Properties of Nanomaterials

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Nanometer

- ✓ **Nano:** The word “Nano” means dwarf in Greek language. Use as a prefix for any unit means a billionth of that unit. For instance,
  - ✓ Nanosecond means a billionth of a second.
  - ✓ Nanogram is a billionth of a gram
  - ✓ Nanometer, which is one billionth of a meter, is used to measure the length of a small object about the length of a few atoms lined up shoulder to shoulder.
    - $\left.\begin{array}{l} 1A^0 = 10^{-10}\ m \\ 1nm = 10^{-9}\ m \end{array}\right\}$ Atomic/Crystallographic
    - $1\ \mu m = 10^{-6}\ m\}$ microstructure
    - $\left.\begin{array}{l} 1\ mm = 10^{-3}\ m \\ 1\ cm = 10^{-2}\ m \end{array}\right\}$ macrostucture

Nanometer ……

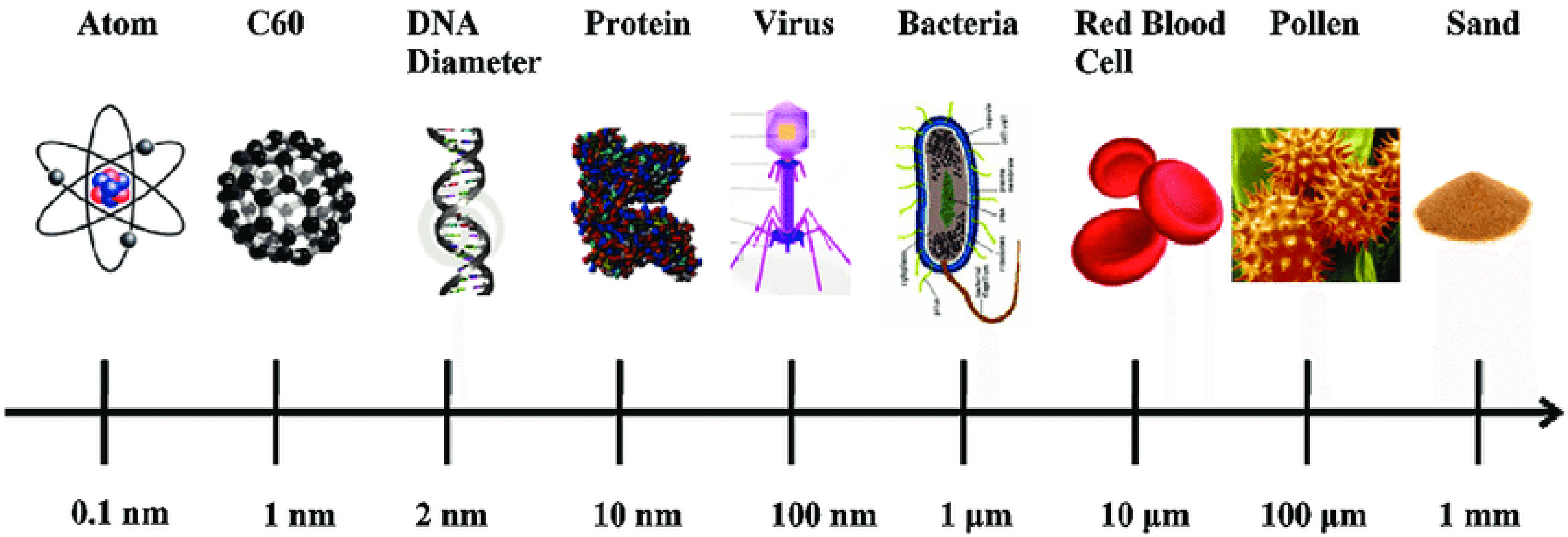
✓ **How small the nanometer is?**

- To understand how small a nanometer is, we typically compare the nanoscale to objects that we know how big or small they are. Here are some examples:
  - ❖ a human hair is about 60,000 - 100,000 nm wide
  - ❖ a fingernail grows 1 nm per second
  - ❖ a DNA molecule is ~2.5 nm in width
  - ❖ The individual components of an Intel Pentium III microprocessor span about 200 nanometers.
  - ❖ a 2 meter person is 6 feet 6 inches tall or 2 billion nanometers

Nanometer … …

✓ How small the nanometer is?

- Another way to help in the understanding of the minuteness of a nanometer is to examine objects on a size scale.



Nanoscale

✓ **What is nanoscale?**

- The nanoscale is the dimensional range of approximately 1 to 100 nanometers.
- In nanoscale, some physical and chemical properties of material can differ significantly from those of the bulk structured materials of the same composition.
- Unique physical and chemical properties arise when the size (d) of material is equal to or less than critical length (d^*), i.e., $d \leq d^*$.
- Critical length (d^*) is a length characteristic of some physical phenomena, such as free path length of electrons, phonons, length of de Broglie wave, length of external electromagnetic and acoustical waves, correlation length, penetration length, diffusion length, etc.

Nanoscale ……

Characteristic length of some physical phenomena

Phenomenon	Physical Quantity	Length Scale
Electronic transport	Fermi wavelength, λ_F	~ 1 Å
	Scatting length, l	10 – 100 nm
	de Broglie wavelength	~ 4 Å
Optical interactions	Wavelength of light in medium, $\frac{\lambda}{2n}$	100-300 nm
Magnetic interactions	Range of exchange interactions	1-100 Å
	Range of magnetic dipole interactions	Few microns
Thermal	Phonon mean free path	100 nm at 300 K

Nanoscale ……

Why is nanoscale so wide (1-100 nm)?

- ✓ The different characteristic physical phenomenon are dictated by different length scale ranging from 1 Å to few hundred nanometers.
- ✓ Materials having length greater than critical length do not exhibit physical and chemical properties remarkedly different from bulk materials.
- ✓ Materials with the same compositions have different critical length for different characteristic physical phenomenon.
- ✓ Nanoscale is defined in the range of 1-100 nm for covering almost all the critical length of characteristic physical phenomenon.

Territory or realm of Nanoscale

- Chemistry is the study of atoms and molecules, a realm of matter of dimensions generally less than one nanometer.
- While condensed matter physics deals with solids of essentially an infinite array of bound atoms or molecules of dimensions greater than 100 nm.
- A significant gap exists between these regimes. Nanoscale falls into this gap and make a bridge between chemistry and solid state physics.

Atoms/ molecules 1	Nanoscale Particles 125-70,000	Condensed Matter 6×10^{6} - ∞N atoms
Quantum Chemistry	?	Solid State Physics

Territory or realm of Nanoscale……

- In this nanoscale regime neither quantum chemistry nor classical laws of physics hold.
- In nanoscale regime, strong chemical bonding is present, delocalization of valence electrons can be extensive, and extent of delocalization can vary with size of the system.
- This effect coupled with structural changes with size variation can lead to different chemical and physical properties that *depend on size.*
- *A* host of properties depend on the size of such nanoscale particles, including magnetic properties, optical properties, melting points, specific heats, and surface reactivity.
- When such ultrafine particles are consolidated into macroscale solids, these bulk materials sometimes exhibit new properties (e.g., enhanced plasticity).

Are the nanoscale materials new?

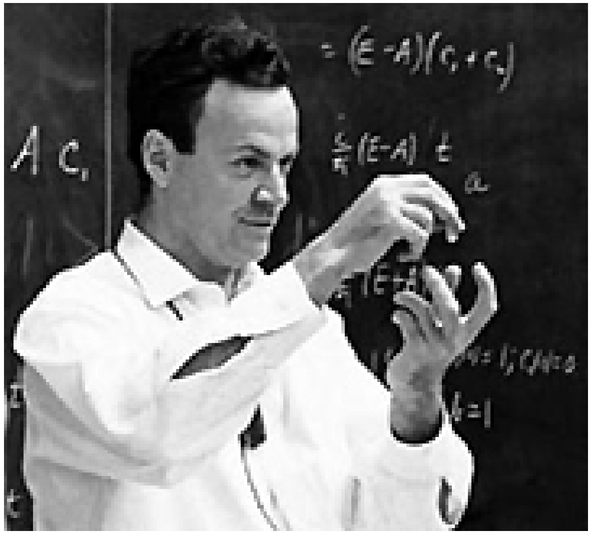
- Romans in the pre-Christian era introduced metals with nanometric dimensions in glass-making: a cup describing the death of King Lycurgus (ca 800 bc) contains nanoparticles of silver and gold; when a light source is placed inside the cup, its color changes from green to red .

Are the nanoscale materials new?

- Art history of India and China is also filled with examples of nanotechnology. Photography, which was developed in the 18th and 19th centuries, provides a more recent example of the use of silver nanoparticles.
- In the early 1940s, precipitated and fumed silica nanoparticles were being manufactured and sold in the United States and Germany as substitutes for ultrafine carbon black for rubber reinforcements.
- In 1857, Faraday had described the use of colloidal gold in his experiments.
- In the early twentieth century Gustav Mie presented the Mie theory, which is a mathematical treatment of light scattering that describes the relationship between metal colloid size and optical properties of solutions containing them.

Are the nanoscale materials new?

- The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used.
- In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules.



Physicist Richard Feynman, the father of nanotechnology.

From these discussion, it can be concluded that the nanoscale materials are not new at all.

But why recently heated up?

- Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term nanotechnology.
- It wasn't until 1981, with the development of the scanning tunneling microscope that could "see" individual atoms, that modern nanotechnology began.

Professor Norio Taniguchi

After discovery of sophisticated instruments to see individual atoms, research in nanoscience, nanotechnology and nanomaterials became heated up or speeded up.

Nanoscience

- **Nanoscience** is the study of phenomena and manipulation of materials at nanoscale, where properties, functionality, and phenomena differ significantly from those at larger scales.
- Important properties of materials, such as the electrical, optical, thermal and mechanical properties, are determined by the way molecules and atoms assemble on the nanoscale into larger structures.
- In nanoscale, these properties often different then on macroscale, because quantum mechanical effects become important.

Nanotechnology

- **Nanotechnology** is the production and application of structures, devices and systems for controlling shape and size nanoscale.
- Nanotechnology concerns with the manipulation, control, and integration of atoms and molecules to form materials, structures, components, devices and systems at the nanoscale with their industrial and commercial applications.
- Nanotechnology covers
  - ✓ Nanoscience – manipulation, control and integration of atoms and molecules
  - ✓ Technology for fabricating material, structures, components and devices at nanoscale
  - ✓ Technology for industrialization and commercialization.

Nanochemistry

Two crucial strands of Nanoscience and Nanotechnology

Investigate and utilize nanoscale materials

Manipulate and manufacture nanoscale things

Chemists

Synthesize & investigate:

- ✓ Nanotubes, coatings, new alloys, composites,
- ✓ Particles for sunscreens, catalysts, colloids and quantum dots and so on.

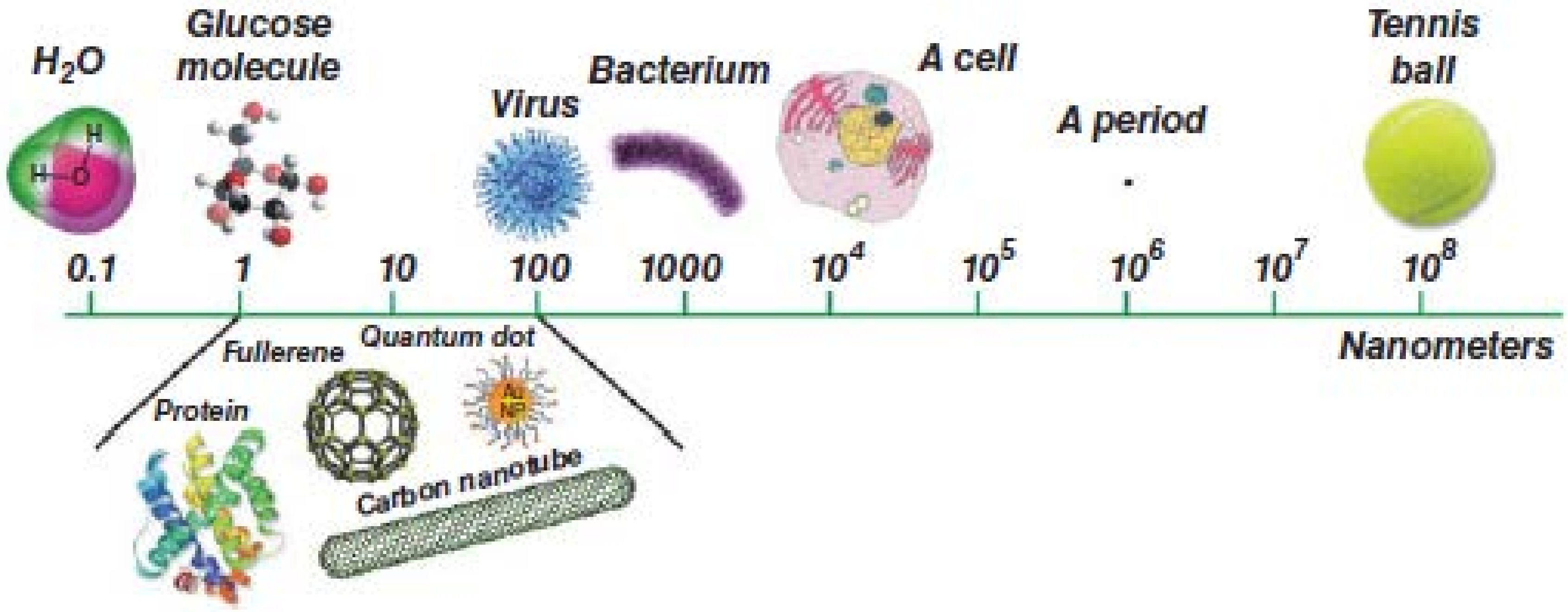
Manipulation & manufacture:

- ✓ Top-down approach (photolithography) uses chemical processes
- ✓ Building structure from atoms or manipulation of atoms into nanostructures -bottom up processes

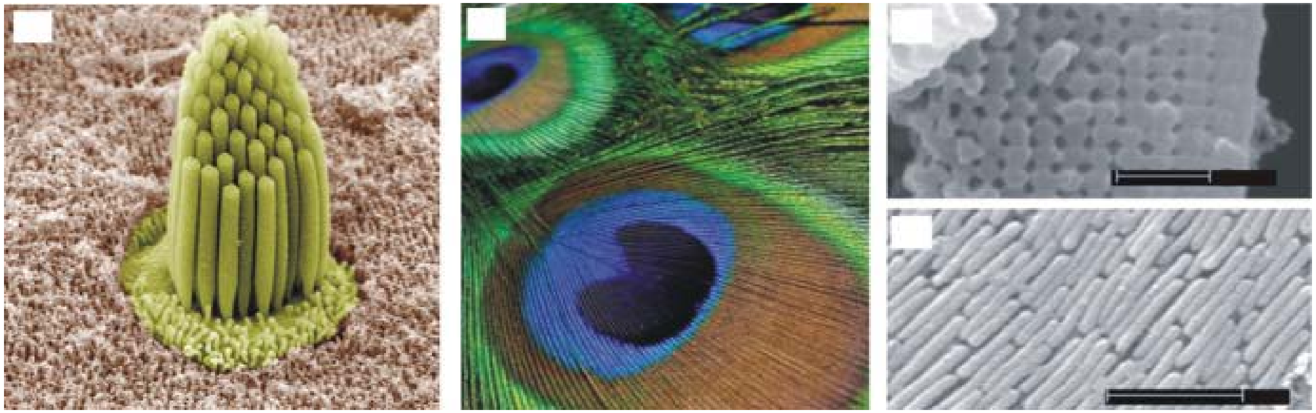
Nanoscale Materials

Nanomaterials:

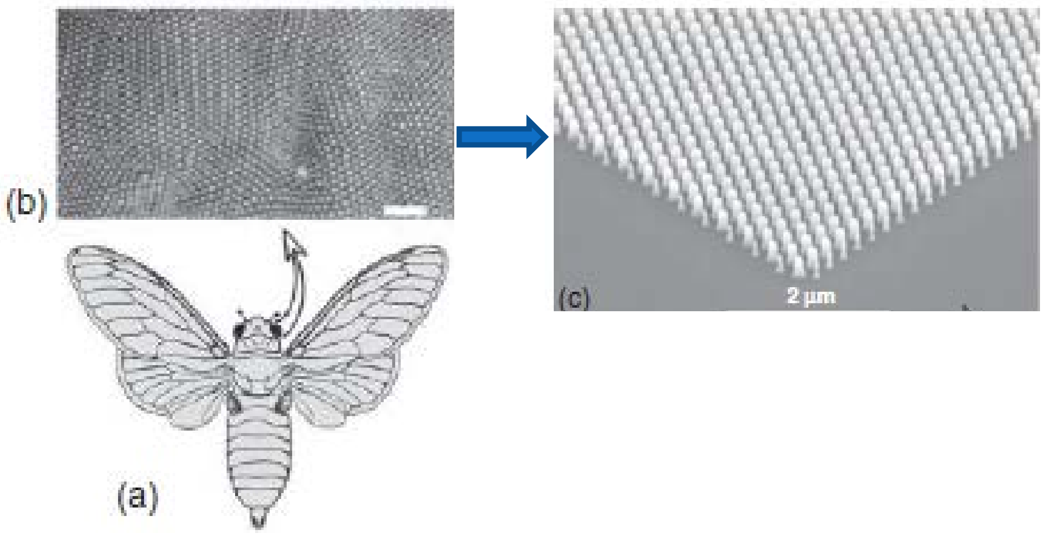
These materials are created from building blocks having at least one dimension in the nanoscale range of 1-100 nm.



