Size Effects in Metals, Semiconductors and Inorganic Compounds

Edited by Grégory Guisbiers and Dibyendu Ganguli
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Special topic volume with invited peer reviewed papers only.

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PREFACE

Nanoscience and nanotechnology are among the most widely used terms in the modern scientific and technological literature. The idea of nanotechnology appeared for the first time in the famous talk “There is Plenty of Room at the bottom” given by the physicist Richard Feynman at the American Physical Society meeting at Caltech on December 29, 1959. Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set and so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important whereas surface effects would become increasingly more significant. The term “nanotechnology” was originally defined by Norio Taniguchi in 1974 as follows “Nano-technology mainly consists of the processing of separation, consolidation and deformation of materials by one atom or by one molecule”. Nanotechnology and nanoscience got started in the early 1980s with two major developments; the advances in computing power and material modeling coupled with significant advances in characterization such as the scanning tunneling microscope (STM) and the atomic force microscope (AFM).

The field of nanoscience and nanotechnology is now growing very rapidly. According to the UK Royal Society, nanoscience is defined as the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale. Nanotechnologies are the design, characterization, production, and application of structures, devices, and systems by controlling shape and size at the nanoscale. Nanomaterials cross the boundary between nanoscience and nanotechnologies and link these both areas together. Generally, nanomaterials deal with sizes of 100 nanometers or smaller in at least one dimension. The material properties of nanostructures are different from the bulk due to the high surface area over volume ratio and possible appearance of quantum effects at the nanoscale. The study of size and shape effects on material properties has attracted enormous attention due to their scientific and industrial importance.
It is the aim of this book to present the size effect on different materials properties like the thermal, electrical, magnetic, optical and mechanical ones. This book gives a rapid overview on size as a new parameter that permits the tuning of material properties. The book is separated into three parts. The first one presents a general overview of the nanoworld. The second part is about the synthesis of nanoparticles and how the materials properties are modified at the nanoscale. The third part concerns applications of nanotechnologies in the real world as the nanostructured solar cells and the light emitting diodes. This book is composed of 11 chapters written by experts in their respective fields. Chapter 1 from Wautelet is an introductory chapter to the nanoworld. In Chapter 2, Pan et al. update the recent progress in dealing with the coordination-resolved energetic and dynamic behavior of bonds in the low-dimensional systems with consideration of the joint effect of temperature and pressure. In chapter 3, Rodriguez et al. discuss size effect and shape stability of nanoparticles. In Chapter 4, Guisbiers, who is one of the Guest editors of this book, discusses how to obtain quantitative information on nanomaterials from thermodynamics. In Chapter 5, Ganguli, who is the other Guest editor of this book, considers the size effect in disordered nanoparticles. In Chapter 6, Delogu et al. describe how to synthesize nanostructures. In Chapter 7, Yang et al. consider the size effect on optical properties of semiconductor nanocrystals. In Chapter 8, Erb discusses the size effect on mechanical properties. In Chapter 9, Zhao et al. examine the size effect on thermal properties. The last two chapters written by Nanda and Vigil are about applications of nanotechnology in particular the light emitting diodes and the nanostructured solar cells respectively.

To present the different authors to the readers, a small curriculum vitae of each author is included below with full contact details. The CVs are presented in alphabetical order.

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It is the hope of the editors and authors that this book will be useful to under-graduated as well as graduated students and confirmed researchers in materials sciences, physics, chemistry, and engineering.

Finally, the editors thank all the authors who have taken time to participate in the realization of this book.
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Introduction to the nanoworld

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Keywords : nanosciences, nanotechnologies, scaling laws, nanogeometry, dimensions

Abstract. Nanosciences and nanotechnology (NST) constitute currently a major research field all over the world. NST deal with the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale. The properties of materials can be different at the nanoscale for two main reasons : size and quantum effects. Effects negligible at the macroscopic level become important at the nanometer scale, and vice versa. Scaling laws are described in order to understand some differences. Moreover, geometric arguments are necessary to understand the origin of some physical and chemical properties of nanosystems. On the other hand, quantum effects can begin to dominate the behaviour of matter at the nanoscale – particularly at the lower end – affecting the optical, electrical and magnetic behaviour of materials. The characteristic dimensions for which the properties change from the “macro-“ to the “nano-“ regimes are discussed.

Introduction

Nanoscience, nanotechnology, nanoparticles, nanostructures are among the most widely used terms in modern scientific and technological literature. The field of nanoscience and nanotechnology (NST) is growing very rapidly. NST are believed to lead to dramatic modifications of many of our activities: technologies of information and communication, medicine, materials, space, energy, water, etc. The reasons for this comes from the definitions.

As defined by the Royal Society [1]: Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale. Nanotechnologies are the design, characterisation, production and application of structures, devices and systems by controlling shape and size at the nanometre scale. The fact that the properties differ significantly from those at the macroscale raises interesting and important scientific questions, from both fundamental and applied points of view.

First, let us briefly examine how the properties vary with size. When one goes from the macroworld to the nanoworld, one passes through two diffuse limits. When the characteristic dimensions of the elements decrease from the macroscopic to the micrometer size, the effects of gravity become negligible as compared with adhesive and friction effects. Surface tension dominates gravity. A characteristic example is the fact that insects or geckos adhere to the ceiling, by means of Van der Waals forces. This implies that our reasoning, based on our experience at the macroscopic level, is no more valid. We have to modify our rules of thinking. The boundary between the macroscopic and microscopic levels is not sharp. It depends on the effect to be considered.

When the characteristic size decreases further to attain the nanometer range, another limit is encountered. While the macroscopic properties of matter remain generally valid at the micrometer size, surface effects become dominant at the nanometer scale. Moreover, when one reaches the interatomic distance range, quantum effects appear.

In order to understand the transition from macroscopic to microscopic dimensions, one obviously needs to consider pluridisciplinary effects. This “top-down” approach may begin with the use of so-
called “scaling laws”. The discussion of scaling laws and their domains of validity are important to understand the origin of the differences between the macroworld, the microworld and the nanoworld [2]. This is the subject of the second chapter.

Another approach consists in starting with the properties of individual atoms or molecules, and to look at the properties of systems with increasing numbers of atoms or molecules. This “bottom-up” approach is not treated here.

As said above, the properties of materials can be different at the nanoscale for two main reasons. First, nanomaterials have a relatively large surface area when compared to the same mass of material produced in a larger form. This can make materials more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties. Various effects may be understood by just looking at the geometry of the systems [3]. This is the subject of the third chapter, entitled “Nanogeometry”.

Second, quantum effects can begin to dominate the behaviour of matter at the nanoscale – particularly at the lower end – affecting the optical, electrical and magnetic behaviour of materials. Materials can be produced that are nanoscale in one dimension (for instance, very thin surface coatings), in two dimensions (for example, nanowires and nanotubes) or in all three dimensions (for example, nanoparticles). The characteristic dimensions for which the properties change from the “macro-” to the “nano-” regimes are discussed in the fourth chapter.

Scaling Laws

Scaling laws are used since a long time by scientists and engineers. In our case, scaling laws illustrate the fact that shrinking a body does not only lead to size reduction, but also to different modifications of physical effects. In the following sections, scaling laws relevant to mechanics, fluids, electromagnetism, thermodynamics and optics are considered. We restrict ourselves to physics. It is obvious that chemical effects would also be interesting.

**Mechanics.** Let us consider elements with a typical linear dimension, L. In the following, except when explicitly stated, it is assumed that all the linear dimensions vary proportionally to L. This implies that all areas, S, vary like $L^2$:

$$S \sim L^2,$$

and all volumes, V, vary like $L^3$:

$$V \sim L^3.$$

This implies that the masses, m, scale to:

$$m \sim L^3.$$  

(3)

Let us start by discussing how forces vary with L. The most common force is gravitation. At the Earth’s surface, the gravitation force, $F_{gr} = mg$, where g is the gravitational acceleration.

$$F_{gr} \sim L^3.$$  

(4)

The pressure exerted by a body on the ground, $p_{gr} = F_{gr}/S$, and:

$$p_{gr} \sim L^3/L^2 = L.$$  

(5)
At the microscopic level, adhesion forces dominate, because the details of the forces at the molecular level are much larger than the gravitational ones [4]. Let us first look at adhesion between two surfaces. It is well known that the adhesion between a solid and another solid (or a liquid) is due to forces between atoms and molecules. The main forces responsible for adhesion are Van der Waals type forces [5]. The attractive force experienced by an infinite flat slab separated by a distance \( x \) from another infinite flat slab is given by [6]:

\[
F_{\text{vdw}}(x) = \frac{H}{6\pi x^3},
\]

where \( H \) is the so-called Hamaker constant. \( H \) depends on the nature of the medium between the slabs. \( H \) is of the order of \( 10^{-19} \) J in air and of \( 10^{-20} \) J in water. This relation is valid for \( x \) between around 2 and 10 nm. It is obvious that \( F_{\text{vdw}}(x) \) varies like the contact area:

\[
F_{\text{vdw}}(x) \sim L^2.
\]

Since \( F_{\text{gr}} \) and \( F_{\text{vdw}} \) behave differently with \( L \), their relative values also vary with \( L \). One obtains easily that:

\[
\frac{F_{\text{vdw}}}{F_{\text{gr}}} \sim L^{-1},
\]

i.e. the adhesion force dominates the gravitational force at low \( L \). The critical value at which both forces are equal depend on \( x \) and on the nature of the medium between the two solids. However, below say \( L = 1 \) mm, \( F_{\text{gr}} \) is much less than \( F_{\text{vdw}} \). Gravitation may then be neglected at such small dimensions, both in the micro- and the nano-worlds.

When two surfaces are sliding about each other, at the macroscopic level, the friction force is given by: \( F_{\text{fr}} = \mu F_{\text{gr}} = \mu mg \), where \( \mu \) is the friction coefficient. Provided \( \mu \) is constant,

\[
F_{\text{fr}} \sim L^3.
\]

\( F_{\text{fr}} \) is independent of the contact area. The generally admitted physical reason is that two rough bodies touch each other only at three points. At the microscopic level, things are different due to surface roughness. As seen above, the adhesive forces are very large. The striction (i.e. the combination of adhesion and friction) forces, \( F_{\text{str}} \), has to be taken into account. These forces scale like the contact area [4,7]:

\[
F_{\text{str}} \sim L^2.
\]

Springs exist at all dimensions. The spring force, \( F_{\text{spring}} = - k \delta L \), where \( k \) is the stiffness or spring constant and \( \delta L \) is the elongation from the equilibrium position. Providing \( k \) remains constant, one obtains:

\[
F_{\text{spring}} \sim L.
\]

The corresponding oscillating frequency, \( \nu_{\text{spring}} = (1/2\pi)(k/m)^{1/2} \) and :

\[
\nu_{\text{spring}} \sim L^{-3/2}.
\]
The period of oscillation then scales like:

\[ T_{\text{spring}} \sim L^{3/2}. \]  

(12)

The kinetic energy of a body, \( E_c \), is given by the well known relation \( E_c = \frac{1}{2}mv^2 \). Thus, at constant \( v \):

\[ E_c \sim L^3 \text{(constant } v). \]  

(13)

When \( v \sim L \), one obtains:

\[ E_c \sim L^5 \text{(when } v \sim L). \]  

(14)

Rotational bodies are characterized by the inertial momentum, \( I = \text{cst.} mL^2 \). Then, one obtains:

\[ I \sim L^5. \]  

(15)

The rotational kinetic energy, \( K = \frac{1}{2}I\omega^2 \), and:

\[ K \sim L^5. \]  

(16)

This implies that, at constant \( \omega \), the rotational energy of small systems decreases very rapidly with size. Conversely, the kinetic energy stored in a rotating system is much smaller in small systems than in large ones.

In nature, one often sees beams, strings or tubes. Such items are characterized by resonance frequencies. The lowest eigenfrequency, \( \nu \), corresponds to a state where the length of the device equals a quarter or half the wavelength, \( \lambda \). From the well-known relation \( \nu = \lambda \cdot v \) (where \( v \) is the phase velocity of the wave), one obtains that:

\[ \nu \sim L^{-1}. \]  

(17)

It turns out that resonance frequencies are large in small systems.

**Fluids.** Fluids are obviously important, since, except in vacuum, all bodies move in a fluid (air, water, ...). It is then interesting to look at the variation with \( L \) of various fluid parameters.

When a body falls « vertically » in a fluid, viscous friction is such that, after a certain time, it falls with constant velocity, \( v_{\text{lim}} \). The transient time, \( \tau \), is proportional to \( v_{\text{lim}} \). If the body is spherical, with radius \( r \), the limiting velocity is given by: \( v_{\text{lim}} = \frac{4\sqrt{gr^3}}{18\eta r} \), where \( \eta \) is the viscosity of the fluid and \( \rho \) is the density.

\[ v_{\text{lim}} \sim L^2. \]  

(18)

\[ \tau \sim L^2. \]  

(19)
Viscous forces then drastically and rapidly damp any motion at small dimension. A very small body remains immobile in air (when there is no air movement). When air moves, the small body follows the air movement, as experienced by us by looking at dust in sunrays.

At high velocities, the hydrodynamics is unstable, and turbulent flow arises. The transition from laminar to turbulent flow is given by the Reynold number, Re. Re = \( \rho v L / \eta \).

If \( v \sim L \), then:

\[
Re \sim L^2. \quad (v \sim L)
\]  

(20)

For flow in pipes, the transition from laminar to turbulent flow occurs when \( Re \geq 10^3 \) [8]. In this case, turbulence disappears in micro- and nanosystems in which liquids flow.

A particle travels a distance \( L \) by diffusion during a diffusion time given by \( \tau_{\text{diff}} = L^2 / \alpha D \), where \( \alpha \) is a geometrical constant and \( D \) is the diffusion constant. One obtains:

\[
\tau_{\text{diff}} \sim L^2. 
\]  

(21)

This is valid for particle and thermal diffusion.

**Electromagnetism.** A conductor of length \( L \) and cross-section \( A \) has an electrical resistance, \( R_{\text{el}} = \rho_{\text{el}} L / A \), where \( \rho_{\text{el}} \) is the specific electrical conductivity. Thus:

\[
R_{\text{el}} \sim L^{-1}. 
\]  

(22)

When one applies a given voltage, \( V_{\text{el}} \), the electric current, \( I_{\text{el}} \), is given by the Ohm’s law, so that:

\[
I_{\text{el}} \sim L. 
\]  

(23)

Consequently, the power dissipated by the element is given by Joule’s law: \( W = R_{\text{el}} I_{\text{el}}^2 \), and:

\[
W \sim L. 
\]  

(24)

The number of elements by unit area varies like \( L^{-2} \). So, the electrical power dissipated by unit area varies like:

\[
W_{\text{un}} \sim L^{-1}. 
\]  

(25)

This is a well known fact in microelectronics, where it is known that the reduction of size of the components leads to more dissipated power [9]. One way to diminish this effect is to reduce the applied voltage.

When \( V_{\text{el}} \) remains constant, while \( L \) varies, the electric field, \( E_{\text{el}} \), obviously varies:

\[
E_{\text{el}} \sim L^{-1}. 
\]  

(26)

When \( E_{\text{el}} \) increases, it attains a range of value where Ohm’s law is no longer valid or, in other words, \( \rho_{\text{el}} \) varies with \( E_{\text{el}} \).

In nanosystems, one also deals with capacitors. Let us consider a capacitance made of two parallel plates of area, \( A \), separated by a distance, \( d \). The capacitance is \( C = \varepsilon_0 A / d \), and:

\[
C = \frac{\varepsilon_0 A}{d}. 
\]
C \sim L. \quad (27)

When one applies a given voltage, V_{el}, the charge on each plate, Q = C.V_{el}, and:

Q \sim L. \quad (28)

Under these conditions, the energy stored in the capacitor, E_{cap} = Q^2/2C, and:

E_{cap} \sim L. \quad (29)

Therefore, the stored energy decreases with the size of the capacitor. One sometimes prefers to deal with capacitors having constant charge density, i.e. Q \sim L^2. In this case:

E_{cap} \sim L^3. \quad (30)

Since the electric force between the capacitor plates, F_{cap}, is given by the derivative of E_{cap} relative to the gap distance, one obtains that:

F_{cap} \sim L^2. \quad (31)

The magnetic field in a solenoid, with n turns of wire, of length L, and a current I_{el} through the coil, is given by:

B = \mu I_{el} n/L. \quad (32)

When one shrinks the solenoid, n may remain constant, but the cross-section of the wire decreases, so that I_{el} varies. It seems reasonable to assume that the current density is constant. Hence, I_{el} \sim L^2, and:

B \sim L. \quad (33)

The magnetic energy stored in the solenoid is E_{magn} = B^2.Vol/2\mu, where Vol is the volume of the magnetic field. Since Vol \sim L^3, one obtains:

E_{magn} \sim L^5. \quad (34)
F_{magn} \sim L^4. \quad (35)

When going to small dimensions, one has to allow for technological problems. For instance, the number of wires is not independent of L at low L, because it is not (yet?) possible to manufacture very thin wires. In practice, it seems that solenoids smaller than 1 mm^3 are hardly feasible [8]. Moreover, the maximum current density is limited by the dissipation of energy, i.e. the maximum temperature the system can have. The dissipation is related to size. Hence, the current density depends on L, in a way that depends on the design of the system.

Thermodynamics. The energy, E_{th}, required to heat a system to a temperature T is proportional to the mass:

E_{th} \sim L^3. \quad (36)
Heat losses occur by conduction, convection and radiation. For conduction and radiation, the power dissipation, \( P_{\text{diss}} \), is proportional to the area of the system, i.e.

\[
P_{\text{diss}} \sim L^2.
\]  

(37)

When using this relation, care has obviously to be taken, owing to the fact that thermal losses are related to temperature differences between the interior and the exterior of the system. Heat diffusion coefficients have to be carefully checked.

The time, \( \tau_{\text{th}} \), needed to homogenize the temperature in a system of given shape is proportional to the square of the linear dimensions of the system [10], i.e. :

\[
\tau_{\text{th}} \sim L^2.
\]  

(38)

When the size of a system decreases down to the nanometer range, the ratio of surface to volume atoms increases, so that the surface influences the properties of the system. Moreover, in the nm range, the validity of some thermodynamical concepts has to be questioned. We will come back to this later.

**Optics.** Optics is interesting both for the study and the manufacturing of small systems. The limitations of optical methods arises from wave optics, in particular diffraction. When a plane wave is shone on an element of linear dimension, \( L \), the reflected wave diverges. The divergence angle, \( \theta \) \( \approx \lambda/L \). Hence :

\[
\theta \sim L^{-1}.
\]  

(39)

This has consequences in various applications [11]. In photolithography, when one irradiates elements with lenses of a fixed numerical aperture (\( \text{NA} = n \sin \theta \)), the minimum diameter of the irradiated zone, \( L = 2\lambda/\pi \cdot \text{NA} \). Hence, the wavelength required to design an element of diameter scales like :

\[
\lambda \sim L.
\]  

(40)

This is why the specialists of microelectronics go to ultraviolet lithography when they decide to diminish the size of the electronic components on chips.

This remains obviously valid as long as the theory is valid, i.e. the dimensions of the optical elements are much larger than \( \lambda \).

**Nanogeometry**

The fact that the physical and chemical properties of nanosystems differ from the ones at the macroscale may sometimes be understood by simple geometrical arguments.

**Specific area.** Let us first examine how the specific area of particles vary when their linear dimension varies. Let us take a cube with sides of length \( C \), with volume \( V = C^3 \). The total area of its 6 faces is equal to \( A_1 = 6C^2 \). Let us divide the cube into \( 2^3 = 8 \) identical cubes. The total volume remains constant. However, the total area of the faces is now equal to \( A_2 = 2A_1 = 12C^2 \). Similarly, when the initial cube is divided \( n \) times into identical small cubes, the total volume is constant, while the total area of the faces varies like \( A_n = nA_1 \). Altogether, the total surface to volume ratio varies like :
\[ A_n/V = 6.n/C \] (41)

The ratio \( A_n/V \) is called the “specific area”, when \( V \) is a unit volume. It turns out that the specific area increases when the size of the nanoparticles decrease. This size effect is important in phenomena taking place at the surface of solids (adsorption, heterogeneous catalysis, etc.).

Let us evaluate the specific area of a powder (of mass equal to 1 g) made of carbon spherical nanoparticles, with radius \( r = 10 \) nm. The density of carbon is equal to \( \rho = 2.26 \) g/cm\(^3\). In the case of spheres, the ratio \( A/V = (4\pi r^2)/(4\pi r^3/3) = 3/r \). Here, \( A/V = 3.10^8 \) m\(^2\)/m\(^3\). One calculates easily that the specific area is equal to 0.133 km\(^2\)/kg = 133 m\(^2\)/g. This principle is currently used in gas masks, so-called sorption pumps and heterogeneous catalysis.

At low temperature, nitrogen may be adsorbed on nanoparticles. From the literature, the area of one nitrogen molecule is equal to 0.162 nm\(^2\). A simple calculation gives the number of nitrogen molecules adsorbed : \( 0.82.10^{24} \) nitrogen molecules per kg of carbon nanoparticles. Given that at standard pressure and room temperature, one mole of gas occupies a volume of 22.4 l, one deduces that 32 l of nitrogen are adsorbed on 1 kg of carbon nanoparticles.

**Nanocrystals.** Geometrical objects made of closed faces satisfy the generalized Euler relation, namely:

\[ F - A + S = K \]

where \( F, A \) and \( S \) are the numbers of faces, edges and summits, respectively. \( K \) is the Euler characteristics and is related to the number of holes, \( g \) (for genus), via \( K = 2(1 - g) \) [12]. For a torus, \( g = 1 \). For polyhedra, \( g = 0 \).

Nanoparticles are often observed as being regular polyhedra. In many cases these are so-called Platonic polyhedra : cube, octahedron, decahedron, dodecahedron, icosahedron [13]. These polyhedra satisfy the well known conventional Euler relation, namely:

\[ F - A + S = 2. \] (42)

The values of \( F, A \) and \( S \) for different polyhedra are given in Table 1.

<table>
<thead>
<tr>
<th>Geometrical shape</th>
<th>F</th>
<th>A</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>4</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Cube</td>
<td>6</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Octahedron</td>
<td>8</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Dodecahedron</td>
<td>12</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>Icosahedron</td>
<td>20</td>
<td>30</td>
<td>12</td>
</tr>
</tbody>
</table>

Let us note that the cube and the octahedron have the same number of edges, and that the number of faces of one is equal to the number of summits of the other one. The same is true for the dodecahedron and the icosahedron. The generalized Euler relation is used in the case of other shapes, like in foams or zeolites [14].

The Euler relation is useful when one studies the chemical reactivity of nanoparticles. Let us consider the case of cubic nanoparticles. Let \( N \) be the number of atoms on the edge of a cube. The total number of atoms on the summits of one cube, \( S_o \), does not depend on the size of the cube : \( S_o = S = 8 \). The total number of atoms on the edges of one cube (excluding the atoms on the summits) is
It is well established experimentally that the chemical reactivity depends on the geometrical environment of the atoms. The reactivity of atoms on the summits, the edges or the faces are often different. This is due to the fact that the number of so-called “dangling bonds” are different. This implies that the reactivity of nanoparticles might depend on their size and shape. Let \( d_0 \) be the diameter of one atom. One obtains that \( N \cdot d_0 = C/n \). In the following, it is assumed that \( N >> 2 \).

The total reaction rate on summits is proportional to the number of summits in the powder:

\[
S_{\text{tot}} = S/N^3 = 8/N^3 \div n^3
\]  

Similarly the total reaction rates on (for reaction taking place at) edges and faces are respectively proportional to:

\[
A_{\text{tot}} = A \cdot (N-2)/N^3 = 12 \cdot (N-2)/N^3 \approx 12N/N^3 = 12N^2/\ N^3 \div n^2
\]

\[
F_{\text{tot}} = F \cdot (N-2)/N^3 = 6 \cdot (N-2)/N^3 \approx 6N^2/N^3 = 6N/\ n
\]

It is then obvious that the reaction rates depend on both the shape (via \( S, A \) and \( F \)) and the size (via \( n \)) of the nanoparticles. The reasoning is easily extended to other shapes.

It is one of the reasons why some materials appear to be chemically inert in the bulk state, while they are chemically active when nanopowders. For instance, it is well known that Au is chemically inert. However, it has been found that Au nanoparticles less than 3-5 nm in diameter are catalytically active for several chemical reactions, like CO oxidation [16]. The variation of the catalytic activity with \( n \) shows that the summits and to a lesser extent edges contribute to this activity.

**Fullerenes.** One of the most important molecules in the nanoscience field is the so-called “buckminsterfullerene” (or “fullerene”) molecule, also known as buckyball or \( C_{60} \). Its shape is like a soccer ball. Each carbon atom is bound to three other carbons in an alternative arrangement of pentagons and hexagons.

Fullerenes satisfy the Euler relation. Fullerenes are made of \( H \) hexagons and \( P \) pentagons. The numbers of faces, edges and summits satisfy:

\[
F = H + P
\]

\[
2A = 6H + 5P
\]

\[
3S = 6H + 5P
\]

Given the Euler relation, a little algebra leads to \( P = 12 \). The value of \( H \) depends on the value of \( S \). In the case of \( C_{60} \), \( S = 60, H = 20 \) and \( F = 32 \). Fullerenes with other values of \( S \) are observed. For instance, \( C_{70} \) is characterized by \( S = 70, H = 25 \) and \( F = 37 \).

It is worth noting that in \( C_{60} \), the 60 atoms are geometrically equivalent. Every carbon is bound to three others. Moreover, every carbon atom is at the vertex of two hexagons and one pentagon. It is not case of \( C_{70} \), in which atoms are divided into five categories. \( C_{70} \) has the form of a rugby ball.

**Carbon nanotubes.** Carbon nanotubes are another important material in NST. It is sometimes called the XXIst century material, due to its particular physical properties. These are long cylindrical tubes, made of carbon [15]. Each carbon nanotube is a single molecule. It may be thought as a graphene sheet (from graphite) with its hexagonal structure rolled back on itself to form a cylinder. The diameter of such single-walled nanotubes varies between 0.671 and 3 nm.
Three types of nanotubes are known, according to the way the graphene sheets are enrolled: arm-chair, zigzag and chiral. One also observes multi-walled carbon nanotubes, made of coaxial single-walled nanotubes. Their diameter may attain 30-50 nm.

Like other nanoparticles, the specific area of carbon nanotubes is large. In the graphene sheet, the interatomic distance is \( d_{CC} = 0.142 \) nm. The area of one hexagon is \( S_{\text{hex}} = 2.6 \times d_{CC}^2 = 0.052 \) (nm\(^2\)). Every atom belongs to three different hexagons. Hence \( S_{\text{hex}} \) corresponds to the area occupied by 2 atoms. Given the fact that one mole of carbon weighs 12 g, one easily calculates that 1 g of carbon nanotubes is characterized by an area of \( 1300 \) m\(^2\).

Given their high specific area, carbon nanotubes are believed to be good candidates for hydrogen storage in future hydrogen tanks. Let us assume that one hydrogen atom may be adsorbed on each carbon atom [16]. One mole (1 g) of atomic hydrogen is adsorbed on one mole of carbon (12 g). One deduces that 1/12 g of hydrogen is adsorbed by 1 g of carbon nanotubes, corresponding to an equivalent gas volume equal to 1.87 l H or 0.93 l H\(_2\). This also means that the so-called maximum mass\% hydrogen adsorbed on carbon nanotubes is equal to \( l/(l + 12) = 7.7\% \). In other words, storing 1 kg of hydrogen by adsorption on carbon nanotubes would require a tank weighting (at least) 13 kg.

The fact that the specific area of carbon nanotubes is very high has a lot of potential applications. Among others, it is argued that carbon nanotubes attached to a surface would increase significantly the area of the plates of capacitors, hence allowing the design of ultracapacitors [17] and the storage of electrical energy. It is also argued that the carbon nanotubes might be major ingredients in adhesive systems (glues) where surface to surface contacts are important, like gecko-like effects [18].

**The limits of the nanoworld**

As said in the introduction, **Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale.** Although interesting for the non-specialist, these definitions are not very useful for practical purposes. Let us evaluate such characteristic dimensions.

The first question to be addressed is: what does “properties differ significantly from those at larger scale” mean? More precisely: how much is significantly different? There is no agreement on the quantities. So, in the following, we choose arbitrarily to state that the properties are “significantly different” when they differ by either 1% or 10%. This allows us to determine the dimension ranges at which “nano”-properties appear. Let us bear in mind that, in this work, we are looking at orders of magnitude of the characteristic dimensions. Moreover, as seen later, the transitions are often temperature dependent. In the following, we consider the properties at room temperature (\( \text{T} = 300 \) K), excepted when noted.

**Geometry.** In a first approach, it may be thought that the properties are related to the number of atoms. Nanoparticles are such that the number of atoms located at their surface, \( A \), is not small as compared with their total number, \( V \). In other words, nanoparticles are such that \( A/V \) is larger than 1% or 10%.

Let us express the diameter, \( D \), of a spherical particle, in units of interatomic distances, \( D_0 : D = 2rD_0 \). \( D_0 \) is typically of the order of 0.2 nm. \( A = 4\pi r^2 ; V = 4\pi r^3/3 ; A/V = 3/r \). Then, \( A/V = 10^{-2} \) when \( r = 300; D_1 \approx 120 \) nm. \( A/V = 10^{-1} \) when \( r = 30; D_2 \approx 12 \) nm.

For a cube (side of length \( L = lD_0 \)), \( A = 6l^2; V = l^3; A/V = 6/l \). Then, \( A/V = 10^{-2} \) when \( l = 600; L_1 \approx 120 \) nm. \( A/V = 10^{-1} \) when \( l = 60; L_2 \approx 12 \) nm.

It may be helpful to deal with the characteristic number of atoms in a nanosystem. In this case, it is more suitable to express \( A/V \) at constant volume. Then, \( A/V = \beta/V^{1/3} \), where \( \beta \) is a purely
geometrical factor, depending on the shape of the system [19]. For a sphere, one obtains \( A/V = 10^{-2} \) when \( V_1 = 1.13 \times 10^5 \) atoms; \( A/V = 10^{-1} \) when \( V_2 = 1.13 \times 10^3 \) atoms.

There are also nanowires, of section \( S \) (with perimeter \( P \)) and length \( L \) (much larger than \( S^{1/2} \)). In this case [20], \( A = PL; V = SL; A/V = P/S = \beta/S^{1/2} \). In the case of cylindrical nanowires, \( A/V = 10^{-2} \) when \( S_1 = 1.25 \times 10^5 \) atoms; \( A/V = 10^{-1} \) when \( S_2 = 1.25 \times 10^3 \) atoms.

**Cohesion.** Since the ratio \( A/V \) is not small in nanosystems, it is expected that the effects of the surface on the cohesive properties cannot be neglected. This is seen in various situations, like the size-dependent melting point depression [21,22, and other chapters of the present book]. In inorganic materials, the melting temperature, \( T_m \), varies with the diameter of the particle, \( D \), like \((T_m \propto \) is the bulk melting point):

\[
T_m = T_{m.\propto} [1 - \alpha/D].
\]  

(49)

\( \alpha \) depends on the material. It is between 0.4 and 3.3 nm [6]. The difference between the bulk and nanocases may be characterized by:

\[
\Delta T = (T_{m.\propto} - T_m)/T_{m.\propto} = \alpha/D
\]  

(50)

For our evaluation, let us take \( \alpha = 1 \) nm. It turns out that \( \Delta T = 10^{-2} \), when \( D_3 \approx 100 \) nm; \( \Delta T = 10^{-1} \), when \( D_4 \approx 10 \) nm. It is worth noting that \( D_3 \) compares with \( D_1 \), and \( D_4 \) compares with \( D_2 \).

**Thermal properties.** In order to describe thermal properties, one usually uses thermodynamics. One generally considers that thermodynamics is valid when the number of atoms is «large». What is “large”? Are nanosystems “large” with respects to thermodynamics definition?

**Thermal fluctuations.** Thermodynamics gives a macroscopic description of a material in thermodynamical equilibrium, defined as a volume where thermal fluctuations are «small». But what is “small”? Let us consider a cube (of volume equal \( L^3 \)), with \( N \) atoms per unit volume. The relative temperature fluctuation within the cube is \( \delta T/T \approx (NL^3)^{1/2} \), or \( L \approx (\delta T/T)^{1/2} N^{1/2} \). Let us assume that the temperature is uniform when it fluctuates by less than \( 10^{-2} \) (10^1). In solids and liquids, \( N \approx 10^{29} m^{-3} \), so that \( D_5 = 4.6 \) nm (\( D_5 = 1 \) nm).

It is worth noting that the reasoning may be applied to phase transitions. In particular, in the case of “bulk” first order phase transitions, the temperature fluctuation means that the transition takes place over a temperature interval given by \( \delta T \). This implies that first order phase transitions disappear in the nanoworld. This is a well known characteristics of the thermodynamics of nanoparticles.

**The definitions of temperature.** In thermodynamics, the basic parameter is the temperature. For macroscopic systems, it is easy to define a local temperature. But the size of the regions over which a local temperature can be defined must be precise. Is it in the nanometer range or above? This has been carefully discussed by Cahill et. al. [23] in the framework of nanoscale thermal transport. In the following, their discussion is summarized, emphasizing the size of the nanosystems. The usual definition of temperature is related to the average energy of a system of particles. There are three ways to define a local temperature.

The first definition is used, for instance, in molecular dynamics. In this method, one calculates the position and the velocity of each atom in each time period. One then calculates the mean kinetic energy, \( E_k \), over \( M \) time steps. \( M \) must be high enough, so that the result is statistically valid. The calculations are classical. The temperature is classically given by:
\[ <E_c> = \frac{<m v_i^2>}{2} = \frac{3kT}{2} \] (51)

In this equation, \( k \) is the Boltzmann constant, and \( v_i \) is the velocity of atom \( i \). The temperature is defined locally, over one atom. This approach neglects quantum effects.

The second approach takes quantum effects into account. The collective motion of atoms is described by the phonon model. They are characterised by their pulsation, \( \omega(\vec{p}, \vec{q}) \), depending on the polarisation, \( \vec{p} \) and wavevector, \( \vec{q} \).

At high \( T \) (well above the Debye temperature), the classical and quantum equations give similar results. However, at low temperature (and near room temperature), when below the Debye temperature, both definitions give different values of \( T \), since the thermal energy as given by the Debye theory differs from the classical one \[24\].

A third definition is to subtract the zero temperature motion from the quantum definition.

Among the three definitions, the correct definition depends on the size of the domain where \( T \) is defined. The classical definition is purely local. \( T \) may be defined for each atom or row of atoms.

With quantum definitions, the length scale is defined by the phonon mean free path, \( l_{ph} \). If two space domains are characterized by different temperatures, the phonon distributions are different. One domain is defined by one phonon distribution. Hence the characteristic length of a local domain at a given fixed \( T \) must be larger than the phonon diffusion length. But this length is a function of the phonon frequency. Low frequency phonons have large mean free paths, while high frequency ones have shorter mean free paths. At high temperature, one may define an average mean free path. From this point of view, \( T \) may not be defined on one atom or row of atoms. It may only be defined over a length larger than \( l_{ph} \). At high temperature, the phonon mean free path is governed by the so-called “Umklapp process”. In this case, \( l_{ph} \propto T^{-1} \). For many materials, at room temperature, \( l_{ph} \) is in the nm range \[24\] (NaCl : 2.3 nm; quartz : 4.0 nm). Let us take \( l_{ph} = 3 \) nm. This implies that \( T \) may then be defined when the characteristic dimensions of the system are in the nm range. It is often stated that the statistical collision theory holds when the dimension of the system is larger than \( D \), such that \( \eta = \exp(-l_{ph}/D) \) is small. Taking \( \eta = 10^{-2} (10^{-1}) \), this criteria is met when \( D_7 = 4.6x l_{ph} = 14 \) nm (\( D_8 = 2.3x l_{ph} = 7 \) nm). In other words, systems with characteristic dimensions below about 10 nm are in a non-thermodynamical regime.

Although this fact, the thermodynamical concepts are often used in the case of numerical simulations of heat transport (for instance) in nanosystems. There is yet no known way to solve this important problem.

**Electrons.** The electronic properties of nanosystems are of tremendous importance for various applications, like nano-electronics and nano-optics. Therefore, it is necessary to look at the effects of the size on some electron properties.

**Coulomb blockade.** When a current is injected into a nanoparticle, or when a nanoparticle is electrically charged, one (or more) electrons have to go from the external part of the particle to the interior. In usual macroscopic situations, this poses no difficulty. However, when dealing with nanoparticles, things may be different. The “Coulomb blockade” refers to an interdiction of an electron transfer into a region where it results in a change of the electrostatic energy greater than the thermal energy, \( kT \) \[25\]. Let us assume this “region” to be a spherical nanoparticle, with radius \( R \). The energy for charging this nanoparticle with one electron is given by the energy of a capacitor: \( E_{cap} = e^2/(4\pi \varepsilon_0 R) \). For macroscopic particles, \( E_{cap} \) is very weak. In nanoparticles, the condition \( E_{cap} > kT \) is easily met. For instance, when \( R = 10 \) nm, \( E_{cap} = 2.3x10^{-20} \) J = 0.14 eV. This energy is not much more important than the thermal energy at room temperature (\( T = 300 \) K; \( kT = 0.025 \) eV). The
probability of charging the nanoparticle is given by \( Pr = \exp(-E_{\text{cap}}/kT) \). \( Pr \approx 1 \) for large nanoparticles. At room temperature, \( 1 - Pr = 10^{-3} \) when \( E_{\text{cap}} = 2.51 \times 10^{-4} \text{ eV} \); \( R = 5.6 \mu\text{m} \) \( (D_0 = 11.2 \mu\text{m}) \); \( 1 - Pr = 10^{-1} \) when \( E_{\text{cap}} = 2.6 \times 10^{-3} \text{ eV} \); \( R = 540 \text{ nm} \) \( (D_{10} = 1.08 \mu\text{m}) \).

This effect is obviously temperature dependent. Since \( Pr \) depends only on \( E_{\text{cap}}/T \), and \( E_{\text{cap}} \sim D^{-1} \), \( Pr \) is constant at fixed \( D, T \). Hence, \( D \) decreases with increasing \( T \).

**Metals.** Let us address the case of metallic nanoparticles. In the quantum free electron theory, the electron energy levels are quantified. At the Fermi level, the level spacing, \( \delta(E_F) \), is derived from the bulk density of states [24]:

\[
\delta(E_F) = \frac{dE_F}{dN_e} = 2 \frac{E_F}{3N_e}, \quad (52)
\]

\[
E_F = \left(\frac{\hbar^2}{2m}\right)(3\pi^2 N_e/V)^{2/3}, \quad (53)
\]

where \( N_e \) is the total number of free electrons. A transition between the metallic continuum and the discreteness of the levels in a nanosystem is observed when the mean level spacing, \( \delta(E_F) \approx kT \). When \( \delta(E_F) > kT \), the nanosystem does not behave like a metal, and the quantification of the energy levels is expected to play a role in the electronic properties. This size-induced metal to insulator transition is often called the “Kubo criterion”.

Let us assume that the bulk-nano transition takes place when \( \exp(-\delta(E_F)/kT) = 10^{-2} \) \( (10^{-1}) \). Let us consider a spherical nanoparticle, with a diameter equal to \( D \). Let \( D_0 \) be the interatomic distance. Let \( n_e = N_e/V \). The condition \( \delta(E_F) = \beta kT \) rewrites:

\[
\beta T D^3 = \frac{\hbar^2}{2m} \left(3\pi^2 n_e\right)^{2/3} D_0^{2/3} / (3mk). \quad (54)
\]

For a monovalent metal (like Ag, where \( n_e = 5.85 \times 10^{28} \text{ m}^{-3} \); \( D_0 = 3.04 \times 10^{-10} \text{ m} \), at \( T = 300 \text{ K} \), one calculates: \( D_{11} = 2.5 \text{ nm} \) \( (\text{when } \exp(-\delta(E_F)/kT) = 10^{-2}) \) or \( D_{12} = 2.0 \text{ nm} \) \( (\text{when } \exp(-\delta(E_F)/kT) = 10^{-1}) \). This effect is temperature dependent. The condition \( \delta(E_F) = \beta kT \) is such that \( T D^3 \) is constant. Hence, \( D \) decreases with increasing \( T \).

**Semiconductors.** From the electronic point of view, a semiconductor is characterized by the existence of an energy band gap, \( E_g \), between an occupied valence band (VB) and an empty (at \( T = 0 \text{ K} \)) conduction band (CB). When an electron is excited from the VB to the CB, the electron and the hole may be bonded electrostatically, and form a so-called Bohr exciton. The quantum description of the Bohr exciton is similar to the case of the electron in a hydrogen atom. The Bohr exciton is characterized by the Bohr radius of the exciton, \( a_B \):

\[
a_B = \frac{\varepsilon \hbar^2}{\mu e^2} \quad (55)
\]

\( \varepsilon \) is the dielectric constant, \( \mu \) is the reduced mass of the electron-hole system \( (\mu^{-1} = m_e^{-1} + m_h^{-1}) \); \( m_e, m_h \) are the effective masses of the electron and the hole, respectively) and \( e \) is the charge of the electron. \( a_B \) is of the order of a few nm. When the radius of the nanoparticle compares with or is less than \( a_B \), the wavefunctions are not delocalized as they are in an infinite (bulk) solid. There is then a transition between the bulk and the localized behavior. In this case, the electron energy levels also become discrete. The exact treatment of the energy levels is out of the scope of the present work [26]. Altogether, it turns out that the optical band gap is shifted to high energy when the radius of the nanoparticle decreases. The shift is obviously dependent on the chemical nature of the system. It becomes significant when the diameter is less than about \( D_{13} \approx 10 \text{ nm} \) [26].

From the previous reasoning, it turns out that the borders between the nano and the classical regimes depend on the studied properties. These are summarized in the Table 2 for geometrical,
cohesive, thermal and electronic cases. Generally speaking, one may conclude that most properties of nanoparticles with diameter less than about 10 nm differ significantly from the bulk case.

Table 2. Characteristic dimensions of the nano to bulk transitions. See text for definitions. (* : Temperature dependent. Taken at T = 300 K)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Remarks</th>
<th>Difference $= 10^{-2}$</th>
<th>Difference $= 10^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>Sphere</td>
<td>$D_1 = 120$ nm</td>
<td>$D_2 = 12$ nm</td>
</tr>
<tr>
<td></td>
<td>Cube</td>
<td>$L_1 = 120$ nm</td>
<td>$L_2 = 12$ nm</td>
</tr>
<tr>
<td>Cohesion</td>
<td>Melting temperature</td>
<td>$D_3 \approx 100$ nm</td>
<td>$D_4 \approx 10$ nm</td>
</tr>
<tr>
<td>Thermal</td>
<td>Temperature fluctuations</td>
<td>$D_5 = 4.6$ nm</td>
<td>$D_6 = 1$ nm</td>
</tr>
<tr>
<td></td>
<td>Phonon mean free path*</td>
<td>$D_7 = 14$ nm</td>
<td>$D_8 = 7$ nm</td>
</tr>
<tr>
<td>Electron</td>
<td>Coulomb blockade*</td>
<td>$D_9 = 11.2$ μm</td>
<td>$D_{10} = 1.08$ μm</td>
</tr>
<tr>
<td></td>
<td>Fermi level*</td>
<td>$D_{11} = 2.5$ nm</td>
<td>$D_{12} = 2.0$ nm</td>
</tr>
<tr>
<td></td>
<td>Bohr exciton</td>
<td>$D_{13} \approx 10$ nm</td>
<td></td>
</tr>
</tbody>
</table>

Summary

Nanosciences and nanotechnologies deal with the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at the larger scale. It is shown here that many differences between the macroworld and the nanoworld are understood in the framework of the “top-down” approach. The use of scaling laws allow to describe how different phenomena are size dependent. Some effects negligible at the macroscopic level become important at the nanometer scale, and vice versa. From the geometric point of view, nanosystems are characterized by the fact that the number of atoms at their surface is not negligible compared with the number of atoms in the inner part. Nanogometry helps to better understand this point. Quantum effects are necessary to define the characteristic dimensions of the nano- to macroworlds.

References


Behind the quantum and size effects: broken-bond-induced local strain and skin-depth densified quantum trapping of charge and energy

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Abstract. Shrinking the size of a solid down to nanometer scale is indeed fascinating, which makes all the otherwise constant physical quantities to be tunable such as the Young’s modulus, dielectric constant, melting point, etc. The variation of size also generates novel properties that can hardly be seen in the bulk such as the conductor-insulator and nonmagnetic-magnetic transition of noble metals at the nanoscale. Although the physics of materials at the nanoscale has been extensively investigated, the laws governing the energetic and dynamic behavior of electrons at such a scale and their consequences on the tunable physical properties of nanostructures have not been well understood [C. Q. Sun, Prog Solid State Chem 35, 1-159 (2007); Prog Mater Sci 54, 179-307 (2009)]. The objective of the contribution is to update the recent progress in dealing with the coordination-resolved energetic and dynamic behavior of bonds in the low-dimensional systems with consideration of the joint effect of temperature and pressure. It is shown that the broken-bond-induced local strain and the associated charge and energy quantum trapping at the defect sites perturbs the atomic cohesive energy, electroaffinity, the Hamiltonian and the associated properties of entities ranging from point defects, surfaces, nanocavities and nanostructures. Application of the theories to observations has led to consistent understanding of the behavior of nanometer-sized materials and the interdependence of these entities as well as the means of determining the bond energy through the temperature-dependent measurements.

Introduction

The process of size reduction has formed the essential entity that can be used to tune the physical properties of nanostructured materials that cannot be realized in the corresponding bulk counterpart. With reduction of solid size, none of the physical properties such as the Young’s modulus, dielectric constant, melting point, the magnitude and frequency of lattice vibration, activation energy for atomic diffusion, etc, of a material remains the bulk constant but change with their shape.

* Associated with an honorary appointment at Xiangtan University.
and size. Properties of nanosolids determined by their dimensionality are indeed fascinating, which form the basis of the emerging fields of nanoscience and nanotechnology that has been recognized as the key significance in science, technology, and economics in the current century.

When examining nanostructures, many of the concepts developed in both molecular chemistry and solid-state physics have to be considered. One may develop a “top-down” theory on the behavior of nanosystems starting from a solid and confining it to a limited size. Another chemical-like “bottom up” approach is to start with a molecular system and expand its size. Each approach has different advantages and limitations. To bridge these two approaches and develop new concepts for nanostructures is a challenge.

The size-induced property change of nanostructures has inspired tremendous theoretical efforts. For instance, a number of models have been developed to explain how the size reduction could induce the blue shift in the photoluminescence (PL) of nanosemiconductors. An impurity luminescent center model\textsuperscript{3} assumed that the PL blue shift arises from different types of impurity centers in the solid and suggested that the density and variety of the impurity centers vary with particle size. Surface states and surface alloying mechanism\textsuperscript{4,5} proposed that the PL blue shift originates from the extent of surface passivation that is subject to the processing parameters, aging conditions, and operation temperatures.\textsuperscript{6} The model of Inter-cluster interaction and oxidation\textsuperscript{7} also claimed the responsibility for the PL blue shift. The most elegant model for the PL blue shift could be the “quantum confinement (QC)” theory.\textsuperscript{8,9,10,11,12} According to the QC theory, the PL energy corresponds to the band gap expansion dictated by electron-hole (e-h) pair (or exciton) production. Electrons in the conduction band and holes in the valence band are confined spatially by the potential barrier of the surface, or trapped by the potential well of the quantum box. Because of the confinement of both the electrons and the holes, the lowest energy optical transition from the valence to the conduction band increases in energy, effectively increasing the $E_G$. The sum of the kinetic and potential energies of the freely moving carriers is responsible for the $E_G$ expansion, and therefore, the width of the confined $E_G$ grows as the characteristic dimensions of the crystallites decrease.

In contrast, a free-exciton collision model\textsuperscript{13} suggested that the $E_G$ expansion arises from the contribution of thermally activated phonons in the grain boundaries rather than the QC effect. During a PL measurement, the excitation laser heats the free excitons that then collide with the boundaries of the nanometer-sized fragments. The laser heating the free-excitons up to the temperature in excess of the activation energy required for the self-trapping gives rise to the extremely hot self-trapping excitons (STE’s). Because the resulting temperature of the STE’s is much higher than the lattice temperature, the cooling of the STE’s is dominated by the emission of phonons. However, if the STE temperature comes into equilibrium with the lattice temperature, the absorption of lattice phonons becomes possible. As a result, the blue shift of the STE-PL band is suggested to originate from the activation of hot-phonon-assisted electronic transitions. The blue shift of the STE-PL band depends on the temperature of laser-heated free-excitons that in turn is determined by the size of nano-fragments. This event happens because the temperature (kinetic energy) of the laser-heated free-exciton increases with the number of boundary collisions, which tends to be higher with decreasing size of the nano-fragments. The energy gained from laser heating of the exciton increases with decreasing nanosolid size in an $\exp(1/R)$ way, with $R$ being the characteristic size of the nanocrystal. It should be noted that all the above-mentioned theories dealt only with the PL blue shift but they cannot explain the size induced blue shift of photoabsorbance.

Another typical issue of nanostructures is their thermal stability. The melting point ($T_m$) of an isolated nanosolid, or a system with weakly linked nanoparticles, drops with solid size (called undercooling), while the $T_m$ may rise (called overheating) for an embedded nano-system due to the interface effect. The $T_m$ is characterized by the Lindemann’s criterion\textsuperscript{14} of atomic vibration
abruption or Born’s criterion\textsuperscript{15} of shear modulus disappearance at the \( T_m \). The \( T_m \) elevation or suppression or the mode of melting in the nanometer regime have been described with numerous models. These models include (i) homogeneous melting and growth;\textsuperscript{16,17} (ii) random fluctuation melting;\textsuperscript{18} (iii) liquid shell nucleation and growth;\textsuperscript{19,20,21,22} (iv) lattice-vibrational instability;\textsuperscript{24,25} (v) surface-phonon instability,\textsuperscript{26,27} and, (vi) the BOLS theory used presently.\textsuperscript{1} Classical thermodynamic theories based on the surface Laplace and the Gibbs-Duhem equations\textsuperscript{28} have derived that \( K_C \) obeys the following relations:\textsuperscript{29,30}

\[
K_C = \frac{-2}{H_m(\sigma)} \times \left[ \sigma_{sv} - \sigma_{l}(\rho_{sv}/\rho_l)^{3/2}, \right. \text{ (Homogeneous growth and melting)} \\
\left. \sigma_{sl} (1 - K_0/K_f)^{-1} + \sigma_{lv}(1 - \rho_{sv}/\rho_l), \right. \text{ (Liquid shell Nucleation)} \\
\left. \left[ \sigma_{sl} 3(\sigma_{sv} - \sigma_{lv} \rho_{sv}/\rho_l)/2 \right] \right. \text{ (Liquid nucleation and growth)}
\]

Where \( H_m \) is the latent heat of fusion. \( \rho \) is the mass density and \( \sigma \) the interfacial energy. Subscripts \( s, l, \) and \( v \) represent the phases of solid, liquid and vapor, respectively. The critical value of \( R_C (= K_CD_0) \) is normally several nanometers. Expressions for \( K_C \) correspond to three outstanding mechanisms in terms of classical thermodynamics, as mentioned above.

It is quite often that numerous modeling arguments exist for a specific phenomenon. The challenge is how to correlate all the outstanding arguments for all the observations to the effect of bond order deficiency that originates the size effect. The origin for one single phenomenon must intrinsically sustain to others. Understanding the mechanisms for size reduction is critical to controlling the behavior of nanostructured materials and related devices.

Recently, a bond order-length-strength (BOLS) correlation theory\textsuperscript{1} has been developed by extending the atomic “coordination-radius” correlation premise of Goldschmidt\textsuperscript{31} and Pauling\textsuperscript{32} to include the energetics and electronics of the spontaneous process of bond relaxation. It has been justified that if one bond breaks, the remainder become shorter and stronger. The broken-bond-induced local strain and skin-depth quantum trapping cause strong localization and densification of charge, energy, and mass nearby defects, resulting in perturbation to the atomic cohesive energy, electroaffinity, Hamiltonian, etc., and associated properties of a substance. This theory has resulted in discoveries of: (i) the factors dictating the size dependency of nanostructures; (ii) the means of determining atomic energy levels; (iii) clarification of the bonding identities in atomic chains, nanoribbons, and nanotubes and; (iv) the unification of the size dependency of nanostructures in mechanical strength, thermal and chemical stability, lattice acoustic dynamics, photonic, electronic, magnetic and dielectric properties and their interdependence in terms of the BOLS correlation.

Subsequently, a local-bond-average (LBA) approach\textsuperscript{33} has been established by connecting the detectable properties of a substance directly to the identities (nature, order, length, strength) of a representative bond and the response of these identities to the applied stimulus such as the coordination environment, pressure, and temperature, complementing the existing quantum and continuum medium approximations. This theory has enabled consistent understanding of: (i) the factors responsible for the thermo-mechanical behavior of atomic chains, nanotubes, nanowires, nanograins, nanocavities, liquid and solid skins, interfaces and nanocomposites; (ii) the means of bond energy determination; (iii) electronic origin for superhydrophobicity, superlubricity, and superfluidity observed in nanometer sized contacts\textsuperscript{34} and; (iv) factors dominating the strongest size in plastic deformation of nanostructures.

The objective of this contribution is to present the latest progress based on the BOLS theory and LBA approach\textsuperscript{35} and further to indicate that the broken-bond-induced local strain and the associated skin-depth charge and energy quantum trapping dictate the observed size dependence of
nanostructures. Bond order loss causes the remaining bonds of the under-coordinated atom to contract spontaneously associated with bond-strength gain or atomic potential well depression, which localize electrons and enhance the density of charge, mass, and energy in the relaxed region. The energy density rise in the relaxed region perturbs the Hamiltonian and the associated properties such as the band-gap width, core-level energy, Stokes shift (electron-phonon interaction), and dielectric susceptibility. On the other hand, bond order loss lowers the cohesive energy of the under-coordinated atom, which dictates the thermodynamic process such as self-assembly growth, atomic vibration, thermal stability, and activation energies for atomic dislocation, diffusion and chemical reaction.

Effects of size and confinement

Basic concepts
Atoms, interactions and the laws of operation. One sort of matters in the universe is the condensed matter that includes those with and without life, organic and inorganic, from tiny small to infinitely large, ordered to disordered, etc. The key elements for the condensed matter are three entities:

(i) the constituent elemental atoms given in the periodic table,
(ii) the interaction among them through charge sharing, nonsharing or polarization or in terms of bonding or nonbonding, and,
(iii) the laws governing the organization of the atoms and their interactions.

The most effective way of describing the bonding or nonbonding static and dynamic nature under the external stimuli:

(i) Static: bond nature, bond order, bond length, and bond strength
(ii) Dynamic: bond formation, dissociation, vibration, and relaxation
(iii) Stimuli: coordination environment, temperature, pressure, composition, electric field, etc

For a large bulk, classical continuum theories such as the Gibbs free energy or the continuum mechanics are sufficient to describe the behavior of the bulk under the external stimuli; for a matter at the atomic scale, quantum mechanics or molecular dynamics approaches work well. However, at the nanometer scale both quantum and continuum approaches are facing serious difficulties because of the boundary conditions. At the grain boundaries, atoms and electrons perform unusually.

Involvement of interatomic interaction causes the performance of a solid to be different from that of an isolated atom; the interaction between the under-coordinated atoms makes a cluster of atoms to behave differently from that of an isolated atom or the bulk. Therefore, interaction between the under-coordinated atoms at sites surrounding atomic defects, dislocations, grain boundaries, terrace edges or at surfaces of skin depth of the differently curved surfaces has been recognized as the key to the unusual behavior of low-dimensional systems such as dimer, atomic chains, nanoribbons, nanotubes, nanowires, nanograins, nanocavities, and the surface skin of a bulk specimen. The low-dimensional systems are characterized by a high fraction of atoms with the effective atomic coordination number (z, or CN) being between 0 and 12. The z equals to zero corresponds to an isolated atom and z = 12 to an atom in the ideal bulk interior with an fcc structure as the standard. Therefore, an atom with partially coordinated neighbors forms the basis that ties the atomic defects, dislocations, terrace edges, grain boundaries, surfaces, nanocavities and nanostructures together with the common nature of the broken-bond-induced local strain and the skin depth charge and energy quantum trapping. The elucidation of the bond structure and the electronic binding energy of such low-dimensional systems are of great importance. The clarification of bonding and the corresponding dynamics can improve our understanding of the origin of the novel physical properties of the low-dimensional systems, such as the mechanical strength, chemical reactivity,
thermal stability, optoelectronic, magnetic and dielectric performance, as compared to those of the bulk counterparts [2].

Intraatomic trapping. Electrons of a single atom confined by the intra-atomic trapping potential, \( V_{\text{atom}}(r) \), move around the central ion core in a standing-wave form inside the potential well. The \( V_{\text{atom}}(r) \) describes the electron-nucleus interaction and it takes a value that varies from several eV to infinity, depending on the orbitals in which electrons are revolving. The Hamiltonian and the corresponding eigen wave functions and the eigen energies for an electron in the isolated atom are given as:

\[
\hat{H}_0 = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r)
\]
\[\phi_n(r) \propto \sin(k_n r), \text{ and} \]
\[E(n) = \frac{\hbar^2 k_n^2}{2m} + \frac{2n\pi}{d_0^2}, n = 1, 2, 3, \ldots \tag{1}\]

the atomic diameter \( d_0 \) corresponds to the dimension of the potential well of the atom. The branch numbers \( (n) \) correspond to different energy levels. The energy separation between the nearest two levels depends on \( (n+1)^2 - n^2 = 2n+1 \). The intra-atomic binding energy is in the range varying from several eV to \( 10^3 \) eV depending on the particular electronic orbit.

Interatomic bonding and intercluster coupling. When two or more atoms join as a whole, interatomic interaction comes into play, which causes the performance of a cluster of atoms to be different from that of an isolated atom. The interatomic binding energy is in the range of several eV; electrons in the inner shells experience weaker interatomic binding energy because of the screening effect. However, the interatomic bonding is essential to make a solid or even a liquid. Considering an assembly composed of \( n \) particles of mean size \( K_j \) and with each particle, there are \( N_j \) atoms, the total binding energy, \( V_{\text{cry}}(r, n, N_j) \), is:

\[
V_{\text{cry}}(r, n, N_j) = \sum_i N_i \sum_{i=1}^{N_i} \sum_{k, l} v(r_{kl})
\]
\[= n \left[ N_j \sum_{i=1}^{N_i} v(r_i) + \sum_{k, l} v(K_{kl}) \right] \tag{2}\]
\[\approx n \left[ \frac{N_j^2 v(d_0)}{2} + nV(K_j) \right]\]

The \( V_{\text{cry}}(r, n, N_j) \) sums over all the \( N_j \) atoms and the \( n \) particles. The high order \( r_{kl} \) is a certain fold of the nearest atomic spacing, \( d_0 \). Interaction between the nearest clusters, \( k \) and \( j \), \( V(K_{kl}) \), is negligible if the \( K_{kl} \) is considerably large. Normally, the intercluster interaction, \( V(K_{kl}) \), is much weaker than the interatomic interaction, if the cluster is treated as an electric or a magnetic dipole of which the Van der Waals or the super-paramagnetic potentials dominate.

Hamiltonian and energy band. According to the band theory, the Hamiltonian for an electron inside a solid is in the form:

\[
\hat{H} = \hat{H}_0 + \hat{H}^* = -\frac{\hbar^2 \nabla^2}{2m} + V_{\text{atom}}(r) + V_{\text{cry}}(r + R_C)
\tag{3}\]

where the \( \hat{H}_0 \) is the Hamiltonian for an isolated atom as given in eq (1). \( \hat{H}^* = V_{\text{cry}}(r) = V_{\text{cry}}(r + R_C) \) is the periodic potential of the crystal, describing the interaction between the specific electron with
the ion cores of all other atoms, including the many-body effect. The term of electron-electron interaction is treated in a mean field as a constant background from the first order approximation. \( R_C \) is the lattice constant. According to the nearly-free-electron approximation, the \( E_G \) between the valence and the conduction bands originates from the crystal potential. The width of the gap depends on the integral of the crystal potential in combination with the Bloch wave of the nearly-free electron, \( \phi(k, r) \):

\[
E_G = 2|V_1(k_j)|, \quad \text{and} \quad V_1(k_j) = \langle \phi(k_j, r)|V(r + R_C)|\phi(k_j, r)\rangle
\]

where \( k_j \) is the wave-vector and \( k_j = 2l\pi/R_C \). Actually, the \( E_G \) is simply twice the first Fourier coefficient of the crystal potential.

As illustrated in Figure 1, the energy levels of an isolated atom will evolve into energy bands when interatomic bonding is involved. When two atoms are bound together, such as \( \text{H}_2 \) dimer-like molecules, the single energy level of the initially isolated atom splits into two sublevels. The presence of interatomic interaction lowers the center of the two sublevels, or termed as the core level shift. Increasing the number of atoms up to \( N_j \), the single energy level will expand into a band within which there are \( N_j \) sublevels.

What distinguishes a nanosolid from a bulk chunk is that for the former the \( N_j \) is accountable, while for the latter the \( N_j \) is too large to be accounted despite the proportion of the under-coordinated atoms in the surface skin. Therefore, the classical band theories are valid for a solid over the whole range of sizes or containing any number of atoms. As detected using x-ray photoelectron spectroscopy (XPS), the density-of-states (DOS) of the valence region for a nanosolid exhibits band-like features rather than the discrete spectral lines of a single atom. If the \( N_j \) is sufficiently small, the separation between the sublevels is resolvable. The energy level spacing between the successive sublevels in the valence band, known as the Kubo gap \( \delta_K = 4E_f/3N_j \), decreases with the increase of the number of valence electrons of the system, \( N_j \), where \( E_f \) is the Fermi energy of the bulk. Because of the presence of the \( \delta_K \) in an individual nanosolid, properties such as electron conductivity and magnetic susceptibility exhibit quantized features.

![Figure 1](image_url)

**Figure 1** The involvement of interatomic interaction evolves a single energy level to the energy band when a particle grows from a single atom to a bulk solid that contains \( N_j \) atoms. Indicated is the work function \( \phi \), band gap \( E_G \), core level shift \( \Delta E_C \), bandwidth \( E_B \). The number of allowed sublevels in a certain band equals the number of atoms of the solid.

According to the tight-binding approximation, the energy dispersion of an electron in the \( v \)th core band follows the relation:
The cohesive energy of a solid containing \( N_j \) atoms equals to the energy dividing the crystal into individually isolated atoms by breaking all the bonds of the solid. If no atomic CN reduction is considered, the \( E_{\text{coh}} \) is the sum of bond energy over all the \( z_b \) coordinates of the \( N_j \) atoms:

\[
E_{\text{coh}}(N_j) = \sum_{N_j} \sum_{z_b} E_i \simeq N_j z_b E_b = N_j E_B
\]  

(6)
directly to the atomic cohesive energy – the product of the bond number and bond energy of the specific atom.

**Boundary conditions**

Barrier confinement vs. quantum uncertainty. The termination of lattice periodicity in the surface normal direction has two effects. One is the creation of the surface potential barrier (SPB), or work function, or contact potential, and the other is the reduction of the atomic CN. The SPB is the intrinsic feature of a surface, which confines only electrons that are freely moving inside the solid. However, the SPB has nothing to do with the *strongly localized* electrons in deeper core bands or with those form sharing electron pairs in a bond. The localized electrons do not suffer such barrier confinement at all as the localization length is far shorter than the particle size.

According to the principle of quantum uncertainty, reducing the dimension (D) of the space inside which energetic particles are moving increases the fluctuation, rather than the average value, of the momentum, p, or kinetic energy, E_k, of the moving particles:

\[
\Delta p D \geq \hbar/2 \\
p = p \pm \Delta p \\
E_k = p^2/(2\mu)
\]  

(7)

where \( \hbar \) being the Plank constant corresponds to the minimal quanta in energy and momentum spaces and \( \mu \) is the effective mass of the moving particles. The kinetic energy of a freely moving carrier is increased by a negligible amount due to the confinement effect on the fluctuation that follows the principle of quantum uncertainty.

Atomic CN reduction. The atomic CN reduction is referred to the standard value of 12 in the bulk of an fcc structure irrespective of the bond nature or the crystal structure. Atomic CN reduction is referred to an atom with coordinate less than the standard value of 12. The CN is 2 for an atom in the interior of a monatomic chain or an atom at the open end of a single-walled carbon nanotube (CNT) or the edge of a graphene ribbon; while in the CNT wall, the CN is 3. For an atom in the fcc unit cell, the CN varies from site to site. The CN of an atom at the edge or corner has differences from the CN of an atom in the plane or the central of the unit cell. Atoms with deformed bond lengths or deviated angles in the CNT are the same as those in amorphous states that are characterised with the band tail states.\(^{40}\) For example, the effective CN of an atom in diamond tetrahedron is the same as that in an fcc structure as a tetrahedron unit cell is an interlock of two fcc unit cells. The CN of an atom in a highly curved surface is even lower compared with the CN of an atom at a flat surface. For a negatively curved surface (such as the inner side of a pore or a bubble), the CN may be slightly higher than that of an atom at the flat surface. Therefore, from the atomic CN reduction point of view, there is no substantial difference in nature between a nanosolid, a nanopore, and a flat surface. This premise can be extended to the structural defects or defaults such as voids surrounding which atoms are suffer from CN reduction. Unlike a nanosolid with ordered CN reduction at the surface, an amorphous solid possesses defects that are distributed randomly.

**Bond order-length-strength (BOLS) correlation**

Bond order-length correlation. As the consequence of bond-order loss, the remaining bonds of the under-coordinated atoms contract spontaneously. As asserted by Goldschmidt\(^{31}\) and Pauling,\(^{32}\) the ionic and the metallic radius of the atom would shrink spontaneously if the CN of an atom is reduced. The CN reduction induced bond contraction is independent of the nature of the specific bond or structural phases.\(^{41}\) For instance, a 10% contraction of spacing between the first and second atomic surface layers has been detected in the liquid phase of Sn, Hg, Ga, and In.\(^{42}\) A substitutional dopant of As impurity has induced 8% bond contraction around the impurity at the Te sublattice in
CdTe has also been observed using EXAFS (extended X-ray absorption fine structure) and XANES (X-ray absorption near edge spectroscopy). Therefore, bond order loss induced bond contraction is universal.

Figure 2a illustrates the CN dependence of bond length. The solid curve, \( c_i(z_i) \), formsulates the Goldschmidt premise which states that an ionic radius contracts by 12%, 4%, and 3%, if the CN of the atom reduces from 12 to 4, 6 and 8, respectively. Feibelman has noted a 30% contraction of the dimer bond of Ti and Zr, and a 40% contraction of the dimer-bond of Vanadium, which is also in line with the formulation.

Figure 2b illustrates the BOLS correlation. Solid curve in (a) is the contraction coefficient \( c_i \), derived from the notations of Goldschmidt (open circles) and Feibelman (open square). Consequently, the bond energy at equilibrium atomic separation will rise absolutely, \( E_i = c_i^{-m}E_b \). However, the atomic cohesive energy, \( z_iE_i \), changes with both the \( m \) and \( z_i \) values. (b) Atomic CN reduction modified pairing potential energy. CN reduction causes the bond to contract from one unit (in \( d_0 \)) to \( c_i \) and the cohesive energy per coordinate increases from one unit to \( c_i^{-m} \) unit.

Bond length-strength correlation. As the atomic-CN reduction induced bond contraction is a spontaneous process, the system energy will be lowered with an association of bond strength gain. The contraction coefficient and the associated bond energy gain form the subject of the BOLS correlation mechanism that is formulated as:

\[
\begin{align*}
\left[ c_i(z_i) \right] &= d_i/d_0 = 2/[1 + \exp[(12-z_i)/(8z_i)]] \\
E_i &= c_i^{-m}E_b \\
E_{B,i} &= z_iE_i
\end{align*}
\]

(BOLS – coefficient \( t \))

(Single – bond – energy)

(atomic – cohesive – energy) \hspace{1cm} (8)

Subscript \( i \) denotes an atom in the \( i \)th atomic layer, which is countered up to three from the outermost atomic layer to the center of the solid as no CN-reduction is expected for \( i > 3 \). The index \( m \) is a key indicator for the nature of the bond. Experience revealed that for Au, Ag, Ni metals, \( m = 1 \); for alloys and compounds, \( m \) is around four; for C and Si, the \( m \) has been optimized to be 2.56 and 4.88, respectively. The \( m \) value may vary if the bond nature evolves with atomic CN. If the surface bond expands in cases, we simply expand the \( c_i \) from a value that is smaller than unity to greater, and the \( m \) value from positive to negative to represent the spontaneous process of which the system energy is minimized. The \( c_i(z_i) \) depends on the effective CN rather than a certain order of CN. The \( z_i \) also varies with the particle size due to the change of the surface curvature. The \( z_i \) takes the following values: \( z_1 = 4(1-0.75/K) \), \( z_2 = z_1 + 2 \) and \( z_3 = 12 \).
Figure 2b illustrates schematically the BOLS correlation using a simple interatomic pairing potential, \( u(r) \). When the CN of an atom is reduced, the equilibrium atomic distance will contract from one unit (in \( d_0 \)) to \( c_1 \) and the cohesive energy of the shortened bond will increase in magnitude from one unit (in \( E_b \)) to \( c_i^{-m} \). The solid and the broken \( u(r) \) curves correspond to the pairing potential with and without CN reduction. The BOLS correlation has nothing to do with the particular form of the pairing potential as the approach involves only atomic distance at equilibrium. The bond length-strength correlation herein is consistent with the trend reported by Bahn and Jacobsen\(^{49} \) though the extents of bond contraction and energy enhancement therein vary from situation to situation.

There are several characteristic energies in Figure 2b, which correspond to the following facts:

1) \( T_{m,i} \) being the local melting point is proportional to the cohesive energy, \( z_iE_b(0) \),\(^{50} \) per atom with \( z_i \) coordinate.\(^{51} \)
2) Separation between \( E = 0 \) and \( E_i(T_m) \), or \( \eta_{1i}(T_{m,i} - T) + \eta_{2i} \), corresponds to the cohesive energy per coordinate, \( E_i \), at \( T \), being energy required for bond fracture under mechanical or thermal stimulus. \( \eta_{1i} \) is the specific heat per coordinate.
3) The separation between \( E = 0 \) and \( E_i(T_m) \), or \( \eta_{2i} \), is the 1/\( z_i \) fold energy that is required for atomization of an atom in molten state.
4) The spacing between \( E_i(T) \) and \( E_i(0) \) is the vibration energy purely due to thermal excitation.
5) The energy contributing to mechanical strength is the separation between the \( E_i(T_m) \) and the \( E_i(T) \), as a molten phase is extremely soft and highly compressible.\(^{52} \)

Values of \( \eta_{1i} \) and \( \eta_{2i} \) can be obtained with the known \( c_i^{-m} \) and the bulk \( \eta_{1b} \) and \( \eta_{2b} \) values that vary only with crystal structures as given in Table 1.

Table 1 Relation between the bond energy \( E_b \) and the \( T_m \) of various structures.\(^{23} \) \( \eta_{2b} < 0 \) for an fcc structure means that the energy required for breaking all the bonds of an atom in molten state is included in the term of \( \eta_{1b}T_m \) and therefore the \( \eta_{2b} \) exaggerates the specific heat per CN.