Some Nanoscale Materials in Nature

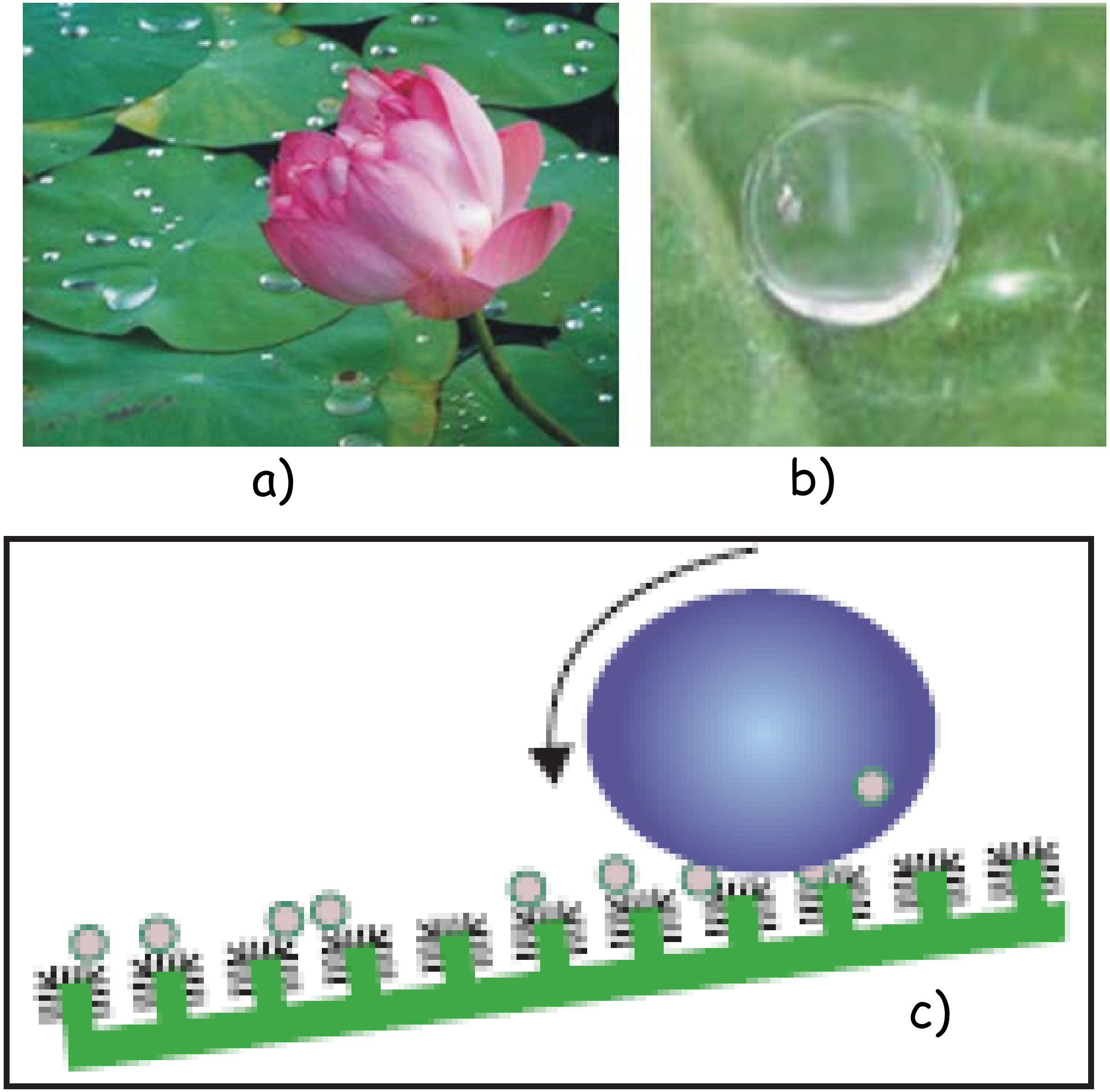


(a) SEM image of a sensory patch in amphibian ears.
(b) Peacock feather showing barbules, representing a photonic lattice;
(c and d) SEM image of barbules (transverse and longitudinal sections)



a) schematic of a moth;
b) SEM micrograph of anti-reflective surface of a moth's eye
c) biomimetic replica of a moth eye fabricated with ion- beam etching. (scale bar = 1 µm);

Some Nanoscale Materials in Nature



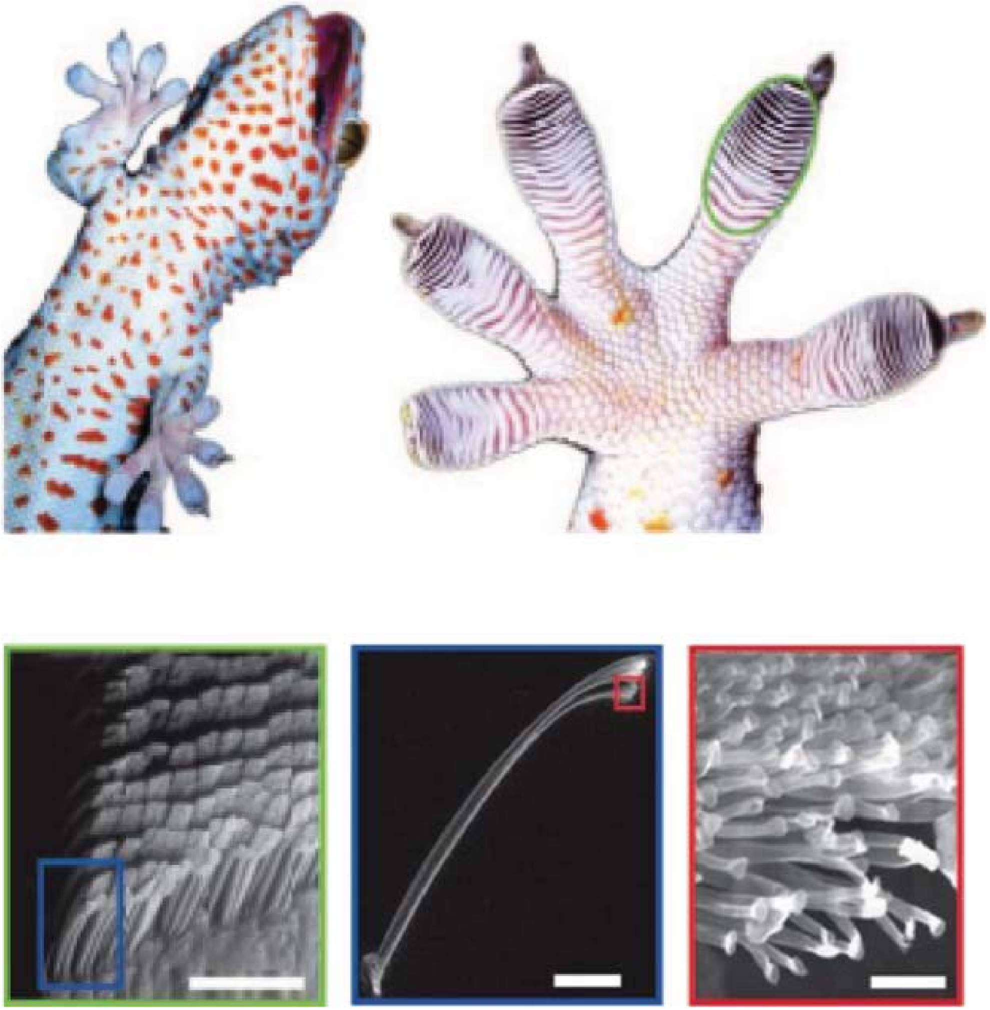
a)

b)

c)

a) Lotus (*Nelumbo nucifera*) plant;
b) spherical water droplet on a non-wettable lotus plant leaf.
c) self-cleaning: a drop picks up the dirt particles as it rolls off the leaf's surface.

Some Nanoscale Materials in Nature



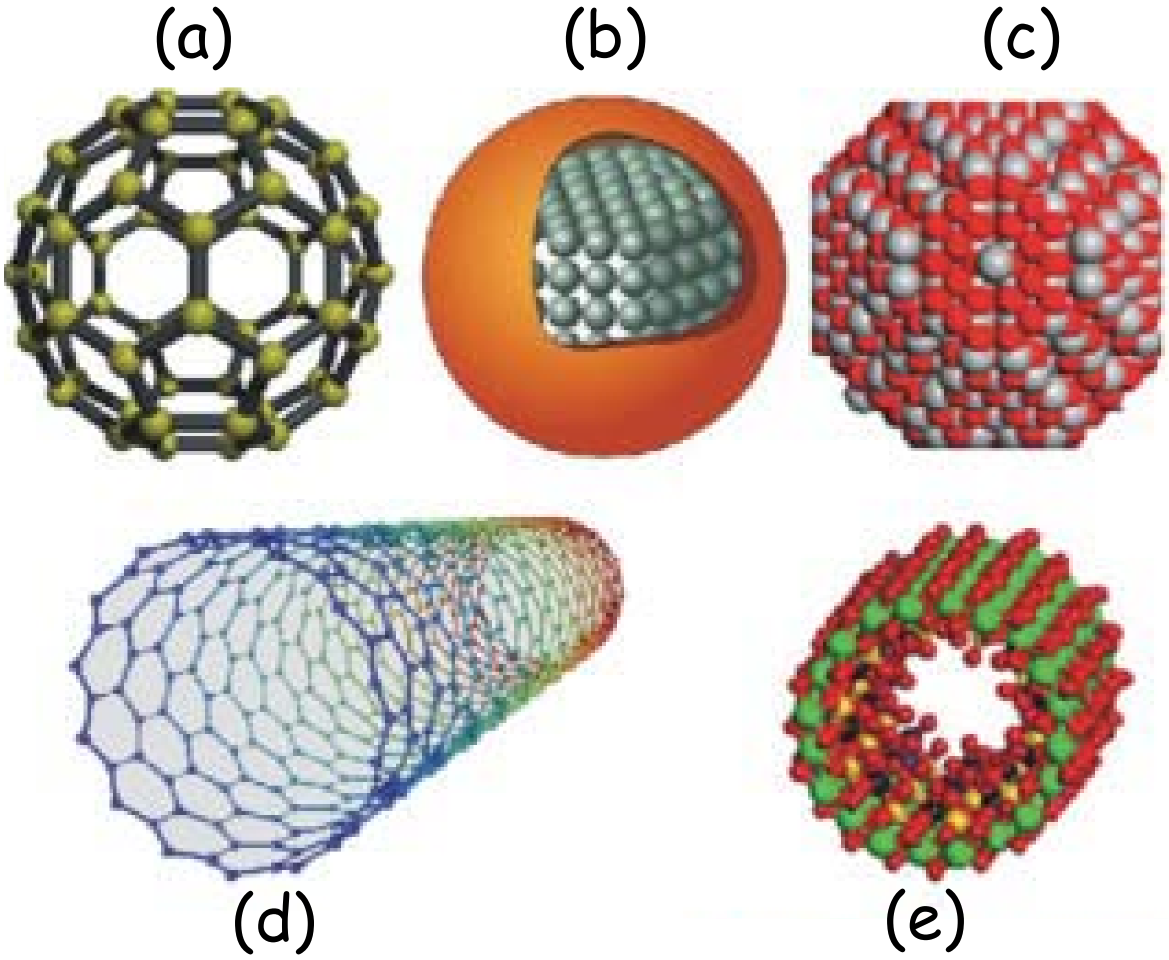
Gecko's adhesive system structure:

a) ventral view of a tokay gecko (*Gekko gecko*);
b) sole of the foot showing adhesive lamellae;
c) microstructure: part of a single lamella showing arrays of setae;
d) (d and e) nanostructure: single seta with branched structure at the upper right area, terminating in hundreds of spatula tips.

Nature is the greatest nanotechnologist.
Plentiful nanomaterials are in nature.

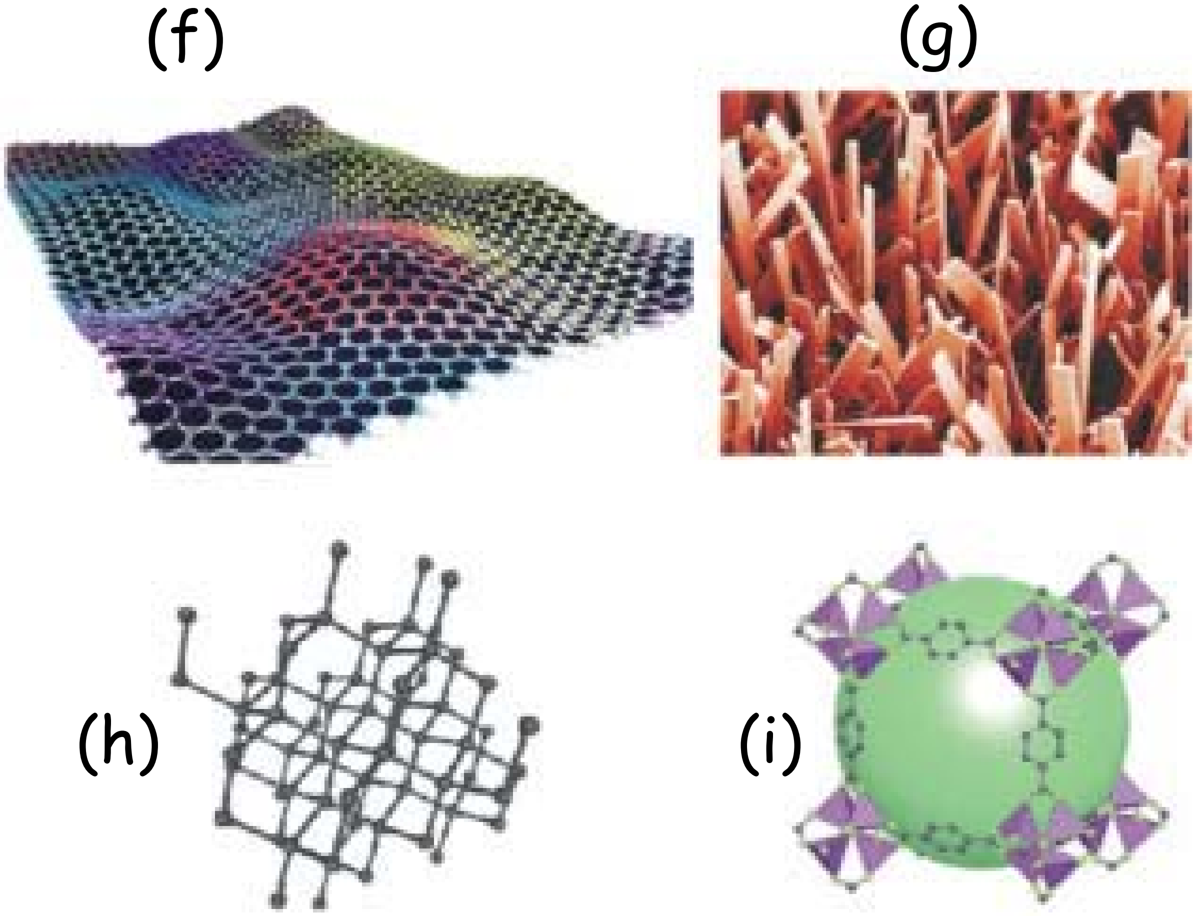
Explain

Artificial Nanoscale Materials



(a) fullerene;(b) quantum dot; (c) metal cluster;
(d) carbon nanotube; (e) metal oxide nanotube;

Artificial Nanoscale Materials



(f) graphene;(g) metal oxide nanobelts; (h) nanodiamond; (i) metal organic frameworks (MOFs).

Classification of nanomaterials

Classification of nanomaterials based on the dimensions out of the nanoscale:

(1) Zero dimensional (0D) nanomaterials have all dimensions in the nanoscale.

(2) One- dimensional (1D) nanomaterials have two dimensions in the nanoscale and other out of the nanoscale.

(3) Two-dimensional (2D) nanomaterials have one dimension in the nanoscale and other two out of the nanoscale.

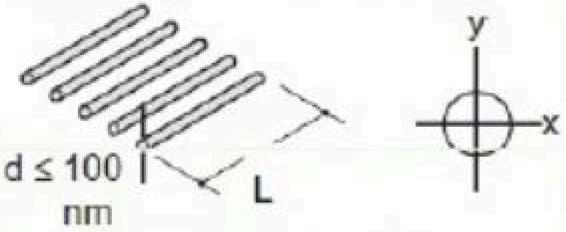
(4) Three-dimensional (3D) nanomaterials have all the dimensions out of the nanoscale.

Classification

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).
- (1) zero-dimensional (0-D),
- (2) one-dimensional (1-D),
- (3) two-dimensional (2-D), and
- (4) three-dimensional (3-D).

1-D

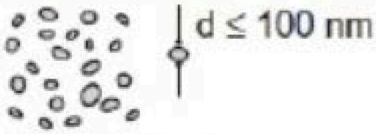
Two dimensions (*x,y*) at nanoscale, other dimension (*L*) is not



Nanowires, nanorods, and nanotubes

0-D

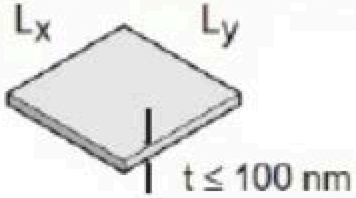
All dimensions (*x,y,z*) at nanoscale



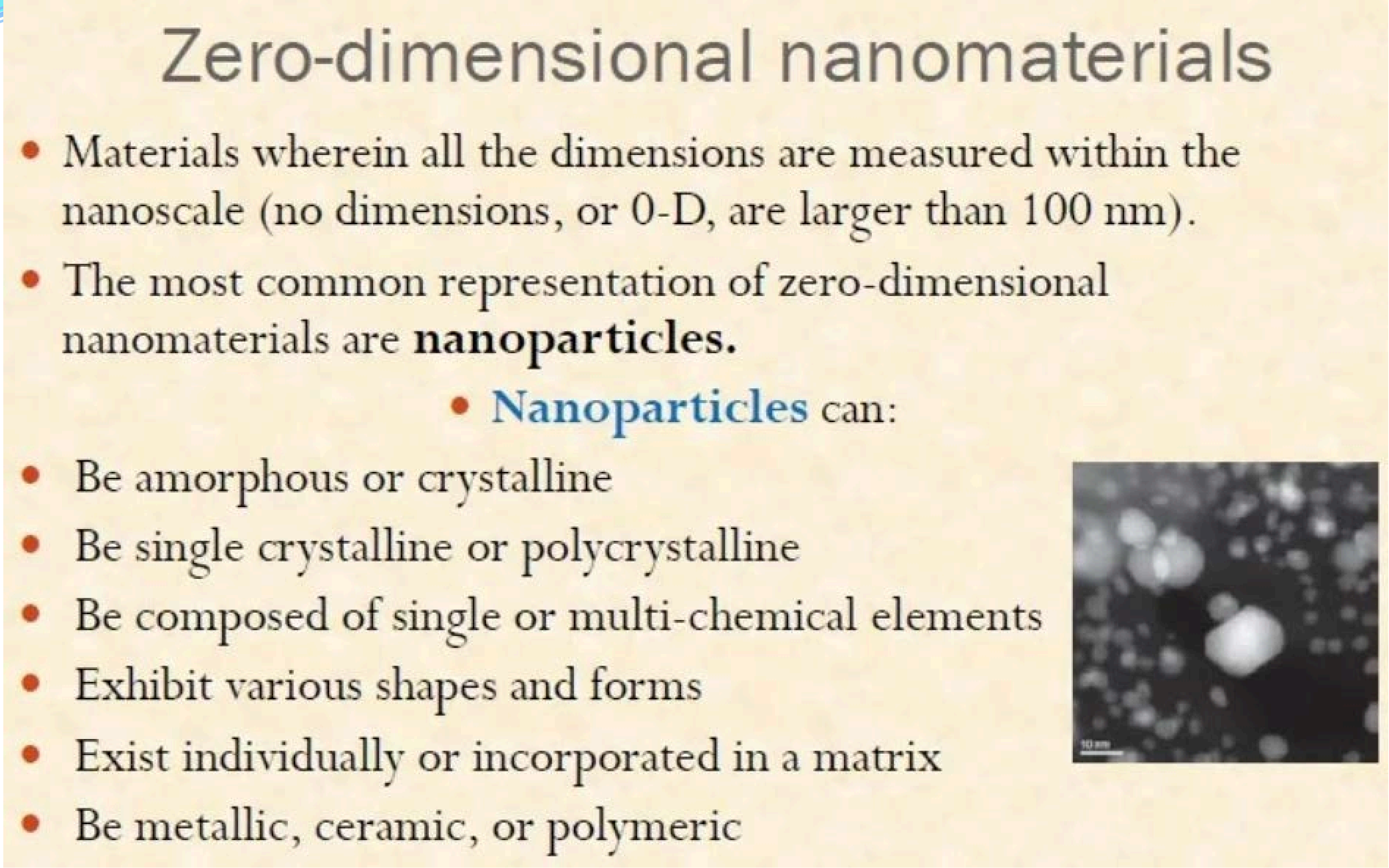
Nanoparticles

2-D

One dimension (t) at nanoscale, other two dimensions- (L_x, L_y) are not

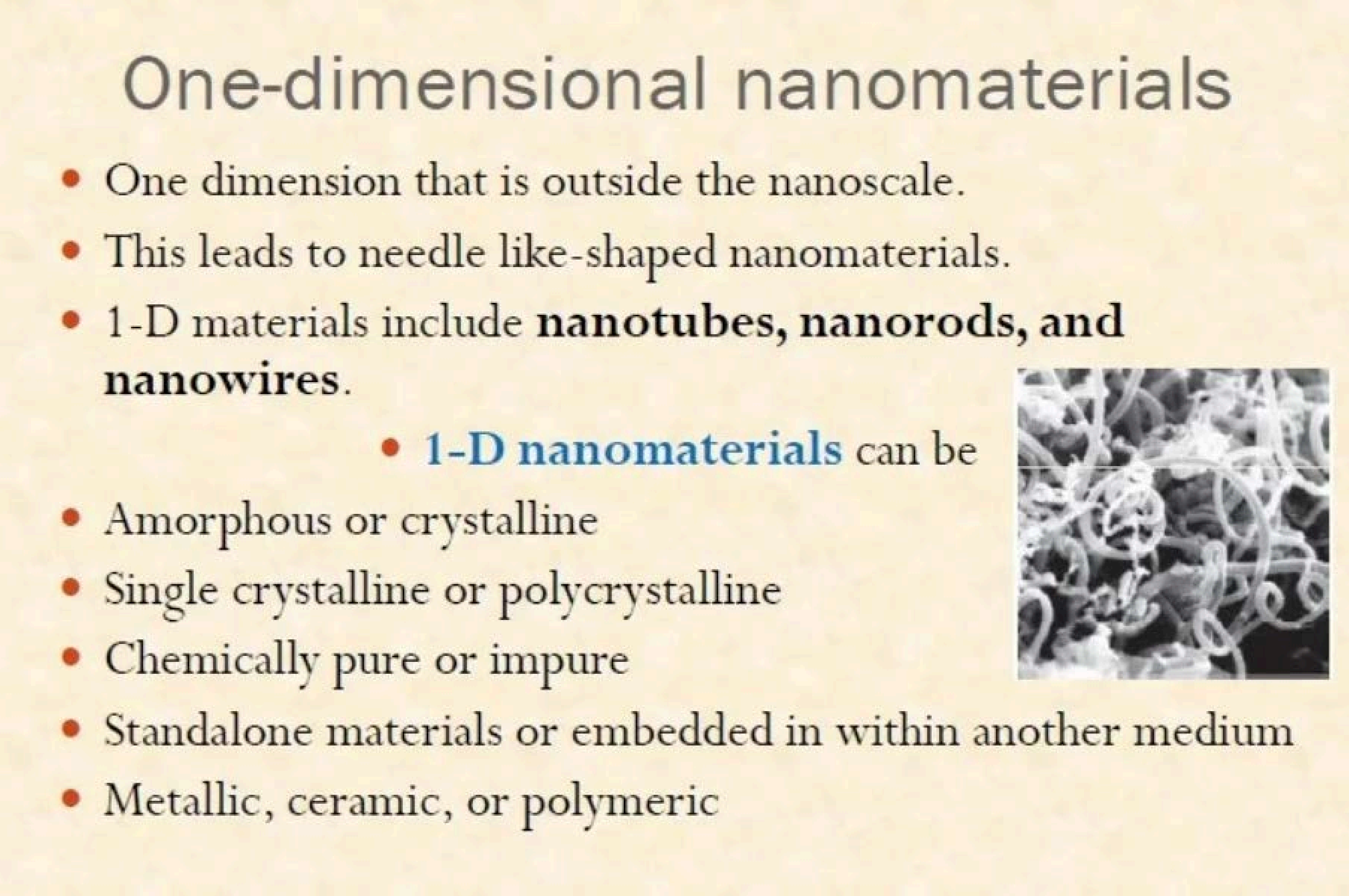


Nanocoatings and nanofilms



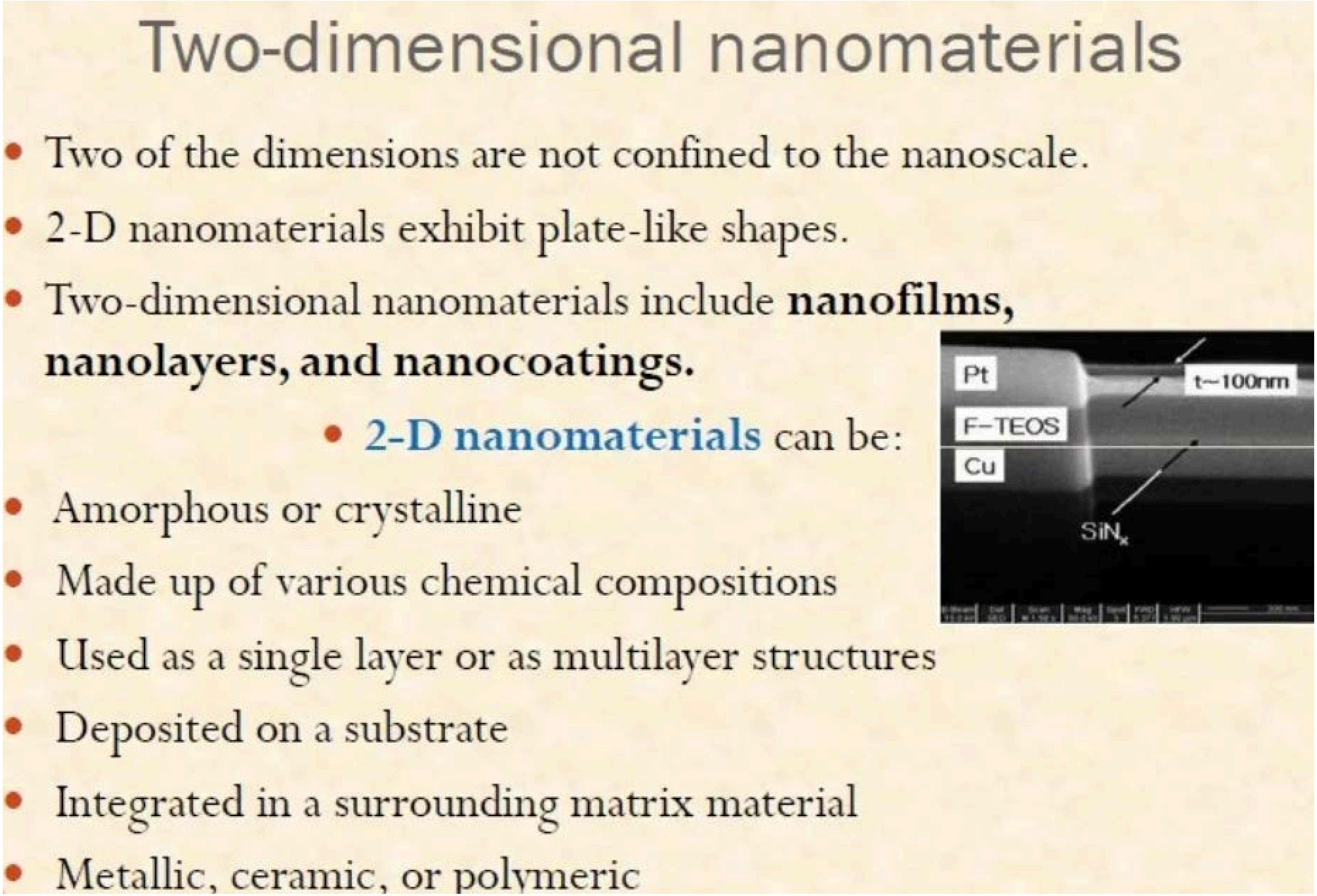
Zero-dimensional nanomaterials

- Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm).
- The most common representation of zero-dimensional nanomaterials are **nanoparticles.**
  - **Nanoparticles** can:
- Be amorphous or crystalline
- Be single crystalline or polycrystalline
- Be composed of single or multi-chemical elements
- Exhibit various shapes and forms
- Exist individually or incorporated in a matrix
- Be metallic, ceramic, or polymeric



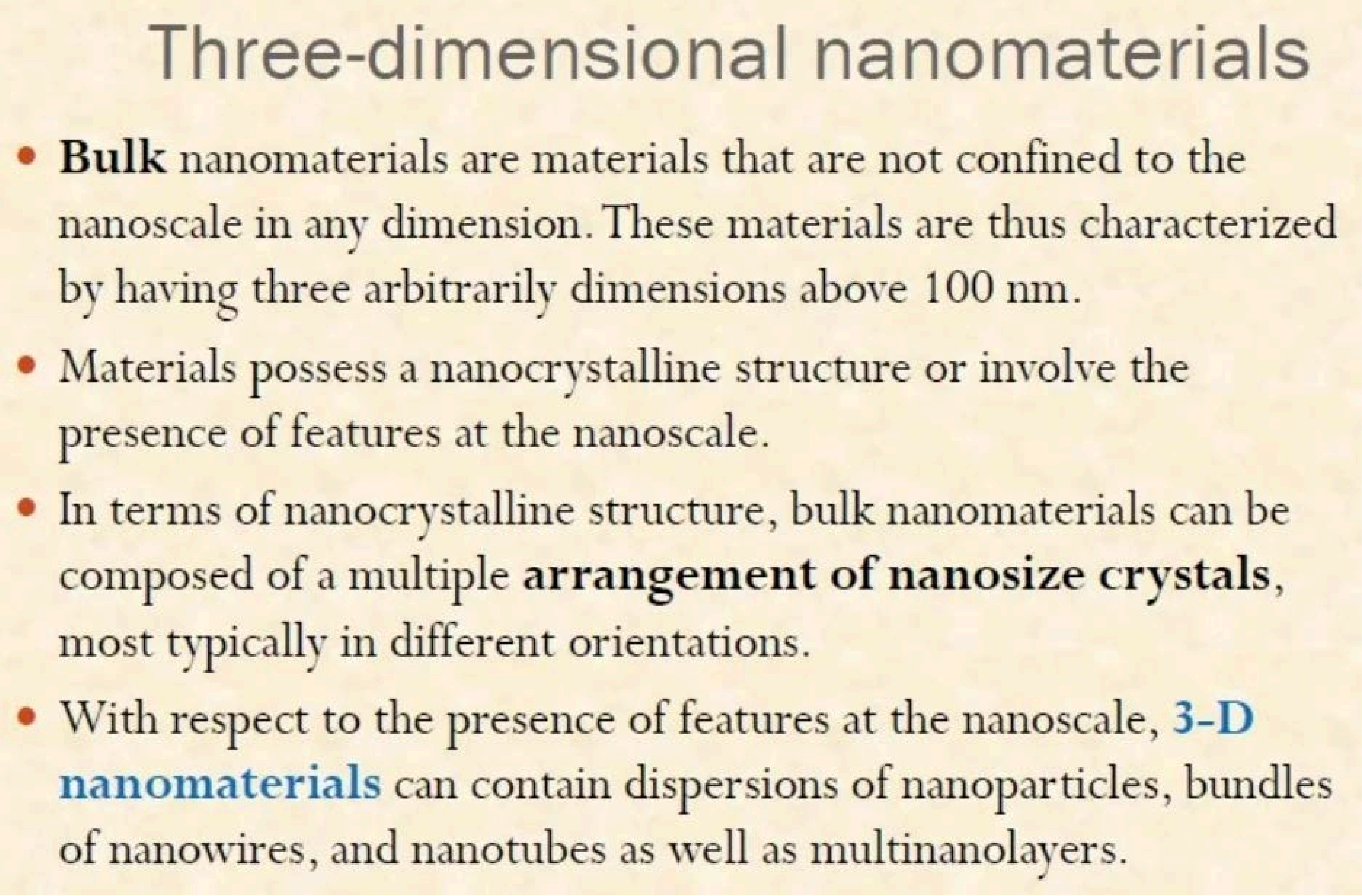
One-dimensional nanomaterials

- One dimension that is outside the nanoscale.
- This leads to needle like-shaped nanomaterials.
- 1-D materials include **nanotubes, nanorods, and nanowires**.
  - **1-D nanomaterials** can be
- Amorphous or crystalline
- Single crystalline or polycrystalline
- Chemically pure or impure
- Standalone materials or embedded in within another medium
- Metallic, ceramic, or polymeric



Two-dimensional nanomaterials

- Two of the dimensions are not confined to the nanoscale.
- 2-D nanomaterials exhibit plate-like shapes.
- Two-dimensional nanomaterials include **nanofilms, nanolayers, and nanocoatings.**
    - **2-D nanomaterials** can be:
- Amorphous or crystalline
- Made up of various chemical compositions
- Used as a single layer or as multilayer structures
- Deposited on a substrate
- Integrated in a surrounding matrix material
- Metallic, ceramic, or polymeric



Three-dimensional nanomaterials

- **Bulk** nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple **arrangement of nanosize crystals**, most typically in different orientations.
- With respect to the presence of features at the nanoscale, **3-D nanomaterials** can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

Types of Nanomaterials

Types of Nanomaterials (NMs)

For understanding, nanomaterials are designed into four types as follows:

(i) Carbon based materials
(ii) Metal based materials
(iii) Dendrimers
(iv) Composites

(i) Carbon based materials: These are composed of carbon, taking the form of hollow spheres, ellipsoids or tubes. The spherical and ellipsoidal forms are referred as fullerenes, while cylindrical forms are called nanotubes.

Types of Nanomaterials

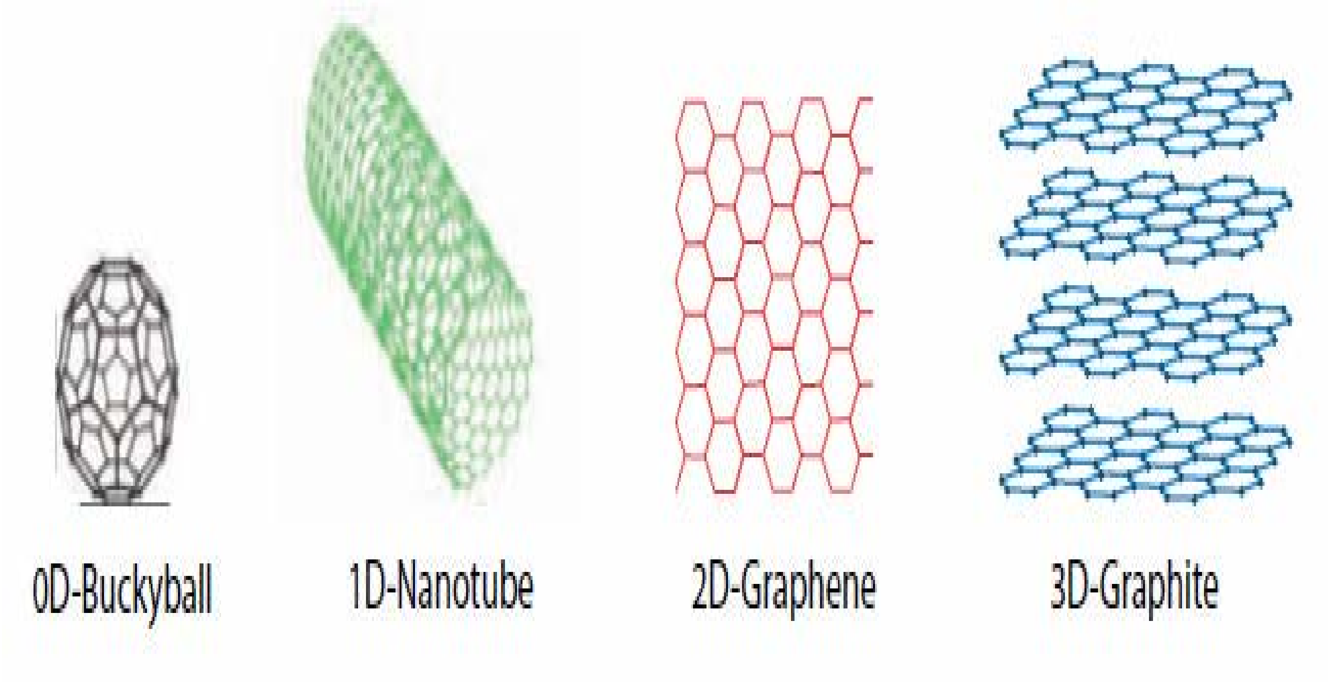


Figure (3)Carbon nanostructures

Types of Nanomaterials

Graphene

Graphene is a crystalline allotrope of carbon with two- dimensional, atomic scale, hexagonal pattren. It is the basic structural element of other allotropes like graphite, fullerene, nanotubes, nanocones, etc. hence called mother of all carbon nanomaterials (Figure 4). Nowdays, it is commonly used in semiconductors, batteries, electronics, composite industries, and many more.

Types of Nanomaterials

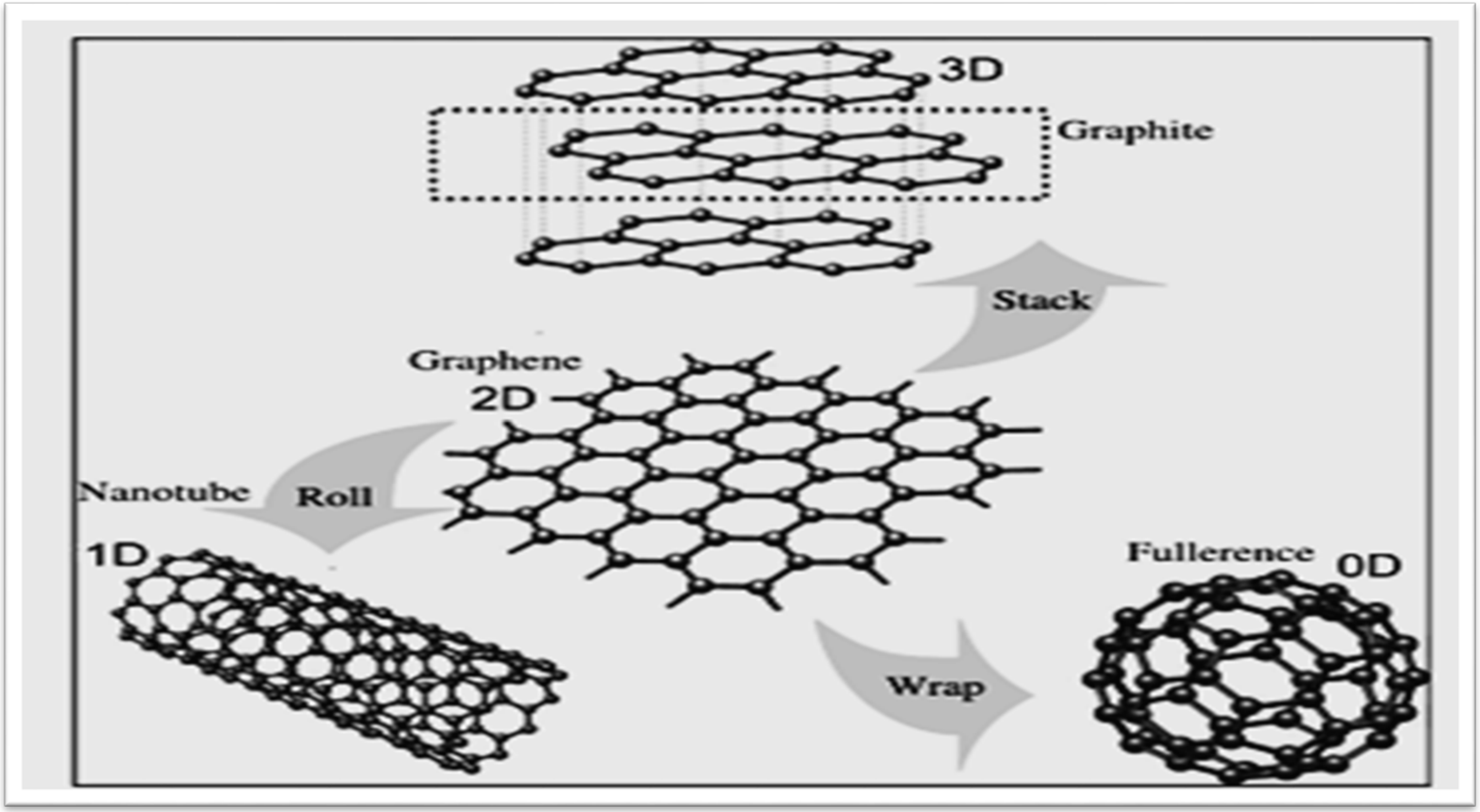


Figure (4) Graphene and other carbon nanomaterials

Types of Nanomaterials

(i) Metal based materials: These include quantum dots, nanogold, nanosilver and metal oxides like TiO_2. A quantum dot is a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, whose size is on the order of a few nanometers to a few hundred nanometers.

(ii) Dendrimers: Dendrimers are repetitively branched molecules. The name comes from the Greek word 'dendron' (tree). These nanomaterials are nanosized polymers built from branched units. The surface of dendrimer has numerous chain ends, which can perform specific chemical functions. Dendrimers are used in molecular recognition, nanosensing, light harvesting, and opto- electrochemical devices. They may be useful for drug delivery.