<table>
<thead>
<tr>
<th></th>
<th>fcc</th>
<th>Bcc</th>
<th>Diamond structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_b = \eta_{1b}T_m + \eta_{2b} )</td>
<td>5.542</td>
<td>5.919</td>
<td>5.736</td>
</tr>
<tr>
<td>( \eta_{1b} (10^4 \text{ eV/K}) )</td>
<td>-0.24</td>
<td>0.0364</td>
<td>1.29</td>
</tr>
<tr>
<td>( \eta_{2b} (\text{ eV}) )</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Densification of mass, charge and energy. Figure 3 compares the potential well in the QC convention with that of the BOLS for a nanosolid. The QC convention extends the monotrapping potential of an isolated atom by expanding the size from \( d_0 \) to \( D \). BOLS scheme covers contribution from individual atoms that are described with multi-trapping-centre potential wells, and the effect of atomic CN reduction in the surface skin. Atomic CN reduction induced bond-strength gain depresses the potential well of trapping in the surface skin. Therefore, the density of charge, energy, and mass in the relaxed surface region are higher than other sites inside the solid. Consequently, surface stress that is in the dimension of energy density will increase in the relaxed region. Electrons in the relaxed region are more localized because of the depression of the potential well of trapping, which lowers the work function and conductivity in the surface region due to boundary scattering,\(^{53,54} \) but enhances the angular momentum of the surface atoms.\(^{56} \)
Surface-to-volume ratio
It is easy to derive the volume or number ratio of a certain atomic layer, denoted i, to that of the entire solid by differentiating the natural logarithm of the volume,\(^5\)

\[
\gamma_i = d(\ln V) = \frac{\int_{V_i} V_i dV}{V} = \frac{4\pi}{4\pi R^3/3} = 1 - \frac{(R - d_i)}{R} \approx \frac{3c_i}{K} \quad (9)
\]

where \(K\) is the number of atoms lined along the radius of the nanosphere or across the thickness of a thin film or the wall thickness of a nanotubes. Generally, \(\gamma_i = \tau c_i / K \cdot \tau = 1, 2, \text{ and } 3\) corresponds to a thin plate, a cylindrical rod and a spherical dot, respectively. The definition of dimensionality (\(\tau\)) herein differs from the convention in transport or quantum confinement considerations in which a nano-sphere is zero-dimension (quantum dot), a rod as one dimension (quantum wire), and a plate two dimension (quantum well). If all bonds in the nanocrystal contribute to the elastic enhancement, the integral over the size of \(R = 0\) to \(R\), becomes unity. Therefore, the measured \(1/K\) dependence of elastic modulus indicates clearly the bonds in the surface shell of limited thickness dominate the size-induced change. For a hollow system, the \(\gamma_i\) should count both external and internal sides of the hollow structure. With reducing particle size, performance of surface atoms become dominant because at the lower end of size limit \((K_j \rightarrow \tau c_i)\), \(\gamma_1\) approaches unity. At \(K_j = 1\), the solid will degenerate into an isolated atom. Therefore, the \(\gamma_i\) covers the whole range of sizes and various shapes. If we count atom by atom, the number ratio and the property change will show quantized oscillation features at smaller sizes, which varies from structure to structure.\(^5\)

Shape-and-size dependency
Scaling relation. Generally, the mean relative change of a measurable quantity of a nanosolid containing \(N_j\) atoms, with dimension \(K_j\), can be expressed as \(Q(K_j)\); and as \(Q(\infty)\) for the same solid without contribution from bond order loss. The correlation between the \(Q(K_j)\) and \(Q(\infty) = N_j q_0\) and the relative change of Q due to bond order loss is given as:
\[
Q(K_j) = N_j q_0 + N_s (q_s - q_0)
\]

\[
\frac{\Delta Q(K_j)}{Q(\infty)} = \frac{Q(K_j) - Q(\infty)}{Q(\infty)} = \frac{N_s}{N_j} \left( \frac{q_s}{q_0} - 1 \right)
\]

\[
\sum_{j=3} \gamma(q_j/q_0) = \Delta_{qj}
\]

The weighting factor, \( \gamma_{ij} \), represents the geometrical contributions from dimension (\( K_j \)) and dimensionality (\( \tau \)) of the solid, which determines the magnitude of change. The quantity \( \Delta q/q_0 \) is the origin of change. The \( \sum_{j=3} \gamma_{ij} \) drops in a \( K_j^{-1} \) fashion from unity to infinitely small when the solid grows from atomic level to infinitely large. For a spherical dot at the lower end of the size limit, \( K_j = 1.5 \) (\( K_j d_0 = 0.43 \text{ nm} \) for an Au spherical dot example), \( z_i = 2, \gamma_{ij} = 1, \) and \( \gamma_{ij} = \gamma_{3j} = 0 \), which is identical in situation to an atom in a monatomic chain (MC) despite the orientation of the two interatomic bonds. Actually, the bond orientation is not involved in the modeling iteration. Therefore, the performance of an atom in the smallest nanosolid is a mimic of an atom in an MC of the same element without presence of external stimulus such as stretching or heating. At the lower end of the size limit, the property change of a nanosolid relates directly to the behavior of a single bond.

Generally, experimentally observed size-and-shape dependence of a detectable quantity follows a scaling relation. Equilibrating the scaling relation to Eq (8), one has:

\[
Q(K_j) - Q(\infty) = \left\{ \frac{bK_j^{-\gamma}}{Q(\infty) \times \Delta_{qj}} \right\} \text{(measurement)}
\]

(11)

where the slope \( b \equiv Q(\infty) \times \Delta_{qj} \times K_j \equiv \text{constant} \) is the focus of various modeling pursues. The \( \Delta_{qj} \propto K_j^{-\gamma} \) varies simply with the \( \gamma_{ij}(\tau, K_j, c_i) \) if the functional dependence of \( q(z_0, c_i, m) \) on the atomic CN, bond length, and bond energy is given.

Cohesive energy modification. The heat energy required for loosening an atom is a certain portion of the atomic \( E_B \) that varies with not only the atomic CN but also the bond strength. The variation of the mean \( E_B \) with size is responsible for the fall (undercooling) or rise (overheating) of the \( T_c \) (critical temperature for melting, phase transition, or evaporation) of a surface and a nanosolid. The \( E_B \) is also responsible for other thermally activated behaviors such as phase transition, catalytic reactivity, crystal structural stability, alloy formation (segregation and diffusion), and stability of electrically charged particles (Coulomb explosion). The cohesive energy also determines crystal growth and atomic diffusion, and atomic gliding displacement that determine the ductility of nanosolids.

Considering both the BOLS correlation in the surface region and long-range bond loss, we have a universal form for the cohesive energy suppression for an oxide nanosolid:57

\[
\frac{\Delta E_B(K_j)}{E_B(\infty)} = \left\{ \sum_{i=3} \gamma_{ij} \left( \frac{c_i}{c_i} \right)^{-1} - 1 \right\} = \Delta_B \quad \text{(BOLS)}
\]

\[
\sum_{i=K_{c}} \gamma_{ij} \left( \frac{-V_{vac}}{V_C} \right) + \Delta_B = \Delta_{coh} \quad \text{(BOLS + long-range)}
\]

(12)

For the short spin-spin interaction, it is sufficient to sum over the outermost three atomic layers while for a ferroelectric and a superconductive solid. The sum should be within the sphere of radius \( K_C \). The BOLS correlation considers only contribution from atoms in the shells of the surface skin,
whereas, long-range contribution involves the concept of correlation radius that is used in ferroelectric systems:

\[ \langle E_{coh}(N_j) \rangle = N_j z_b E_b + \sum_{i \leq 3} N_i (z_i E_i - z_b E_b) \]

\[ = N_j E_B(\infty) + \sum_{i \leq 3} N_i z_b E_b (z_b E_{ib} - 1) \]

\[ = E_{coh}(\infty) \left[ 1 + \sum_{i \leq 3} \gamma_i (z_i c_i^{-m} - 1) \right] = E_{coh}(\infty)(1 + \Delta_B) \quad (13) \]

or, \( \frac{\Delta E_B(K_j)}{E_B(\infty)} = \sum_{i \leq 3} \gamma_i (z_i c_i^{-m} - 1) = \Delta_B \)

where \( E_{coh}(\infty) = N \tilde{z} E_b \) represents the ideal situation without CN reduction. The \( z_{ib} = z_i/z_b \) is the normalized CN and \( E_{ib} = E_i/E_b \equiv c_i^{-m} \) is the normalized binding energy per coordinate of a surface atom. For an isolated surface, \( \Delta_B < 0 \); for an intermixed interface, \( \Delta_B \) may be positive depending on the strength of interfacial interaction. Therefore, the relative change of \( T_C(K_j) \) and activation energy, \( E_A(K_j) \) for thermally and mechanically activated process can be expressed as:

\[ \frac{\Delta T_C(K_j)}{T_C(\infty)} = \frac{\Delta E_A(K_j)}{E_A(\infty)} = \frac{\Delta E_B(K_j)}{E_B(\infty)} = \Delta_B \quad (14) \]

Interestingly, the critical temperature for sensing operation could be lowered from 970 to 310 K of SrTiO\(_3\) by ball milling to obtain 27 nm-sized powders. The resistivity of the SrTiO\(_3\) increases when the SrTiO\(_3\) particle size is decreased. Decreasing the particle sizes of ferroelectric BaTiO\(_3\) could lower the \( T_C \) to 400 K and the refractive index (dielectric constant), and hence the transmittance of BaTiO\(_3\) infilled SiO\(_2\) photonic crystals, as a consequence. The suppression of the critical temperatures for sensing and phase transition results and the modulation of resistivity and refractive index could be consequences of energy densification and cohesive energy suppression in the surface skin.

Hamiltonian perturbation. The perturbation to the energy density in the relaxed region that contributes to the Hamiltonian upon assembly of the nanosols is,

\[ \Delta_H(K_j) = \frac{V_{cr}(r, n, N_j)}{V_{cr}(d_0, n, N_j)} - 1 \]

\[ = \sum_{i \leq 3} \gamma_i \frac{\Delta v(d_i)}{v(d_0)} + \delta_{ij} \]

\[ = \sum_{i \leq 3} \gamma_i (c_i^{-m} - 1) + \delta_{ij} \]

where, \( \delta_{ij} = \frac{n V(K_j)}{N_j^2 v(d_0)} \quad (15) \)

With the perturbation, the \( \hat{H}' \) in eq (3) becomes, \( \hat{H}'(\Delta_H) = V_{cr}(r) \left[ 1 + \Delta_H(K_j) \right] \), which dictates the change of not only the \( E_G \) width, but also the core-level energy:

\[ \frac{\Delta E_G(K_j)}{E_G(\infty)} = \frac{\Delta E_v(K_j)}{E_v(\infty)} = \Delta_H(K_j) \quad (16) \]
where $\Delta E_{\nu}(K_j) = E_{\nu}(K_j) - E_{\nu}(1)$. This relation also applies to other quantities such as the bandwidth and band tails.\(^{39}\)

Most strikingly, without triggering electron-phonon interaction or electron-hole generation, scanning tunneling microscopy/spectroscopy (STM/S) measurement at low temperature revealed that the $E_G$ of Si nanorod varies from 1.1 to 3.5 eV with decreasing the rod diameter from 7.0 to 1.3 nm associated with $\sim$12% Si-Si bond contraction from the bulk value (0.263 nm) to $\sim$0.23 nm. The STS findings concur excitingly with the BOLS premise: CN reduction shortens the remaining bonds of the under-coordinated atoms spontaneously with an association of $E_G$ expansion.

Electron-phonon coupling. Electron-phonon (e-p) interaction contributes to the processes of photoemission, photoabsorption, photoconduction, and electron polarization that dominates the static dielectric constant. Figure 4 illustrates the effect of e-p coupling and crystal binding on the energy of photoluminescence and absorbance, $E_{PL}$ and $E_{PA}$. The energies of the ground state ($E_1$) and the excited state ($E_2$) are expressed in parabola forms:\(^{40}\)

\[
\begin{align*}
E_1(q) &= Aq^2 \\
E_2(q) &= A(q - q_0)^2 + E_G
\end{align*}
\]

Constant $A$ is the slope of the parabolas. The $q$ is in the dimension of wave-vector. The vertical distance between the two minima is the true $E_G$ that depends uniquely on the crystal potential. The lateral displacement ($q_0$) originates from the e-p coupling that can be strengthened by lattice contraction. Therefore, the blue shift in the $E_{PL}$ and in the $E_{PA}$ is the joint contribution from crystal binding and e-p coupling.

In the process of carrier formation, or electron polarization,\(^{40}\) an electron is excited by absorbing a photon with $E_G+W$ energy from the ground minimum to the excited state with creation of an electron-hole pair. The excited electron then undergoes a thermalization and moves to the minimum of the excited state, and eventually transmits to the ground and combines with the hole. The carrier recombination is associated with emission of a photon with energy $E_{PL} = E_G - W$. The transition processes (e-h pair production and recombination) follow the rule of momentum and energy conservation though the conservation law may be subject to relaxation for the short ordered nanosolid. Relaxation of the conservation law is responsible for the broad peaks in the PA and PL.

The insertion illustrates the Stokes shift, $2W = 2Aq_0^2$, or the separation from $E_{PL}$ to $E_{PA}$. The $q_0$ is inversely proportional to atomic distance $d_i$, and hence, $W_i = A'(c_i d_i)^2$, in the surface region. Based on this premise, the blue shift of the $E_{PL}$, the $E_{PA}$, and the Stokes shift can be correlated to the CN reduction-induced bond contraction.\(^{63,61}\)

\[
\begin{align*}
\frac{\Delta E_{PL}(K_j)}{E_{PL}(\infty)} &= \frac{\Delta E_G(K_j) + \Delta W(K_j)}{E_G(\infty) + W(\infty)} \approx \sum_{i=3} \gamma_j [c_j^{-m} - 1] \mp B(c_j^{-2} - 1) \\
\frac{\Delta E_{PA}(K_j)}{E_{PA}(\infty)} &= \Delta H \mp B \Delta e^{-p} \\
B &= \frac{A}{E_G(\infty) d_i^2}; \quad W(\infty) = 0.007 \times 1.12 \approx 0
\end{align*}
\]

Compared with the bulk $E_G(\infty) = 1.12$ eV for silicon, the $W(\infty) \sim 0.007$ eV obtained using tight-binding calculations\(^{62}\) is negligible. One can easily calculate the size dependent $E_{PL}$, $E_{PA}$, and $E_G$ =
Mechanical strength. The mechanical yield strength is the strain-induced internal energy deviation that is proportional to energy density or the sum of bond energy per unit volume. Considering the contribution from heating, the strength (stress, flow strength), the Young’s modulus, and the compressibility (under compressive stress) or extensibility (under tensile stress) at a given temperature can be expressed by:

\[
P_i(z_i, T) = -\frac{1}{V} \frac{\partial u(r, T)}{\partial V} \bigg|_{d_i, T} - \frac{N_j \eta_i (T_{m,i} - T)}{d_i^2}
\]

\[
\beta_i(z_i, T) = -\frac{1}{N_j \eta_i (T_{m,i} - T)} \left[ \frac{d_i}{d_i^2} \right]^{-1} = \frac{d_i}{N_j \eta_i (T_{m,i} - T)} \left[ \eta_i (z_i, T) \right]^{-1}
\]

(19)

`\beta` is an inverse of dimension of the Young’s modulus or the hardness. `N_j` is the total number of bonds in `d_i` volume. If calibrated with the bulk value at `T` and using the size dependent specific heat, melting point, and lattice parameter, the temperature, bond nature, and size dependent strength and compressibility of a nanosolid will be:
The bond number density between the circumferential neighbouring atomic layers does not change upon relaxation \((N_i = N_0)\). Eq (20) indicates that the mechanical strength is dictated by the value of \(T_m(K_j) - T\) and the specific heat per bond. At \(T\) far below the \(T_m\), a surface or a nanostructure is harder than the bulk interior. However, the \(T_m\) drops with size \(K_j\) and therefore, the surface or nanosolid become softer when the \(T_m(K_j) - T\) value becomes smaller. This relation has led to quantification of the surface mechanical strength, the breaking limit of a single bond in monatomic chain and the anomalous Hall-Petch relationship in which the mechanical strength decreases with size in a fashion of \(D^{0.5}\) and then deviates at 10 nm from the Hall-Petch relationship.\(^{52}\)

**Temperature and pressure dependence**

![Figure 5 Schematic illustration of the pressure enhanced bond energy. The integration area is the energy pumped in the crystal that enhances the bond energy, under the conditions of bond number unchanged.\(^{64}\)](image)

In the case of nanosolids under externally applied pressure and temperature, the perturbation to the bond length and bond energy can be expressed as,

\[
d(z_i, T, P) = \prod (1 + \Delta_{d_j})
\]

\[
d_0(1 + (z_i - 1))\left(1 + \int_0^T \alpha_i(t)dt\right)\left(1 + \int_0^P \beta_i(p)dp\right)
\]

\[
E_i(z_i, T, P) = E_0\left[1 + \sum \Delta_{E_j}\right]
\]

\[
= E_0\left[1 + (z_i - 1) - \int_0^T C_i(t)dt - \int_{\nu_s}^\nu p_i(\nu)d\nu\right]
\]

where the subscript \(j\) denotes the component of \(T, P\) and \(z_i\). \(\alpha, \beta, C\) are the thermal expansion coefficient, compression coefficient and the specific heat per bond. Physically, the external pressure would enhance the unit-cell distortion energy. So, the \(\Delta_{E_p}\) can be expressed as the integral area of \(V_0\Delta S\) in the \(v-p\) state equation,
\[
\Delta_{EP} = - \int_{1}^{V/V_0} p(v)dx = \left[ \int_{0}^{P} vdp - VP \right]/V_0
\]

(22)

where \( p \) and \( V_0 \) are, respectively, the external pressure and the unit cell volume at zero pressure and zero temperature.

On the other hand, the pressure, temperature and size dependence of the cohesive energy of nanocrystals can be integrated based on the superposition principle of energy. It is clear to see that the external stimuli such pressure and temperature can be taken as the perturbations of the Hamiltonian.\(^{63}\) Following the consideration, the cohesive energy of a spherical nanoparticle under the condition of coupling stimuli of pressure and temperature is given by

\[
E_{coh}(K,P,T) = \sum_{i \leq 3} N_i \left( E_i + \Delta E_i^P + \Delta E_i^T \right) + \sum_{i \leq 3} N_i z_i E_i
\]

(23)

where \( E_{i0} \) and \( E_{b0} \) are the cohesive energy with and without the external stimuli.

From the above deductions, we can obtain the size-, temperature- and the pressure-dependent cohesive energy shown as follows,

\[
\frac{E_{coh}(K,P,T)}{E_{coh}(\infty,0,0)} = \left[ 1 + \sum_{i \leq 3} \gamma_i \left( z_i c_i^{m-1} - 1 \right) \right] \frac{\Delta E_b^P + \Delta E_b^T}{E_{b0}} + \sum_{i \leq 3} \gamma_i \left( z_i \frac{\Delta E_i^P + \Delta E_i^T}{E_{b0}} - 1 \right)
\]

(24)

If consider more independent parameters, \( x (= P, T, \text{ etc}) \), the cohesive energy can generalized in the form,

\[
\frac{E_{coh}(K,P,T)}{E_{coh}(\infty,0,0)} = \left[ 1 + \sum_{i \leq 3} \gamma_i \left( z_{ib} c_i^{m-1} - 1 \right) \right] \frac{\Delta E_b^x}{E_{b0}} + \sum_{i \leq 3} \gamma_i \left( z_{ib} \frac{\sum^x \Delta E_i^x}{\sum^x \Delta E_b^x} - 1 \right)
\]

(25)

Where, \( z_{ib} = z_i / z_b \); \( z_i \) and \( z_b \) are the CN of atoms in \( ith \) atomic layer and the bulk, respectively. The first part represents the effect of size and the second part the joint effect of pressure and temperature on the atomic cohesive energy. As a first order approximation, we assume the same elastic thermal energy of the individual bond in the surface shell to those in the core interior,
atomic cohesive energy change is,

\[
\frac{\Delta E_{coh}(K, p, T)}{E_{coh}(\infty, 0, 0)} = \sum_{i\leq 3} \gamma_i \left( z_{ib} c_{i-m} - 1 \right) + \frac{\Delta E_p + \Delta E_T}{E_0} \tag{26}
\]

Considering the local bond average, the cohesive energy per bond as the size, temperature and pressure dependence, on which the band gap and the core level shift depend. Therefore, we can calculate the band gap expansion or the core level shift of nanostructures as a function of size, temperature and pressure using the master equation,

\[
\frac{\Delta E_C(K, p, T)}{E_C(\infty, 0, 0)} = \left( z \right) \left[ \sum_{i\leq 3} \gamma_i \left( z_{ib} c_{i-m} - 1 \right) + \frac{\Delta E_p + \Delta E_T}{E_0} + 1 \right]^{-1} \tag{27}
\]

where \( \langle z \rangle \) being the average atomic CNs that can be obtained using the core-shell configuration,\(^6^3\)

\[
\langle z \rangle = z_b \left[ 1 + \sum_{i\leq 3} \gamma_i (z_{ib} - 1) \right]
\]

**Summary**

For a given specimen, the bond nature and the total number of bonds do not change before the phase transition takes place. However, the bond length and bond strength will respond to the external stimulus such as coordination environment, temperature, and pressure. Therefore, we can focus on the representative bonds or their average to approach the behavior of the entire specimen. Using this approach of local bond average, we are free from considering the concepts such as surface stress, surface energy, and the entropy, as implemented in the classical theories of thermodynamics.

If one could establish the functional dependence of a detectable quantity \( Q \) on atomic separation or its derivatives, the size dependence of the quantity \( Q \) is then certain. One can hence design a nanomaterial with desired functions based on such prediction. Physical quantities of a solid can be normally categorized as follows:

1) Quantities that are directly related to bond length, such as the mean lattice constant, atomic density, and binding energy.

2) Quantities that depend on the cohesive energy per discrete atom, \( E_{B,i} = z_i E_i \), such as self-organization growth, thermal stability, Coulomb blockade, critical temperature for liquidation, evaporation and phase transition of a nanosolid and the activation energy for atomic dislocation, diffusion, and bond unfolding.\(^6^5\)

3) Properties that vary with the binding energy density in the relaxed continuum region such as the Hamiltonian that determines the entire band structure and related properties such as band-gap, core-level energy, photoabsorption and photoemission.

4) Properties that are contributed from the joint effect of the binding energy density and atomic cohesive energy such as mechanical strength, Young’s modulus, surface energy, surface stress, extensibility and compressibility of a nanosolid, as well as the magnetic performance of a ferromagnetic nanosolid.

Using the scaling relation and the BOLS correlation, we may derive solutions to predict the size and shape dependence of various properties. Typical samples are given in Table 2 and Figure 6, 7 and 8.
Table 2 Summary of functional dependence of various quantities on particle size and derived information.

<table>
<thead>
<tr>
<th>Quantity Q</th>
<th>[ \Delta Q(K_j)/Q(\infty) = \Delta_q(K_j) ]</th>
<th>Ref</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant (d)</td>
<td>( \sum_{i=3} \gamma_q(c_i - 1) )</td>
<td>45</td>
<td>Only outermost three atomic layers contribute</td>
</tr>
<tr>
<td>Bond energy ((E_i)) Band gap ((E_G)) Core-level shift ((\Delta E_o))</td>
<td>( \sum_{i=3} \gamma_q(c_i^{-m} - 1) = \Delta_H )</td>
<td>35,9</td>
<td>( \Delta_H ) - Hamiltonian perturbation</td>
</tr>
<tr>
<td>Electron-phonon coupling energy (Stokes shift, (W))</td>
<td>( B \sum_{i=3} \gamma_q(c_i^2 - 1) = B\Delta_{\epsilon - p} )</td>
<td>63</td>
<td>B-constant</td>
</tr>
<tr>
<td>Photoemission and photoabsorption energy ((E_{PL}, E_{PA}))</td>
<td>( \Delta_H \mp B\Delta_{\epsilon - p} )</td>
<td>63</td>
<td>( E_G = \frac{(E_{PA} + E_{PL})}{2} )</td>
</tr>
<tr>
<td>Critical temperature for phase transition ((T_C)); activation energy for thermally and mechanically activated processes</td>
<td>[ \begin{aligned} \sum_{i} \gamma_q(z_a c_i^{-1} - 1) = \Delta_a \ \sum_{i} \gamma_q(-\frac{V_{\text{vac}}}{V_c}) + \Delta_a = \Delta_{\text{corr}} \end{aligned} ] (Ferromagnetic) (else)</td>
<td>50</td>
<td>( \Delta_B ) - Atomic cohesive perturbation ( V_{\text{vac}} ) - volume loss ( V_C ) - correlation volume.</td>
</tr>
<tr>
<td>Mechanical modulus and Young’s modulus of monatomic bond ((P, Y))</td>
<td>( \frac{\eta_1 d^3(T_{mi} - T)}{\eta_0 d^3(T_{m(\infty)} - T)} - 1 )</td>
<td>66</td>
<td>( \eta_1 ) - specific heat per bond ( T_m ) – melting point</td>
</tr>
<tr>
<td>Inverse Hall-Petch relation; solid-semisolid-liquid transition</td>
<td>( \frac{\eta_1(K_j)^3(T_{j} - T)}{\eta_0 d^3 \left( \frac{K_j}{T_{m(\infty)} - T} \right)} - 1 )</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>Optical phonon frequency ((\omega))</td>
<td>( \sum_{i} \gamma_q(z_a c_i^{-m/2 + 1} - 1) )</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Fermi level</td>
<td>( \sum_{i} \gamma_q(c_i^{-2/3} - 1) )</td>
<td>68,</td>
<td></td>
</tr>
<tr>
<td>Dielectric permittivity ((\chi = \varepsilon - 1))</td>
<td>( \Delta_d - (\Delta_H - B\Delta_{\epsilon - p}) )</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6 Comparison of BOLS predictions with measured size dependence of
a) Lattice contraction of Pr$_2$O$_3$ films on Si substrate.\textsuperscript{71}
b) Atomic cohesive energy of Mo and W.\textsuperscript{72}
c) Mechanical strength (Inverse hall-Patch relationship, IHPR) of TiO$_2$\textsuperscript{73} nanosolids; Straight line is the traditional Hall-Petch relationship (HPR).
d) $T_m$ suppression of Bi\textsuperscript{74, 75, 76, 77, 78} and CdS,\textsuperscript{79} and

e) $T_c$ suppression of ferromagnetic Fe$_3$O$_4$ nanosolids;\textsuperscript{80}
f) $T_c$ suppression of ferroelectric PbTiO$_3$,\textsuperscript{81} SrBi$_2$Ta$_2$O$_9$,\textsuperscript{82} BaTiO$_3$,\textsuperscript{83} and anti-ferroelectric PbZrO$_3$\textsuperscript{84} nanosolids. High order CN reduction is considered for dipole-dipole interaction.
Figure 7  Comparison of BOLS predictions with measured size dependence of
a) $E_G$-expansion measured using STS $^{85}$ and optical method, Data –1 ($E_G = E_{PA} - W$), $^{86}$ Data –2 ($E_G = (E_{PL} + E_{PA})/2$) $^{87}$
b) Core level shift of Au caped with Thiol $^{88}$ and deposited on Octan $^{89}$ shows three-dimensional features while core level shift of Au deposited on TiO$_2$ $^{90}$ and Pt $^{91}$ show one-dimensional pattern.
c) Raman acoustic frequency shift of TiO$_2$-a and TiO$_2$-b $^{92}$ SnO$_2$-a $^{93}$ nanostructures due to interparticle interaction.
d) Raman optical frequency shift of CeO$_2$, $^{94}$ SnO$_2$-1, $^{95}$ SnO$_2$-2, $^{93}$ InP, $^{96}$ and

e) Dielectric suppression of nanosolid silicon with Data 1, 2, and 3; $^{97}$ Data 4 and 5; $^{98}$ and Data–6. $^{99}$
f) Temperature and size dependence of magnetization.
Figure 8 Theoretical reproduction of
(a) Temperature dependence of the thermal expansion coefficient\(^{100}\) of AlN,\(^{101}\) GaN\(^{102,103}\) and Si\(_3\)N\(_4\).\(^{101}\)
(b) Size and pressure dependence of the phase transition at room temperature of CdSe nanocrystals.\(^{104,105}\)
(c) Pressure dependence of the Raman shift of the E\(_1\)(LO) and E\(_2\)(high) modes of AlN.\(^{106,107}\)
(d) Size and pressure induced blue shift of the photoluminescence energy of CdSe nanocrystals.\(^{64,108,109}\)
(e) Temperature dependence of the Raman shift of Si\(^{110,111,112,113}\)
(f) Temperature dependence of the elastic modulus of Si\(^{110,114}\)
The impact of the often-overlooked effect of atomic CN reduction is tremendously propounding, which unifies the performance of a point defect, a surface, a nanosolid and a solid in amorphous state consistently in terms of broken-bond-induced local strain and the associated skin-depth charge and energy quantum trapping. The unusual behavior of a surface and a nanosolid has been consistently understood and systematically formulated as functions of atomic CN reduction and its derivatives on the atomic trapping potential, crystal binding intensity, and electron-phonon coupling. The properties include the lattice contraction (nanosolid densification and surface relaxation), mechanical strength (resistance to both elastic and plastic deformation), thermal stability (phase transition, liquid-solid transition, and evaporation), and lattice vibration (acoustic and optical phonons). They also cover photon emission and absorption (blue shift), electronic structures (core level disposition and work function modulation), magnetic modulation, dielectric suppression, and activation energies for atomic dislocation, diffusion, and chemical reaction. Structural miniaturization has given indeed a new freedom that allows us to tune the physical properties that are initially non-variable for the bulk chunks by simply changing the shape and size to make use of the effect of atomic CN reduction.

Using the approach of local bond average, we can connect directly the physical quantities of a specimen to the bonding identities (nature, order, length and strength) and their response to the external stimuli to avoid using the continuum thermodynamics to deal with the pressure and temperature effect on the physical properties. The advantage of using this approach is that we are able to derive quantitative information of atomic bonding energy, which is beyond the scope of existing approaches. The LBA may complement the difficulties of both the quantum and continuum approaches in the low-dimensional systems.

It is necessary to point out that the shorter and stronger bonds between undercoordinated atoms perturb the atomic cohesive energy and the Hamiltonian. The former defines the thermal stability and the activation energy of dislocation and diffusion and the latter defines the entire band structure including the dispersion relation the allowed states. However, the actual occupation of the allowed states by those relating to nonbonding electrons is quite another, as the nonbonding states of the lone pairs, unpaired electrons and the andibonding dipoles neither contribute significantly to the Hamiltonian nor follow the regular dispersion relation but they add states in the mid gap or in the vicinity of Fermi energy. Further study on the impact of nonbonding states would be even more fascinating and rewarding than dealing with the core and valence electrons alone. It would be more effective to consider the low-dimensional systems in terms of bond and nonbond formation, dissociation, relaxation and vibration and the associated dynamics and energetics of charge
repopulation, polarization, localization and densification. Grasping with the factors controlling the process of bond making, breaking and relaxing would be more interesting and rewarding.

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Size Effect and Shape Stability of Nanoparticles

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Keywords: Nanostructures; geometrical characteristics; shape stability; clusters; crystallography; metallic particles; transmission electron microscopy (TEM).

Abstract. Nanoparticle research disciplines—chemical synthesis, applied physics and devices based on their physical-chemical properties, and computational physics—have been very active fields for the last 15 years or so, because of the potential and current applications in medicine, catalysis, energy storage, environment and electronics applications. This wide spectrum of disciplines and their applications keep metallic nanoparticles as one of the most promising nanostructures and their research as one of the cornerstones of nanotechnology. In this contribution we present a comprehensive and extended geometrical description for the most common shapes and structures for metallic nanoparticles, as well as experimental results for these geometries with some variations given by truncations.

Introduction

All Nanotechnology is a leading interdisciplinary science that is emerging as a distinctive field of research. Its advances and applications will result in technical capabilities that will allow the development of novel nanomaterials with applications that will revolutionize the industry in many areas [1,2]. It is now well established that dimensionality plays a critical role in determining the properties of materials and its study has produced important results in chemistry and physics [3]. Nanoparticles are one of the cornerstones of nanotechnology. Indeed, even when the research on this field has been going on for a long time, many present and future applications are based on nanoparticles. For instance, the electron tunneling through quantum dots has led to the possibility of fabricating single electron transistors [4-9]. One concept particularly appealing is a new three-dimensional periodic table based on the possibility of generating artificial atoms from clusters of all the elements [10]. This idea is based on the fact that several properties of nanoparticles show large fluctuations, which can be interpreted as electronic or shell closing properties with the appearance of magic numbers. Therefore, it is conceivable to tailor artificial super-atoms with given properties by controlling the number of shells on a nanoparticle. This idea is illustrated in Fig. 1.
The periodic table of the elements in 3D. The first dimension represents the knowledge about atoms, molecules and low dimensional systems (surfaces and clusters); the second dimension represents the well known bulk properties of the elements. The third dimension represents hierarchical systems based on nanostructures—clusters, nanostructures and arrays of so called super-atoms—with periodicity and crystal structure, with totally new, unexpected and relevant chemical and physical properties.

The development of nanotechnology can be approached from several directions; mesoscopic physics, microelectronics, materials nanotechnology and cluster science. The different fields are now coming together and a completely new area is emerging [11,12]. Figure 2 illustrates how the different approaches are converging; it exhibits the domains of clusters and nanoparticles with different structures that result from an increase on the number of atoms. The different possible structures include nanorods, nanoparticles, fullerenes, nanotubes, and layered materials.

One of the most remarkable advances in this field has been the synthesis of ligand-capped metallic clusters. In a seminal contribution Brust et al.[13] used the classical two-phase Faraday colloid separation combined with contemporary phase transfer chemistry to produce small gold nanoclusters coated with alkanethiolate monolayers. Several groups have pursued this technique [14-21] and introduced improvements and modifications to the original technique it has to be mentioned Whetten and his group [15,16] for important contributions in this field.

A significant property of ligand-capped clusters is that they can be repeatedly isolated from and re-dissolved in common organic solvents without irreversible aggregation or decomposition. The properties of the monolayer-protected nanoparticles (MPNs and MPANs) allow handling in ways that are familiar to the molecular chemist since they are stable in air conditions. MPN of some metals such as Pt [22], Ag [23], Rh and Pd [24] have been synthesized.
Geometric considerations

Clusters and nanoparticles. Since pioneering work of Ino and Ogawa [25,26] it was clear that in most cases the structure of nanoparticles can not be described by the bulk crystallography of the used material. The concept of multiple twins was used to explain many of these structures at the nanoscale, such as the icosahedron and the decahedron. This concept was directly imported from the macroscopic metallurgical studies and was certainly very useful for a first understanding of the structure of nanoparticles. Another related research field was the study of clusters formed by few atoms. From that field we learned that atomic structures are made by shells and the concept of magic number was introduced [27]. Nanoparticles are referred to particle sizes of ~5-100 nm and clusters are referred to sizes ~1 nm. In recent times the computational tools for study clusters allow the analysis of a large number of atoms and the methods to study nanoparticles allow interrogating smaller nanoparticles. The two fields are merging in one and in this paper we will use the term particle and cluster indistinctly.

Clusters with cubic symmetry. When considering atom clusters of nanometric dimensions, they can be classified into a corresponding symmetry point groups, mainly tetrahedral (T₈), octahedral (O₁₆), decahedral (D₅₀) and icosahedral (I₅₅). In previous works, small clusters (up to tens of atoms) of diverse forms: tetrahedron, hexahedron, octahedron, decahedron, dodecahedron, trigonal, trigonal prism and hexagonal antiprism (with and without a central site) have already been studied [28]. Partially and totally capped clusters were also considered (clusters to which a site has been added to each face of the polyhedron, equidistant to every site of the face), in order to vary the number of sites for all the polyhedrons and thus allowing the comparison as a function of the number of sites.

Geometric characteristics of the clusters formed by concentric layers can be considered as formed by equivalent sites: sites located at the same distance from origin, which occupy the same geometric place and have the same environment, i.e., the same number and type of neighbors. These layers can arrange in such a way that they group in shells forming clusters of different sizes, retaining the original geometric structure. The number of shells in the cluster is called the order of the cluster and is represented by the greek letter ν. The studied structures were the icosahedron (ICO), the face-centered cubic structure, fcc (the cubo-octahedron, CO); and simple cubic, sc [29]. In order to determine the stability of the structures from an energetic point of view, a study of the cubo-octahedral and icosahedral structure was performed using the embedded atom method (EAM) for the transition metals Cu, Pd, Ag, and Ni [29]. It was determined that for sizes smaller than 2000 atoms, the icosahedron is the most stable structure, and for larger sizes, the cubo-octahedron.
For this study, the advantage of having equivalent sites in the clusters was used to reduce computation time. In a latter study, based upon the same metals, small clusters of less than 100 atoms with regular polyhedron geometries were used, and to change the cluster size, partially and totally capped clusters were considered. Tetrahedral clusters showed the highest stability for sizes of less than 18 atoms, and icosahedra for larger sizes [31].

In this work, the structural stability competition among different regular structures of the concentric shell type is searched. The studied geometries consider also some other arrays of the layers in shells, which give raise to other geometries. The \textit{fcc} structure considers many structures, which are divided in two groups: a) with a central site, and b) without a central site. Among the centered ones, the cubo-octahedron (CO), octahedron (c-O) and truncated octahedron (ct-O) are considered. For the ones not centered, the octahedron (s-O) and the truncated octahedron (st-O) are considered.

**Geometric characterization.** The following procedure was used to determine the geometric characteristics of the structures: a) Identify the structures or their geometric shape; b) the nature of the site coordinates which conform the structures; c) their neighbors with surrounding layers, in order to identify the equivalent sites and generate the concentric shell type structures. Once this previous stage is completed, the geometric properties to be determined are defined, the structures are presented and the geometric properties of each structure are numbered. Afterwards, based on the geometric characteristics of each structure, the analytic expressions are deducted in function only of the cluster order for the defined properties.

An example of the concentric shell type structures (onion-like) is shown in Fig. 3, which presents the cubo-octahedron in three different sizes. In this figure, a central site surrounded by 12 sites forming a CO with one first shell can be seen, Fig. 3a. Then it is covered with another shell of sites distributed in three layers of equivalent sites, as will be seen later, but retaining the original geometric shape, Fig. 3b. And finally, Fig. 3c presents a three-shell cubo-octahedron.

The structure considered in Fig. 4a is the face-centered cubic \textit{fcc}. Although it does not seem to be cubic, joining 8 units or 27 it gives place to the \textit{fcc} structures in Figs. 4b and 4c, respectively. The structure in Fig. 4b has a central site, \textit{fccc}, and the ones in Figs. 4a and 4c do not have, so they are going to be referred as \textit{fccs}. They have a cubic shape: 8 vertices, 6 square faces and 12 edges.

From Fig. 4a it is evident that it is a completely capped octahedron, then truncating each one of the structures in a certain direction, non-cubic structures are obtained. They present besides vertices (V), edges (E) and square faces (S); faces of different shapes: triangular face (T) and hexagonal face (H). Therefore, the resulting structures are: the cubo-octahedron (CO, Fig. 3), the octahedron (c-O, Fig. 4d) and the truncated octahedron (ct-O, Fig. 4e).

Table 1 presents the number of characteristic sites of each structure. The information is presented in such a way that for each structure, \textit{V} represents the vertices attached by \textit{E} edges forming \textit{X} faces of different types, where \textit{X=\{S, T, H\}}, as it corresponds. The icosahedron is included (Fig. 4f), because it can be obtained by an adequate distortion of the CO, and it is useful as a reference for comparison of results. Both ICO and CO structures present a central site. Some octahedra and truncated octahedra may also present central site.
Figure 4. Structures a) face-centered cubic, fcc; b) face-centered cubic with central site, fccc; and c) face-centered cubic without central site, fccs. Polyhedra resulting from truncation of fcc structures. d) octahedron and e) truncated octahedron. f) as a result of an adequate distortion of the cubo-octahedron, the icosahedron is obtained.

<table>
<thead>
<tr>
<th></th>
<th>V</th>
<th>E</th>
<th>S</th>
<th>T</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>fcc</td>
<td>8</td>
<td>12</td>
<td>6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cubo-octahedra</td>
<td>12</td>
<td>24</td>
<td>6</td>
<td>8</td>
<td>—</td>
</tr>
<tr>
<td>Octahedra</td>
<td>6</td>
<td>12</td>
<td>—</td>
<td>8</td>
<td>—</td>
</tr>
<tr>
<td>Truncated octahedra</td>
<td>24</td>
<td>36</td>
<td>6</td>
<td>—</td>
<td>8</td>
</tr>
<tr>
<td>Icosahedra</td>
<td>12</td>
<td>30</td>
<td>—</td>
<td>20</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 1. Number of geometric sites corresponding to the structures of the first column, all with a central site.

**First neighbors.** There will be different types of equivalent sites, depending on the geometric structure, and each type will occupy a geometric position which will be of type vertex (V), edge (E), square face (S), triangular face (T) and hexagonal face (H), and it will have a total number of neighbors, coordination \( z \), which will correspond to the structure, but the number of neighbors with layers of its same shell, with interior and exterior shells will be characteristic of each site. Table 2 presents the different types of sites in the studied structures, as well as the number of first neighbors with layers of interior shells (\( \downarrow \)), in the same shell (\( \forall \)), and with exterior shells (\( \uparrow \)). Also, total coordination \( z \) in the structure is presented. The truncated octahedron with a central site (ct-O) presents two types of edges, the edges between squared and hexagonal faces, ES, with coordination (2, 5, 5), and the edges between hexagonal faces, EH, with coordination (1, 6, 5), not in the table, while all the other structures have only one.

**Definition of geometric properties.** The geometric characteristics to be considered here are the number of atoms in a given site \( N_X \), with \( X = V, T, S, \) and \( E \); the total number of atoms \( N \) in a cluster of order \( v \); the number of atoms in a crust or on the surface \( N_\sigma \), and the dispersion \( D \), defined as the rate of the surface atoms to the total number of atoms, \( N_\sigma/N \). These properties can be expressed analytically as a function of only the order of the cluster \( v \), for each structure or geometric array, and only \( N_\sigma \) and \( N \) are presented in Table 5.

**fcc structure**

A face-centered cubic structure, fcc is that in which the unit cell is a cube with sites in the vertices and in the center of squared faces, this means that there are 14 sites on a cube, 8 vertices and 6 squared faces (see Fig. 4a). Also, it can be seen as a completely capped octahedron. When attaching many of these arrays with common or shared sites in faces and vertices, clusters are obtained with
sites in vertices, edges and squared faces. The origin of coordinates can be chosen to be at the center of the cube or on a vertex, obtaining structures with and without a central site respectively.

<table>
<thead>
<tr>
<th>Faces</th>
<th>S</th>
<th>T</th>
<th>H</th>
<th>E</th>
<th>V</th>
<th>z</th>
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<tr>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
<td>$\uparrow$</td>
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<tr>
<td>$\sqrt{3}$</td>
<td>$\Box$</td>
<td>$\triangle$</td>
<td>$H$</td>
<td>$\setminus$</td>
<td>$\bullet$</td>
<td></td>
</tr>
<tr>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
<td>$\downarrow$</td>
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<td></td>
</tr>
</tbody>
</table>

| Octahedra          | 6 | 6 | 4 | 12 |
|                    | 3 | 1 | 0 |    |
| Truncated octahedra| 4 | 6 | 5 | 5  | 12 |
|                    | 4 | 3 | 2 | 1  |    |
| Cubo-octahedra     | 4 | 6 | 5 | 4  | 12 |
|                    | 4 | 3 | 2 | 1  |    |
| Icosahedra         | 6 | 6 | 5 | 12 |
|                    | 3 | 2 | 1 |    |

Table 2. Number of first neighbors with shell on external layers $\uparrow$ (internal $\downarrow$) and with shells on the same layer $\sqrt{3}$, for the different types of sites of the structures fcc and icosahedral. The total coordination $z$ is given by ($\uparrow$) + ($\downarrow$) + ($\sqrt{3}$).

Figure 5. The successive truncations of a octahedron with a central site (a), (b) first truncation, (c) second truncation, (d) third truncation and (d) last truncation that gives place to a cubo-octahedron.

Truncating the fcc structure in the (111) direction the octahedron is obtained, Fig. 4d, and truncating the octahedron in the (100) direction (by the vertices), the truncated octahedron is obtained, Fig. 4e. The octahedron has 6 vertices (V), 12 edges (E) and 8 triangular faces (T), Fig. 5a. It is an onion-like structure and there are two types of these structures: with even and odd number of sites in the edge. The odd number type is with a central site (c-O). The geometric
characteristics for the octahedron with and without a central site are listed on Table 3, the first column, $N_V$, is common to both structures. From this table, the general expressions of the geometric characteristics for the octahedron with (c-O) and without (s-O) a central site can be deducted and are presented in Table 5.

The successive truncations of a octahedron with a central site is presented in Fig. 5. It is observed that the last truncation gives place to a cubo-octahedron while the truncation of a octahedron without a central site does not. Also, this series is not an onion-like structure. Each one of the truncation made to the octahedron present different shapes, therefore there is not a unique onion-like structure for the truncated octahedron. In Fig. 6 the family of the first truncation for various octahedra is presented, but this is not an onion-like structure. On the other hand, in Fig. 7 an onion-like structure is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different octahedra is presented, but this is not an onion-like structure. In Fig. 6 the family of the first truncation for various octahedra is presented, they correspond to two truncations before the last truncation of different...
octahedron without a central site, the common characteristic is that the edge among hexagonal faces has 6 sites. Then for each type of truncation exists a table of geometrical characteristics.

<table>
<thead>
<tr>
<th>v</th>
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<th>NE</th>
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<td>216</td>
<td>720</td>
<td>270</td>
<td>1002</td>
<td>3871</td>
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</table>

Table 4. Geometric characteristics for the cubo-octahedra and icosahedra.

![Figure 8. Cubo-octahedron of a) order 1 of 13 sites, b) order 2 of 55 sites, c) order 3 of 147 sites, and d) order 6 of 923 sites. Observe the distortion of CO d) to obtain e) icosahedron of order 6 of 923 sites.](image)

**Cubo-octahedron.** The cubo-octahedron (CO) can be obtained by the complete truncation of a fcc structure with a central site in direction (111), as is shown in Fig. 5e. In Fig. 8b a cubo-octahedron of 55 sites is presented, and is the result of removing the 8 corners of a cube of 63 sites. It is formed by 8 triangular faces and 6 squared ones, attached by 24 edges and 12 vertices, see Table 1. Consequently, the surface sites are localized in squared faces (S), triangular faces (T), edges (E) and vertices (V). The CO of order 1 has a central site and a first shell with one single layer of 12 vertices, Fig. 8a. The CO of order 2 is formed by adding one shell formed by 42 sites in order to complete 55 sites (Fig. 8b), distributed in three layers: one layer of 6 S sites, another of 24 E sites and a third one of 12 V sites. When adding a third shell of 92 sites, the third order CO of 147 sites is completed (Fig. 8c), the sites are distributed in four layers: one of 24 S sites, another of 8 T sites, one more of 48 E sites and a fourth one of 12 V sites. Successively, complete shells are added in this way, forming clusters of order v.

The number of neighbors for each site can be found in Table 2, the geometric characteristics are enumerated in Table 4 and from this table it is possible to obtain the general expressions for the geometric characteristics of the cubo-octahedron which are presented in Table 5.

Figure 8e presents an icosahedron of 923 sites of order 6. When comparing with the CO, which has the same number of sites, from Fig. 8d it can be observed the distortion made to obtain the ICO. Table 2 has the number of neighbors for each site, and Table 4 reproduces the geometric characteristics corresponding to the icosahedron, which have been reported previously [29]. A great similarity can be noticed between cubo-octahedra and icosahedra, the number of vertices, \( N_v \), the number of surface atoms, \( N_s \), and the total number of atoms, \( N \), is the same. Then the general expressions for the geometric characteristics in Table 5 are the same for both structures.
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### Energy stability of nanoparticles through the embedded atom method scheme.

The Embedded Atom Method is applied, in the Foiles version [32] using the parameters for copper, to fcc clusters with and without a central site, in order to calculate the cohesion energy per atom, determining in this way the stability of the clusters. The results are compared with the ones from the icosahedra and cubo-octahedra previously reported [30]. Figure 9 presents the results for cohesive energy as a function of \( N^{1/3} \) for the octahedron and truncated octahedron clusters, for sizes from 300 to 3400 atoms. From Fig. 9 it can be seen that the truncated octahedra with a central site (\( \Delta \)) have higher stability than the icosahedra (\( \bullet \)) and cubo-octahedra (\( \Box \)), while the octahedra with a central site (\( \Diamond \)) present stability until sizes larger than 900 atoms. The truncated octahedra without a central site (\( \triangleleft \)) as well as the octahedra without a central site (\( \nabla \)) compete in stability with the icosahedra (\( \bullet \)) and cubo-octahedra (\( \Box \)). Further more, the truncated octahedra without a central site show a higher stability than the octahedra.

### Clusters and nanoparticles with pentagonal symmetry \((D_h \ & \ I_h)\)

**Introduction.** A cluster is defined as an aggregate of atoms; this can lead to clusters from 2 atoms (diatomic molecules), a lineal array of atoms, bidimensional or three-dimensional arrays. This part presents the study of clusters with pentagonal symmetry, with sizes up to thousands of atoms in arrays of spherical or concentric layers type.

Arrays of linked atoms forming three-dimensional clusters are considered here as sites in geometric positions attached by the edges in such a way that faces of diverse forms are generated (triangular, squared, rombohedral, etc.). Distance between the sites is considered as the distance to first neighbors, \( d_{NN} \), which is normalized to one. There could be sites in the vertices, edges and faces, either in the surface or internals; also there could be different types of sites, depending on its position and the number and type of neighbors in the geometric array. There could be also equivalent sites, which present the same geometric characteristics: to the same distance from the center of the geometric array, in the same type of site and with the same number and type of neighbors.

<table>
<thead>
<tr>
<th></th>
<th>( N )</th>
<th>( N_S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO, ICO</td>
<td>( 10/3 \nu^3 + 5\nu^2 + 11/3 \nu + 1 )</td>
<td>( 10 \nu^2 + 2 )</td>
</tr>
<tr>
<td>c-O</td>
<td>( 16/3 \nu^3 + 8\nu^2 + 14/3 \nu + 1 )</td>
<td>( 16 \nu^2 - 48\nu + 2 )</td>
</tr>
<tr>
<td>s-O</td>
<td>( 16/3 \nu^3 + 2/3 \nu )</td>
<td>( 16 \nu^2 - 16\nu + 6 )</td>
</tr>
</tbody>
</table>

Table 5. Particular expressions of the geometric characteristics for the icosahedra and fcc with and without a central site structures.
Figure 9. Cohesive energy per atom as a function of the cubic root of the number of atoms in the cluster, for the icosahedra, and fcc with and without a central site type clusters.

Figure 10. Decahedral polyhedra, a) bicapped hexahedron or decahedron of 7 atoms of order 1, without a central site; b) Decahedron of 23 atoms of order 1 with a central site; c) Decahedron of 835 sites of order 5, without a central site and d) Decahedron of $N = 1111$ atoms of order 5 with a central site.

From the bicaped hexahedron or decahedron, Fig. 10a, pentagonal symmetry structures can be obtained. Among the clusters with structures of pentagonal symmetry the following structures are considered: decahedra with ($c$-$D_{h}$) and without ($s$-$D_{h}$) a central site, pentadecahedra, truncated decahedra (Marks decahedra) $m$-$D_{h}$, and modified and developed decahedra.

**Decahedra ($D_{h}$).** Decahedra are obtained from the bicapped hexahedra and also from attaching two pentagonal based pyramids from their bases and sharing their sites (which form the equator of the cluster), yielding geometrical bodies of seven vertices (2 at poles and 5 at equator), 15 edges (all from the same length, 5 at the equator) and 10 triangular equilateral faces, 5 of them converge on each pole and by pairs they form the edges of the equator. Decahedra can be without a central site, Figs. 10a and 10c, and with a central site, Figs. 10b and 10d, without losing the decahedral form. So, decahedra have the vertices at the poles, VP, vertices at the equator, VE, at the edges over the equator, EE, edges at poles, EP, and triangular faces T. It has to be noticed that the coordination, i.e., distribution of the first neighbors (NN) is what makes the difference in each type of sites, although total coordination is the same for all the sites of the corresponding cluster. Table 6 presents the coordination of each site, for example the poles (VP) have 5 first neighbors (NN) with sites at their same shell, 1 NN towards the inner shell and 6 towards the exterior shell. The decahedron of order 1, without a central site, Fig. 10a, has only 7 vertices in two layers; the one from order 2, is obtained from covering that of order one with a shell of 47 sites distributed as
Table 6. Coordination or number of first neighbors (NN), of the different types of sites in the decahedron and the pentadecahedron with sites in shells in external, the same and internal shells.

Table 7. Geometrical characteristics for the decahedra with and without a central site. The parameter \( v \) is the order of the cluster, \( N_i \) with \( i = T, E \) and \( V \), is the number of sites \( i \). The number of sites in the cap, \( N_{cap} \), the number of surface sites, \( N_o \), and \( N \) is the total number of sites in the cluster.

follows: 7 V sites of two types, 30 E sites in three layers (10 sites of one type at the equator) and 10 at triangular faces (sites T, one for each triangular face) in one single layer, for a total of 54 sites in the cluster. Decahedra of superior order are formed by coverage of this cluster of order two with successive shells of many layers each one.

The decahedron with central site of order 1, Fig. 10b, has 15 sites E, one per edge, of two types, 5 sites of one type at the equator, and 7 sites V, giving a total number of 22 sites and the central one in five layers. The cluster of second order results from the cluster of order one, covered by a shell of 82 sites distributed in 8 layers; 45 E sites in 5 layers, 30 T sites in one single layer and 7 V sites in two layers, for a total of 105 sites in the cluster, and so on for cluster of superior order.

Table 7 presents the geometric characteristics of decahedra with and without a central site. First column, common for all decahedra, lists the cluster order \( v \). This is followed by two groups of 9 columns each one, which correspond to the decahedron with and without a central site. The three first columns of each group list the number of sites on each type of site in the cluster, triangular face (T), \( N_T \), edge (E), \( N_E \), and vertex (V) \( N_V \). The next column shows the number of sites that form a cap of the decahedron; a cap is formed for the surface sites from the equator to the poles, which will be needed afterwards. Finally, the two last columns of each group represent the number of sites in the shell, \( N_o \), and the total of sites in the cluster, \( N \). Decahedra with (without) a central site, have an odd (even) number of sites per edge.
From Table 7 it is observed that for both decahedron types the number of vertices per shell is 7, two of type VP and five of type VE. The dependence with the cluster order of \( N_o \) and \( N \) is expressed in the following relations for the decahedra with a central site,

\[
N_o(\nu) = 20\nu^2 + 2, \quad (1)
\]
\[
N(\nu) = 20/3\nu^3 + 10\nu^2 + 16/3 \nu + 1, \quad (2)
\]
and for decahedra without a central site:

\[
N_o(\nu) = 20\nu^2 - 20 \nu + 7, \quad (3)
\]
\[
N(\nu) = 20/3\nu^3 + 1/3\nu. \quad (4)
\]

**Pentadecahedra.** The cap, defined below, or several caps are added to the decahedron to form the pentadecahedra, Fig. 11. This is, a decahedron with a wide waist or developed decahedron.

The pentadecahedra are polyhedra of 12 vertices (2 poles and 10 in vertices at the waist), 25 edges (10 from the poles to the waist, 10 at the waist and 5 of other type, which join the vertices of the two pyramids, and whose length depends on the number of caps added), 10 equilateral triangular faces and 5 rectangular lateral faces (or squared, depending on the number of intermediate layers added) Fig. 11. The number of sites in these pentadecahedra depends on the size of the original decahedron and of how many caps are added, also, with and without central site are considered depending on the original decahedron from which they were generated. So, at the surface of the pentadecahedra there are the same type and number of sites as in the decahedra, plus the waist sites, which are divided in sites type VE, sites EE, sites at vertical edges at the width of the waist, EV and in rectangular faces, RF. Table 6 presents the coordination of each type of site in the pentadecahedron. Notice that, as expected, only the sites corresponding to the pentadecahedron are added and not for those of the decahedron.

For pentadecahedron order it can be used \( v \mu, v \) for the decahedron order which it comes from and \( \mu \) for the number of layers at the waist, so, regular decahedra would be pentadecahedra with \( \mu =1 \). The number of caps which are added to the decahedron referred to generate the pentadecahedron is \( \mu -1 \). So, in order to have the pentadecahedron of order 65 without a central site, Fig. 11, that is a 2766-atom pentadecahedron one has to start with a decahedron without a central site of order 6, with 1442 atoms, and add four caps with 331 atoms each.
Table 8. Geometric characteristics for the pentadecahedra with and without a central site, obtained from the corresponding decahedron of order \( v \). The parameter \( \mu \) is the number of equatorial layers in the cluster. The number of EV sites, \( N_{EV} \), RF sites, \( N_{RF} \), of sites added, \( N_{ag} \), surface sites, \( N_{\sigma} \) and of total number of sites, \( N \), in the cluster of order \( v \mu \) are listed. Notice that for \( \mu = 1 \) values of Table 7 are obtained. Even when \( \mu \) can have any value higher than zero, here only some values are presented.

The number of sites T, EP and VP is the same as in the decahedron which originated the pentadecahedron. The number of sites EE and VE is duplicated respect to the original decahedron. The number of EV and RF sites for the pentadecahedra with and without a central site is the same, and are presented in Table 8, which presents the geometric characteristics of the pentadecahedra with and without a central site respectively, and only some of \( \mu \) values are presented. There are three groups: one of three columns and two of four columns respectively. In the columns of the first group, the quantities common to the two types of pentadecahedra are listed as: cluster order \( v \) and \( \mu \), and the number of sites EV, \( N_{EV} \). For both polyhedra, in each following group, the geometric characteristics for each polyhedron are presented, being those of the pentadecahedra with and without a central site. A list of the number of RF sites, \( N_{RF} \), the number of sites added, \( N_{ag} \), of sites at the surface, \( N_{\sigma} \) and the total of sites, \( N \), in the cluster of order \( v \mu \) are listed. Note that for \( \mu = 1 \) the values from Table 7 are obtained.

The analytical expressions for those numbers shown in Table 8, are for the number of sites which are added, the sites in the surface and the total number of sites for pentadecahedra with a central site

\[
N_{ag}(v,\mu) = (\mu - 1)(10v^2 + 5v + 1),
\]

\[
N_{\sigma}(v,\mu) = 20v^2 + 2 + 10v(\mu - 1),
\]

\[
N(v,\mu) = 20/3v^3 + 10v^2 + 16/3v + 1 + N_{ag}(v,\mu),
\]

and for pentadecahedra without central site

\[
N_{ag}(v,\mu) = (\mu - 1)(10v^2 - 5v + 1),
\]

\[
N_{\sigma}(v,\mu) = 20v^2 - 20v + 7 + 5(2v - 1)(\mu - 1),
\]

\[
N(v,\mu) = 20/3v^3 + v/3 + N_{ag}(v,\mu).
\]
Figure 12. Decahedron of order 4 with 609 sites and with a central site, with 360 sites aggregated for a mrdec of 969 sites. (b) mrdec decahedron with a central site of order 4 (609 sites), with surface reconstruction (969 sites) and three caps (181 sites each one) for a total of 1331 sites in the polyhedron, or pentadecahedron with surface reconstruction.

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<th>N</th>
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<td>1285</td>
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Table 9. Geometric characteristics for the mrdec, decahedra with and without a central site, modified with surface reconstruction. $\nu$ is the cluster order. The number of added sites, $N_{ag}$, of surface sites, $N_a$, and of total number of sites, $N$, in the cluster are listed.

It must be noticed that for $\mu = 2\nu + 1$ ($\mu = 2\nu$) in the decahedron with (without) a central site the Ino's decahedra are obtained.

**Modified decahedra with surface reconstruction.** The triangular faces in the decahedron are (111) type, as in a fcc structure the layers follow the sequence ...ABCABC..., i.e., a layer is equal to the three before one. Modification of surface reconstruction of a decahedron is obtained if for each triangular face of the decahedron a stacking fault is made, that is, a triangular face equal to the one before the last is added to the decahedron, following a sequence as ...ABCABA. Hereafter these polyhedra are called mrdec (Montejano's reconstructed decahedron)[33]. Figure 12a shows the example of a decahedron with a central site of 609 sites of order 4, to which 36 sites are added per face, this is 360 sites in total, for a mrdec of 969 sites. It should be noticed that it seems that a decahedron with a surface channel is obtained, although the sites which seem to form the channel are at a distance of 1.13 $d_{NN}$. This is why in this modification a long bond is considered and the EP sites of the interior decahedron do not form part of the surface. In fact, the surface of the resulting polyhedron is formed by the added sites and the sites VE, VP and EE of the internal decahedron, which are those which can be considered also as surface, because the remain with free bonds.

The characteristics of these polyhedra are presented in Table 9. The parameter $\nu$ is the original cluster order, $N_{ag}$ is the number of sites added, $N_a$ is the number of sites in the surface and $N$ is the total number of sites in the cluster.

From Table 9, is possible to obtain the analytic expressions as a function of the order of the original cluster, for the different characteristics listed here and are presented next for the polyhedron with central site:
The adequate elimination of sites is equivalent to eliminate the end sites of the edges which converge in the vertices of the equator of the corresponding decahedron. Notice that in each elimination the equatorial edges loose two sites, while the edges which converge also towards the poles only loose one, this causes that edges converging to the poles are larger than the equatorial ones, but shorter than the ones from the original decahedron.

**Truncated decahedra (Marks decahedra).** These structure results from the adequate elimination of some sites of a certain decahedron. The resulting geometry is a figure of 22 vertices (of three types), 40 edges (of 4 types, 15 from the original decahedron but shorter, and 25 which are generated by elimination of the adequate sites), 10 pentagonal faces (triangular faces from the original decahedron are converted to irregular pentagons) and 10 equilateral triangular faces (at the equator and joint by pairs), Fig. 13a.

The adequate elimination of sites is equivalent to eliminate the end sites of the edges which converge in the vertices of the equator of the corresponding decahedron. Notice that in each elimination the equatorial edges loose two sites, while the edges which converge also towards the poles only loose one, this causes that edges converging to the poles are larger than the equatorial ones, but shorter than the ones from the original decahedron.
The number of eliminated sites, third column of Table 11, is the same for the two polyhedra, 
the number of sites per equatorial edge are eliminated, and one of the rest 
of the edges, 20 sites that whit the previous stage are converted in 25. Third step, n=3, the step of 
the edges of the last shell is repeated, 20 sites, plus two sites of each triangular face, 20 sites, 
besides, in one shell before the last, interior decahedron, the equator vertices are eliminated, 5 more 
sites in order to obtain 40 sites to be eliminated in this step, and complete a total of 70 eliminated 
sites in three steps. And so on, for n<ν, because \( N_{EE} = \frac{5(2\nu-1)}{(2\nu-2)} \) for decahedra with 
[without] a central site, for ν=1, there are only 3 [2] sites EE (see Table 11).

Table 11 lists the truncated decahedron, resulting from decahedra with and without a central site respectively. The order of the truncated decahedron consists of two numbers corresponding to the 
first and second column of Table 11, first column is the order of the decahedron generated, ν, and second column is the number of steps, \( n \), needed to eliminate the adequate sites, or is the half of sites eliminated from each edge at the equator, \( n=1 \) means that only the vertices at the equator are eliminated, first step in the elimination process. Third column lists the total number of sites eliminated from the original decahedron to obtain the truncated decahedron of order \( \nu n \), \( N_{(c)} \), in the 
fourth [eighth] the number of sites per equatorial site EE remaining in the originals (take into account that in these sites are included the two new vertices VE) per edge, for the polyhedra with a central site [without a central site] (for \( n=1 \) is the number of sites in edges in the original decahedron); finally, the fifth, sixth and seventh columns [ninth, tenth and eleventh] present the number of sites of the cap, \( N_{cap} \), the number of surface sites, \( N_0 \) and the total number of sites in the 
resulting truncated decahedron with a central site [without a central site]. For example, the truncated 
decahedron without a central site of order 63, Fig. 13a, is generated from the decahedron with 
central site of order 6 (1442 sites, 10 sites per edge, 386 sites in cap, are eliminated the 5 sites VE, 4 
sites EE of each one of the equatorial edges of the surface, 2 sites EP from each edge towards the 
poles ant the 5 VE sites from the immediate interior shell, so the truncated decahedron of order 63 
has 6 sites per equatorial edge, 70 sites are eliminated and it has 1372 in total.

The number of eliminated sites, third column of Table 11, is the same for the two polyhedra, 
with and without a central site, and depends only on the number of steps \( n \) given and is obtained by 

\[
N_{(c)}(n) = \frac{5}{6} n (n + 1) (2n + 1).
\]  

(17)

Expressions for the number of surface sites and in total for the truncated decahedra with central site:

\[
N_0(\nu, n) = 20\nu^2 - 5n^2 + 2,
\]

(18)

\[
N(\nu, n) = \frac{20}{3}\nu^3 + 10\nu^2 + 16/3\nu + 1 - N_{(c)}(n),
\]

(19)
The truncated decahedron is a polyhedron formed by 22 vertices, joint by 40 edges forming 10 pentagonal faces and 10 triangular. Vertices are of three types: VP, VE, and V'; VP (2 vertices) are the same as in the original decahedron, VE and V' (10 vertices each one) resulted by pairs from elimination of original VE and from elimination of sites from EE and EP; sites V' are found were the end of the edges converge towards the poles, this is, the edges EP join sites VP and V'. Edges are of 4 types: the original EP edges (10 edges) and EE (5 edges), but the shorter, ET (20 edges) and EV' (5 edges) which form the triangular faces TF (10 faces) formed upon elimination of the equatorial sites, the edges EV' join the vertices V' by pairs, and the edges ET join sites VE and V'. So, any truncated decahedron will have vertex sites type VP, VE, V', edges type EP, EE, ET, EV' and faces type TF and pentagonal face PF. The number of VP sites is 2, of V' is 10 and VE is also 10. The number of remaining sites is variable and is listed in Table 12 for the truncated decahedra with and without central site. The number of surface sites is also listed as well as the total sites of the polyhedron. Columns 1 and 2 correspond to the order of the cluster v and n respectively. Columns 3 to 8 [11 to 16] correspond to sites EP, N_{EP}, EE, N_{EE}, ET, N_{ET}, EV', N_{EV'}, PF, N_{PF}, and TF, N_{TF}, respectively, and the two last columns to the surface sites, N_{S}, and the total of sites N for truncated decahedra with [without] a central site.

Table 11. Geometric characteristics for the truncated decahedra, constructed from a certain decahedra of order v, with and without a central site. n is the half of sites eliminated from each equator edge.

| order \(v\) | n | \(N(v,n)\) | \(N_{EE}\) | \(N_{cap}\) | \(N_{g}\) | N | Without a central site | N | N_{cap} | N_{g} | N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 5 | 11 | 17 | 18 | — | — | — | — | — | — | — |
| 2 | 1 | 5 | 3 | 46 | 77 | 100 | 2 | 26 | 42 | 49 | — | — | — | — |
| 2 | 25 | 1 | 31 | 62 | 80 | — | — | — | — | — | — | — | — | — |
| 3 | 1 | 5 | 5 | 101 | 177 | 282 | 4 | 71 | 122 | 176 | — | — | — | — |
| 2 | 25 | 3 | 86 | 162 | 262 | 2 | 56 | 107 | 156 | — | — | — | — | — |
| 3 | 70 | 1 | 61 | 137 | 217 | — | — | — | — | — | — | — | — | — |
| 4 | 1 | 5 | 7 | 176 | 317 | 604 | 6 | 136 | 242 | 423 | — | — | — | — |
| 2 | 25 | 5 | 161 | 362 | 584 | 4 | 121 | 227 | 403 | — | — | — | — | — |
| 3 | 70 | 3 | 136 | 277 | 539 | 2 | 96 | 202 | 358 | — | — | — | — | — |
| 4 | 150 | 1 | 100 | 240 | 459 | — | — | — | — | — | — | — | — | — |
| 5 | 1 | 5 | 9 | 271 | 497 | 1106 | 8 | 221 | 402 | 830 | — | — | — | — |
| 2 | 25 | 7 | 256 | 482 | 1086 | 6 | 206 | 387 | 810 | — | — | — | — | — |
| 3 | 70 | 5 | 231 | 457 | 1041 | 4 | 181 | 362 | 765 | — | — | — | — | — |
| 4 | 150 | 3 | 186 | 422 | 961 | 2 | 156 | 327 | 685 | — | — | — | — | — |
| 5 | 275 | 1 | 151 | 377 | 835 | — | — | — | — | — | — | — | — | — |
| 6 | 1 | 5 | 11 | 386 | 717 | 1828 | 10 | 326 | 602 | 1437 | — | — | — | — |
| 2 | 25 | 9 | 371 | 702 | 1808 | 8 | 311 | 587 | 1417 | — | — | — | — | — |
| 3 | 70 | 7 | 346 | 677 | 1763 | 6 | 286 | 562 | 1372 | — | — | — | — | — |
| 4 | 150 | 5 | 311 | 642 | 1683 | 4 | 251 | 527 | 1292 | — | — | — | — | — |
| 5 | 275 | 3 | 266 | 597 | 1558 | 2 | 206 | 482 | 1167 | — | — | — | — | — |
| 6 | 435 | 1 | 211 | 542 | 1378 | — | — | — | — | — | — | — | — | — |

\[ N_{g}(v, n) = 20v^2 - 20v - 5n^2 + 7. \]  
\[ N(v, n) = 20/3 \, v^3 + v/3 - N(v,n). \]
Experimental Results

In this section we will present the most common shapes of large particles and that are in accordance with the material presented above. These particles were gold and produced by wet chemical methods and correspond to shapes that might be approaching the equilibrium structure. Images were obtained using a High resolution SEM Hitachi 5500 with field emission gun. The apparatus can achieve a resolution of 0.5 nm. Samples were observed on the secondary electron mode. A drop of solution of the particles was deposited on a regular TEM grid for observation.

The experimental images obtained for each particle is presented besides to the corresponding geometrical hard-ball model, where the type of facets are described. The first particle observed is a regular solid, the structure has (111) and (110) facets, these facets result from the truncation of a octahedron by the vertices until to get 8 triangular faces and six square faces. The cubo-octahedron can be also obtained from the truncation of a cube in a similar way. Bulk gold has an fcc structure and this shape is consistent with these structures.

We have observed that as the growth of the particle advances truncations are produced on the structure. This is shown in Figs. 14b that correspond to a truncated octahedron.

Table 12. Geometric characteristics for the truncated decahedra with and without a central site. The number of surface sites for each type of site, the number of total surface sites and in the polyhedron are listed.