(iii) Composites: Composites are combination of nanoparticles with other nanoparticles or with larger., bulk- type materials. Nanoparticles like nanosized clays are added to products (auto parts), packaging materials, etc.) to enhance mechanical, thermal, and flame–retardant properties.

Types of Nanomaterials

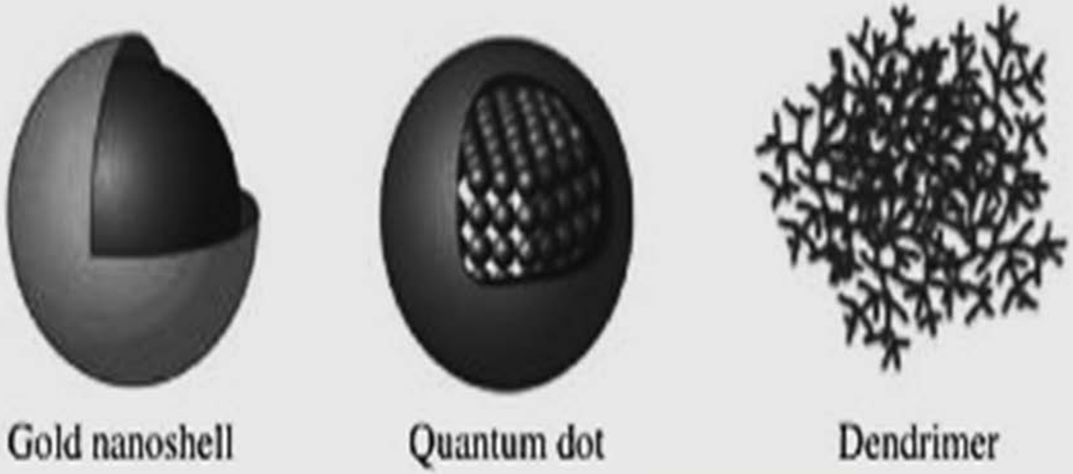


Figure 9.2 Some types of nanomaterials.

Figure (5) Some types of nanomaterials

Some Vocabulary in Nanoscale

Matter:

- ✓ Matter is anything that has **mass**.
- ✓ Therefore, everything around us comes under the definition of the matter.
- ✓ Elements like sulfur, gold, and potassium; compounds like water, air and coffee — everything is matter and matter can exists in a number of states.

Material:

- ✓ Material is any kind of matter for intention to use. Material is just a word for referring to the matter which has a specific purpose.
- ✓ For example, construction material.
- ✓ If a log of wood is just lying on the roadside as you drive-by, it is matter. But if you pick-up that wooden log with the intention of crafting something out of it, then the log becomes wooden material. Such matter is basically *raw material* which becomes some useful object after we take it through a process.

Some Vocabulary in Nanoscale

Nano-object:

- ✓ Material confined in one, two, or three dimensions at the nanoscale. This includes nanoparticles (all three dimensions in the nanoscale), nanofiber (two dimensions in the nanoscale), and nanoplates (one dimension in the nanoscale). Nanofiber are further divided into nanotubes (hollow nanofiber) nanorods (solid nanofiber) and nanowire (electrically conducting or semiconducting nanofiber)

Cluster:

- ✓ A collection of units (atoms or reactive molecules) of up to 50 units. Cluster compounds are such moieties surrounded by a ligand shell that allows isolation of a molecular species (stable, isolable, soluble).

Some Vocabulary in Nanoscale

Nanostructured or nanoscale material:

- ✓ Any solid material has at least one dimension in the nanoscale. Three dimensions → particles; Two dimensions → thin films; and One dimension → thin wire.

Nanophase Materials:

- ✓ The same as nanostructured materials.

Quantum Dot:

- ✓ A particle that exhibits a size quantization effect in at least one dimension.

Nanostructure:

- ✓ It is a structure with at least one dimension in the nanoscale. It is the same as nanostructured, or nanoscale, or nanophase material.

Some Vocabulary in Nanoscale

Nanocrystal:

✓ It is a solid particle that is a single crystal with all three dimension in the nanoscale.

Particle:

✓ It is a minute piece of matter with defined physical boundaries. A particle can move as a unit. This general particle definition applies to nano-objects.

Nanoparticle:

✓ It is a solid particle with all three external dimensions in the nanoscale. Nanoparticles can be amorphous, an aggregate of crystallites or a single crystallite.

Nanoparticulate matter:

✓ It refers to a collection of nanoparticles, emphasizing their collective behavior.

Some Vocabulary in Nanoscale

Agglomerate:

✓ It is a group of particles held together by weak forces such as van der Waals forces, some electrostatic forces, and surface tension. It should be noted that agglomerate will usually retain a high surface-to-volume ratio.

Aggregate:

✓ It is a group of particles held together by strong forces such as those associated with covalent or metallic bonds. It should be noted that an aggregate may retain a high surface-to-volume ratio.

Colloid:

✓ A stable liquid phase containing particles in 1-1000 nm range. A colloidal particle is one such 1 – 1000 nm sized particle.

Some Vocabulary in Nanoscale

3D bulk materials:

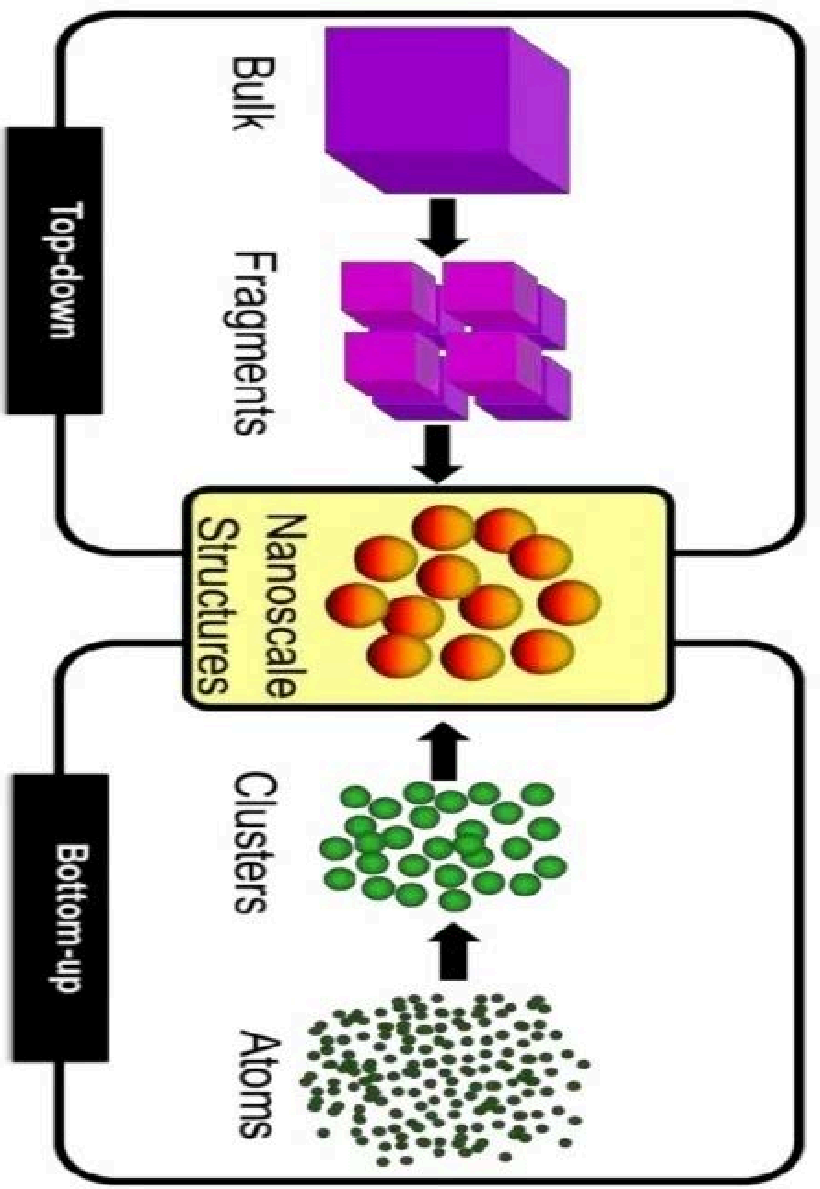
- ✓ A stable liquid phase containing particles in 1-1000 nm range. A colloidal particle is one such 1 – 1000 nm sized particle.

3D nanostructured materials:

Synthetic routes of nanomaterials

- **Top-down approach**
  - Begin with a pattern generated on a larger scale, then reduced to nanoscale
  - By nature, are not cheap and quick to manufacture
  - Slow and not suitable for large scale production.

- **Bottom-up approach**
  - Start with atoms or molecules and build up to nanostructures
  - Fabrication is much less expensive.



Methods of synthesis

Top-down

1) Ball milling
2) Lithography
3) Laser ablation
4) Sputtering deposition
5) Pulsed electrochemical etching
6) Vapor deposition
7) Molecular bean epitaxy
8) Nanografting
9) Polymer Pen Lithography (PPL)

Bottom-up

1) Co-precipitation
2) Sol-Gel Process
3) Microemulsions
4) Hydrothermal/Solvothermal Methods
5) Templated Synthesis
6) Self-assembly
7) Chemical vapor deposition
8) Plasma or flame spraying
9) Laser pyrolysis

Characterization of Nanomaterials

Acronym	Technique	Analytical Values
Optical (imaging) probe characterization methods		
CLSM	Confocal laser-scanning microscopy	Imaging/ultrafine morphology
SNOM	Scanning near-field optical microscopy	Raster imaging
DLS	Dynamic light scattering	Particle sizing
PCS	Photon correlation spectroscopy	Particle sizing
Electron Probe Characterization Methods		
SEM	Scanning electron microscopy	Raster imaging/topology morphology
FESEM	Field emission scanning electron microscopy	Raster imaging/topology morphology
TEM	Transmission electron microscopy	Imaging/particle size-shape
STEM	Scanning transmission electron microscopy	Imaging/particle size-shape
AES	Auger electron microscopy	Chemical surface analysis

Characterization of Nanomaterials

Acronym	Technique	Analytical Values
Scanning probe characterization methods		
AFM	Atomic force microscopy	Topology/imaging/surface structure
STM	Scanning tunneling microscopy	Topology/imaging/surface structure
Photon (Spectroscopic) Probe Characterization Methods		
SPR	Surface plasmon resonance spectroscopy	Surface/adsorbate analysis
RS	Raman spectroscopy	Vibrational analysis
SERS	Surface enhanced Raman spectroscopy	Chemical analysis/bond structure
XRD	X-ray diffraction	Crystal structure
XRF	X-ray florescence	Elemental analysis
XPS	X-ray photoelectron spectroscopy	Surface analysis/depth profile
Thermodynamic Characterization Methods		
TGA	Thermal gravimetric analysis	Mass loss vs. temperature
DSC	Differential scanning calorimetry	Reaction heats, heat capacity
BET	Brunauer-Emmett-Teller method	Surface area analysis

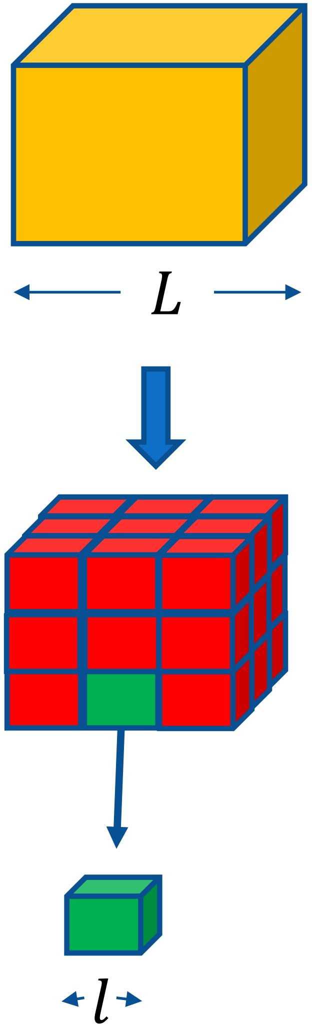
Consequence of nanoscale

There are three basically size dependent effects

- Surface effect
  - ✓ Increase in surface to volume ratio and specific surface area
  - ✓ Increase in the fraction of surface atoms
  - ✓ Increase in specific surface free energy
- Quantum confinement effect
- Reduced imperfections in crystal

A. Surface Effect

A.1 Surface to volume ratio & surface area



- Let L be the length of a large cubical particles

  Surface to volume ratio, $F = \frac{a}{V} = \frac{6L^2}{L^3} = \frac{6}{L}$

- If the large cubical particle is sub-divided to n_c small cubical particles of edge, l, then from mass balance equation, assuming no mass losses during conversion,

$$\text{Mass of large cube} = \text{total mass of small cube}$$

$$V \times \text{density} = n_c \times v \times \text{density}$$

$$n_c = \frac{V}{v} = \frac{L^3}{l^3}$$

$$\text{Specific surface area} = \frac{n_c \times a}{\rho L^3} = \frac{L^3}{l^3} \times \frac{6l^2}{\rho L^3} = \frac{6}{\rho l}$$

- Ratio of surface area $= \frac{n_c \times a}{A} = \frac{L^3}{l^3} \times \frac{6l^2}{6L^2} = \frac{L}{l}$

A. Surface Effect

A.1 Surface to volume ratio & surface area

- Let R be the radius of a large spherical particles

Surface to volume ratio, $F = \frac{a}{V} = \frac{4\pi R^2}{\frac{4}{3}\pi R^3} = \frac{3}{R} = \frac{6}{D}$

- If the large cubical particle is sub-divided to n_c small particles of radius, r, then from mass balance equation, assuming no mass losses during conversion,

$$\text{Mass of large sphere} = \text{total mass of small sphere}$$

$$V \times \text{density} = n_c \times v \times \text{density}$$

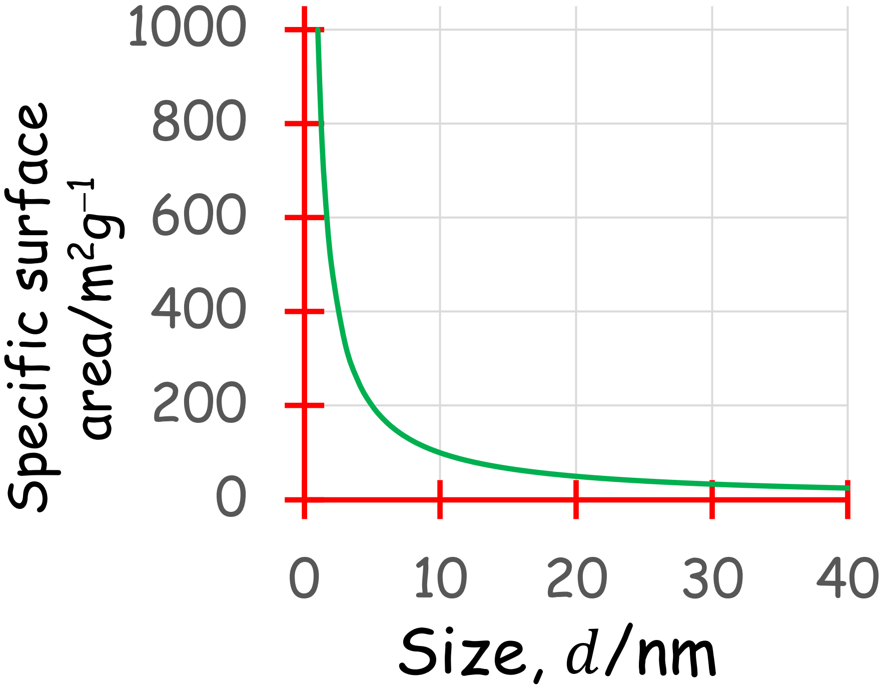
$$n_c = \frac{V}{v} = \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi r^3} = \frac{R^3}{r^3}$$

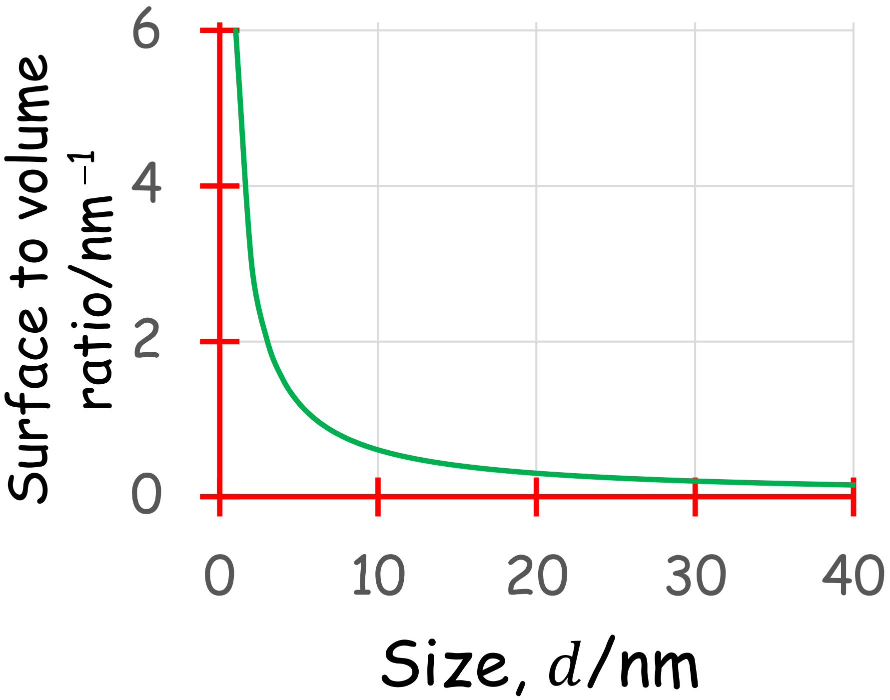
$$\text{Specific surface area} = \frac{n_c \times a}{\rho V} = \frac{R^3}{r^3} \times \frac{4\pi r^2}{\frac{4}{3}\pi\rho R^3} = \frac{3}{\rho r} = \frac{6}{\rho D}$$

- Ratio of surface area $= \frac{n_c \times a}{A} = \frac{R^3}{r^3} \times \frac{4\pi r^2}{4\pi R^2} = \frac{R}{r}$

A. Surface Effect

A.1 Surface to volume ratio & surface area





- It is apparent that both surface to volume ratio & specific surface area increase drastically when the size of material is reduced to or below 10 nm.

A. Surface Effect

A.1.2 Fraction of surface atoms

Cubical Particles

- Let the number of atoms along edge $= n$
- Total number of atoms in the cube, $N = n^3$
- The atoms at the edge share between two surface, while at the corner among eight surfaces. Thus, overcounting the edge and corner atoms need to be corrected. For large N, this correction is negligible. However, for nanoparticle, it is dominated.
- Total number of atoms on six surfaces including double counting at the edges $= 6n^2$
- Total number of double counted atoms at 12 edges $= 12n$
- Total number of atoms on eight corners $= 8$
- Subtraction of edge atoms from $6n^2$ also removes the corner atoms, which is to be added to count net total surface atoms.
- Thus, the net total number of surface atoms $= 6n^2 - 12n + 8$
- The fraction of surface atoms, F

$$F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{\frac{1}{3}}} - \frac{12}{N^{\frac{2}{3}}} + \frac{8}{N} \approx 6N^{-\frac{1}{3}}$$

A. Surface Effect

A.1.2 Fraction of surface atoms

Spherical Particles

- Let the number of atoms in a spherical particle $= N$, volume of sphere $= V_c$, radius of sphere $= R_c$, volume of each atom, $V_a = \frac{4}{3}\pi r_a^3$, r_a is the radius of atom & number of surface atoms $= N_s$.
- For spherical particle,

  The volume of spherical particle = total volume of N atoms

$$\frac{4}{3}\pi R_c^3 = N\left(\frac{4}{3}\pi r_a^3\right) \Rightarrow N = \left(\frac{R_c}{r_a}\right)^3$$

- Surface area of particle, $S_c = 4\pi R_c^2 = 4\pi\left(N^{\frac{2}{3}} r_a^2\right) = N^{\frac{2}{3}} S_a$

  where, S_a = surface area of an atom $= 4\pi r_a^2$
- Approximate number of surface atoms,

$$\mathrm{N_s} = \frac{\text{Surface area of a particle}}{\text{Central cross} - \text{sectional area of an atom}} = \frac{4\pi N^{\frac{2}{3}} r_a^2}{\pi r_a^2} = 4N^{\frac{2}{3}}$$

- The fraction of surface atoms *called dispersion* is given by

$$F = \frac{N_s}{N} = \frac{4N^{\frac{2}{3}}}{N} = 4N^{-\frac{1}{3}}$$

A. Surface Effect

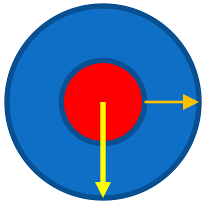
A.1.2 Fraction of surface atoms

Spherical Particles

- Volume of the layer or shell with a thickness δ at the surface of a spherical particle of a radius R can be determined from the following equation,

$$V_{shell} = \frac{4}{3}\pi R^3 - \frac{4}{3}\pi(R-\delta)^3 = \frac{4}{3}\pi[R^3 - (R-\delta)^3]$$

$$V_{sphere} = \frac{4}{3}\pi R^3$$



- The ratio of the volume of surface layer or shell to total volume of a particle can be determined by

$$F = \frac{V_{shell}}{V_{sphere}} = \frac{\frac{4}{3}\pi[R^3 - (R-\delta)^3]}{\frac{4}{3}\pi R^3} = 1 - \left(\frac{R-\delta}{R}\right)^3$$

- Ratio, F approaching to 1 implies that all atoms are on the surface. F becomes 1 when $R = \delta$.

A. Surface Effect

A.1.2 Fraction of surface atoms

From structural magic numbers

- ✓ Most metals in the solid form close packed lattices
- ✓ Ag, Al, Cu, Co, Pb, Pt, Rh are Face Centered Cubic (FCC)
- ✓ Mg, Nd, Os, Re, Ru, Y, Zn are Hexagonal Close Packed (HCP)
- ✓ Cr, Li, Sr can form Body Centered Cubic (BCC) as well as (FCC) and (HCP) depending upon formation energy
- ✓ How does crystal structure impact nanoparticles?
- ✓ Nanoparticles have a "**structural magic number**", that is, the optimum number of atoms that leads to a stable configuration while maintaining a specific structure.
- ✓ Structural magic number = minimum volume and maximum density configuration
- ✓ If the crystal structure is known, then the number of atoms per particle can be calculated.

A. Surface Effect

A.1.2 Fraction of surface atoms

From structural magic numbers

- ✓ For *n* layers, the number of atoms N in an approximately spherical FCC nanoparticle is given by the following formula:

$$N = \frac{1}{3}(10n^3 - 15n^2 + 11n - 3)$$

- ✓ The number of atoms on the surface N_{surf}

$$N_s = 10n^2 - 20n + 12$$

- ✓ The fraction of surface atom,

$$F = \frac{N_s}{N}$$

- ✓ The diameter of cluster

$$D = 2d(2n - 1)$$

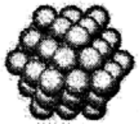
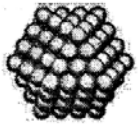
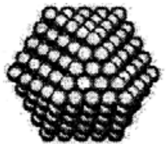
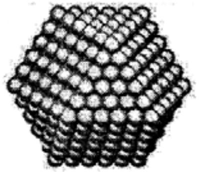
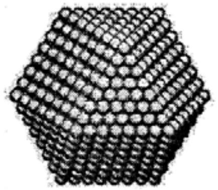
Where $d = \frac{a}{\sqrt{2}}$, a is lattice constant.

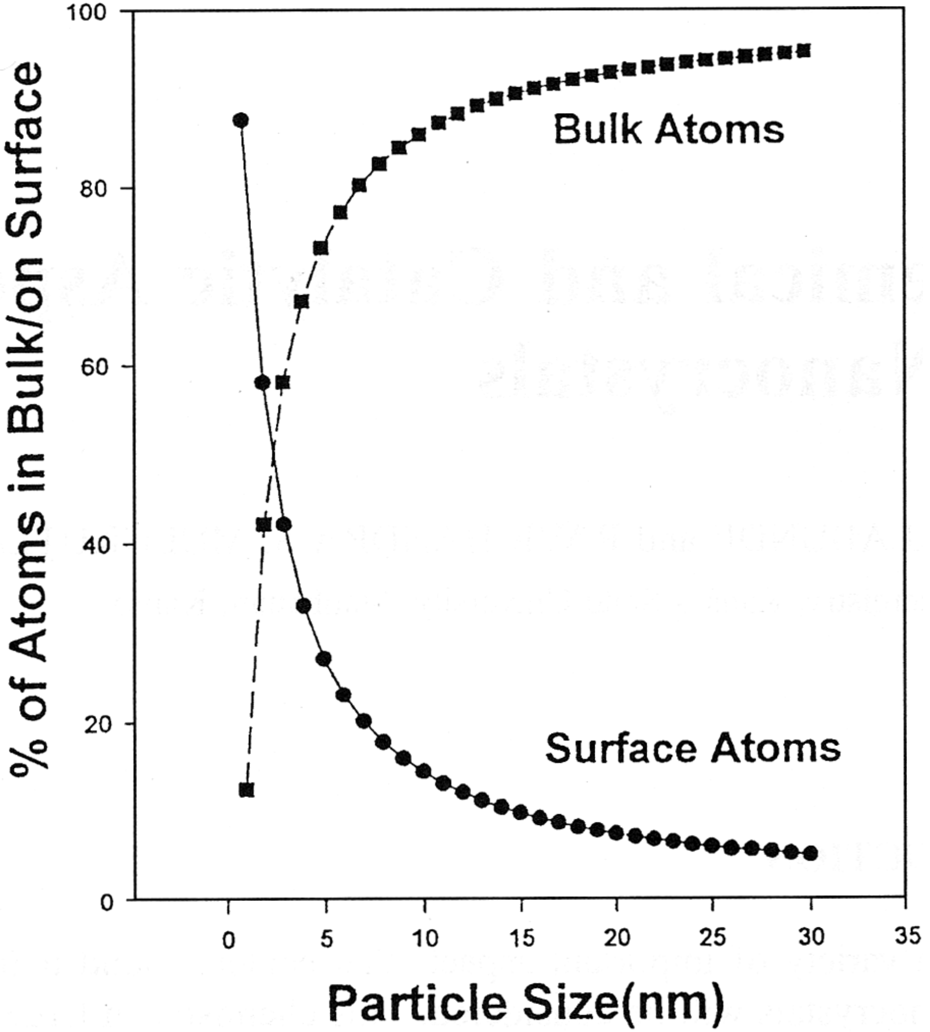
- ✓ For bcc crystal

$$N = 4n^3 - 6n^2 + 4n - 1, \; N_s = 12n^2 - 24n + 14$$

A. Surface Effect

A.1.2 Fraction of surface atoms

Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35



A. Surface Effect

A.1.3 Specific surface energy

- The energy required to create a new surface containing N_b atoms is given by $\frac{N_b u}{2}$, where u is the bonding energy between two atoms.
- If the A is the surface area, then its contribution to specific surface energy is

$$\gamma_0 = \frac{N_b u}{2A}$$

- Within the interior of a particle, an atom or ion is held in a mechanical equilibrium by binding forces, which fix the ions in their lattice positions.

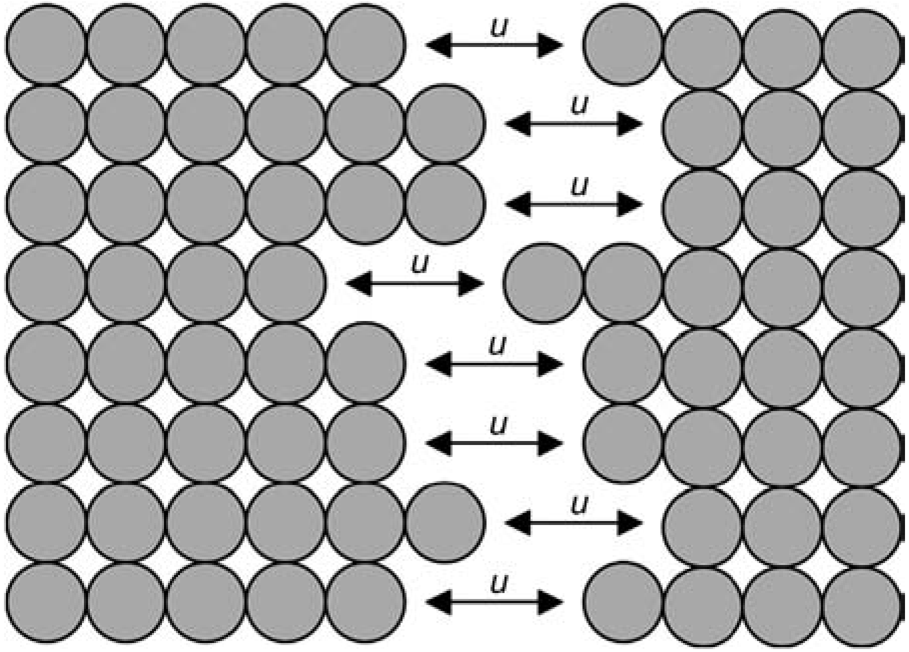


Fig. Creation of new surfaces (e.g., by breaking a larger portion into smaller pieces) requires energy u for each bond to be broken.

A. Surface Effect

A.1.3 Specific surface energy

- Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers. They have dangling or unsatisfied bonds exposed to the surface.

- Due to the reduced number of neighbors, at each surface of the atom, a force f acts perpendicular to the surface. It leads stress in the plane. Surface stress is given by

$$\sigma = \frac{f}{A}$$

- δ deforms the surface and results in surface stretching. δ contributes to the specific surface energy as function of stretching, ε_s. The specific surface energy is given by

$$\gamma = \gamma_0 + \gamma_s(\varepsilon_s)$$

Where γ_s is the contribution of the surface stress to the surface energy.

A. Surface Effect

A.1.3 Specific surface energy

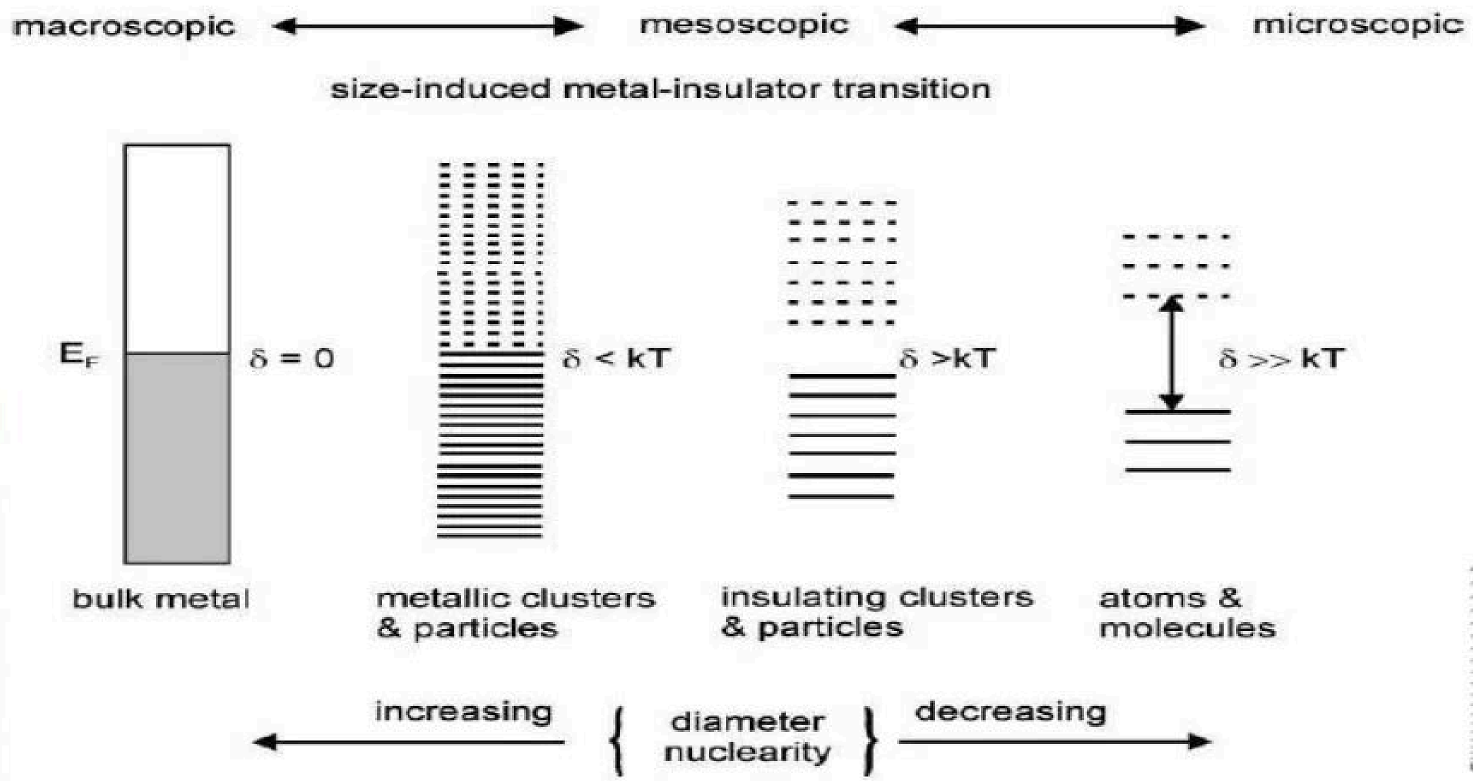
- The amount of surface energy per particle $u_{surface}$ is equal to γA, where γ is the specific surface energy and A is the surface area of one particle.
- For thermodynamic considerations, the surface energy per mole of material is the essential quantity.
- Hence, if N is the number of particles per mole, one obtains $N\gamma A = \left(\frac{M}{\rho v}\right)\gamma A$, where ρ is the density of the material, M is the molar mass, v is volume of particle $= \frac{\pi d^2}{6}$, $A = \pi d^2$, and d is the diameter of particle.
- Finally, one obtains the surface energy of particles with diameter d per mole:

$$U_{surface} = \frac{M}{\rho}\frac{6}{\pi d^3}\gamma\,\pi d^2 = \left(\frac{6M}{\rho}\right)\frac{\gamma}{d}$$

- From equation, the surface energy per mole increases with 1/d and in some cases, especially those related to very small particles, this may have dramatic consequences.

B. Quantum confinement effect

- The valence atomic orbitals form energy bands in the solids, while core atomic orbitals remain confined in a small volume.
- Width of the bands increase with number (N) of atoms added, and density of states (DOS) is proportional to N.
- Thus, the reduction in size of materials leads to reduce the DOS and separate the energy states in the bands as shown in **Fig**.

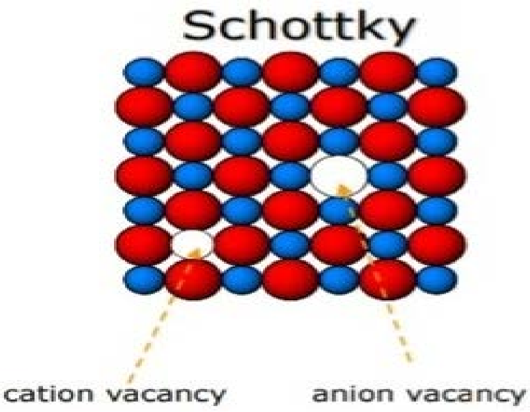


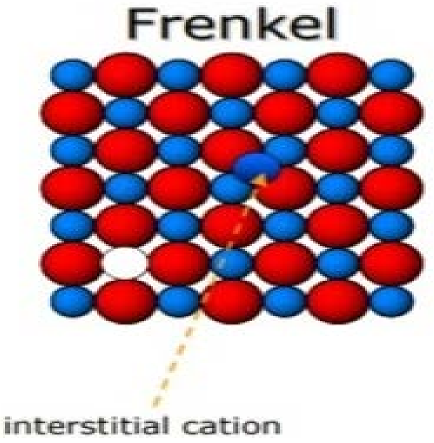
B. Quantum confinement effect

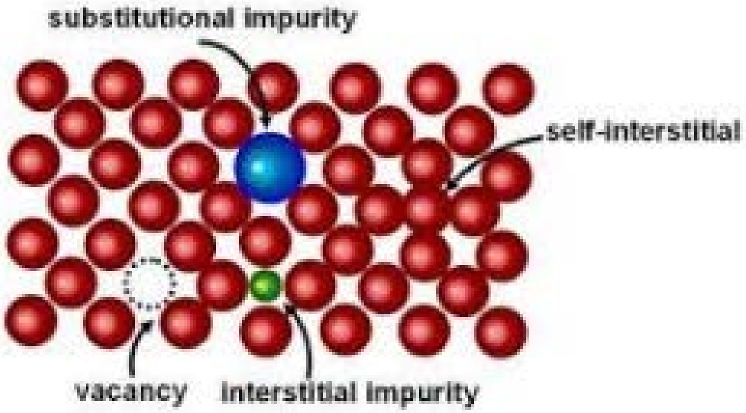
- When the size of materials is smaller than the de Broglie wavelength, electrons and holes are spatially confined and electric dipoles are formed, and discrete electronic energy level would be formed in all materials.
- The threshold size of material below which electrons and holes are spatially confined is quantum size.
- The phenomenon of confinement of electrons and holes is quantum confinement or quantum confinement effect, or quantum effect.
- The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies.