<table>
<thead>
<tr>
<th>V</th>
<th>n</th>
<th>(N_{ET})</th>
<th>(N_{EV})</th>
<th>(N_{TF})</th>
<th>(N_{E})</th>
<th>(N_{EE})</th>
<th>(N_{PF})</th>
<th>(N_{\sigma})</th>
<th>(N)</th>
<th>(N_{E\text{p}})</th>
<th>(N_{EE})</th>
<th>(N_{PF})</th>
<th>(N_{\sigma})</th>
<th>(N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>5</td>
<td>30</td>
<td>77</td>
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<td>10</td>
<td>42</td>
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<td>0</td>
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<td>40</td>
<td>15</td>
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<td>282</td>
<td>30</td>
<td>10</td>
<td>60</td>
<td>122</td>
<td>176</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>80</td>
<td>25</td>
<td>210</td>
<td>317</td>
<td>604</td>
<td>50</td>
<td>20</td>
<td>150</td>
<td>242</td>
<td>423</td>
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<tr>
<td>5</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>160</td>
<td>50</td>
<td>340</td>
<td>482</td>
<td>1086</td>
<td>60</td>
<td>20</td>
<td>260</td>
<td>387</td>
<td>810</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>320</td>
<td>100</td>
<td>700</td>
<td>1041</td>
<td>2270</td>
<td>70</td>
<td>30</td>
<td>280</td>
<td>402</td>
<td>830</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>640</td>
<td>150</td>
<td>1400</td>
<td>2082</td>
<td>4570</td>
<td>80</td>
<td>40</td>
<td>280</td>
<td>504</td>
<td>1640</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1280</td>
<td>200</td>
<td>2800</td>
<td>4162</td>
<td>8140</td>
<td>100</td>
<td>50</td>
<td>360</td>
<td>708</td>
<td>3280</td>
</tr>
</tbody>
</table>

We have observed that as the growth of the particle advances truncations are produced on the structure. This is shown in Figs. 14b that correspond to a truncated octahedron.
Another family of shapes is the tetrahedral structures that have facets (111). However is very difficult to find a non truncated structure, four variations can be seen in Fig. 15. In the first case, Fig. 15a, a truncation by the vertices gives rise to a triangular facet on top and a small truncation by the edges gives rise to a (100) facets. In Fig. 15b there are big edge truncations and another to give (110) facets. In Fig. 15c there are not truncations at the top and only on the edges. Finally a more complex shape can be produced such a truncated bipyramid shown in Fig. 15d containing again (111) and (110) facets.

It might happen that faceting produces a very flat (111) facet with six facets of (110) type that result in a truncated hexagonal pyramid as shown in Fig. 16.
All the above shapes can be considered as normal fcc shapes. However the non-crystallographic shapes with five-fold symmetry are often observed. The most common are the decahedron, Fig. 17a, and the icosahedron shown in Fig. 17b. However, this kind of shapes also tend to be truncated and produce very well known shapes such as the truncated decahedron Fig. 18a, the Ino’s decahedron, Fig. 18b, and the Mark’s decahedron, Fig. 18c, in all the cases the facets are (111) and (110).

The marks decahedron will have additional truncations with respect to the Ino. However, the icosahedron can show additional truncations two of those are shown in Fig. 19a and Fig. 19b.

The first structure is truncated in all the icosahedrons corners and has been described as the Chui icosahedrons. The second will correspond to a truncated facet. The Chui icosahedron has been discussed at length by Barnard et al. [33] and is a stable structure. So it appears that in both fcc and non fcc structures the truncation is a very common phenomena. It is clear that most of the growth of the particles results in truncations. This might be the result of growth kinetics or might represent an
approach to equilibrium condition. In the first case facets in different orientations will grow at a
different rate.

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(TACC) at UT-Austin, TX USA.

Glossary

v Order of the cluster or Number of crusts in
the cluster
z Total coordination
N_s Number of surface sites
N Total number of sites in the cluster
S Squared face
T Triangular face
H Hexagonal face
RF Rectangular face
TR Trapezoidal face
PF Pentagonal face
TF Equatorial triangular face
E Edge
EE Edge on the equator
EV Vertical edges on the equator
ET Edges between PF and TF
EP Edge toward pole sites
EH Edges between hexagonal faces in
truncated octahedrons
EV' Edges joining V'

V Vertex
V' Vertex at the end of truncated EP
VE Vertex on the equator
VP Vertex on pole sites
N_i Number of I sites, I= S, T, H, R, RH,
-Type fcc
fcc Face-centered cubic
-fcc Face-centered cubic with a central site
OCTAC Octahedron with a central site
type fccs
OCTAS Octahedron without a central site
OCTAC Octahedron without a central site
type fccs
ICO Icosahedron
mrdc Montejano’s reconstructed decahedron, described
originally by J.M. Montejano-Carrizales and J.L.
Rodriguez-Lopez.

References

1999).
2000).
\( \alpha_{\text{shape}}, \) birth of one universal parameter?

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Keywords: size effect, shape effect, melting temperature, phase diagram, segregation, melting enthalpy, energy bandgap, Debye temperature, Curie temperature, superconductive temperature, diffusion, creep, activation energy, Thornton & Hoffman’s criterion, residual stress, nanomaterial, nanostructure, nanoparticle, nanowire, nanofilm.

Abstract. The description of different effects observed in nature by only one general equation is the “Holy Grail” for all physicists. This goal has been achieved for characteristic temperatures through a top-down approach (studying size effects from macroscopic laws) and is presented in this chapter. Here, we show the general equation based on the surface area to volume ratio of nanostructures and statistics (Fermi-Dirac or Bose-Einstein) followed by the particles involved in the investigated phenomena. From the distinction between fermions and bosons, so-called particles which follow a Fermi-Dirac or a Bose-Einstein statistics respectively, this equation indicates the universal behaviour of size and shape effects on different material properties like melting, ferromagnetism, vibration and superconduction. The same shape parameter used in this universal equation can be used to determine the melting enthalpy, the phase diagrams of alloys, the energy bandgap and also the creep behavior of nanomaterials. Theoretical predictions show satisfactory agreement with experimental data taken from literature.

Introduction

When size of materials decreases down to the nanometer range, new properties arise. The properties of materials evolves with size and shape for two main reasons [1].

1) Nanomaterials have a relatively large surface area when compared to the same mass of material produced in a larger form.
2) Quantum effects can begin to dominate the behavior of matter at the nanoscale.

To study the materials properties at the nanoscale, there are two approaches bottom-up and top-down. The first makes use of computational methods like molecular dynamics and the second relies on classical thermodynamics. Molecular dynamics generally consider less than \( 10^5 \) atoms [2], in order to keep calculation time within reasonable values. This factor limits the nanostructure size modeled to a maximum size of tens of nanometers, but the chemical environment of the nanostructure can be modeled by this approach. Therefore, the top-down approach where bigger size of nanostructures can be considered appear as a complimentary method that may provide useful insights into nanotechnology. In this chapter, we adopt the top-down approach using classical thermodynamics to study size-dependent materials properties.

Origin of the \( \alpha_{\text{shape}} \) parameter

The \( \alpha_{\text{shape}} \) parameter was first defined in 1998 by Wautelet [3] who studied the size and shape effects on the melting temperature.

\[
\frac{T_m}{T_{m,\infty}} = 1 - \frac{\alpha_{\text{shape}}}{D}.
\]

(1)
Where \( T_m \) is the melting temperature of the nanomaterial, \( T_{m,\infty} \) is the bulk melting temperature and \( D \) is the size of the nanomaterial.

Eq. 1 has been established by describing the liquid-solid phase transition with the Gibbs free energy. The Gibbs free energy of a nanostructure can be expressed as a sum of the bulk free energy, \( G_s \), with a term considering the effect of the surface at the nanoscale [4], assuming that the surface may be characterized by a single value of the surface energy

\[
G = G_s + \left( \frac{A}{V} \right) \gamma .
\]  

(2)

Where \( A \) and \( V \) are the surface area and the volume of the nanostructure, respectively, and \( \gamma \) is the surface energy.

By expressing Eq. 2 for a nanostructure in the liquid and then solid state, we can evaluate the Gibbs free energy difference between the liquid and solid state of a nanostructure at a fixed temperature [4].

\[
G_l - G_s = G_{l,\infty} - G_{s,\infty} + \left( \frac{A}{V} \right) (\gamma_l - \gamma_s) .
\]  

(3)

The phase transition occurs when the Gibbs free energy difference equals to zero. At \( T = T_m \), \( G_l - G_s = 0 \) and we know that \( G = H - TS \). Therefore, \( G_l - G_s = \Delta H_m - T_m \Delta S_m \) where \( \Delta H_m \) is the melting enthalpy of the nanomaterial and \( \Delta S_m \) the melting entropy of the nanomaterial respectively. Therefore, Eq. 3 becomes [4]:

\[
0 = \Delta H_{m,\infty} - T_m \Delta S_{m,\infty} + \left( \frac{A}{V} \right) (\gamma_l - \gamma_s) .
\]  

(4)

A little algebra leads to the equation describing the size and shape effects on the melting temperature [4]:

\[
\frac{T_m}{T_{m,\infty}} = 1 + \frac{A}{V} \left( \frac{\gamma_l - \gamma_s}{\Delta H_{m,\infty}} \right) .
\]  

(5)

The \( \alpha_{\text{shape}} \) parameter is defined as [4]:

\[
\alpha_{\text{shape}} = \frac{AD (\gamma_s - \gamma_l)}{V \Delta H_{m,\infty}} .
\]  

(6)

The \( \alpha_{\text{shape}} \) parameter depends on the shape of the nanostructure, on the surface energies in the liquid and solid states and also on the bulk melting enthalpy. But it is size-independent. When \( \alpha_{\text{shape}} \) is known, it can be used to predict the melting temperature of a nanomaterial whatever its size. The \( \alpha_{\text{shape}} \) parameter is always positive except when a surfusion phenomena occurs. For free-standing nanostructures (Fig. 1), there are useful links between shape parameters as \( \alpha_{\text{film}} / \alpha_{\text{sphere}} = 1/3 \);
\( \alpha_{\text{wire}} / \alpha_{\text{sphere}} = 2/3 \) [3]. The values of ratios \( \alpha_{\text{tetrahedron}} / \alpha_{\text{sphere}} \approx 2.45 \) and \( \alpha_{\text{hexagon}} / \alpha_{\text{cylinder}} \approx 0.58 \) have been confirmed by Lu et al. [5].

Fig. 1: Melting temperature versus the size of nanostructures for aluminium. The following materials data have been used: \( T_{m,\infty} = 933K \), \( \Delta H_{m,\infty} = 1.07 \times 10^9 J/m^3 \), \( \gamma_s = 0.86 J/m^2 \) and \( \gamma_s = 1.14 J/m^2 \).

As \( G = H - TS \), the most stable shape for a given material is the one which exhibits the highest melting temperature because it minimizes the Gibbs free energy. Thus, the lowest value of \( \alpha_{\text{shape}} \) gives the preferentially adopted shape for isolated nanostructures, considering an isotropic value for the surface tension \( \gamma_s \). A sphere and a cylinder are the preferentially adopted shapes respectively for nanoparticles and nanowires which is in agreement with the Wulff’s construction of nanostructures exhibiting an isotropic surface tension. For other shapes of nanoparticles and nanowires \( \alpha_{\text{shape}} \) is always higher than \( \alpha_{\text{sphere}} \) and \( \alpha_{\text{cylinder}} \), respectively. This approach can be used to understand the shapes experimentally observed by Yacaman et al. [6].

<table>
<thead>
<tr>
<th>Material</th>
<th>( T_{m,\infty} ) [K]</th>
<th>( \alpha_{\text{sphere}} ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>933</td>
<td>1.56</td>
</tr>
<tr>
<td>Au</td>
<td>1337</td>
<td>1.83</td>
</tr>
<tr>
<td>InAs</td>
<td>1215</td>
<td>1.71</td>
</tr>
<tr>
<td>Ge</td>
<td>1211</td>
<td>1.72</td>
</tr>
<tr>
<td>Si</td>
<td>1687</td>
<td>1.16</td>
</tr>
</tbody>
</table>

Table 1: \( \alpha_{\text{shape}} \) parameter for some spherical nanoparticles of metals and semiconductors [7].

**Size effect on the melting enthalpy**

Let us evaluate Eq. 3 for a temperature corresponding to the bulk melting one. At \( T = T_{m,\infty} \), \( G_{l,\infty} - G_{s,\infty} = 0 \) and we know that \( G = H - TS \). Therefore, \( G_{l,\infty} - G_{s,\infty} = \Delta H_{m,\infty} - T_{m,\infty} \Delta S_{m,\infty} \) where \( \Delta H_{m,\infty} \) is the bulk melting enthalpy and \( \Delta S_{m,\infty} \) the bulk melting entropy respectively. Therefore, Eq. 3 becomes [4]:

\[
\Delta H_m - T_{m,\infty} \Delta S_m = \frac{A}{V} (\gamma_l - \gamma_s).
\] (7)
Inserting Eq. 5 into Eq. 7 gives:

\[
\Delta H_m = \left( \frac{T_m}{T_{m,\infty}} - 1 \right) \Delta H_{m,\infty} + T_{m,\infty} \Delta S_m. \quad (8)
\]

Knowing that \( T_m = \Delta H_m / \Delta S_m \) and \( T_{m,\infty} = \Delta H_{m,\infty} / \Delta S_{m,\infty} \), we can simplify Eq. 8 and write:

\[
\frac{\Delta H_m}{\Delta H_{m,\infty}} = \frac{T_m}{T_{m,\infty}}. \quad (9)
\]

This result means that with the same \( \alpha_{\text{shape}} \) parameter defined to describe the size and shape effects on the melting temperature, it can be used to describe the size and shape effects on the melting enthalpy. A similar result has been obtained by Lu et al. [8] through a different approach by using the cohesive energy.

**Size effect on alloys**

As the melting temperature decreases with size for free-standing nanostructure, the phase diagram of metallic or semiconductors alloys will also be modified when the size of nanostructure will be reduced implying a dependence of the \( \alpha_{\text{shape}} \) parameter with composition (Fig. 2). For an ideal solution, the nano phase diagram is described with the following liquidus-solidus curves (Eq. 10) [9].

\[
\begin{align*}
kt \ln \left( \frac{x_{\text{solidus}}}{x_{\text{liquidus}}} \right) &= \Delta H_m^A \left( 1 - \frac{T}{T_m^A} \right) \\
kt \ln \left( \frac{1 - x_{\text{solidus}}}{1 - x_{\text{liquidus}}} \right) &= \Delta H_m^B \left( 1 - \frac{T}{T_m^B} \right)
\end{align*}
\quad (10)
\]

Where A and B are the two considered materials. \( x_{\text{solidus}} \) and \( x_{\text{liquidus}} \) are the composition of the solidus and liquidus, respectively. \( T_m \) is the size-dependent melting temperature. \( \Delta H_m \) is the size-dependent melting enthalpy. \( T \) is the considered temperature. By solving Eq. 10, we obtain \( x_{\text{solidus}} \) and \( x_{\text{liquidus}} \).

At the nanoscale, a surface segregation is possible (Fig. 2). It refers to the phenomenon by which the chemical composition at the surface of alloys differs from the composition in the core. According to the model from Williams & Nason [10], the surface compositions of the liquid and solid phase are given by:

\[
\begin{align*}
\frac{x_{\text{surface}}}{x_{\text{solidus}}} &= \left( \frac{x_{\text{solidus}} / 1 - x_{\text{solidus}}}{1 + (x_{\text{solidus}} / 1 - x_{\text{solidus}}) e^{-(\Delta H_{\text{solidus}} \gamma_s) / (kt)}} \right) \\
\frac{x_{\text{surface}}}{x_{\text{liquidus}}} &= \left( \frac{x_{\text{liquidus}} / 1 - x_{\text{liquidus}}}{1 + (x_{\text{liquidus}} / 1 - x_{\text{liquidus}}) e^{-(\Delta H_{\text{liquidus}} \gamma_s) / (kt)}} \right)
\end{align*}
\quad (11)
\]
Where \( z_i \) is the first nearest-neighbor atoms. \( z_{iv} \) is the number of first nearest atoms above the same plane (vertical direction). \( \Delta H_{vap} \) is the difference between the vaporization enthalpies of the two pure elements, \( \Delta H_{vap} = \Delta H_{vap}^A - \Delta H_{vap}^B \). \( \Delta H_{sub} \) is the difference between the sublimation enthalpies of the two pure elements, \( \Delta H_{sub} = \Delta H_{sub}^A - \Delta H_{sub}^B \). Element A is chosen to be the one with the highest vaporization and sublimation enthalpies. If the two components are identical, \( \Delta H_{vap} = 0 \) and \( \Delta H_{sub} = 0 \), there is no segregation and we retrieve Eq. 10.

![Phase diagram of the system Si-Ge.](image)

**Fig. 2:** Phase diagram of the system Si-Ge. The phase diagram is plotted for the bulk case and the case of a spherical nanoparticle with a diameter equal to 4nm. The segregation phenomenon is represented for the nanoparticle surface. The surface is enriched with the component having the lowest surface energy i.e. Ge.

**Universal relation**

The description of different effects observed in nature by only one general equation is the “Holy Grail” for all physicists. This goal has been achieved for characteristic temperatures through our top-down approach. Indeed, we propose the following equation as a general equation to describe size and shape effects on characteristic temperatures at the nanoscale\([11]\):

\[
\frac{T_X}{T_{X,\infty}} = \left(1 - \frac{\alpha_{shape}}{D}\right)^{s \gamma/2}.
\]  

(12)

\( T_X \) and \( T_{X,\infty} \) are the size-dependent characteristic temperature and the characteristic bulk temperature, respectively. Where \( X \) represents melting, Debye, Curie or superconductive. \( S \) is equal to one-half or one depending if the particles involved in the considered phenomena follows a Fermi-Dirac (particles with half-integer spin, called fermions) or Bose-Einstein (particles with integer spin, called bosons) statistics respectively. \( D \) is the diameter of the nanostructure.

Among the considered phenomena, superconductivity is described by Cooper pairs of electrons which are characterized by integer spins and then follow Bose-Einstein statistics \([12]\). The vibration behaviour of materials is described by phonons, following a Bose-Einstein statistic \([12]\). In the case of ferromagnetism, only partially filled shells can experience a net magnetic moment in absence of external magnetic field. As the valence spins are unpaired and the electrons are fermions (so called particles with half-integer spin), they follow a Fermi-Dirac statistic \([13]\). Ordinary melting is a
result of thermal breaking of interatomic bonds and then electrons become unpaired which is described by the Fermi-Dirac statistic [14, 15]. Indeed, the cohesive energy which is the energy required to break the atomic bonds of a solid into isolated atomic species is proportional to the melting temperature. To resume, if the particles follow a Fermi-Dirac statistic then $T_{\text{Debye}} \propto \sqrt{T_X}$. Otherwise, if the particles follow a Bose-Einstein statistic then $T_{\text{Debye}} \propto T_X$. More generally, for a given material and a given size and shape, here is the relation between the considered characteristic temperatures: $T_m \propto T_{\text{Curie}} \propto T_{\text{Debye}}^2 \propto T_{\text{superconductive}}^2$ which is confirmed by Refs.[16-19].

$$\frac{T_X}{T_{\text{shape}}} = 1 - \alpha_{\text{shape}} / D$$

Fig. 3: Melting, superconductive, Curie and Debye temperatures versus the diameter of nanostructures respectively for silicium, lead, nickel and gold nanostructures.

Table 2: Summary concerning characteristic temperatures.

<table>
<thead>
<tr>
<th>Characteristic temperature</th>
<th>Spin</th>
<th>Statistics</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting</td>
<td>1/2</td>
<td>Fermi-Dirac</td>
<td>$T_m / T_{m,\infty} = 1 - \alpha_{\text{shape}} / D$</td>
</tr>
<tr>
<td>Superconductive</td>
<td>1</td>
<td>Bose-Einstein</td>
<td>$T_{\text{superconductive}} / T_{\text{superconductive,\infty}} = \sqrt{1 - \alpha_{\text{shape}} / D}$</td>
</tr>
<tr>
<td>Curie</td>
<td>1/2</td>
<td>Fermi-Dirac</td>
<td>$T_{\text{Curie}} / T_{\text{Curie,\infty}} = 1 - \alpha_{\text{shape}} / D$</td>
</tr>
<tr>
<td>Debye</td>
<td>1</td>
<td>Bose-Einstein</td>
<td>$T_{\text{Debye}} / T_{\text{Debye,\infty}} = \sqrt{1 - \alpha_{\text{shape}} / D}$</td>
</tr>
</tbody>
</table>

Another group of authors lead by Nanda [20], has published also a universal relation between the cohesive energy and the size of nanoparticles, based on the liquid-drop model [21]. The cohesive energy evolves with the inverse of particle size independently of the materials suggesting then a universal relation.

**Size effect on the energy bandgap**

Moreover, the $\alpha_{\text{shape}}$ parameter can be used to predict the energy bandgap of nano-semiconductors [22].
\[
\frac{E_{g}}{E_{g,\infty}} = 1 + \frac{\alpha_{\text{shape}}}{D}.
\]

(13)

Where \( E_g \) and \( E_{g,\infty} \) are the size-dependent energy bandgap and the bulk energy bandgap, respectively.

The energy bandgap is well known to be temperature dependent [23]. The energy bandgap of semiconductors increases when the temperature is decreased \( E_g = \Delta H_{cv} - T\Delta S_{cv} \) [24]. \( \Delta H_{cv} \) and \( \Delta S_{cv} \) represent the enthalpy and entropy variation between the conduction and valence electronic bands. This behaviour can be better understood if one considers that the interatomic spacing decreases when the amplitude of the atomic vibrations decreases due to the decreased thermal energy. A decreased interatomic spacing increases the potential seen by the electrons in the material, which in turn increases the size of the energy bandgap. Therefore, such temperature-dependent property is also size-dependent due to the size effect on the melting temperature (Eq. 1).

Indeed, the melting temperature indicates the maximal temperature accessible by a solid nanostructure, therefore when \( D \) decreases, the limit temperature \( T \) decreases also \( (T \propto 1 - \alpha_{\text{shape}}/D) \) which increases \( E_g \) \( (E_g \propto T) \). Explicitly, using the equation

\[
\left( E_g - E_{g,\infty} \right)/E_{g,\infty} = 1 - T_m/T_{m,\infty} \quad [25, 26],
\]

this means that with the same \( \alpha_{\text{shape}} \) parameter, we can describe the size effect on the energy bandgap of semiconductors, \( E_g \), with Eq. 13 (Fig. 4).

![Fig. 4: Energy bandgap of several semiconductors versus the size of spherical nanoparticles.](image)

**Size effect on diffusion and creep**

Before analysing the diffusion at the nanoscale, let us remember what is the diffusion at the macroscale. The displacement of atoms due to thermal energy, \( kT \), is called diffusion. This process is governed by an Arrhenius’ equation [27]:

\[
D_\infty = D_{0,\infty}e^{\frac{Q_\infty}{RT}}.
\]

(14)

Where \( D_{0,\infty} \) is a pre-exponential factor, \( Q_\infty \) is the thermal activation energy without considering size and shape effects, \( R \) is the ideal gas constant, and \( T \) is the temperature.
There are four types of diffusion: surface, grain boundary, dislocations and lattice (bulk) [27-29]. Each type of diffusion is characterized by a thermal activation energy. All of these thermal activation energies \( Q_{\alpha} \), are related to the melting temperature, \( T_{m,\infty} \), via a coefficient \( C \) which is different for each type of diffusion, \( Q_{\infty} = CT_{m,\infty} \). \( C \) is constant for a given class of materials and a given type of diffusion process (considering dislocations movements C~18R for metals).

Adopting a top-down approach and assuming no size effect on \( C \), we can write the thermal activation energy at the nanoscale, \( Q \), as [30]:

\[
Q = CT_{m,\infty}
\]

Where \( T_{m} \) is the nanoscale melting temperature. Indeed, as there is a size effect on the melting temperature at the nanoscale, the bulk melting temperature is replaced by the nanoscale melting temperature. Therefore, at the nanoscale, the activation energy decreases when the size decreases. It means that diffusion is more easily activated at the nanoscale.

Assuming no size and shape effects on \( D_{0,\infty} \), the diffusion coefficient at the nanoscale can be evaluated by [30]:

\[
D(L,T) = D_{0,\infty} e^{-\frac{CT_{m,\infty}}{RT_{D}}\left(1 - \frac{\alpha_{\text{shape}}}{D}\right)}
\]

(16)

The creep can begin when the grain boundaries can move over distances of the order of the grain size by diffusion processes. At the macroscale, creep can be neglected when the following condition is satisfied, \( T < 0.3T_{m,\infty} \). As the diffusion coefficient is higher at the nanoscale, this condition has to be adapted considering the size effect on the melting temperature. Therefore, we define the threshold temperature at the nanoscale, \( T_{c} \) as \( T_{c} = 0.3T_{m} \) and combining this definition with Eq. 1, it becomes [30]:

\[
T_{c} = 0.3T_{m,\infty}\left(1 - \alpha_{\text{shape}}D^{-1}\right)
\]

(17)

Of course with this definition, we retrieve when \( D \) is very large the macroscale threshold, \( T_{c} = 0.3T_{m,\infty} \). The term \( 0.3T_{m,\infty}\alpha_{\text{shape}}D^{-1} \) contains the size and shape effects on the creep threshold temperature.

The rate of diffusion along the grain boundaries is limited by the emission and absorption of atoms at grain boundaries. This process needs energy to emit and absorb atoms at grain boundaries resulting in a threshold stress. Combining the expression from Cai et al. [31], \( \sigma_{c} = \sigma_{0}\left(1 - T/T_{c}\right) \), and Eq. 17, the threshold stress for creep appearance is given by [30]:

\[
\sigma_{c} = \sigma_{0}\left[1 - \frac{T}{0.3T_{m,\infty}}\left(1 - \frac{\alpha_{\text{shape}}}{D}\right)^{-1}\right]
\]

(18)

Where \( \sigma_{0} \) is the threshold stress at \( T=0K \) and \( T_{c} \) is the threshold temperature and \( T \) is the temperature.
Dividing $Q = CT_m$ by $Q_\infty = CT_{m,\infty}$, we get $Q/Q_\infty = T_m/T_{m,\infty}$ which is the same theoretical result as already obtained by Jiang et al. [32]. Furthermore, our calculated diffusion coefficient for a gold spherical nanoparticle with a radius of 2nm is in agreement with the value announced by Dick et al. $\sim 10^{22}$ cm$^2$s$^{-1}$ [33].

**Size effect on the Thornton & Hoffman criterion**

Generally, the total residual stress within a material is the sum of two components: intrinsic and thermal. The intrinsic component is due to the growth process itself, whereas the thermal one appears due to the thermal expansion coefficients mismatch between the deposited material and substrate. The Thornton & Hoffman’s criterion [34] traditionally separates the materials into two categories: the low melting point materials ($T_{\text{substrate}}/T_{m,\infty} > 0.25$) and the high melting point materials ($T_{\text{substrate}}/T_{m,\infty} < 0.25$). The low/high melting point materials are characterized by a low/high intrinsic residual stress compared to the thermal one.

As there is a size effect on the melting temperature, there should be a size effect also on the Thornton & Hoffman criterion. In brief, the separation point at -0.25 is only valid at the macroscale. Therefore, the Thornton & Hoffman’s criterion can be generalized at the nanoscale according the following equation [35]:

$$T_{\text{substrate}}/T_m = 0.28 + 0.62D^{-1} \tag{19}$$

Where $D$ is expressed in nanometers. This relation provides the separation point as a function of the nanostructure size. To establish this equation, we have calculated the intrinsic residual stress due to a liquid-solid phase transition (Fig. 5) and described by this equation [35]:

$$\sigma_{\text{intrinsic}} = \frac{E}{1-\nu} \alpha_{th} (T_m - T_{\text{substrate}}) \exp \left( \frac{-E\tau}{\eta} \right) \tag{20}$$

Where $E$, $\nu$ and $\alpha_{th}$ are the Young’s modulus, Poisson’s ratio, and thermal expansion coefficient of the material. $T_m$ is the size-dependent melting temperature. $T_{\text{substrate}}$ is the substrate temperature. $\eta$ is the viscosity of material. The plasticity time is defined as $\tau = h_p/k_BT_m$ where $h_p$ is the Planck’s constant and $k_B$ is the Boltzmann’s constant.

By calculating the intrinsic residual stress for all the transition metals with three different sizes, we can deduced for a given size when the thermal stress will dominate the intrinsic residual stress by assuming that this is the case when the intrinsic residual stress equal to zero. Therefore, from the above figure, we deduce $T_m$ corresponding to a null intrinsic residual stress. By dividing the substrate temperature, $T_{\text{substrate}}$, by $T_m$ we get the value of the ratio $T_{\text{substrate}}/T_m$ corresponding to the transition between a domain where the intrinsic residual stress dominates and a domain where the thermal stress dominates (Fig. 6).
Combining Eq. 1 and 19, we obtain:

\[
T_{\text{substrate}} / T_{m,n} = 0.28 + \left( 0.62 - 0.28 \alpha_{\text{shape}} \right) D^{-1} - 0.62 \alpha_{\text{shape}} D^{-2}
\]  

(21)

Where \( D \) is expressed in nanometers. So the term \( \left( 0.62 - 0.28 \alpha_{\text{shape}} \right) D^{-1} - 0.62 \alpha_{\text{shape}} D^{-2} \), where the size effects are included, allows to generalize the Thornton & Hoffman’s criterion down to the nanoscale (Fig 7). When this term tends to zero (large values of \( D \)) we retrieve the Thornton & Hoffman’s criterion at the macroscale. Note that the value of the separation point at the macroscale originally proposed (~0.25) is not a strict value; it may vary between 0.2 and 0.3 as discussed by Thompson [36].
For given deposition conditions, the proportion of intrinsic residual stress increases when the size of nanostructures decreases.

**Summary**

Nanomaterials exhibit different properties from their bulk behavior. It is due to the increasing surface area to volume ratio when size decreases and to possible quantum effects when size goes down to nanometers length scales. It has been shown all along this chapter that there exist a universal relation between many materials properties and the reciprocal size of nanostructures. Furthermore, from a top-down approach, a shape parameter called $\alpha_{\text{shape}}$ has been defined and has been used to predict several different materials properties exhibiting the “universal” character of this parameter. Eq. 12 is a first step on the way of a universal equation describing the size and shape effects on materials properties. Work is now in progress to find the same kind of equation in other fields.
References

Size Effects in Amorphous Nanosolids

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Abstract. Compared to information on nanocrystals, that on amorphous nanosolids is on the whole much less organized. On the other hand, growth of structural data in recent years on the latter, that deal with the range of atomic order (short range order and beyond), coordinations of core and surface atoms and similar aspects in amorphous nanoparticles through computer simulation and other techniques, has been very impressive. Similar generation of information is also true for physical phenomena like crystallization and melting. Finally, interesting properties revealed through experimentations point toward important applications. The present article makes a brief survey of these areas and attempts at reaching certain conclusions mostly specific for amorphous nanostructures with respect to the crystalline counterparts. The article analyzes the structural data to try and explain different properties of amorphous nanosolids and also their position in the applications scenario.

Introduction

Externally symmetrical solids have attracted attention through ages; relatively large and colorful gems and other undisturbed, e.g. uncut single crystals found in Nature are typical examples [1]. A similar place is occupied by colored or completely transparent cut-and-polished slabs or other shapes and sizes of glass. These of course derive their shape and surface smoothness from human endeavor. The former thus possessed a “morph”, i.e. form or external character since the time they were born. The latter on the other hand lacked this before processing, and have been qualified as “amorphous”, i.e. devoid of “morph”. At some stage of their appreciation, the “amorphicity” of glass has been supported by instrumental proof of disorder in its atomic structure [2]. This is also true for various other natural and artificial amorphous solids. It should be mentioned here that through this article, disorder will not include discussion on line or volume defects (basically observed in crystalline structures), voids or any other similar features to avoid possible confusion.

Amorphous or atomically disordered substances have since been identified in large numbers and selectively produced in large quantities; some of them e.g many kinds of glasses [3] and species like amorphous (a-) Si with surface passivation by hydrogen [4-6] have proved to be technologically very important. So in addition to inquisitive experimentations on them, new amorphous substances have been synthesized continuously through various techniques, from simple sol-gel procedures to sophisticated procedures like plasma-enhanced CVD [7]. In parallel, their atomic structures have also been revealed or suggested in great details [8-10]. Such substances can be metalloids like Si and Ge, various oxides, sulfides and other compounds, atomic or molecular clusters, metallic alloys, glasses etc. Their nanosolid forms i.e. particles of various geometries from dots to nanowires, deposited films, particles embedded in amorphous or crystalline matrices and allied configurations are being looked into with great interest and some have proved to exhibit exploitable properties.

The main intentions of this article are to offer selected information on amorphous nanosolids, especially in the following areas: the range of order that can be observed in the disordered substances, atomic arrangements in nanoparticles (taking into consideration the surface and core atomic species), their physical properties, and how they are controlled by their own size (“size effect”). The properties
are divided in two classes, i.e. (a) transformation characteristics of e.g. amorphous nanoparticles to crystals or melts, and (b) technically useful characteristics like photoluminescence.

**Nomenclature: Short Range Order and Beyond**

A discussion on properties of “amorphous” solids needs an introduction to the historically evolved ideas about disorder in their building blocks, atomic and molecular units, and the corresponding terminology. The need becomes important because of probable confusions that might follow the debate on (see below) and exchangeable use of terminology defining such solids. We therefore start with a discussion on the basic characteristics of substances which are, for certain, not crystalline in character. The first point in tune with this discussion is the 1915 comment of P. Debye that no assemblage of molecules of finite size can be completely random; a “most random” assemblage could be that in a monatomic gas [11]. It is planned to present the evolution of this concept in the following paragraphs.

W.H. Zachariasen’s seminal work of 1932 [12], widely accepted for its success in explaining the structural aspects of glass, introduced the concept of “continuous random network” (CRN) in the atomic structure of glass. This aspect of “randomness” of structure in Zachariasen’s work has been debated on the basis of experimental revelations in later years. The first and conceptually simple indication that an amorphous atomic structure need not be random comes from the fact that depending on the degree of covalency in the structure-building polyhedra, they can exhibit so-called “directional bonds”. This means a near-constancy (on an average) of internal bond angles, e.g. Si-O-Si in SiO₄ tetrahedra, though the tetrahedra are likely to be distorted to a small degree [13]. While a structure constructed of such building blocks may lack a global atomic order that characterizes a crystal (e.g. crystalline silica and silicon), bond distances and coordination numbers are not expected to be very different [14,15].

On the face of it, a regular polyhedron is by itself a piece of “order”. However, the local features like nearest neighbor bond lengths and dihedral bond angles e.g. O-Si-O in the above example, which is short range order (SRO), become the most important points to consider in a structure that forms out of the connectivity of the polyhedra (corner- or edge-sharing, like in a-SiC [16]). A well-employed tool which has been resorted to since long for understanding the degree of order or disorder in such structures is X-ray diffraction study and data on (partial) radial distribution function [9,14-17] and the related pair correlation functions that in an amorphous substance, e.g. silica glass, can comment on the absolutely local connectivities like Si-O, O-O and Si-Si (SRO). Such analytical techniques, however well-tested, cannot go farther, as the peaks with increasing angles go on becoming broader and broader [17]. Similar observations hold good for e.g. electron and neutron diffraction. Small angle X-ray scattering (SAXS), extended X-ray absorption fine structure (EXAFS), and Raman spectroscopy are some techniques which on the other hand yield results indicative of the structure beyond the short range, i.e. intermediate range order (IRO) in specific cases [14,17], but cannot claim to meet the overall needs.

As has been observed as a general phenomenon, the “order” in “disordered” substances does not end at SRO, but can extend to an intermediate or medium range order (IRO or MRO) that goes beyond the local atomic interactions. Such structural correlations can be valid in the length scale range of 0.5 nm to 1 nm [17], or even somewhat more. Compared to SRO which is linked with only the nearest neighbors and the related bond length and angle distribution (2- and 3-body correlation functions), IRO can go to 4-body correlation functions [18]. However, as indicated above, an overall IRO structural description for amorphous substances is an elaborate task [19].

Families of materials that have been studied in detail for their IRO include a variety of glasses and other disordered materials [8,17,19-22]. In many of these, the IRO is indicated by the so-called first sharp diffraction peak (FSDP) in the X-ray diffraction pattern, though not in all cases [15]. Based on
FSDP, several models have been proposed for specific amorphous substances, as above [15]; however, none of these are equipped for explaining all the details of the obtained atomic order.

The above and other reasons related to measurements and models led around the mid-1990’s to the development and use of the now well-utilized fluctuation electron microscopy [FEM] in transmission electron microscopes [14,18,19]. The procedure is based on statistical analysis of image variance as against the scattering vector: this can yield information on nm-sized “ordered” local areas (~1-2 nm) in disordered materials. The overall advantage of FEM is its sensitivity to 3- and 4-body correlation functions. The importance and necessity of this in understanding intermediate stage order in amorphous materials is pointed out above. General applications include the ability of FEM to obtain signals due to fluctuations represented by inhomogeneities; varying numbers of nm-sized voids or grains of relative order are examples. A well-studied case is a-Si [19].

Finally, the basic individuality of disordered materials with respect to various ordered forms and the necessary steps required to understand their structures have been taken up currently in depth by various researchers. Modeling for disordered materials has been considered to take care of e.g. the following major factors [23]: (i) The model of the atomic structure must be essentially large to avoid overlap between atoms and use “adequate sampling” (up to thousands of atoms) of all possible/expected variations in disorder, e.g. various local structures so as to obtain the most realistic scenario; (ii) Accurate interatomic forces for simulations; this is a very vital choice for obtaining, as above, a trustworthy picture of the structure; (iii) temporally extended MD simulations; (iv) “accurate approximation” of structural changes taking place in excited states, as might be required for evaluating various e.g. electronic and optical properties, considered to be a difficult proposition. Extensive discussions based on crystal chemical considerations, experiments and computer simulations are available on the special considerations demanded by disordered structures [23-27].

Atomic Structures of Amorphous Nanosolids: Size-dependence

Oxide nanoparticles

Extensive computer simulation has been used for obtaining relatively clear pictures of atomic structures that form in various amorphous oxide nanoparticles as a function of factors like temperature and size [13,28-31]. The major conditions and accomplishments in most of these investigations are: (i) the particles (2-6 nm) are spherical with a specific density value (generally the bulk density, obtained experimentally), (ii) structural properties e.g. coordination numbers (CN) obtained not only for a particle in totality, but also separately for surface and core atom assemblages, (iii) instead of the earlier concepts e.g [32], that of a division between the atoms belonging to the shell and those belonging to the core has been used; this is based on “the largest radius of the coordination spheres [13,29]” found in individual systems. The thickness of the shell constituted of the outer atoms is thus taken as, e.g. 3.30Å for SiO2 [13] and 4.00Å for TiO2 [29]. (iv) information is obtained through systematic cooling of the mother liquid into the particles (the overall temperature range is 7000 to 350/300K) at a relatively high cooling rate. Here we shall discuss mainly the results obtained at 300 or 350K.

AO2 compositions

Investigations on amorphous silica [13] centers round 4 nm particles, and the major conclusions are as follows:
The tetrahedral network structure becomes slightly distorted when the particle size is “large enough”, so that the CN of silicon achieves the bulk value of 4. It has been shown on the other hand that the percentage of CN = 4 reaches the maximum value of about 93 (4 nm, 350K); larger particles have not been considered. A major defect that reveals itself is an excess concentration of oxygen atoms at the
surface of a particle, causing oxygen deficiencies in the core region. Expectedly, germanium oxide shows several trends [28] that match with those observed in case of silica. Thus, the network structure is distorted for particles of specific size; for a size of 4 or 5 nm, the percentage of tetrahedral coordination records a value of around 94. In comparison, the CN (=4) has a value of about 87% for 2 nm particles, the rest of the Ge atoms being 3-coordinated. Similar to that observed in case of silica, oxygen atoms tend to concentrate at the surface of germania particles; germanium atoms also concentrate, in a layer just below the surface, apparently as a sign of maintaining charge neutrality.

The coordination number of bulk TiO₂ being 6, there are some clear differences in character between TiO₂ [29] and SiO₂ or GeO₂ (CN = 4). The main units at the shell are TiO₅, while the same at the core has the value of about 6 (even with a size of only 2 nm); the structure is, of course, clearly size-dependent. The connectivity, unlike in case of silica and germania, involves both corner- and edge-sharing.

A₂O₃ composition

The average CN of Fe-O for Fe₂O₃ nanoparticles [30] is recorded to be on increase with size, i.e. ~ 4.9 (2 nm) to 5.5 (5 nm). The main structural units are taken as FeO₄ in surface shells, and FeO₆ in the core regions; when the CN values are considered separately, the surface atoms exhibit a range (with increasing particle size) of 4.81 to 5.27 and the core atoms, 5.59 to 5.66. There may thus be a possibility of oxygen depletion in the core and a corresponding accumulation at the surface, as found in case of SiO₂ and GeO₂.

A₂O₃.2BO₂ composition

The relative complexity of structure and composition in nanosized Al₂O₃.2SiO₂ [31] is obvious in some of the atomic relationships in the amorphous form: while the difference in tetrahedral coordination of Al between the core and shell (2 nm to 3 nm size) is about 20%, the same for Si is very little. The difference in case of Al seems to even up with increasing size. This mainly indicates a large number of under-coordinated surface atoms. As in the other cases discussed above, a tendency of oxygen atoms to concentrate at the surface is noted.

Metal nanoclusters (ncl)

An interesting source of disorder among a group of units in inorganic substances is the so-called clusters of atoms, molecules, chemical units representing non-molecular compounds etc. These entities represent a wide variety of assemblages both ordered and disordered, and have attracted attention due to a number of important properties and applications [33,34]. A cluster represents aggregates that are too large to be described as molecules and too small to be called crystals particles etc., though such divisions are often terminologically transgressed. By definition, amorphous particles (our concern here) can also exhibit sizes that match the same of many types of clusters generally expressed by the number (n) of constitutional units like atoms; but a boundary line can possibly never be drawn. The simple reason is that boundaries of clusters have been set at 1 nm [35] to tens of nm [36]. In this article, we shall discuss mostly “small” clusters built of metal atoms.

How many atoms, then, constitute a cluster in a scientifically accepted sense? The minimum number is a few atoms, while the maximum can go up to a few thousands of them [36]. In this wide range is included a variety of ordered structures of metal nanoclusters; a compact list is presented in Table 1 [37-42]. As the major goal is a discussion of partially or fully disordered metal nanoclusters, no detailed discussion will be made here on the contents of Table 1.
It has been observed [43] that disorder in the structure of nanoclusters could be a general feature. Questions that immediately come up are: What are the most stable cluster configurations in a system? Which ones are the lowest-lying isomers and how do they compare with the other isomers? And finally, how do the ordered and disordered clusters compete — if at all — with one another in respect of stability? Based on these and similar questions, a variety of metal atom nanoclusters have been examined from various angles through experiments and simulations. Selected examples are discussed below with some indications.

Table 1. Common structurally ordered forms among metal nanoclusters

<table>
<thead>
<tr>
<th>Basic Symmetries</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Icosahedra</td>
<td>37,38,39,</td>
</tr>
<tr>
<td>Mackay</td>
<td>40</td>
</tr>
<tr>
<td>Anti-Mackay</td>
<td>40</td>
</tr>
<tr>
<td>Hendy</td>
<td>40</td>
</tr>
<tr>
<td>B. Decahedra</td>
<td>40</td>
</tr>
<tr>
<td>Marks</td>
<td>38-41</td>
</tr>
<tr>
<td>Ino</td>
<td>40</td>
</tr>
<tr>
<td>C. Cuboctahedra</td>
<td>40</td>
</tr>
<tr>
<td>D. Truncated Forms</td>
<td></td>
</tr>
<tr>
<td>Octahedra</td>
<td>40</td>
</tr>
<tr>
<td>Decahedra</td>
<td>39</td>
</tr>
<tr>
<td>E. Face-Centered Cubic (fcc)</td>
<td>40,41</td>
</tr>
<tr>
<td>F. Hexagonal Close-Packed (hcp)</td>
<td>40</td>
</tr>
<tr>
<td>G. Capped and Twinned Forms</td>
<td>39,42</td>
</tr>
</tbody>
</table>

Several observations (based on essentially simulation work) require mention as an introduction to disordered metal nanoclusters, referred to as “ncl” in the following.

(a) “Disordered” clusters are those that do not exhibit any detectable overall order, but some kind of local order [41], as already discussed above for bulk materials. Stabilization of disordered forms has been explained to occur through energy gain in the central part of a cluster [44,45]. A “rigorous” condition proposed for a structure to be totally disordered, is that there should not be any locally identified space region in the cluster where the atomic density is significantly low [37].

(b) A conclusion with reservations has been drawn that disordered clusters could be relatively small in size [41]. However, all small clusters are not disordered. Thus, while Al_{147} can have “disordered configurations without symmetry” [46], current work [47] finds Al clusters with n = 13-22 to have icosahedral growth and n = 23-34 to exhibit a “competition” among forms like decahedral, fcc (relaxed fragments) and hexagonal prismatic.

(c) Though difficult to accept on the face of it, many disordered clusters represent lowest-energy structures (global minima) out of a large number of ordered/disordered clusters and isomers. It
has been suggested [45] that disordered structures can represent global minima if the potential well is “sufficiently wide”. Further, this stabilization has been considered to be assisted by the elastic energy [45].

**Sodium nanoclusters (IA)**

Among the small clusters of sodium (Na\(_n\) and Na\(_n^+\)), where \(n = 8\) to 55, the lowest-energy isomers are generally symmetrical, e.g. icosahedral forms [48,49]. With increasing values of \(n\), disordered clusters are identified. Examples are \(n = 92\) and 142 [37,50,51]; of the two, again, Na\(_{92}\) is truly disordered, while Na\(_{142}\) is only partially so, as indicated by the nature of melting that shows an identifiable atomic shell structure [37,51]. The anomalies in the structural properties of metal clusters, indicated above, have been examined from the point of view of melting of sodium [52], where \(n = 142\) shows relatively high melting point, apparently supporting the “partial” disorder (see later). As \(n\) increases to 147, a complicated Mackay icosahedron (Table 1) is recorded as the lowest energy isomer [49].

**Gold nanoclusters (IB)**

Gold ncl-s are one of the major groups where lack of symmetry is a significant feature, especially for relatively small clusters. A limited study on Au\(_n\) (\(n = 38, 55, 75\)) clusters (1-1.5 nm) [53], i.e. magic number clusters [54-56] finds a number of lowest-lying isomers, most of which are disordered in structure. This however does not indicate complete amorphicity to be conclusively in relative favor. Of the above, with \(n = 38\), the ground state is represented by two amorphous parts that are, however, placed symmetrically (a plane of reflection symmetry [57]). An atomic arrangement (“fluxional” cluster [58]) observed in Au\(_34\) has 3-4 inner atoms and ~ 30 outer atoms which are likely to be disordered. With \(n = 55\), on the other hand, a large number of amorphous states of lower energy than that in an icosahedral structure is predicted; in fact, no other symmetric forms with lower energy than those exhibited by the amorphous forms could be identified. It is concluded that the apparently relative abundance of disorder is linked with “low coordinated and well separated” surface atoms and their short range interactions, leading to disordered building blocks of an amorphous structure [53].

In contradistinction, relatively large clusters (\(n = 923, 1415, 3871\) and 10179; 3-8 nm) present a different picture. It has been concluded [59] that amorphous configurations in large clusters, from all relevant aspects, i.e the total internal energy (U), vibrational entropy (S\(_{\text{vib}}\)), and the Gibbs free energy (G), as obtained from the equation

\[
G = U - TS_{\text{vib}} + PV
\]  

are thermodynamically the most unstable.

**Zinc and cadmium nanoclusters (IIB)**

Nanoclusters of Zn and Cd represent a special case where all the “magic size” [54-56] clusters up to about 147 atoms (\(n = 13, 38, 55, 75\) and 147) with the most stable configurations are found to be disordered or exhibit hardly any symmetry [38]. In parallel, it is predicted that the global minima in case of all the magic sizes are disordered [38]. It is also observed that in between a series of ncl-s (\(n = 18, 49, 100, 176\)) identified with their association with “complete” Marks decahedra (Table 1) there are a number of clusters without an overall order [41].

**Aluminum and gallium nanoclusters (IIIA)**

Aluminum nc-s show relatively rich symmetrical forms at different cluster size levels. Thus, a current work [60] on Al\(_n^+\), Al\(_n\) and Al\(_n^-\) (\(n = 13-34\)) reports icosahedral growth for \(n = 23-34\) and a competition
among decahedral, relaxed fragments of fcc and hexagonal prismatic forms. Specifically, Al\(_{13}\) can be termed a “slightly” distorted icosahedron with a minimum-energy configuration [48]. Indications of amorphicity are also obtained from the nature of melting (see also below for Ga) in nanoclusters. For Al, a direct 2-state (i.e. solid→ melt) transition [61] is observed in case of most clusters with \(n = 25\)-83 atoms, while with \(n = 51, 52, 56, 61\) and 63, intermediate states are expected. Following the results of Ga nc-s [62], one can infer order for the former in case of Al nc’s too, and partial or complete disorder in case of the latter. In comparison, an Al cluster of 147 atoms has been shown to exhibit disordered nature in an early work [46].

Apart from the structural studies - mainly computer simulation - that indicate partial or complete disorder of specific clusters (which must be critically dependent on the selection of potentials), experimental investigations also indicate order/disorder rather convincingly. Order or lack of it is understood in gallium clusters, as an example, by examining their melting behavior [62-64]. The main signatures are observed in heat capacity measurements. A sharp peak in plots of heat capacity [62] as a function of temperature indicates a first order solid-liquid transition, as also a ground state symmetric, ordered geometry [63]; steps in the plot of the “peak” indicate a second order transition of amorphous clusters in ground state. The former (e.g. Ga\(_n^+\) with \(n = 31, 33, 36\) and 46) are more in number in the group of 29-55 atoms; amorphous clusters include Ga\(_{30}^+\) and Ga\(_{55}^+\). Among smaller-sized clusters, Ga\(_{17}^+\) records no significant peak in specific heat, while Ga\(_{29}^+\) does record so [63].

Vanadium nanoclusters (VB)

Structural simulation and experimental investigations of vanadium clusters \(V_n\) (\(n = 2\)-17, 55, 147, 309) yield a large number of structures and energetically favored forms. Only the following basic results for smaller clusters are given here [45,65-67]:
(i) The most stable structures are obtained in the size range of 3-17 atoms; some of these structures are symmetrical, e.g., isosceles triangle for \(V_3\) and tetrahedron for \(V_4\), but several others may be distorted e.g. distorted trigonal bi-pyramid for \(V_5\). Some other distorted forms in the above range are \(n = 5, 7\)-9, 11, 12. Basically disordered structures are exhibited by \(V_{15} - V_{17}\).
(ii) Among the “most stable” but disordered structures are \(V_{55}, V_{147}\) and \(V_{309}\), though signs of order (e.g. features of icosahedral symmetry) are observed.
(iii) The stable forms of disordered structures are considered to originate from the energy gain in the core regions of the clusters.
(iv) For small cationic clusters \(V_n^+\), energetically favored structures are simple forms like isosceles triangle, as also trigonal and tetragonal bipyramid, strongly distorted pentagonal bipyramid and icosahedron (up to \(n = 14\)). Apparently the lowest energy forms in the overall range here are not disordered.

Amorphous ncl-s, some of them energetically most stable as mentioned through this section, raise an obvious question: how do amorphous clusters form, and how do they gain the stability? It has been concluded [62] that this can be due to relatively fast kinetics in favor of a disordered form where an ordered structure cannot form or “cannot be accessed on the relevant time scale”. There can also be a thermodynamic effect where the relevant ordered structures are destabilized, making way for large numbers of disordered forms [57,62].
Conversions of Amorphous Nanosolids: Size Effect
Solid-liquid Conversion

Size effect in melting is a widely studied subject, but most of the research concerns conversion of crystalline nanoparticles [68-70], because they generally show sharp solid-liquid transitions. However, there are also records – though limited – of melting behavior of disordered substances with respect to their ordered counterparts.

An early experimental work [71] on bulk amorphous (190 nm thick) and single crystal Si shows a significant drop in the melting temperature: 1170 ± 100K in case of the former, as against 1685K for the latter. The large difference in the free energies is thought to be directly responsible for this variation. In comparison, a molecular dynamics (MD) simulation [72] indicates a depression of about 230K. A current MD simulation [73] predicts “a remarkably lower solid-to-liquid temperature than that of nanocrystal” for Ag nanosolids.

Melting behavior of both ordered and disordered nanoclusters has been widely studied [62, 74, 75]. Values for several parameters are determined or calculated to arrive at the size factor and depression in melting temperature: (a) normalized heat capacity (normalized to $3Nk$, where $3N = 3n - 6 - 3/2$, and $k = \text{Boltzmann constant}$ [62]) as a function of temperature; (b) caloric curves [74]; (c) Lindemann index [75]. Relations of these parameters with disorder are briefly indicated here: (i) While heat capacity of ordered nc-s is indicated by and easily measurable from a sharp peak, that of an amorphous nc is rather wide and forms in steps [62]. (ii) The caloric curve, which exhibits the changes in the total energy with temperature, shows a significantly sharp jump as a function of temperature in case of bulk materials, a moderately sharp jump for ordered nanoclusters and hardly any jump for disordered nanoclusters (top, middle and bottom curves respectively of Figure 1). (iii) The Lindemann index [75] indicates root-mean-square relative bond length fluctuations at the atomic and cluster levels. For a cluster, Lindemann index can be defined by $\{ \frac{1}{N} \Sigma i \}$, where $*\text{cl}$ indicates the overall cluster, $*i$, an individual atom, and $N$ indicates (same as n through this text) the number of atoms in the cluster.

It should be noted that melting point is basically a thermodynamic property irrespective of sample size. Depression of this parameter for a finite crystal size does, in a way, belong to a different regime, though the transition is generally sharp. For disordered substances of finite size, the melting occurs far from at a unique temperature (as discussed above). This has been fixed in some cases at the onset temperature of melting [75].

![Figure 1: Hypothetical caloric curves showing total energy U as a function of temperature T (dependent on individual cases); top: bulk, middle: ordered cluster, bottom: disordered cluster.](image-url)
Disorder-order Conversion

Crystallization of bulk to nanometric amorphous materials can be assumed to be based on the available surface energy and its minimization through nucleation of (specific) crystalline phases. This apparently puts a thermal restriction related to the type and/or degree of disorder on the starting substance. Also, crystallization can take place as an obvious function of a possible critical size (see below) as in various other conversions.

Disorder-order conversions have various kinds of known examples: the main controlling parameter is of course the size of the disordered probe material. The other factors that demand consideration here (only in conjunction) are temperature and atmosphere, though in specific cases. Some typical examples from different classes of substances are assembled below to present an overall scenario, and possibly come to a size-based boundary between the two structural states.

Among the elemental substances, a-Si provides a clear size dependence of a→c (amorphous to crystalline) transition temperature [76]; the nature of the shift is shown in Table 2. As expected, the smallest particle size (4 nm) matches the lowest transition temperature. In case of the transition a→Ag→c-Ag, MD simulation predicts the minimum size to exceed 3 nm (more than 640 atoms) [76,77].

The transition size from a- to c-CdS has proved to be a debatable point, especially for sizes below 6 nm. With a size less than 1.5 nm diameter, the particles are reported to be amorphous, transforming to the zinc blende structure at 2.5 nm [78]. This, however, is not uniformly confirmed: the crystalline phase can also be wurtzite-type, or a phase not clearly determinable [79]. In comparison with the above, MD simulation concludes [80] that very small (≤2 nm), uncapped CdS nanoparticles should be amorphous in nature; larger particles around 6 nm crystallize with wurtzite structure. Note that below 6 nm, the scenario remains rather diffuse. However, with the information at hand, 2-2.5 nm may be considered a boundary. Similarly, crystallization experiments on a-CdSe nanoparticles also cannot indicate any clear size control [81,82]. There are, however, hints [82] that particles of the smallest size (1.9 ± 0.2 nm) are likely to remain amorphous at 150° (2h). In comparison, hexagonal CdSe crystallizes from amorphous particles 2.3 ± 0.3 nm or larger in size under similar (not same) conditions. Such crystallization starts at the core.

A strong effect of size on the conversion is shown by CoPt: while a particle size of ≤ 2 nm is disordered in character, another with a size of ≥ 3 nm is ordered [83]. Similarly, a chemical order in FePt is also dependent on size [84,85]. The required ordering is accomplished at 600°C with the particle size apparently at ~7nm, but not less than ~4 nm. Below a size of ~3nm, the long range order parameter \( S = k_B \ln W_{sub}^{3\theta} \) (entropy related to the FePt structure), where \( k_B = \) Boltzmann constant and \( W_{sub} = \) number of arrangements of Fe and Pt for one sublattice decreases, and reaches a value of zero at a size <2 nm. The correspondingly low annealing temperature does not achieve the required ordering.
Table 2. Amorphous-crystalline conversion in silicon as a function of size [76]

<table>
<thead>
<tr>
<th>Size (nm)</th>
<th>Conversion temperature (K)</th>
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<tbody>
<tr>
<td>4</td>
<td>773</td>
</tr>
<tr>
<td>6</td>
<td>1073</td>
</tr>
<tr>
<td>8</td>
<td>1173</td>
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<tr>
<td>10</td>
<td>1273</td>
</tr>
</tbody>
</table>

The examples cited above indicate clearly that a direct $a \to c$ conversion should be dependent on the size parameter, though an exact boundary of size separating $a$ and $c$ is not always indicated. It is pointed out [86] that the long-range order of the smallest crystalline structure with a minimum diameter $D_{\text{min}}$ demands at least half of the atomic volume to be inside the core. This is expressed by the simple relationship

$$D_{\text{min}} = 2D_0$$

(2)

where $D_0$ is the so-called critical diameter (i.e. the boundary mentioned above), which can be shape-dependent as well. Another important point is that below a critical minimum size $D_{\text{min}}$, the nanosized crystal is “thermodynamically unstable with respect to the amorphouslike structure” [86]. In the reverse case, i.e. with $D > D_{\text{min}}$, the atomic structure of the nanocrystal matches that of its bulk form. There are, however, instances where the conversion may not exactly follow the above principle. One example is non-epitaxial growth of spherical Sb islands on crystalline substrates where, for transition of low-coverage amorphous deposits to crystalline forms at higher thickness, the suggested critical diameter is as large as about 120 nm [87].

**Core-shell Particles**

Examples are known of core-shell products obtained during conversion of amorphous nanoparticles above a critical size: while the shell still retains its amorphicity, crystallization sets in at the core region. The case is simple for $a$-alumina particles > 20 nm that change into composite, core-shell products with a $\gamma$-$\text{Al}_2\text{O}_3$ core on electron irradiation [88]; a likely reason is the similarity of the two phases from energetic viewpoint, but more importantly, the elastic strain energy with the nucleation of the $\gamma$-phase. In nano-sized amorphous titania, likewise, the core can be like the crystal phase anatase, while the shell exhibits a highly distorted atomic arrangement [89].
Apart from such factors as above, the size factor is also likely to play an important role in core-shell systems. The completely oxygen-coordinated cations in the core region (as discussed above) should find it easier, e.g. on application of energy, to arrange themselves into a partially or fully organized segment, and the under-coordinated cations would be unable to become as sufficiently ordered. It is, however, to be noted that the boundary between the core and the shell may not have a generally matching value; one of the likely reasons is that the set of parameters related to the formation of one particular crystal form are different for another.

Size-dependent Property of Practical Interest in Amorphous Nanosolids

Photoluminescence

One of the most important areas of practical application where property relates itself with size of amorphous nanosolids is luminescence. This conception is supported by both theoretical [90-92] and experimental [93-95] studies. Some examples of photoluminescence in amorphous nano silicon, the most studied substance in this context are discussed below.

Amorphous silicon

A family of materials that occupies an important position in the above domain includes nanosized amorphous silicon, designated a-Si, and a-Si:H where hydrogen ions passivate the surface of the particle (taking care of the dangling bonds [5]), as also the group that is doped with various concentrations of erbium [93,96] (see below). Additional examples of dopants include carbon [97] and lithium [98]. The passivation of dangling bonds is clearly a step that links itself with self-luminescence of a-Si. It is proposed [5] that the density of state in the energy gap of a-Si:H is reduced significantly by adding 10-15 of atom% of hydrogen, increasing its importance as a luminescent substance. The essential role of hydrogen has been demonstrated [5] by using partial substitution of hydrogen by the isotope tritium (T) in glow discharge deposited a-Si:H. It is shown that the radioactive decay of tritium with time leads to a corresponding increase in non-passivated dangling bonds, and as a result, decreasing efficiency of self-luminescence of the (originally) a-Si:H:T.

In a model proposed by Estes and Moddel [91,92] on radiative recombination in photoluminescence (PL) was addressed for a-Si:H with 0D to 2D shapes (spheres to slabs respectively). Predictions of relevance here are: (i) The peak energy of room temperature luminescence should increase with decreasing “diameter”, whatever the shape (as above), and the sharpest increase should be shown by the 0D spheres. Such spheres of 1-5 nm size should exhibit luminescence parallel to that of porous silicon (1.6-2.0 eV); (ii) Considering only spheres of different sizes, large (20 nm) samples should exhibit asymmetric peaks as in bulk hydrogenated Si, and relatively small sizes (down to 1.25 nm), symmetric peaks; narrow PL bands are expected in the size range, say, 2.5 to 10 nm; (iii) The size dependence is thus clearly accepted, even when the model does not necessarily accept the density of states of a-Si:H to be so (size dependent).

In spite of the advantages offered by a-Si and a-Si:H, light-induced degradation (Staebler-Wronski effect [99-102]) of the material, leading to a (metastable) change seems to be a significant problem that is yet to be solved properly. Apparently the major material properties that are involved are: (i) disorder in the Si network, (ii) hydrogen concentration and (iii) concentration of impurities [100-102]. Of these, only the hydrogen concentration deserves attention here because of the limited scope of this article. The relevant point in this context is the observation that the light-induced degradation should be noted in H-poor, rather than H-rich regions. Among the various points that attract attention [103], again, are the local hydrogen concentration fluctuation, and the number density...
(and its distribution) of a-Si:H nanodots as a function of the flow rate of hydrogen during synthesis; in parallel, as the nanodot concentration increases, the dot size can decrease significantly [104].

Undoped a-Si nanoparticles confined in silicon nitride or oxide layers, or a-Si nanolayers show characteristics like: (a) strong room temperature luminescence through practically the entire visible spectrum [104-107], (b) relatively high number density of a-Si: \( \sim 10^{12} \) cm\(^{-2} \) (\( x = -1 \) to 7) which can increase to \( 10^{13} \) cm\(^{-2} \) under specific conditions [105]. The size relationships controlling the product characteristics are expressed in the following way: (i) relatively small particles indicate relatively high number density [104,105], (ii) band gap can be tuned within limits by controlling the dot size, i.e. \( E(\text{eV}) \propto 1/d \) (nm), (iii) progressively smaller particles are linked with corresponding blue shifts of the PL peak [108,109], demonstrating a relationship between the quantum dots and PL and the possibility of tuning of the color of the latter.

Based on effective mass theory (originally for crystals, but reformulated for amorphous substances too [110]) and assuming an infinite potential barrier, the energy gap \( E \) for confined size (3-dimensional) a-Si is often expressed in the following way:

\[
E(\text{eV}) = E_{\text{bulk}} + C/a^2
\]

where \( E_{\text{bulk}} \) = bulk a-Si band gap (taken as 1.5-1.6 [111]), \( a = \) dot size and \( C = \) confinement parameter [104,111]. Using obtained or available data the equation has been rewritten as

\[
E(\text{eV}) = 1.56 + 2.40/a^2
\]

Various devices exploiting the above are on trial [112,113]. Quantum dots (~2 nm) of a-Si (controllable for control of PL color) in silicon nitride films have been used in an orange light-emitting device (LED) [112]. Another recent advancement [113] in fabrication of LED is a multilayer stack of a-Si/Si\(_3\)N\(_4\); with a fixed, about 10 nm layer of the nitride, variations in the a-Si layer (thickness about 7 to 3 nm) can fine tune the emitting color through blue shift of the PL peak. Reduction in the layer thickness of a-Si also leads to increased PL intensity.

The erbium ion (Er\(^{3+}\)) is in essence the major dopant for development of luminescent a-Si; the main photoluminescence (PL) band is observed at 1.54 \( \mu \text{m} \) - intra-4f shell excited state-to-ground-state transition: \( ^{4}I_{13/2} \rightarrow ^{4}I_{15/2} \). [114] for all such optical materials [4,93,96,115]. The choice behind the selection of the rare earth ion looks forward to possible application as LED’s and laser systems that function at around 1.54 \( \mu \text{m} \) [93,96], and the extensive work [4,93,96,115] on Er-doped a-Si is based on the advantages over crystalline Si [96] The common configuration is Er-doped a-Si quantum dots (QD) in silicon nitride films. An additional (restricted) dopant can be oxygen, used for reduction of luminescence quenching [96].

Effective Er luminescence as a function of size limit is worked out at a boundary above which the relatively large area of the particle allows larger and closer presence of Er ions. This crowding, leading to enhanced Er-Er interaction (concentration quenching), causes diminished intensity of the PL peaks. The boundary (devoid of quenching phenomena) lies at a dot size of ~ 2 nm, at which high PL intensity is expected [93]. The Er-Er interaction (and the relatively large dot size as the cause factor) is considered to be related to nonradiative quenching [93], so that the size affects both the PL intensity and the decay time. The latter becomes nearly double as the dot size decreases from 2.5 to 1.4 nm. Thus, a relatively large dot size is predicted to show high PL intensity at relatively low Er concentration; the reverse is also predicted to be true. The obtained results [93] that demonstrate the ideas mentioned above are presented in room temperature PL spectra (Figure 2).
Figure 2. PL spectra of a-Si:Er; concentration of Er: (a) Er $10^{21}$ cm$^{-3}$, (b) Er $10^{19}$ cm$^{-3}$. Dot size: 2.5 nm (solid line), 1.8 nm (dashed line), 1.4 nm (dashed-dotted line). Reprinted with permission from N.M. Park et al., J. Electrochem. Soc. 152, G445 (2005). Copyright (2005), The Electrochemical Society.

Additional examples

Various other materials in amorphous form are known to exhibit luminescence; a few specific examples of non-oxides are introduced here for the sake of offering a more extended picture. It should, however, be mentioned that such examples do not always represent results with nanoparticles (see below), and the amorphous nature of the material is not always strictly so.

Early work [94] reports room temperature PL spectra of a-Si$_{1-x}$C$_x$ films at 2.61 eV (475 nm). Subsequent work on a-SiC shows examples of tailoring in experimentations to control the PL peak position (300 – 700 nm, as also 1540 nm) and width [116-118]. A recent technology uses low temperature and pressure microwave plasma reactors for successfully producing amorphous nanoparticles (4-6 nm) of SiC [119]. The technology takes help of the amorphous nature of this material to adjust the ratio of Si and C and achieve flexibility. Er-doped oxycarbide (a-SiC$_x$O$_y$:Er, C = 0.5, O = 1.0) shows strong room temperature luminescence at 1540 nm with different experimental procedures [120].

Quantum confinement effect is recorded in a-GaN dots (mean size 7.9 nm, less than the Bohr radius) deposited by pulsed laser ablation. The room temperature PL is marked by a strong band at 3.9 eV [95]. Amorphous thin films can also exhibit a blue emission at ~ 2.8 eV [121]. Doped with Er, a film shows PL spectrum (room temperature) with a shift to the green region [122]. Among other non-oxides, rare earth-doped amorphous AlN has currently become important for its varied characters in luminescence and their applications in optical devices [123-125].

Concluding Comments

This paper assembles and re-states the following important points about inorganic amorphous nanosolids:

[a] Amorphous or disordered solids are marked by relative order of atoms at the short and intermediate extents (SRO and IRO respectively, but not a long range order or LRO) of length scale (from fractions
of 1 nm to a few nm), which is far from an absolutely random arrangement of the structural (atomic and polyhedral) units.

This also indicates a degree of reproducibility of the average structural characteristics, e.g. effect of size (a few nm scale) on the structure, and hence the properties like amorphous-crystalline and solid-liquid transitions.

Such size-dependent transitions, however reproducible, are not as sharp (first-order transition) as expected for highly ordered nanomaterials; a finite size analogue of second-order transition has been proposed in melting of disordered counterparts.

The SRO and IRO, and their overall reproducibility (essential for applications) has been exploited significantly in case of materials like nanofilms/nanoparticles of a-Si:H and a-Si:Er for fabrication of optical and other devices.

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References

The synthesis of nanostructured and nanometer-sized systems

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Pulsed laser ablation; Wet chemical synthesis; Sol-gel processing; Microwave processing; Spray pyrolysis;
Flame synthesis; Inert gas condensation; Vapor deposition; Vapor-liquid-solid growth.

Abstract. The present chapter deals with the difficult task of giving a brief survey of the synthetic routes
employed to prepare materials with characteristic features on the nanometer scale. Definitions and general
concepts regarding nanostructured and nanometer-sized materials are shortly tackled in the introductory
part, which is followed by an overview of the most important approaches developed to synthesize such materials. No attempt is made to create a comprehensive and detailed synopsis of the experimental methods currently available. Rather, attention is focused on a selected number of general methodologies, the choice of which can be usually motivated by a mix of historical perspective, scientific significance and technological potential. So-called “top-down” approaches are discussed first, whereas the second part of the chapter is devoted to “bottom-up” ones. The former group includes mechanical processing, melt quenching, and de-vitrification methods. Sonochemistry, pulsed laser ablation, wet chemical synthesis, sol-gel processing, microwave processing, spray pyrolysis, flame synthesis, inert gas condensation, vapor deposition, and vapor-liquid-solid growth form instead the latter group.

Introduction

Nanostructured and nanometer-sized materials can be generically defined as synthetic materials exhibiting a spatial arrangement such that at least one of their characteristic lengths is below 100 nm [1-3]. Such definition implies the existence of different classes of materials, the identification of which relies upon the number of lengths in the above mentioned size range [1-3]. When only one length is below 100 nm, nanometer-sized materials have the shape of two-dimensional sheets or layers. Nanometer-sized wires or tubes are instead systems with two lengths in the appropriate size range. Finally, nanometer-sized clusters or particles have all the three characteristic lengths down to the nanometer scale. Precisely for their spatial characteristics nanometer-sized layers, wires and clusters are also commonly termed two-, one- and zero-dimensional solids respectively [1-3]. Nanostructured materials must be instead regarded as three-dimensional solids, even though composed of individual nanometer-sized domains [1-3].

The simple size constraint can be often indicated as the only responsible for the emergence of qualitatively new physical and chemical behaviors in nanometer-sized materials and structures [1-4]. In fact, any given physical process undergoes a significant perturbation when its characteristic length scale becomes comparable with the size of the portion of matter under investigation [1-4].
For example, the coherence length of phonons affects heat conduction, whereas magnetic properties are determined by the size of magnetic domains [1-4]. Nevertheless, the nature of the emerging behaviors is generally far beyond the experience and intuition of scientists. Under this perspective, the physics and chemistry of nanometer-sized systems can be reasonably regarded as a new subject of scientific investigation [1-5].

At present, scientists and technologists are seriously involved in the challenging attempt of rationalizing the unusual properties of nanometer-sized systems and finding for them practical applications. For this purpose, concentrated efforts have been, and are, devoted to a number of intertwined experimental tasks including the development of synthetic routes, the improvement of available characterization techniques and the identification of novel investigation methods [1-5].

The present chapter will focus on the different strategies developed to synthesize nanostructured and nanometer-sized systems of given size and shape.

**General overview**

The properties and functionalities of nanomaterials are intimately connected with their size and structure. Then, achieving the capability of manipulating matter on the nanometer scale represents a strategic goal for fundamental physics and chemistry, destined to promote crucial breakthroughs in nanotechnology applications.

In the recent past, the methods devised to specifically address a particular synthetic demand have undergone a considerable increase in both number and variety. This is not surprising since the methodologies to synthesize a given nanomaterial can be in principle as various as the combination of size, shape, structure, properties and functionalities specifically required for that given material. Of course, an important role has been also played by the continuous technological advance in the design and realization of experimental apparatuses.

The first commonly accepted systematic classification of synthetic routes focuses on the general strategy applied by the synthetic method and identifies two major categories, usually termed “top-down” and “bottom-up” [1-5]. The conceptual framework is schematically described in Fig. 1.

![Figure 1. “Top-down” and “bottom-up” approaches for the synthesis of nanometer-sized materials.](image)

The “top-down” strategy relies upon the synthesis of nanometer-sized systems by the progressive fragmentation of a massive crystal. This generally results in an increase of the number of coherent crystalline domains accompanied by a decrease of their average size. Therefore, the experimental “top-down” processes typically generate a nanostructured phase characterized by individual nanometer-sized coherent crystalline domains separated by thin structurally disordered boundaries.

In contrast, the “bottom-up” approach is based on the gradual assembly of small building blocks consisting of either individual atoms and molecules or suitable nanometer-sized systems. Accordingly, individual nanomaterials are prepared starting from precursors or reactants at the atomic or molecular level. Depending on the fundamental mechanisms, these methods allow the
fabrication of systems with various architectures such as particles, wires and tubes. It follows that, at least in general terms, the “bottom-up” approach exhibits the highest synthetic versatility.

The two above mentioned strategies find application in a number of experimental techniques exploiting the physical, chemical or physic-chemical processing of gaseous, liquid and solid phases as well as of their possible different mixtures. The different synthetic methods considered in this chapter are summarized in Table 1, where the acronyms used are also indicated.

Table 1. The “top-down” and “bottom-up” synthetic methods discussed in the present chapter.

<table>
<thead>
<tr>
<th>Synthetic method</th>
<th>Acronym</th>
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<tr>
<td>Top-down</td>
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<tr>
<td>Mechanical processing</td>
<td>MP</td>
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<tr>
<td>Melt quenching</td>
<td>MQ</td>
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<tr>
<td>De-vitrification</td>
<td>DV</td>
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<tr>
<td>Bottom-up</td>
<td></td>
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<tr>
<td>Sonochemistry</td>
<td>SC</td>
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<tr>
<td>Pulsed laser ablation</td>
<td>PLA</td>
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<tr>
<td>Wet chemical synthesis</td>
<td>WCS</td>
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<tr>
<td>Sol-gel processing</td>
<td>SGP</td>
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<tr>
<td>Microwave processing</td>
<td>MWP</td>
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<tr>
<td>Spray pyrolysis</td>
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<tr>
<td>Flame synthesis</td>
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<tr>
<td>Inert gas condensation</td>
<td>IGC</td>
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<tr>
<td>Vapor deposition</td>
<td>VD</td>
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<tr>
<td>Vapor-liquid-solid growth</td>
<td>VLS</td>
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Only a short qualitative description of such experimental methods will be given. In fact, the present chapter aims at providing a general overview of the different synthetic routes to nanomaterials, and not a detailed discussion of the underlying mechanisms and potential in terms of specific applications. Rather, the existing literature will be used to address interested readers.

Before starting the description of the above mentioned methods, a few words of comment on the cumbersome absence of an important technique such as nanolithography. Nanolithography is currently regarded, in its different configurations, as the analogous of optical lithography on the nanometer scale [5-9]. In conventional optical lithography a light beam is directed through a detailed mask onto a film of photoresist material deposited on the surface of a Si wafer [10,11]. The mask produces on the photoresist material the desired patterns of illumination [10,11]. These are utilized to selectively induce chemical modifications on specific regions of the photoresist material, which finally result in the different features of modern integrated circuits [10,11]. Nanolithography still takes profit of suitable masks to promote the formation of nanometer-sized features on the surface of a given substrate [6-9]. However, different from conventional optical lithography, masks consist of standing waves of light [6-9]. The standing wave allows a spatial modulation of the atom-light interaction and determines the concentration of atomic fluxes on specific regions of the substrate surface [6-9]. Actually, a number of alternative methods have been developed based on near-field optics, electron beam, imprint, scanning probe and dip pen [6-9]. In all of the cases, the final result is the formation of surface patterns with characteristic features on the nanometer scale.
[6-9]. However, it must be noted that all of the lithography methods mentioned above exhibit various limitations [6-9]. For example, leveling the imprint template in imprint lithography is an extremely challenging issue. Also, in advanced deep ultraviolet photolithography the minimum size of surface features is limited by the diffraction of light. Instead, the evanescent near field lithography, originally developed to overcome light diffraction limits, is affected by light intensity attenuation phenomena. In summary, the method is still far from a mature implementation in industry, and even in laboratory it is not easy to perform, requiring relatively expensive apparatuses [6-9]. In addition, nanolithography represents the natural evolution of conventional optical lithography, a mature technology applied since decades in electronic industry. Dealing with all the interconnected aspects of lithography and nanolithography in a relatively short overview would be very difficult. Furthermore, it would necessarily result in a confuse and quite limited description of all of the other methods selected. It is for these reasons that lithography has not been included in the present chapter, which has been instead suitably oriented to cover the as large as possible number of general physical and chemical methods for the preparation of nanostructured and nanometer-sized materials.

Mechanical processing
The mechanical processing (MP) of materials is a powder metallurgy technique widely employed to synthesize metallic alloys starting from pure elements [6]. Nanostructured phases are also easily formed [6]. MP is usually performed in suitably designed ball mills, inside which milling tools undergo a series of collisions between each other [6].

MP is apparently simple [6]. At each deformation event, powders are submitted to mechanical loading and shearing processes taking place on a local scale. Such processes involve random configurations of particles, which are brought into intimate contact and plastically deformed. The mechanical load is sustained by the force network formed by the points of contact between different particles, where most severe plastic deformation phenomena occurs. The whole process is schematically depicted in Fig. 2, where different length scales are considered.

![Figure 2](image-url)

**Figure 2.** The processes taking place during deformation events. Different length scales have been considered ranging from particle assembly to individual atoms.

It is at the points of contact between particles that microstructural modifications mostly occur. In fact, local deformation events induce a sudden increase in the population of crystalline defects that progressively determines the significant change of structural, physical and chemical properties of the material processed [7-10]. Under such conditions, a hierarchy of processes can be roughly identified including morphological, microstructural and chemical changes as well as a general enhancement of chemical reactivity [7-10]. Among the others, the formation of disordered regions separating coherent portions of crystalline lattices is observed [7-12]. In other words, MP is able to
promote the formation of a nanostructured phase whose microstructure depends on the system properties as well as on the detailed processing features [13].

Three fundamental features characterize MP. First, the mechanical energy is transferred to powders at local deformation events, i.e. when powder particles are trapped between colliding surfaces. Second, only a small fraction of the total amount of powder inside the reactor is involved in each deformation event. Third, powders move according to a granular flow that effectively remixes the powder fraction involved in individual deformation events with the rest of the powders. These three points clearly indicate that MP exhibits an intrinsic statistical character.

The structural transformations induced by MP were initially thought to proceed through the accumulation of structural defects in crystalline lattices and the intimate mixing of elemental species at interfaces consequent to the mechanical deformation of powder particles trapped between the surfaces of colliding milling tools [6]. However, such hypothesis has been recently seriously questioned, so that the atomic-scale mechanisms are still matter of lively debate. At present, hypotheses range from the oldest scenarios of hot spot theory [14] and defect-enhanced diffusion [15] to the most recent ones of shear-induced mixing, interface roughening and contact melting [7-11]. More specifically, the emphasis has gradually shifted from inherently thermal processes to coupled thermally and mechanically induced phenomena. MP mechanisms can be thus tentatively connected with local rearrangements activated by non-hydrostatic mechanical stresses operating on the atomic scale [7-11]. The resulting far-from-equilibrium conditions have been shown to be able to promote a transient enhancement of chemical reactivity and the formation of a nanostructured phase [7-12], provided that the solid is not exceedingly ductile and malleable [6].

Melt Quenching (MQ)
Quenching techniques have been used since the 1950s to produce amorphous metallic alloys [16]. Initially, amorphous films were grown on a cryogenically cooled substrate by quenching the vapors of either elemental species or a mixture of metals [16]. Shortly after, it was observed that the same amorphous alloys could be prepared by rapidly cooling a melt down to the room temperature [17].

Provided that cooling rates on the order of $10^6$ K s$^{-1}$ are achieved, a number of molten alloys can be forced to take an atomic arrangement similar to the one of frozen liquids [17,18]. The amorphous solids obtained, generally referred to as metallic glasses, are successfully synthesized as a consequence of the kinetic constraints imposed to the liquid dynamics by the high cooling rate [18]. Under such conditions, the usual nucleation and growth of crystalline phases are indeed by-passed and the atoms are unable to take the lowest energy configuration [18], forming a metastable phase.

![Figure 3](image_url). A cross sectional view of a Ni-Zr nanocrystalline domain with average diameter around 2 nm embedded in the surrounding amorphous phase.

However, metallic glasses are not the only metastable phases that can be synthesized by MQ. On the contrary, a suitable tuning of experimental conditions permits the synthesis of nanocrystalline systems [19]. More specifically, nanocrystalline phases can be obtained starting from a metallic
alloy melt provided that a suitable window of cooling rate is identified [19], thus carrying out a controlled crystallization of metallic, oxide or ceramic melts [20]. The obtained nanostructured phases exhibit crystalline domains in the size range between 10 and 50 nm, generally partially embedded in a residual amorphous matrix [20]. Such structure is exemplified in Fig. 3.

Controlling the kinetics of nucleation and growth of crystalline grains under far-from-equilibrium conditions represents a valuable opportunity for the design and preparation of innovative nanostructured materials [20]. The method exploits the phase selection mechanisms intrinsically involved in processes based on the relative kinetic stability of different competing phases, the crystallization of which represents a compromise between thermodynamic driving forces and atomic mobility on the microscopic scale [20]. It also exploits the competition between nucleation and growth processes to suitably obtain the final desired result in terms of average size, size distribution and morphology of crystalline domains [20].

De-vitrification (DV)

Solid phases with nanocrystalline features can be easily synthesized by crystallization of the amorphous alloys prepared by MP or MQ. The process is generally referred to as de-vitrification (DV) and is based on the accurate control of the crystallization kinetics by finely tuning the factors driving the crystallization such as temperature and time interval of annealing and heating rate [21]. This results in the partial or complete conversion of the amorphous into a nanostructured phase.

The crystallization of metallic glasses is known to proceed according to a nucleation and growth kinetics [21,22]. The crystalline phases produced by the crystallization process as well as their morphology and microstructure depend on the transformation mechanism, which in turn depends on the chemical composition of the metallic glass and on the relative thermodynamic stability of the possible crystalline phases [21,22]. Due to the temperature dependence of the thermodynamic driving forces and of the atomic diffusivity, the maximum growth rate is observed close to the melting point. In contrast, the nucleation rate increases as the temperature decreases in a temperature range well below the melting point. It follows that obtaining a nanocrystalline phase requires in principle that nucleation and growth are respectively as faster and as slower as possible. Depending on the chemical composition of the metallic glass, three different transformation paths are possible, namely the polymorphous, eutectic and primary crystallization [21,22]. It is in the latter case that the finest nanocrystalline structure is generally obtained.

Primary crystallization is governed by the long-range diffusion of atomic species and exhibits a time-dependent growth rate. In fact, the rate of individual crystalline domains growth decreases with the domain size. In the final growth stages, the growth domains overlap and the different grains impinges with each other. A simplified description of the process is given in Fig. 4.

![Figure 4. The formation of a nanostructured phase during primary crystallization.](image)

Initially, the nuclei are embedded in apparently random positions inside the amorphous matrix. During their growth, the residual amorphous phase undergoes a continuous compositional change connected with local driving forces and diffusivities. Finally, the residual amorphous phase transforms into a nanostructured phase by either eutectic or polymorphous crystallization [21,22].
Sonochemistry (SC)

The term sonochemistry (SC) identifies the form of chemistry resulting from the interaction of sound waves with matter [23]. Such interaction is mediated by cavitation, which can be defined as the multistage process including the nucleation, growth and implosive collapse of bubbles in a liquid phase [24,25]. Cavitation phenomena are generally induced by generating intense sound waves into a liquid phase, which can be done by immersing a suitably designed piezoelectric horn into the liquid [24,25]. To be effective, the sound waves must have wavelength in the range between 0.001 and 10 cm, i.e. must fall within the wavelength domain of ultrasounds [24,25].

As the sound wave passes through the liquid phase, it creates a succession of compression and depression stages. Accordingly, the liquid is submitted to pressure cycles during which the local pressure harmonically changes from positive to negative values [24,25]. Provided that the ultrasound intensity is sufficient, the local expansion associated with the negative pressure stage induces the nucleation of a cavity inside the liquid. More specifically, this occurs when the negative pressure is higher in absolute value than the tensile strength of the liquid phase [24,25]. The cavity typically nucleates where the system exhibits favorable conditions, e.g. at local impurities or small bubbles of gas, and is filled by solute gases and vapor of the liquid phase. A schematic description of the cavitation process is given in Fig. 5.

Once nucleated, the bubbles can grow in size as a consequence of the superimposed ultrasound bombardment. Provided that the intensity of travelling sound waves is not exceedingly high, any single cavity undergoes a size oscillation spanning over various pressure cycles [24,25]. However, on the average the size of the cavity increases. This must be ascribed to the dynamics of the vapor phase inside the cavity, and in particular to the different rates of vaporization and dissolution at the vapor-liquid interface delimiting the cavity [24,25]. The capability of the cavity of absorbing energy depends on its size. In particular, an effective absorption of ultrasound energy is only possible when the cavity attains a critical size. When this occurs, energy absorption induces a rapid growth of the cavity during a single pressure cycle [24,25]. Due to the marked size increase, no ultrasound energy can be further absorbed. Therefore, the cavity can no longer sustain the external pressure of the liquid and undergoes a rapid implosion involving the penetration of high speed liquid jets.

![Diagram of cavitation process](image)

**Figure 5.** The relationship between pressure cycles and cavity size during a cavitation process originated from the bombardment of a liquid phase with ultrasounds.

The result is a local hot spot with temperature and pressure roughly on the order of 5000 K and $10^8$ Pa respectively [24-27]. Heating and cooling rates amount to about $10^9$ K s$^{-1}$ and the hot spot...
exhibits a lifetime considerably shorter than 1 μs [24,27]. Precisely the above mentioned far-from-equilibrium conditions promote the occurrence of chemical processes. These can possibly take place on solid surfaces, where the energy barrier to nucleation is lower [24,25]. The concentration of ultrasound energy into hot spots also induces the electronic excitation of chemical species, with the consequent emission of electromagnetic radiation [26,27]. The emission in the visible region of the electromagnetic spectrum is generally referred to as sonoluminescence [26,27].

Sonochemical processes can involve homogeneous liquid systems as well as liquid-liquid and liquid-solid heterogeneous mixtures. In both cases, nanometer-sized materials can be successfully synthesized [24,25]. In the case of a homogeneous liquid phase, the extreme conditions imposed by cavity implosion can promote the decomposition of suitable chemical precursors and the formation of nanometer-sized crystalline domains [28]. In the presence of solid particles, the turbulent flow and shock waves produced by the bombardment of the liquid phase with intense ultrasounds induces high-velocity collisions between particles. The energy of collisions is such that particles can even melt at the points of contact [24,25]. The mechanical loads can also produce the fragmentation of brittle materials, which produces a suspension of nanometer-sized particles [24,25].

**Pulsed laser ablation (PLA)**

The laser ablation of materials from solid targets under vacuum conditions was first applied in the early 1960s, i.e. as soon as ruby lasers became available [29]. The method generally referred to as pulsed laser ablation (PLA) was developed shortly after [29]. PLA immediately attracted attention due to its versatile applications in the processing of solid materials by laser, which includes cleaning of surfaces, preparation of thin films and synthesis of nanometer-sized systems [29,30].

The apparatus for PLA is schematically depicted in Fig. 6. PLA is typically carried out under ultra-high vacuum conditions, but background gases can be also suitably used to assist the deposition of particular materials.

![Figure 6. A schematic of the experimental apparatus employed to carry out PLA deposition.](image)

The physical processes underlying the interaction between laser pulses and solid target are quite complex and still not completely understood [31]. The PLA mechanism is often described as a sequence of at least four different stages [29-32]. The first one involves the irradiation of the solid target with the consequent localized heating of the irradiated surface and the evaporation of material. The second is strictly connected with the intrinsic dynamics of the ablation plume, which contains plasma and still undergoes intense irradiation. The third stage concerns the interaction between the ablated material and the substrate to be coated, with the incident material that can accommodate on the surface, rebound back in the gas phase or induce surface modifications. Finally, the fourth stage concerns the kinetics of nucleation and growth of the different possible modifications.
nanocrystalline phases after deposition on the substrate. It is however worth noting that the different steps are intimately correlated and often overlapped [29-32].

The ablation of the solid target takes place as a consequence of the vaporization processes occurring at the surface. Evaporation mostly originates from a so-called Coulomb expansion under far-from-equilibrium conditions. In general terms, the absorption of the laser pulse by the target is followed by a series of intertwined conversions. First, the absorption of electromagnetic radiation promotes the excitation of electronic states, which subsequently relax transferring energy to the crystalline lattice [29-32]. Under such circumstances, the lattice undergoes a fast phonon excitation producing thermal, chemical and mechanical effects, which in turn result in the ablation of at least the mostly irradiated portion of the target [29-32]. The penetration depth of the laser pulse depends on the laser wavelength and on the refraction index of the solid material at such wavelength, and typically amounts to about 10 nm [29-32]. The intense laser irradiation is sufficient to induce the local ionization of the target surface, the electrons being ejected in the vacuum within roughly the first 10 ps of a laser pulse lasting 1 ns. Then, the free electrons oscillate under the action of the electromagnetic radiation field and collide with the target surface, thus inducing the local heating responsible for the material vaporization [29-32].

The material ejected in the ultrahigh vacuum forms a plasma plume with characteristic features depending on the details of the ablation process [29-32]. The plasma region exhibits a complicated internal dynamics related to the different kinetic energy of electrons, ions, atoms, molecules and other species. Furthermore, Coulomb repulsion also plays an important role in governing the progressive modification of the plume shape [29-32].

The energetic species in the plume move in a direction roughly perpendicular to the surface of the ablated solid target and gradually impinge on the substrate. Here a number of different processes can take place depending on the kinetic energy possessed by the colliding species. For example, highly energetic species can penetrate the substrate, giving rise to crystalline lattice defects [29-32]. The deposition on the substrate of the different species in the plume occurs at relatively high rates, so that the deposited material generally experiences a considerable degree of supersaturation. It is under such conditions that the nucleation and growth of the new crystalline phases takes place [29-32]. The nucleation and growth kinetics can be further influenced by a number of factors, including the characteristics of laser irradiation, the substrate temperature and the pressure of background gases if present. PLA finds numerous applications in different fields of science and technology and it has shown the capability to synthesize nanometer-sized systems more complex than thin solid films, such as nanowires and nanotubes [29-33].

**Wet chemical synthesis (WCS)**

The terms “wet chemical synthesis (WCS)” generically refer to a set of chemical methods applied to synthesize materials by homogeneous chemical reactions in liquid phases [34,35]. Being the chemical reactions in liquid environments a considerable part of classical solution chemistry, the number of available synthetic procedures is quite large [34,35]. When specifically referred to the preparation of nanometer-sized materials, WCS must be intended as the set of chemical methods developed to synthesize nanometer-sized solid systems starting from precursors and reactants dissolved in a liquid solvent [5,36].

The methods exploiting WCS exhibit considerable variety and versatility, taking advantage of the broad literature devoted to solution chemistry [5,36,37]. Experimental conditions can be easily varied not only in connection with thermodynamic variables such as temperature, pressure and stoichiometry of solutions, but also with the chemical nature of solvent phases, of precursors and reactants and of possible surfactants to be used to govern the nucleation and growth of nanometer-sized systems [5,36,37]. Size, structure, shape and crystallographic features of nanomaterials are strictly controlled by WCS conditions, so that even small differences can remarkably alter the final products [5,36,37]. For example, different surfactants can promote the formation of spherical nanoparticles rather than faceted nanotubes or vice versa [5,36,37].
The preparation of metallic nanoparticles in solution can be regarded as a classical example of WCS [5,36-38]. Such methods generally involve the preparation of a colloidal phase of zero-valent metallic species as an intermediate stage [5,36-38]. A colloid can be defined as a chemical mixture in which an internal phase is suspended in a dispersion medium in the form of particles [5,34,35,39]. The suspended particles, typically in the size range between 1 and 200 nm, are characterized by an intrinsic thermodynamic stability preventing their complete dissolution [5,34,35,39]. Depending on the nature of the dispersion medium, the colloidal solution can be referred to as an aerosol, an emulsion, a foam, a dispersion or a hydrosol [5,34,35,39].

Colloidal phases can be easily obtained by reductive processes carried out by adding reducing agents to the solution of metallic ions [5,39]. A very large number of reducing agents can be used for this purpose, including inorganic species such as lithium aluminiumhydride, sodium borohydride and organic ones such as alcohols, hydrazine, hydroquinone and formaldehyde [5,36-39]. Size, size distribution, shape and morphology of nanoparticles can be considerably affected by the nature and reductive potential of the reducing agent and by the rate at which reduction occurs [5,36-39].

The process of particle formation by reduction involves various stages that can be described in terms of nucleation and growth [5,36-39]. Accordingly, the reduced species, e.g. the zero-valent metal atoms, initially aggregate with each other to form the first embryos of crystalline phase. Once a critical size threshold is overcome, such nuclei grow under the effects of local concentration gradients [5,36-39]. When present, nuclei also interact with surfactants, which can significantly affect the faceting processes and, in turn, the nuclei growth and coalescence. A schematic description of this mechanism is shown in Fig. 7.

In principle, the colloidal phase cannot be regarded as a stable phase [5,36-39]. In fact, interaction forces operate between the particles suspended in the liquid, with features and intensity depending on the nature of the system [5,36-39]. Typically, particles interact with each other via electrostatic and Van der Waals forces [5,36-39]. Such forces determine an instability that finally results in the flocculation of the colloid, i.e. in the mutual aggregation of particles that gradually precipitate from the solution [5,36-39].

![Figure 7. The nucleation and growth of a nanoparticle in solution in the presence of surfactant molecules.](image)

The above mentioned aggregation process can be generally avoided by either electrostatic or steric stabilization [5,36-39]. In the former case, the different affinity of suspended and dispersion phases for electrical charges results in the formation of an electric double layer at the interface. When the colloidal particles have the same chemical nature, all of them bear the same electric charges. The resulting repulsive interaction prevents the aggregation and precipitation of particles. A similar effect can be obtained by capping the particle surface with specific surfactants [5,36-39].
Bonding selectively the atoms at the particle surface, the surfactant forms a layer of tunable thickness that physically obstacles the direct contact between particles. In addition, it can protect the surface from further undesired reactions allowing at the same time the possibility of functionalizing the particle for successive utilizations [5,36-39].

**Sol-gel processing (SGP)**

The so-called sol-gel process (SGP) is a WCS method widely employed to prepare ceramic and glass materials [40,41]. The method is based on the thermally-induced transition from a colloidal liquid phase, referred to as the “sol”, to a solid phase, referred to as the “gel” [40,41]. The sol can be defined as a dispersion of solid particles with characteristic size on the order of 1 µm or below suspended in a liquid phase as a consequence of Brownian motion [40,41]. The gel can be instead regarded as an interconnected or percolating solid network containing a liquid phase [40,41]. In the light of the above mentioned definitions, SGP can be described as a multistage process including the initial solid particle dispersion, the sol polymerization and the final pyrolysis of the gel material to produce a solid system [40,41].

![Figure 8. The different synthetic possibilities offered by SGP.](image-url)
The synthetic methodology is extremely versatile. Depending on the experimental conditions governing the transition, ceramic and glass materials can be synthesized in the form of nanometer-to micron-sized particles, thin films, elongated fibers, porous membranes, aerogels as well as massive ceramics and glasses [40,41]. These possibilities are schematically shown in Fig. 8.

The applications of the materials obtained by SGP range from optical coatings and insulators to superconductors and chemical catalysis, also including reinforcement fibers, protective films and electronic coatings [40,41]. Thin film coatings are usually produced by spin- or dip-coating procedures [40,41]. Aerogels, i.e. extremely porous systems, can be instead obtained by removing the liquid from a wet gel under supercritical conditions [40,41]. A suitable adjustment of the sol viscosity allows the fabrication of elongated fibers, whereas powders can be synthesized by a variety of approaches including precipitation processes, spray pyrolysis and emulsions [40,41].

The first evidences of SGP date back to the late 1800s and the process has been extensively studied since the 1930s [40-42]. It attracted renewed interest in 1970s, due to the preparation of massive gels at relatively low temperatures and their subsequent transformation into glasses [40-42]. Currently, SGP represents one of the most attractive methods to synthesize homogeneous inorganic materials with a number of tailored properties including hardness and porosity as well as chemical and thermal resistance [40,41]. Allowing a low-temperature synthesis, SGP exhibits considerable advantages over the conventional thermal treatments employed to prepare inorganic glasses [40,41].

As briefly mentioned above, the physics and chemistry of SGP involve the formation of a colloidal suspension of solid particles, the sol, and the successive sol gelation to create a solid network inside a continuous liquid phase, the gel [40,41]. The colloidal suspension is synthesized starting from chemical precursors that usually consist of metallic or metalloid species suitably coordinated to reactive ligands [40,41]. Metal alkoxides are the most commonly employed precursors due to their chemical reactivity with water, in particular alkoxysilanes such as tetramethoxysilane and tetraethoxysilane [40,41]. Aluminates, titanates and borates also find general utilization [40,41].

The chemistry of the functional groups surrounding the metal or metalloid centers can be schematically described by considering the three fundamental reactions referred to Si and showed in the scheme below:

- Si – OR + HOH $\rightarrow$ Si – OH + ROH (Hydrolysis)
- Si – OH + Si – OH $\rightarrow$ Si – O – Si + HOH (Water condensation)
- Si – OH + Si – OR $\rightarrow$ Si – O – Si + ROH (Alcohol condensation)

**Scheme 1.** Hydrolysis, water condensation and alcohol condensation processes involved in SGP of alkoxysilanes.

From top to bottom, the alkoxysilane undergoes so-called hydrolysis, alcohol condensation and water condensation processes [40,41]. These reactions induce the formation of a solid network inside the liquid phase. However, the characteristics of any given solid framework are determined by a number of intertwined factors influencing the rate of hydrolysis and condensation reactions [40,41]. These include the pH of the colloidal solution, the temperature at which SGP is carried out, the rate of the above mentioned processes, the relative amounts of reactants and precursors, the H₂O-to-Si molar ratio, the concentration of possible catalysts [43,44].
The hydrolysis reaction is mediated by the addition of water, which gradually shifts the equilibrium governing the stability of alkoxide groups –OR and favors their replacement with hydroxyl groups -OH [40,41]. In the case of condensation processes, silanol groups Si–OH react with each other or with esterified silanol groups Si–OR to form siloxane bonds Si–O–Si [40,41]. Under usual conditions, hydrolysis and condensation take place concurrently [40,41]. However, a suitable adjustment of experimental parameters can permit the completion of hydrolysis and then the separation of the two above mentioned stages [40,41,45].

As condensation proceeds and the number of siloxane bonds increases, individual molecules aggregate into larger assemblies and gradually create the sol phase. The gel phase is formed when the individual colloidal particles suspended in the sol phase interact with each other and bridge into a network of siloxane bonds. The process of particle aggregation continues as the gel undergoes drying, which further promotes condensation [40,41].

According to such simplified description, SGP can be substantially regarded as a three-stage process involving first the polymerization of monomers to form individual particles in solution, the growth of individual particles as a consequence of surface aggregation processes and finally the interconnection of individual particles to form a gel phase. This latter stage implies forming networks of increasing complexity, ranging from linear and branched chains extending into the liquid phase to three-dimensional porous assemblies [40,41].

The network geometry depends on a number of factors, most of which have been already mentioned above. However, it is possible to recognize a few general features that can be usefully exploited to control the synthesis process, particularly with Si-based systems [40,41]. When the condensation processes is carried out under acid catalysis conditions, silicon oxide networks with chain and branched chain topology are mostly obtained [40,41]. In contrast, alkaline catalysis favors the formation of individual clusters with highly branched surfaces, which prevent their direct interaction and aggregation before gelation [40,41].

Even though SGP exhibits in principle considerable advantages over most conventional techniques for the preparation of ceramic materials, it also suffers of various limitations, which substantially hinder at present its industrial application. In particular, the materials synthesized by SGP generally exhibit unsatisfactory mechanical performances, low resistance to wear, high permeability to liquids and gases [40,41]. In addition, the solvent phases used in SGP are often trapped in porosity, which can give rise to undesired failures during thermal treatments [40,41]. Also, the performances of thin films are strongly affected by the nature of the underlying substrate and usually their use requires a relatively large thickness [40,41].

**Microwave processing (MWP)**

The processing of materials by microwave irradiation substantially relies upon their gradual heating [46]. However, microwave processing (MWP) is completely different from conventional thermal treatments. In the latter case, the transfer of thermal energy to a solid is typically mediated by the interaction of the solid surface with either electromagnetic radiation fields or convective currents inside a liquid phase. It is the heat conduction that allows the gradual temperature rise in the solid bulk. Conversely, the heating process induced by the absorption of microwaves is connected with the direct interaction of molecules with the electromagnetic field [46]. It follows that microwave heating better correspond to an energy conversion process rather than to heat transfer [46].

A direct consequence of the capability of microwaves of penetrating materials is that a uniform heating of the bulk is produced [46]. This also means that the temperature gradient is usually reversed with respect to conventional thermal treatments, with the solid bulk experiencing higher temperatures than the surrounding [46].

Penetrating microwave radiation, controllable distribution of electric fields, rapid temperature rises, selective heating of materials consequent to differential absorption of microwaves and self-limiting chemical reactions represent a few of the advantageous characteristics of microwave radiation over conventional material processing methods by heat transfer [46,47]. MWP also
provides promising alternatives for the processing of chemicals, ceramics, composites and minerals both in bulk and powder form.

Of course, MWP also involves challenging questions related to the difficulty of processing specific materials. For example, massive samples of materials characterized by relatively high ionic and metallic conductivities cannot undergo any effective MWP due to exceedingly limited penetration of microwaves in the bulk. Insulating systems with low dielectric loss factors are also difficult to heat as a consequence of the limited absorption of microwaves. It must be also noted that materials characterized by permittivity or loss factors steeply changing with temperature generally undergo a non-uniform heating and possibly thermal failures or undesired degradation [46,47].

The technological potential of MWP directly originates from the properties of microwaves. First employed during the World War II in radar applications, microwaves are electromagnetic waves in the wavelength domain between 300 MHz and 300 GHz. Industrial microwave processing is usually accomplished at the frequencies specifically set aside for industrial utilization, namely 915 MHz, 2.45 GHz, 5.8 GHz and 24.124 GHz [46,47]. However, microwave furnaces with variable frequencies, usually in the range between 0.9 and 18 MHz, have been also developed for fundamental research applications [46,47].

MWP is commonly carried out inside so-called furnaces, which consist of a microwave radiation source, a waveguide, an applicator to deliver the power to the sample, and a system to control heating [46-48]. A schematic description of a typical furnace for MWP is shown in Fig. 9.

![Figure 9. A typical furnace employed to submit materials to MWP.](image)

Most widespread microwave generators consist of vacuum tubes, but solid state devices are sometimes used. The magnetron is the most common microwave source in materials processing applications [46-48]. The waveguide system delivers the electromagnetic waves generated by the source to the applicator, typically a metallic reactor inside which the energy of the electromagnetic field is either absorbed or reflected by the material sample [46-48]. The most common applicators work under either multi-mode or single-mode conditions. In the former case numerous modes of the electromagnetic microwave field are simultaneously excited, whereas in the latter excitation concerns a single resonant mode [46-48]. The choice of the applicator to employ to perform MWP depends on the properties of the material to be processed. Single-mode and traveling-wave applicators can be successfully used to treat materials with a relatively simple geometry [46-48]. Industrial MWP employs instead multi-mode applicators, which permit the processing and production of materials of largest size and more complex shapes [46-48].

Apart from the sample geometry and applicator architecture, the absorption of the microwave electromagnetic field is directly connected with the dielectric properties of the material [46-48]. The interaction of microwaves with the material at a molecular level induces the translational and vibrational motion of both free and bound electric charges as well as the rotational motion of dipolar structures [46-48]. The distribution of kinetic energy on the different translational, rotational and vibrational modes determines a general excitation of the solid, which induces a
response mediated by inertial, elastic and local frictional forces [46-48]. The result is a temperature rise uniformly distributed inside the sample volume [46-48]. The heating rate, i.e. the rate at which temperature increases, depends on the strength of interaction between the material and the electromagnetic field [46-48]. The electromagnetic power absorbed by the material exhibits a linear dependence on the frequency of the microwave, on the relative dielectric constant, on the so-called loss tangent that measures microwave absorptivity, and on the square of the electric field amplitude [46-48]. The penetration depth, i.e. the distance at which the power of the incident electromagnetic waves is reduced by one half, is also dependent on such factor. More specifically, it changes linearly with the electromagnetic radiation wavelength [46-48].

A fundamental issue concerning the precise nature of interaction between microwaves and solid materials concerns the enhancement of chemical processes. This can be in principle ascribed to specific effects originated from the microwave irradiation, which would imply a secondary role for heating [46-48]. The experimental evidences accumulated until now did not succeed in a satisfactory definition and clarification of the question, mainly due to difficulties in local temperature measurements and to the fragmentary characterization of reactive processes. However, an extremely recent work seems to provide a definite negative response to such question [49]. In fact, a technology has been developed based on the use of SiC reaction vessels and single-mode microwave reactor that does not point out any a-thermal detectable effect [49]. The experimental evidences indicate indeed that the chemistry of reactions carried out in Pyrex glass and in SiC reactors is exactly the same, even though the material inside the SiC reactor is effectively prevented from interacting with the electromagnetic field [49]. It follows that MWP relies exclusively on thermal effects [49].

Provided that the material effectively interacts with microwaves, MWP can be carried out over a considerable variety of conventional and innovative materials. MWP applications range from the solution heating and drying to the synthesis of polymers and polymer composites, from the sintering of ceramics and ceramic composites to the preparation of functionally-graded materials [48]. Chemical synthesis processes have also suitably profited of MWP [50]. Along with the above mentioned conventional applications, MWP can be also employed to fabricate advanced materials such as micrometer- and nanometer-sized powders and tubes [48].

For example, MWP has been utilized to synthesize hexagonal hollow ZnO tubes with wall thickness of about 1 μm and sub-micron-sized hydroxyapatite whiskers [51,52]. Carbon as well as semiconductors nanotubes have been synthesized [54,54]. Nanometer-sized materials prepared by MWP also include a number of oxides [55].

MWP seems to have a future in specialty applications within the areas of science and technology in which it has considerable advantages over conventional thermal processing methods. Although most research efforts focused only on the laboratory scale, the potential benefits of MWP will be exploited only through a suitable process industrialization and the design of innovative reactors.

The development of so-called microwave plasma processing represents an example in such direction [56]. This technique represents an ancillary application of chemical vapor deposition and permits to couple the microwave electromagnetic field with a plasma discharge suitably generated in the reactor chamber [56]. As a consequence, kinetic energy is transferred to the electron gas, which is then imparted to ionic and neutral species by an energetic collision dynamics [56]. The final result is a considerable improvement of the deposition process, with particular reference to the case of diamond thin films [56].

**Spray pyrolysis (SP)**

Spray pyrolysis (SP) is a powerful methodology that can be applied to synthesize a wide variety of high-purity, chemically homogeneous fine and nanometer-sized powder particles as well as thin films [57,58]. It represents a variant of the so-called gas phase or aerosol method [57,58], with the term “aerosol” referring to a suspension of solid or liquid particles in a gaseous phase. Whereas physical and vapor deposition methods employ a gas-to-particle conversion route with a so-called
build-up approach, SP is a liquid-to-particle conversion route characterized by a break-down strategy for aerosol processing [57,58]. Starting from liquid phase or a sol, SP must be regarded as a liquid phase process [57,58].

The SP methodology is generally employed to produce large amounts of metal oxide powders with homogeneous particle size and high crystallinity degree [57,58]. However, various functional and multi-component materials can be also successfully fabricated [57,58].

The synthesis of fine and nanometer-sized particles by SP relies upon the use of a starting solution containing the salt of the desired metallic component. The starting solution is nebulized before entering the furnace and the resulting droplets processed at high temperatures. A number of consecutive reaction stages can take place, including the evaporation of the solvent phase, the precipitation of salts, the chemical reaction between the precursors and the surrounding gaseous atmosphere, the pyrolysis of solid phases and possibly their sintering [57,58].

A variant of the spray route, generally referred to as spray drying, makes use of precursors formed by colloidal solutions [57,58]. In this case, the final product can also consist of a nanostructured phase formed as a consequence of agglomeration processes involving the primary nanometer-sized particles present in the sol phase [57,58].

Figure 10. The experimental apparatuses employed to carry out SP processes with the aim of producing fine powders (a) or depositing thin films on a hot substrate (b).

The experimental apparatus for SP for the production of nanoparticles generally includes a nebulizer to convert the starting solution into droplets, a system for the circulation of the gaseous phase employed as a carrier, a furnace in the shape of a tubular reactor where temperatures up to 1200 °C can be reached and a so-called precipitator for the collection of powder particles [57,58]. Depending on the size and configuration, a SP apparatus can be fed at a rate as high as 10 liters of solution per minute of processing, which corresponds to a residence time of a few seconds, and
attain a production capacity on the order of 0.1 to 3 kg per day. The apparatus is schematically depicted in Fig. 10. An apparatus for the production of thin films is also schematically shown. Of course, it must be noted that different experimental conditions are necessary for producing nanometer-sized particles and thin films. Despite the identical general principles underlying their operation, SP apparatuses can exhibit significant differences in size, design and performances. These originate from the different choices that can be made in the attempt to suitably tailor the device capabilities in view of the desired final product. Since all of the parts of the experimental apparatuses are virtually susceptible of different choices, a considerable variety of SP processing systems are available in research laboratories and pre-industrial applications. The nebulization of the initial solution containing the chemical precursors can be performed by so-called air-assisted nebulizers, two-fluids nozzles, ultrasound irradiation and vibration [57,58]. The total length of the furnace reactor can vary considerably depending on the droplet or particle residence times associated with the heating process. In addition, the furnace can be designed to exhibit different temperature zones, aimed at allowing the best processing conditions in terms of axial temperature distribution [57,58]. Various instruments can be placed in intermediate position between nebulizer and precipitator in order to gain information on the dynamics of droplets and particles as well as on their chemical reactivity [57,58]. The precipitator can consist of a simple filter, of an electrostatic device as well as of a thermophoretic camera [57,58].

Depending on a number of different factors, SP can produce particles with tailored morphology, microstructure, size and chemical composition [57,58].

Of course, starting solutions play an important role. In fact, the chemical composition of the final product critically depends on the relative stoichiometric amounts of precursors dissolved in the solvent phase. Chemical precursors typically consist of inorganic salts of metallic species such as chlorides, nitrates and acetates. These are dissolved in the solvent phase, usually water or ethanol. Organic complexing agents can be used to enhance the low solubility of inorganic salts in the selected solvent phase. Similar considerations hold for the differential precipitation of the precursors, which must be suitably suppressed [57,58].

The generation of liquid droplets by atomization or nebulization represents another stage of outstanding importance to control the SP process. As a matter of fact, the average value as well as the statistical distribution of powder particle size are significantly affected by the average size of the initial droplets produced by the nebulizer as well as by the initial concentration of the chemical precursors in the starting solution. The number density and the velocity of droplets generated by nebulization can also affect the average size and the morphology of the final product [57,58].

Morphology is mostly affected by the chemical features of the precursor species, by the flow rate of the carrier gas inside the furnace and by the temperature profile of the furnace. A suitable variation of these parameters can induce a change of the final particle morphology from dense to hollow or from a single crystal to a mosaic system [57,58].

The synthetic opportunities offered by the SP method are schematically summarized in Fig. 11. The scheme permits to point out a few fundamental concepts lying at the basis of SP. First, the importance of relative time scales governing the evaporation of the solvent phase and the mobility of solutes. Depending on the predominance of one or the other of these factors, the droplet and the successive solid particle can exhibit different structural features and undergo different evolution. Second, the intimate relationship between droplets and particles that permeates all the mechanistic studies on SP processing. Indeed, SP is generally thought as a liquid phase processing method in which any individual solid particle originates from an individual droplet [57,58]. On the one hand, such idea comes from the intuitive connection of the number of droplets with the number of particles at relatively low nebulization rates. On the other, it is somewhat supported by the evidence that it is virtually impossible to synthesize nanometer-sized particles unless nanometer-sized, or at least extremely fine, droplets are generated [57,58].
The synthesis of solid particles by SP when the time scale of solvent evaporation is comparable with the one of solute diffusion (left) or significantly shorter (right).

The need of obtaining very fine, possibly nanometer-sized, droplets introduces a further degree of complication and represents a stringent limit on the performances of the nebulization process. However, such difficulty has been at least partly by-passed by mixing suitable fuels with the chemical precursors in the starting solution [57,58]. Dissolved fuels typically consist of alcohols, urea, nitrates and sugars. The use of fuel additives is based on the evidence that the evolution of heat and gases connected with their combustion induces a considerable fragmentation and disaggregation of solid particles, also assisted by the rapid solvent evaporation and consequent reaction under conditions relatively similar to vapor deposition processes [57,58].

The different strategies applied to develop SP processes effective in the synthesis of nanometer-sized systems has brought to the creation of different SP applications such as the flame-assisted spray pyrolysis, electrospray pyrolysis, low-pressure SP and salt-assisted aerosol decomposition [57,58]. The electrospray pyrolysis copes directly with the difficulty of generating very fine droplets by conventional nebulization processes. Rather than exploiting ultrasonic nebulizers or similar conventional devices, electrospray apparatuses employ very high electric voltages at the surface of the liquid meniscus formed at the end of a capillary tube. These induce the conical deformation of the liquid meniscus that exhibits a fine jet extending toward the counter electrode. As a consequence of the high electric potential difference, the jet breaks up and forms droplets with very small size, even down to a few nanometers. This allows the synthesis of nanometer-sized metallic, oxide, semiconductor and polymer systems [57-62].
Low-pressure SP is based instead on the utilization of a so-called filter expansion aerosol generator [63]. This generator is formed by a two-fluids nozzle for effectively dispersing a liquid phase, a filter consisting of porous glass and a vacuum pump [63]. The generator works in a very simple manner. First, a small amount of liquid phase is sprayed onto the glass filter in order to form a thin layer. Then, the liquid filters through the accessible porosity of the glass and reaches the opposite side, assisted by the diffusion of the carrier gas. Finally, the liquid phase expands into the low-pressure chamber forming very fine droplets, on the order of a few microns [63]. The successive processing of such small droplets easily results in the formation of nanometer-sized particles [63].

Salt assisted aerosol decomposition focuses on the agglomeration processes typically occurring when a pair of nanometer-sized particles formed in the furnace come into contact [64]. More specifically, the method exploits specific salts easy to remove in successive processing that are able to distribute on the surface of the nanometer-sized particles and then to prevent their coalescence [64]. Once the processing temperature exceeds the melting points of the added salts, these melt and behave like a sort of high-temperature solvent [64]. The material to be processed by SP can thus dissolve into the molten phase and react, eventually precipitating when the solubility degree of the product in the molten phase is exceeded [64]. At the end of the process, nanometer-sized particles of product are embedded into a salt matrix, the removal of which can be easily accomplished by washing the powders [SP8]. A variety of one- and multi-component oxide nanometer-sized particles have been already synthesized by this method [64].

SP represents one of the rare techniques for the synthesis of nanometer-sized systems susceptible of industrial application. It is a relatively low cost processing route, can be performed under continuous production conditions and can reach high production rates in suitably designed reactors [57,58]. It has been shown that SP can be profitably used as a chemical processing technique to produce a huge number of different powders as well as to deposit a considerable variety of materials in the form of thin films. In both cases, the substrate temperature, the spray rate, the concentration of the starting solution, the nature of chemical precursors as well as the nebulization method represent the most critical parameters to control the size of the nebulized droplets and their distribution inside the reactor chamber. A review of the existing literature on SP clearly demonstrates the versatility of the method to obtain metal oxides, metallic spinel oxides, binary, ternary and quaternary chalcogenides and superconducting oxides [57-64]. The properties of the materials produced, and then the future applications of SP methods, depend on the capability of adjusting or optimizing the SP processing conditions [57,58].

Flame synthesis (FS)
The utilization of flames underlies one of the most promising methodologies for the production of nanometer-sized materials on a large scale [65-68]. Most of its potential can be ascribed to the unique processing conditions imposed to reactants by flame combustion [65-68]. In fact, flame synthesis (FS) is characterized by rapid heating and cooling stages that allow the formation of materials with particular chemical composition, microstructure and morphology [65-68].

The recent progress in the comprehension of combustion processes is pushing the capabilities of FS further, permitting the preparation of materials with specifically tailored properties, including nanometer-sized particles [65-68]. In addition, carrying out a FS process is quite easy and this provides a considerable economic advantage over the various technologies developed to prepare nanometer-sized systems [65-68]. The process is intrinsically scalable on the industrial level, the heat of combustion can be suitably utilized to activate reactants and precursors, evaporate solvents and pyrolyze materials when necessary [65-68]. Also, the production of particles does not require a specifically designed reactor, but rather just a suitably designed container to collect the particles after the synthesis [65-68]. Finally, FS takes place on relatively short times, thus ensuring on the one hand the possibility of carrying out a continuous production process and on the other a high production rate [65-68]. It follows that FS can be regarded as the method for the synthesis of
nanometer-sized particles which exhibits the greatest potential for industrial development [65-68]. On the other hand, it already accounts for more than 90% of fine and nanometer-sized particles synthesized in a gaseous environment [65-68].

The success of FS and its great potential for future development mainly relies upon the availability of many variables to control the process [65-68]. These include the structure and temperature of the flame, the stoichiometry of precursors and reactants, the pressure of gases, the relative position of reactant injection and product extraction systems and a number of other specific factors related to both the combustion process and the design of the experimental apparatus [65-68].

FS has been shown to be a valuable and reliable method to fabricate a variety of nanometer-sized structures ranging from quantum dots to tubes [65-68]. The chemical nature of materials is not limited to metal or semiconductor ceramic oxides [65-68]. On the contrary, FS has been successfully applied to the preparation of nanometer-sized particles of pure metals, semimetals and semiconductors, borides, carbides, nitrides and alloys [65-68]. For this purpose, considerable attention is paid to the innovative design for combustors and to the utilization of non-conventional fuels and oxidizers [65-68].

Consequent to the versatility and flexibility of the method, FS processes exhibit a considerable variability in the reactor design and the details of flame processing. It is in connection with the state of the chemical precursors that FS processes are usually identified and classified [69].

Liquid-fed aerosol flame synthesis represents the most versatile methodology. It is based on the use of liquid solutions in which chemical precursors are dissolved, of emulsions in which two liquid phases are suitably mixed or of suspensions of solid particles in the liquid [65-69]. The complete evaporation of the liquid results in the formation of solid nanoparticles, whereas the incomplete evaporation of the liquid droplets induces the formation of hollow structures [65-69]. The solution can be sprayed through nozzles and the combustion possibly assisted by an external flame, being the resulting process generally referred to as flame-assisted spray pyrolysis [69,70].

Figure 12. The vapor-fed aerosol flame synthesis of nanometer-sized particles.

Vapor-fed aerosol flame synthesis can be instead defined as the combustion of volatile precursors [65-69]. In this case, nanometer-sized particles are formed as a consequence of the chemical reaction of the precursors in the gaseous phase, followed by nucleation and growth stages.
[69,70]. Although limited to some extent by availability of suitable chemical precursors and associated costs, this process finds industrial application for the preparation of fumed silica, alumina and titania [65,69]. It is schematically depicted in Fig. 12.

The final nanometer-sized particles, or their aggregates, can be collected by employing filters, so-called cyclone separators and electrostatic precipitators [69]. Otherwise, the combustion products can be deposited on a suitable substrate [69].

Although the individual fundamental stages of FS processes can exhibit considerable complexity, their general description can be relatively simple [65-69].

The chemical precursors are injected into the combustion chamber in the form of gaseous phases, liquid droplets or solid particles. Due to the high flame temperature, both liquid and solid phases undergo rapid evaporation processes. The resulting vapors can readily react to form the first nuclei of products, which subsequently grow as a consequence of surface and coalescence processes as well as of agglomeration ones. In the former case, the individual particle grows as a result of the chemical interaction between precursors or nuclei at the particle surface. These processes are usually favored by high temperatures, so that typically take place in the highest temperature region of the flame. As the particles reach a lower temperature zone, coalescence processes between different particles and nuclei are no longer possible and aggregation phenomena predominate.

The properties of the materials involved as well as the processing conditions determine to a large extent the degree of particle coalescence and agglomeration, the microstructure of the solid and the final morphology of individual particles and aggregates. The characteristics of the final product are affected by the chemical reactivity of precursor species, the flame temperature and the time of residence inside the combustion chamber.

As briefly mentioned before, the final products can be in the form of either particles or films [69]. The various process parameters allow the production of materials with tailored characteristic size, structure and morphology [69]. It is also possible to control the chemical composition through a suitable mixing of initial reactants and a control of the gaseous atmosphere [69]. Depending on the residence times, porous or dense films can be obtained [69].

The number of different materials synthesized by FS processes has exponentially grown in recent times [69]. Materials range from conventional oxides to the salts of metallic species and from pure metals and metallic alloys to metallic phases supported on oxide substrates [69]. Borides, carbides, nitrides have been obtained together with fullerences and carbon nanotubes [68,69].

Of course, the availability of a methodology such as FS represents a considerable opportunity for manufacturing nanometer-sized systems in an efficient and economic manner. Although the FS process is relatively well understood from a fundamental point of view, there are still various open questions and niches of application that propose serious challenges. For example, a better control of combustion and evaporation processes, as well as a suitable control on the atomistic scale of local composition in the case of multi-component functional materials [69]. Nevertheless, FS is a mature technology ready for industrialization.

**Inert gas condensation (IGC)**

Inert gas condensation (IGC), also referred to in the specific literature as gas phase condensation, is one of the most popular methodologies to fabricate nanometer-sized and nanostructured massive materials [71]. Its considerable success is substantially motivated by the unusual control that the method allows on the particle size and size distribution [71].

The first experiments on IGC date back to 1930s, when the synthesis of extremely fine particles by nucleation and growth was attempted starting from an inert gaseous phase containing the vapors of a selected metal [71]. With various successive modifications, the method was shown able to synthesize electrically insulated metal particles with average diameter below 10 nm and narrow size distribution [71]. Staring from 1960s, the IGC process was intensively used to produce a variety of metallic particles with size in the range from 10 to 100 nm in a low pressure gaseous environment [71]. However, it was only after the 1980s that the IGC method attracted widespread interest as a
consequence of its capability of producing nanostructured materials by consolidation of the nanometer-sized particles created by nucleation and growth processes in the gaseous phase and subsequently deposited on a suitable substrate [71-73].

Although the IGC method was initially employed to only synthesize metal nanoparticles, the process has been now extended to a variety of materials including both metallic and ceramic systems as well as semiconductors and ionic salts [71].

The IGC process is based on a relatively simple two-stage mechanism. The selected material is first evaporated in a low pressure reactor chamber and then submitted to a rapid condensation process under controlled conditions, which allows obtaining the selected average particle size.

A typical apparatus for IGC is shown in Fig. 13. The material to be evaporated is placed in suitable crucibles inside the chamber and slowly heated to undergo the necessary degassing process. At the same time, the chamber is evacuated to a residual pressure on the order of $10^{-4}$ Pa. After evacuation, a suitable amount of inert gas is introduced into the chamber in order to reach a pressure of about 100 Pa. The crucible containing the material, generally in the form of powder, is then heated at high rates and the solid evaporated. The dynamics of atomic species in the vapor phase is such that nucleation processes rapidly occur, with consequent formation of the first nuclei of solid particles. These undergo a relatively fast growth by surface condensation and particle coalescence processes, that finally produce the nanometer-sized particles in the desired size range. The particles are then collected typically on a cooled substrate [71-74].

In the most recent configurations, the reactor chamber is evacuated to ultrahigh vacuum levels. In addition, various evaporative sources are available inside the chamber. Among the others, evaporation can be induced by electrical resistive heating, radiofrequency energy injection, electron beam energy transfer, ion sputtering and laser irradiation. The reactor chamber is possibly equipped with a powder compaction device to obtain nanostructured massive samples [71-74].

![Figure 13. A typical IGC reactor for the synthesis of nanometer-sized particles.](image)

The dynamics of the atomic species in the gaseous phase is qualitatively simple [75]. The evaporated atoms collide with inert gas atoms as well as with each other. Once a pair of collided atoms loses a sufficient amount of kinetic energy, it remains in a bound state and form a dimer. The dimer can interact with another atom and form then a trimer. The process continues with individual atom or cluster addition until the necessary supersaturation degree is reached, which allows the nucleation of a nanocrystal. Inside the chamber, both particles and clusters are submitted to a convective regime due to the temperature difference between the crucible and the cold substrate employed to deposit and collect the solid material formed in the gaseous phase. Precisely such
convective currents determine the gradual deposition of the particles over the substrate. The material deposited on the substrate exhibits a very irregular structure characterized by fractal features, i.e. very loose packing.

Based on the above mentioned description, the final particle size is to a large extent governed by the relative rates of three fundamental processes. In particular, the rate at which vapor phase attains supersaturation, the rate at which atoms loose energy by interaction with the inert gas and the rate at which particles and clusters move apart from the supersaturation region inside the chamber [71-74].

Such rates can be controlled by suitably tuning experimental parameters. For example, a high pressure of inert gas accelerates the loss of kinetic energy loss and then atomic recombination and coalescence processes. Also, local temperatures can be suitably adjusted to control convective currents and then average residence times in the region of vapor supersaturation [71-74].

**Vapor deposition (VD)**

The deposition from a vapor phase represents one of the most versatile methods to obtain uniform thin films and coatings on solid substrates as well as nanometer-sized systems [76,77]. The terms substantially identify any given process in which the coating is obtained through the deposition on a substrate of materials initially in the vapor phase [76,77]. In turn, this can be accomplished either by a thermodynamic transition from the vapor to the solid phase or by a chemical process [76,77].

The outstanding importance of vapor deposition (VD) processes is motivated by their capability of controlling the structure of deposited material on the atomic level [76,77]. This permits the manipulation of the physical and chemical properties of deposited materials and therefore a tailoring of their functionality, which finds valuable application in a variety of fields ranging from giant magnetoresistance to photovoltaics and from chemical protection to microelectronics [76,77].

Depending on the fundamental characteristics of the deposition process, VD methods are further subdivided into physical VD (PVD) and chemical VD (CVD) categories [76,77]. In the former case, the methods rely upon a condensation process from the vapor phase with no intervention of chemical driving forces [76,77]. In the latter, instead, the deposition is allowed precisely by the occurrence of chemical reactions involving vapor phase and substrate [76,77].

PVD methods are conceptually the simplest ones [78,79]. Essentially, they consist of two fundamental stages [78,79]. First, the desired material is brought into the vapor phase into a reactor chamber under ultra high vacuum conditions. Then, it is deposited on a suitable substrate.

In the most widely employed PVD technologies, the desired vapor phase is obtained by evaporation or sputtering processes [78,79]. Evaporation based PVD methods are mostly employed to deposit metallic species. The starting material is placed into a crucible, which is subsequently heated typically by electrical resistance, inductive or electron-beam methods [78,79]. The crucible is generally given a shape such that evaporated atoms have a restricted number of allowed linear trajectories. This permits a so-called line-of-sight deposition on the cold substrate due to the ultra high vacuum conditions and the consequent collision-free atomic dynamics in the vapor phase.

An evaporation PVD reactor is shown in Fig. 14. PVD processes driven by thermal evaporation essentially employ low energy atoms, which results in a relatively low deposition rate, a relatively large size of individual crystalline domains and a relatively poor adhesion of the obtained thin film [78,79].

In the case of PVD processes based on sputtering, the desired atoms are brought into the vapor phase by localized ablation phenomena involving the surface of the selected solid material. Ablation is driven by the impingement of positive ions of chemically inert species, typically Ar cations, accelerated through an electric field and directed to the target. The collisions of cations with the target surface displace the surface species, which successively deposit on the substrate.
The emission of atoms, molecules and possibly clusters from the solid target is a relatively complex process that involves the formation of a plasma of cationic species and electrons. In general terms, localized ablation phenomena involve a surface layer about 1 nm thick. About the 95% of incident kinetic energy is absorbed by the target, which then needs suitable cooling. The residual 5% of energy is transferred to displaced atoms, the kinetic energy of which ranges roughly from 5 to 100 eV. As a consequence, sputtering PVD methods involve more energetic species than evaporation ones. This results in higher deposition rates, a deposition less controlled by line-of-sight directions as a consequence of the collision dynamics in the plasma region, a smaller size of individual crystalline domains and a better adhesion of the produced coating [78,79]. Moreover, sputtering PVD can be carried out on a wider range of materials and assures a called better shape coverage [78,79].

Another PVD methodology is the molecular beam epitaxy (MBE) [78,79]. MBE is based on evaporation, but the deposition process is carried out at very low rates in ultra high vacuum conditions. This permits a considerable control of the processes occurring inside the reactor chamber, which allows the growth of thin films with tailored structure and properties [78,79].

Contrary to PVD, CVD methods involve either the dissociation or the chemical reaction of gaseous precursors and reactants under thermal, radiant or plasma activation conditions [80-82]. The deposition process can be based both on homogeneous chemical events in the gas phase and heterogeneous chemical reactions at, or in proximity of, the surface of the heated substrate [80-82]. Depending on the processing conditions, the final result is a thin film or a fine powder [80-82].

In the last four decades, CVD methodologies have benefited enormous advances from both scientific and technological points of view. CVD is now a mature technology for the deposition of thin films and coatings [80-82]. These have found application in a number of different areas concerned with wear, corrosion, and oxidation phenomena as well as with thermal insulation and neutron shielding [80-82]. A considerable variety of chemical compositions is now available for coatings obtained by CVD, including pure elements, borides, carbides, nitrides, oxides, silicides and sulfides as well as their combinations [80-82].

CVD processes can be carried out in both “open” and “closed” systems [80-82]. In a “closed” system, both reactants and products can be re-utilized. This is the case of reactive systems in which the chemical reactions are reversible depending on the processing temperature [80-82]. Although “closed” systems can be important for the purification of metals, at present CVD methods essentially employ “open” systems in which the reaction products are removed after deposition with no recovery attempt [80-82].
The CVD process consists of different consecutive steps [80-82]. In the first place, the gaseous reactant species are suitably generated. Second, such species are transported to the reaction chamber. Third, the reactants undergo one or more chemical reactions in the gas phase.

In some cases, the above mentioned homogeneous chemical reaction is followed by the formation of solid products consequent to further reaction or decomposition of the intermediate species. When this occurs, the CVD process results in the formation of powder particles [80-82]. Alternatively, the intermediate species formed by the homogeneous chemical process can be brought into contact with a solid substrate. They can here undergo a heterogeneous chemical reaction with the substrate surface, on which the solid reaction products form a deposit. The different deposits act as nucleation centers for the crystalline thin films, which form gradually as the deposition proceeds [80-82].

Once the CVD process is interrupted, both reaction by-products and unreacted materials are removed from the deposition chamber [80-82].

The precursors commonly used in CVD must satisfy a number of requisites including room temperature stability, low evaporation temperature, high vapor phase saturation and stability of the generated vapor at relatively low temperature [80-82]. In addition, they must exhibit suitable deposition rates and allow the desired chemical reactivity [80-82].

The precursors commonly employed in CVD consist of pure metals and metal hydrides, halides and halohydrides as well as of metallorganic compounds [80-82]. These precursors can typically undergo thermal decomposition, reduction, oxidation, nitridation, hydrolysis, and metathesis chemical reactions [80-82]. Such reactions normally take place under non-equilibrium conditions. In fact, CVD spontaneously tends to far-from-equilibrium processing conditions [80-82].

![Diagram of CVD process](image-url)

**Figure 15.** The reactor chamber for the deposition of thin films by CVD (top) and a simplified representation of the reaction stages in the case of the deposition of polycrystalline Si starting from the SiH₂Cl₂ halohydride.
The CVD reactor consists of a reaction chamber equipped with a mobile sample holder for the transport and placement of the desired substrate into the chamber, a substrate holder, and a heating system with temperature control [80-82]. CVD reactors usually employ a “cold wall” configuration, in which only the substrate is heated to avoid generalized deposition of products onto the reaction chamber [80-82]. An effluent gas handling system, possibly comprising a vacuum system, is also employed to suitably deal with exhaust gases and reaction by-products [80-82]. A typical CVD reactor is schematically described in Fig. 15.

The CVD process is controlled by a number of parameters including the temperature of the substrate, the total gas pressure, the relative reactant concentration, and the total gas flow [80-82]. Of course, a suitable knowledge of the general thermodynamic and kinetic features of the chemical reactions involved is necessary to control CVD [80-82]. In addition, the transport of reactants and precursors to the substrate is influenced by the reactor geometry and the substrate shape [80-82].

In the light of the above mentioned considerations, it is not surprising that CVD conditions exhibit a considerable variability [80-82]. Depending on the physical and chemical properties of reactants and precursors, the CVD process can be performed under vacuum or relatively high pressure conditions, and require relatively low or relatively high substrate temperatures or reactant partial pressures [80-82]. This originates a number of CVD variants of the simple thermally activated CVD process [80-82]. Depending on the method employed to activate the chemical reactions, the so-called plasma enhanced and photo-assisted CVD methodologies have been developed [80-82]. Atomic layer epitaxy is a CVD method allowing the layer-by-layer growth of the desired crystalline phase [80-82]. Pulsed injection metallorganic and aerosol assisted CVD are further variants as well as the flame assisted vapor deposition and the electrochemical vapor deposition [80-82].

The materials obtained by CVD methods are extremely variegated and include semiconductors, dielectrics, metallic phases, ceramics, and optical fibers [80-82]. Among the others, a variety of nanometer-sized and nanostructured materials have been synthesized by CVD, including carbon nanotubes [80-82].

**Vapor-liquid-solid growth (VLS)**

The so-called vapor-liquid-solid (VLS) process specifically addresses the synthesis of one-dimensional nanometer-sized structures, i.e. nanowires [83-86]. It substantially represents a variant of CVD processes [83-86]. In fact, also VLS is based on the chemical interaction between precursors in the vapor phase and the solid substrate supporting the one-dimensional structure [83-86]. However, different from CVD, the VLS process allows the fabrication of oriented single crystals of semiconductor systems with a good control of diameter, length and chemical composition [83-86]. In addition, it is also possible to modulate both longitudinal and axial substructures in terms of chemical composition profiles [83-86].

The VLS synthesis relies upon the catalytic effects of a nanometer-sized droplet of a liquid metallic phase deposited on a solid substrate [83-86]. The droplet interacts with the chemical precursors in the surrounding vapor phase, dissolving a fraction of them [83-86]. As the droplet becomes supersaturated with precursors, a precipitate phase is formed [83-86]. This subsequently gives rise to a crystalline domain with roughly the same surface area of the liquid droplet [83-86].

In the light of the above mentioned considerations, the mechanism of the VLS synthesis can be summarized by a few fundamental stages [83-86]. First, a cluster of the metallic phase is deposited on the selected solid planar substrate. Second, the system temperature is raised above the metallic phase melting point. Third, the liquid droplet is exposed to the vapor phase containing the desired chemical precursors, so that precursors are absorbed at the droplet surface and then diffuse in its interior. Fourth, the concentration of precursors inside the droplet attains supersaturation and a novel crystalline phase nucleates. It can consist of one or more chemical species contained in the absorbed precursor molecules. Since nucleation takes place at the interface between the liquid droplet and the solid substrate, the crystal can grow only along the direction perpendicular to the
substrate surface. The result is a nanowire, the length of which depends on the amount of precursors feeding the liquid droplet. The sequence of elementary stages is schematically given in Fig. 16.

The first mechanistic interpretation of the VLS process was proposed in 1964 to explain the growth of Si whiskers from a vapor phase when liquid Au droplets were deposited on a Si substrate [87]. In such case, an Au layer a few nanometers thick was deposited onto a Si substrate by thermal evaporation. The Si substrate was then annealed at temperatures above the eutectic point of the Au-Si alloy, which induced the formation of Au-Si liquid droplets on the substrate surface. The system was then exposed to a vapor phase of SiCl₄ and H₂ at a temperature of about 950 °C. Due to the favorable thermodynamic driving force, Si first underwent absorption into the liquid droplet and then a precipitation under supersaturation conditions.

![Figure 16](image1.png)

**Figure 16.** Growth mechanism of a crystalline nanowire synthesized by VLS process.

The result was the formation of a Si crystal precisely in correspondence of the surface area occupied by the liquid droplet, which was therefore raised from the initial substrate surface. The VLS mechanism is to a large extent dominated by surface energetic at the liquid-solid interface between supersaturated droplet and growing nanowire [5,83-87]. Despite this generic statement, various questions remain still open, particularly in connection with the dependence of overall saturation degree and surface energies on the droplet size [5].

**A few final considerations**

The short, and necessarily incomplete, overview of the different methods heretofore considered represents an attempt to provide a brief description of the general ideas underlying the synthesis of nanostructured and nanometer-sized systems. It can be readily seen how any process in principle capable of producing reduced portions of matter can be substantially utilized to this aim. “Top-down” and “bottom-up” approaches, arrested nucleation processes and controlled growth phenomena, selective deposition and energetic degradation reactions as well as a number of other methodologies must be regarded as the results of conceptual and practical efforts devoted to obtain a suitable control of matter on a length scale quite far from usual. Further progress is expected in the next future, particularly in the research areas dealing with nanometer-sized materials for energy harvesting and conversion, environmental remediation and protection, biochemistry and biotechnology.

Providing the most suitable response to the questions posed by the challenging issues mentioned above will require a careful choice of synthetic methods and a considerable refinement of general knowledge. It is quite easy to see the number of questions usually arising when a researcher is called in choosing a synthetic method to prepare the desired material. How can be the selected size range of products attained? How can be the morphology of products controlled? What are the advantages offered by a given methodology? What are instead the disadvantages? Can be a given synthetic process suitably modified and oriented to yield a product that is not the most common one?
All of these questions, and similar ones, can receive a response only after a detailed study of existing literature aimed at clarifying the physical and chemical aspects of the researcher’s ideas. The response will be often a compromise between acquired knowledge and acceptable risk, which comes out from a suitable weighting of advantages and disadvantages as well as by an adequate evaluation of feasibility.

In view of such situations, a summary of significant features of the synthetic methods discussed in the present chapter can be useful. It is given in Table 2, where the size range and morphology of products as well as the most evident advantages and disadvantages are indicated.

Of course, Table 2 only gives general indications. It must be therefore intended that exceptions to the information provided are always possible.

**Table 2.** Size range and morphology of products, advantages and disadvantages for the synthetic methods discussed in the present chapter.

<table>
<thead>
<tr>
<th>Synthetic method</th>
<th>Size range (nm)</th>
<th>Product morphology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>MQ</td>
<td>5 - 500</td>
<td>Powders, ribbons</td>
<td>Short processing times. Accessibility to metastable states. Castability.</td>
<td>Small samples. Control of processing conditions. Large energy consumption.</td>
</tr>
<tr>
<td>DV</td>
<td>5 - 100</td>
<td>Powders, ribbons</td>
<td>Controlled microstructure.</td>
<td>Applicability restricted to glassy substrates.</td>
</tr>
<tr>
<td>SC</td>
<td>1 - 100</td>
<td>Particles, powders</td>
<td>Versatility.</td>
<td>Control of local processing conditions. Low efficiency.</td>
</tr>
<tr>
<td>PLA</td>
<td>1 – 50</td>
<td>Thin films, nanowires, nanotubes</td>
<td>Deposition of high-melting point systems.</td>
<td>Ultrahigh vacuum processing conditions.</td>
</tr>
<tr>
<td>Method</td>
<td>Equivalent Concentration</td>
<td>Products</td>
<td>Versatility</td>
<td>Material Properties</td>
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<tr>
<td>--------</td>
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</tr>
<tr>
<td>SGP</td>
<td>1 - $1 \times 10^5$</td>
<td>Powders, nanoparticles, nanowires, nanotubes</td>
<td>Versatility. Variety of accessible structures. Control of porosity. Broad range of synthesizable materials.</td>
<td>Restricted to soluble species. Long processing times.</td>
</tr>
<tr>
<td>MWP</td>
<td>10 - $1 \times 10^5$</td>
<td>Powders, nanoparticles, nanowires, nanotubes</td>
<td>Short processing times. Heating homogeneity. Versatility. Broad range of synthesizable materials. Industrial scaling.</td>
<td>Restricted to materials with suitable dielectric properties. Use of MW transparent reactors.</td>
</tr>
<tr>
<td>IGC</td>
<td>10 - 100</td>
<td>Powders, nanoparticles</td>
<td>Versatility. Control of experimental conditions.</td>
<td>Ultrahigh vacuum processing conditions</td>
</tr>
<tr>
<td>VLS</td>
<td>5 - 100</td>
<td>Nanowires</td>
<td>Control of experimental conditions. Selective modulation of the compositional profile.</td>
<td>Restricted to specific precursors.</td>
</tr>
</tbody>
</table>

A final word of comment about the processes underlying the synthetic methods dealt with. All of them exhibit a considerable degree of complexity, even in the apparently roughest cases. Mastering all of their most intimate aspects represents a challenging issue well beyond the possibility of individual researchers’ life. Physical and chemical features are often inextricably intertwined, offering on the one hand infinite opportunities, on the other unavoidable difficulties. It is precisely...
the complex dynamics of scientific progress that allows the necessary exchanges between different areas, ideas and philosophies. Often, the complexity of the individual processes underlying the synthesis of nanometer-sized materials does not permit the identification of solutions on a strictly scientific basis, however complicated they could be. For this reason, there is still considerable room for expertise and imagination, which make in combination the synthesis of advanced nanometer-sized materials something close to artistic creation.

References


Size dependence of optical properties in semiconductor nanocrystals

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Abstract. An extension of the classic thermodynamic theory to nanometer scale has generated a new interdisciplinary theory - nanothermodynamics. It is the critical tool for the investigation of the size-dependent physicochemical properties in nanocrystals. A simple and unified nanothermodynamic model for the melting temperature of nanocrystals has been established based on Lindemann’s criterion for the melting, Mott’s expression for the vibrational melting entropy, and Shi’s model for the size dependence of the melting point. The developed model has been extensively verified in calculating a variety of size- and dimensionality-dependent phase transition functions of nanocrystals. In this work, such a model was extended to explain the underlying mechanism behind the bandgap energy enhancement and Raman red shifts in semiconductor nanocrystals by (1) investigating the crystal size $r$, dimensionality $d$, and constituent stoichiometry $x$ dependences of bandgap energies $E_g$ in semiconductor quantum dots (QDs) and quantum wires (QWs); and (2) revealing the origin of size effect on the Raman red shifts in low dimensional semiconductors by considering the thermal vibration of atoms. For $E_g$, it is found that: (1) $E_g$ increases with a decreasing $r$ for groups IV, III-V and II-VI semiconductors and the quantum confinement effect is pronounced when $r$ becomes comparable to the exciton radius; (2) the ratio of $\Delta E_g(r, d)_{QW}/\Delta E_g(r, d)_{QDs}$ is size-dependent, where $\Delta E_g(r, d)$ denotes the change in bandgap energy; (3) the crystallographic structure (i.e. zinc-blende and wurtzite) effect on $E_g$ of III-V and II-VI semiconductor nanocrystals is limited; and (4) for both bulk and nanosized III-V and II-VI semiconductor alloys, the composition effects on $E_g$ are substantial, having a common nonlinear (bowing) relationship. For the Raman red shifts, the lower limit of vibrational frequency was obtained by matching the calculation results of the shifts with the experimental data of Si, InP, CdSe, CdS$_{0.65}$Se$_{0.35}$, ZnO, CeO$_2$, as well as SnO$_2$ nanocrystals. It shows that: (1) the Raman frequency $\omega(r)$ decreases as $r$ decreases in both narrow and wide bandgap semiconductors; (2) with the same $r$, the sequence of size effects on $\omega(r)$ from strong to weak is nanoparticles, nanowires, and thin films; and (3) the Raman red shift is caused by the size-induced phonon confinement effect and surface relaxation. These results are consistent with experimental findings and may provide new insights into the size, dimensionality, and composition effects on the optical properties of semiconductors as well as fundamental understanding of high-performance nanostructural semiconductors towards their applications in optoelectronic devices.