C. Reduced imperfections

Point Defects (0D Defects)



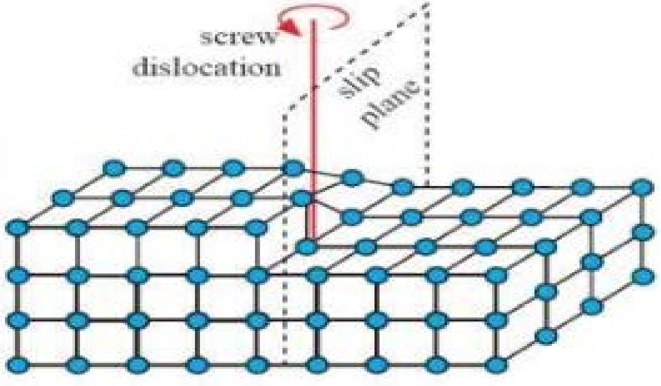


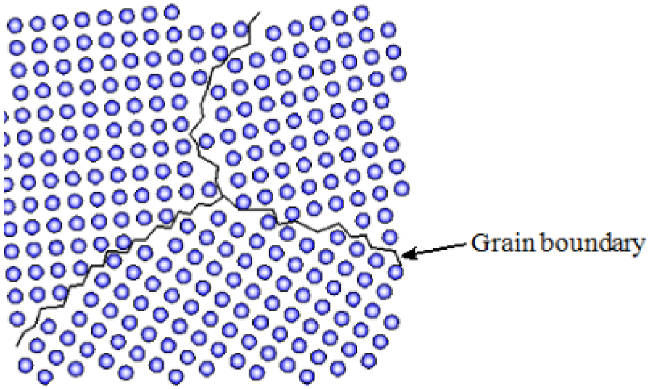


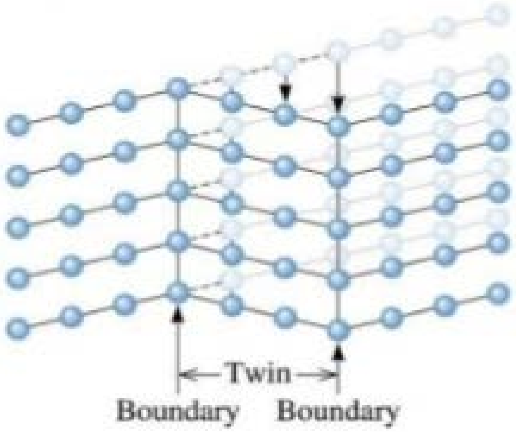
Line Defects (1D Defects)

Surface Defects (2D Defects)

Volume Defects (3D Defects)



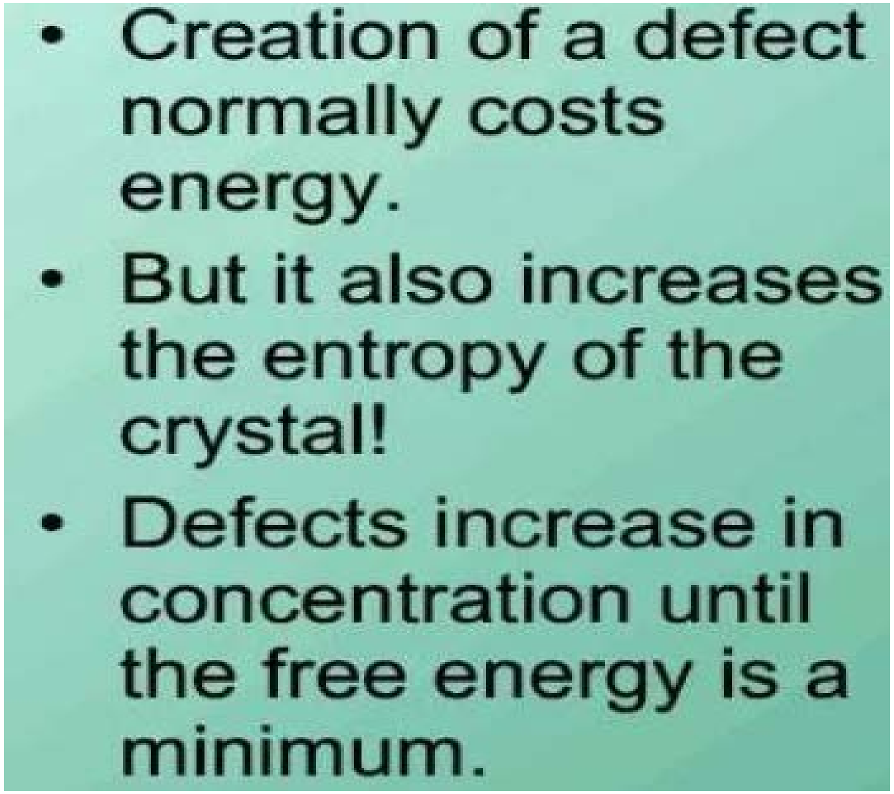




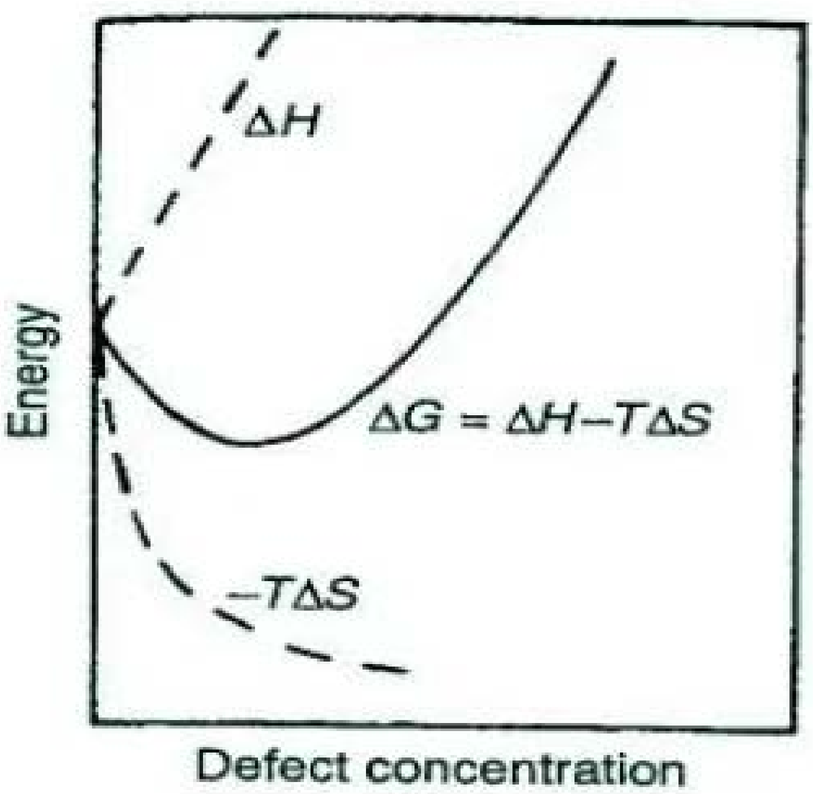
C. Reduced imperfections

At Constant P, $\Delta V = 0$

- Defect stability
  - ✓ Free energy: $\Delta G = \Delta \underset{\uparrow}{U} + P\Delta V - T\Delta \underset{\uparrow}{S}$
  - ✓ G decreases if $U < TS$



- Creation of a defect normally costs energy.
- But it also increases the entropy of the crystal!
- Defects increase in concentration until the free energy is a minimum.



C. Reduced imperfections

- Critical size of crystal
  - ✓ Concentration of defects

$$\frac{N_V}{N} = \exp\left(\frac{-Q_V}{kT}\right)$$

N_V is the No. of defects
N is the No. of potential defects
Q_V is activation energy

  - ✓ Critical size

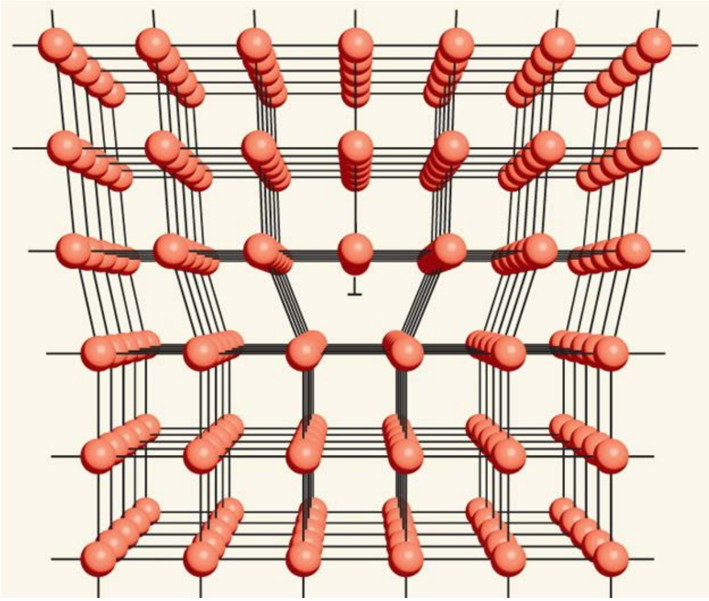
$$d_c = 2\left[\frac{3\exp\left(\frac{Q_V}{kT}\right)}{4\pi n_V}\right]^{\frac{1}{3}}$$

n_V is number of atoms per unit volume

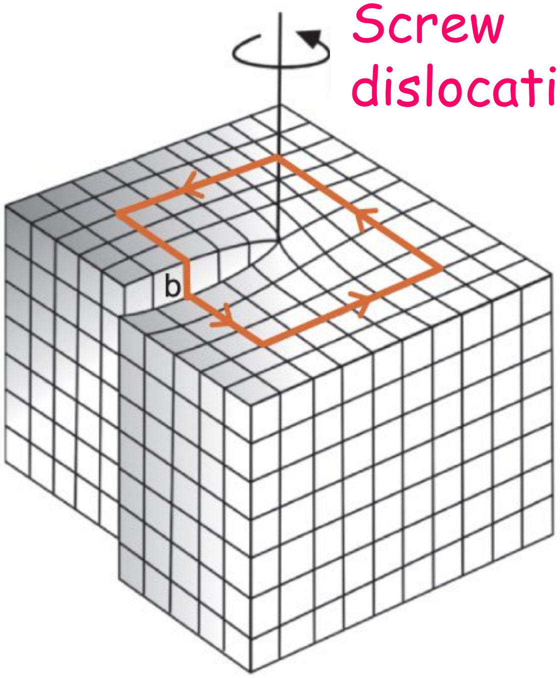
  - ✓ For Al at 900 K with Q_V = 0.66 eV, d_c is 6 nm
  - ✓ For Cu at 900 K with Q_V = 1.29 eV, d_c is 86 nm
- It is to be noted that nanocrystals below d_c (1- 100 nm) the crystal becomes free of vacancies

C. Reduced imperfections

- Line defects
  - ✓ Line defects are the irregularities of deviations from ideal arrangement in entire rows of lattice points.
  - ✓ Interatomic bonds significantly distorted in immediate vicinity of dislocation line.
  - ✓ Dislocation affects the mechanical properties.



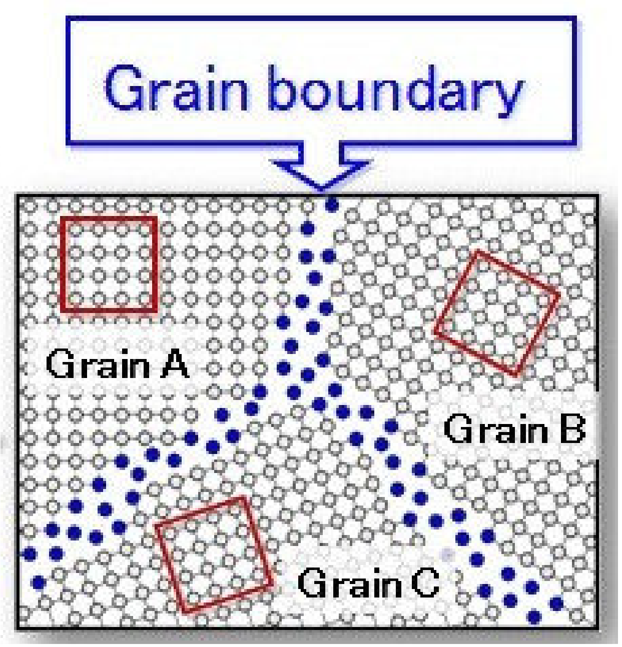
Edge dislocation

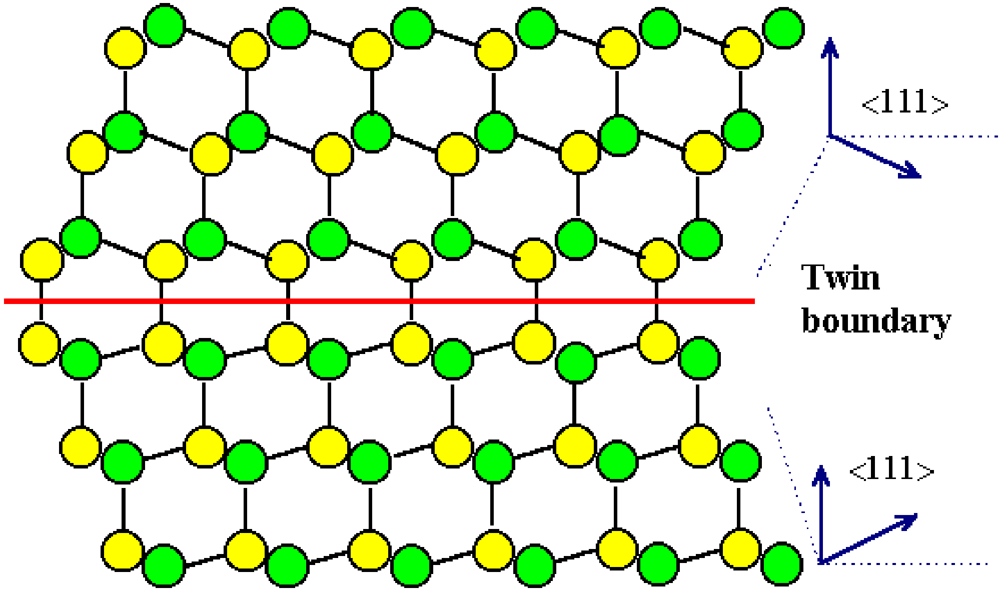


Screw dislocation line

C. Reduced imperfections

- Surface defects
  - ✓ Surface defects are boundaries that have two dimensions and normally separate regions of the materials that have different crystal structures
  - ✓ Defects are slightly disorder, low density, high mobility, high diffusivity and high chemical reactivity





C. Reduced imperfections

- Movement of dislocation
  - ✓ It is almost impossible to create a dislocation free crystal but if the size is sufficiently reduced then the dislocations will be pinned by the grain boundaries and the interior of the grain would be essentially dislocation free.
  - ✓ The stress required to move a dislocation is

$$\tau = \frac{2\alpha G b}{\lambda}$$

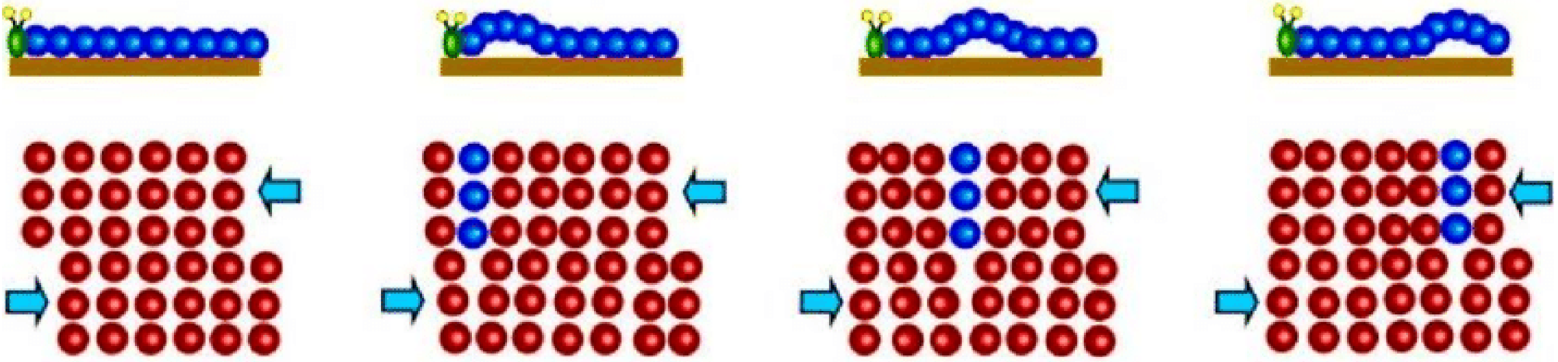
Where, *G* is the shear modulus of the crystal, *b* is the Burgers vector of the dislocation, α is a constant (0.5 - 1.5) depending upon the type of dislocation.

C. Reduced imperfections

- Movement of dislocation
  - ✓ The grain size at which the dislocation will be pinned at both ends by the grain boundary of the crystallite comes out is

$$d_c = \frac{2\alpha G b}{\tau_s}$$

where τ_s is the theoretical strength. Here again the critical size is in the nanometer range.



  - ✓ Crystal with size less than d_c is free from dislocation

Size dependent properties

The properties that depend on the size of materials is called size dependent properties. There are various size dependent properties, such as

A. Crystal properties
   1. Transition of crystal structure
   2. Lattice constant

B. Mechanical properties

C. Thermal properties
   1. Melting point
   2. Specific heat

D. Optical properties

E. Electrical properties

F. Magnetic properties

G. Chemical properties

A. Crystal properties

A.1 Transition of crystal structure

- ✓ Different facets of crystal have different surface energies.

$$\text{Total surface energy}, E_s = \sum \gamma_i A_i$$

where the index *i* represents the different facets with areas A_i and specific surface energy γ_i.

- ✓ Surface Properties of Different Crystal Planes in FCC Structures (*a* is the lattice constant and ε is the bonding energy) is

	(111)	(100)	(110)
Number of dangling bonds	3	4	5
Interatomic layer spacing	0.577*a*	0.5*a*	0.354*a*
Surface energy per atom	$3*0.5\varepsilon$	$4*0.5\varepsilon$	$5*0.5\varepsilon$
Number of atoms per unit area	2 atoms/ $(0.866a^2)$	2 atoms/ a^2	1 atom/ $(0.747a^2)$
Surface energy per unit area	$3.464\varepsilon/a^2$	$4\varepsilon/a^2$	$3.347\varepsilon/a^2$

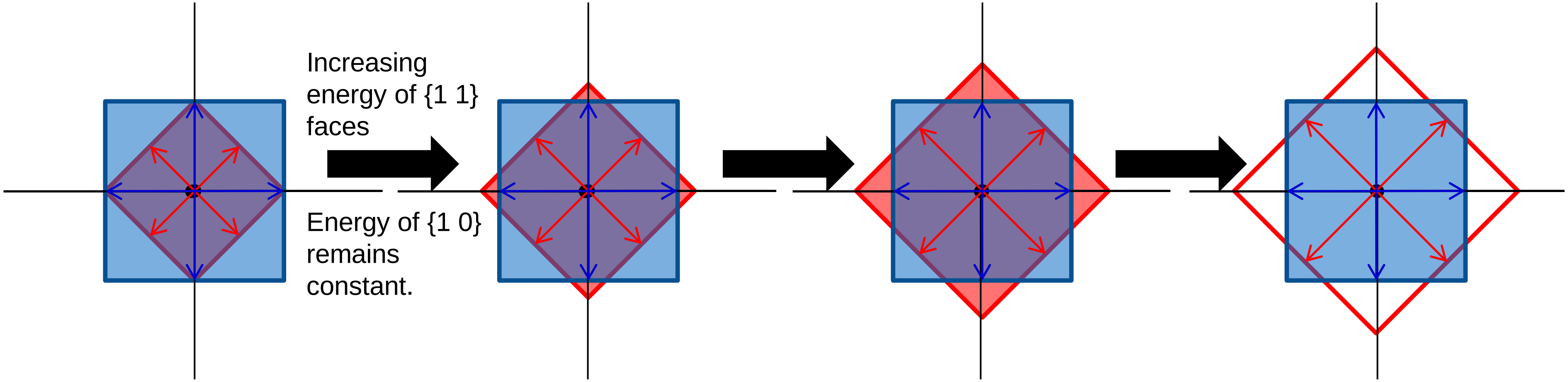
A. Crystal properties

A.1 Transition of crystal structure

- ✓ According to Wulff, the minimal energy is obtained for a polyhedron in which the central distances h_i to the faces are proportional to their surface energies γ_i, i.e.,

$$\frac{\gamma_i}{h_i} = \text{Constant}$$

- ✓ Wulff Plots: Length of arrow is proportional to surface energy of that face. Longer arrows denote higher energy surfaces.



Increasing energy of {1 1} faces

Energy of {1 0} remains constant.

A. Crystal properties

A.1 Transition of crystal structure

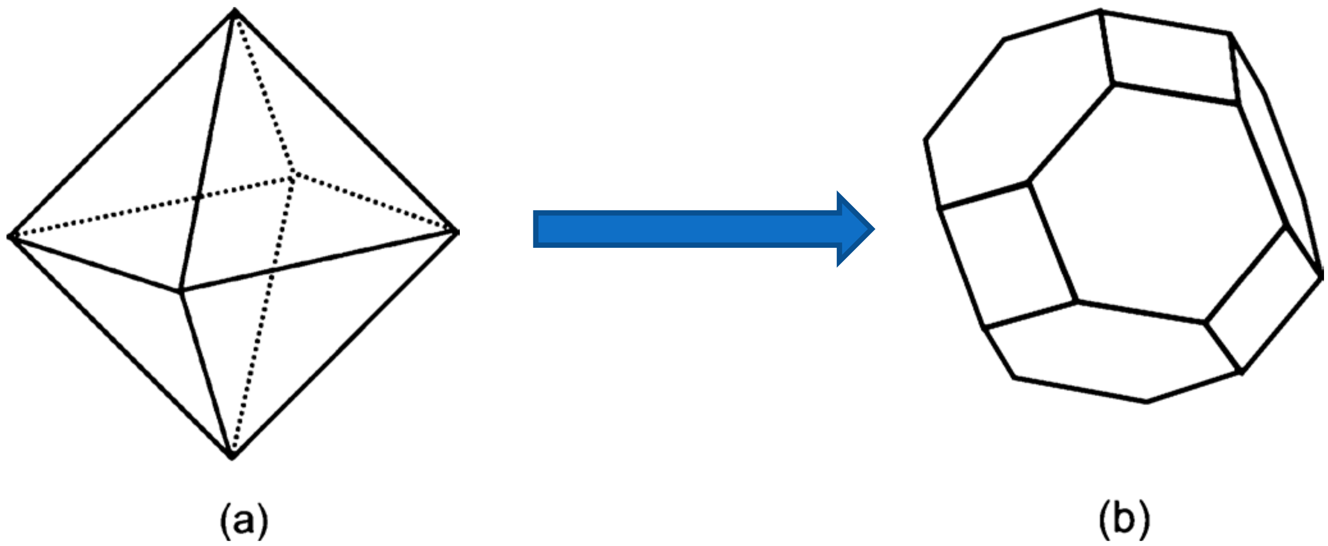


Fig. (a) An FCC crystal with only the {111} planes making the surface; the surface to volume ratio is high and so the total surface energy is high even though the {111} planes have the lowest energy, (b) the surface energy can be reduced by truncating the corners of the octahedron; this exposes some high energy {100} planes but reduces the total surface area.

A. Crystal properties

A.1 Transition of crystal structure

<u>Examples</u>

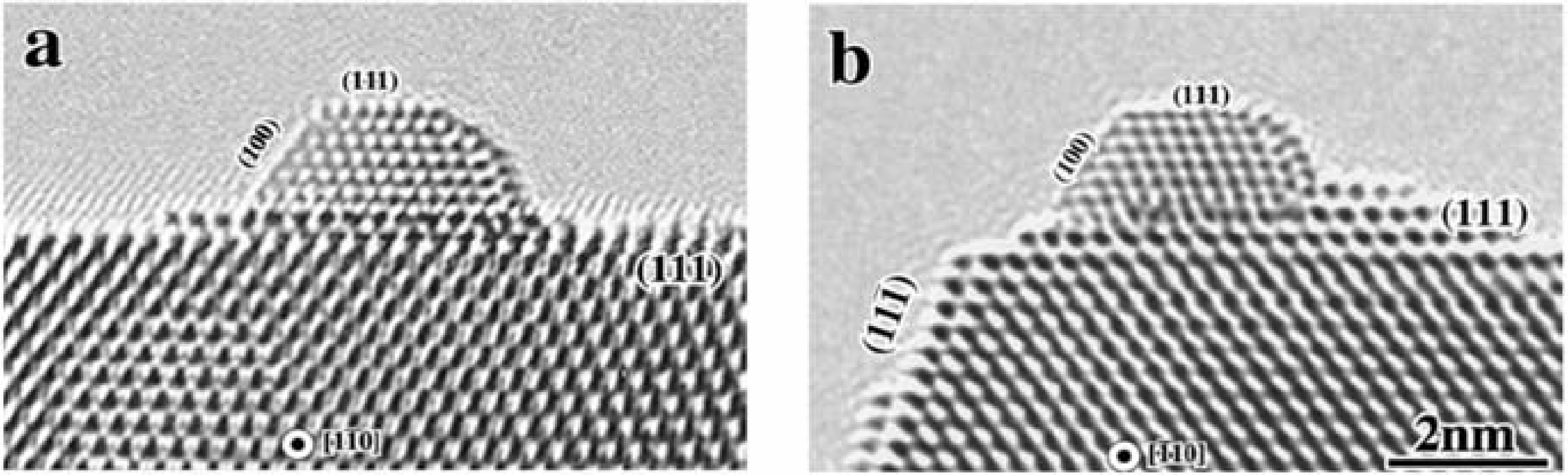


Figure (a, b) Nano FCC metallic particles (Au) showing (111) and (100) surface.

A. Crystal properties

A.2 Lattice parameters

- ✓ As the size of the nanocrystal is reduced, surface tension effects tend to dominate
- ✓ This leads to a reduction in the lattice parameter of nanocrystal.
- ✓ The difference of internal and external pressure of crystal is given by

$$\Delta P = \frac{2\gamma}{d}$$

Where, d is diameter of spherical particle and γ is surface energy

- ✓ The compressibility, $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Longrightarrow \Delta P = -\frac{3}{K}\frac{\Delta a}{a_0}$

Where a_0 is the lattice constant of bulk crystal

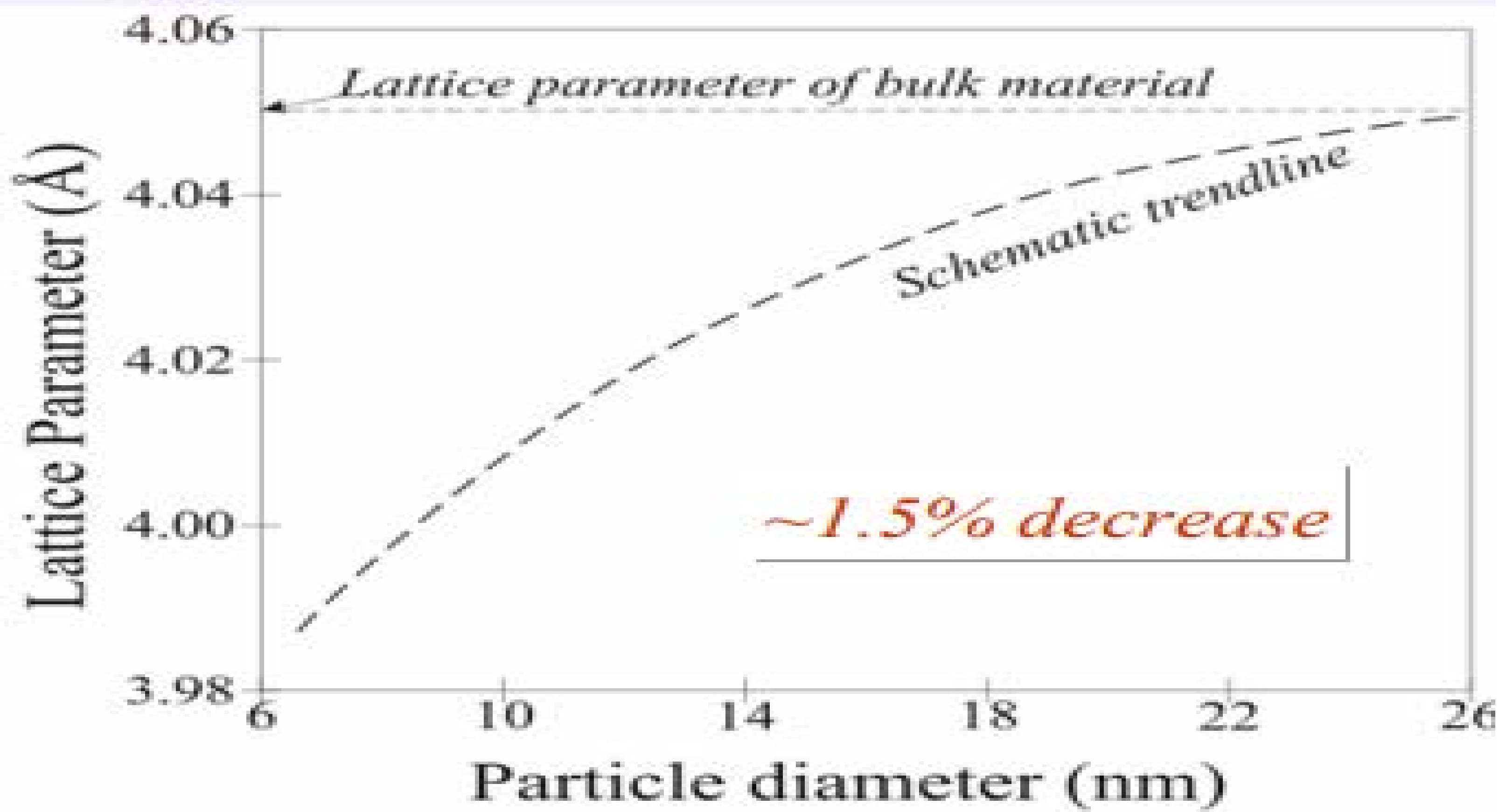
A. Crystal properties

A.2 Lattice parameters

- ✓ Eliminating ΔP gives

$$\frac{\Delta a}{a_0} = -\frac{2K}{3}\frac{\gamma}{d}$$

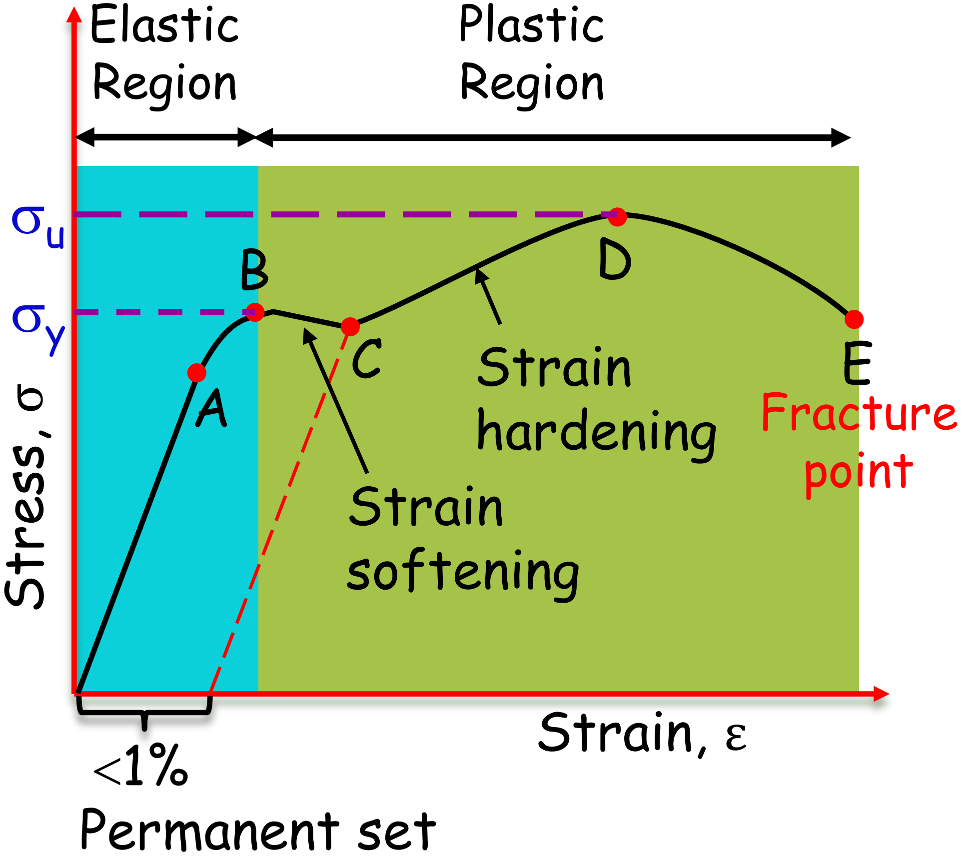
- o $d \longrightarrow \infty \Longrightarrow \Delta a = 0,$
  $d \downarrow \Longrightarrow \Delta a \downarrow$



B. Mechanical properties

Stress – strain curve

- ✓ $\sigma = \frac{F}{A}$ and $\varepsilon = \frac{\Delta l}{l_0}$
- ✓ A → Proportional limit
- ✓ B → Yield point (Elastic limit) corresponding stress is yield strength (σ_y).
- ✓ After B → permanent deformation.
- ✓ D → Ultimate tensile strength (σ_u).
- ✓ E → Fracture point



- ✓ If D and E are close, the material is said to be brittle, whereas if they are far apart, the material is said to be ductile.

B. Mechanical properties

The mechanical properties of materials usually increase with decreasing size. →not always true.

(C-1) Whiskers and Nanowires

(A) a whisker can have a mechanical strength approaching to the theoretical.

- The increase of mechanical strength becomes appreciable only when the diameter of a whisker is less than 10 microns.
  - The enhancement in mechanical strength starts in micron meter scale, which is noticeably different from other property size dependence.

B. Mechanical properties

(B) Two possible mechanisms to explain the enhanced strength :

- high internal perfection of the nanowires or whiskers :

  Imperfections in crystals are highly energetic and small size makes elimination of imperfections possible. Some imperfections in bulk materials, such as dislocations are often created to accommodate stresses generated in the synthesis and processing of bulk materials due to temperature gradient and other inhomogeneities. Such stresses are unlikely to exist in small structures.

- perfection of the side faces of whiskers or nanowires :

  In general, smaller structures have less surface defects.

  For example, It was found that vapor grown whiskers with diameters of 10 microns or less had no detectable steps on their surfaces whereas irregular growth steps were revealed on whiskers with diameters above 10 microns.

B. Mechanical properties

(C-2). Nanostructured materials (polycrystalline with nano-sized grains

- Yield strength, σ_{TS}, and hardness, H, of polycrystalline materials are known to be dependent on grain size on the micrometer scale, following the Hall-Petch relationship:

$$\sigma_{TS} = \sigma_0 + \frac{K_{TS}}{\sqrt{d}}$$

$$H = H_0 + \frac{K_H}{\sqrt{d}}$$

$\sigma_0$and H_0 : constants, d : average grain size, and K_{TS} and K_H : material-dependent constants.

- The Hall-Petch model treats grain boundaries as barriers to dislocation motion
- Nano-materials possess high perfection and no dislocations Therefore, the Hall-Petch model would be invalidated in the nanometer regime.
- Experimentally, it has been found that nanostructured metals have higher or lower strength and hardness compared to coarse-grained materials, (There is no solid understanding on the size dependence of the mechanical properties.)

C. Thermal properties

C.1 Melting point

- ✓ Nanoparticles (metallic, semiconductors or oxide) are found to have lower melting temperatures when the particle size decreases below 100nm.
- ✓ The relationship between the melting points of a bulk material, T_b, and a particle, T_m is given by

$$T_b - T_m = \left[\frac{2T_b}{\Delta H \rho_s r_s}\right]\left[\gamma_s - \gamma_l\left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right] \qquad (8.12)$$

r_s is radius of the particle, ΔH is molar latent heat of fusion; γ and ρ are surface energy and density, respectively.

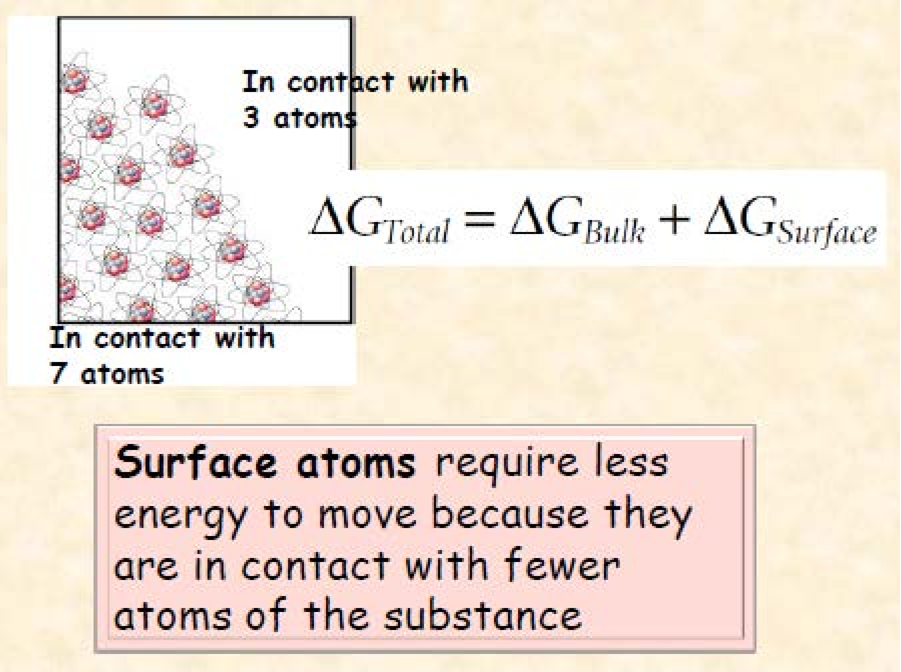
C. Thermal properties

C.1 Melting point

- Melting Point (Microscopic Definition) Temperature at which the atoms, ions, or molecules in a substance have enough energy to overcome the intermolecular forces that hold the them in a “fixed” position in a solid
- At macroscopic length scales, the melting temperature of materials is size-independent. For example, an ice cube and a glacier both melt at the same temperature.
- Melting starts from the surface.
- Bulk materials have negligible surface atoms

✓ Surface atoms becomes dominate factor in Nano materials

✓ Surface atoms requires less energy to move.



$$\Delta G_{Total} = \Delta G_{Bulk} + \Delta G_{Surface}$$

Surface atoms require less energy to move because they are in contact with fewer atoms of the substance

C. Thermal properties

C.1 Melting point

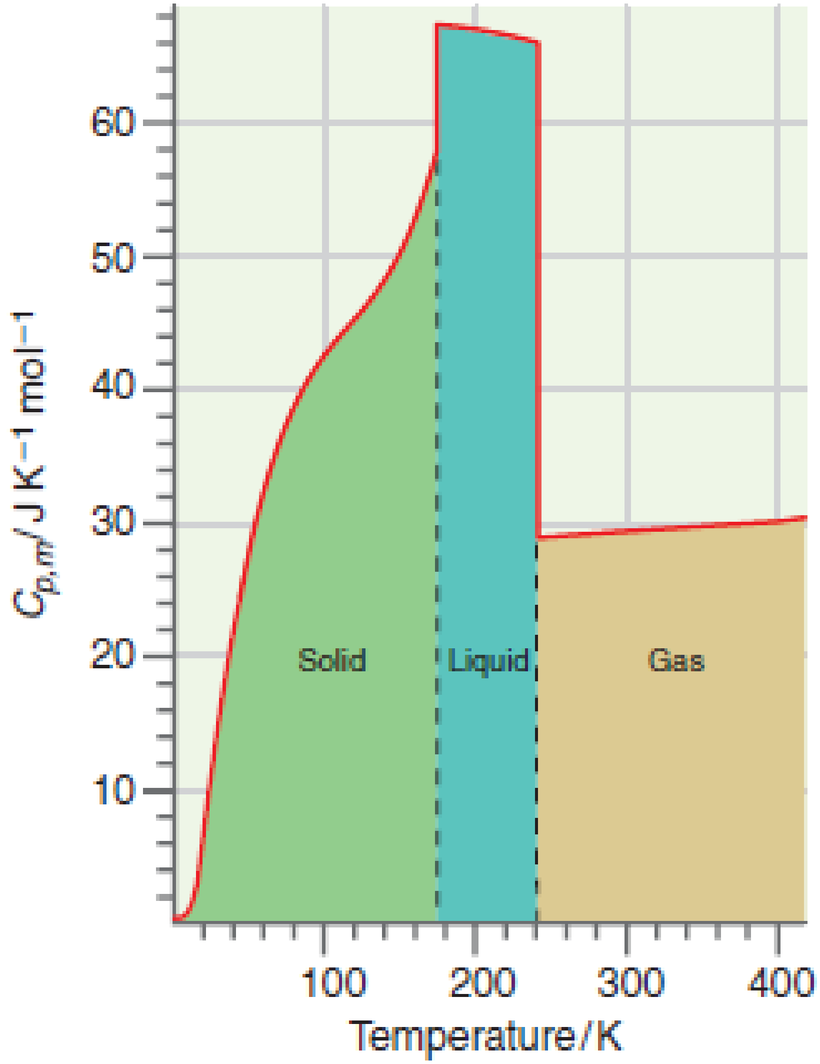
✓ However, it is not always easy to determine or define the melting temperature of nanoparticles. Because,

- Evaporation effectively reduces particle size
- Oxidation changes the surface composition and thus melting temperature.