1. Introduction

1.1 Scope. This report starts with Section 1 that presents a brief overview on the experimental and theoretical progress of size-dependent bandgap energy and Raman red shifts in semiconductor nanocrystals. A consistent insight into the mechanism behind the size effect on optical properties in semiconductor nanocrystals is essential for their practical applications in optoelectronic devices. In Section 2, a simple and unified nanothermodynamic model for the melting temperature and cohesive energy of nanocrystals was established based on Lindemann’s criterion for the melting, Mott’s expression for the vibrational melting entropy, and Shi’s model for the size dependence of the melting temperature with considerations of size and dimensionality effects. The developed model was
extended to illustrate the size, dimensionality, and constituent stoichiometry dependences of bandgap energies as well as the size- and dimensionality-dependent Raman red shifts in semiconductor nanocrystals. In Section 3, the accuracy of the developed model was verified by using the available experimental data and other theoretical results of semiconductor nanocrystals reported in open literatures. Section 4 summarizes the main contribution and challenge of this work. Further investigation of structural evolution and physicochemical properties in cluster-based materials would stimulate new discoveries in materials research community.

1.2 Overview. When the size of low-dimensional materials approaches the nanometer scale, the electronic, magnetic, optic, catalytic, and thermodynamic properties of the materials diverge significantly from those of isolated atom as well as bulk materials [1]. The reasons lie in the so-called specific and smooth size effects. The former is responsible for the existence of “magic numbers” and related irregular variation of properties in clusters, whereas the latter pertains to nanostructures in the size domain between clusters and bulk systems [2]. The discovery of novel nanostructured materials has generated enormously ever-increasing interests for scientific insight [3]. Moreover, owing to the change of the properties, the fabrication of nanostructural materials and devices with unique properties in atomic scale has become an emerging interdisciplinary field involving solid state physics, chemistry, biology, and materials science [1]. Understanding the physical and chemical nature behind the new properties in nanocrystals is desired for fabricating the materials for practical applications. In this report, special attention is paid to the optical behaviours of semiconductor nanocrystals, bandgap energy enhancement and Raman red shifts, which have triggered great interests due to their scientific and industrial importance.

1.2.1 Bandgap energy of semiconductor nanocrystals. In last two decades, a diverse range of semiconductor nanocrystals have been vigorously developed in order to exploit their physical properties for high-performance optoelectronic devices. When the size of semiconductor nanocrystals approaches 1-5 nm and hence becomes comparable to their exciton radius, quantum confinement becomes a significant determinant of their physicochemical properties [4-6]. Both quantum dots (QDs) and quantum wires (QWs) have demonstrated quantization effects under these conditions. Semiconductor nanocrystalline materials have been used in many applications as advanced functional materials, especially in optoelectronic devices, such as laser diodes, high-speed field-effect transistors, solar cells, UV photodetectors, and biomedical tags [4-6]. Many of these applications are related to the most identifiable aspect of quantum confinement of semiconductor QDs and QWs: the valence-conduction bandgap energy $E_g$ increases as the radius $r$ of QDs and QWs decreases [4-6]. Such enhanced bandgap energy has been reported experimentally in covalent Si (IV) [7-10] with diamond structure, III-V (GaAs [11,12]), GaP [12-14], GaAs [15,16], InN [17], InP [18-20], InAs [19,21-25] etc.) and II-VI (ZnS [26-30], ZnSe [31-33], ZnTe [34], CdS [19,35-41], CdSe [38,42-47], CdTe [38,48,49] etc.) semiconductors, which have zinc-blende (ZB) or wurtzite (WZ) crystallographic lattice structures. As a result, an understanding of the size effect on the bandgap energy is one of the most important topics in the QD and QW research community. Asides from the change of size, differences in the dimensionality also result in different $E_g$ values of semiconductor nanocrystals due to the various dimensionalities of confinement [5,20,25,46,47]. Moreover, for certain applications, QWs exhibit more potential technological advantage over QDs, which has been experimentally demonstrated by the observation of linearly polarized emission and lasing from QWs [25]. However, in contrast to QDs, studies of QWs are still in their infancy and the related research publications are limited [5]. With rapid developments in nanocrystals synthesis technologies, the size and dimensionality of nanocrystals can be manipulated in a controlled fashion. This provides the opportunity to study the dimensionality dependence of the quantum confinement effects and also the difference of bandgap structures between the QDs and QWs.

Recently, efforts toward new materials development have focused primarily on the fabrication of semiconductor nanocrystals of various sizes and dimensionalities [5]. However, variations in nanocrystal size may also affect the performance of optoelectronic devices on account of the variation of thermal stability induced by the size reduction. As a result, recent advances have led to the
exploration of tunable optical properties in nanosized alloys where both the nanocrystal size and the constituent stoichiometries in materials may be altered to select multiple desirable qualities simultaneously [50-52]. It is reported that these nanoalloys have superior luminescent properties comparable to or even better than the best-reported binary semiconductor nanocrystals and that they are the promising materials for optoelectronic devices [53]. Recently, several III-V (In,Ga1-x,N [54-56], GaxAl1-x,N [57], InxAl1-x,N [58], etc. with 0 ≤ x ≤ 1 being the atomic fraction) and II-VI (Zn,Cdx,Se [53,59] and Zn,Cdx,S [60,61]) semiconductor alloyed nanocrystals have been fabricated and their tunable optical properties have been investigated experimentally. It is found that a nonlinear (bowing) relationship between \( E_g \) and \( x \) is discernible in nanosized alloy systems. However, the nature behind the variation of \( E_g \) in semiconductor nanoalloys is not clear.

In complement to experimental efforts, numerous theoretical approaches have been implemented to investigate the \( E_g \) enhancement in semiconductor nanocrystals. The first model is the quantum confinement theory based on the effective masses of electron and hole [62]. Based on this theory, the size-dependent bandgap energy \( E_g(r) \) is expressed as

\[
E_g(r) = E_g(\infty) + \hbar^2 \pi^2/(2\mu r^2),
\]

where \( E_g(\infty) \) denotes the bandgap energy of bulk materials and \( \mu \) (1/\( \mu \) = 1/\( m_e \) + 1/\( m_h \) with \( m_e \) and \( m_h \) being the effective masses of electron and hole, respectively) is the reduced mass of an electron-hole pair. Eq. (1) has been further extended by including the Coulomb energy and the correlation energy between the electron and the hole [63,64],

\[
E_g(r) = E_g(\infty) + \hbar^2 \pi^2/(2\mu r^2) - 1.786e^2/(\varepsilon r) - 0.248E_r
\]

where \( \varepsilon \) denotes the dielectric constant of crystals and \( E_r \) is bulk exciton Rydberg energy. Due to the confinement effect, the electrons in the conduction band and the holes in the valence band are confined spatially by the potential barrier of the surface. This results in the increase of the transition energy from the valence to the conduction band, effectively increasing the \( E_g \) [62-64]. Moreover, other theoretical models, the free-exciton collision [65], impurity centers [66], surface states [67], surface alloying [68], cluster interaction and oxidation effect [69], bond-order-length-strength (BOLS) correlation [3,42] etc., have also been proposed to describe the size dependence of \( E_g \) on the nanometer scale. On the other hand, with rapid development of semiconductor nanoalloys in experiments [53-61,70,71], several thermodynamic models have been developed to investigate the composition-induced \( E_g \) variation in these alloys [72-74]. For example, the composition and size-dependent atomic interaction energy \( b(x, r) \), also called bowing parameter, was introduced to investigate the bowing relationship between \( E_g \) and \( x \) in nanosized semiconductor alloys [72]. On the basis of this consideration, the \( E_g(x, r) \) function is given as

\[
E_g(x, r) = xE_g(1, r) + (1-x)E_g(0, r) + b(x, r)x(1-x).
\]

Based on Eq. (3), it is found that the bowing behavior of \( E_g(x, r) \) is weaker than that in the bulk counterpart, especially when \( r \) is in the deep nanometer scale, since the \( b(x, r) \) of nanocrystals decreases with decreasing \( r \). This is beneficial for the materials design of nanosized alloys due to the difficulty in determining the \( b \) experimentally and theoretically. All above models developed from various perspectives can contribute significantly to understanding the mechanism of \( E_g \) variation in semiconductor nanocrystals and have established a framework for the \( E_g \) function on the nanometer scale.

1.2.2 Raman red shifts of semiconductor nanocrystals. In recent times, the vibration of atoms in both narrow (Si, InP, CdSe etc.) and wide (ZnO, CeO2, SnO2 etc.) bandgap semiconductor nanocrystals has been widely researched due to its influence on electrical and optical properties as phonon scattering in nanostructured materials and devices [3,75]. It is believed that understanding of electron-phonon interaction is critical for manipulating the nonlinear optical properties and also
revealing the relaxation mechanism of the excited carriers. The phonon scattering in semiconductor nanocrystals is one of the most important topics in optoelectronic and thermoelectric research communities. It is known that Raman spectroscopy is one of the advanced non-destructive characterization tools to acquire information on local atomic arrangements and atomic vibrations in materials. This tool has been widely used to investigate the vibrational and structural properties of the nanosized materials [76,77], such as the confinement effect on optical phonons. Recently, it has demonstrated that the corresponding Raman frequency \( \omega \) undergoes a red shift with the decreasing of \( r \) [78-92]. Note that \( r \) here is either the radius of nanoparticles (NPs) and nanowires (NWs), or the half-thickness of thin films. In this case, understanding the Raman red shifts in semiconductor nanocrystals and the corresponding mechanism behind the new physical properties is essential for the advanced applications of semiconductors in optoelectronic devices. In general, the size-dependent Raman shift can be expressed as \( \Delta \omega(r) \equiv \omega(r)-\omega(\infty) \), where \( \omega(r) \) is the size-dependent Raman frequency and \( \Delta \) denotes the difference. The size-induced Raman red shifts have been reported in experiments in both narrow (Si [78-80], InP [81], CdSe [82], and CdS$_{0.65}$Se$_{0.35}$ [83]) and wide (ZnO [84], CeO$_2$ [85], and SnO$_2$ [86,87]) bandgap semiconductor nanocrystals. The findings from these experiments show that \( r \) plays an important role in the modification of \( \omega(r) \) and the \( \omega(r) \) decreases with \( r \) decreasing due to the phonon confinement effects. Moreover, \( \omega(r) \) is also a function of dimensionality due to different dimensional confinement in NPs, NWs and thin films. As a result, the study of the differences in \( \omega(r) \) among semiconductor nanocrystals is beneficial to the understanding of the nature of Raman red shifts in nanostructures and hence to industry applications. Except for the experimental progress, several analytical models have also been developed to study the size and dimensionality dependence of Raman frequency in nanostructural semiconductors [3,93-96]. For example, the BOLS correlation mechanism indicates that the Raman red shift arises from the cohesive bond weakening of the surface atom with lower coordination number (CN) [3]. Based on this correlation, the \( \omega(r) \) function is given as,

\[
\frac{\omega(r)-\omega(\infty)}{\omega(\infty)-\omega(1)} = \sum_{i=3}^{\gamma_i \left( \frac{Z_i}{Z} \right)} C_i^{-\frac{(m/2+1)}{2}} - 1
\]

where \( \omega(1) \) is the vibrational frequency of an isolated dimer, \( \gamma_i \) denotes the portion of atoms in the \( i \)-th atomic layer over the total number of atoms in the entire solid, \( Z_i \) is the CN of the \( i \)-th atomic layer and \( Z \) is the corresponding bulk value, \( C_i \) shows CN-dependent reduction of bond length, and \( m \) is a parameter recognizing the bond nature [3]. Moreover, several factors, such as phonon confinement effect [97,98], surface stress [78,99], and structural defects [77,85,87,91], were suggested to be the determinants of the Raman red shifts in semiconductor nanocrystals. However, the underlying mechanism behind the Raman shifts on the nanometer scale is still unclear.

**1.3 Challenge and objectives.** As described above, there are relatively extensive investigations on \( E_g \) of semiconductor nanocrystals. However, (1) theoretical and experimental efforts have been primarily focusing on investigating the variation of \( E_g \) as a function of size [3-5]; and (2) the reports related to the dimensionality, constituent stoichiometry, and crystallographic lattice structure (ZB and WZ structures) effects on the \( E_g \) of QDs and QWs are limited. These challenges have become impediments to the rapid development of advanced optoelectronic devices. Therefore, a general quantitative model needs to be developed for: (1) revealing the intrinsic factor that dominates the variation of \( E_g \) in the strong quantum confinement regime, and (2) calculating the \( E_g \) of IV, III-V, and II-VI semiconductor QDs and QWs with respect to size, dimensionality, and composition effects.

In order to reveal the underlying mechanism behind the Raman shifts, a quantitative nanothermodynamic model needs to be established for (1) determining the \( \omega(r) \) function of semiconductors on the nanometer scale; and (2) investigating the origin of size and dimensionality effects in the \( \omega(r) \) of semiconductors. Moreover, understanding the lower limit of \( \omega(r) \) in
semiconductor nanocrystals, which is very difficult to be determined with current experimental technologies, will provide a new insight into the fundamental mechanism behind the Raman red shift.

An extension of the classic thermodynamic theory to nanometer scale has generated a new interdisciplinary theory - nanothermodynamics, which is beneficial for the investigation of the size-dependent physicochemical properties in nanocrystals. In this work, a nanothermodynamic model is established to calculate the size-, dimensionality-, and composition-dependent $E_g$ of semiconductor nanocrystals on the basis of the cohesive energy function of nanocrystals. Moreover, the size-, and dimensionality-dependent $\sigma(r)$ of semiconductor nanocrystals is investigated with nanothermodynamics based on the size dependence of root-mean-square (rms) average amplitude of atomic thermal vibration. The calculated results are in good agreement with experimental data reported in open literatures. An expanded understanding of the optical properties of semiconductor nanocrystals and their related quantum and phonon confinement effects will advance the development of their practical applications in optoelectronic devices.

2. Methodology

2.1 Principle: atomic vibrational instability. It is believed that understanding of the melting temperature of low-dimensional solids is beneficial not only to the theoretical exploitation of phase transition, but also to the applications in modern industries [100]. This is because their thermal stability against melting is increasingly becoming one of the major concerns in the upcoming technologies. Numerous theoretical methods have been developed to model the size-dependent melting temperature $T_m(r)$ of nanocrystals [2]. These models could provide considerable references for investigating the mechanism of size effects on the physicochemical properties in nanocrystals. On the basis of Shi’s model [101] for $T_m(r)$, the rms average amplitude $\sigma(r)$ of a nanocrystal can be written as, $\sigma^2(r) = \alpha^2 V_0 r^2 + (1 + \beta) V_0 (r/h)^2$ where $h$ is the atom number and the subscripts $S$ and $V$ denote atoms located on surface and within the crystals, respectively. The ratio of the atom numbers on the surface to that in the interior can be expressed as $\chi = n_S/n_V = r_0/r_0 - r_0$ where $r_0$ is a critical radius for which all atoms of a low-dimensional material are located on its surface. This parameter depends on dimensionality $d$ and atomic or molecular diameter of $h$ through $r_0 = (3-d)h$ with $d = 0$ for QDs or NPs, $d = 1$ for QWs, NWs, nanorods, or nanocolumn, and $d = 2$ for thin films [102]. The crystal is considered to be long-range ordering. Therefore, the crystal with the minimum size, which can remain the crystallographic structure to be the same as its bulk counterpart, should have at least a half volume of the atoms within the crystal [102]. In this case, the minimum radius, $r_{min}$, is twice of the critical radius, having $r_{min} = 2r_0$. This size correlation could be verified below. To determine the $\alpha^2(r)$ function, it is assumed that (1) $\sigma^2(r)/\sigma^2(\infty) = \sigma^2_{S}(r)/\sigma^2_{S}(\infty) = \alpha$ is size-independent although $\sigma^2_{V}(r)$ and $\sigma^2_{V}(\infty)$ are size-dependent; and (2) the variation of $\sigma^2(r)$ is considered phenomenologically to be dependent on the value of $\sigma^2(r)$ due to the importance of the cooperative coupling between the surface and the interior regions for nanocrystals [101]. Thus, a change in $\sigma^2$ with $\chi$ can be given by $\sigma^2(\chi) = \alpha^2(\chi) d\chi$. Integrating this equation yields, $\sigma^2(r)/\sigma^2(\infty) = \exp(\alpha - 2)/(r/\chi_n) - 1$. From Lindemann’s melting criterion, a crystal melts when the $\sigma$ reaches to a certain fraction of the equilibrium atomic distance $h$ [103], i.e. $\sigma/h = c$ with $c$ being a constant. This criterion is a kinetic consideration for single component crystals. Thus, it is much simpler than the usual phase equilibrium consideration based on the general thermodynamics theory. The Lindemann’s criterion was verified experimentally and is applicable for both bulk materials and nanocrystals [2,100-102,104], providing the base for the establishment of $T_m(r)$ function. Since $T_m(r)$ is usually higher than the bulk Debye temperature $\Theta_B(\infty)$, the high temperature approximation can be utilized [101,102], $\sigma^2(r, T) = F(r, T)$, where $F(r)$ is a size-dependent function and $T$ denotes the absolute temperature. As a result, at any $T$, $\sigma^2(r, T)/\sigma^2(\infty) = F(r)/F(\infty)$. Moreover, when $T = T_m$, $F(r)/F(\infty) = [\sigma^2(r, T_m)/h^2]/[\sigma^2(\infty, T_m)/h^2] = T_m(\infty)/T_m(r)$ on the basis of the Lindemann’s
criterion if the size dependence of $h$ is neglected. Therefore, $$\sigma^2(r)/\sigma^2(\infty) = T_m(\infty)/T_m(r) = \exp\{(\alpha-1)/[(r/r_0)-1]\}.$$ 

The value of $\alpha$ was determined by considering size-dependent vibrational entropy $S_{\text{vib}}(r)$ deduced by Mott’s expression for $S_{\text{vib}}(\infty) [105,106]$, $S_{\text{vib}}(r) = S_{\text{vib}}(\infty) - (3R/2)(\alpha-1)/[(r/r_0)-1]$, where $R$ is the ideal gas constant. When $r = 2r_0$, both the crystal and the liquid have the same short-range ordering and the structural difference between them is negligible, resulting in $S_{\text{vib}}(2r_0) = 0$ [102]. In this case, $\alpha = 2S_{\text{vib}}(\infty)/(3R)+1$. Note that this $\alpha$ value is only applicable for isolated nanocrystals.

With the above considerations, the $\sigma(r)$ function can be written as

$$\sigma(r)/\sigma(\infty) = \sqrt{\exp\{2S_{\text{vib}}(\infty)/(3R)\}/[(r/r_0)-1]}.$$  \hspace{1cm} (5)

Accordingly, the $T_m(r)/T_m(\infty)$ function can be obtained as

$$T_m(r)/T_m(\infty) = \exp\{-2S_{\text{vib}}(\infty)/(3R)\}/[(r/r_0)-1].$$  \hspace{1cm} (6)

The non-linear relationship between $T_m(r)$ and $1/r$ shows that both surface and interior atoms of nanocrystals contribute to the reduction of $T_m(r)$ on the nanometer scale.

As a first-order approximation, the size-dependent melting entropy $S_m(r)$ has the same size dependence of $S_{\text{vib}}(r)$, $S_m(r) = S_m(\infty) - (3R/2)(\alpha-1)/[(r/r_0)-1]$ [2]. Thus, $S_m(r)/S_m(\infty) = 1-1/[(r/r_0)-1]$ with the consideration of $S_m(2r_0) = 0$ [2,102]. From the general thermodynamics, the size-dependent melting enthalpy $H_m(r)$ can be expressed as $H_m(r) = T_m(r)S_m(r)$. Based on the above $T_m(r)$ and $S_m(r)$ functions, we have $H_m(r)/H_m(\infty) = \exp\{-2S_{\text{vib}}(\infty)/(3R)\}/[(r/r_0)-1]$. As a natural consideration, the size effect on the $H_m(r)$ function should be applicable for the cohesive energy $E_c(r)$, which is defined as the difference between the average energy of the atoms in a solid and the isolated vapor.

$$E_c(r) = H_m(r) - H_m(\infty) = \exp\{-2S_{\text{vib}}(\infty)/(3R)\}/[(r/r_0)-1].$$  \hspace{1cm} (7)

Note that Eqs. (6) and (7) in nature show the similar relationship at least for metals (their $S_{\text{vib}} \approx S_m \approx R$) since $S_b \approx 12S_m \approx 12R$. As a result, $E_c \propto T_m$ can be obtained, which is also applicable on the nanometer scale, $E_c(r)/E_c(\infty) = T_m(r)/T_m(\infty)$. This is consistent with the general understanding. It is discernible from Eq. (7) that the $E_c(r, d)$ increases with decreasing $r$, indicating the instability of nanocrystals compared with the corresponding bulk crystals. This trend is expected since the surface/volume ratio increases with the reduction of nanocrystals size, resulting in a higher energetic state of surface atoms and thus enhancing the cohesive energy [2,107,108]. Moreover, although the $E_c(r, d)$ is deduced from the expression of $T_m(r)$ function, $E_c(r, d)$ determines the variation of the potential profile for nanocrystals, which is related to the crystallographic structures and the corresponding transition functions. As a result, $E_c(r, d)$ dominates the size effect on a number of physicochemical properties in low-dimensional materials, including the $T_m(r)$ [100].
The principle of atomic vibrational instability has been utilized to determine size-dependent phase transition functions (melting temperature, melting entropy, melting enthalpy, cohesive energy, Debye temperature, glass transition temperature, ferromagnetic transition temperature, ferroelectric transition temperature, superconductor transition temperature, and ferromagnetic-antiferromagnetic transition temperature), phase diagrams (continuous binary solution phase diagrams, bi-layer transition diagrams of metallic multilayer, and solid transition phase diagrams), and kinetic properties (diffusion activation energy and diffusion coefficient) [2]. The model predictions are consistent with the experimental and other theoretical results, verifying the accuracy of the principle. In this work, this principle will be extended to investigate the optical properties of semiconductor nanocrystals.

2.2 Bandgap energy enhancement. According to the nearly-free-electron approximation, \( E_g \) originates from the crystal potential \( V \). The width of the bandgap is dependent on the integration of \( V \) and the Bloch wave of the nearly free electron. As a result, the bandgap energy is determined by the first Fourier coefficient of the crystalline field \( V_1 \), namely \( E_g = 2|V_1| \) [3,6,109]. This relationship is applicable for both bulk and nanosized materials. Therefore, \( \Delta E_g(r, d) / E_g(\infty) = \Delta V(r, d) / V(\infty) \), where: (1) \( V(\infty) \) is bulk crystalline field, (2) \( \Delta E_g(r, d) = E_g(r, d) - E_g(\infty) \) expresses the size- and dimensionality-dependent energy change, and (3) \( \Delta V(r, d) = V(r, d) - V(\infty) \) is the corresponding crystalline field change. Recently, it has demonstrated that the cohesive energy \( E_c(r, d) \) determines the size dependence of a variety of physicochemical properties in low-dimensional nanocrystals, such as melting temperature, evaporation temperature, Debye temperature, critical temperature for ferromagnetic, ferroelectric, and superconductor transition, formation enthalpy, surface energy, interface energy, diffusion activation energy, vacancy formation energy, and thermal conductivity [107]. Moreover, since \( E_c \) is related to the total \( CN \) of a particular atom and also the interatomic interaction, it provides the crystal potential. Therefore, \( E_c(\infty) \propto V(\infty) \) and \( E_c(r, d) \propto V(r, d) \) [3,6,109] can be obtained. With above considerations, we have:

\[
\Delta V(r, d) / V(\infty) = \Delta E_c(r, d) / E_c(\infty) = 1 - E_c(r, d) / E_c(\infty)
\]

and the size- and dimensionality-dependent \( E_g(r, d) \) function can be expressed as follows,

\[
E_g(r, d)/E_g(\infty) = 2 - E_c(r, d)/E_c(\infty).
\]

From Eqs. (7) and (8), we have,

\[
\frac{E_g(r, d)}{E_g(\infty)} = 2 - \left\{ 1 - \frac{1}{12r/[3-(3-d)h]-1} \right\} \exp\left\{ -\frac{2S_b}{3R} \frac{1}{[3-(3-d)h]-1} \right\}.
\]

For bulk semiconductor alloys, the \( E_g(x, \infty) \) function can be determined by the Fox equation as follows [110],

\[
1/E_g(x, \infty) = (1-x)/E_g(0, \infty) + x/E_g(1, \infty).
\]

As a first-order approximation, this relationship can be extended to the nanometer scale due to similar structure and optoelectronic properties of the binary semiconductors in group III-V or II-VI. Thus, the \( E_g(x, r, d) \) function for semiconductor nanoalloys is given as,

\[
1/E_g(x, r, d) = (1-x)/E_g(0, r, d) + x/E_g(1, r, d).
\]

2.3 Raman red shift. For the Raman red shift, the total energy resulting in the lattice vibration is the sum of interatomic binding energy and lattice thermal vibrational energy \( E_v \). Based on the BOLS correlation mechanism [3], the \( E_v \) function can be expressed as \( E_v = \mu_d (\nu \sigma^2/(2Z)) + k \sigma^2/(6Z^2) + \ldots \) for a certain atom, where \( \mu_d \) is the reduced mass of the dimer, \( \nu \) denotes the light speed, and \( k \) is a prepositive coefficient for lattice vibration. In this relationship, the contribution from all neighboring
bonds of a particular atom has been included and the mean contribution from each coordinate has also been considered. As a first order approximation, the high-order terms in the above relation can be negligible. Thus, we have $E_v \approx \mu_d(v_0)^2 \sigma^2/(2Z)$. On the other hand, $E_v$ can also be expressed as $k_B T$, where $k_B$ is the Boltzmann constant [3,111]. In this case, $\mu_d(v_0)^2 \sigma^2/(2Z) \approx k_B T$ and $\omega \approx Z^{1/2}/\sigma$ can be obtained at a particular temperature. As noted above, the atomic periodical close pack arrangement in bulk may be varied as crystal size approaches to the nanometer scale. When $r < r_{\text{min}}$, the nanocrystals become thermodynamically unstable with respect to the amorphouslike structure [78,112,113]. This is caused by the structural revolution with the collapse of long-range-ordered lattice structure in nanocrystals and the heavily reconstructed geometries of atomic clusters since the increase of broken bonds in deep nanometer scale causes localized structural distortion or variation [100,102]. In the other words, the nanocrystals have the same crystallographic structure with their bulk counterparts when $r > r_{\text{min}}$, resulting in $Z(r) = Z(\infty)$ [78,112,113]. Based on the discussion above, $\omega \propto 1/\sigma$ could be derived at a certain temperature when $r > r_{\text{min}}$. Assuming this relationship can be extended to the nanometer scale as a first-order approximation, the $\omega(r)$ function is given as

$$\frac{\omega(r) - \omega(\infty)}{\omega(\infty) - \omega(r_{\text{min}})} = \frac{1/\sigma(r) - 1/\sigma(\infty)}{1/\sigma(\infty) - 1/\sigma(r_{\text{min}})} \quad (12)$$

where $\omega(r_{\text{min}})$ is the lower limit of vibrational frequency in the nanocrystals and it can be considered as a reference point for the Raman red shift.

Combining Eqs. (5) and (12) as well as the consideration of $r_{\text{min}} = 2r_0$, we have

$$\frac{\omega(r) - \omega(\infty)}{\omega(\infty) - \omega(2r_0)} = \frac{1}{1 - \sqrt{\exp[-2Z_{\text{rb}}(\infty)/(3R)]}} - 1 \quad (13)$$

As shown in Eq. (13), the both understandable asymptotic limits are provided: $\omega(r) \to \omega(\infty)$ when $r \to \infty$ and $\omega(r) \to \omega(2r_0)$ when $r \to 2r_0$, demonstrating the validity of Eq. (13).

3. Results and discussions

3.1 Size-, dimensionality-, and composition-dependent bandgap energy. Figure 1 plots the calculation result from Eq. (9) and experimental data of $E_g(r, d)$ for Si QDs with diamond structure. The related parameters used in the modeling are listed in Table 1.

Fig. 1. $E_g(r, d)$ of Si QDs with diamond structure. The solid line denotes the model prediction from Eq. (9). The symbols • [7], Δ [8], ∇ [9], × [10], and ♦ [10] are experimental results.
It is discernable that the calculated $E_g(r, d)$ of Si QDs are in good agreement with the experimental data even when $r < 2$ nm, thereby confirming the accuracy of the developed model. As shown in the figure, the $E_g(r, d)$ function increases with a decreasing $r$ and the quantum confinement effect is pronounced when $r \ (< 5$ nm) becomes comparable to the exciton radius. Due to the strong confinement effect in this size regime, both the electrons and the holes are confined spatially by the potential barrier of the surface [109]. It is known that the surface/volume ratio increases with the reduction in crystal size, which results in higher energetic state of surface atoms compared with the interior ones [100]. As a result, the cohesive energy as well as the related transition energy from the valence band to the conduction band increase, effectively enhancing the bandgap energy.

Table 1. Parameters used in the model predictions of Eq. (9).

<table>
<thead>
<tr>
<th></th>
<th>$E_g(\infty)$ [eV]</th>
<th>$h$ [nm]$^a$</th>
<th>$S_b$ [J g-atom$^{-1}$ K$^{-1}$]$^b$</th>
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</thead>
<tbody>
<tr>
<td>For Figs. 1-13</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Si</td>
<td>1.12 [10]</td>
<td>0.2352 [115]</td>
<td>144</td>
</tr>
<tr>
<td>GaP (ZB)</td>
<td>2.78 (direct) [14]$^c$</td>
<td>0.2373 [13]</td>
<td>13R</td>
</tr>
<tr>
<td>GaP (ZB)</td>
<td>2.22 (indirect) [14]$^c$</td>
<td>0.2373 [13]</td>
<td>13R</td>
</tr>
<tr>
<td>InAs (ZB)</td>
<td>0.90 [3]</td>
<td>0.2624 [5]</td>
<td>13R</td>
</tr>
<tr>
<td>ZnS (ZB)</td>
<td>3.16 [29]</td>
<td>0.2343 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>ZnSe (ZB)</td>
<td>2.58 [115]</td>
<td>0.2455 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>ZnTe (ZB)</td>
<td>2.26 [115]</td>
<td>0.2641 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>CdS (ZB)</td>
<td>2.42 [115]</td>
<td>0.2520 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>CdSe (ZB)</td>
<td>1.74 [115]</td>
<td>0.2620 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>CdTe (ZB)</td>
<td>1.61 [49]</td>
<td>0.2806 [116]</td>
<td>13R</td>
</tr>
<tr>
<td>For Figs. 14-21</td>
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<td>CdS (WZ)</td>
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<td>13R</td>
</tr>
<tr>
<td>ZnSe (WZ)</td>
<td>2.63 [52]</td>
<td>0.2037 [117]</td>
<td>13R</td>
</tr>
<tr>
<td>CdSe (WZ)</td>
<td>1.67 [52]</td>
<td>0.2192 [5]</td>
<td>13R</td>
</tr>
<tr>
<td>InN (ZB)</td>
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<td>0.2156 [118]</td>
<td>13R</td>
</tr>
<tr>
<td>GaN (ZB)</td>
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<td>0.1949 [118]</td>
<td>13R</td>
</tr>
<tr>
<td>AlN (WZ)</td>
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<td>13R</td>
</tr>
<tr>
<td>InN (WZ)</td>
<td>0.70 [58]$^d$</td>
<td>0.1793 [119]</td>
<td>13R</td>
</tr>
</tbody>
</table>

$^a$ $h = a^2/(6c)+c/4$ and $h = (\sqrt{3}/4)a$ for WZ and ZB structures, respectively with $a$ and $c$ being the corresponding lattice constants. For Si with diamond structure, $h = (\sqrt{3}/4)a$.

$^b$ For Si, $S_b = E_b/T_b$ with $E_b = 456$ kJ g-atom$^{-1}$ and $T_b = 3173$ K [114]. For III-V and II-VI semiconductor compounds, $S_b \approx 13R$ as a first-order approximation, which is equal to that of the mean value of most elements (70-150 J g-atom$^{-1}$ K$^{-1}$) [114].

$^c$ Note that the direct and indirect $E_g(\infty)$ values of GaP are different.

$^d$ Note that different experimental data of $E_g(\infty)$ are used for InN with WZ lattice structure, which are obtained from different sources.

Figures 2-7 and 8-13 plot the results calculated using Eq. (9) for $E_g(r, d)$ of III-V and II-VI QDs and QWs with ZB or WZ structures, where the parameters (Table 1) used in the modeling are derived from the open literatures. The experimental data are also included in these figures for comparison.
Fig. 2. $E_g(r, d)$ of GaN QDs with WZ structure. The solid line denotes the model prediction from Eq. (9). The symbols $\bullet$ [11] and $\bullet$ [12] are experimental data.

Fig. 3. $E_g(r, d)$ of GaP QDs with ZB structure. The solid lines denote the model predictions from Eq. (9). The symbols $\bullet$ [13] and $\circ$ [12,14] are experimental results.

Fig. 4. $E_g(r, d)$ of GaAs QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols $\bullet$ [15] and $\circ$ [16] are experimental data.
Fig. 5. $E_g(r, d)$ of InN QWs with WZ structure. The solid line denotes the model prediction from Eq. (9). The symbol $\blacklozenge$ [17] is experimental result.

Fig. 6. $E_g(r, d)$ of InP QDs and QWs with ZB structure. The solid lines denote the model predictions from Eq. (9). The symbols $\blacklozenge$ [18] and $\odot$ [19] are experimental results of QDs while the symbols $\triangle$ [20] denote experimental data of QWs.

Fig. 7. $E_g(r, d)$ of InAs QDs and QWs with ZB structure. The solid lines denote the model predictions from Eq. (9). The symbols $\triangledown$ [19], $\bullet$ [21], $+$ [22], $\odot$ [23], and $\triangle$ [24] are experimental results of QDs while the symbols $\bullet$ [25] denote experimental data of QWs.
Fig. 8. $E_g(r, d)$ of ZnS QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols $\bigtriangleup$ [26], $\bullet$ [27], $\nabla$ [28], $\Delta$ [29], and $\bigcirc$ [30] are experimental data.

Fig. 9. $E_g(r, d)$ of ZnSe QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols $\bigtriangleup$ [31], $\bigcirc$ [32], and $\Delta$ [33] are experimental results.

Fig. 10. $E_g(r, d)$ of ZnTe QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols $\bigtriangleup$ [34] are experimental data.
Fig. 1. $E_g(r, d)$ of CdS QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols ▲ [19],  [35], + [36], V [37], Δ [38], O [39], ● [40], and × [41] are experimental results.

Fig. 2. $E_g(r, d)$ of CdSe QDs and QWs with ZB structure. The solid lines denote the model predictions from Eq. (9). The symbols × [38], ● [42], V [43], O [44], and Δ [45] are experimental results of QDs while the symbols + [46] and ● [47] denote experimental results of QWs.

Fig. 3. $E_g(r, d)$ of CdTe QDs with ZB structure. The solid line denotes the model prediction from Eq. (9). The symbols ● [38], Δ [48], and O [49] are experimental results.
It is believed that the III-V semiconductors have stronger covalent bonding compared to II-VI semiconductors due to their lower extent of ionic lattice and larger exciton radii. For example, the exciton radius in III-V GaAs is 19 nm whereas it is only 6 nm for II-VI CdS [13]. In this case, the quantum size effects on the optical properties of III-V semiconductors are expected to be stronger than as is the case for II-VI semiconductors due to their greater $E_g(\infty)$. Accordingly, for the same values of $r$, the $E_g(r, d)$ in GaN and GaP as shown in Figs. 2 and 3 are greater than those of CdS and CdSe in Figs. 11 and 12. However, there is negligible difference between the values of $E_g(r, d)/E_g(\infty)$ when comparing III-V and II-VI semiconductors because of their similar $S_h$ and $h$ values in Eq. (9).

As shown in Figs. 1-13, a little deviation can be found between our model predictions and experimental results of $E_g(r, d)$ for some semiconductor nanocrystals, InP, InAs, ZnTe etc., although they have the same trend within the measurement errors. A possible reason for such a difference is that parts of the experimental data were directly determined with the photoluminescence (PL) or the photoabsorption (PA) spectrometry. The corresponding energies $E_{PL}$ and $E_{PA}$ differ each other with a difference called as Stoke shift, or $E_{PL} = E_g - W$ and $E_{PA} = E_g + W$ where $W$ denotes the energy for electron-phonon coupling [109]. As a result, for PL and PA, the mentioned bandgap should be contributed by both crystal potential and electron-phonon coupling. It is believed that only the crystals potential contributes to the actual bandgap [$E_g = (E_{PL} + E_{PA})/2$] whereas the electron-phonon coupling causes the Stoke shift (2$W$). For bulk semiconductors, $W(\infty)$ is much smaller than $E_g(\infty)$ and thus can be negligible [109]. Therefore, $E_g(\infty) \approx E_{PL}(\infty)$ [or $E_{PA}(\infty)$]. However, $W(r)$ abruptly increases as $r$ decreases on the nanometer scale, resulting in the enhanced difference between $E_g(r)$ and $E_{PL}(r)$ [or $E_{PA}(r)$] especially when $r < 1$ nm [109]. Further efforts will be focused on the size dependence of the Stoke shift in order to accurately calculate the size-dependent $E_{PL}(r)$ and $E_{PA}(r)$ functions for PL and PA. Moreover, the deviation may also arise from (1) the size-dependent solid-solid phase transformations in nanocrystals [104,120]; and the H-terminated dangling bonds at the surface of nanocrystals, which lowers the potential level of the nanocrystals [3].

![CdSe](image)

**Fig. 14.** $\Delta E_g(r, d)_{QW}/\Delta E_g(r, d)_{QDs}$ of CdSe. The solid and dash lines denote the model predictions from Eq. (9) for ZB and WZ structures, respectively.

It has been demonstrated in experiments that the quantum confinement effect in QWs is weaker than that observed in QDs due to the loss of one dimension of confinement [17,20,25,46,47]. This has been verified by the calculation by means of a simple effective-mass approximation model, which indicates that the ratio of $\Delta E_g(r, d)_{QW}/\Delta E_g(r, d)_{QDs}$ for a particular semiconductor is given by a constant, $\lambda = 0.586$ [5,20]. On the other hand, $\lambda = 0.62, 0.66$ was determined experimentally while $\lambda = 0.75$ was calculated using a semiempirical pseudopotential method for III-V semiconductor InP [20]. Moreover, the calculations using an *ab initio* method demonstrated that $0.495 \leq \lambda \leq 0.971$ in the case
of III-V and II-VI semiconductors [5]. Figure 14 plots the λ values of CdSe with ZB and WZ crystallographic structures as a function of nanocrystal size as calculated using Eq. (9). It was found that λ is size-dependent and that it increases with a decreasing \( r \). When \( r > 10 \text{ nm} \), λ approaches to 0.67, which is consistent with the aforementioned experimental and other theoretical results.

Figure 15 plots the \( \beta = \Delta E_g(r, d)_{\text{WZ}}/\Delta E_g(r, d)_{\text{ZB}} \) values of CdSe QDs and QWs in order to compare the influence of crystallographic structure on the bandgap energy of semiconductor nanocrystals. As shown in the figure, it is discernible that the nanocrystal size effects on the β can be divided into two segments, namely the size-dependent and size-independent regions. We can see that β decreases with increasing \( r \) sharply and subsequently approaches a saturation value of 0.83 when \( r > 5 \text{ nm} \). In this case, the bandgap energies determined by Eq. (9) for these two crystallographic structures are similar despite differences in the wave function symmetry and the fine structures of the energy spectrum for ZB and WZ structures. This implies that the crystallographic structure effects on the bandgap energy of CdSe QDs and QWs are negligible, and that the bandgap is dominated by the parameters of size and dimensionality in semiconductor nanocrystals.

![Fig. 15. \( \Delta E_g(r, d)_{\text{WZ}}/\Delta E_g(r, d)_{\text{ZB}} \) of CdSe. The solid and dash lines denote the model predictions from Eq. (9) for QDs and QWs, respectively.](image)

Experimental findings in the field of semiconductor alloys have led to the conclusion that the \( E_g(x, \infty) \) varies smoothly and monotonically (but not linearly) with \( x \) changing over the whole range of composition [51-61,121]. The \( E_g(x, \infty) \) function is often described by an empirical formula, \( E_g(x, \infty) = E_g(0, \infty) + [E_g(1, \infty) - E_g(0, \infty)]x + bx^2 \) [5,51,121]. The value of \( b \) is a measure of the fluctuation magnitude of the crystal field, or the nonlinear effect caused by the anisotropic nature of binding. As noted above, \( b \) is size- and composition-dependent when the alloy components have different lattice constants [72,122]. Moreover, the value of \( b \) is difficult to measure experimentally, with limited means of calculation using theoretical methods [5,51,121]. Except for the above empirical formula, Vegard formula has also been used to determine the \( E_g(x, \infty) \), where \( E_g(x, \infty) = xE_g(1, \infty) + (1-x)E_g(0, \infty) \) [53,60,61]. However, the calculated results are not consistent with the experimental data [5,51,121]. Figure 16 plots the calculated results from Eq. (10) and the experimental data of the \( E_g(x, \infty) \) in bulk Zn\(_x\)Cd\(_{1-x}\)S and Zn\(_x\)Cd\(_{1-x}\)Se alloys. The calculated results obtained using the empirical formula \( b = 0.22 \) [51] and 0.45 [52] eV for Zn\(_x\)Cd\(_{1-x}\)S and Zn\(_x\)Cd\(_{1-x}\)Se, respectively, and those derived from the Vegard formula are also plotted in Fig. 16 for comparison. It can clearly be seen that the variation of \( E_g(x, \infty) \) deviates slightly from a linear dependence, displaying a downward bowing relationship. This demonstrates that the results calculated with the developed model as Eq. (10) are in good agreement with the experimental data and also the empirical formula. However, the unique
advantage of Eq. (10) is that it does not have any adjustable parameters in the equation, thereby substantially simplifying the calculation of $E_g(x, \infty)$ for semiconductor alloys.

![Graph showing $E_g(x, \infty)$ for bulk Zn$_x$Cd$_{1-x}$S and Zn$_x$Cd$_{1-x}$Se alloys.](image)

Fig. 16. $E_g(x, \infty)$ of bulk Zn$_x$Cd$_{1-x}$S and Zn$_x$Cd$_{1-x}$Se alloys. The solid, dash, and dot lines denote the model predictions from Eq. (10), empirical formula, and Vegard formula, respectively. The symbols $\Delta$ [51] and $\nabla$ [52] are experimental results of bulk Zn$_x$Cd$_{1-x}$S and Zn$_x$Cd$_{1-x}$Se alloys, respectively.

Figures 17-21 plot the $E_g(x, r, d)$ as a function of constituent stoichiometry $x$ for Zn$_x$Cd$_{1-x}$S QDs, Zn$_x$Cd$_{1-x}$Se QDs, In$_x$Ga$_{1-x}$N NPs and thin films, Ga$_x$Al$_{1-x}$N nanorods, and In$_x$Al$_{1-x}$N nanocolumns as calculated using Eq. (11) for different nanocrystal sizes. Experimental data are also included in these figures for comparison. As shown in Figs. 17-21, it can be observed that the $E_g(x, D, d)$ plots have downward shifts as $r$ increases and that the bandgap energy varies non-linearly with $x$ changing. The model predictions from Eq. (11) match perfectly with experimental data. Moreover, the composition effects on the bandgap energy of nanoalloys are much stronger than that of the size effects, in particular for the mixture of narrow-gapped and wide-gapped semiconductors. It is noted that the crystal size of III-V semiconductor nanoalloys discussed in this paper is large, which results in weak quantum confinement effect. A comparison of the results in Fig. 16 with the data in Figs. 17-21 indicates a similar bowing behavior in both bulk and nanosized alloy systems. This is because the studied alloy components have similar lattice constants and also the optical properties. These findings are in agreement with recent experimental observations [53,60].

![Graph showing $E_g(x, r, d)$ for Zn$_x$Cd$_{1-x}$S nanoalloy QDs with WZ structure.](image)

Fig. 17. $E_g(x, r, d)$ of Zn$_x$Cd$_{1-x}$S nanoalloy QDs with WZ structure. The solid lines denote the model predictions from Eq. (11). The symbols $\Delta$ (2.4 nm) [53], O (2.9 nm) [53], • (3.2 nm) [53], • (4.0 nm) [53], and $\nabla$ (10 nm) [59] are experimental data.
Fig. 18. $E_g(x, r, d)$ of Zn$_x$Cd$_{1-x}$Se nanoalloy QDs with WZ structure. The solid lines denote the model predictions from Eq. (11). The symbols $\bullet$ [60], O [60], $\Delta$ [60], $\triangledown$ [60], $\bullet$ [60], and $\times$ [61] are experimental results.

Fig. 19. $E_g(x, r, d)$ of In$_x$Ga$_{1-x}$N alloyed NPs and thin films with ZB structure. The solid lines denote the model predictions from Eq. (11). The symbols $\bullet$ [56] are experimental results of NPs while the symbols O [55], $+$ [55], $\bullet$ [55], $\Delta$ [55], $\triangledown$ [55], and $\times$ [54] denote experimental data of thin films.
The size-, dimensionality-, and composition-induced variation of bandgap energy are common phenomena in semiconductor nanocrystals. The theoretical findings of this work indicate that the bandgap structure has the potential for quantitative modification through the precise manipulation of the size, dimensionality, and also composition of nanosized semiconductors. This understanding may provide essential information for the future application of these nanostructured materials in optoelectronic devices. Moreover, the developed model could also be used to calculate the bandgap energies of other II-VI and III-V semiconductors if the relevant parameters are available. The
parameters used in the modeling have distinctive physical meanings, which makes it possible to reveal the physical and chemical nature behind the properties in the nanometer scale.

3.2 Size- and dimensionality-dependent Raman red shifts. The values of $\omega(r_{\text{min}})$ or $\omega(2r_0)$ can be determined by matching the experimental data of $\omega(r)$ with the results calculated from Eq. (13), where the parameters used in the modeling are listed in Table 2. Figures 22-28 plot the calculation and experimental results of $\omega(r)$ for Si, InP, CdSe, CdS$_{0.65}$Se$_{0.35}$, ZnO, CeO$_2$, and SnO$_2$ nanocrystals. It is discernible that our model predictions are in good agreement with the experimental data of $\omega(r)$ even when $r < 3$ nm.

Table 2. Parameters used in the model predictions of Eq. (13).

<table>
<thead>
<tr>
<th></th>
<th>$\omega(\infty)$ [cm$^{-1}$]</th>
<th>$h$ [nm]$^a$</th>
<th>$S_{\text{vib}}(\infty)$ [J g-atom$^{-1}$ K$^{-1}$]$^b$</th>
<th>$\omega(2r_0)$ [cm$^{-1}$]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>520 [78]</td>
<td>0.2352</td>
<td>6.7</td>
<td>513</td>
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<td>InP</td>
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<td>0.2555</td>
<td>6.248</td>
<td>194.4</td>
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<td>CdS$<em>{0.65}$Se$</em>{0.35}$-2$^d$</td>
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<td>0.2555</td>
<td>6.248</td>
<td>294</td>
</tr>
<tr>
<td>ZnO-1$^d$</td>
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<tr>
<td>ZnO-2$^d$</td>
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<td>7.261</td>
<td>1045</td>
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<td>CeO$_2$</td>
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<td>SnO$_2$</td>
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<td>0.2057</td>
<td>4.098</td>
<td>618</td>
</tr>
</tbody>
</table>

$^a$ For ZnO (WZ structure, $a = 0.325$ nm, $c = 0.531$ nm), $h = a^2/(6c) + c/4$ [5]. For SnO$_2$ (rutile structure, $a = 0.4737$ nm), $h = 2^{1/2} \times 0.307a$ [87,123]. For CeO$_2$ (fluorite structure, $a = 0.54087$ nm) [85], $h = (3^{1/2}/4)a$. For Si with diamond structure, InP, CdSe and CdS with ZB structures, $h$ values are listed in Table 1. For CdS$_{0.65}$Se$_{0.35}$, $h = 0.65h_{\text{CAS}} + 0.35h_{\text{CASE}}$.

$^b$ For InP, CdSe, CdS, and ZnO, $S_{\text{vib}}(\infty) \approx S_m(\infty)$ with $S_m(\infty)$ being 18.787 [106], 14.938 [106], 14.360 [106], and 15.575 J g-atom$^{-1}$ K$^{-1}$ [124], respectively. For CdS$_{0.65}$Se$_{0.35}$, $S_{\text{vib}}(\infty) = 0.65S_{\text{vib}}(\infty)_{\text{CAS}} + 0.35S_{\text{vib}}(\infty)_{\text{CASE}}$. For CeO$_2$ and SnO$_2$, $S_{\text{vib}}(\infty) \approx S_m(\infty)$ with the values of $S_m(\infty)$ are $9.686$ and $4.098$ J g-atom$^{-1}$ K$^{-1}$ [124], respectively.

$^c$ $\omega(2r_0)$ is determined by matching the experimental data of the size-dependent $\omega(r)$ with the results calculated from Eq. (13).

$^d$ 1 and 2 are two different Raman optical modes with different $\omega(\infty)$ values.

As shown in Figs. 22-28, the $\omega(r)$ function decreases with $r$ decreasing. This is consistent with the experimental findings, demonstrating the accuracy of the developed model and the approximation of $r_{\text{min}} = 2r_0$. Precisely $r_{\text{min}} = fr_0$ with $f \sim 2$, where $f$ is associated with the crystallographic lattice structure. The first principle will be used to investigate the $f$ values of nanocrystals with different crystallographic structures. As noted above, with the reduction of $r$ in semiconductor nanocrystals, the surface/volume ratio increases, resulting in higher energetic state of their surface atoms [100,102]. The phonon confinement effect induced by the size reduction plays a critical role in determining the physical properties of semiconductor nanocrystals. As a result, the atomic vibrational amplitude increases as $r$ decreases, effectively decreasing the atomic vibrational frequency. When $r < 5$ nm, which is comparable to the exciton radius of the semiconductor nanocrystals, the confinement effect becomes pronounced. This leads to a rapid decrease of $\omega(r)$ as shown in Figs. 22-28. Moreover, Fig. 25 shows that the developed model could also be used to calculate the $\omega(r)$ of nanosized semiconductor alloys if the relevant thermodynamic parameters are available. It is believed that such an alloy has better photonic properties than the best-reported binary semiconductors and they are the promising materials for optoelectronic devices. Therefore, the developed model could be used to design the advanced nano-optoelectronic materials through changing the constituent stoichiometries and to tune the optical properties [6].
Fig. 22. $\omega(r)$ of Si NPs. The solid line denotes the model prediction from Eq. (13). The symbols $\triangledown$ [3,79], $\triangle$ [80], and $\bigcirc$ [80] are experimental results.

Fig. 23. $\omega(r)$ of InP QDs. The solid line denotes the model prediction from Eq. (13). The symbols $\blacklozenge$ [81] are experimental data.

Fig. 24. $\omega(r)$ of CdSe NPs. The solid line denotes the model prediction from Eq. (13). The symbols $\blacklozenge$ [82] are experimental results.
Fig. 25. $\omega(r)$ of CdS$_{0.65}$Se$_{0.35}$ NPs with 1 and 2 denoting two different optical modes: (a) CdSe-like longitudinal optical (LO) mode; and (b) CdS-like LO mode. The solid lines denote the model predictions from Eq. (13). The symbols $\Delta$ and $\nabla$ are experimental data [83].

Fig. 26. $\omega(r)$ of ZnO NPs with 1 and 2 denoting two different optical modes: (a) 1LO mode; and (b) 2LO mode. The solid lines denote the model predictions from Eq. (13). The symbols $\Delta$ and $\nabla$ are experimental results [84].
The model prediction from Eq. (13) is in good agreement with the experimental and computer simulation results, which verifies the accuracy of Eq. (13).

Moreover, the developed model can also be used to determine the dimensionality dependence of \( \omega(r) \) in semiconductor nanocrystals with different surface/volume ratios, of \( 3/r, 2/r, \) and \( 1/r \) for NPs, NWs, and thin films, respectively.

It was reported that the crystalline Si NPs transform into amorphous phase when \( r \approx 1.5 \) nm [78]. Moreover, the molecular dynamics simulations on Ag NPs [113] and Au NWs [112] also show that: (1) a size-dependent amorphous to crystalline structural transition of Ag occurs at \( r = 1.5 \) nm; and (2) the amorphouslike structures of Au NWs are formed when \( r < 1.1 \) nm. For Si NPs, as \( h = 0.2352 \) nm (see Tables 1 and 2) and \( r_{\text{min}} = 2r_0 \), we have \( r_{\text{min}} = 6h = 1.4112 \) nm. For the face-centered-cubic Ag and Au, their lattice constants \( a \) are 0.4086 and 0.4079 nm [124], having \( h \) of 0.2889 and 0.2884 nm \( [h = (2^{1/2}/2)a] \), respectively. As a result, \( r_{\text{min}} = 6h = 1.7334 \) nm for Ag NPs, and \( r_{\text{min}} = 4h = 1.1536 \) nm for Au NWs. These results mentioned above are further evidence that our simple approximation of \( r_{\text{min}} = 2r_0 \) is in good agreement with the experimental and computer simulation results, which verifies the accuracy of Eq. (13).
When \( r < r_{\text{min}} \), the crystallographic structure becomes unstable due to the bond deficit, which causes localized structural distortion or variation and the material has cluster characteristics [100]. For example, a helical structure was proposed for Pb [125], Al [125], and Au [112] NWs by the computer simulations, as well as observed in carbon nanotube [126] and Au NWs [127] in experiments. In this case, with the structural revolution, the long-range-ordered characteristics of the crystalline materials disappear, resulting in different bonding structures from their bulk counterparts. As a result, \( Z(r) \neq Z(\infty) \) due to the increase of broken bond in these clusters. In this work, the developed model is only suitable for crystalline materials based on the consideration of a continuous medium and further efforts will be focused on the structures and physicochemical properties of clusters.

For \( r/r_0 > 10 \), \( y = (2S_{\text{vib}}(\infty)/(3R))/[(r/r_0)-1] \) is small enough, which leads to \( \exp(-y) \approx 1-y \) and \( \sqrt{1-y-1} = \frac{-y}{\sqrt{1-y+1}} \approx -y/2 \) as a first order approximation. Therefore, Eq. (13) can be rewritten as,

\[
\frac{\omega(r) - \omega(\infty)}{\omega(\infty) - \omega(2r_0)} = -\frac{r_0S_{\text{vib}}(\infty)l(3R)}{1-\exp[-2S_{\text{vib}}(\infty)/(3R)]} / r.
\]  

(14)

Eq. (14) obeys the thermodynamic law of low-dimensional materials, in which the alternation of size-dependent quantity is associated with the surface/volume ratio, or \( 1/r \) [3,100-102]. This supports the notion that the size-dependent properties of nanocrystals are most likely affected by the severe bond dangling, which is induced by the crystal size reduction in nanoscale. The nonlinearity correlation of Eq. (13) is a consequence of an essential assumption that the ratio of \( \sigma \) for surface atoms against the underneath atoms in nanocrystals is size-independent [100-102]. Moreover, it is evident that the dimensionality dependence of \( \omega(r) \) as presented in Eq. (14) is 3:2:1 for NPs, NWs, and thin films as a first order approximation.

The phonon confinement model has been widely used to investigate the size effects on the phonon Raman spectra of low-dimensional semiconductors [97,98]. When the crystal size approaches to the nanometer scale, the Raman scattering would not be confined at Brillouin zone center (wavevector \( q = 0 \)) and the optical phonons with \( q \neq 0 \) from an extended region other than the Brillouin zone center also contribute to the Raman spectra. As a result, the phonon vibrational frequency decreases with the wavevector increasing. However, the discrepancy between the calculation results and the experimental data shows that the phonon confinement model cannot describe phonon behavior.
precisely [85,87,88,91]. The accuracy of the developed model in this work indicates that the Raman red shift is the consequence of the combination of the effects of size-induced phonon confinement and surface relaxation, which was considered in the $S_{\text{ vib}}(\infty)$. The structural defects may also contribute to the Raman red shifts. This should be associated with the reduction of the disordered regions and the partial influence on the atomic vibration [77,85,87,91]. Further experimental work will be implemented to study the correlation of specific defects, such as oxygen vacancies, and photonic properties in ZnO nanocrystals. This can also be used to investigate the contribution of specific defects to Raman red shifts.

4. Summary

Nanothermodynamic modeling for recent progress on size-dependent optical properties in semiconductor nanocrystals is comparatively reviewed. A simple and unified model of size- and dimensionality-dependent melting point of nanocrystals has been established based on the Lindemann’s criterion for the melting, Mott’s expression for the vibrational melting entropy, and Shi’s model for the size dependence of the melting temperature. The underlying mechanism behind the bandgap energy enhancement and Raman red shifts in semiconductor nanocrystals is clarified on the basis of an extension of such model to calculate the bandgap energy and Raman frequency. For $E_g$, it was found that (1) $E_g$ increases with decreasing $r$; (2) the ratio of $\Delta E_g(r, d)_{\text{QW}}/\Delta E_g(D, d)_{\text{QD s}}$ increases from 0.67 to 1 with decreasing the nanocrystal size; (3) the structure effects on bandgap energy are negligible while the composition effect in semiconductor alloys is substantial; (4) a similar nonlinear (bowing) relationship between bandgap energies and the composition is discernable in both bulk and nanosized alloy systems; and (5) the composition effect play an important role in determining the bandgap energy of the nanosized semiconductor alloys while the size and dimensionality effects are also substantial. These findings are consistent with experimental data. It reveals that the cohesive energy change is an intrinsic factor to dominate the size, dimensionality, and composition effects on the bandgap energy of semiconductors. For $\omega$, the calculation results show that: (1) $\omega(r)$ decreases with $r$ decreasing for both narrow and wide bandgap semiconductors; (2) the lower limit of the vibrational frequency can be determined theoretically; and (3) the sequence of size effects on Raman red shifts from strong to weak is NPs, NWs, and thin films. The developed model is also in good agreement with experimental data. It reveals that the Raman red shift is caused by the combination of the effects of size-induced phonon confinement and surface relaxation. This review may provide new insights into the size, dimensionality, and composition effects on the optical properties of semiconductors as well as the fundamental understanding of high-performance nanostructural semiconductors towards the applications in optoelectronic devices.

Our model based on the principle of atomic vibrational instability has been utilized to describe a variety of size-dependent physicochemical properties in nanocrystals. This model covers all essential considerations of early models and thus has wider suitability. The unified form of the size-dependent functions reveals that the physical nature behind the new properties of nanocrystals are the increase of surface/volume ratio and also the related bond dangling, which is caused by the reduction of crystal size in the nanoscale. Further extension of this general model to other fields would be more beneficial and the understanding of the mechanism behind the new properties on the nanometer scale should be able to help us in designing and fabricating nanomaterials with desired functions.

The nanothermodynamic model developed in this work has established a good basis for the top-down calculation, which is beneficial for the determination of macroscopic, mesoscopic and even microscopic properties. The model is also a good complementarity for the widely used bottom-up method of computer simulation at the electronic level. It is well known that thermodynamics has a statistic mechanics basis and thus the developed models are only suitable for crystalline structural materials based on the consideration of a continuous medium. For the clusters, up to now, only computer simulation could be used to exactly determine their structures and the related properties, which have no direct correlation with their bulk counterparts and cannot be described by an analytical
solution. Moreover, in this work, most of the discussed nanocrystals are isolated NPs, NWs, or thin films on inert substrate, where the interface effect or the interface interaction is negligible. For the thin films on substrate with strong interaction between them, the interface effect should play an important role on the thermodynamic properties of nanocrystals. Further attention is needed to address the film/substrate interaction on the nanometer scale.

With the progress of the nanothermodynamics, a more complete understanding of the thermodynamic and the kinetic aspects for nanomaterials could be achieved. However, the aforementioned challenges have become impediments to the rapid development of advanced nanodevices and should be solved. It is believed that the structures and properties of clusters are remarkably different from their counterparts in bulk and also in the nanometer scale. Recently, this has become an important subject as the continuing miniaturization of electronic devices will make the minimal device features eventually reach the size regime of atomic clusters [128]. Moreover, the cluster assembled materials also offer the attractive proposition to develop materials tailored physicochemical properties [129-133]. To realize novel nanostructured or cluster-assembled materials associated with their potential technological applications in nanodevices, fundamental and challenging issues need to be addressed. For example, how do the structural arrangement of atoms and the electronic states of the system change with aggregation size increasing from single atom to bulk condensed matter? What are the determinants of the physicochemical properties in such nanocrystals and nanoclusters? Recently, an approach was implemented to combine nanothermodynamics and ab initio density functional theory (DFT) to investigate the structural evolution and size-dependent cohesive energy $E_c(n)$ of Sn from bulk to a dimer where $n$ denotes the number of atoms in the material of a particular size [107]. With the classification of material structure evolution caused by decreasing $n$, $E_c(n)$ could be divided into four regimes: (1) NPs with bulk crystallographic structure ($n \geq 1000$), $E_c(n)$ increases nonlinearly with the decrease of $n$; (2) large-sized clusters with spherical-like structure ($35 < n < 1000$), $E_c(n)$ is proportional to $n^{-1/3}$; (3) medium-sized clusters with prolate structure ($10 \leq n \leq 35$), $E_c(n)$ is size-independent; and (4) small-sized clusters with specific structure ($2 \leq n < 10$), $E_c(n)$ increases with decreasing $n$ rapidly. The calculated and simulated results are in good agreement with the experimental and other simulation results. To the best of our knowledge, this may be the first systematic investigation of the size-dependent $E_c(n)$ of materials. However, the studies of clusters are just beginning because some fundamental issues, such as cluster growth kinetics and nonequilibrium effects are still unresolved. Moreover, in order to understand the structural and property evolution from a single atom to condensed matter, the studies of larger clusters containing dozens or hundreds of atoms and even NPs in several nanometers are required. However, this is difficult to be achieved at present due to the limited computation power. With ever-increasing computer power and the advance of experimental techniques, the above challenge could be overcome in the near future. In addition, the combination of nanothermodynamics and ab initio DFT has provided a new methodology to investigate the size-dependent properties in the full size range. This method should be able to be extended to calculate other properties of nanocrystals and nanoclusters. For the strong interaction between thin films and substrates, the studies on the interfacial energy, interfacial stress, interfacial strain, as well as the size dependence of these properties could provide important information to clarify the interfacial behaviours.

Acknowledgements

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Size Effects in Electroformed Nanomaterials

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Key Words: Electrodeposition; fully dense nanomaterials; grain size-dependent properties; grain size-independent properties; intercrystalline volume fractions; grain boundaries; triple junctions

Abstract
This paper reviews size effects in nanocrystalline metals and alloys made by electroforming, a particular form of electrodeposition. The main size effects in these fully dense, three-dimensional nanomaterials come from grain size reduction to less than 5 nm and down towards the limit of the amorphous structure. Details will be given on the synthesis of such materials and their microstructural characteristics including reduced crystal size and intercrystalline defect density. Properties which show either weak or strong grain size dependence will be discussed and compared with the structure-sensitivity of various properties in conventional polycrystalline materials.

1) Introduction

Nanomaterials can be made by numerous synthesis methods. On the basis of the physical and chemical principles involved in their synthesis, five basic approaches can be used: vapour phase processing, liquid phase processing, solid state processing, chemical synthesis and electrochemical synthesis. For each basic approach there are then several distinct methods. For example, solid state processing methods such as ball milling, equal channel angular pressing, crystallization of amorphous precursors, accumulative roll bonding or shot peening can all result in considerable structure refinement to less than 100 nm. Electroforming is a processing method that belongs to the general category of electrochemical synthesis, and is a specific form of electrodeposition. Electroforming is the electrodeposition of metals, alloys or composites onto a temporary substrate cathode (mandrel or mold) to make a product with a very specific shape [1]. For example, Fig. 1 shows the deposition of a cone shape object using a reusable cathode made of stainless steel or titanium. After the desired cone thickness has been deposited, the electroforming process is stopped and the cone is stripped from the mold by mechanical means, often involving the immersion of the object into liquid nitrogen. Thermal stresses due to the difference in the thermal expansion of the object material and the mold are sufficient to separate them. Mold materials such as titanium and stainless steel have a very thin surface oxide layer which, while electrically conductive to allow for electron transfer during the electrodeposition process, presents a physical barrier between the mold material and the electroform to prevent a strong metallurgical bond between the two materials. A finished cone-shaped nickel electroform is shown in Fig. 2.

Electroforming has been used to make near net shape products ranging considerably in size. Examples include large objects such as erosion shields for helicopter blades, thrust chambers for rocket nozzles and precision reflectors, and microcomponents, for example gears and cantilevers, used in microelectromechanical systems (MEMS).

For many of the materials examined for size effects in this chapter, a very simple arrangement was used in the electroforming process. The cathode was a flat piece of titanium, typically 30 x 30 x 0.5 cm onto which flat nanomaterials were deposited to various thicknesses (typically 0.1–5 mm).
Subsequently the nanomaterial sheets were mechanically stripped from the titanium cathode and machined into various shapes for very specific property measurements. For example, Fig. 3 shows a typical tensile specimen cut from a 1 mm thick nanocrystalline nickel electroform. In another version of the process, the cathode is a rotating titanium drum which allows for a continuous production of nanomaterial foil in the 50 – 100 μm thickness range. This process is useful for products that require materials as relatively thin foils such as for transformer core or printed circuit wiring applications.

While conventional electroforming has been used in industrial applications for many decades [1], it was only recently recognized that this method can be used to i) make nanomaterials in which critical size effects in solids can be studied and ii) produce advanced materials with unique mechanical, physical and chemical property combinations not available in conventional polycrystalline and amorphous materials [2-4].

This chapter is organized as follows. First, the synthesis of nanocrystalline materials by electroforming will be briefly reviewed. Next, details on the microstructural scale effects in this group of materials will be given. This will be followed by an analysis of several properties showing either weak or strong grain size dependence. Whenever possible, comparisons will be given for properties measured on nanomaterials made by other synthesis materials.
2) Synthesis of Nanomaterials by Electroforming

The electroplating bath (electrolyte) is an aqueous solution containing a dissolved salt (Me\(^{z+}\) ions) of the metal (Me) to be electroformed on the cathode (Figure 1). Usually the same metal is also immersed as a solid into the bath as a dissolvable anode. When a potential is applied between anode and cathode, metal is dissolved at the anode and deposited at the cathode. While the anodic and cathodic reactions for specific electroforming operations can be quite complex and involve many intermediate steps, the most important reactions in low pH solutions are as follows:

\[
\begin{align*}
\text{Me}^{z+} + ze^- & \rightarrow \text{Me} \quad \text{cathodic reaction.} \quad (1) \\
H^+ + e^- & \rightarrow \frac{1}{2} \text{H}_2 \quad \text{cathodic reaction.} \quad (2) \\
\text{Me} & \rightarrow \text{Me}^{z+} + ze^- \quad \text{anodic reaction.} \quad (3)
\end{align*}
\]

In other words, at the cathode the reduction of metal and hydrogen ions occurs at the same time. The ratio of metal to hydrogen formation is usually referred to as the current efficiency of the process. As the potential difference (current density) between the anode and cathode increases more electrons will be used to produce hydrogen because metal ions are being depleted in the close vicinity (Nernst diffusion layer) of the cathode.

In order to produce nanocrystalline metals, electrodeposition should be carried out under conditions that promote crystal nucleation and reduce crystal growth i.e. very high current densities [5, 6]. To overcome the depletion of metal ions in the Nernst diffusion layer, pulse current electroforming is usually used. In this process the deposition current is on for only short periods of time at very high current densities to form small crystals, followed by a current-off time during which metal ions can diffuse back into the Nernst diffusion layer from the bulk of the electrolyte. Using this pulsed current approach, very high current densities can be applied to induce massive crystal nucleation.

3) Structure of Electroformed Nanomaterials

In this section the most relevant structural features of nanocrystalline electroforms important for size effect considerations will be summarized. These include grain shape and size, volume fractions of intercrystalline defects and types of grain boundaries in such materials.

3.1 Grain Shape and Intercrystalline Volume Fractions

Fig. 4 shows brightfield and darkfield transmission electron micrographs of a nanocrystalline nickel-2.8% phosphorus electroform. Also shown are the corresponding selected area diffraction pattern and a grain size distribution histogram, the latter being based on measuring several hundred
grain diameters in the darkfield micrograph. Several features can be observed in Fig. 4. First, the grain size is very uniform throughout the microstructure with an average size of 6.1 nm. Second, the grain size histogram shows a log-normal grain size distribution. Third, the diffraction pattern shows continuous rings for the fcc structure of nickel.

Figure 4: TEM brightfield, darkfield and diffraction images, and grain size distribution for a nanocrystalline Ni-2.8 wt% P electroform.

Figure 5 presents a high resolution electron micrograph of a nanocrystalline Ni-1.9 wt% P electroform having an average grain size of 8.1 nm. At this magnification grains in different orientations can be clearly seen, separated by grain boundaries across which the lattice orientation

Figure 5: High resolution electron micrograph of a nanocrystalline Ni-1.9 wt% P electroform with an average grain size of 8.1 nm (original micrograph courtesy of S. Mehta and D.A. Smith, Stevens Institute of Technology, Hoboken, NJ).
changes in the crystals. There are also several triple junctions visible in this figure. Triple junctions are distinct defects at which three grains in different orientations meet. It can be further seen in Fig. 4 that the material is free of coarse porosity.

The grain structure shown in Fig. 5 is very similar to the grain structure observed in conventional polycrystalline materials. It is known that individual crystals in equiaxed polycrystalline materials consist of polyhedra which are joined on crystal facets to form a three-dimensional aggregate. However, there are two main differences between conventional polycrystalline and nanocrystalline materials. First, the grain size in polycrystalline material is much larger than in the nanocrystalline electroforms shown in Figs. 4 and 5. This is the main size effect to be discussed later in this chapter. Second, because of the small crystal size in nanocrystalline material, the relative volume fraction of atoms associated with the interfacial component (i.e. grain boundaries and triple junctions) is much larger in nanomaterials than in polycrystalline materials. This is of considerable importance when considering size effects in such materials because the structural order at grain boundaries and triple junctions is quite different than for the grain interiors. It is the deviation from regular lattice sites which imparts a certain atomistic disorder at grain boundaries and triple junctions. Therefore, when the grain size of a polycrystalline aggregate is reduced, the fraction of atoms at structurally disordered sites increases while the number of atoms at perfect lattice sites decreases.

In order to quantify the volume fractions of grain boundary and triple junction atoms, Palumbo et al. [7] presented a detailed analysis which was based on the following assumptions. First, a representative polyhedron was used to approximate the grain shape: the regular 14-sided tetrakaidecahedron (Fig. 6). Second, a polycrystalline aggregate consists of closely packed tetrakaidecahedra as shown in Fig. 7, whereby two facets are joined together at grain boundaries and the lines where three crystals come together form the triple junctions. Third, the thickness of the grain boundaries was assumed to be 1 nm. In other words, all atoms located within a thickness of 1 nm belong to the interface component and are not located at perfect crystal sites. A geometric analysis was then performed to express the volume fractions for the intercrystalline ($V_{ic}$) and crystalline ($1-V_{ic}$) components of the system as a function of grain size. $V_{ic}$ is given by equation (4):

$$V_{ic} = 1 - \left[\left(\frac{d-\Delta}{d}\right)^3\right].$$  \hspace{1cm} (4)

where $\Delta$ is the grain boundary thickness and $d$ is the grain size of the material. Table 1 shows that for a crystal size of 1000 nm this volume fraction is rather small (~0.3%). At 100 nm it reaches ~3% and then rapidly increases with decreasing grain size, reaching ~27% at 10 nm and ~88% at 2 nm.

![Figure 6: The regular 14-sided tetrakaidecahedron used as the grain shape in volume fraction calculations.](image)
hows the grain boundary and triple junction contributions for grain sizes $\Delta d - \Delta / d$.

$V = V_{gb} - V_{tj}$.

Figure 7: Arrangement of several 14-sided tetrakaidecahedra to form a polycrystalline structure. GB: grain boundary; TJ: triple junction.

Table 1: Volume fractions of atoms associated with interfaces in the bulk ($V_{ic}$) and at the surface ($S_{ic}$), and total grain boundary area per cm$^2$ ($S$) of a 3-D nanomaterial as a function of grain size for a grain boundary thickness of 1 nm.

<table>
<thead>
<tr>
<th>Grain Size [nm]</th>
<th>$V_{ic}$ [%]</th>
<th>$S_{ic}$ [%]</th>
<th>$S$ [m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.29</td>
<td>0.35</td>
<td>2.37</td>
</tr>
<tr>
<td>100</td>
<td>2.97</td>
<td>3.40</td>
<td>23.7</td>
</tr>
<tr>
<td>50</td>
<td>5.88</td>
<td>6.80</td>
<td>47.4</td>
</tr>
<tr>
<td>20</td>
<td>14.26</td>
<td>16.57</td>
<td>118.5</td>
</tr>
<tr>
<td>10</td>
<td>27.10</td>
<td>31.64</td>
<td>237</td>
</tr>
<tr>
<td>5</td>
<td>48.80</td>
<td>57.28</td>
<td>474</td>
</tr>
<tr>
<td>3</td>
<td>70.40</td>
<td>82.14</td>
<td>790</td>
</tr>
<tr>
<td>2</td>
<td>87.75</td>
<td>98.21</td>
<td>1185</td>
</tr>
</tbody>
</table>

For some properties (e.g. mechanical properties, electrochemical properties) it was observed that triple junctions and grain boundaries behave differently and should be considered as two distinct microstructural constituents. Palumbo et al. [7] showed that the volume fraction of grain boundaries ($V_{gb}$) and triple junctions ($V_{tj}$) are given by equations (5) and (6):

$$V_{gb} = \left[3\Delta (d - \Delta)^2\right] / d^3. \quad (5)$$

$$V_{tj} = V_{ic} - V_{gb}. \quad (6)$$

Table 2 shows the grain boundary and triple junction contributions for grain sizes $\leq 50$ nm. This table demonstrates that at 50 and 20 nm the triple junction contribution is relatively small and most of the intercrystalline volume fraction is due to grain boundaries. However, with decreasing grain size triple junction atoms become more and more important. At the smallest grain size of 2 nm in Table 2, triple junctions actually make a bigger contribution to the intercrystalline volume fraction than grain boundaries. The cross over from grain boundary volume fraction dominated to triple junction dominated structures occurs at a grain size just above 2 nm (Figure 8).
Table 2: Contributions of grain boundaries ($V_{gb}$) and triple junctions ($V_{tj}$) to total intercrystalline volume fractions ($V_{ic}$).

<table>
<thead>
<tr>
<th>Grain Size [nm]</th>
<th>$V_{ic}$ [%]</th>
<th>$V_{gb}$ [%]</th>
<th>$V_{tj}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5.88</td>
<td>5.76</td>
<td>0.12</td>
</tr>
<tr>
<td>20</td>
<td>14.26</td>
<td>13.53</td>
<td>0.73</td>
</tr>
<tr>
<td>10</td>
<td>27.10</td>
<td>24.30</td>
<td>2.80</td>
</tr>
<tr>
<td>5</td>
<td>48.80</td>
<td>38.40</td>
<td>10.40</td>
</tr>
<tr>
<td>3</td>
<td>70.40</td>
<td>44.44</td>
<td>25.95</td>
</tr>
<tr>
<td>2</td>
<td>87.75</td>
<td>37.50</td>
<td>50.25</td>
</tr>
</tbody>
</table>

Also shown in Table 1 are two other important structural features in such materials: the volume fraction of atoms associated with grain boundaries at surfaces ($S_{ic}$) and the total grain boundary area per cm$^3$ of material (S). $S_{ic}$ is given by equation (7):

$$S_{ic} = 1 - \left[1 - \frac{\sqrt[3]{3\Delta}}{d}\right]^2. \quad (7)$$

This volume fraction is important for many surface properties such as catalysis, corrosion, passivation, or oxidation.

The total grain boundary area (S) per unit volume (V) for the tetrakaidecahedron grain shape is given by equation (8) [8]:

$$\frac{S}{V} = \frac{2.37}{d}. \quad (8)$$

The total grain boundary area is important to assess i) the free energy of the system in the form of stored grain boundary energy which, in turn, has a strong influence on the thermal stability of such materials or ii) the electrical resistivity as will be discussed in section 4.2.1.

Figure 8: Volume fractions of total interface ($V_{ic}$), grain boundary ($V_{gb}$) and triple junction ($V_{tj}$) components.
3.2 Grain Boundary Structures

The structure and properties of grain boundaries have been studied for nearly a century and numerous models have been proposed over the years [e.g. 9, 10]. These include dislocation models, amorphous structure models, structural unit models and the coincidence site lattice model. The challenge with these models in to account for the large body of experimental evidence that grain boundaries exhibit many properties (e.g. energy, segregation of impurities, diffusion, migration, fracture, corrosion rate) which are strongly dependent on the misorientation between adjacent crystals. On this basis, grain boundaries can be grouped into three different categories: i) low angle boundaries, ii) general high angle grain boundaries and iii) special grain boundaries.

Low angle boundaries, also referred to as small angle or sub boundaries, are grain boundaries with small orientation changes of typically less than 10-15°, depending on the material. These boundaries have been found to consist of dislocation (Burgers vector b) networks in which the misorientation (θ) increases with decreasing dislocation spacing (d) according to the following equation:

\[
\sin \frac{\theta}{2} = \frac{b}{2d}.
\]  (9)

Since each dislocation in the sub boundary contributes to the total strain energy of the dislocation network it is easy to understand why the energy of sub boundaries increases more or less linearly with increasing misorientation angle / dislocation density.

One of the most successful models to describe special high angle boundaries is the coincidence site lattice (CSL) model. In this model grain boundaries are analyzed in terms of superlattices generated for crystals with different orientation relationships [11]. These superlattices cover both crystals in contact with each other and have unit cells with lattice constants larger than the unit cell of the two crystals. They have the property that they extend over both crystals having a certain fraction of atoms, \(\frac{1}{\Sigma}\), in both crystals coinciding within the \(\Sigma\) - times larger unit cell. With x and y being coordinates of the superlattice unit cell, expressed as distances in the coordinate system of one of the crystals, hkl giving the Miller indices of the rotation axis and \(\theta\) describing the misorientation angle between the two crystals, the generating equations for coincidence site lattices are given as follows [12]:

\[
\Sigma = x^2 + y^2N.
\]  (10)

\[
N = h^2 + k^2 + l^2.
\]  (11)

\[
\theta = \left(2 \tan^{-1} \left(\frac{y}{x}\right)\right)^{1/2}.
\]  (12)

In principle, \(\Sigma\) could take on any value. However, it has been shown in numerous studies that only relatively low \(\Sigma\) boundaries show special properties. Grain boundaries are considered special when their \(\Sigma\) value is \(\leq 29\). Structurally, low \(\Sigma\) boundaries exhibit relatively good atomic fit as demonstrated in Fig. 9. In this Figure, two dimensional [111] twist grain boundary structures are presented for the case of two (111) oriented crystals placed on top of each other and rotated by 21.8°, 25.0° and 27.8°, respectively about the plane normal[111]. Note that this arrangement is for the cubic crystal structure. It can be seen in Figs. 9a and 9c that misorientations of 21.8° and 27.8° yield superlattices with relatively small unit cells in which atoms of the two crystals coincide i.e. are located at the same sites. These two cases correspond to \(\Sigma7\) and \(\Sigma13\) boundaries, respectively. On
the other hand, for the $25^0$ rotation (Figure 9b), coincidence is only observed for the two atoms located in the center of the drawing. While several atom pairs show relatively close positions, no other pair in the drawing shows exact coincidence. The next pair with exact coincidence is located far away from the center pair and outside the range covered in this drawing. Therefore, the $\Sigma$ value for the $25^0$ boundary is very high.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Two-dimensional twist grain boundaries in cubic material generated by rotations of (111) oriented crystals by different angles about the [111] rotation axis.}
\end{figure}

The same pair of crystals can be rotated to higher angles and further $\Sigma$ boundaries are obtained for the following misorientations:

$$38.21^0 (\Sigma 7), 46.83^0 (\Sigma 19), 60^0 (\Sigma 3), 73.17^0 (\Sigma 19), 81.79^0 (\Sigma 7)$$
$$92.2^0 (\Sigma 13), 147.8^0 (\Sigma 13), 158.21^0 (\Sigma 7), 166.83^0 (\Sigma 19), 180^0 (\Sigma 3)$$

What is shown in Fig. 9 for the case of $[111]$ tilt boundaries, and the two-dimensional case, can be extended to the three-dimensional case with basically any rotation axis. In other words, the generating equations (11), (12), (13) apply to all possible grain boundary scenarios. The reason that low $\Sigma$ boundaries often exhibit special properties is that atomistically these interfaces have a better structural order than high $\Sigma$ boundaries as can be easily seen in Figure 9.

It has been shown that in a polycrystalline aggregate with crystals having a random orientation distribution, the fraction of boundaries with low $\Sigma$ values ($\leq 19$) is on the order of 10%. However, this number can be substantially increased to over 80% in what is referred to as grain boundary engineering. The ultimate goal of grain boundary engineering is to increase the overall properties of polycrystalline materials by creating high frequencies of special grain boundaries with better properties. However, this is beyond the scope of this chapter.

In summary, the most important structural features in nanocrystalline electroformed materials are the high volume fractions of grain boundary and triple junction defects, the type of grain boundaries and the reduced crystal size. These aspects are of considerable importance in the analysis of size effects in such materials.

4) **Effect of Crystal Size on Properties of Electroformed Nanomaterials**

The properties of nanocrystalline electroforms have been studied extensively over the past two decades in particular for nickel, cobalt and copper, and some of their alloys such as nickel-phosphorus, nickel-iron, cobalt-phosphorus, cobalt-tungsten, etc. [4]. In order to concentrate mainly on the effect of crystal size, the remainder of this chapter will focus on properties of electroformed
nickel. It should be noted, however, that similar trends as discussed here for nickel have also been observed for other electroformed materials.

In terms of grain size dependence, two groups of properties have been observed for nickel. The first group of properties showed weak grain size dependence as listed in Table 3. On the other hand, numerous other properties exhibited strong grain size dependence (Table 3). In the following sections several properties of each group will be discussed in more detail. These include the Young’s modulus (E), saturation magnetization (M_S) and thermal expansion (α) from the group of grain size independent properties, and hardness (H), yield strength (σ_y) abrasive wear resistance as expressed by the Taber wear index (TWI) and electrical resistivity (ρ) from the group of grain size dependent properties. These are summarized in Table 4. The data presented in Table 4 were taken from comprehensive property-grain size graphs published earlier in reference 4.

In the following sections size effects will be discussed as follows. Section 4.1 will cover properties with weak grain size dependence of electroformed nanomaterials for which size effects are fairly well established as seen in Table 4. In section 4.2, the focus will be on those properties presented in Table 4 for which strong grain size effects are observed. Finally section 4.3 will address properties which do show grain size dependence but for which clear size effects have not yet been established.

Table 3: Grain size dependence of various properties for nanocrystalline electroformed nickel.

<table>
<thead>
<tr>
<th>Strong Grain Size Dependence</th>
<th>Weak Grain Size Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>Young’s Modulus</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>Fatigue Performance</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>Thermal Expansion</td>
</tr>
<tr>
<td>Elongation to Fracture</td>
<td>Specific Heat</td>
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<tr>
<td>Coefficient of Friction</td>
<td>Saturation Magnetization</td>
</tr>
<tr>
<td>Abrasive Wear Resistance</td>
<td>Curie Temperature</td>
</tr>
<tr>
<td>Adhesive Wear Resistance</td>
<td>Salt Spray Corrosion Resistance</td>
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<tr>
<td>Localized Corrosion</td>
<td>Passivity in Corrosion</td>
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<tr>
<td>Hydrogen Diffusivity</td>
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<tr>
<td>Electrical Resistivity</td>
<td></td>
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<tr>
<td>Coercivity</td>
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</table>

4.1 Properties with Weak Grain Size Dependence

Several properties of nanocrystalline nickel electroforms show weak grain size dependence over very large crystal size ranges (Tables 3 and 4). These include the Young’s modulus, thermal expansion and saturation magnetization. In this section it will also be shown that materials produced by other synthesis techniques exhibited quite different responses for these properties when their crystal size was reduced to the nanometer range.

4.1.1 Young’s Modulus

Earlier studies using nanocrystalline metals prepared by compacting individual nanometer-sized powder particles made by the inert gas condensation technique showed significant (as high as 82%) reductions in the Young’s modulus in comparison with conventional materials with grain sizes in the micrometer range. These reductions were interpreted in terms of interfacial effects and residual porosity [13-15].

Krstic et al. [16] and Zugic et al. [17] showed that large reductions in such materials can indeed by the result of the intrinsic porosity often observed in compacted nanopowders. By applying a porosity model originally developed for strong solids such as ceramics, Krstic et al. [16] and Zugic
et al. [17] were able to explain the reduced Young’s modulus on the basis of the crack opening displacement of annular flaws associated with the pores as shown in Figure 10.

Table 4: Young’s modulus (E), hardness (H), Yield strength (σy), Taber wear index (TWI), electrical resistivity (ρ), saturation magnetization (Ms), and thermal expansion coefficient (α) for nickel as a function of grain size and intercrystalline volume fraction.

<table>
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</thead>
<tbody>
<tr>
<td>10000</td>
<td>0.03</td>
<td>207</td>
<td>1.3</td>
<td>200</td>
<td>37</td>
<td>8.5</td>
<td>502</td>
<td>11.2</td>
</tr>
<tr>
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<td>0.29</td>
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<td>400</td>
<td>30</td>
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<tr>
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<td>3.7</td>
<td>680</td>
<td>26</td>
<td>8.8</td>
<td>500</td>
<td>11.0</td>
</tr>
<tr>
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<td>5.88</td>
<td>207</td>
<td>4.5</td>
<td>720</td>
<td>23</td>
<td>9.0</td>
<td>495</td>
<td>10.8</td>
</tr>
<tr>
<td>20</td>
<td>14.26</td>
<td>200</td>
<td>5.8</td>
<td>780</td>
<td>22</td>
<td>13.0</td>
<td>489</td>
<td>10.7</td>
</tr>
<tr>
<td>10</td>
<td>27.10</td>
<td>190</td>
<td>6.4</td>
<td>920</td>
<td>20</td>
<td>20.0</td>
<td>488</td>
<td>10.6</td>
</tr>
<tr>
<td>5</td>
<td>48.80</td>
<td>185</td>
<td>5.5</td>
<td>780</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>70.40</td>
<td>170</td>
<td>5.3</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
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</tr>
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</table>

Figure 10: Annular flaws, associated with pores, open up with increasing stress, effectively reducing the stiffness (Young’s modulus) of a strong solid.

In contrast Table 4 shows that the Young’s modulus in porosity-free nanoelectroforms is unaffected by grain size down to 50 nm grain size. For grain sizes less than 20 nm, some reductions were observed, from 207 GPa to 170 GPa, i.e. by about 18% which is much smaller than the over 80% reported for gas condensed materials.

In order to explain this relatively small reduction, Zhou et al. [18] used a composite model previously developed by Shen et al. [19] to describe the change in the Young’s modulus measured on nanomaterials made by mechanical attrition. In this model, the nanomaterial is treated as a composite structure consisting of grain interiors (i.e. perfect crystals), grain boundaries and triple junctions. Using the measured Young’s modulus values for nanocrystalline nickel and nickel-phosphorus electroforms, Zhou et al. [18] determined the upper bound and lower bound solutions as per equations (13) and (14):
\[ E = E_g V_g + E_{gb} V_{gb} + E_{ij} V_{ij}. \]  

(13)

\[ \frac{1}{E} = \frac{V_g}{E_g} + \frac{V_{gb}}{E_{gb}} + \frac{V_{ij}}{E_{ij}}. \]  

(14)

where \( V_g \), \( V_{gb} \) and \( V_{ij} \) are the volume fractions of atoms associated with the perfect grain interiors, grain boundaries and triple junctions, respectively, and \( E_g \), \( E_{gb} \), \( E_{ij} \) the corresponding Young’s moduli for the three components.

With this approach the following upper-bound / lower-bound solutions were obtained:

\[ E_g : 201 - 220 \text{GPa}; E_{gb} : 142-172 \text{GPa}; E_{ij} : 134-187 \text{GPa}. \]  

(15)

With respect to size effects, these results have shown the following. First, with decreasing crystal size in the electroformed nickel, the Young’s modulus of the nanocrystalline interiors is more or less the same as for large nickel grains, both in the form of random crystal aggregates with isotropic behavior averaged over many differently oriented crystals. Second, the Young’s modulus values of the grain boundaries and triple junctions show some reductions which can be explained on the basis of the larger interatomic separations at these defects as compared to the perfect crystal. It is therefore not surprising that the Young’s modulus of materials with grain sizes between 1 \( \mu \text{m} \) and 50 nm is more or less the same, as the total intercrystalline volume fraction changes only from \( \sim 0.3 \) to \( \sim 5.0\% \) (Table 1). On the other hand, for grain sizes less than 20 nm these volume fractions increase very rapidly and the influence of grain boundaries and triple junctions is much more important, consistent with the decrease in the Young’s modulus at the smallest grain sizes, \( \leq 20 \text{nm} \).

In summary, over large grain size ranges the Young’s modulus is not strongly affected by grain size in electroformed nanocrystalline materials.

### 4.1.2 Thermal Expansion

Thermal expansion coefficient measurements on nanocrystalline nickel electroforms cover the range from 10 \( \mu \text{m} \) to 10 nm (Table 4). The \( \alpha \) values change from 11.2 – 10.6 [x 10\(^{-6}\) /K] over this range, i.e. a reduction by about 5.3%. This is in contrast to earlier studies which showed considerable increases in the thermal expansion for nanocrystalline materials produced by the inert gas condensation technique [20] or crystallization of amorphous precursor material [21]. Rupp and Birringer [20] found that the thermal expansion of gas condensed copper with 8 nm grain size (90\% density) was almost twice the expansion value of conventional polycrystalline copper. Lu et al. [21] reported an increase in \( \alpha \) by 60\% for Ni-P alloys crystallized from amorphous precursors. It should be noted, however, that these materials were two phase materials consisting of fcc Ni and a bct Ni\textsubscript{3}P phase. Therefore, a direct comparison with pure single phase Ni nanomaterial may be difficult.

Szpunar et al. [22] used a molecular – dynamics approach with interactions represented by the embedded – atom method to calculate the thermal expansion coefficients for two special grain boundary types in nickel: \( \Sigma 5 \) ([100] 36.9\%) and \( \Sigma 13 \) ([100] 22.6\%). They found that for both grain boundary cases the thermal expansion coefficient is only slightly different from the bulk value (<1\%). Therefore, the total effect of grain boundaries on the thermal expansion coefficient would be rather small, consistent with the data presented in Table 4 for nickel electroforms.

The reason why nanocrystalline materials produced by inert gas condensation showed significantly increased thermal expansion values is not known. However, Gleiter [23] presented further results on gas condensed copper which suggests that porosity may be responsible for this effect. In this study, Gleiter [23] presented thermal expansion data as a function of the applied pressure during powder consolidation. The general trend was that the difference between the thermal expansion coefficients for nanocrystalline and polycrystalline copper decreased with
increasing compaction pressure. Some compacted materials even showed a slight reduction of $\alpha$ from the value of polycrystalline material. These observations are consistent with the results reported for nanocrystalline nickel electroforms.

### 4.1.3 Saturation Magnetization

Table 4 shows that the saturation magnetization in nickel electroforms changes from 502 kA/m at 10 $\mu$m grain size to 488 kA/m at 10 nm, a small reduction of about 2.8%. As for the case with thermal expansion, these results are in contrast to saturation magnetization values observed for materials made by the inert gas condensation technique. Gleiter [24] reported a 40% reduction in saturation magnetization for gas condensed nanocrystalline iron with 6 nm grain size compared to bulk polycrystalline $\alpha$-iron. Gong et al. [25] also observed considerable reductions for nanocrystalline particles of Ni, Co and Fe with particle sizes in the 10-50 nm range, as did Yao et al. [26] and Schaefer et al. [27] for nickel, and Krill et al. [28] for gadolinium nanoparticles. Various explanations for this effect were presented including differences in the magnetic microstructure [24], the presence of antiferromagnetic oxide layers on the ultrafine metal particles [25] or structural disorder at interfaces [27].

In order to shed further light on this discrepancy, Szpunar et al. [29-31] conducted a theoretical study using the linear muffin-tin orbital, atomic sphere approximation method to evaluate the effect of structural disorder introduced by grain boundaries on local magnetic moments. Different grain boundary types were examined covering a wide range of structural disorder (Figure 11). At one end of the spectrum, the high angle boundary with the least structural disorder considered was the $\Sigma 3$ coherent twin boundary (Figure 11a). The other extreme case with the maximum structural disorder was a totally amorphous grain boundary structure (Figure 11c). As a boundary with structural disorder between the two extreme cases, a $\Sigma 5$ special grain boundary was considered.

![Figure 11: The structures of grain boundaries used in the calculation of magnetic moments: a) $\Sigma 3$; b) $\Sigma 5$; c) completely amorphous (from reference 29, with permission).](image)

The results of these calculations have shown the following. First, for the $\Sigma 3$ boundary, no effect on the local magnetic moments in the vicinity of the boundary was found. Second, for the amorphous grain boundary structure, the local moments varied between 0.35 and 0.71 $\mu_B$ with an average of 0.5 $\mu_B$ compared to 0.6 $\mu_B$ for atoms located in a single crystal. Third, for the $\Sigma 5$ boundary, the local moments were 0.48 $\mu_B$, 0.59 $\mu_B$, 0.60 $\mu_B$, 0.59 $\mu_B$ and 0.6 $\mu_B$ for nickel sites 1, 2, 3, 4 and 5 in Figure 11b. It should be noted that the value of 0.48 $\mu_B$ for site 1 does not significantly reduce the total moments associated with the $\Sigma 5$ boundary, since Ni (1) sites constitute only a small portion of the total number of atoms in this boundary. Overall these calculations have shown that the magnetic moments are rather insensitive to the degree of structural disorder.
associated with grain boundaries. Even for the worst possible scenario of a 18% reduction in the local moment for a completely amorphous boundary and a 27.1% intercrystalline volume fraction (Table 1), the overall reduction in saturation magnetization for nickel with 10 nm grain size should not exceed 5%. Considering the fact that for special grain boundaries the local moment reduction is much less than 18%, the effect of grain boundaries on saturation magnetization is therefore rather small, in good agreement with the results presented in Table 4.

More recently there have been other reports that support the findings presented in Table 4. For example, Daroczi et al. [32] showed that for nanocrystalline nickel made by mechanical attrition the saturation magnetization for 7 nm grain size is essentially the same as for 50 μm grain size. Kisker et al. [33] showed that for gas condensed materials saturation magnetization is independent of grain sizes long as the material is not exposed to air. This supports the idea that the relatively large reductions reported earlier for gas-condensed nanomaterials were indeed due to the formation of nickel oxide layers on individual powder particles and not the crystal size per se.

4.2. Properties with Strong Grain Size Dependence

In contrast to properties that are relatively structure-insensitive, many other properties of Ni electroforms are strongly influenced by either the presence of intercrystalline defects alone or, more importantly, the interactions of intercrystalline defects with other structural elements such as vacancies, dislocations, surfaces or ferromagnetic domain walls.

4.2.1 Electrical Resistivity

Table 4 shows that the room temperature electrical resistivity of nanocrystalline nickel electroforms is relatively constant for the grain size range from 10 μm to about 100 nm. However, below 100 nm resistivity increases considerably from 8.8 μΩcm at 100 nm to 20 μΩcm at 10 nm. This increase in electrical resistivity is due to electron scattering at the intercrystalline defects, the volume fraction of which increases rapidly at grain sizes less than 100 nm (Table 1).

McCrea et al. [34] presented equation (16) to express the electrical resistivity of a nanomaterial in terms of a specific grain boundary resistivity ($\rho_{SGBR}$):

$$\rho_T = \rho_o + \rho_{SGBR} \frac{2.37}{d}. \quad (16)$$

where $\rho_T$ is the total resistivity of the material and $\rho_o$ the resistivity due to electron scattering on phonons and other defects such as vacancies, dislocations, impurity atoms, etc. In other words, it is the second term that adds to the resistivity when the grain size of the material is reduced. For the specific case of the room temperature resistivity of nickel the experimentally determined values for $\rho_o$ and $\rho_{SGBR}$ are given in equation (17):

$$\rho_T = \left(8.33 + \frac{2.37 \times 2.82 \times 10^6}{d}\right) \mu\Omega cm. \quad (17)$$

where $d$ is the grain size in centimeters.

Using equation (17) it can be shown that, for the case of nickel, the electrical resistivity of a single crystal is increased by 1% at a grain size of 835 nm, by 2% at 400 nm and by 10% at 80 nm. The largest increases are then observed at very small grain sizes ≤80 nm as seen in Figure 12.

A very similar effect of crystal size on the electrical resistivity was also observed in materials prepared by the inert gas condensation technique [24]. There is also a good agreement in terms of
the temperature coefficient for resistivity for materials made by electrodeposition [4] and inert gas condensation [24]. In both cases, the temperature coefficient was observed to decrease with decreasing grain size.

**Figure 12:** Effect of grain size on electrical resistivity of nanocrystalline nickel at 295K and 4.2K (from reference 34, with permission).

### 4.2.2 Hardness and Yield Strength

Both hardness and yield strength show strong grain size dependence in nanocrystalline nickel. Table 4 shows that both properties initially increase with decreasing grain size. Hardness increases from 1.3 GPa at 10 µm grain size to 6.4 GPa at 10 nm grain size. For even smaller grain sizes the hardness decreases somewhat to 5.3 GPa at the smallest grain size of 3 nm. Similarly, the yield strength at 10 µm grain size is 200 MPa and increases to a maximum of 920 GPa at 10 nm grain size. Again a small reduction down to 780 GPa is observed for the smallest grain size of 5 nm.

The initial increase in hardness ($H$) and yield strength ($\sigma_y$) can be explained by using the Hall-Petch relationship [35, 36] given in equations (18) and (19):

$$H = H_o + k \cdot d^{1/2}. \tag{18}$$

$$\sigma_y = \sigma_o + k' \cdot d^{1/2}. \tag{19}$$

where $H_o$, $\sigma_o$ are the hardness and yield strength values at large grain sizes, $d$ is the grain size and $k$, $k'$ are constants for each material, respectively. These equations, originally developed for polycrystalline materials, explain hardness/yield strength increases in terms of grain boundary/dislocation interactions. Smaller grain sizes introduce higher grain boundary densities and, therefore, higher concentrations of obstacles for dislocation slip. As can be seen in Table 4, this trend continues down to the nanocrystalline range. However, both hardness and yield strength show a maximum at a grain size of ~10 nm. For grain sizes below 10 nm, a softening is observed for both properties.
This phenomenon is known as the inverse Hall-Petch relationship which was originally observed in nanocrystalline Cu made by the inert gas condensation technique [37] and nanocrystalline Ni-P prepared by electrodeposition [2]. In other words, for very small grain sizes, \( k \) and \( k' \) in equations (18) and (19) become negative. This behavior has been observed in numerous studies on electroformed Ni and Ni-based alloys as summarized, for example, in reference 38. The results of one particular study [39] on the microhardness of polycrystalline and nanocrystalline nickel is shown in Figure 13. Note that the hardness values in this figure are given in units of Vickers Hardness Numbers (VHN). A similar curve for the yield strength as a function of \( d^{-1/2} \) can be found elsewhere [40].

The main question is why the classical Hall-Petch relationship breaks down at very small grain sizes and is replaced by an inverse relationship between hardness / strength and grain size? This behavior is not unique to electroformed and gas condensed nanomaterials but has also been reported for materials produced by other synthesis techniques. Numerous experimental and theoretical papers have addressed this issue, and it is now generally agreed that the change from regular to inverse Hall-Petch behavior is due to changes in deformation mechanisms [41].

For large grain sizes the two major room temperature deformation mechanisms are dislocations slip and twinning (in some materials) (Figure 14a). For the case of deformation by dislocation slip, grain boundaries act as barriers and usually create dislocation pile-ups of dislocations generated inside the grain by dislocation multiplication sources. However, with decreasing grain size it becomes more and more difficult for these dislocation sources to operate. Therefore, other deformation mechanisms become more dominant at very small grain sizes. Figure 14b shows some of the alternative deformation mechanisms including Coble creep, Nabarro-Herring creep, grain boundary sliding and grain rotation likely to operate in nanomaterials.

Wang et al. [40] examined the creep behavior in nanocrystalline nickel electroforms and analyzed the data using the constitutive equations for diffusion-dependent mechanisms. They generated an Ashby-type deformation map, showing the effect of grain size (from 34 \( \mu \)m to 10 nm) on the various deformation mechanisms. The major conclusions from this work were as follows. First, the mechanical behavior of nanocrystalline nickel electroforms can be described on the basis of a composite model [40, 42], in which the total strength of the material is the sum of contributions coming from different structural components including grain interiors, grain boundaries and triple junctions. Second, grain boundary sliding and diffusive matter transport in the intercrystalline regions play an important role in the deformation of nickel with very small grain size.
Palumbo et al. [43] observed that the onset of decreasing hardness in electroformed Ni-P alloy electroforms occurred at a grain sizes less than 20 nm where triple junctions begin to contribute significant volume fractions to the structure (Table 2) and introduced the concept of triple junctions softening for nanomaterials. Triple junction softening was earlier reported for conventional polycrystalline Al, Cu and W with various grain sizes by comparing the room temperature tensile properties of wire samples with and without triple junctions [44]. For all three materials, increases in strength and decreases in ductility were observed in samples containing no triple junctions. Triple junction softening was also observed for polycrystalline Ni [45].

The importance of this effect for nanocrystalline materials was further demonstrated by the smooth transition of the decreasing hardness, in the inverse Hall-Petch region, of nickel-phosphorus electroforms with grain sizes in the range of 8 nm to less than 2 nm and towards the limit of the amorphous structure [43]. This phenomenon was explained in terms of the high density of disclinations, defects that have been used to describe both triple junction structures as well as the amorphous structure [46-48].

Comprehensive computer modeling work over the past several years has shown that several new inter-grain and intra-grain deformation mechanism can occur in nanocrystalline materials. As summarized by Derlet et al. [49], these include the emission of full or partial dislocations from grain boundaries or deformation twins.

In the early years of research on nanocrystalline structures, materials were often available only in small quantities, insufficient to measure their mechanical properties by tensile testing. Therefore, the hardness test was frequently used and, as summarized by Brooks et al. [50], the yield strength was then estimated form various hardness (H) / yield strength ($\sigma_y$) relationships including the following:

\[ H \approx 3\sigma_y, \quad (20) \]
\[ H \approx \sigma_y. \quad (21) \]
Brooks et al. [50] analyzed tensile test and hardness test data for a large number of electroformed metals and alloys including nickel, nickel-molybdenum, nickel-silicon carbide, nickel-iron cobalt and cobalt-phosphorus. They found that the relationships (20) and (21) are not applicable to this class of nanomaterials and result in significant over-estimations of the intrinsic yield strength of electroformed materials. On the other hand, they found that the relationship given in equation (22) is a more reliable expression:

\[ H_v = 3\sigma_{UTS}. \]  (22)

where \( H_v \) is the Vickers hardness and \( \sigma_{UTS} \) the ultimate tensile strength. As long as the material has sufficient ductility (>5%) to sustain tensile deformation to a discernible peak load, equation (22) can be used to estimate tensile strength from hardness measurements. However, for more brittle materials (<5% elongation to fracture), this relationship was also found to be invalid.

### 4.2.3 Wear Properties

Several studies have reported the wear properties of electroformed nanomaterials [39, 51-53]. These studies used various wear tests including pin-on-disk, Taber wear or scratch tests. One of the earliest studies on the tribological properties of nanocrystalline Ni electroforms used the pin-on-disk method [39]. In this study it was shown that the wear rate was reduced by two orders of magnitude when the grain size was reduced form 10 \( \mu \text{m} \) to 10 nm. At the same time the coefficient of friction dropped by a factor of 2.

Pin-on-disk testing measures the wear properties under adhesive wear conditions. The Taber wear test, on the other hand, is designed for the much harsher conditions of abrasive wear. In this test a test piece is abraded by a rubber wheel with embedded hard alumina particles. The wear rate is expressed as the Taber wear index which is the weight loss in milligrams per 1000 cycles of rotational abrasion. The Taber wear index is usually given as a unitless number: the lower the Taber wear index the higher the material’s resistance to abrasive wear.

Jeong et al. [51] measured the Taber wear index as a function of grain size in electroformed Ni. As can be seen in Table 4, the Taber wear index decreases from 37 at 10 \( \mu \text{m} \) grain size to 20 at a grain size of ~10 nm. Figure 15 shows scanning electron micrographs of both polycrystalline and nanocrystalline nickel after 10,000 wear cycles. The polycrystalline nickel shows deep abrasion grooves demonstrating excessive material loss by the hard alumina particles. On the other hand, the wear grooves on the nanocrystalline nickel are relatively shallow and much narrower demonstrating reduced material removal compared with polycrystalline nickel.

The study by Jeong et al. [51] showed that the Taber wear resistance for nickel electroforms follows the well established Archard’s law which states that the wear loss of a material is inversely proportional to its hardness as per equation (23):

\[ \Delta V = k \cdot \frac{L \cdot S}{H}. \]  (23)

where \( \Delta V \) is the wear volume loss, \( L \) the applied load, \( S \) the sliding distance, \( k \) the wear coefficient and \( H \) the hardness of the material.

In another study, Jeong et al. [54] reduced the grain size of nickel electroforms to values below 10 nm by alloying with a few percent phosphorus. This produced materials with hardness values in both regions of regular and inverse Hall-Petch behavior (Figure 16a). As expected from Archard’s law, the Taber wear index showed a minimum at the grain size at which the hardness reached the maximum (Figure 16b). The studies by Jeong et al. [51, 54] have therefore shown that for electroformed nickel and nickel-phosphorus alloys there are direct relationships between crystal size, hardness and Taber wear index.
Figure 15: Polycrystalline (left) and nanocrystalline (right) nickel after Taber wear testing of 10,000 cycles (from reference 55, with permission).

It should be noted, that the same relationships were not observed for cobalt electroforms [55]. Instead, for cobalt ductility also played an important role in wear resistance: higher ductility giving lower abrasive wear resistance. This phenomenon is currently not well understood and needs further study.

Figure 16: Hardness and Taber wear index as a function of $d^{-1/2}$ for nanocrystalline nickel and nickel-phosphorus (from reference 55, with permission).

4.3 Other Properties Showing Size Effects

In this section, several other properties will be discussed which clearly show grain size effects in electroformed nanomaterial, but for which a comprehensive treatment in terms of grain size and intercrystalline volume fractions is currently not yet available. These include ductility, precipitation hardening and corrosion properties.

4.3.1 Ductility

At this time it is impossible to quantitatively analyze ductility of nanocrystalline metals, alloys and composites with straight forward equations relating ductility with grain size, intercrystalline volume fractions or any other microstructural features. This is the case not only for nanocrystalline electroforms but for all nanomaterials, regardless of synthesis method. A good review of our
understanding of ductility in all types of nanomaterials was recently published by Koch [56]. The main reasons for the lack of a better understanding of the intrinsic effect of grain size on ductility include i) insufficient quantities of nanomaterials in the early studies to perform testing according to standard procedures as established, for example, by the American Society for Testing and Measurements (ASTM), ii) flaws in the materials due to processing (e.g. porosity, impurities) and iii) incomplete knowledge of deformation mechanisms in nanocrystalline materials. Nevertheless, considerable progress has been made over the past 10 years in understanding the ductility of nanocrystalline electroforms, in particular nickel, nickel-iron and cobalt electroforms. Early measurements [40, 57] showed that the ductility of nickel decreases from about 50% at a grain size of 100 μm to about 15% at a grain size of about 80 nm. Further grain size reduction to about 10 nm, at which the maximum is observed in hardness and yield strength (Table 4) resulted in a disappointing ductility of less than 1%. Again it should be emphasized that nanomaterials produced by other synthesis methods showed very similar low ductility values at this grain size [56]. However, it is unlikely that the ductility values reported in these earlier studies are indicative of the intrinsic ductility of nanocrystalline electroforms. In fact, upon scaling up the electroforming process from a laboratory scale to the industrial scale [50], it was observed that the ductility of Ni increased considerably. Also, with a better control of detrimental impurity elements, such as sulfur in Ni, better ductility values were achieved in electroformed materials [50, 58]. More recent improvements in the electroforming process have resulted in much higher ductilities of electroformed Ni, Co and Ni-Fe alloys reaching values in excess of 10% at grain sizes in the 10-20 nm range [50, 59, 60].

Another important aspect in ductility of nanomaterials is grain size distribution. Early research efforts in nanostructured materials were often concerned with achieving relatively narrow grain size distributions such as shown in Figure 4 for electroformed nickel-phosphorus nanomaterials. While this approach is of great benefit to study intrinsic properties of nanomaterials, it is not necessarily the best approach for optimizing all properties of the material. In fact, in order to obtain a good compromise for optimized strength/ductility, materials with much broader grain size distributions or even bimodal distributions may be much better [4, 56]. In such structures the smaller grains would give rise to increased strength/hardness, while the larger grains would provide the material with reasonable ductility (Figure 17). A recent study has shown that this is indeed possible for electroformed nickel with broad grain size distributions which had ultimate tensile strength values of ~1400 – 1900 MPa and ductilities of ~ 6 – 11% [61].

![Schematic diagram showing a bimodal grain size distribution in nanomaterials.](image)

**Figure 17:** Schematic diagram showing a bimodal grain size distribution in nanomaterials.

### 4.3.2 Precipitation Hardening

Precipitation hardening has been used for many years in conventional polycrystalline alloys to considerably increase their strength by precipitate/dislocation interactions. The basic requirement in terms of alloy composition is that the solid solubility limit decreases with decreasing temperature. Examples of conventional precipitation-hardening alloys include Al-Cu, Al-Ag, Cu-Be, Cu-Co, Ni-Al and Ni-Ti.
Nanocrystalline electroforms can be deposited as supersaturated solid solutions, e.g. Ni-P, Co-P, Co-W or Zn-Ni [4]. These alloys can be heat treated to induce some grain growth in addition to the precipitation of the equilibrium second phase particles [62]. An example of Ni$_3$P precipitation on the hardness on Ni-1 wt% P alloys is shown in Figure 18. The as-electroformed material had a grain size of about 7 nm and a hardness of ~7 GPa. After 15 minutes of annealing at 400°C the grain size grew to about 21 nm and many very small Ni$_3$P particles precipitated in the alloy. This increased the hardness quite substantially to over 12 GPa. Further annealing at 400°C resulted in the growth of the grain size, e.g. to 64 nm after 60 minutes, and coarsening of the Ni$_3$P particles. Consequently, the hardness decreased with increasing grain size/particle size, as expected from conventional precipitation-hardening theory. This effect is referred to as overaging.

Figure 18 further shows that annealing the same alloy at 500°C and 600°C did not increase the hardness, regardless of annealing time. At these temperatures the grain size and particle size grew so rapidly that for the higher annealing temperatures chosen in this study the phenomenon of overaging was observed for all annealing times.

A similar precipitation hardening effect was also reported for nanocrystalline Co-P electroforms [4]. In this case, the second phase particle is Co$_3$P. The hardness of the electroformed supersaturated Co-5.2 wt% P alloy was ~8 GPa in the as-deposited state and increased to 10.5 GPa after an annealing treatment of 5 minutes at 400°C.

![Figure 18: Precipitation hardening in annealed nanocrystalline nickel-1% phosphorus alloy.](image)

### 4.3.3 Corrosion Behavior

When nanocrystalline electroforms were first developed, their corrosion behavior was initially of great concern because of the high densities of grain boundaries in triple junctions. In many conventional polycrystalline metals these defects are often attacked preferentially leading to intergranular corrosion. The reason for this form of corrosion is that grain boundaries and triple junctions have higher energies than the perfect crystal and are prone to segregation of impurity atoms. Therefore, by extrapolation from the polycrystalline to the nanocrystalline case, the initial expectation was that the corrosion resistance of nanocrystalline materials would be very poor.

Extensive research on the corrosion behavior of nanocrystalline nickel, cobalt, copper and zinc electroforms over the past two decades has shown that this is not the case as summarized recently by Kim et al. [63] and Erb et al. [4]. A detailed analysis of the findings in these studies is beyond the scope of this current review. However, the main results can be summarized as follows. First, contrary to the early concerns, the high grain boundary and triple junction densities found in
Electroformed nanomaterials do not compromise their corrosion performance. The general shapes of polarization curves for various materials in acidic, basic or neutral chloride solutions were not strongly affected by grain size. This is shown in Figure 19 for the example of the corrosion of nanocrystalline and conventional polycrystalline Co electroforms in 0.1M NaOH (pH=13) solution. Both materials show basically the same active-passive-transpassive corrosion behavior. Of particular importance is that materials that show passivity in the polycrystalline form also show passivity in the nanocrystalline form.

Figure 19: Potentiodynamic polarization curves in 0.1 M NaOH (pH=13) for polycrystalline and nanocrystalline cobalt (from reference 63, with permission).

Second, for systems that do show passivity, the structure and chemical composition of the passive layer depends on the grain size of the material. This can be understood on the basis of the high defect concentrations (Si in Table 1) intersecting the free surface of the material. This defective structure has a strong influence on the defect structure of the passive layer. Impurity atoms were
also found to have a strong effect on the nature of the passive film. Nevertheless, even the defective passive layer structure provides considerable protection of the nanocrystalline metal.

Third, metals which show clear intergranular attack in polycrystalline form can benefit enormously from grain size reduction because corrosion attack in nanomaterials is more evenly spread out over the entire surface, instead of being concentrated in narrow channels along grain boundaries and triple junctions. This is clearly seen for the case of the surface morphologies of polycrystalline and nanocrystalline nickel corroded potentiodynamically in 2N H₂SO₄ solution (pH=0) at room temperature (Figure 20).

5) Size Effects in Nanomaterials and Structure-Sensitivity of Properties in Polycrystals

In section 4 it has been shown that size effects in nanocrystalline electroforms are observed for some properties but not for others (Tables 3, 4). It is perhaps instructive to compare these findings with what has been known for a long time for conventional polycrystalline metals and alloys in terms of structure-sensitivity of properties.


<table>
<thead>
<tr>
<th>Type of Property</th>
<th>Structure-Insensitive</th>
<th>Structure-Sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical</td>
<td>Density</td>
<td>Mechanical loss angle</td>
</tr>
<tr>
<td></td>
<td>Elastic moduli</td>
<td>Tensile yield stress</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fracture strength</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Plasticity</td>
</tr>
<tr>
<td>Thermal</td>
<td>Thermal expansion (high temperature)</td>
<td>Thermal conductivity (at high temperatures)</td>
</tr>
<tr>
<td></td>
<td>Melting point</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Specific heat (high temperature)</td>
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<tr>
<td></td>
<td>Heat of fusion</td>
<td></td>
</tr>
<tr>
<td>Electrical</td>
<td>Resistivity (metallic) at high temperatures</td>
<td>Resistivity at low temperatures in semiconductors and metals</td>
</tr>
<tr>
<td></td>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Saturation polarization of ferroelectric materials</td>
<td>Electrical loss angle</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Paramagnetic and diamagnetic properties</td>
<td>Ferromagnetic properties (including magnetostriction) except saturation induction</td>
</tr>
<tr>
<td></td>
<td>Saturation induction of ferromagnetic materials</td>
<td></td>
</tr>
<tr>
<td>Superconductive</td>
<td>Transition temperature</td>
<td>Current carrying capacity</td>
</tr>
</tbody>
</table>

Table 5 is a summary table listing structure-insensitive and structure-sensitive properties for polycrystalline materials, modified from the classical materials science textbook by A.L. Ruoff [65]. As can be seen in this table, properties such as elastic modulus, specific heat, thermal expansion or saturation induction (magnetization) are structure-insensitive properties, i.e. properties that show no major changes when the microstructure is modified (for example by grain size reduction, increases in dislocation density, low concentration solute additions). On the other hand, tensile strength, plasticity and low temperature electrical resistivity are structure-sensitive and depend strongly on the defect structure in the material. This is more or less the same what is observed for nanocrystalline electroforms: the same properties are either not strongly affected by grain size or show considerable changes when the microstructure is refined.

In summary, electroforming technology developed over the past two decades has made it possible to push the grain size of metals and alloys down to the nanometer range and therefore allows for
considerable improvements of some properties (strength hardness, wear resistance) compared with conventional polycrystalline materials with grain sizes in the micrometer range. At the same time, those properties which have long been known to be structure-insensitive in polycrystalline materials (the Young’s modulus, thermal expansion, saturation magnetization) continue to be relatively independent of grain size even in nanocrystalline materials.

6) Conclusions

Fully dense nanocrystalline metals and alloys made by the electroforming technology have unique microstructures consisting of nanometer-sized perfect crystals and large volume fractions of grain boundary and triple junction defects. It has been shown that several properties (e.g. the Young’s modulus, thermal expansion and saturation magnetization) are not strongly affected by the presence of high concentrations of these defects. On the other hand, properties that depend on the interactions of intercrystalline defects with other structural characteristics (e.g. dislocations, precipitates, electrons) show significant grain size effects. These include strength, hardness, wear resistance, electrical resistivity and several other properties.

7) Acknowledgements

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Size effect on thermal properties in low-dimensional materials

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Abstract. An extension of the classical thermodynamics to nanometer scale has been conducted to elucidate information regarding size dependence of phase transition functions and binary phase diagrams. The theoretical basis of the extension is Lindemann’s criterion for solid melting, Mott’s expression for vibrational melting entropy, and Shi’s model for size dependent melting temperature. These models are combined into a unified one without adjustable parameters for melting temperatures of nanocrystals. It is shown that the melting temperature of nanocrystals may drop or rise depending on interface conditions and dimensions. The model has been extended and applied to size dependences of melting enthalpy, melting entropy, atomic cohesive energy. Moreover, the above modeling has been utilized to determine the size-dependent continuous binary solution phase diagrams. These thermodynamic approaches have extended the capability of the classical thermodynamics to the thermodynamic phenomena in the nanometer regime.

Introduction

As nanoscience and nanotechnology develop in recent years, sizes of materials come into nanometer size range at least in one dimension, which lead dramatic increase of surface(interface)/volume ratio and corresponding changes of physical, chemical and mechanical properties. To understand these properties and related physical bases, which are the necessary premises for correct industrial application, theoretical considerations on these size dependent phenomena become important due to partly absence of accurate measuring techniques on these properties of materials. Among different theoretical approaches, the thermodynamic theories as classic ones are powerful tools to study these phenomena following the top-down way, which will benefit materials design as well the corresponding manufacture and fabrication techniques and processes.

In this chapter, size dependences of several thermodynamic amounts are systematically modeled without adjustable parameters, which include models for size dependent melting temperature, for surface meting, for size dependence of melting entropy and enthalpy in different dimension and environment. Experimental evidences confirm these models. In light of these general thermodynamic models, several typical size-dependent transition phenomena, such as freezing temperature, the evaporation temperature, Debye temperature and volume thermal expansion coefficient, Solid transition and Phase diagram are considered and discussed. These model predictions are in agreement with the experimental results. All of these simple analyses imply that the classic thermodynamic are still important even in nanometer size range to supervise, interpret, and even predict physical, chemical and mechanical properties.

Basic thermodynamics

The classical thermodynamics on macroscopic systems has long been well established [1,2], which describes adequately the macroscopic behaviors of bulk systems with the change of macroscopic parameters where the astrophysical objects and small systems at the nanometer scale are excluded [3]. The basic thermodynamic relationship for a macroscopic system at equilibrium is [4],

\[
dU = TdS - PdV.
\]

where \( U \) is the internal energy, \( T \) denotes the absolute temperature, \( S \) is the entropy, \( P \) the pressure, and \( V \) the volume. This equation connects incremental changes of internal energy, heat, and work.

In 1878, the monumental work of Gibbs first formulated a detailed thermodynamic phase equilibrium theory [1] where he transformed the previous complicated thermodynamics of cycles into the simpler thermodynamics of potentials and introduced chemical potentials [2]. Gibbs generalized Eq. 1 by allowing, explicitly, variations in the number of molecules \( N_i \) of the different components in the system [4]. As a result, Eq. 1 became, \( dU = TdS - PdV + \mu_i dN_i \), or in a more general and modernized form,

\[
dG = -SdT + VdP + \gamma dA + \sum_i \mu_i dN_i.
\]

where \( G \) and \( \mu_i \) denote Gibbs free energy and the chemical potential of the component \( i \), \( A \) denotes surface(interface) area and \( \gamma \) shows surface(interface) energy. Eq. 2 thus could treat various equilibria (chemical, phase, osmotic, surface, etc.) and examine many other topics, such as the equilibrium condition of a solid and a surrounding medium [2]. Eq. 2 is much less difficult to use than to understand although it is very simple mathematically. Although Eq. 2 has wide application ranges, it is essentially used to treat phase equilibrium and related phenomena, such as phase diagrams.

Note that Eq. 2 with a statistic basis is only valid for materials being at least larger than submicron size while the parameter "size" in Eq. 2 is actually a constant of bulk. Since nanomaterials and nanotechnology go into the scientific and technical worlds now, extending the validity of thermodynamics into nanometer size range thus becomes an urgent task. Namely, a further term or variant of size must be introduced into Eq. 2.

It is well-known that thermodynamic properties of nanometer-sized systems largely differ from those of single molecules as well as bulk materials. The reasons lie in the so-called specific and smooth size effects. The former is responsible for the existence of "magic numbers" and related irregular variation of properties in clusters, whereas the latter pertains to nanostructures in the size domain between clusters and bulk systems. Within this broad size range, mechanical, physical and chemical properties are often seen to change according to relatively simple scaling equations involving a power-law dependence on the system size due to the energy contributions of \( \gamma \) to the total \( G \) of the system with a high surface/volume ratio \( \chi = A/V \) [5]. These properties changes lead to, on one hand, an emerging interdisciplinary field involving solid state physics, chemistry, biology and materials science to synthesize materials and/or devices with new properties by controlling their microstructures on the atomic level, on the other hand, understanding the physical and chemical natures behind the new properties in order to guide the fabrication of new materials and their possible industrial applications [6].

Among the above properties of solids, thermal stability of materials and devices are especially important, which is related to the corresponding \( T_m \). The melting denotes a solid-liquid phase transition process at \( T_m \) under a certain \( P \) where \( G_m = G_l - G_s = 0 \). The melting, as a first order phase transition, requires \( H_m \not= 0 \) and \( V_m \not= 0 \). Since the value of \( H_m \ll H_b \) with \( H_b \) being the vaporization enthalpy, the values of cohesive energy \( E_c \) and \( C_p \) of liquid and solid phases should be similar [7].

The melting entropy \( S_m \) and \( H_m \) are also essential thermodynamic parameters for melting. \( H_m \) is mainly produced by the internal energy change while \( S_m \) is induced by a structural change. Since \( T_m =
As a variable for the melting thermodynamics, the size effect has only been studied in recent years due to the rapid progress in nanoscience and nanotechnology [7,8]. It is now known that \( T_m(r) \) of metallic [9,10], semiconductor [11,12], and organic [13,14] nanocrystals are size dependent where \( r \) denotes the size of the materials. While \( T_m \) of a free nanocrystal is known to decrease as \( r \) decreases [15], nanocrystals embedded in a matrix can melt below or above the corresponding \( T_m(\infty) \) depending on interface structure between embedded nanocrystals and the matrix [16-18]. If the interfaces are coherent or semi-coherent, an enhancement of \( T_m(r) \) is present. Otherwise, there is a depression of \( T_m(r) \) [19]. Some molecular dynamics (MD) simulations have also shown that the same tendency [20-22]. To address these findings, the corresponding nanoscale thermodynamics — nanothermodynamics is needed where a larger \( \chi \) value with decreasing \( r \) leads to increasing of \( G \) but with different speeds for distinct phases [23].

Size Dependence of Solid-liquid Transition

It is known that melting is the most general phenomenon and is also a typical phase transition, which could be well described by thermodynamics, which is so obvious in nature that even the ancient speculative physicists might expect to discuss it. The phenomenon even stimulates the development of classical thermodynamics in the nineteenth century [7]. Up to the volume change of the melting \( V_m \) and the bulk melting enthalpy \( H_m(\infty) \) were measured, where \( \infty \) denotes the bulk size, the first and the second laws of thermodynamics were established during 1700’s and 1800’s, where a compact mathematical expression for melting thermodynamics can be presented.

An alternative for studying the melting transition was carried out in 1910 by Lindemann for single component crystals with a kinetic consideration [24]. This quantitative model was based on Einstein’s explanation of the low-temperature specific heats of crystals \( C_p(\infty) \) where the bulk characteristic Einstein temperature of the low-temperature specific heat of solids \( \Theta_e(\infty) \) is proportional to the Einstein frequency \( \nu_e(\infty) \), by \( p \nu_e(\infty) = k \Theta_e(\infty) \) where \( p \) is Planck’s constant and \( k \) is Boltzmann’s constant. This, as the first application of quantum theory to condensed matter physics, suggests that the atoms vibrate as quantized harmonic oscillators. At the melting for a given bulk crystal, the typical vibrational displacement \( \sigma(\infty) \) or root-mean-square (rms) average amplitude of atomic thermal vibration should be some fixed fraction of the atomic or molecular diameter (the nearest atomic or molecular spacing) \( h \), or \( \sigma(\infty)/h = c \) where \( c \) is a constant. Lindemann pointed that the ratio should be about a half, implying direct collisions between the atoms constituting the lattice would become possible, leading to the lattice’s demise. Lindemann’s argument accounts for anharmonicities in the problem but in a very generic fashion, through the existence of collisions. The theory relates the average thermal vibrational energy to the temperature by the equipartition relation [7],

\[
m_s \left[ 2 \pi \nu_e(\infty) \right]^2 \sigma(\infty)^2 = kT.
\]

where \( m_s \) is the atomic mass, \( T \) in K denotes the absolute temperature. Combining Eq. 3 and the above equation in the text, a simple expression in its modern form is present [7],

\[
\Theta_e (\infty) = c \left[ T_m(\infty)/(MV_s^{2/3}) \right]^{1/2}.
\]

where \( M \) is the atomic or molecular molar weight, \( V_s \) denotes the molar volume of solids, \( T_m(\infty) \) is the bulk melting temperature.
The empirical value of \( c \) varies slightly with crystal structure: It is 0.13 for fcc crystal and 0.18 for bcc crystal [25]. This difference is partly due to the change of \( h \), which depends on the coordination number \( (CN) \) of the specific atom [26]. The \( h \) reduces with \( CN \) [27]. In order to eliminate or reduce this difference among distinct lattices or \( CNs \), \( h \) can be determined not by the nearest atomic spacing, but by atomic volume that depends little on the lattice structure [26], and hence \( c \) is almost lattice-independent [28].

There are also other classic models for melting. Grüneisen correlates \( T_m(\infty) \) with the reciprocal of the linear thermal expansion coefficient [29], while Born relates \( T_m(\infty) \) to the absence of elastic resistance against shearing stress [30]. Both of the models share a similar physical nature of Lindemann’s model [31] and thus will not be further discussed.

The most melting experiments, such as calorimetric measurements, indicated that there are gradual changes of melting peak near \( T_m \) [7]. The broad melting transition peaks can be induced by dissolved impurities, by surfaces, and by polycrystallinity. The first produces a progressive lowering of \( T_m \) as the atomic concentrations in the liquid and solid change along the phase boundary. The second and the third produce a combination of surface energy or grain-boundary energy and size effects. Both contribute to the dropping of \( T_m \). Since surface-melting is more evident, which is in nature a second order transition and occurs below \( T_m \), this phenomenon has been specially studied [7]. The related model will be shown and discussed later.

However, the Lindemann’s model has its limitation. The model is based on harmonic forces, whereas melting must involve bond breaking or loosening [8,27]. The model, which depends on properties of the solid phase alone, cannot predict \( T_m \) convincingly. In fact, Lindemann did not intend to provide a "melting criterion" at all in his original paper, but rather pointed out the possibility to estimate the frequency of oscillators to support Einstein’s model for explaining the drop of \( C_p \) of solids at low temperatures [8]. Melting may be due to the intrinsic disorder created by thermal excitations, such as vibrational modes, point defects such as vacancies and interstitials, dislocations, and, in the case of molecular crystals, orientational defects [32,33]. Each type has a characteristic excitation energy dictating an exponential increase of the energy of solid with temperature. This leads also to lowering of \( T_m \), where solid and liquid has the same \( G \) value. In addition, as we now understand, a proper analysis of dynamical melting should proceed with reference to process at the liquid/solid interface. Despite the unsolved problems for the modeling of melting, Lindemann’s criterion has provided the most bases for predicting the melting behavior as it has been experimentally confirmed [28]. In the following, size dependent melting is thus still modeled in terms of Lindemann’s model.

The Comparison between Existing Models. \( T_m(r) \) functions have been experimentally measured since 1954 by Takagi [15]. A linear relationship of \( T_m(r) \sim 1/r \) is usually modeled, which is simply deduced from \( \chi = hA/V \). Both depression and enhancement of \( T_m(r) \) have been found to depend on \( r \), dimension \( d \), and surface conditions of nanocrystals [16,18,19,31,34-39]. Since 1940’s, surface melting below \( T_m(\infty) \) with a thickness of several atomic layers is widely studied, which is a process proceeding under the condition of \( \gamma_v > \gamma_s+\gamma_l \) [7,40-42]. The physical nature of the surface melting is that although \( \Delta G(T< T_m) = G(T< T_m) - G(T< T_m) > 0 \), the condition of \( \gamma_v > \gamma_s+\gamma_l \) leads to formation of a liquid surface layer, which neutralizes the positive \( \Delta G(T< T_m) \). This effect has naturally been enhanced due to the increase of \( \chi \) [41,42].

The earliest thermodynamic consideration to interpret the above phenomena was firstly derived by Pawlow in 1909 only takes into account the relative change from \( T_m(\infty) \) [43], which was even one year earlier than the modeling of \( T_m(\infty) \) by Lindemann in 1910 [24] and much early than the experimental result in 1954 [15], which has the following form,

\[
T_m(r)/T_m(\infty) = 1 - 2V_s[\gamma_v - \gamma_l (\rho_s/\rho_l)^{2/3}]/(rH_m).
\]
where $\rho$ denotes mass density respectively. For the most cubic metals [44,45],

$$\gamma_{sv} - \gamma_{lv} = \gamma_{sl}. \quad (6)$$

With $\rho_s \approx \rho_l$ and thus $(\rho_s/\rho_l)^{2/3} \approx 1$ and in terms of Eq. 6, Eq. 5 can be expressed as,

$$T_m(r)/T_m(\infty) \approx 1 - 2V_s\gamma_{sl}/rH_m. \quad (7)$$

Actually, Eq. (7) is identical to the Gibbs-Thomson equation [46],

$$T_m(r)/T_m(\infty) = 1 - (1/r_1 + 1/r_2)V_s\gamma_{sl}/H_m. \quad (8)$$

where $r_1$ and $r_2$ are principal radii of curvature of the interface that bound a solid. For a spherical particle, $1/r_1 = 1/r_2 = 1/r$, Eq. 8 = Eq. 7.

A quantitative equation from Couchman and Jesser [47] to model this phenomenon in 1977 has the following form before the most experimental results were present in 1990's,

$$T_m(r)/T_m(\infty) = 1 - [3(V_s + V_t)(\gamma_{sl} - \gamma_{th})/2r - \Delta U]/H_m, \quad (9)$$

where subscript M denotes matrix, $\Delta U$ shows energy density difference between the nanocrystal and the nanoliquid. If $\Delta U$ is negligible, $T_m(r)$ can either higher or lower than $T_m(\infty)$, depending on the sign of $\gamma_{sl} - \gamma_{IM}$, which is closely related to the nature of the interface. Generally, $\gamma_{IM} - \gamma_{sl} = \gamma_{sl}\cos \theta$, where $\theta$ is the contact angle between a particle and the matrix ranged from 0° to 180° [48]. For a particle wetted by the matrix, $0 \leq \theta < 90^\circ$ and $0 < \gamma_{IM} - \gamma_{sl} \leq \gamma_{sl}$ where coherent or semi-coherent interface between the matrix and the solid should be formed. Consequently, superheating happens and $T_m(r)$ increases with the decreasing of $r$. For a nanocrystal with $\theta \geq 90^\circ$, $\gamma_{IM} - \gamma_{sl} \leq 0$ and undercooling occurs.

Superheating has also been interpreted through various pressure effects, such as a capillary effect due to the decreasing size, the differential thermal expansion between the matrix and the nanocrystals, and the effect due to volume change during the melting [16]. However, these models underestimate experimental observations since they can predict only a very small superheating up to 6 K [16]. The reason is that they have only considered mechanical effects while the dominant chemical interfacial effect is neglected.

If the surface-melting phenomenon is taken into account, $T_m(r)$ function has different expressions [40-42,45],

$$T_m(r)/T_m(\infty) = 1 - 2V_s[\gamma_{sl}/(1 - \delta/r) - \gamma_{lv}(1 - \rho_s/\rho_l)]/(rH_m). \quad (10)$$

$$\frac{T_m(r)}{T_m(\infty)} = 1 - 2V_s[1 - \exp(-\delta/\xi)] - V_s[\gamma_{sv} - \gamma_{lv} - \gamma_{sl}(1 - \delta/r)^2]\exp(-\delta/\xi)/H_m(1 - \delta/r)^2. \quad (11)$$

$$T_m(r)/T_m(\infty) = 1 - 2V_s\gamma_{sl}/[rH_m(1 - \delta/r)]. \quad (12)$$

where $\delta$ is layer thickness of surface liquid, $\xi$ in Eq. 11 shows correlation length of solid-liquid interface. Note that when $\delta \ll r$, $\delta \ll \xi$ [40,41], $\rho_s \approx \rho_l$, and in terms of Eq. 6, Eqs. 10, 11, and 12 have essentially predicted the same trend as given by Eq. 7. This result implies that when $r$ is large enough, the surface-melting phenomenon does not change the melting behavior of the nanocrystals although it indeed exists. However, when $r < 5$ nm ($\chi > 10\%$), Eqs. 10, 11, and 12 indicate a stronger melting point depression than Eq. 7 does. Note that once Eq. 7 comes into play, the surface-melting
Another way to calculate $T_m(r)$ was made by Semenchenko [49] who has considered melting of a small solid particle embedded in the corresponding liquid, which has an exponential form,

$$T_m(r)/T_m(\infty) = \exp[-2V_s\gamma_{sl}/(rH_m)].$$

(13)

Eq. 13 almost gives the same $T_m(r)$ value of Eqs. 10, 11, and 12 in the full size range of nanocrystals. As $r$ increases, with a mathematical relation of $\exp(-x) \approx 1-x$ where $x$ is small, Eq. 13 $\approx$ Eq. 7. Since some variables in Eqs. 10, 11, and 12 come from fitting experimental results [40,41,44], Eq. 13 is more convenient to predict $T_m(r)$ when $r < 5$ nm with the same level of accuracy.

In the above equations, $\gamma_{sl}$ value, as an important thermodynamic amount to determine $T_m(r)$ function, has been deduced recently according to Gibbs-Thomson equation [46],

$$\gamma_{sl} = 2hS_{vib}(\infty)H_m/(3V_sR).$$

(14)

where $S_{vib}(\infty)$ denotes vibrational melting entropy of bulk crystals and $R$ is the ideal gas constant. Eq. 14 is capable of predicting $\gamma_{sl}$ values quite accurately for element and compound crystals when the crystalline anisotropy is negligible [46,50]. Substituting Eq. 14 into Eq. 7,

$$T_m(r)/T_m(\infty) = 1 - 4hS_{vib}(\infty)/(3Rr) = 1 - (\alpha - 1)r_0/r.$$

(15)

where $\alpha = 2S_{vib}(\infty)/(3R)+1$ and $r_0 = 2h$. The exact meanings of them will be discussed later. Although any surface reconstruction decreases $\gamma_{sv}$, such as roughing and surface melting, which seems to be neglected in Eq. 15, $S_{vib}(\infty)$ itself indeed has included the surface relaxation phenomenon. This is because $S_{vib}(\infty)$ value measured denotes the vibrational entropy difference at $T_m(\infty)$ between the solid and liquid where various surface relaxations have occurred in the solid. However, Eq. 15, or Eq. 7 fails for smaller nanocrystals where $\chi > 20\%$.

In Eq. 15, there is a size limit of $r = (\alpha - 1)r_0$, at which $T_m(r) = 0$ K. If $r \leq (\alpha - 1)r_0$, $T_m(r) \leq 0$, which is strictly forbidden in the physics. As indicated above, when $r < 5-10$ $r_0$, Eq. 7 or 15 is no longer valid. In contrast, Eqs. 10, 11, 12, and 13 can be applied to $(\alpha - 1)r_0 < r < 5-10$ $r_0$ due to the non-linear parts between $T_m(r)$ and $1/r$ in these equations.

It is interesting that although $H_m$ function appears in above equations, it disappears in Eq. 15 since it is included in $S_{vib}(\infty)$. Thus, the detailed form of $H_m$ is not of immediate concern.

Based on an analogy with the liquid-drop model [51,52] and empirical relations among $E_c(\infty)$, $\gamma$, and $T_m(\infty)$, for free nanocrystals and nanocrystals embedded in the matrix, $T_m(r)$ functions are determined recently [53],

$$T_m(r)/T_m(\infty) = 1 - (c_2/r)(1 - \gamma_{sl}/\gamma_{sv}).$$

(16)

where $c_2$ is a constant relating to atomic volume, $T_m(\infty)$ and $\gamma_{sv}$. Eq. 16 is very similar to Eq. 9 and could describe both undercooling and superheating of nanocrystals. Note that for the case of undercooling, $\gamma_{sl} = 0$.

Sun et al [54] attributes $T_m(r)$ function to the CN-imperfection of the lower coordinated atoms near the surface. It is suggested that the CN-imperfection causes the remaining bonds of the lower-coordinated atoms to contract spontaneously with an association of magnitude increase of the bond energy, i.e., bond-order-length-strength (BOLS) correlation [55], which contributes to $E_c$ (the sum of bond energy $\varepsilon$ over all coordinates of a specific atom with the coordination $z$, $E_c = zN_a\varepsilon/2$ with $N_a$ being the Avogadro constant), and hence to $G$ that determines the thermodynamic behavior of a system. The thermal energy required to loosen the bonds of the specific atom is a portion of $E_c$. Thus, $T_m(r) \sim E_c(r)$, which leads to [56],
\[ T_m(r)/T_m(\infty) = 1 + \sum_{i=1}^{3} \beta_i (x_{ib}c_i^{-m} - 1). \]  

where \( \beta_i \) is the volume or number ratio of the \( i \)th atomic layer to that of the entire crystal, \( x_{ib} = z_i/z_b \) where \( z_i \) and \( z_b \) are the coordinates with and without \( CN \) imperfection, \( c_i \) shows \( CN \)-dependent reduction of bond length, and \( m \) is a parameter varying with the bond nature.

Moreover, the surface-phonon instability model [57,58] suggests that \( T_m(r) \) is a function of two bulk parameters: \( T_m(\infty) \) and the energy of formation of intrinsic defects. The shape effect on \( T_m(r) \) for polyhedral nanocrystals, which is in nature also related to \( \chi \), is also considered and the corresponding shape factor is introduced [59,60].

Wautelet and Guisbiers et al. [61-63] obtained a theoretical model using classical thermodynamics. Applying the energy conservation law, the melting temperature, \( T_m \), can be expressed as a function of the bulk melting temperature, \( T_m(\infty) \),

\[ T_m(r)/T_m(\infty) = 1 + (\gamma_l/\gamma_s)/H_m(\infty)(A/V), \]

where \( A \) and \( V \) are the surface area and volume, respectively, for a given shape. To describe the size effect with only one parameter, a more convenient equation is

\[ T_m(r)/T_m(\infty) = 1 + \alpha_{\text{shape}} / 2L, \]

where the shape parameter \( \alpha_{\text{shape}} \) is defined as \( \alpha_{\text{shape}} = 2AL(\gamma_s - \gamma_l)/[VH_m(\infty)] \), where \( L \) is the smallest dimension of the structure. This \( \alpha_{\text{shape}} \) parameter, for a given material, depends only on the shape. This allows us to compare the magnitude of the size effect on the melting temperature of a particular material for different shapes. So Eq. (19) describes size effect and introduces a \( A/V \) ratio to investigate the action of different shapes, for examples, ZnO nanoparticles, nanowires with circular, rectangular (nanobelts) and hexagonal sections and nanotubes with circular and hexagonal sections [64].

In summary, all above models developed from various perspectives can contribute significantly to understanding the mechanism of \( T_m(r) \) function. These models predict the same linear relationship between \( T_m(r) \) and \( 1/r \) due to the surface effect when \( r \) is large enough. However, as \( \chi > 10\% \), the dramatic drop of \( T_m(r) \) is present because the energetic state of internal atoms also changes, which has been considered by Eqs. 10, 11, 12, and 13 in different approaches although their considerations are not directly related to energetic state of atoms, but \( \chi \). Since the superheating phenomenon was realized later than the undercooling one, the later models of Eqs. 9, 16, 17 attempted to determine both undercooling and superheating with also a similar linear relationship of \( T_m(r) \sim 1/r \). The sign of the \( 1/r \) term is negative for undercooling but positive for superheating. Note that if the \( CN \) imperfection of the second surface layer is considered, Eq. 17 becomes a nonlinear function and could describe the melting behavior of smaller size of nanocrystals. Moreover, for nanoscale materials with different shapes, Eq. 19 is an effective model to investigate size effect on \( T_m \).

**Size dependence of melting temperature.** There are many theoretical and experimental investigations showing that the melting point of nanocrystals with free surfaces or deposited on inert substrates, including metallic [10,15,65-69], organic [13,28], inert gas [70] and semiconductor [11,12] crystals, decreases with decreasing their size. The melting point depression of the crystals is roughly proportional to their reciprocal radius \( r^{-1} \) written as [10,11,68,70],

\[ T_m(r)/T_m(\infty) = 1 - C/r. \]

where \( C \) denotes an unknown material constant obtained only by fitting experimental data. Eq. (20) reflects the fact that the essential factor to influence the properties of nanocrystals is the surface/volume ratio where the energetic changes of interior atoms of nanocrystals are as a second
effect neglected. This neglect becomes serious when \( r \) is in 1-5 nm size range. Thus, a better modeling for \( T_m(r) \) function especially when \( r \) is small is needed.

\( T_m(r)/T_m(\infty) \) functions can be deduced by considering the averaged mean square displacement (msd) of atoms in a nanocrystal \( \sigma^2(r) \) with [10],

\[
\sigma^2(r) = \sigma^2_S(r) + [\sigma^2_S(r) - \sigma^2_V(r)]n_S/n_V .
\]

where the subscripts \( S \) and \( V \) denote surface and interior atoms of a particle, \( n \) is the atom number of a nanocrystal with

\[
\frac{n_S}{n_V} = \frac{(4\pi^2h/V_0)[(4/3)\pi^3/V_0-(4\pi^2h/V_0)]}{3h/(r-3h)}
\]

when the shape of the particle is considered to be spherical or quasi-spherical where \( V_0 \) and \( h \) show the volume and the atomic diameter of the nanocrystal. The msd of the nanocrystal is larger than the corresponding bulk value not only on its surface, but also in its core, or the both \( \sigma^2_S(r) \) and \( \sigma^2_V(r) \) are size-dependent. However, it is assumed that \( \sigma^2_S(r)/\sigma^2_V(r) = \sigma^2_S(\infty)/\sigma^2_V(\infty) = \alpha \) is size-independent [10]. Since the cooperative coupling between the surface region and the interior region may be important for small particles, the variation of \( \sigma^2(r) \) is considered phenomenologically to be dependent on the value of \( \sigma^2(r) \) itself [10], which leads to,

\[
\sigma^2(x+dx) - \sigma^2(x) = (\alpha - 1)\sigma^2(x)dx .
\]

where \( x = n/n_v = r_0/(r-r_0) \) with \( r_0 = 3h \). Integrating Eq. 22,

\[
\int_0^\infty \frac{1}{\sigma^2(x)}d\sigma^2(x) = (\alpha - 1)\int_0^\infty dx ,
\]

\[
\sigma^2(r)/\sigma^2(\infty) = \exp[(\alpha - 1)x] = \exp[(\alpha - 1)/(r/r_0 - 1)]
\]

In Eq. 23, \( r_0 \) as a critical radius of a nanoparticle where almost all atoms are located on the surface has been further extended for different dimensions of all low-dimensional crystals \[28,68,71\]. Let \( d \) denote the dimension and \( d = 0 \) for nanoparticles where \( r \) has a usual meaning of radius, \( d = 1 \) for nanowires with \( r \) being taken as its radius and \( d = 2 \) for thin films with \( r \) denoting its half thickness. \( r_0 \) is roughly given by (i) \( r_0 = 3h \) for \( d = 0 \) since \( 4\pi r^2h = 4\pi r_0^2h/3; \) (ii) \( r_0 = 2h \) for \( d = 1 \) since \( 2\pi rh = \pi r_0^2h \); and (iii) \( r_0 = h \) for \( d = 2 \) since \( h = r_0 \). In short, the relationship between \( d \) and \( r_0 \) is given by \[28,68,70\],

\[
r_0 = (3-d)h .
\]

A nanocrystal is deposited on substrate may wet or not wet the substrate. When the nanocrystal does not wet the substrate, the deposit prefers taking a spherical shape with the smallest surface/volume ratio where \( d = 0 \). If the nanocrystal wets the substrate, an island-like or disc-like particle may be present [68]. Because the shape of a disk-like particle is between that of a film and that of a particle, the disk-like particle is assumed to have an equivalent dimension of \( d = 1 \) between a film of \( d = 2 \) and a particle of \( d = 0 \) [68].

To find a convenient means for correlating \( T_m(r) \) to measurable physical properties such as \( \sigma^2 \), Lindemann criterion \[7,24,25\], which says that a crystal will melt when \( \sigma/h \) reaches a certain fraction of \( c \), is useful and is known to be valid qualitatively for small particles,

\[
\sigma / h = c .
\]

Although \( c \) varies a bit with crystal structure: It is 0.13 for fcc crystal and 0.18 for bcc crystal [25]. This difference is partly induced by the change of \( h \), which depends on the coordination number of a lattice CN [26]. A smaller CN corresponds to a smaller \( h \) [27]. In order to reduce or eliminate this difference among distinct lattices or CNs, \( h \) here is calculated by atom volume that is little dependent on the lattice structure [26]. With this \( h \), \( c \) is almost lattice-independent. This method has an
additional advantage that atomic volume is measurable in any structure, no matter how complex, by dividing the volume of the unit cell by the number of atoms in the unit cell.

Since \( T_m(r) \) is usually higher than the bulk Debye temperature \( \Theta_\text{D}(\infty) \), the high temperature approximation can be utilized [10,72,73], \( \sigma^2(r,T) = f(r)T \), where \( f(r) \) is a size-dependent function. Thus, at any temperature \( T \) near \( T_m(r) \), \( \sigma^2(r,T)/\sigma^2(\infty,T) = f(r)/f(\infty) \). Moreover, when \( T = T_m(r) \), \( f(\infty) = \{\sigma^2[r,T_m(r)]/h^2\}/[\sigma^2[\infty,T_m(\infty)]/h^2]\}[T_m(\infty)/T_m(r)] = T_m(\infty)/T_m(r) \) in terms of Eq. 23. As results,

\[
T_m(r)/T_m(\infty) = \sigma^2(r)/\sigma^2(\infty) = \exp[-(\alpha-1)/(r/r_0-1)].
\] (26)

In Eq. 26, if \( \alpha > 1 \), which is determined solely by vibrational entropy of melting \( S_{\text{vib}}(\infty) \), \( T_m(r) \) decreases with decreasing \( r \); When \( \alpha < 1 \), which is related to the relative size of \( h \) and \( T_m(\infty) \) between the nanocrystals and the matrix, \( T_m(r) \) increases with decreasing \( r \).

**Nanocrystals with Free Surface.** \( \alpha \) in Eq. 26 may be determined by considering \( S_{\text{vib}}(r) \) deduced by Mott’s expression for \( S_{\text{vib}}(\infty) \) [28,74,75]. \( S_{\text{vib}}(\infty) \) at \( T_m(\infty) \) was shown as,

\[
S_{\text{vib}} = \frac{3k}{4}\ln\left[\frac{T_m(\infty)[C_s(\infty)/C_1(\infty)]^2[\pi^4/(6N_0)^2]}{M}\right].
\] (27)

where \( C_1(\infty) \) and \( C_s(\infty) \) the ultrasound propagation velocities of the bulk liquid and the bulk crystal, respectively, \( N_0 \) is Avogadro’s number, \( M \) is the molecular number, \( k \) denotes the Boltzmann constant. The size-dependent vibrational entropy of melting \( S_{\text{vib}}(r) \) of a nanocrystal with a radius of \( r \) can be obtained as a generalization of Eq. 25, i.e., \( S_{\text{vib}}(r) - S_{\text{vib}}(\infty) = (3k/2)\ln\{[T_m(r)/T_m(\infty)] [C_s(r)/C_s(\infty)]^2[C_s(\infty)/C_s(\infty)]^2\} \). Instead of treating \( C_s(r) \) and \( C_1(r) \) to be size-dependent, respectively, the ratio of \( C_s(r)/C_1(r) \approx C_s(\infty)/C_1(\infty) \) is approximately taken as a size-independent value. Hence,

\[
S_{\text{vib}}(r) - S_{\text{vib}}(\infty) = (3R/2)\ln[T_m(r)/T_m(\infty)].
\] (28)

Substituting Eq. 26 into Eq. 28, it reads,

\[
S_{\text{vib}}(r) = S_{\text{vib}}(\infty) - (3R/2)(\alpha - 1)/[(r/r_0) - 1].
\] (29)

For a free-standing or a quasi-free-standing nanocrystal, \( S_m(2r_0) = S_{\text{vib}}(2r_0) = 0 \) is assumed for the smallest nanocrystal as stated above, which leads to,

\[
\alpha = 2S_{\text{vib}}(\infty)/(3R) + 1.
\] (30)

Eliminating the parameter \( \alpha \) from Eq. 29 by means of Eq. 30, one has,

\[
S_{\text{vib}}(r) = S_{\text{vib}}(\infty)[1 - 1/(r/r_0 - 1)].
\] (31)

It is known that the overall melting entropy \( S_m \) consists, at least, of three components: positional \( S_{\text{pos}} \), vibrational \( S_{\text{vib}} \) and electronic \( S_{\text{el}} \) [74]. If the structural difference of two structures is only the appearance of vacancies, \( S_{\text{pos}} = -R(x_A\ln x_A + x_B\ln x_B) \) [74] where \( x_A \) and \( x_B \) are the mole fractions of the atoms and vacancies, respectively. This is the case of a melting process when liquid is roughly assumed to be produced by crystals through increasing vacancies where the bond length and bond strength remain constant, which leads to \( x_A = 1/(1 + \Delta V_m/V_m), \) \( x_B = 1 - x_A \) where \( \Delta V_m \) is the molar volume difference between the liquid and the crystal.
For metallic and organic crystals, the type of chemical connection does not vary during the melting transition, $S_d \approx 0$ [74]. Thus,

$$S_{\text{vib}} = S_m + R(x_A \ln x_A + x_B \ln x_B).$$

(32)

For semiconductors, if the melting is accompanied by the semiconductor-to-metal transition, the entropy of electronic origin should strongly contribute the overall entropy of melting [74], while $S_d$ value is large and $S_{\text{vib}}$ must be considered in another way. $S_{\text{vib}}$ is directly given by Mott [75],

$$S_{\text{vib}} = 3R\ln(\nu_e/\nu_l) = (3/2)R\ln(\eta_e/\eta_l).$$

(33)

where $\nu$ and $\eta$ are characteristic vibration frequencies and electrical conductivity of the particles, respectively. For semiconductors, $S_m = R[1+3\ln(\Theta_D/\Theta_{DI})]$ where $\Theta_D$ and $\Theta_{DI}$ are the Debye temperatures of the solid and liquid phases [76]. Since $\Theta_D/\Theta_{DI} = \nu_e/\nu_l$, it reads,

$$S_{\text{vib}} = S_m - R.$$  

(34)

Because $2r_0$ is a critical size where the smallest nanocrystal can exist, the entropy difference between the crystal and liquid or amorphous states below $2r_0$ will disappear, i.e.,

$$S_{lc}(2r_0, T) = 0.$$  

(35)

Now, we will derive the melting temperature for the smallest free-standing nanocrystal of size $2r_0$, $T_m(2r_0)$. Since the entropy of melting for metallic crystals is mainly vibrational in nature [74], one may suggest that $S_m(r)$ for metallic nanocrystals follows the same size dependence as Eq. 31 $S_{\text{vib}}(r)$,

$$S_m(r) = S_m(\infty)-(3R/2)(\alpha-1)/(r/r_0-1).$$  

(36)

An expression for the size dependence of the melting entropy for nanocrystals which is related to the lower limit of melting temperature of nanocrystals. Since $S_{lc}(2r_0, T) = 0$, i.e., Eq. 35, the entropy of melting for a free-standing nanocrystal of size $2r_0$ should also be zero,

$$S_m(2r_0) = S_m[2r_0, T_m(2r_0)].$$  

(37)

which enables us to obtain an expression for $\alpha$ (for a free-standing nanocrystal, $\alpha = \alpha_{\text{max}}$ ) from Eq. 36,

$$\alpha_{\text{max}} = 2S_m(\infty)/(3R) +1.$$  

(38)

Eq. 38 implies that $\alpha_{\text{max}} > 1$ since $S_m(\infty) > 0$. In terms of Eq. 26 and 38, the melting temperature for the free-standing nanocrystal in a size of $2r_0$ is obtained,

$$T_{\text{min}} = T_m(2r_0)\alpha^{-1} = T_m(\infty)\exp[-2S_m(\infty)/(3R)].$$  

(39)

It is interesting to point out that as a first-order phase transition, melting degenerates into a continuous second-order transition as the nanocrystal size reaches its limiting value of $2r_0$. This is because $T_{\text{min}}$ is a crystal-liquid equilibrium transition temperature, the Gibbs free energy of melting, $g_m(T_{\text{min}}) = 0$, and consequently, the enthalpy of melting, $h_m(T_{\text{min}}) = 0$. This result that $g_m(T_{\text{min}}) = h_m(T_{\text{min}}) = S_m(T_{\text{min}}) = 0$ is similar to the suggestion by Lam and Okamoto that the crystal-glass enthalpy difference is equal to zero at the highest crystal-glass transition temperature [77].

Because of the above transition characteristics at $T_{\text{min}}$, $T_{\text{min}}$ is certainly associated with glass transition temperatures (a second-order transition), i.e., Kauzmann temperature ($T_k$) and the glass
transition temperature ($T_g$). According to Kauzmann, $S_{lc}(\infty, T_k) = 0$ [78]. Since $S_{lc}(r, T)$ decreases as $r$ and $T$ decrease [78], $S_{lc}(\infty, T_{min}) > 0$ or $T_{min} > T_k$. In addition, $S_{lc}(2r_0, T_{min}) = 0$, $T_{min}$ is determined as [79], a glass-liquid transition at $T_{min}$ can thermodynamically occur with the smallest size of the liquid in $2r_0$. Thus, $T_{min}$ can be considered as the lowest glass transition temperature that can be obtained only by a zero cooling (or heating) rate without crystallization. Therefore, it is lower than usual measured glass transition temperature, $T_g$, for instance, by heating a glass with a rate of 20 Kmin$^{-1}$ on a calorimeter. Hence, there is,

$$T_k < T_{min} < T_g.$$  

(Nanocrystals Embedded in a Matrix). For nanocrystals embedded in a matrix with coherent or semi-coherent interfaces, under the assumption that $\sigma$ of the interfacial atoms of the nanocrystals has an algebraic average value between that of interior atoms of the nanocrystals and that of the matrix, $\alpha$ is determined as [79], $\alpha$ is a ratio between the mstd of atoms on the surface [$\sigma_s^2(r)$] and of those inside [$\sigma_i^2(r)$] of the nanocrystals [10,80], i.e., $\alpha = \sigma_s^2(r)/\sigma_i^2(r)$ where $\sigma_i^2(r) \approx \sigma_i^2(\infty)$ [10]. For the nanocrystals embedded in a matrix with coherent interfaces, it is expected that the mstd value of surface atoms of nanocrystals falls between that of the interior atoms of nanocrystals and of the matrix, which thus could simply be estimated as a mean value between them,

$$\alpha = \frac{\sigma_s^2(\infty)}{\sigma_i^2(\infty)} = \frac{\sigma_M^2(T_m(\infty))}{\sigma_M^2(\infty)+1}/2. \tag{41}$$

where $\sigma_M^2(T_m(\infty))$ is the averaged mstd value of the matrix at $T_m(\infty)$ and is approximately equal to the mstd value of the interior atoms of the matrix.

According to Lindemann’s criterion Eq. 25, $h, c$ is almost lattice-independent. Thus, $\sigma_M[T_M(\infty)]/h_M = \sigma(\infty)/h$ where $\sigma_M[T_M(\infty)]$ denotes the root msd of atoms of the matrix at the corresponding melting temperature $T_M(\infty)$, $h_M$ shows atomic diameters of the matrix.

Since $T_m(\infty)$ is usually higher than the bulk Debye temperatures of the matrix, the high-temperature approximation for $\sigma_M^2(T)$ at a temperature $T$ can be utilized [7],

$$\sigma_M^2(T) = k/[m(2\pi v_E)^2]T. \tag{42}$$

where $m$ is atomic mass, $v_E$ is the Einstein frequency, $k$ is Boltzmann’s constant. Substituting $T = T_M(\infty)$ and $T = T_m(\infty)$ into Eq. 42, $\sigma_M^2[T_m(\infty)]/\sigma_M^2[T_M(\infty)] = T_m(\infty)/T_M(\infty)$. In terms of Eq. 25, this gives $\sigma_M[T_M(\infty)]/h_M = \sigma(\infty)/h$, $\sigma_M^2[T_M(\infty)] = [h_M^2/h]^2[\sigma_i^2(\infty)]$ or $\sigma_M^2[T_m(\infty)]/\sigma_M^2(\infty) = [h_M^2/h]^2[T_m(\infty)/T_M(\infty)]$, and thus $\alpha = \frac{[h_M^2/h]T_m(\infty)+1}{2}$ in terms of Eq. 41. Since the difference between $T_m(\infty)/T_M(\infty)$ and $T_m(\infty)/T_M(\infty)$ is small, $\alpha$ is a weak function of $r$. As a first order approximation, $T_m(\infty)$ takes the place of $T_m(\infty)$, or $\alpha$ takes its smallest value. Finally, it reads,

$$\alpha = \frac{[T_m(\infty)/T_M(\infty)](h_M/h)^2 + 1}{2}. \tag{43}$$

Note that the validity of Eqs. 26, 43 depends on stability of interfaces between the matrix and the nanocrystals. When a liquid layer on the interface is formed, which results in the replacement of nanocrystal-matrix interface by two solid-liquid interfaces, melting of the total nanocrystals occurs at once. Thus, the stability of the interface is controlled by the interface energy change $\Delta \gamma$ during the above transition. Only when $\Delta \gamma > 0$, superheating of nanocrystals can exist. We assume the liquid layer on the interface only consists of the component of nanocrystals, since the temperature is lower than the melting temperature of the matrix and the mutual solubility in any superheating system is negligibly small [16]. $\Delta \gamma$ may be read by [81]

$$\Delta \gamma = [h_MS_m^M H_m^M/V_g^M - h_NS_m^N H_m^N/V_g^N]/(3R). \tag{44}$$
Where superscripts M and N denote matrix and nanocrystals, respectively. $V_g$ is the molar volume.

Up to $\Delta \gamma$ is balanced with volume Gibbs free energy of the nanocrystals $\mu = S_m^N[T_{\text{max}}(r) - T_m(\infty)]$ where $T_{\text{max}}(r)$ is the size-dependent maximal superheating temperature, or $(h_N/r_0)S_m^N[T - T_m(\infty)]/V_g^N = \Delta \gamma$ with $h_N/r_0$ suitting different dimensions, the interface remains stable. In terms of Eq. 44, we get

$$T_{\text{max}}(r)/T_m(\infty) = 1 + r_0[(h_N/h_M)(H_m^M/H_m^N)(V_g^M/V_g^N)S_m^M - S_m^N]/(3Rr).$$

(45)

**Surface Melting.** For surface melting, It can be considered as a second-order transition [7]. This assumption is also supported by the structure of the melting film on the solid surface, which is similar to a crystalline order [7]. If the above crystal-liquid film transition may be considered as a second transition where a liquid film with a thickness of $2r$ is deposited on its own crystalline substrate, The surface melting temperature $T_{\text{sm}}(r)$ function can be achieved from Eq.26 when $S_{\text{vib}}(\infty)$ in Eq. 30 is substituted by $C_{\text{pm}}(\infty)$, which is the heat capacity difference between the liquid and the crystal at $T_m(\infty)$. The corresponding $\alpha$ value is shown as [82],

$$\alpha = [2C_{\text{pm}}(\infty)/(3R)] + 1.$$  

(46)

Note that the surface melting is similar to melting of a film epitaxial grown from own substrate where the free surface number of the film is unity, which leads to, $r_0 = h/2$.

Substituting Eqs. 30 or 43 or 46 into Eq. 26 in terms of Eq. 24, undercooling, superheating, and surface melting of nanocrystals can be quantitatively determined when the related materials constants of $h$, $T_m(\infty)$, $S_{\text{vib}}(\infty)$, or $C_{\text{pm}}(\infty)$ are known.

**Results.** Fig. 1 shows $T_m(r)$ functions of Au and Ag with free-standing or quasi-free-standing surfaces based on Eq. 26 and the corresponding experimental results. As shown in Fig. 1, the model predictions are in good agreements with the both experimental and computer simulation evidences where dimension difference could also lead to distinct drops of $T_m(r)$. This is because at the same $r$, different $d$ values have different $\chi$.

![Fig. 1. $T_m(r)$ functions of noble metals nanocrystals in terms of Eqs. 24, 26 and 30 shown as the solid lines. For Au, $T_m(\infty) = 1337.33$ K [83], $S_{\text{vib}}(\infty) = 7.74$ J-mol$^{-1}$-K$^{-1}$ in terms of Eq. 28 where $\Delta V_m/V_s = 5.1\%$ [84] and $S_m(\infty) = 9.35$ J-mol$^{-1}$-K$^{-1}$ determined by $S_m(\infty) = H_m(\infty)/T_m(\infty)$ with $H_m(\infty) = 12.5$ KJ-mol$^{-1}$ [83], and $h = 0.2884$ nm [26]. The symbols $\circ$ denote experimental results with $d = 1$ and $d = 0$, and the symbol $\bigcirc$ denote computer simulation results with $d = 0$, respectively [85]. For Ag, $T_m(\infty) = 1234.93$ K [83], $S_{\text{vib}}(\infty) = 7.98$ J-mol$^{-1}$-K$^{-1}$ where $\Delta V_m/V_s = 3.3\%$ [84] and $S_m(\infty) = 9.15$ J-mol$^{-1}$-K$^{-1}$ with $H_m(\infty) = 11.3$ KJ-mol$^{-1}$ [83], and $h = 0.2889$ nm [26]. The symbol $\blacklozenge$ denotes experimental results with $d = 0$ [85].](image)

Fig. 2 shows the model predictions of Eq. 26 for melting point suppression of Pb nanocrystals. Melting point enhancement of experimental results of Pb/Al system [16,18,37] (referring to Pb nanoparticles embedded in Al matrix, the following expressions have a similar meaning) and Pb/Zn system [86] are also compared with Eq. 26 where $\alpha$ is calculated by Eq. 46. It is obvious that the predictions for different systems with distinct dimensions show good agreement with the
Fig. 2 $T_m(r)$ functions of Pb nanocrystals where the solid lines are the model predictions of Eq. 26. For spherical ($d = 0$) and disc-like ($d = 1$) particles, $r_0 = 3h = 1.1694$ nm and $r_0 = 2h = 0.7796$ nm respectively with $h = 0.3898$ nm [26]. $T_m(\infty) = 600.6$ K [83] and $S_{\text{vib}} = 6.77$ Jmol$^{-1}$K$^{-1}$ in terms of Eq. 32 with $S_m = 7.99$ Jmol$^{-1}$K$^{-1}$ [83] and $\Delta V_m/V_e=3.5\%$ [84]. The symbols + and denote the measured $T_m(r)$ values [42,87]. For the Pb/Al system, $\alpha = 0.71$ in terms of Eq. 43 where $h_M = 0.3164$ nm [26], $h = 0.3898$ nm [26], and $T_M = 933.25$ K [83]. $r_0 = 3h = 1.1694$ nm. $V_v^N = 18.17$ cm$^3$/mol and $V_g^M = 10$ cm$^3$/mol [83], $H_m^N(\infty) = 4799$ J/mol and $H_m^M(\infty) = 10790$ J/mol [83]. The experimental results of Pb particles shown as • [37], ▲ [18] and ▼ [16], are given. For the Pb/Zn system, $\alpha = 0.77$ in terms of Eq. 43 where $h_M = 0.3076$ nm [26] and $T_M = 692.73$ K [83]. $V_v^N = 9.2$ cm$^3$/mol and $H_m^M(\infty) = 7322$ J/mol [83]. The symbol ○ denotes the experimental data [86]. $T_{\text{max}}(r)$ functions in terms of Eq. 45 for Pb/Al and Pb/Zn systems shown as the dash lines.

Figs. 3 and 4 show the model predictions of Eq. 26 and the experimental observations for semiconductor nanocrystals Si [12], Bi [87,88] and CdS [11] for the $T_m(r)$. It is evident that the model predictions are consistent with the experimental results. The evident drops of $T_m(r)$ with decreasing of $r$ are due to the energetic increase of crystals while this increase of the corresponding liquid is smaller. The variation of $T_m(r)$ indicates that as size of materials decreases, the thermal stability of the materials must be reexamined and considered in the industrial application.

Fig. 3 $T_m(r)$ of Si and Bi nanocrystals. The solid line is the prediction of Eq. 26. ▲ denotes the experimental results of Si nanocrystals [12]. ● and ■ do that of Bi nanocrystals [87,88]. For disk-like Si nanocrystals, $r_0 = 2h = 0.6676$ nm since $d = 1$ and $h = 0.3338$ nm [87]. $T_m(\infty) = 1685$ K and $S_m = 30$ Jmol$^{-1}$K$^{-1}$ [88]. For disk-like Bi, $r_0 = 2h = 0.8144$ nm with $d = 1$ and $h = 0.4072$ nm [26]. $T_m(\infty) = 544.52$ K and $S_m = 20.75$ Jmol$^{-1}$K$^{-1}$ [86]

Fig. 4 $T_m(r)$ of CdS nanocrystals. The solid line is obtained by Eq. 26. ● denotes the experimental results of CdS [11]. $r_0 = 3h = 0.75$ nm in terms of Eq. (7) since $d = 0$ and $h = 0.25$ nm where $h$ is taken as the averaged covalent diameter of Cd ($h = 0.296$ nm) and S ($h = 0.204$ nm) [86]. $T_m(\infty) = 1678$ K [11] and $S_m = 20.482$ Jmol$^{-1}$K$^{-1}$ [11].

experimental data of different authors. In addition, all stability temperatures of the interfaces are higher than thermodynamic melting temperatures in the measured size range.
$T_m(r)$ functions of molecular nanocrystals are shown in Fig. 5. Since the chemical bond among molecules is Van der Waals type, all thermodynamic amounts of melting, namely $T_m(\alpha)$, $S_m(\alpha)$ and $H_m(\alpha)$, are smaller than those of metallic, ionic and covalent bond nature. Thus, the corresponding dropping tendency of $T_m(r)$ is weak, which reacts through $S_{vib}(\alpha)$ value in Eq. 26 and is introduced from Eq. 30. Thus, Eq. 26 can distinguish and describe $T_m(r)$ functions of all chemical combinations in a unique equation.

Fig. 6 presents $T_m(r)$ function of H$_2$O embedded in MCM-41 in terms of Eq. 26. The value of $\alpha$ is different from the above since the interaction between surface molecules and the molecules on the pore wall must be considered.

Fig. 7 presents a comparison between model predictions of Eq. 26 and the experimental results for nanowires with $d = 1$. For Ke, $T_m(\infty) = 116.0$ K, $S_{vib}(\infty) = 14.14$ J-g-atom$^{-1}$K$^{-1}$, and $h = 0.206$ nm. The symbol + denotes experimental results for nanowires with $d = 1$. For O$_2$, $T_m(\infty) = 54.4$ K, $S_{vib}(\infty) = 4.073$ J-g-atom$^{-1}$K$^{-1}$, and $h = 0.278$ nm. The symbol $\times$ denotes experimental results for nanowires with $d = 1$. For Ne, $T_m(\infty) = 24.6$ K, $S_{vib}(\infty) = 13.54$ J-g-atom$^{-1}$K$^{-1}$, and $h = 0.102$ nm. The symbol $\bullet$ denotes experimental results for nanowires with $d = 0$ and the symbol $\circ$ denotes experimental results for nanoparticles with $d = 1$.

$T_m(r)$ functions of all chemical combinations are shown in Eq. 26 and is introduced from Eq. 30. Necessary parameters and experimental data are all cited from the references [70] and [89]. For H$_2$O, $T_m(\infty) = 273.15$ K, $S_{vib}(\infty) \approx S_m(\infty) = 7.37$ J-g-atom$^{-1}$K$^{-1}$, $\alpha = [2S_{vib}(\infty)/(3R)+1](1-\beta) = 1.39$ with $\beta = 12.7\%$ denoting a ratio of the surface molecules that interact with the molecules on the pore wall to the total number of surface ice molecules. The symbol $\bigcirc$ denotes the experimental results with $d = 1$ since the morphology of MCM-41 is cylindrical.

Fig. 7 presents a comparison between model predictions of Eq. 26 and the experimental results of melting and surface melting temperatures for In crystals in different dimensions and different surroundings. There are good agreements between the model predictions and the experimental results. The size dependence of $T_{sm}(r)$ function is evidently weaker than that of $T_m(r)$ function even its $r_0$ is only a half of that of a film. This difference is induced by the fact that $C_{pm}$ is only about one eleventh of $S_m$ as shown in the figure caption, which implies that the size of the driving force for the surface melting is much smaller than that for the melting. It is interesting that our model for $T_{sm}(r)$ function has just a logarithmic rule when $T$ is far below $T_m$, which corresponds to a long-range atomic interaction where $r$ is smaller, but an exponential law at $T \approx T_m$ corresponds to a short-range atomic interaction where $r$ is larger.
Size Dependences of Melting Enthalpy and Entropy. Since the size-dependent thermodynamic amounts of nanocrystals have been found to be proportional to $1/r$ [91], the determination of $H_m(r)$ function [92] will benefit us to understand suitability of this universal relationship. However, the experimental results on $H_m(r)$ show that the relationship between $H_m(r)$ and $1/r$ is nonlinear [92]. To understand this phenomenon, theoretical work [93,94] for $H_m(r)$ function is needed. A direct explanation for this divergence can be understood through the following thermodynamic relationship,

$$H_m(r) = T_m(r)S_m(r) \tag{47}$$

where $S_m(r)$ is size-dependent melting entropy. Since the both of $T_m(r)$ and $S_m(r)$ functions are linearly proportional to $1/r$ [28], $H_m(r)$ should drop more strongly than this linearity as $r$ decreases especially when $r$ is in mesoscopic size range.

$T_m(r)$ function has been determined in terms of Eq. 26. Thus, for free nanocrystals, in terms of Eqs. 30 and 36, there is [90],

$$S_m(r) = S_m(\infty)[1-1/(r/r_0-1)] \tag{48}$$

In terms of Eqs. 47, 26 and 48, $H_m(r)$ function is determined,

$$H_m(r)/H_m(\infty) = T_m(r)/T_m(\infty)[1-1/(r/r_0-1)] \tag{49}$$
where \( H_m(\infty) = T_m(\infty)S_m(\infty) \) is the bulk melting enthalpy.

Fig. 8 presents a comparison between the model prediction of Eq. 49 and the experimental results of \( H_m(r)/H_m \) for In nanoparticles having free surface. As shown in the figure, a good agreement between them has been found. The size dependence of \( H_m(r) \) is stronger than that of \( T_m(r) \) because \( H_m(r) \) is a product of \( T_m(r) \) and \( S_m(r) \) where the both functions are size-dependent. The confirmation of Eq. 49 with experimental results indicates that the size-dependent melting is indeed a thermodynamic transition. The physical nature of the drop of \( H_m(r) \) is related to the increase of the internal energy of atoms of nanocrystals while the corresponding increase of the liquid is weaker. Guisbiers and Shandiz’s models are shown in the figure too. All the models show relative good agreement with experimental points.

Figs. 9 and 10 compares the model prediction and the experimental observation for \( H_m(r) \) and \( S_m(r) \) of Sn [95] and Al [96] nanoparticles. The experiment was performed for Al nanocrystals in an oxygen atmosphere where the interaction among Al nanocrystals is avoided due to the oxide film on the surface of the particle. It is evident that the model predictions are consistent with the experimental observation: enthalpy and entropy of melting decrease with a decrease in size.

**Fig. 9.** The size dependence of melting enthalpy and entropy for Sn nanocrystals. For Sn, \( r_0 = 3h = 1.1172 \text{ nm} \) where \( h = 0.3724 \text{ nm} \) [26]. The solid line denotes the model prediction of \( H_m(r) \) and \( S_m(r) \) by Eqs. 49 and 48. Symbols ● and ■ denote experimental data [95] of \( H_m(r) \) and \( S_m(r) \), respectively.

**Fig. 10.** The size dependence of melting enthalpy and entropy for Al nanocrystals. For Al, \( r_0 = 3h = 0.9492 \text{ nm} \) since \( h = 0.3164 \text{ nm} \) [26]. The solid lines denote the model prediction of \( H_m(r) \) and \( S_m(r) \) by Eqs. 49 and 48. Symbols ● and ■ show experimental data of \( H_m(r) \) and \( S_m(r) \), respectively [96]. The size of Al nanocrystals does not include the thickness of the surface oxide layer that was experimentally determined [96].

### Liquid-solid Transitions

It is well known that the melting temperature is higher than the freezing temperature [97]. A series of systematic experiments on the freezing behavior of isolated micrometer-sized metallic droplets first began to appear in the late 1940s and 1950s where the undercooling \( \Delta T(\infty) \) [a temperature difference between \( T_m(\infty) \) and the freezing temperature \( T_f(\infty) \) ] remains a constant of about 0.27 \( T_m(\infty) \) [97]. As the size of crystal decreases to nanometer, the size-dependence of undercooling \( \Delta T(r) \) [a temperature difference between \( T_m(r) \) and the size-dependent freezing temperature of a liquid particle \( T_f(r) \) ] is present, which decreases with particle size [42, 98-100]. To predict \( \Delta T(r) \), we introduce the critical spherical nucleus size \( r_c \) in bulk liquid in terms of classical crystallization theory [42],

\[
r_c = \frac{[2\gamma_s(r)T_m(\infty)]}{[\rho_sH_m(\infty)\Delta T(\infty)]}.
\]  

(50)
where \( \rho_s \) is the density of the solid, \( \gamma_{sl}(r) \) denotes the size-dependent solid-liquid interface energy. Although Eq. 50 is derived for homogeneous crystallization of a spherical nucleus in bulk liquid, it can also be applied to heterogeneous nucleation when the liquid does not wet the surface.

Since \( \gamma_{sl}(r) \) is unknown, \( \gamma_{sl}(r) \approx \gamma_{sl}(\infty) \) in Eq. 50 is assumed where \( \gamma_{sl}(\infty) \) is the bulk value of \( \gamma_{sl}(r) \) \cite{46,101}. However, \( \gamma_{sl}(\infty) \) is also difficult to measure \cite{46}. Thus, some theoretical works are carried out to predict \( \gamma_{sl}(\infty) \) values \cite{46,101}. Among many theoretical and phenomenological models, an empirical relationship of \( \gamma_{sl}(r) = cH_m(\infty)/V_g \) \cite{102} proposed by Turnbull is widely used where \( c \) is a constant, \( V_g \) is molar volume. This equation is recently found to be Gibbs-Thomson equation and is expressed as \cite{46},

\[
\gamma_{sl}(\infty) = 2hS_m(\infty)H_m(\infty)/(3V_gR).
\]  

(51)

\( \gamma_{sl}(r) \approx \gamma_{sl}(\infty) \) is valid only when \( r > 10 \text{ nm} \) \cite{46,101}. If \( r < 10 \text{ nm} \), \( \gamma_{sl}(r) \) function itself must be utilized. \( \gamma_{sl}(r) \) function could be obtained by substituting Eqs. 48 and 49 into Eq. 51:

\[
\gamma_{sl}(r) = 2hS_m(r)H_m(r)/(3V_gR)
\]  

(52)

where \( \gamma_{sl}(r \rightarrow \infty) = \gamma_{sl}(\infty) \) and \( \gamma_{sl}(r \rightarrow 2r_0) = 0 \). The latter implies that the interface between the liquid and the nucleus at \( r = 2r_0 \) is diffuse and disappears since a half of atoms of the particle is located on its surface and thus the nucleus has a similar structure of the liquid.

Since a particle is usually obtained by depositing it on an inert substrate, it may wet or not wet the substrate. When the deposit does not wet the substrate, the deposit prefers taking a spherical shape with the smallest surface-to-volume ratio. In this case, Eq. 50 can be written as:

\[
r_c = [2\gamma_{sl}(r)T_m(r)]/[[\rho_sH_m(r)\Delta T(r)]
\]  

(53)

where all bulk values are substituted by the corresponding size-dependent values. Substituting Eqs. 52 and 53 into Eq. 50, one has:

\[
\Delta T(r)/\Delta T(\infty) = H_m(r)/H_m(\infty).
\]  

(54)

During the deduction of Eq. 54, \( r_c \) is treated as the same for the bulk liquid and for the nano-sized liquid as the first order approximation. This is because that \( r_c \) value must be near \( 2r_0 \) where the nucleus is in fact a cluster with a liquid-like structure \cite{28,103}. Here we take Pb as an example. In terms of Eq. 50, \( r_c \approx 1.99 \text{ nm} \) is obtained by use of values of \( \gamma_{sl}(\infty) = 0.05 \text{ Jm}^{-2} \), \( H_m(\infty) = 22990 \text{ Jkg}^{-1} \), \( \rho_s = 10950 \text{ kgm}^{-3} \), \( T_m(\infty) = 600.6 \text{ K} \) and \( \Delta T(\infty) = 0.2T_m(\infty) = 120 \text{ K} \) \cite{42} while \( 2r_0 = 6h = 2.3388 \text{ nm} (h = 0.3898 \text{ nm} \text{ [26]}) \) in terms of Eq. 30. This agrees also with the experimental observation of the size, \( r = 2.5 \text{ nm} \) where the melting and freezing points meet \cite{99}, which means that the nucleation barrier at this size is zero where \( \gamma_{sl}(2r_0) = 0 \).

In terms of definition of \( T_f(r) \), it reads:

\[
T_f(r) = T_m(r) - \Delta T(r).
\]  

(55)

With Eqs. 26, 49, 54 and 55, the size-dependent freezing temperature can be predicted. Since experimental data for Pb nanoparticles are abundant, Pb nanoparticles have no strong chemical interaction with substrate and they thus have a spherical shape. Pb nanoparticles are taken as an example to confirm our model.

The calculated \( T_m(r) \) and \( T_f(r) \) curves of Pb crystals are shown in Fig. 11 where \( \Delta T(\infty) \approx 0.2T_m(\infty) \) is taken \cite{101}. The decreases of \( T_m(r) \) and \( T_f(r) \) of Pb are evident as \( r \) decreases while \( \Delta T(r) \) decreases with decreasing size too. As shown in Fig. 11, the model predictions for \( T_m(r) \) in terms of Eq. 26 and \( T_f(r) \) in terms of Eq. 55 are consistent with experimental evidence \cite{42,99}. This correspondence
confirms also that homogenous nucleation dominates the solidification process of nanoparticles [42]. As \( r \to 2r_0 \), nucleation barrier decreases to zero and the melting point and the freezing point meet. When \( r < 2r_0 \), there is only the glass transition [28,103].

![Graph showing \( T_m(r) \) and \( T_f(r) \) functions of Pb nanoparticles. The solid lines are theoretical predictions in terms of Eqs. 26 and 55. For Pb nanoparticles, \( r_0 = 3h = 1.1694 \) nm in terms of Eq. 28 since \( h = 0.3898 \) nm [26]. Symbols + and \( \times \) denote the experimental results of \( T_m(r) \) values of Pb nanocrystals [42,99] while symbols • and ■ represent the experimental results of \( T_f(r) \) of Pb nanocrystals [42,91].](image)

### Solid-vapor Transitions: Cohesive Energy

**Model.** Being similar to the function of the size-dependent melting temperature of nanocrystals, solid-vapor transition is no longer constant. According to Kelvin equation [104], the vapor pressure of nanoparticles due to their curved surface is higher than that of a flat surface. Thus, the vapor pressure and the related evaporation of nanocrystals are size-dependent. As predicted by Kelvin equation, the evaporation temperature \( T_{ev}(r) \) of nanocrystals is experimentally found indeed to be size-dependent and decreases with decreasing size [56,105-108]. From the technological point of view, it is possible to evaporate different materials at the same temperature by taking different nanomaterials with distinct sizes. This is meaningful for the synthesis of nanoparticles or thin films of compounds from a single temperature source. Thus, knowing \( T_{ev}(r) \) function of nanocrystals is valuable in industry.

Based on the Lindemann’s criterion of melting, an expression for the bulk melting temperature \( T_m(\infty) \) of crystals is derived [109], which shows that \( T_m(\infty) \) is proportional to atomic cohesive energy \( E_c(\infty) \), or \( T_m(\infty) \) characterizes the bond strength [27,110,111]. The fact that \( T_m(\infty) \) varies linearly with \( E_c(\infty) \) agrees with experimental data for metals [41].

According the Trouton’s rule [112], the ratio of latent heat of vaporization \( H_v(\infty) \) to the liquid-vapor transition temperature \( T_v(\infty) \) is a constant or vaporization entropy \( S_v \). As results, \( H_v(\infty) \propto T_v(\infty) \). It is known that compared with the gas, the bond strength and coordination number of liquid are similar to the crystal and their energetic differences are very small where \( H_v(\infty) \approx E_c(\infty) \) and \( T_v(\infty) \approx T_{ev}(\infty) \) [113,114], liquid-vapor transition entropy \( S_v(\infty) = E_c(\infty)/T_v(\infty) \). Since \( E_c(\infty) \) is directly equal to the product of the bond number and the bond energy, which is the energy that divides a crystal into isolated atoms by destroying all bonds. This is just the energetic requirement for the solid-vapor transition. Thus, similar to \( T_m(\infty) \) and \( T_v(\infty) \), \( T_{ev}(\infty) \) characterizes even better the bond strength and \( T_{ev}(\infty) \propto E_c(\infty) \) [56,98]. This relationship has been extended to nanosize [56,106],

\[
T_{ev}(r)/T_{ev}(\infty) = E_c(r)/E_c(\infty). \tag{56}
\]

As a natural consideration, by Eq. 49 \( H_m(r) \) function is also applicable for the determination of \( E_c(r) \) function if the corresponding transition entropy term for the solid-vapor transition \( S_v(\infty) = E_c(\infty)/T_{ev}(\infty) \) is used to substitute \( S_m(\infty) \). In light of this consideration, \( E_c(r)/E_c(\infty) \) function is given as [115],

\[
\frac{E_c(r)}{E_c(\infty)} = \frac{T_{ev}(r)}{T_{ev}(\infty)} = \frac{T_m(r)}{T_m(\infty)}.
\]
\[ E_c(r)/E_c(\infty) = \left[ 1 - 1/(r/r_0 - 1) \right] \exp \left\{ (-2S_c(\infty) / 3R) [1/(r/r_0 - 1)] \right\}. \tag{57} \]

In Eq. 57, \( E_c(2r_0) = 0 \) where the structure of the solid and the vapor is indistinguishable. Since a single atom/molecule cannot be identified whether it is in a solid or a vapor state, \( 2r_0 = h \), or, \( r_0 = h/4 \). This equation differs from Eq. 24 with a factor of 1/12 where \( d = 0 \) has been taken, which is induced by the structural characteristic of vapor.

Note that although the solid-vapor transition entropy should be used here, which is difficult to find in literatures, \( S_c \) as a first order approximation is acceptable since the structural difference between solid and liquid is much smaller than the correspondence with vapor.

It is evident from Eq. 57 that \( E_c(r) \) increases (the absolute value decreases) with a decrease in size, which reflects the instability of nanocrystals in comparison with the corresponding bulk crystals. This trend is expected since the surface/volume ratio increases with decreasing size while the surface atoms have lower coordinates and thus higher energetic state, and consequently \( E_c(r) \) as a mean value of all atoms increases [115]. Using Eq. 57, \( E_c(r) \) values of W and Mo nanoparticles are predicted and are in agreement with the experimental results [115]. Substituting Eq. 57 into Eq. 56, we get,

\[ T_n(r)/T_n(\infty) = \left[ 1 - 1/(r/r_0 - 1) \right] \exp \left\{ (-2S_n(\infty) / 3R) [1/(r/r_0 - 1)] \right\}. \tag{58} \]

Results. Comparisons between model predictions in terms of Eq. 57 and experimental results for \( E_c(r) \) functions of free Mo and W nanoparticles is shown in Fig. 12.

Fig. 12. \( E_c(r) \) functions of Mo and W nanoparticles in terms of Eq. 57 shown as the solid lines and the symbols ▲ and ■ denote the corresponding experimental results of Mo and W, respectively [116]. For Mo, \( E_c(\infty) = 659 \text{ KJ-mol}^{-1} \) [83], \( S_c(\infty) = 122.15 \text{ J-mol}^{-1} \text{K}^{-1} \) with \( H_c(\infty) = 600 \text{ KJ-mol}^{-1} \) and \( T_c(\infty) = 4912 \text{ K} \) [83], and \( h = 0.2745 \text{ nm} \) [26]. For W, \( E_c(\infty) = 860 \text{ KJ-mol}^{-1} \) [83], \( S_c(\infty) = 137.27 \text{ J-mol}^{-1} \text{K}^{-1} \) with \( H_c(\infty) = 800 \text{ KJ-mol}^{-1} \) and \( T_c(\infty) = 5828 \text{ K} \) [83], and \( h = 0.2741 \text{ nm} \) [26].

Fig. 13. \( T_{ev}(r) \) functions for Ag, Au and PbS nanocrystals where the solid lines denote the model prediction of \( T_{ev}(r) \) in terms of Eq. 58 and the symbols ■, ▲ and ▼ show the experimental data of Ag, Au and PbS nanocrystals, respectively [106]. For Ag, \( S_B(\infty) = 105.5 \text{ J-mol}^{-1} \text{K}^{-1} \) with \( H_c(\infty) = 255 \text{ KJ-mol}^{-1} \) and \( T_c(\infty) = 2435 \text{ K} \), and \( h = 0.2889 \text{ nm} \) [83]. \( T_{ev}(\infty) = 1097 \text{ K} \) [106]. For Au, \( S_B(\infty) = 105.5 \text{ J-mol}^{-1} \text{K}^{-1} \) with \( H_c(\infty) = 330 \text{ KJ-mol}^{-1} \) and \( T_c(\infty) = 3129 \text{ K} \), and \( h = 0.2884 \text{ nm} \) [83]. \( T_{ev}(\infty) = 953 \text{ K} \) [106]. For PbS, \( S_B(\infty) = 13R = 105.5 \text{ J-mol}^{-1} \text{K}^{-1} \), \( h = 0.2970 \text{ nm} \) [117], \( T_{ev}(\infty) = 805 \text{ K} \) [106].
As shown in Fig. 12, except $E_c(r = 0.5 \text{ nm})$ value of W nanoparticles, Eq. 57 is consistent with the experimental observations. $E_c(r)$ increases with a drop in size, which reflects the instability of nanocrystals in comparison with the corresponding bulk ones due to the increase of surface/volume ratio $\chi$ and thus higher energetic state on average [115]. When $r < 1-1.5 \text{ nm}$ where the particles consist of only several ten to hundred atoms, a cluster structure is formed, which differs from the corresponding bulk structure, while Eq. 57 is valid only when the particle has the same structure of the bulk. This is the reason why the experimental $E_c(r = 0.5 \text{ nm})$ value of W nanoparticles differs from the model prediction of Eq. 57.

Fig. 13 presents comparisons of $T_{ev}(r)$ between the model predictions in light of Eq. 58 and available experimental results for Ag, Au and PbS nanocrystals. As shown in Fig. 13, $T_{ev}(r)$ decreases as $r$ drops, and prediction of Eq. 58 agrees well with the experimental results.

### Size Dependence of Debye Temperature and Volume Thermal Expansion Coefficient

The Debye temperature of nanocrystals $\Theta_D(r)$ has received considerable attention since it is an essential physical quantity to characterize many materials properties, such as thermal vibration of atoms and phase transitions [118-128]. Moreover, some important physical properties and their size effects, such as the Einstein temperature $\Theta_E(r)$ and the volume thermal expansion coefficient $\alpha_v(r)$, are all related to $\Theta_D(r)$ function [120,123,129]. At once $\Theta_D(r)$ function is known, the other two are determined. Therefore, it is important to determine this function.

#### Model

In terms of the Debye model, the $\Theta_D$ function is related to the rms $\sigma$ by [120,130],

$$\sigma^2 \propto T/\Theta_D^2$$

(59)

when $T > \Theta_D(\infty)/2$. By Eq. 23 $\sigma^2(r)/\sigma^2(\infty) = \exp[(-1)\alpha x] = \exp[(\alpha - 1)/(r/r_0 - 1)]$. It is assumed that $\Theta_D(r)$ has the same size dependence of $1/\sigma(r)$ as a first order approximation since the nature of any phase transition is related with the potentials of the two related phases of the crystals. Thus,

$$\Theta_D(r)/\Theta_D(\infty) = \sigma(\infty)/\sigma(r).$$

(60)

Substituting Eq. 23 into Eq. 60, it reads,

$$\Theta_D(r)/\Theta_D(\infty) = \sqrt{\exp\{-(\alpha - 1)/[(r/r_0 - 1)]\}}.$$ (61)

Since $\alpha_v(\infty) \propto 1/\Theta_D^2(\infty)$ [123], Eq. 61 can be extended for $\alpha_v(D)$ functions as follows,

$$\alpha_v(r)/\alpha_v(\infty) = \exp\{(\alpha - 1)/[(r/r_0 - 1)]\}.$$ (62)
Results. Comparisons between model predictions in terms of Eqs. 30, 43 and 61 and the available experimental and computer simulation results for \( \Theta_0(r) \) functions of Fe, \( \beta \)-Sn, Se, Cu, Co, Au, and Ar/Al (Ar nanocrystals embedded in Al matrix) nanocrystals are shown in Fig. 14 where the related parameters are listed in Table 1. It is obvious the model predictions for different kinds of nanocrystals in different surroundings correspond to the experimental and computer simulation results in the full size range, which implies that Eq. 61 is reasonable.

As shown in Fig. 14(a) to Fig. 14(d), \( \Theta_0(r) \) with \( \alpha > 1 \) decreases for free nanocrystals as \( r \) decreases. \( \alpha > 1 \) implies decrease of \( \Theta_0(r) \) with increase of the rms. Note that Fe and \( \beta \)-Sn films in Figs. 14(a) may refer to finely granular structures with high densities of inner surface/grain boundaries and cannot be described by a continuous film [130]. This granular structure is similar to a random structure of a chain polymer modeled by a trajectory of a self-avoiding walk with a fractal dimension of \( d = 4/3 \) [130]. It is obvious that the depression for \( \Theta_0(r) \) of films with \( r \) is weaker than that of nanoparticles as shown in Figs. 1(a), which is induced by different \( d \) and thus different values of \( r_0 \) in Eq. 24. Consequently, our model can also predict the dimension dependence of \( \Theta_0(r) \) while different dimensions of nanocrystals have different surface/volume ratios.

**Table 1** Necessary parameters used to determine \( \Theta_0(r), \Theta_E(r) \) and \( \alpha_s(r) \) functions [131]

<table>
<thead>
<tr>
<th></th>
<th>( \Theta_0(\infty) ) [K]</th>
<th>( T_m(\infty) ) [K]</th>
<th>( \Delta H_m(\infty) ) [kJ mol(^{-1})]</th>
<th>( \Delta V_m/V_s )</th>
<th>( \Delta S_vib(\infty) ) [J mol(^{-1}) K(^{-1})]</th>
<th>( h ) [nm]</th>
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<tr>
<td>Fe</td>
<td>388.00</td>
<td>1811.00</td>
<td>13.80</td>
<td>3.4</td>
<td>6.42(^a)</td>
<td>0.2482</td>
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<tr>
<td>( \beta )-Sn</td>
<td>140.00</td>
<td>505.08</td>
<td></td>
<td></td>
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<tr>
<td>Se</td>
<td>135.90</td>
<td>494.00</td>
<td>5.4</td>
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<td></td>
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<tr>
<td>Cu</td>
<td>343.00</td>
<td>1357.77</td>
<td>13.10</td>
<td>4.9</td>
<td>8.08(^a)</td>
<td>0.2556</td>
</tr>
<tr>
<td>Co</td>
<td>400.00</td>
<td>1768.00</td>
<td>16.20</td>
<td>3.9</td>
<td>7.83(^a)</td>
<td>0.2507</td>
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<tr>
<td>Au</td>
<td>184.59</td>
<td>1337.33</td>
<td>12.50</td>
<td>5.1</td>
<td>7.74(^a)</td>
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<tr>
<td>Ar</td>
<td>70.00</td>
<td>83.80</td>
<td></td>
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<td></td>
<td>0.3500</td>
</tr>
<tr>
<td>Pb</td>
<td>600.61</td>
<td>4.77</td>
<td>3.5</td>
<td></td>
<td>6.71(^a)</td>
<td>0.3500</td>
</tr>
</tbody>
</table>

\( a \) The values are calculated by Eq. 32, where \( \Delta S_m(\infty) = \Delta H_m(\infty)/T_m(\infty) \) and \( R = 8.314 \) J mol\(^{-1}\) K\(^{-1}\).

\( b \) The value is determined by Eq. 33 with \( n_s/n_l = 2.10 \) [74].

\( c \) The values are approximately equal to \( \Delta S_m(\infty) \).
Fig. 14. $\Theta_D(r)$ functions of Fe, $\beta$-Sn, Se, Cu, Co, Au, and Ar/Al. The solid lines in (a)-(c) denote the model predictions in terms of Eqs. 30 and 61 while in (d) denote the model predictions based on Eqs. 43 and 61 and $r_0$ is determined by Eq. 24. (a) The symbols ● (nanoparticles, $d = 0$) [118], + [119], ○ [120] and ■ [120], (films with finely granular structures, $d = 4/3$) show the experimental results of Fe. The symbols ▲ (films with finely granular structures, $d = 4/3$) [121] and Δ (nanoclusters embedded in SiO$_2$ layers, $d = 0$) [123] show the experimental results of $\beta$-Sn. (b) The symbol ■ (nanoparticles, $d = 0$) [123] shows the experimental results of Se. The symbol ▲ (thin films on mica substrate, $d = 2$) [126] shows the experimental results of Au. (c) The symbol ● (thin films on graphite substrate, $d = 2$) [124] shows the experimental results of Cu. The symbols ■ [125] and □ [125] (nanoclusters, $d = 0$) show the experimental and computer simulation results of Co, respectively. (d) For the Al matrix, $h_M = 0.2863$ nm [26] and $T_{M(\infty)} = 933.47$ K [83]. The symbol ■ (Ar nanoparticles embedded in Al matrix, $d = 0$) [127] shows the experimental results of Ar/Al.
As shown in Fig. 15, comparisons between the model predictions based on Eqs. 30 and 62 and experimental results for \( \alpha_v(r) \) of Se and Pb nanocrystals are present. The model predictions correspond to the experimental results of Se nanocrystals in the full size range. For Pb nanocrystals, the model can predict the \( \alpha_v(r=8 \text{ nm}) \) value accurately in comparison with the experimental results while a big divergency between them is found for \( \alpha_v(r=8 \text{ nm}) \) value. One possible reason is the approximation of \( \alpha_v(r) = 3\alpha_B(r) \) could collapse in smaller size range (such as \( r=8 \text{ nm} \)). As mentioned above, \( \alpha_v(r) \) increases with decreasing \( r \). It is known \( E_B \propto 1/\alpha_v \) and \( E_v(r) \) decreases with decreasing \( r \) [115], which confirms Eq. 62.

\[ \text{Fig. 15. } \alpha_v(D) \text{ functions of Se and Pb. The solid lines denote the model predictions in terms of Eqs. 43 and 62 and } r_0 \text{ is determined by Eq. 24. For Se, } \alpha_v(x) = 9.45 \times 10^{-5} \text{ K}^{-1} \text{ is a mean value of } 7.8 \times 10^{-5} \text{ K}^{-1} [123] \text{ and } 11.1 \times 10^{-5} \text{ K}^{-1} [132] \text{ as a first order approximation. The symbol } \blacksquare \text{ (nanoparticles, } d = 0) [123] \text{ shows the experimental results of Se. For Pb, } \alpha_v(x) = 8.7 \times 10^{-5} \text{ K}^{-1} [132]. \text{ The symbol } \bigcirc \text{ (nanoparticles, } d = 0) [129] \text{ shows the experimental results of Pb. Note that the original experimental results is the linear expansion coefficient } \alpha_f(r) \text{ of Pb nanocrystals. As a first order approximation, } \alpha_v(r) = 3\alpha_B(r) \text{ is used} [132]. \]

**Solid-solid Transitions and Phase Diagrams**

**Continuous binary solution phase diagram.** It is well known that phase transition properties of metallic, semiconductors and organic nanocrystals differ from those of the corresponding bulks, while a systematic study on phase equilibria among nanometer-sized components related to phase diagrams is scarce [133,134]. The study of nanophase diagram may deepen phase transition theory and extend possible industry applications. Since nanophase equilibrium is metastable in nature and is difficult to measure, a theoretical work may be an alternative.

To calculate nanophase diagrams, size dependences of melting temperature and melting enthalpy of components, and that of atomic interaction energy among components are basic thermodynamic quantities. A kind of consideration on the size effect is to separate the thermodynamic quantities into a bulk item and a surface item, which is related with the contribution of the surface/volume ratio [133,134]. However, when the size of nanophase decreases to mesoscopic size range, the size effect is stronger than the surface/volume ratio [135]. Moreover, the known studies on nanophase diagram have neglected the size effect of the atomic interaction energy [133,134]. Thus, the nanophase diagram needs to be further studied.

**Model.** A general thermodynamic frame for a binary regular solution system consisting of components A and B is introduced firstly. When the liquid and solid of the binary system are in equilibrium, the chemical potentials \( \mu \) of component A in the both phases are equal, or,

\[ \mu_A^L = \mu_A^S. \tag{63} \]

where the superscripts L and S denote the liquid and solid phases respectively, and the subscripts A and B denote the components (for the component B, there is the same equation but with subscript B). It is known that,

\[ \mu_A^L = G_A^L + RT\ln \alpha_A^L. \tag{64a} \]
\[ \mu_A^S = G_A^S + RT \ln a_A^S. \]  

(64b)

where \( a \) is activity, \( R \) denotes the ideal gas constant, \( T \) is temperature and \( G \) shows the molar Gibbs free energies. In Eq. 64,

\[ G_A^L - G_A^S = G_{mA} = H_{mA} - TS_{mA} = H_{mA} - TH_{mA}/T_{mA}. \]

(65)

with \( G_m, H_m, S_m \) and \( T_m \) being the melting Gibbs free energy, melting enthalpy, melting entropy and melting temperature, respectively. Combining Eqs. 63 to 65,

\[ \ln (a_A^S/a_A^L) = H_{mA}(T_{mA} - T)/(T_{mA}RT). \]

(66)

Similarly, for component B,

\[ \ln (a_B^S/a_B^L) = H_{mb}(T_{mb} - T)/(T_{mb}RT). \]

(67)

Let \( a_A = f_Ax_A \) and \( a_B = f_Bx_B \) with activity coefficient \( f \) and atomic percentage \( x \) of a component where \( x_A + x_B = 1 \). For a regular solution, \( \ln f_A = (\Omega/RT)x_A^2 \) and \( \ln f_B = (\Omega/RT)x_B^2 \) in a quasi-chemical approach where \( \Omega \) is atomic interaction energy [128]. Substituting the above relations into Eqs. 66 and 67,

\[ H_{mb}(T_{mb} - T)/T_{mb} = \Omega^S(x_B^2 - x_A^2) - \Omega^L(x_B^L - x_A^L) + RT \ln(x_B^S/x_B^L), \]

(68)

\[ H_{mA}(T_{mA} - T)/T_{mA} = \Omega^S(x_B^2 - x_A^2) - \Omega^L(x_B^L - x_A^L) + RT \ln[(1 - x_B^S)/(1 - x_B^L)]. \]

(69)

When \( T \) is certain, \( x_B^L \) and \( x_B^S \) in a bulk phase diagram are respective unique and can be determined through Eqs. 66 and 67 when other quantities are known. Eqs. 68 and 69 can in return be utilized to determine \( \Omega^S \) and \( \Omega^L \) when \( T, x_B^L \) and \( x_B^S \) are known besides \( H_m \) and \( T_m \). Thus, through taking values of \( T, x_B^L \) and \( x_B^S \) from the corresponding bulk phase diagrams, bulk \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) can be determined through Eqs. 68 and 69. Since \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) are weak functions of composition, as a first order approximation, \( \Omega^S(x) \) and \( \Omega^L(x) \) will be determined at \( T \approx (T_{mA} + T_{mb})/2 \) in this work with the corresponding \( x_B^L \) and \( x_B^S \) in the bulk phase diagrams. With the determined \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) values, the bulk phase diagrams are replotted in terms of Eqs. 68 and 69 which are shown in Fig. 16. It can be seen from the figures that the bulk solidus and liquidus curves in the binary regular solution phase diagrams are in agreement with the experimental results. This agreement in return confirms that the fitted \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) values have minor error.

The above discussion has introduced how to determine the solidus and liquidus curves in a binary regular solution phase diagram and the method to determine \( \Omega^S(\infty) \) and \( \Omega^L(\infty) \) through the known bulk phase diagrams. If \( T_m(r) \) and \( H_m(r) \) of each component and \( \Omega^S(r) \) and \( \Omega^L(r) \) may be determined and substituted for the corresponding bulk values \( T_m(\infty), H_m(\infty), \Omega^S(\infty) \) and \( \Omega^L(\infty) \) based on Eqs. 68 and 69, nanophase diagrams could be given.

To obtain \( T_m(r) \) and \( H_m(r) \) functions has been deduced by Eq. 26 and 48. Moreover, it is well known that \( \Omega = N_a Z[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})]/2 \) with \( \varepsilon \) being interaction bond energy where the subscripts have the same meaning of the above. \( N_a \) is Avogadro’s number and \( Z \) coordinate number of an atom. The values of all \( \varepsilon \), which are negative, decrease with reducing \( r \) [115,137]. If decreasing rates of \( \varepsilon \) are different, \( \Omega \) is size-dependent. According to general quantum chemistry consideration [138], all thermodynamic quantities are roughly linear function of \( 1/r \) that corresponds to the surface/volume ratio of particles. It is assumed that \( \Omega \) has the same relationship. Because \( H_m(2r_0) = 0 \) in terms of Eq. 49, \( \Omega(r) \) should have the same limit and thus is assumed to have the following form,

\[ \Omega(r)/\Omega(\infty) = 1 - 2r_0/r. \]

(70)
Since \(2r_0 = 6h\) in terms of Eq. 24 where \(h\) is component dependent, different components have different \(r_0\) values, a larger \(h\) value of two components will be taken to calculate \(2r_0\), which avoids physically unreasonable negative \(H_m(r)\) in terms of Eq. 49 without evident error. In light of Eq. 70, \(\Omega^S(r)\) and \(\Omega^L(r)\) have the same size-dependence and are composition independent as a first order approximation.

**Results.** Fig. 16 show continuous solution phase diagrams of different binary systems of metals Cu-Ni, semiconductors Ge-Si, ceramics Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\) in terms of Eqs. 68 and 69. Note that \(\Omega^S(\infty)\) and \(\Omega^L(\infty)\) are firstly determined by Eqs. 68 and 69 through introducing the corresponding known bulk phase diagrams [139-141]. To determine \(\Omega^S(\infty)\) and \(\Omega^L(\infty)\), \(T = 1573.15\) K, \(x_{Ni}^{L} = 0.45\) and \(x_{Ni}^{S} = 0.57\) are used in calculation in Fig. 16 (a); \(T = 1506.5\) K, \(x_{Si}^{L} = 0.40\) and \(x_{Si}^{S} = 0.73\) in Fig. 16 (b); \(T = 2430\) K, \(x_{Cr2O3}^{L} = 0.44\) and \(x_{Cr2O3}^{S} = 0.67\) in Fig. 16 (c); For nanophase diagrams based on Eqs. 68 and 69, \(T_m(D), H_m(D)\) and \(\Omega(D)\) functions are calculated respectively in terms of Eqs. 26, 49 and 70. Except for Fig. 16(b) where \(S_{vib}(\infty)\) is cited from reference [74], \(S_{vib}(\infty) \approx S_m(\infty) = H_m(\infty)/[nT_m(\infty)]\) where \(n\) is the atom number in a molecule since the unit of \(S_{vib}(\infty)\) is Jg-atom\(^{-1}\)K\(^{-1}\) [28]. \(n = 1\) in Figs. 16 (a) and 16 (b); \(n = 5\) in Fig. 16 (c). To determine \(2r_0\) in Eq. 70, larger \(h\) values between two component counterparts are always taken in all figures as illustrated above. For molecules, \(h = \frac{3}{V_c}\) where \(V_c\) is volume of the cell [28]. Necessary other parameters during the calculations and the calculated results are shown in Table 2.

Fig. 16. Cu-Ni, Ge-Si and Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\) nano and bulk phase diagram where the solid lines show the theoretical calculation for regular solution in terms of Eqs. 68 and 69 and the symbol denotes the bulk experimental results for Cu-Ni and Ge-Si system [139], for Al\(_2\)O\(_3\)-Cr\(_2\)O\(_3\) system [140]. The necessary parameters see Table 2.

As \(r\) decreases, solidus and liquidus curves drop since \(T_m(r)\) of each component decreases. When \(r \to 2r_0\), \(T_m(2r_0) = T_m(\infty)\exp[-2S_{vib}(\infty)/(3R)]\) in terms of Eq. 24, which implies that \(T_m(2r_0)\) is determined by \(T_m(\infty)\) and \(S_{vib}(\infty)\). The latter reflects the size of the structural difference between the liquid and the solid. Because \(S_{vib}(\infty)\) of semiconductors are small, their drops of \(T_m\) are also small.
Another evident change comparing with the bulk phase diagram is that the two-phase zone of the nanophase diagram becomes small. As \( r \rightarrow 2r_0 \), which is about several nanometers, the zone even approaches zero. This is a direct result of \( \Omega(2r_0) = 0 \) where the regular solution deteriorates into the ideal solution and the structures of liquid and the solid become similar due to the short range order.

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<th>( H_m [\text{J mol}^{-1}] ) ([83])</th>
<th>( \Omega^g [\text{J mol}^{-1}] ) ([26])</th>
<th>( \Omega^h [\text{J mol}^{-1}] ) ([26])</th>
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| To determine \( h \) value of \( \text{Al}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \), the related data are \( V_{\text{Al}_2\text{O}_3} = 0.2548 \text{ nm}^3 \) \([132]\), \( V_{\text{Cr}_2\text{O}_3} = 0.2898 \text{ nm}^3 \)

**Summary**

Modeling for recent progress on \( T_m(r) \) function is comparatively reviewed. Without any free parameter, our model based on Lindemann’s criterion, or enhancement or suppression of thermal vibrations of atoms of nanocrystals, has described both undercooling and superheating phenomena of nanocrystals. This model covers all essential considerations of early models with wider size range suitability and may be extended to predict \( S_m(r) \), \( H_m(r) \), \( E_B(r) \), \( T_\alpha(r) \), \( \Theta_D(r) \) and \( \alpha_s(r) \) functions. The obtained unified form of the functions reveals the physical nature of size dependence of materials properties and internal relationship among different types of phase transitions. Based on the above models, size-dependent continuous binary solution phase diagrams, and solid transition phase diagrams have been constructed. As \( r \) decreases, phase diagrams exhibit evident difference from the corresponding bulk and are theoretically and experimentally meaningful due to its utility of prediction on phase structures of nanocrystals.

In all of the above extensions, reasonable agreements between model predictions and experimental data from systems with various bond natures have been reached, evidencing the validity of the model. Further extension of this general model to other fields would be more beneficial.
It is found that the size dependence of properties of a system is indeed an independent thermodynamic amount. This result brings out an evident extension of the classic thermodynamics where the studied system of the thermodynamics can cover all size range from microscopic, along mesoscopic, to macroscopic size, as long as the solid remains the bulk stable structure or other metastable structure. This is not only the most progress of the thermodynamics, but also especially beneficial for the research on nanoscience and nanotechnology nowadays. This progress clarifies also the always importance of the classic thermodynamics, which could keep up with the time.

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[83] Information on http://www.webelements.com/


Direct White Light Nanophosphors

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**Keywords:** White light emission, nanostructured materials, nanophosphors

**Abstract.** White light emission based on semiconductor nanostructures represents a new technology platform for solid state lighting. The major advantages are the easy synthesis and tuning of color emission in the visible range and the high optical stability of nanostructures. This chapter summarizes the materials that can be used as white light nanophosphors.

**Introduction**

Approximately 20% of the global electricity production is currently consumed for lighting and solid state-based light sources potentially offer 50% reduction in the global electricity consumption for illumination. Light emitting devices (LEDs) are gaining popularity as the cost and power consumption of are less. In this regard, white LEDs can replace the conventional lighting sources and are in great demand. LED lights are more rugged and damage-resistant than compact fluorescents and incandescent bulbs. LED lights don't flicker. However, they are very heat sensitive; excessive heat or inappropriate applications dramatically reduce both light output and lifetime. The potential benefits of solid state light sources have been discussed in Ref. [1].

Several promising strategies [2] to generate white light that includes di- tri- and tetrachromatic approaches are shown in Fig. 1. There are two main approaches to white light generation: direct mixing of monochromatic sources (combining blue, green and red chips) and phosphor conversion. Direct mixing of monochromatic sources results in the highest efficiency and best color rendering. However, efficiently extracting all three colors in such a device requires costly chip designs, which likely cannot compete with conventional fluorescent lighting but can be attractive for more specialized lighting applications. They are expensive and each chip degrades at a different rate.

The phosphor converted white LEDs are highly promising because they consist of a single InGaN chip and possess high luminescence efficiency and cost effective. Color conversion scheme for white light emission have been the mostly used and those based on phosphor coatings have been commercially available since 1996 [3]. These white LEDs produce white light by mixing the yellow light emitted by a phosphor with the blue light emitted by a LED chip.

Commercially available phosphor conversion sources use blue LED and yellow phosphor [3]. Phosphor based LEDs involves coating an LED of one color (mostly blue LED made of InGaN) with phosphor of different colors (a yellow phosphor or a combination of green and red phosphors) to produce white light. A common yellow phosphor material is cerium-doped yttrium aluminum garnet (Ce$^{3+}$:YAG). High efficiency yellow phosphors such as YAG:Ce are readily available. Single-chip white-LEDs typically based on yttrium aluminium garnet (YAG) doped with cerium combine low fabrication costs and high efficiency.

There are other approaches to achieve white light emission. One of the schemes explores the coating of nanophosphores on UV-LEDs that can be achieved through (i) blending blue, green
and red phosphor in appropriate ratio, (ii) by blending blue and yellow phosphors or (iii) a direct phosphor that emits white light when coated onto an UV LED. White light can also be generated from IR-LEDs.

![Diagram of LED-based and LED-plus phosphor-based approaches for white light sources](image)

**Fig. 1.** LED-based and LED-plus phosphor-based approaches for white light sources (Ref. [2], permission obtained).

Recently, white light emission from nanostructures has become the research of general interest as a motive to replace the conventional phosphors of white light emission because of their size-tunable luminescence, high quantum yields and high photostability. Recent progress in nanoscience and nanotechnology offers alternative approaches to achieve increase in the efficiency and cost reduction. With improved quantum confinement, efficiency can be increased. This nanophosphor-based device is quite different from an alternative approach based upon growth of blue, green, and red emitting semiconductor materials that requires careful mixing of the those primary colors to produce white illumination. It has been shown that quantum dots exhibit more than one order of magnitude higher photoluminescence than quantum wells [4,5]. Nanophosphors based upon quantum dots have two significant advantages over the use of conventional bulk phosphor powders. First, while the optical properties of conventional bulk phosphor powders are determined solely by the phosphor’s chemical composition, in quantum dots the optical properties such as light absorbance are determined by the size of the dot. Changing the size produces dramatic changes in color. The small dot size also means that, typically, over 70 percent of the atoms are at surface sites so that chemical changes at these sites allow tuning of the light-emitting properties of the dots, permitting the emission of multiple colors from a single size dot.

Nanophosphors have additional advantages. The small size of the quantum dots — much smaller than the wavelength of visible light — eliminates all light scattering and the associated optical losses. Optical backscattering losses using larger conventional phosphors reduce the package efficiency by as much as 50 percent. Other advantages of nanostructured based white light emission are: (1) they do not emit in the infrared radiation unlike light bulbs and (2) the energy loss by backscattering can be reduced as the size is few nm. Taking into consideration these properties, semiconductor nanocrystals are attractive candidate materials for applications in solid state lighting. Semiconductor nanocrystals exhibit high fluorescence quantum efficiencies and large molar
absorptivities. Unlike commercial phosphors, their emission colors can be tuned by controlling the nanocrystal size and the chemical composition.

Recent publications on a new class of inorganic phosphors, oxynitride and nitride luminescent materials, report promising results and encourage the use of these phosphors in solid-state lighting applications [6]. Li et al. [7] have reviewed the recent progress on the fabrication of white LEDs using semiconductor nanocrystals. A review on advances in LED technology can be found in [8]. Blue light emission emission and device application has been reviewed in [9]. The development and demonstration of a highly efficient nitride, and oxynitride based phosphors of blue, green for white light sources have been presented in Ref. [6,10]. There is also a review article on the development of nanophosphors [11]. In this article, we review the nanostructured materials that can be used as direct phosphors for white light sources. In the future, the use of quantum dots as light-emitting phosphors may represent a major application of nanotechnology.

Size-effect of nanocrystals
In order to achieve efficient phosphors for the generation of white light, it is essential to tune the color and the efficiency. Nanostructured materials have attracted interest because they have high luminescence efficiency (quantum yield > 50%) and size-tunable band-gap characteristics.

Phosphors based on semiconductor nanoparticles offer advantages compared to conventional powder phosphors including negligible optical backscattering due to the small diameter of the dots. More importantly, direct white emission from a single size dot is possible, obviating the need to blend two or more dots of differing size. Use of a single size dot eliminates self-absorbance of the emitted light while maintaining optical transparency in the visible, 450 to 700 nm regime.

**Band gap tuning.** Based on the effective mass approximation, the change in band gap (ΔEg) of a semiconductor particle of size D, is given by [12]

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2D^2} \left[ \frac{\eta_e^2}{m_e^*} + \frac{\eta_h^2}{m_h^*} \right] + \Delta E_{e-h}$$

where $m_e^*$ and $m_h^*$ are the effective mass of electron and hole, respectively. This indicates that the band gap increases with decreasing size and has been verified by numerous nanostructured materials. It is evident from Eq. (1) that change in the band gap is significant for materials with smaller effective masses. The effective masses of CdSe are small ($m_e^* = 0.11 m_0$ & $m_h^* = 0.44 m_0$ where $m_0$ is free electron mass). The band gap of CdSe/ZnS core/shell nanocrystals increases from 2.126 to 2.683 eV when the crystal size is reduced from 5.2 to 1.9 nm [13]. This suggests that specific size of the crystal is required to imitate white light emission as observed in Ref. [14]. The tuning of colour of emission from green to red has been demonstrated by controlling the size of CdTe nanocrystals [15]. On the other hand, wide band gap semiconductors such as Ga$_2$O$_3$, ZnO, ZnS, In$_2$O$_3$, etc. depends very weakly on the size of the crystals as the effective masses are large and can be more appropriate for this kind of applications.

**Enhancement of quantum efficiency.** The luminescence not only depends on the band gap but also on the surface states. As the size decreases, the band gap increases and the energy levels associated with the surface states also get modified.

The quantum efficiency $\eta_{bb}$ for the band-to-band recombination is given by [16]

$$\eta_{bb} = \frac{\tau_{bb}^{-1}}{\left(\tau_{bb}^{-1} + \tau_{NR}^{-1}\right)}$$

(2a)
where $\tau_{bb}^{-1}$ and $\tau_{NR}^{-1}$ are the band-to-band recombination and surface recombination rate, respectively. $\tau_{NR}$ depends on the number of surface atoms per unit volume and is inversely proportional to the size of the particle. On the other hand, $\tau_{bb}^{-1}$ should depend weakly on the size of the particle. Therefore, quantum efficiency $\eta_{bb}$ is expected to decrease with particle size. Similarly, the surface recombination rate is given by

$$\eta_{NR} = \frac{\tau_{NR}^{-1}}{\tau_{bb}^{-1} + \tau_{NR}^{-1}} = \frac{1}{1 + \alpha D}$$

This indicates that the surface recombination rate increases with decreasing size. This has been proven for ZnO nanowires [17]. The weight of the surface luminescence increases as the radius of ZnO nanowires decreases.

Now, we discuss the quantum efficiency of doped nanoparticles. The quantum efficiency of luminescence depends strongly on the diameter [16] as

$$QE \alpha \frac{1}{1 + \beta D^2}$$

where $\beta$ is related to the ratio between $\tau_{bb}$ and $\tau_{NR}$ and is a constant. This indicates that the QE increases with decreasing size. Overall, the color of emission can be tuned and the QE can be enhanced by lowering the crystallite size.

**Materials as direct white light nanophosphors**

White-light emitting ultra-small nanocrystals present exciting possibilities in the area of solid-state lighting technology. New high-efficiency phosphors, which can be excited with blue/UV light, are now being developed. In this section, we have summarized the materials that can be used as white light nanophosphors.

The use of recently discovered single-size, ultra-small (~1.5 nm diameter) white-light emitting CdSe nanocrystals as a phosphor eliminates the need for multiple phosphor layers, reducing the limitations common in other devices, such as poor efficiencies and low CRI values. These white-light nanocrystals possess a well-balanced broad-spectrum emission that spans the majority of the visible spectrum.

**Surface state controlled CdSe based phosphors.** White-light emitting ultra-small CdSe nanocrystals present exciting possibilities in the area of solid-state lighting technology. CdSe being a semiconductor with a bulk band gap of 1.74 eV, the band gap of CdSe nanocrystals depends significantly on the crystal size [12]. Browers II et al. [14] have demonstrated the generation of white light by combining the broad surface state emissions and the band edge emission frommagic sized nanocrystals. This suggests that specific size of the crystal is required to imitate white light emission as observed in Ref. [14] and a high degree of control on the nanocrystal size is required.

The material has been proven to demonstrate good photostability. Thin films of magic-sized CdSe (neat on a glass slide) were able to maintain their optical properties after 10 days of exposure to intense UV light under ambient conditions.

White-light emitting CdSe nanocrystals encapsulated in the biphenylperfluorocyclobutyl polymer exhibit luminescence in the visible region and coating on various UV-LEDs creates a white light source with chromaticity coordinates of (0.324, 0.322) and a high color-rendering index of 93 [18].

The approach is based on encapsulating semiconductor quantum dots and engineering their surfaces so they efficiently emit visible light when excited by UV LEDs. The quantum dots strongly absorb light in the near UV range and re-emit visible light that has its color determined by both their size and surface chemistry.

**ZnO based phosphors.** ZnO commonly exhibits luminescence in the visible region due to different intrinsic defects. It has been shown that the color of luminescence depends on the...
excitation wavelength [19]. White light from porous ZnO nanotubes has been demonstrated [20]. A polychromatic PL band consisting of blue, green and orange emissions was realized by introducing the unwanted native defects into the ZnO lattice.

White light emission has been reported for polyvinyl alcohol/ZnO hybrid nanofibers. Simultaneous emission of three bands covering from UV to visible range gives the impression of white light [21].

It has been shown that porous ZnO nanotubes prepared by a two-step hydrothermal method show photoluminescence consisting of blue, green and orange emissions when excited with UV light [20]. The wide-spectrum PL band is considered to be related to complex defect species such as vacancies of oxygen and zinc, interstitial oxygen and zinc and antisite oxygen $O_{Zn}$ in ZnO lattice.

The energy from the interstitial zinc energy level to the valence band and the conduction band to the antisite oxygen $O_{Zn}$ defect energy level depends on the band gap of ZnO and is 2.9 eV and 2.38 eV, respectively for a band gap of 3.26 eV. The energy between the conduction band and the oxygen interstitials level is about 2.28 eV [22] and the defect energy level of zinc interstitial is about 0.22 eV below the conduction band edge [23,24]; therefore, the energy between the oxygen and zinc interstitial energy levels is about 2.06 eV, which is in good agreement with the energy of the orange emission (2.07 eV). The orange emission is hence considered to originate from the transition of electrons between these two interstitial defect levels. The polychromatic emission might be closely related to the co-existence of the interstitial zinc and oxygen defects as well as the antisite oxygen $O_{Zn}$ defect in ZnO lattice.

![Energy band diagram depicting the emissions in ZnO](image)

From the above discussion, the energy level diagram of the defect in the band gap of the porous ZnO nanotubes can be drawn, as shown in figure 2. The origin of the blue emission is related to the transition of electrons between the zinc interstitial defect level and the valence band, while the green emission to that between the conduction band and the antisite oxygen $O_{Zn}$ defect level, and the orange emission originates from the electrons’ transition from the zinc interstitial defect level to the oxygen interstitial defect level. Therefore, the polychromatic visible PL results from zinc and oxygen interstitial defects and oxygen antisite $O_{Zn}$ defects. Please note that the band gap and hence, the energy of the transitions depends on the oxygen deficiency in ZnO.

**$Ga_2O_3$ based phosphors.** Visible blue-green emission is common for $Ga_2O_3$ nanoparticles [25,26], while nanorods emit UV-blue light extended to green region [27-29] when irradiated with an UV light. It may be noted here that a red emission along with blue-green emission is required for
the generation of white light. Red emission has been reported for Ga$_2$O$_3$ nanostructures doped with N, Cr or Eu [30-34].

It has been suggested that nitrogen doping generates deep acceptor levels in the band gap of Ga$_2$O$_3$, and the position of the doping-induced subbands is about the center of the band gap [35]. The red-light emission originates from the recombination of an electron trapped on a donor due to oxygen vacancies and a hole trapped on an acceptor due to nitrogen doping. The bluish emission is attributed to the recombination of an electron on a donor with a hole on an acceptor formed by gallium vacancy or gallium oxygen vacancy pair [34,35].

**CdS/ZnS based phosphors.** Nanoparticles doped with rare earth atoms enable utilizing quantum confinement to enhance efficiency without change in the emission wavelength with nanostructure size [16]. Nanocrystal lighting corporation has been formed recently to exploit doped nanoparticles for phosphors in solid state lighting.

White light from a simple transition-metal-doped semiconducting nanocrystal namely, Mn$^{2+}$-doped CdS is possible by suitably tuning the relative surface-state emissions of the nanocrystal host and the dopant emission [36]. White light emitted by these nanocrystals remains unchanged both in solution form as well as in the solid state and can be excited by a wide range of UV lights without disturbing the chromaticity. The emission depends on the doping amount and not on the monodispersity.

White light emission is observed at room temperature from Cd-rich CdS nanoparticles and the intensity increases manifold when cooled to 77 K [37]. Trapped-rich CdS nanoparticles are shown to act as a white phosphors [38].

![Energy band diagram depicting the emissions in Mn-doped ZnS.](image)

It may be noted that Mn doped ZnS emits in the yellow-orange light [39,40] while Cu doped ZnS emits blue light [41]. White light emission from surface-oxidized manganese-doped ZnS nanorods has been demonstrated [42,43]. The emitted white light was found to be the result of blue, green and orange emission bands. The blue bands were attributed to sulfur vacancies and surface states, the green band is attributed to the singly ionized oxygen vacancy of the ZnO shell layer. The orange emission originated from the Mn$^{2+}$ ions.

Photoluminescence (PL) in the range of 400-700 nm is reported from Mn-doped ZnS nanocrystals (NCs) capped with ZnS (ZnS:Mn/ZnS core-shell NCs) and thioglycolic acid (TGA) (ZnS:Mn/ZnS core-shell NCs dispersed in an alkaline TGA solution) [44].
A series of ZnMgO thin-film nanophosphors [45] with varied Zn:Mg ratio has been prepared by chemical bath deposition. ZnMgO films absorb light efficiently in the near UV (330–400 nm) and the emission covers a large part of the visible spectrum. Luminescence enhancement is maximum for 25% Mg. Measured colorimetric coordinates of (0.28, 0.32) when excited by 350 nm light make them suitable for generation of white light in conjunction with near UV LEDs.

**Si/SiO₂ based phosphors.** Chlorine capped silicon colloids luminescence in the wide range between 340 nm and near 700 nm and showed white color with commercial low-intensity UV-lamp exposure [46]. Fumed silica exhibits visible luminescence in the green red region when excited with a UV laser. Recently, white light emission has been reported from SiO₂ glass [47,48] though the origin of luminescence is not yet clear.

**ZnSe nanophosphors.** Organic capped ZnSe nanocrystals can also be used as white light phosphors [49]. Blue emission is attributed to the quantum confinement effect of ZnSe nanocrystals, while the green-red band is ascribed to the radiative deep levels generated by extremely strained surface lattice of the ZnSe nanocrystals. Chen et al have demonstrated the use of organic capped ZnSe nanocrystals as phosphors by coating on an InGaN chip that exhibited a CIE of (0.38,0.41).

**CdSe-ZnS heteronanocrystals.** Unfortunately, a large fraction of atoms are located on or near the surface of nanoparticles because of high surface-to-volume ratio, which cause the surface states that quench the luminescence resulting in low luminance efficiency. In order to conquer such shortcomings, core/shell nanoparticles have been developed and shown dramatic enhancement in the luminance behavior. High luminescence efficiency and stability have been demonstrated for core–shell nanoparticles [50,51].

However, the investigation reveals an increase in the emission intensity followed by a steady decline with the shells thickness [52-55]. It is believed that the decrease in the intensity is due to the strain caused by the lattice mismatch between the core and shell [54]. However, similar behavior has been predicted for a radiative transition at the core/shell interface [54,55].

Magic sized CdS nanocrystals [14] rely on the surface state emission and emit white light which has been referred to “emission by chance”. Recently, core-shell type of multilayer structure has been used. The material and the size of the core and that of shells are chosen such that emission of different colors combine to give white light. White light emission from CdSe/ZnS/CdSe/ZnS onion-like nanocrystals has been demonstrated and has been referred as “emission by design” [38]. It relies upon the combination of orange and blue band-edge emission from the CdSe core and CdSe shell of onionlike NCs with a CdSe core and three shells comprised of ZnS/CdSe/ZnS [56,57].

**Dy³⁺ doped nanocrystals.** There are reports on Dy³⁺ doped materials that can be used as direct white phosphors [58-60]. The GdAl₃(BO₃)₄:Dy³⁺ nanorods with an average diameter of 60 nm show intense emissions centred at 480, 575, and 665 nm upon excitation by both ultraviolet-blue and infrared light, which are associated with the typical transitions of 4F₉/₂→6H₁₅/₂, 4F₉/₂→6H₁₃/₂ and 4F₉/₂→6H₁₁/₂ of Dy³⁺, respectively [58].

A novel white light emitting long lasting phosphor Cd₁₋ₓDyₓSiO₃ is reported [59]. The Dy³⁺ doped CdSiO₃ phosphor emits white light. The phosphorescence can be seen with the naked eye in the dark clearly even after the 254 nm UV irradiation have been removed for about 30 min. In the emission spectrum of 5% Dy³⁺ doped CdSiO₃ phosphor, there are two emission peaks of Dy³⁺, 580 nm (4F₉/₂→6H₁₃/₂) and 486 nm (4F₉/₂→6H₁₅/₂), as well as a broad band emission located at about 410 nm. All the three emissions form a white light with CIE chromaticity coordinates x=0.3874, y=0.3760 and the color temperature is 4000 K under 254 nm excitation. Dy³⁺ doped GAP (gadolinium aluminum perovskite) powder nanophosphors also show photoluminescence consisting...
of a blue band and a yellow band [60]. The yellow to blue intensity ratio of GAP:Dy$^{3+}$ nanophosphors varies from 1.19 to 1.03.

**Other complex systems.** White-light emission has been observed from Bi$^{3+}$ and Eu$^{3+}$ co-doped $Y_4MgSi_3O_{13}$ nanophosphors upon excitation of 350 nm ultraviolet light [61]. It is noted that Bi$^{3+}$ ions can occupy two different $Y^{3+}$ sites and generate different emissions from the $3p_1→1s_0$ transition. The results indicate that $Y_4MgSi_3O_{13}:0.08Bi^{3+}, \ 0.04Eu^{3+}$ are potential nanophosphors for white light-emitting diodes (LEDs) applications. Other materials that can be used for direct white light nanophosphors are $Y_2SiO_5:Ce,Tb$ [62] and Eu$^{2+}$-doped phosphors with nominal composition of $2SrO.MgO.xSiO_2$ [63].

**Summary**

The use of UV LEDs in white light illumination sources requires novel phosphors. A wide band gap material or band gap tuning in the suitable range is required for the materials to qualify as direct white light phosphors. Nanostructures as phosphors appear promising for improving the efficiency of solid state lighting sources. In some cases, though the efficiency is low, it is believed that a particular approach can be fine-tuned to enhance the efficiency.

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Nanostructured Solar Cells

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Abstract

Novel types of solar cells based on nanostructured materials are intensively studied because of their prospective applications and interesting new working principle – essentially due to the nanomaterials used. They have evolved from dye sensitized solar cells (DSSC) in the quest to improve their behavior and characteristics. Their nanocrystals (ca. 10-50 nm) do not generally show the confinement effect present in quantum dots of size ca. 1-10 nm where electron wave functions are strongly confined originating changes in the band structure. Nonetheless, the nanocrystalline character of the semiconductor used determines a different working principle; which is explained, although it is not completely clear so far,. Different solid nanostructured solar cells are briefly reviewed together with research trends. Finally, the influence of the photoelectrode electron-extracting contact is analyzed.

I. Introduction

I.1. Photovoltaic energy imperious need

Humanity faces a highly dangerous environmental crisis caused mainly by the employment of fossil fuels. CO₂ and other gases produced as by-products in their always incomplete combustion are responsible for:

- contamination in cities with a large concentration of motor vehicles and/or non-electric boilers;
- acid rains that threaten life of corals, fishes, forests and other living species;
- the highly worrisome global warming accompanied by all its known devastating effects [1].

At the same time, an oil crisis, which most probably would bring about an economic crisis, must occur in the not so distant future. According to the International Energy Agency (IEA) for several years oil discoveries have been less than annual consumption [2]. This will make impossible to maintain in the future the oil production increasing trend and the so-called peak-oil will come about. This ever increasing demand is caused by new technological needs, population increase and the improvement of living standards in general and particularly, in some developing countries. Energy used per capita is a basic index of living conditions. About three quarters of the world population lives in developing countries and they use less than half of the total energy produced worldwide [3].

Very high oil prices will result in the not so distant future when oil demand surpasses oil production. Some predictions say we have already reached the peak-oil and a great majority says it will be reached before 2020 [4]. These predictions refer to oil from conventional sources which is relatively light oil, easy to extract and therefore, cheaper (cheap oil in the past made possible accelerated technological development). This conventional oil constitutes over 95% of current world oil production. Regarding non-conventional oil, for example from deep-waters, artic or sand-oil, the International Energy Agency (IEA) has warned that worldwide investment in expanded oil production has been considerably less than needed to continue world oil production that is adequate to meet expected world demand[4]. At the present moment, 85% of the energy used by the total population comes from fossil fuels: oil 34.6%, gas 23.4% and coal 27.6% [5]. Oil high prices have
and will increase consumption of natural gas and coal. These fossil fuels will also peak, though later, especially coal - which is much more dangerous and contaminant than oil.

It is urgent to develop a new energy infrastructure to avoid contamination, acid rains and irreversible global warming consequences together with a fuel crisis. Sources for today’s nuclear energy production are non-renewable and also contaminant. Renewable sources of energies like hydro, eolic, geothermal, solar, etc are not only renewable but affect the environment to a much lesser extent. Until recently, practically only hydro could compete in price with fossil fuels. Today the situation is changing in spite that funds for research have been insufficient and much less that those devoted to fossil fuels or nuclear energy[6]. Electricity coming from eolic or photovoltaic energy shows a very rapid growth. Photovoltaic is the fastest growing renewable energy market, specially its “grid-connected” application [7] Direct solar energy conversion to heat also show a significant incremen in certain regions. Among all renewable energy sources, solar energy has by far the greatest potential and the wider distribution in the Planet. It is much larger than the present energy consumption and capable of covering future demands of world population [8] Electricity coming from photovoltaic energy could in the future also substitute present needs of liquid fuels if stored in the form of hydrogen. One must conclude that it is urgent and highly convenient to develop photovoltaic energy.

I.2. Photovoltaic energy brief history

This is a rather recent history, beginning in the 19th Century, though for practical purposes it only begins in the last part of the 20th Century. Curiously, the first demonstration of the photovoltaic effect was observed in a photochemical solar cell, to which category belong not silicon but nanocrystalline dye sensitized solar cells. Alexandre-Edmund Becquerel, a young experimental physicist in France, was only 19 years old in 1839 when he discovered the photovoltaic effect while assisting his father, who was engaged in electrolytic cells work. But it was not until 1953 that the first silicon solar cell was obtained by D. Chapin, C. Fuller and G. Pearson. This 2 cm² cells had an efficiency of 4% [9] This efficiency value was immediately improved to 6% in 1954 as demonstrated by AT&T in Murray Hill, New Jersey [10].

Solar cells development is closely linked to space race between the former Soviet Union and the United States. On October 4, 1957, the USSR successfully launched Sputnik I; world’s first artificial satellite, about the size of a basketball. Soon later, on November 3, 1957, Soviets scientists successfully launched, Sputnik II, with a dog named Laika on board; that became the first living creature in space. United States answer followed few months later, on January 31, 1958, when Explorer I was successfully launched. These three pioneer satellites worked with batteries and carried no solar cells. On March 17, 1958, United States takes the lead in the use of solar cells in space when the satellite named Vanguard I is set in orbit around the Earth. This satellite had four solar cells on its outer hull. Only two months later, on May 15, 1958, Sputnik III, powered with solar cells, is also successfully launched by the soviet. After these successes, solar cells were established as the energy supply for satellites and space laboratories.

The space race is paralleled by a solar cells race toward higher efficiencies in order to reduce weight to be lifted by space rockets. From 1957–1959, Hoffmann Electronics achieves 8, 9 and 10% efficiency and developed the grid contact, significantly reducing the series resistance of the device [10]. In 1960 they jumped to 14% efficient silicon solar cells, mainly used for satellite technology and space applications. In 1970 Zh. I. Alferov, V.M. Andreev and a team at Ioffe Institute in Leningrad, USSR (today St. Petersburg, Russia) demonstrated the first high-efficiency GaAs heterostructure solar cell [11].

Interest in solar cells for terrestrial uses rouse because of the first oil crisis in the 70’s. As early as 1974, Japan, a country that has no oil of its own, formulated its Project Sunshine. Worldwide several research institutions were devoted to photovoltaic and solar cells research in this period. In 1980 the One thousand solar roof program started in Switzerland [10]. Highly efficient AlGaAs solar cells developed for space applications were demonstrated for the first time for terrestrial applications in 1981 using solar light concentrators at Ioffe Institute [12]. In 1985, M. Green at the
University of New South Wales, Australia, broke the 20% efficiency barrier for silicon solar cells under one sun; after developing one year earlier with S. Wenham the LGBC solar cell (laser-grooved buried-contact) [10].

Solar cells that absorb the light more effectively allowing the use of thin films were also developed, though not as successfully as silicon solar cells. CdTe thin film solar cell with 6% efficiency was reported as early as 1966 [13]. In 1973, first solar powered residence in Delaware, USA, used Cu2S solar cells and in 1980 the first thin-film Cu2S/CdS solar cell with efficiency higher than 10% was reported [14]. In 1998 Cu(InGa)Se2 thin-film solar cell reached 19% efficiency [14] comparable with multicrystalline silicon.

In 1991 M. Grätzel and collaborators report the dye-sensitized photoelectrochemical solar cell (DSSC) based on nanocrystalline TiO2 [15] and in 1996 more than 10% efficiency is achieved [16]. From these early starting points in the last century, each type of solar cell has continued its development through scientific and technological research with the aims of increasing efficiency, increasing life time and decreasing costs. We will refer in Sections II and III to DSSC and nanostructured solar cells evolved from them.

I.3. Advantages of DSSC and nano-solar cells evolved from them

The main advantage of DSSC is its low cost together with a higher than 10% efficiency; unfortunately, life-time is its Achilles’ heel. This low cost is essentially due to its different working principle determined by its nanostructured nature. As will be seen in the next Sections, they do not require high purity materials or highly clean rooms for their fabrication. Rather simple technologies can be used at room temperature or not very high temperature. This means less expensive technological equipments and much less energy used in their fabrication. It must be mentioned that their flexible options imply less weight and allows for a wider range of possible uses. DSSC appearance and possible colors favor architectural and other applications where besides producing electricity, expensive decorative materials are substituted. Even though the use of photovoltaic energy is probably the most environmental-friendly form of renewable energy, materials and reagents used in their fabrication could have a small (though avoidable) contaminant effect. This could also be true when solar panels become old and have to be discarded (also avoidable through recycling). DSSC are the less contaminant of all different types of solar cells because they are based on innocuous materials.

Feltrin and Freundlich [17] estimate energy production limits for several mature photovoltaic technologies based on available global material reserves. DSSC stand out in that material shortages would not prevent their scale-up even to the terawatt range if the Sn conducting oxide contact is substituted.

Finally, regarding future market projection W. Hoffmann [18], president of the European Photovoltaic Industry Association (EPIA), predicts that by 2030 DSSC and “new concepts” solar cells production will surpass crystalline silicon (mono- and poly-) production.

II. From conventional to nano in photovoltaics

In order to understand the advantages and opportunities of nanostructured materials in “new concepts” solar cells one must recall traditional solar cells working principle for comparison.

II.1. How do conventional solar cells work?

II.1.A. The p-n junction

A traditional solar cell, as a semiconductor diode, is usually composed of two semiconductors of different conductivity type in contact giving rise to the so-called p-n junction. Semiconductors with n-type conductivity are good electron conductors and p-type semiconductors are good hole conductors (a positive charge conductor). To explain how they work let us use a simplified energy levels scheme as represented in Fig. II.1. Widely used silicon solar cells and other thin films solar cells in the market today are based on a p-n junction.
Energy levels for the n- and p-type semiconductors with respect to vacuum energy are represented in Fig. II.1a when they are not in contact. The highest energy value of the valence band and the lowest energy value of the conduction band are marked with band initials; their difference is equal to the energy bandgap, $E_G$. The Fermi energy level $E_F$ (equal to the chemical potential) has an occupation probability of practically one half. (Of course, if it coincides with a forbidden energy level, the value of the density of states is zero and anyhow the occupation will be zero). The number of electrons at a given energy $n(E)$ is given by:

$$n(E) = D(E) \frac{1}{\exp\left(\frac{E - E_F}{KT}\right) + 1}$$

(1)

$D(E)$ is the density of electronic states (DOS) and $f(E)$ is the Fermi-Dirac distribution function. Due to the abrupt decrease of the Fermi-Dirac probability function at $E_F$ (it is practically a step function) most of the states with energy above $E_F$ are empty and most of the states with energies below $E_F$ are full. In n-type semiconductors states with energy very close to the bottom of the conduction band (shaded area in Fig. II.1a) are occupied. In p-type semiconductors states with energy very close to the top of the valence band are empty. Accordingly, the Fermi energy level will be closer to one or the other band in each of the two semiconductors. Nonetheless, there are both types of charge carriers in both types of semiconductors. In n-type semiconductors, electrons are called majority carriers and holes are called minority carriers and vice versa for p-type semiconductors. Notice that when apart, states with equal energy in each type of semiconductor do not have the same occupation probability.

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**Fig. II.1** The p-n junction of traditional solar cells. a. Spatial dependence of energy levels corresponding to the top of the valence band VB, the bottom of the conduction band CB and Fermi energy levels $E_F$ (or chemical potential) of n- and p-type semiconductors. b. Same as a. but after the two semiconductors are brought into contact.
They are shown in contact in Fig. II.1b. The Fermi levels will line up so that the occupation probability of states with equal energy would be the same in both semiconductors. (The Fermi level defines the position of the Fermi-Dirac distribution function; the function moves as a whole with the Fermi level giving the occupation probability for all energies). This implies that electrons in the conduction band of the n-type semiconductor will move to the p-type semiconductor to occupy empty lower energy states; i.e., the system tends to an equilibrium state of minimum energy. Therefore, there will be a charge transfer from one to the other. Charge movement from one semiconductor to the other causes that a narrow region in the n-type semiconductor becomes positively charged and a narrow region in the p-type semiconductor becomes negatively charged. These regions define the p-n junction and they form the so-called depletion region where an electric field exists similar to the situation in a parallel-plate capacitor.

II.1.B. Origin of the photocurrent in p-n junction solar cells

If the junction is illuminated with photons of energy higher than the bandgap, electron-hole pairs will be created by photon absorption. If they are generated in the depletion region, these carriers will be separated by the electric field present: electrons toward the n-type side and holes to the p-type side according to the electric field direction. If photons create electron-hole pairs close enough to the depletion region, they can diffuse to this region and contribute also to the photocurrent. This is important because usually the depletion region is very narrow and the majority of electron-hole pairs are created outside it (in the n- or p-type bulk material). The electron-hole pair concentration created by light practically does not change the majority carriers concentration but the much smaller minority carriers concentration changes significantly with respect to the equilibrium value that corresponds to a given temperature. Minority carrier diffusion currents toward the depletion region originate, i.e., currents due to light-generated carrier concentration gradients in the device. These tend to recombine with majority carriers so it is very important to have a big diffusion length (average distance traveled before recombination). Diffusion length value decreases because of impurities and defects present in the semiconductor which favor recombination. Therefore, purity and crystalline perfection contribute to allow more minority carriers to reach the junction where the electric field exists; i.e., to improve efficiency. This implies using materials with high purity and lack of structural defects. These characteristics are also required for obtaining an n-type or p-type semiconductor with a given value of conductivity, i.e., a given value of doping impurity concentration. The several technological processes needed to guarantee all this are performed by highly qualified personnel at high temperatures and in especially clean environments; all of which contributes to increase costs.

From the continuity equations it is possible to obtain minority carrier concentrations in the n-type and p-type regions [19]:

For electrons in the p-type region:

\[ D_e \frac{d^2n_p(x)}{dx^2} - \left( \frac{n_p(x) - n_0}{\tau_e} \right) + G(x) = 0 \]  

(2)

For holes in the n-type region:

\[ D_h \frac{d^2p_n(x)}{dx^2} - \left( \frac{p_n(x) - n_0}{\tau_h} \right) + G(x) = 0 \]  

(3)

The first term represents the change in minority carrier concentration per second due to diffusion caused by concentration gradient; the second term represents the number of carriers that are lost by recombination per second and the third term represents the number of carriers generated by the incident radiation per second. \( G(x) \) depends on light absorption coefficient, the solar cell geometry and radiation intensity; i.e., the number of electron-hole pairs created by the incident radiation depends on the number of incident photons. From the solutions of equations (2) and (3) it is possible to obtain the diffusion currents for the minority carriers:
\[ J_{n}^{\text{diff}} = -eD_{e} \frac{dn_{p}(x)}{dx} \] (4)
\[ J_{p}^{\text{diff}} = -eD_{h} \frac{dp_{n}(x)}{dx} \] (5)

The total current will be the sum of these diffusion currents plus the contribution of drift currents originated by electron-hole pairs created by light absorption in the depletion region where an electric field exists.

\[ \bar{J} = J_{n}^{\text{diff}} + J_{p}^{\text{diff}} + J_{n}^{\text{drift}} + J_{p}^{\text{drift}} \] (6)

II.1.C. Origin of the photovoltage in p-n junction solar cells

For a constant radiation value, a steady state is reached for which carrier concentrations in the regions where electron-hole pairs are created by light differ from those corresponding to the semiconductors temperature and doping. For not intense incident radiation, e.g. solar light intensity, concentration of majority carriers practically does not change but minority carrier concentration changes significantly. A quasi-equilibrium situation is reached for which quasi-Fermi energy levels (QFL) are defined to give carriers distribution. Since majority carriers concentration practically does not change, the QFL of electrons in the n-type semiconductor \( F_{n} \) and of holes in the p-type semiconductor \( F_{p} \) will practically be the same as their equilibrium value \( E_{F} \); although they will no longer line up as in the dark. On the contrary, QFL for electrons in the p-type semiconductor and for holes in the n-type semiconductor will be very different in the region where photons are absorbed. Energy bands in an illuminated p-n junction are represented in Fig. II.2 (surface recombination is not considered) QFL for majority carriers, practically equal to thermal equilibrium Fermi level energies, are also shown. The energy available to do work in the external circuit is limited by the energy difference between the two Fermi levels in the n- and p-side, \( F_{n} - F_{p} \). This difference, caused by the incident radiation, is the driving force that, when the circuit is externally connected, will cause movement of electrons through the connecting circuit from higher energy states in the n-side to lower energy states in the p-side.

**Fig. II.2** Spatial dependence of energy levels in an illuminated p-n junction. Carrier concentrations no longer correspond to those of thermal equilibrium and it is necessary to define the quasi-Fermi energy levels \( F_{n} \) and \( F_{p} \).
Electrons decrease their energy in going from the n-side to the p-side through the external circuit and this energy can be transformed to work in the external load. At open-circuit, this difference $F_n - F_p$ determines the open-circuit photovoltage, $eV_{oc} = F_n - F_p$.

**II.1.D Efficiency in p-n junction solar cells**

In a solar cell radiation energy is converted to useful power. This power is given by the product of the photocurrent $I_{\phi}$ flowing from the solar cell multiplied by the voltage difference across its terminals or photovoltage $V_{\phi}$. For a given light intensity, $I_{\phi}$ and $V_{\phi}$ change according to the external load, $R_L$. A very important characteristic of a solar cell is the dependence of $I_{\phi}$ vs $V_{\phi}$ as $R_L$ changes (the illumination intensity remains constant). This dependence is called the volt-amperic characteristic or I-V curve. It determines the values of photocurrent $I_m$ and photovoltage $V_m$ that correspond to the maximum possible power $P_m$ that the solar cell can give. In a solar cell the I-V curve is given by the expression [19]:

$$I = I_o \left( \exp \left( \frac{-eV_{\phi}}{nKT} \right) - 1 \right) - I_{\phi}$$

(7)

The first term corresponds to the known I-V dependence for p-n junctions, where $I_o$ is the saturation current; $n$ is the so-called ideality factor (theoretically $1 < n < 2$); $K$ is the Boltzmann constant and $T$ the temperature. Of course, an analogous expression holds for the current density. A solar cell I-V curve is shown in Fig. II.3. As explained before, it is clear from Fig. II.2 that electrons in a solar cell flow in the external circuit from the n-side to the p-side; i.e., as they do for a negatively biased diode. In spite of this, even though the current is negative by usual convention, photocurrent in solar cells is considered positive for I-V graphs (as shown in Fig. II.3 for a constant light intensity). The current corresponding to the short-circuit condition, $R_L=0$, is called short-circuit current $I_{sc}$ and the voltage corresponding to open-circuit, $R_L=\infty$, is called open-circuit photovoltage $V_{oc}$. Taking into account that for open circuit conditions, $I=0$ and $V_{\phi}=V_{oc}$, it follows from Eq. (7) that:

$$V_{oc} = \frac{nKT}{e} \ln \frac{I_o}{I_{\phi}}$$

(8)

Since $P=IV$, the maximum power that can be extracted from a solar cell $P_m$ at a given incident light intensity corresponds to the maximum value of the IV product (see Fig. II.3). The maximum efficiency is given by:

$$\eta_m = \frac{P_m}{P_{in}} = \frac{I_m V_m}{P_{in}}$$

(9)

where $P_{in}$ is the incident radiation energy per second.
Fig. II.3 I-V characteristic for a solar cell. The product IV=P is also shown as a function of photovoltage. The ratio of the two rectangles gives the fill factor FF

The fill factor FF, is the ratio of the areas of two rectangles defined by the points $I_m, V_m$ and $I_{sc}, V_{oc}$ with the coordinates axis (see Fig. II.3). FF characterizes the shape of the I-V curve and it is related to its efficiency:

$$FF = \frac{I_m V_m}{V_{oc} I_{sc}} = \frac{P_m}{V_{oc} I_{sc}}$$

(10)

Therefore:

$$\eta_m = \frac{V_{oc} I_{sc} FF}{P_{in}}$$

(11)

If light intensity changes, a family of I-V curves will be obtained corresponding each to a given light intensity. In order to compare solar cells, the I-V curve that is taken as reference is that corresponding to what is defined as 1 sun intensity or Air Mass 1.5 (AM1.5) equivalent to 100 mW/cm$^2$ of solar light; i.e., 1KW/m$^2$.

The efficiency of a p-n junction solar cell relies on carriers that do not recombine before being separated, i.e., that do not give up the energy acquired from photons as heat in their interaction with the transporting medium. Notice that in polycrystals, grain boundaries are populated with defects and adsorbed impurities which act as traps that favor recombination and conspire against efficiency in traditional solar cells. Therefore, as crystal size decreases, recombination centers concentration increases and efficiency decreases. On this basis, it is a wonder the efficiency obtained for nanocrystalline solar cells. Necessarily they have to be based on different working principles.

II.2. Why nanomaterials for solar cells?

In a quest to obtain higher-efficiency, more stable, longer lived and cheaper solar cells, different types of nanostructured solar cells have come up after O’Reagan and Grätzel’s first report in 1991 [15] [19] To realize the advantages of using nanostructured materials in solar cells, it is convenient to understand how dye sensitized solar cells work (DSSC, also sometimes called Grätzel’s cells or DSC).

II.2.A. Component parts of a DSSC

A DSSC consists of the following parts as shown in Fig. II.4: the electron-extracting electrode; the dye-sensitized, mesoporous, nanocrystalline TiO$_2$ penetrated by the electrolyte; and the counter electrode.
conducted glass counter-electrode

contact

sensitized

TiO₂

contact

sealant

conducted glass photoelectrode

assembled solar cell

**Fig. II.4** Component parts of a DSSC. The two electrodes are fixed together by the sealant that serves to contain the electrolyte and to avoid contact of the counter electrode with the TiO₂.

*The electron-extracting electrode* is usually a transparent conducting oxide (TCO) on glass in order to allow light penetration from that side. Surface resistivity of TCO used is between 8-15 Ω/square. The conducting oxide more frequently used is SnO₂:F (known as FTO) [20] It behaves better than ITO (In₂O₃:Sn) whose conductivity decreases significantly during the thermal treatment of TiO₂ film at ca. 500°C. FTO is known to be thermally stable above this temperature. Studies are conducted to employ other substrates; especially for using high-throughput industrial roll-to-roll production of large area, flexible DSSC. Research includes conducting transparent plastic sheets [21], as well as non-transparent metallic foils with light penetrating from the other side [22].

TiO₂ is the *mesoporous, nanocrystalline, wide bandgap metal oxide* used in DSSC for best results (nanocrystalline anatase, bandgap E₉=3.2 eV). The TiO₂ layer thickness is typically between 5-15 μm and nanoparticles average size ranges from 15–30nm [23]. The porosity is approximately 50% [24], which together with particle size give rise to a real area or roughness factor of approximately 100-fold area enhancement per μm. This is very important to increase light absorption by the dye monolayer attached to the TiO₂ but also in determining a different working principle as will be discussed in II.2.B. There has been interest in replacing TiO₂ with other metal oxides such as SnO₂ [25] [26], SrTiO₃ [27] and ZnO [28]-[31]. Efficiencies obtained using TiO₂ have not been improved, even when the SnO₂ electrode is coated with a wide bandgap metal oxide such as MgO [32].

*Dyes or sensitizers* are chemisorbed onto the surface of the TiO₂. Sensitizers that have given best results so far are ruthenium bipyridyl complex with the general formula RuL₅L₅SCNₓ, where L and L’ are polypyridyl ligands. The 3 more frequently used complex are known by their commercial names: red dye N-3, black dye N-749 and Z-907. The last two absorb a wider spectral range than the red dye N-3. Efforts have been made to find alternative less expensive sensitizing compounds. Natural dyes have been studied [33], as well as sensitizers based on metal-free organic dyes [34], [36]. Research reports on sensitizers are very abundant in the literature. Different goals have been and are being pursued as: improved molar absorption coefficients; longer-term stability; extension of the spectral absorption range; and sensitizers with different colors for special applications. It has...
also being reported [37] that the dye plays an important secondary role in passivating the semiconductor oxide surface and inhibiting the recombination with acceptors. The suitability of ruthenium bipyridyl complex then depends on both: the ligand and the nature of the oxide (TiO₂).

The electrolyte plays an essential role in DSSC [38]. The electrolyte typically used consists of the redox pair iodide-triiodide (I⁻/I₃⁻) dissolved in an organic solvent. No other redox pair has been found to give higher efficiencies than I⁻/I₃⁻ even though there has been efforts to find less corrosive redox pairs, with lower light absorption and a more convenient redox potential energy [39][40]. DSSC with highest efficiency employ a low-viscosity solvent, usually acetonitrile; but these electrolytes are not appropriate for achieving the best long-term stability characteristics, especially for outdoors. There are several reports regarding liquid electrolytes for DSSC [41]-[43] though there is no optimum solution. Solvent-free DSSC constitute an important direction of research and different solutions are studied for replacing the volatile liquid electrolyte with solid or quasi-solid hole conductors, such as p-type semiconductors, ionic liquid electrolyte and polymer electrolyte. It must be mentioned that in order to increase efficiency, liquid electrolytes also contain additives such as 4-tert-butylpyridine (TBP) or N-methylbenzimidazole (NMBI) [44] although their exact mechanism of action is not firmly established [45].

The counter-electrode is normally a conducting glass with a small amount of platinum adsorbed on the conducting-thin-film oxide that acts as catalyst in the I₃⁻ reduction; i.e., it facilitates electron exchange of the counter-electrode with the iodide/triiodide redox couple. The TCO is used as electrode because the redox couple I⁻/I₃⁻ corrodes many metals. Graphite [46][47], carbon materials [48]-[50] and polymers [51]-[53] have been employed as counter electrode although lower efficiencies have been obtained. These materials have the advantage that they are stable to corrosion and that they can be employed at low cost in roll-to-roll fabrication of flexible DSSC.

A hot melt polymer sealant serves to join together both electrodes. It is shaped to surround the sensitized TiO₂ (see Fig. II.4). The sealant is 25-50μm thick and it also serves to avoid contact of the sensitized TiO₂ with the counter-electrode.

II.2B. How do dye sensitized solar cells work?

In a traditional semiconductor-electrolyte interface a junction also forms (a depleted region where an electric field exists). It is due to charge transfer between the two contacting materials and it occurs in an analogous way as described before for the p-n junction; it is very similar to the semiconductor-metal junction produced by the contact of these two types of materials. In DSSC, nanocrystals are surrounded by electrolyte. According to calculations the electric field in the TiO₂ nanocrystals-electrolyte interface is very small; it is not capable of separating charges as in conventional solar cells [54] Because of nanocrystals size then, DSSC must be based on a different working principle if compared with traditional solar cells associated with the absence of macroscopic electric field (notice that nanocrystals ca. 10-50 nm do not show confinement effect). It has been discussed to a great extent in the literature whether a macroscopic field to drive carriers toward the contact exists or not. There is a lot of evidence and it is widely accepted now that such field does not exist and that carriers move by diffusion, i.e., due to charge carriers concentration gradients in the device [55]-[59].

a. Origin of the photovoltage in DSSC

In the electrolyte there are allowed energy ranges for reduced and for oxidized species. Their Gaussian probability distribution is exemplified in Fig. II.5. Both distributions cross at the energy origin of the photovoltage in DSSC is ½. This can be thought of as a “Fermi level” for redox species and it is known as the redox potential E_{redox}.
**Fig. II.5** Energy levels in a DSSC under illumination. CB, conduction band. VB, valence band. $S^*$, electron excited state in the dye. $S_0/S^*$, electron HOMO state in the dye: $S_0$ is the ground state and $S^*$ the state without an electron. The Gaussian distributions of iodide/triiodide ($I^-/I_3^-$) species become equal at the redox potential $E_{\text{redox}}$ that is practically equal to the Pt Fermi energy. The following processes take place: 1. An electron in the dye absorbs a photon and occupies the excited state $S^*$. 2. The highest probability of the electron in the excited state $S^*$ is to be injected to lower energy states in the nanocrystalline TiO$_2$ conduction band. 3. The electron is transported in the TiO$_2$, in the TCO, in the external circuit, arriving finally at the counter electrode. 4. The electron passes to the electrolyte reducing a triiodide ion to iodide. 5. The electron is returned to the dye by an iodide ion that oxidizes to triiodide.

In the dark all “Fermi energies” line up; as explained before for p-n junctions. When the device is illuminated, electrons in the dye absorb photons and occupy energy levels in the dye which lie above the TiO$_2$ conduction band empty states (process 1 in Fig. II.5). Electrons are injected on a subpicosecond timescale [60] from the dye to the TiO$_2$ conduction band states that have lower energies (process 2 in Fig. II.5). This process competes and it needs to be faster (higher probability) than the excited state decay, typically 100 ps – 1 ns [61]. A quasi equilibrium state is reached for a constant light intensity, i.e., a quasi-equilibrium excess electron concentration appears in the TiO$_2$ conduction band and the electron distribution is no longer described by the Fermi energy but by the quasi-Fermi energy. In the dark, because of its wide bandgap, TiO$_2$ is practically an isolator; free electron concentration at room temperature is negligible. Therefore, majority carrier concentration increases due to concentration of electrons injected from the dye and QFL $F_n$ is significantly different from the Fermi energy level in the dark. If the external circuit is open and no current flows, the open-circuit photovoltage $V_{oc}$, is given by the difference between the TiO$_2$ electrons QFL and the electrolyte redox potential:

$$eV_{oc} = F_n - E_{\text{redox}} \quad (12)$$

The oxidized dye left behind by the electron injected to the TiO$_2$ ($S^+$ in Fig. II.5) is rapidly regenerated by the electrolyte (process 5 in Fig. II.5). This process is essential in DSSC. When trying to substitute the $I^-/I_3^-$ redox pair, it has been demonstrated that the lower efficiencies obtained were related to a slower dye regeneration rate [62]. $I^-$ oxidizes to $I_3^-$ while at the counter-electrode $I_3^-$ is reduced to $I^-$ (process 4 in Fig. II.5). Therefore, $I_3^-$ is produced at the photoelectrode.
and consumed at the counter-electrode (it is often considered as the “hole carrier” by analogy with traditional solar cells). \( I^- \) is produced at the counter-electrode and diffuses to the photoelectrode. Notice that equilibrium hole concentration in the TiO\(_2\) does not change, contrary to what happens in traditional solar cells. Light is absorbed by the dye and absorption by the TiO\(_2\) is negligible because it only absorbs photons with energy higher than \( E_C=3.2 \text{ eV} (\lambda<387 \text{ nm}) \). The absence of holes in non-equilibrium avoids electron-hole recombination in the semiconductor. This is a situation very different to that existing in p-n junctions where minority carriers must diffuse to the depletion region before recombining. As said before, pure and defect-free materials are optimum for conventional solar cells. That light is absorbed in one medium and electrons are transported in other different media determines the absence of minority carriers in non-equilibrium. This is the reason why semiconductor purity is not crucial in DSSC; there is no need to avoid impurities and defects that favor recombination.

b. Origin of the photocurrent in DSSC
If the two electrodes of the device are joined through an external circuit, electrons at higher energies in the TiO\(_2\) will travel to the counter-electrode through the external circuit giving rise to a photocurrent (process 3 in Fig. II.5). The energy that electrons can give, i.e. that can be converted to work in the external circuit, is equal to the energy difference between the electron QFL and the electrolyte redox potential (see Fig. II.5). The QFL position depends on light intensity but also on the external load. As the external load is changed for constant incident radiation intensity, a dependence of photocurrent on voltage is obtained. DSSC show I-V and P-V curves similar to those of conventional solar cells (see Fig. II.3). Eq. 7 is equally valid for DSSC. Since DSSC photocurrent dependence on photovoltage is given by expression (7), expressions (8) to (11) will follow also; DSSC efficiency is equally obtained from the I-V dependence. Notice that Eq. 8-11 are valid for both but Eq. 6 is not because no drift currents exist in DSSC. Efficiencies higher than 11% at one sun illumination have so far been obtained with DSSC [63].

II.2.C. Implications of nano-structure in DSSC
Nanocrystals in DSSC (in the range 10-50 nm) do not generally show the confinement effect present in quantum dots of size ca. 1-10nm. In these electron wave functions are strongly confined, so that the electron energy levels are discrete and their separation is determined by the crystal size. Nonetheless, the nanocrystalline character of the semiconductor in DSSC determines a different working principle. Let us summarize the implications of having a nano-sized three-dimensional (3D) structure in DSSC.

1. Light absorption by the sensitizer or dye is enormously enhanced since the real internal area of the semiconductor-oxide with the attached dye is orders of magnitude larger than the visibly apparent area.
2. It allows the electrolyte to penetrate and surround the semiconductor-oxide nanocrystals. Therefore, a 3D semiconductor-electrolyte interface is formed. It is not a 3D heterojunction, i.e., there is no macroscopic electric field at this 3D interface, so only diffusion current exists. There are no drift currents as in traditional solar cells.
3. It allows charge carriers to be transported in media different from the medium in which photon absorption creates them.
4. It is a majority carrier device. There are no excess minority carriers in the oxide-semiconductor where electrons are transported. Electron-hole recombination does not play an important role in decreasing efficiency as in traditional solar cells. Therefore, no highly perfect and highly pure materials are required. This leads to the most important characteristic of DSSC: they are cheaper than traditional solar cells while having efficiency above 10%. This is not only because raw materials required are cheaper but also technological procedures: very high temperature processes are not needed; clean-room conditions are less necessary (high purity materials are not employed); technological equipment is not as expensive.
Notice that the electrolyte creates a perfect 3D interface because it can penetrate very well the pores and interstices. This is a great advantage of the liquid electrolyte. But, on the other hand, a perfect seal has not been accomplished; i.e., a sealant resistant to the highly reactive electrolyte that
prevents leakage and/or evaporation of the solvent for several years. Also permeation of water or oxygen molecules that react with the electrolytes worsens cell performance. Therefore, a great disadvantage of DSSC is that they do not last long due to electrolyte and dye degradation. They have passed 1000h stability test at 80°C in the shelf maintaining 94% of its initial performance (efficiency value \( \eta \geq 6\% \)) at one sun illumination and 1000h at 55°C in a solar simulator (100 mW cm\(^{-2}\)) [64]. (Silicon solar cells in the market today last over 20 years.)

II.3. Other nanostructured solar cells

II.3.A. Solid and quasi-solid sensitized solar cells (SSSC)

Difficulties caused by the liquid electrolyte in DSSC has motivated research to replace it with solid or quasi-solid hole conductors, such as ionic electrolytes, p-type semiconductors or polymers. A brief review follows of some published reports on solid nanostructure sensitized solar cells (SSSC).

a. Ionic liquid electrolytes

Ionic liquids constitute the source of both, the redox pair and the solvent. Although most of them are in the liquid state at room temperature, they have good chemical and thermal stability, as well as negligible vapor pressure; thus decreasing problems encountered with organic solvents.

Several ionic liquid electrolytes have been reported while imidazolium compounds have been the most frequently employed:
- methyl-hexyl-imidazolium iodide (MHImI) [65]
- 1-methyl-3-propylimidazolium iodide (PMII) [65]
- 1-dodecyl-3-methylimidazolium iodide (C12MImI) which is an ionic liquid crystal [66]
- 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMIm-TFSA) [67]
- 1-ethyl-3-methylimidazolium tetrafluoroborate(EMImBF4) [68]
- 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) [69]
- trialkylsulphonium iodides, such as (Et2MeSi), (Bu2MeSi), and (Bu2EtSi) [70], [71]

High viscosity imidazolium iodides have yielded high stability cells with efficiencies around 6%. Quasi-solid and solid electrolytes with low ion mobility and low conductivity (associated with medium viscosity) represent an obstacle for developing ionic electrolyte SSSC with high conversion efficiency. Some polymers [72], [75], gelators [76]-[78], and composites [79]-[81] have been used as framework materials to solidify ionic liquid-based electrolyte; they also favor triiodide/iodide diffusion.

An outstanding result has been obtained with the lower-viscosity 1-ethyl-3-methylimidazolium selenocyanate (EMISeCN), a SeCN\(^{-}/(SeCN)\(^{-}\) based ionic electrolyte. Power conversion efficiency ca. 8% has been achieved for SSSC with EMISeCN under AM 1.5 sunlight [82].

b. p type semiconductors

High band-gap inorganic semiconductors have been used as hole conductors to replace the liquid electrolyte. Technologically this is a much harder task than with liquid electrolytes. It must be guaranteed that the hole conductor penetrates pores all along the thickness of the mesoporous TiO\(_2\) in order to contact the sensitizer but it must not contact the electron-extracting conducting electrode. CuI was the first p-type semiconductor to be used in a SSSC [83] [84]. These CuI SSSC are not very stable [85][86][87]. In trying to improve the stability of these CuI-based SSSC, MgO capped TiO\(_2\) [88], [89] has been used. Also incorporation of small quantity of 1-methyl-3-ethylimidazolium thiocyanate (MEISCN) improved the stability [90] and 3.8% efficiency was obtained [91].

Other p-type semiconductor used as hole conductor is CuSCN. It has been found to give more stable and durable SSSC but efficiencies obtained are lower than with CuI [85], [92]-[95].

NiO has been reported as hole conductor in SSSC [96], [97], as well as, CuAlO\(_2\) [98].Complete pore filling represents a problem if available fabrication techniques were to be used for wide-bandgap p-type oxides.

Organic p-type semiconductors are used as substitutes of inorganic ones for different devices in microelectronics and optoelectronics. They have also been studied as hole conductors in SSSC [99] [100], [101]. Efficiency values of 3.2% have been obtained using 2,2',7,7'-tetrakis(N,N-di-p- methoxyphenyl-amine)9’90-spirobifluorene (spiro-OMeTAD) [102]. There are several organic
hole-conductors that have been utilized: pyrrole or polypyrrole [103],[104]; thiophene and polythiophene [105] [106]; poly(3,4-ethylenedioxythiophene, PEDOT [107], [108]; the polyanilines (PANIs) [109], [110].

**c. Polymer electrolytes**

Polymer electrolytes have the advantages of relatively high ionic conductivity and easy solidification. They have been used before in lithium batteries and in redox type laminated supercapacitors. In SSSC the polymer plays the role of the organic solvent in DSSC; the $\Gamma/I_3^-$ redox couple is used dissolved in the polymeric medium [111]. Polymerization must occur in the presence of iodine and at an adequate temperature for the dye not to decompose. The two polymers that have been more frequently used in polymer electrolytes for SSSC are poly(ethylene glycol) (PEO) [112]-[114] and poly(epichlorohydrin-co-ethylene oxide), Epichlomer-16 [115]-[117]. Studies continue to improve results obtained with electrolytes based on these polymers, as well as on other polymers [72],[73], [118]- [123].

**II.3.B. Extremely thin absorber (eta) solar cells**

This solar cell type is similar to the p-type semiconductor SSSC. The difference is that also the sensitizer is replaced by a semiconductor. The eta solar cells consist of an extremely thin light-absorbing semiconductor sandwiched between two transparent, highly interpenetrated, nanostructured semiconductors – an n-type and a p-type [124]. Nanostructure wide-bandgap mesoporous oxide semiconductors are used also in eta solar cells, mainly TiO$_2$. Good coverage of the nanostructure electrode by the extremely thin film absorber, as well as, the filling of the pores with the hole-transporting semiconductor is essential for device efficiency. The absorber must be extremely thin so that electron-hole pairs are created by photons next to the wide-band gap semiconductors or extremely close; i.e., so that electron-hole pairs do not recombine before been injected to the wide-bandgap semiconductors. Different narrow bandgap semiconductors have been proposed as light absorbers like CdTe [125], CdSe [126], CuO [127], CuInS$_2$ [124][128]. Several wide bandgap semiconductors have been studied as hole conductors, e.g., CuI [129], CuSCN [130], [131], NiO [132], CuAlO$_2$ [133]. Efficiency so far is below 4% [134],[135].

**II.3.C. Other trends in the development of nanostructured solar cells**

DSSC efficiency value of ca. 11% is acceptable if it were accompanied by solar cell long life. As mentioned before, the very reactive liquid electrolyte plus dye degeneration attempt against it. SSSC and eta solar cells show higher stability in general but lower efficiency. Charge transport in their respective hole conductors is not as efficient as in the electrolyte; either because of the viscosity of the solvent if ions are transported (ionic and polymer SSSC) or the poor pore filling and contact in the case of electronic conductivity (p-type semiconductor SSSC and eta solar cells). These problems lead to incomplete dye regeneration and low charge generation efficiencies [136]. An appropriate morphology of the porous wide-bandgap n-type semiconductor (TiO$_2$ most frequently) can help to minimize these difficulties. Therefore, different structures are been studied like nanorods [137], nanowires [138], electrospun TiO$_2$ [139] and nanotubes [140]-[142]. All cases may ease penetration of the hole conductor in the mesopores and its contact with the sensitizer.

At present studies of quantum dots as sensitizers are being conducted. The energy bandgap value depends on quantum dot size; so the optical absorption spectrum can be tailored to obtain different color solar cells. Besides, they may have a large extinction coefficient which implies good light absorption efficiency. Different semiconductors with energy bandgap adequate for absorbing a significant part of the solar spectrum have been studied: CdSe [143]-[145]; CdTe [146], [147]; PbS [148],[149]; and CdS, that although it has a less appropriate bandgap value, it nicely renders nanocrystals of controlled size [150]-[152].

Another trend we will examine in the next section is the use of double layer TiO$_2$ structures to avoid the recombination of electrons in the TCO with acceptor species in the electrolyte, as well as, to improve electrical contact of the TiO$_2$ with the TCO.
III. The electron-extracting contact

In traditional solar cells, ohmic metal-semiconductor contacts used to extract photogenerated carriers are very important. In DSSC not much attention has been given to electrical contact between the TiO$_2$ and the conducting glass (TCO) [153], [154], which is used instead of a metal contact to extract electrons. In Fig. II.5 we must look in more detail to what happens between process 2 and 3, i.e. to electron transfer from the TiO$_2$ to the TCO. In this TiO$_2$-TCO interface two loss mechanisms can be present: First, recombination of electrons in the TCO with species in the electrolyte. Since the TiO$_2$ is porous, the electrolyte can penetrate and contact the TCO allowing this recombination to occur. Second, a barrier exists at this interface due to differences in oxides work functions and affinity values [154]-[155]. Defects at this interface would affect this barrier. Therefore, contact resistivity could be affected. Conducting oxide type (ITO, FTO, etc), TiO$_2$ crystal structure and morphology, as well as, the technology used when forming the TiO$_2$/TCO contact, should influence electron extraction efficiency at the TiO$_2$-TCO interface. For example, a different electrical contact to the TCO is to be expected according to the TiO$_2$ porosity (electron recombination with the electrolyte changes) and adherence (contact resistivity plus electron recombination with the electrolyte change). Layers obtained by “doctor blading” a nanocrystalline TiO$_2$ suspension are porous as required but they do not adhere so well as sprayed films which are not nanocrystalline, for example. The use of TiO$_2$ layers to block electron recombination (TCO-electrolyte) has been proposed and studied as a way to reduce electron losses and increase cells efficiency [155]-[157]. A thin and dense TiO$_2$ film is placed in contact with the transparent conducting glass (TCO) underneath the porous layer. These are called blocking layers and only TCO-electrolyte recombination has been considered regarding the two mentioned loss mechanisms.

III.1 TiO$_2$-TCO interface

We have characterized electron extraction as a whole by modeling and fitting experimental solar cell spectral quantum efficiency, also called IPCE (incident photon to current efficiency). To do this, we use unsensitized photoelectrodes [153] These structures are no longer solar cells because they absorb a very small part of the solar spectrum. They are photoelectrochemical cells but they differ from conventional planar photoelectrochemical cells in that they have a 3-D interface like DSSC do. We compare results for two structures: a single layer photoelectrode and a double layer photoelectrode. In the first, the mesoporous layer is obtained by “doctor blading” a nanocrystalline TiO$_2$ suspension of Degussa P-25 [158]. For the double layer structure a new technique has been proposed for depositing the thin contacting film between the TCO and the mesoporous layer: microwave activated chemical bath deposition (MW-CBD) [159]. The purpose is to have a better mechanical and therefore electrical contact between this film and the TCO, as well as blocking TCO-electrolyte electron recombination. Films obtained using MW-CBD are sonication resistant, while often nanocrystalline TiO$_2$ layers deposited by other techniques are not. To study electron extraction at the TiO$_2$-TCO interface MW-CBD has been used for obtaining the TiO$_2$ nanostructured thin film on ITO and FTO [153], [160]. But it can be used with other conducting or semiconducting substrates [161]-[163]. When using MW-CBD, the TiO$_2$ grows on the substrate because it heats up preferentially. Preferential heating of the substrate is due to the interaction of free electrons with microwaves [164], [165]. Since TiO$_2$ nucleates directly on the TCO, very well adhered films are obtained [162], [166].
Fig. III.1 a (left) Scanning electron microscope photo of a TiO$_2$ thin film grown with precursor solution based on TiOSO$_4$ and H$_2$SO$_4$. b (right) Idem for a TiO$_2$ thin film grown with precursor solution based on (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$. Both films were grown on ITO. Shown white point line below each of the photos is 300nm long.

It should be noted that although microwave processing for sintering TiO$_2$ layers has been used by other authors [167], [168], MW-CBD is different. It can be considered a crystal growth process of TiO$_2$ on the conducting substrate rather than a deposition one. Using MW-CBD, double layer structures have been found experimentally to have higher external quantum efficiency as compared to TiO$_2$ single layers when using a precursor solution based on TiOSO$_4$ and H$_2$SO$_4$ [160] which leads to an amorphous nanostructured TiO$_2$ film [162] (see Fig. III.1.a). This experimental result is also obtained when using a precursor solution that leads to nanocrystalline films based on (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$ [153] (see Fig. III.1.b).

III.2 Evaluating electron extraction efficiency

In order to analyze the effectiveness of MW-CBD contacting layers, IPCE experimental results were simulated. Though different models have been reported for simulating DSSC characteristics [169], the diffusion model [170]-[176] is straight forward for modeling IPCE. For our unsensitized photoelectrodes, the TiO$_2$ absorption coefficient spectral dependence was considered. Most important is that a finite electron extraction rate at the TiO2/TCO interface, disregarded on occasions, is introduced. In ref. [175], [176] a constant electron extraction rate is used but IPCE decrease for higher photon energies in TiO$_2$ photoelectrochemical cells had not been considered before by authors using the diffusion model. IPCE values should tend to zero as light penetration is negligible due to absorption increase for higher energy photons and surface recombination becomes predominant. IPCE decrease for higher photon energies has been observed experimentally for non-sensitized photoelectrodes [153], [160][164]. To model this decrease, the electron extraction rate had to be considered a function of electron concentration at the TiO2/TCO interface, pointing to the TiO$_2$/TCO contact importance, which has not been sufficiently considered so far [154].
The model substitutes TiO₂ photoelectrode particle network by rods (with diameter equal to particles dimensions and length equal to film thickness) placed perpendicular to the TCO and surrounded by electrolyte as in Fig. III.2. This is commonly accepted and it allows a one dimensional treatment [177]. Electron concentration at position x refers to an imaginary plane parallel to the TiO₂/TCO plane and at a distance x from it. These imaginary planes cut at x numerous electron paths. The following assumptions were made to obtain the electron concentration n(x) in the stationary state when light penetrates through the TCO: 1. electron transport occurs due to diffusion; 2. redox species concentration is high enough to remain constant during illumination; 3. light creates electron-hole pairs but photogenerated holes are extracted from the TiO₂ by the electrolyte effectively (as in DSSC, the unsensitized photoelectrochemical cell is also a majority-carrier-photovoltaic device); 4. electron diffusion length does not show a spatial dependence; 5. photon concentration decreases exponentially as light travels according to an effective extinction coefficient α(λ) determined by radiation absorption and dispersion; 6. only a fraction of electrons reaching the TiO₂/TCO contact are collected, i.e., extraction rate of electrons at the TiO₂/TCO contact is not infinite. Extraction rate should be affected by electron losses when crossing this interface and it should depend on TiO₂/TCO interface characteristics. According to these assumptions, continuity equation for the stationary case is [170], [172][176]:

$$D_e \frac{d^2 n(x)}{dx^2} - \frac{(n(x) - n_0)}{\tau} + \Phi(\lambda) \alpha(\lambda)e^{-\alpha(\lambda)x} = 0$$

where n(x) is the electron concentration at x, Dₑ is the electron diffusion coefficient, τ is the recombination time, Φ(λ) the photon flux and n₀ the electron concentration at equilibrium. Boundary conditions for diffusing electrons are given by:

$$\frac{dn(x)}{dx} \bigg|_{x=d} = 0$$

where d is the layer thickness. This condition has been used as boundary condition by different authors. They have considered that electrons arriving at the end of the TiO₂ film (x = d) are reflected [170], [172][176]. It means that no net electron flow exists at x=d. The other boundary condition we have used is:

$$D_e \frac{dn(x)}{dx} \bigg|_{x=0} = s \left[n(0) - n_0\right]$$

Fig III.2 Nanostructured TiO₂ single (left) and double (right) layer photoelectrodes. The mesoporous TiO₂ is shown as cylindrical rods according to model assumptions.
That is, electrons arriving at x=0 (TiO$_2$/TCO) are extracted with a rate characterized by s which is dependant on interface characteristics.

Using these boundary conditions and the well-known relation $\tau = L_e^2 / D_e$ (where $L_e$ is the electron diffusion length), solution of equation (13) gives the excess electron concentration $\Delta n(x)$:

$$
\Delta n(x) = n(x) - n_0 = C_1 e^{-\frac{x}{L_e}} + C_2 e^{\frac{x}{L_e}} + \frac{\Phi(\lambda) \alpha(\lambda) L_e^2}{[1 - \alpha^2 \lambda L_e^2]} e^{-\frac{\alpha(\lambda) x}{L_e}}
$$

(16)

where:

$$
C_1 = \left[ \frac{\Phi(\lambda) \alpha(\lambda) L_e^2}{[1 - \alpha^2 \lambda L_e^2]} \right] \left[ \frac{1 - \frac{sL_e}{D_e} \alpha(\lambda) L_e e^{-\alpha(\lambda) d} - \left( \alpha(\lambda) L_e + \frac{sL_e}{D_e} \right) e^{-\alpha(\lambda) x}}{2 \frac{sL_e}{D_e} \cosh \frac{d}{L_e} + 2 \sinh \frac{d}{L_e}} \right]
$$

(17)

$$
C_2 = \left[ \frac{\Phi(\lambda) \alpha(\lambda) L_e^2}{[1 - \alpha^2 \lambda L_e^2]} \right] \left[ \frac{1 + \frac{sL_e}{D_e} \alpha(\lambda) L_e e^{-\alpha(\lambda) d} - \left( \alpha(\lambda) L_e + \frac{sL_e}{D_e} \right) e^{-\alpha(\lambda) x}}{2 \frac{sL_e}{D_e} \cosh \frac{d}{L_e} + 2 \sinh \frac{d}{L_e}} \right]
$$

(18)

Equations (16)-(18) show that excess electron concentration $\Delta n(x)$ can be obtained numerically substituting absorption spectral dependence and known parameters. Also current at x=0, $J_e$, can be found since:

$$
J_e = qD_e \frac{dn(x)}{dx} \Big|_{x=0}
$$

(19)

IPCE values for each wavelength can be obtained from electron flow at x=0 corresponding to one-photon flux:

$$
\text{IPCE} = \frac{J_e}{q \Phi(\lambda)} = \left[ \frac{\alpha(\lambda) L_e}{[1 - \alpha^2 \lambda L_e^2]} \right] \left[ \frac{\frac{sL_e}{D_e} \alpha(\lambda) L_e e^{-\alpha(\lambda) d} + \left( \alpha(\lambda) L_e + \frac{sL_e}{D_e} \right) \sinh \frac{d}{L_e} - \alpha(\lambda) L_e}{2 \frac{sL_e}{D_e} \cosh \frac{d}{L_e} + \sinh \frac{d}{L_e}} \right]
$$

(20)

$\Phi(\lambda)$ is the photon flux, i.e., the number of incident photons per unit area and per second.

The $\alpha(E)$ dependence used in equation (8) for fitting IPCE experimental values is a linear combination of absorption coefficient spectral dependences for different TiO$_2$ crystalline phases. Rutile indirect band gap dependence was used since it absorbs radiation at lower energies than anatase. Both phases are present in TiO$_2$ Degussa P-25 nanocrystalline powder. For anatase (main crystal phase, concentration ≥70%) both indirect and direct band gap dependence were used:

$$
\alpha(E) = A_1 \left( E - E_{giA} \right)^{\gamma_1} + A_2 \left( \frac{E - E_{grA}}{E} \right)^{\gamma_2} + A_3 \left( \frac{E - E_{drA}}{E} \right)^{\gamma_3}
$$

(21)

$E_{giA}$ and $E_{grA}$ are the fundamental indirect energy-gap in anatase and rutile, respectively. $E_{giA}$ corresponds to anatase direct energy-gap. $A_1$, $A_2$ and $A_3$ are constants that depend on crystal order and mass density. All these 6 parameters are also obtained from adjusting equation (20) to IPCE experimental results.
In Fig. III.3 experimental IPCE spectra for single and double layer photoelectrodes show that double layer structures have higher IPCE values. The thin nanocrystalline TiO$_2$ film in the double structure was obtained using precursor solution based on (NH$_4$)$_2$TiF$_6$ and H$_3$BO$_3$. Results obtained from fitting experimental IPCE spectra are shown by continuous line in Fig. III.3. Bandgap energies found from this fitting for anatase and rutile agree with their known values [153]. When fitting equation (20) to experimental data, a constant $s$ value, as employed by other authors, could be used only up to photon energy $E_{\text{max}}$, which corresponds to maximum IPCE value. In order to explain IPCE decrease for short wavelengths experimentally observed in non-sensitized photoelectrodes (Fig. III.3), a decreasing tendency of $s$ on photon energy must be considered for $E>E_{\text{max}}$. In Fig. III.4 one can observe $s$ values that were found for different photon energies from fitting the model to the experimental data shown in Fig. III.3 for the four different photoelectrode structures. The highest electron extraction rate corresponds to double layers (porous/MW/TCO); i.e., electron extraction is more efficient when TiO$_2$ is deposited on TCO using MW-CBD than when “doctor blade” technique is used for layer deposition. This is valid for FTO, as well as, for ITO, though FTO contacts show higher extraction rates than ITO contacts. This can indicate different defect concentrations at the TiO$_2$/TCO interface.

Why should $s$ be a function of photon energy as shown in Fig. III.4?

Fig. III.5 shows the result of evaluating equation (16) (the spatial dependence of excess electron concentration) for three different incident photon energies for porous/MW/ITO double layer structure. Parameters for absorption and $s$ values obtained from IPCE mathematical fitting were used in this calculation.
Fig. III.4 Values of $s$ for different photon energies found by fitting the theoretical IPCE to experimental data for the four types of photoelectrode structures studied.

Since shorter wavelengths (higher energy photons) penetrate less, more excess electrons are created next to the TiO$_2$/TCO contact, as shown in Fig. III.5. Higher excess electron concentration should increase probability of electron losses through recombination at defects in the interface and therefore, extraction rate decreases. This explains that $s$ changes for higher photon energies.

Fig. III.5 Spatial distribution of excess electron concentration $\Delta n(x)$ for different photon energies calculated using $\Phi = 1.8 \times 10^{15}$ photons/s-cm$^2$ and parameters obtained from IPCE mathematical fitting.

III.3 Conclusions

Experimental results show that MW-CBD TiO$_2$ films used as contacting layers in TiO$_2$ double layer photoelectrodes increase IPCE values relative to porous TiO$_2$/TCO single layer structures. Results obtained from modeling show that this behavior is explained by differences in electron extraction rate at different TiO$_2$/TCO interfaces. Therefore, MW-CBD TiO$_2$ contact to TCO is better not only mechanically, but also electrically. Experimentally observed IPCE values decrease for the high photon energy spectral range in non-sensitized photoelectrodes is explained by excess electron concentration increase at the TiO$_2$/TCO contact. Results confirm the importance of the electron-extracting contact.
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