C. Thermal properties

C.2 Heat Capacity

- ✓ Molecules can take up energy by moving faster, by rotating in three-dimensional space, by periodic oscillations (known as vibrations) of the atoms around their equilibrium structure, and by electronic excitations.
- ✓ Energy is gained or lost by a molecule through collisions with other molecules.
- ✓ A given degree of freedom in a molecule can only take up energy through molecular collisions if the spacing between adjacent ΔE and T satisfies the relationship, $\Delta E \approx k_b T$



C. Thermal properties

C.2 Heat Capacity

- ✓ The amount of energy needed to move up the ladder of energy levels is very different for the different degrees of freedom: $\Delta E_{electronic} \gg \Delta E_{vibration} \gg \Delta E_{rotation} \gg \Delta E_{translation}$.
- ✓ A given degree of freedom in a molecule can only take up energy through molecular collisions if the spacing between adjacent energy levels and the temperature satisfies the relationship, $\Delta E \approx k_b T$
- ✓ At 300 K, $\Delta E \approx k_b T$ is always satisfied for translation and rotation, but not for vibration and electronic excitation.
- ✓ A solid can be thought of as a set of interconnected harmonic oscillators, and heat uptake leads to the excitations of the collective vibrations of the solid.

C. Thermal properties

C.2 Heat Capacity

- A solid can be thought of as a set of interconnected harmonic oscillators, and heat uptake leads to the excitations of the collective vibrations of the solid.
- At very low temperatures these vibrations cannot be activated, because the spacing of the vibrational energy levels is large compared to . As a consequence, energy cannot be taken up by the solid.
- Reducing material size activates more and more vibration modes to take up more energy.

Size reduction

- Increage ΔE leads decrease in C_m
- Increase number of vibration mode satisfy $\Delta G \approx k_b T$ which increased C_m
- The increased number of vibration modes dominate over the ΔE.
- Thus reduction in size leads to higher C_m

D. Optical properties

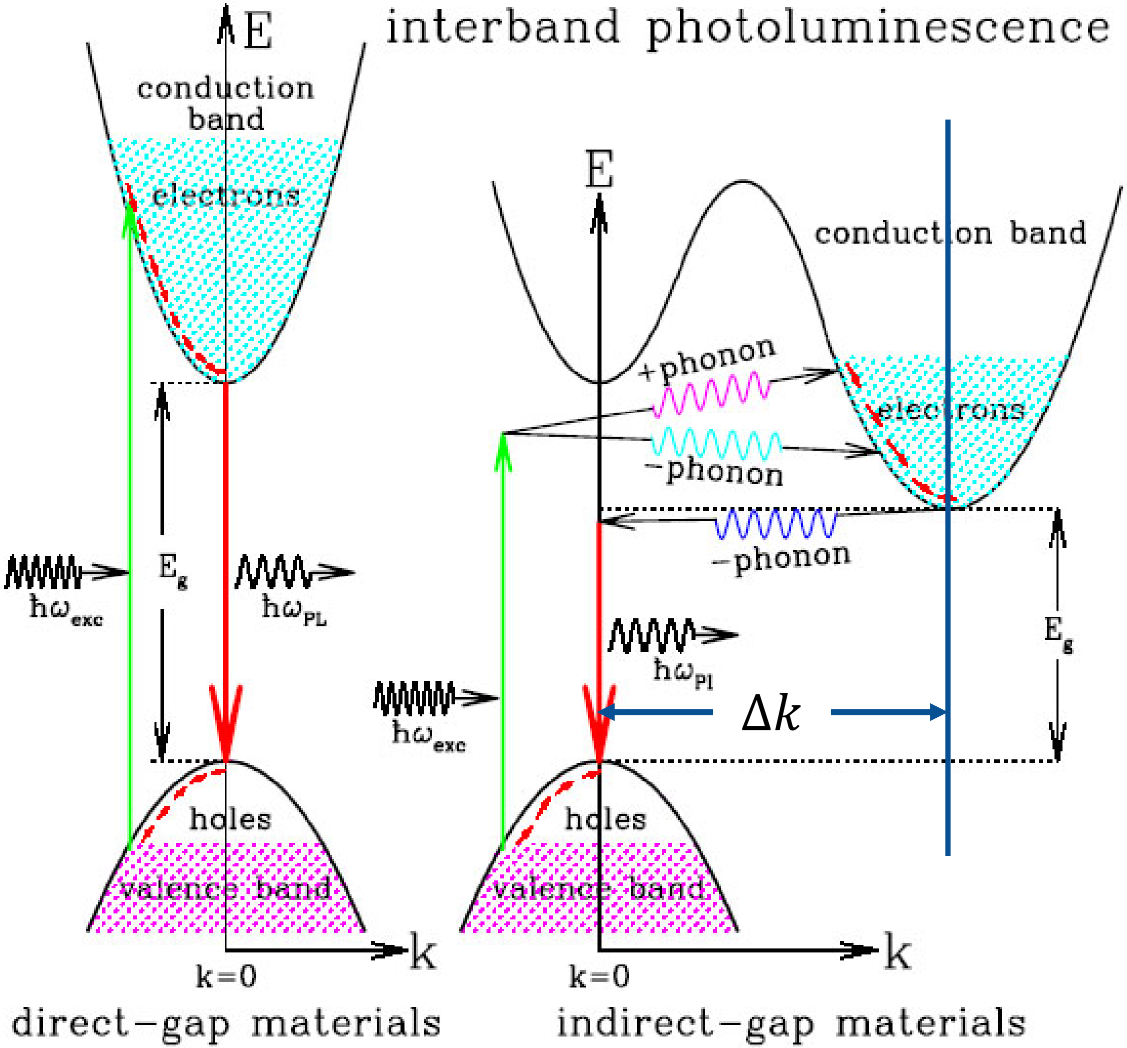
The reduction of materials' dimension has pronounced effects on the optical properties

D-1 One is due to the increased energy level spacing →quantum size effect. It is pronounced in semiconductor or insulation materials

D-2 The other is related to surface plasmon resonance. It dominates in metallic nanomaterials

D. Optical properties

D-1 Photoluminescence



$$E = \frac{k^2\hbar^2}{2m^*} \;\&\; k = \frac{2\pi}{\lambda}$$

- Optical transition:

$$E_i = E_f \;\&\; \hbar k_i = \hbar k_f$$

Direct band gap:

$$\hbar k_i + \hbar k_{phot} = \hbar k_f$$

$$k_{phot} \ll k_i \Longrightarrow \hbar k_i \simeq \hbar k_f$$

$$k_i \simeq k_f = 0$$

- Likely to photoluminescence

Indirect band gap:

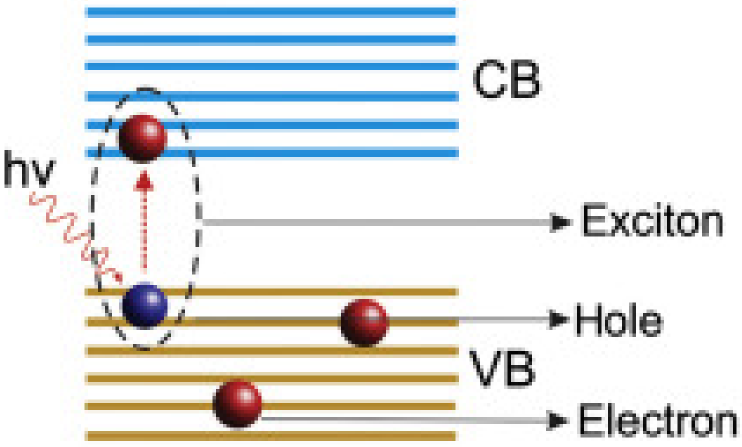
$$\hbar k_i + \hbar k_{phot} \pm \hbar k_{phon} = \hbar k_f$$

$$\Delta k = k_f - k_i \simeq \pm k_{phon}$$

- Transition must requires excitation or de-excitation of phonon.
- It is non-radiative and less likely photoluminescence.

D. Optical properties

D-1 Bohr exciton radius and confinement

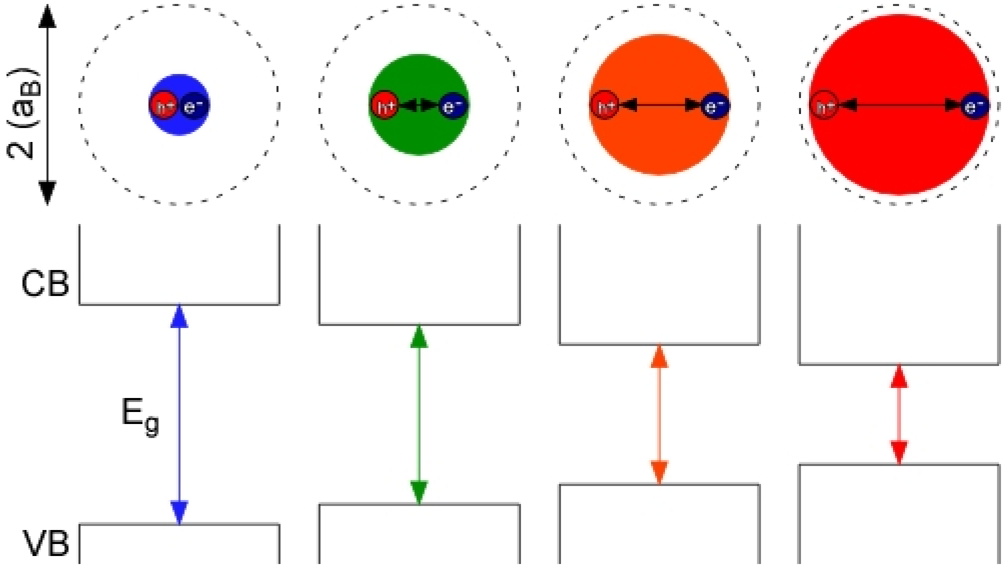


- Exciton→ Bound state of electron and hole

$$r_B^{ex} = \frac{\varepsilon r_B m_0}{\varepsilon_0 \mu} \quad \text{where} \left[\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}\right]$$

$$F_c = -\frac{e^2}{4\pi\varepsilon_0 r^2} \;\&\; E_g = E_g^{bulk} - \frac{e^2}{4\pi\varepsilon_0 r^2}$$

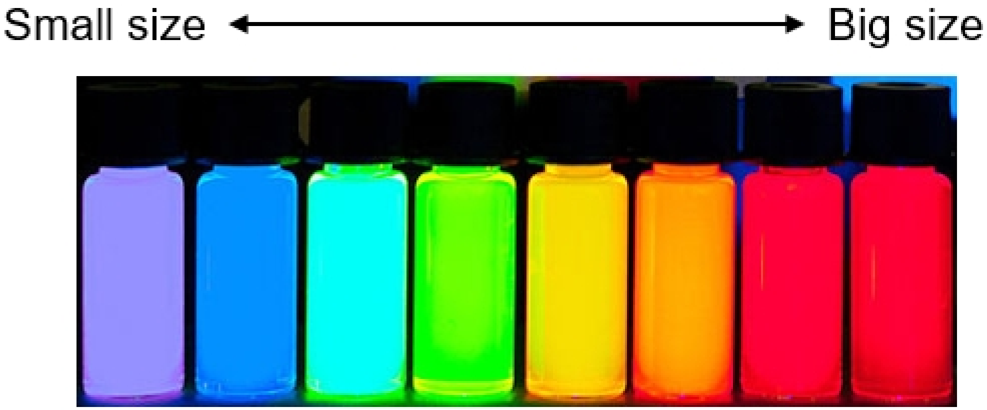
- For bulk material: $F_c \ll kT$, less likely to formation of exciton at RT

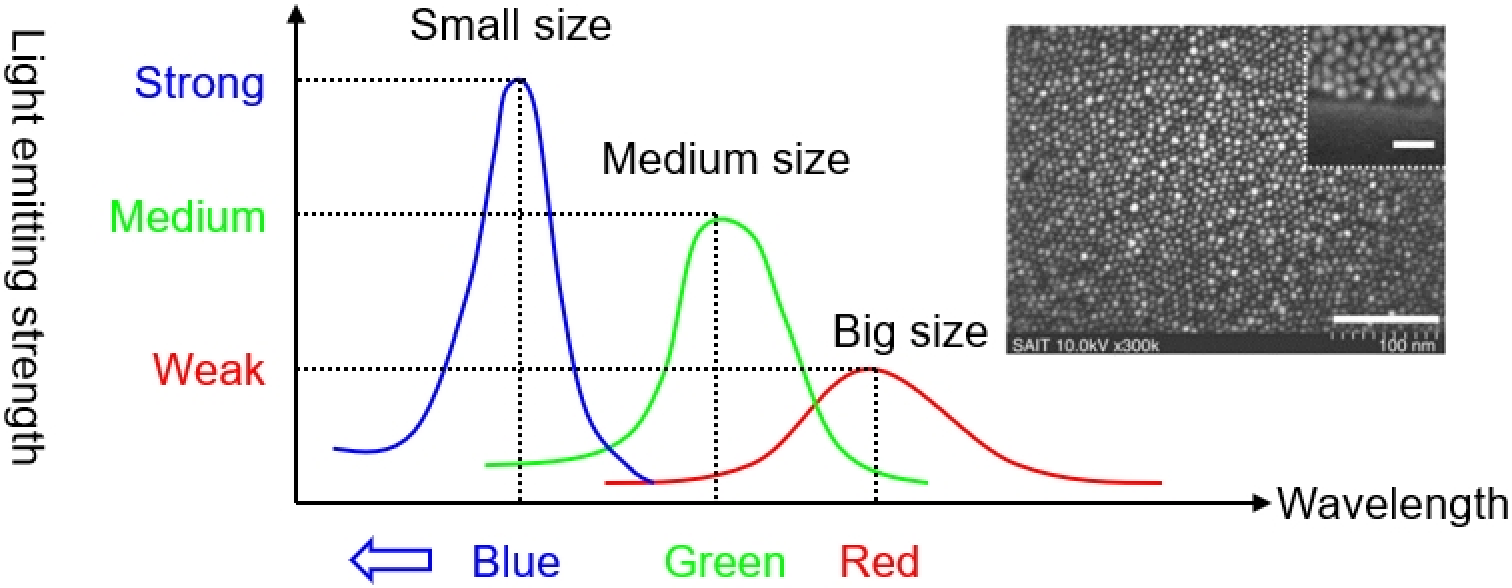


- ✓ $d \ll r_B^{ex} \rightarrow$ electron and hole are confined.
- ✓ E_g increases with $d \downarrow$ and absorption → blue shift.
- ✓ F_c favors radiative recombination and hence photoluminescence.
- ✓ $\Delta k = \frac{\hbar}{\Delta x} \rightarrow$ reduce non-radiative transition

D. Optical properties

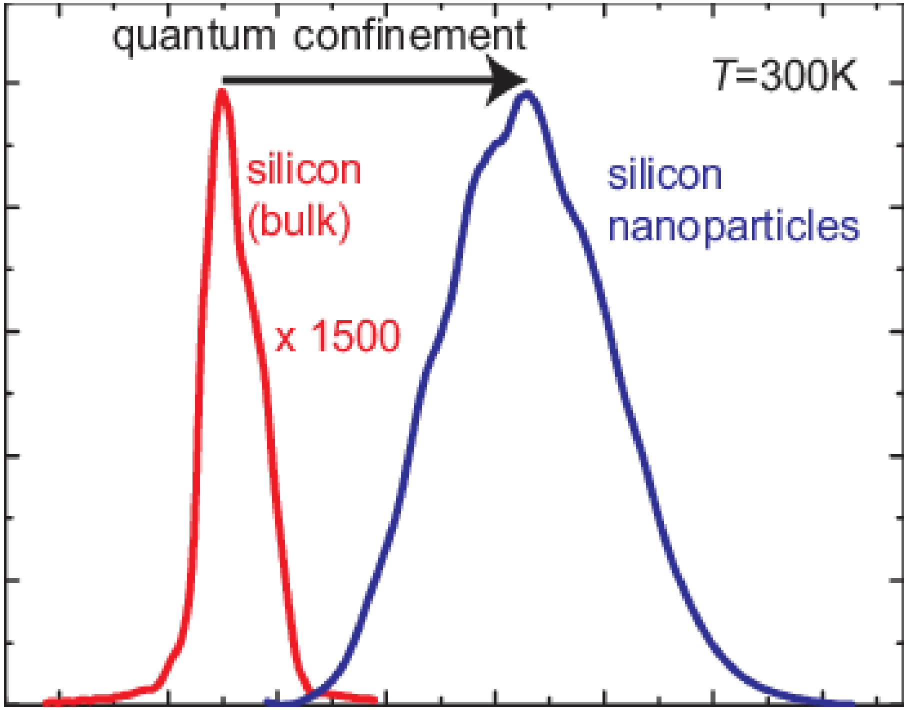
D-1 Bohr exciton radius and confinement





D. Optical properties

D-1 Bohr exciton radius and confinement

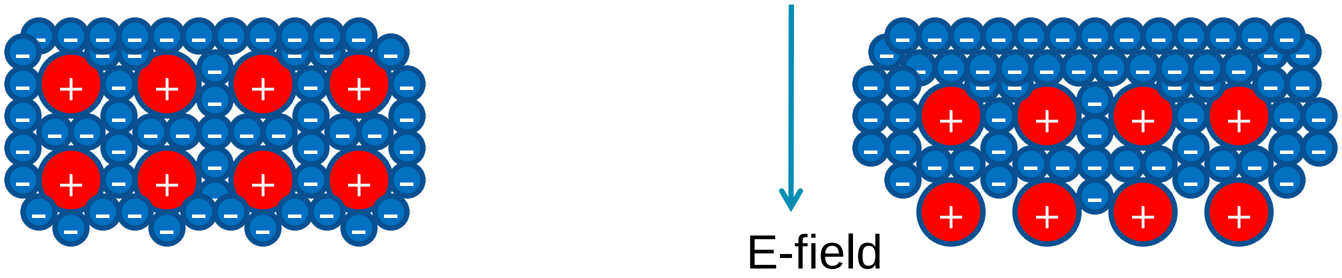


Room temperature photoluminescence of bulk silicon and silicon nanoparticles.

- ✓ Electron-hole recombination rate increases with *d*↓ due to increasing coulombic force between them.
- ✓ Small confinement distance increases the uncertainty in momentum that reduces the non-radiative emission.
- ✓ The increased recombination rate and reduced non-radiative emission enhanced the photoluminescence of semiconductor nanomaterials (quantum dot)

OPTICAL PROPERTIES

- Surface Plasmons
  - Recall that metals can be modeled as an arrangement of positive ions surrounded by a sea of *free electrons*.
  - The sea of electrons behaves like a fluid and will move under the influence of an electric field

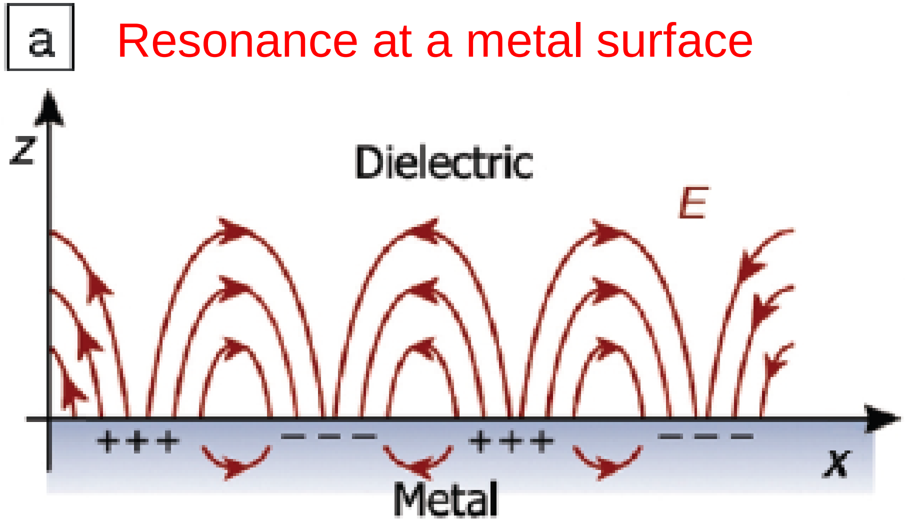


OPTICAL PROPERTIES

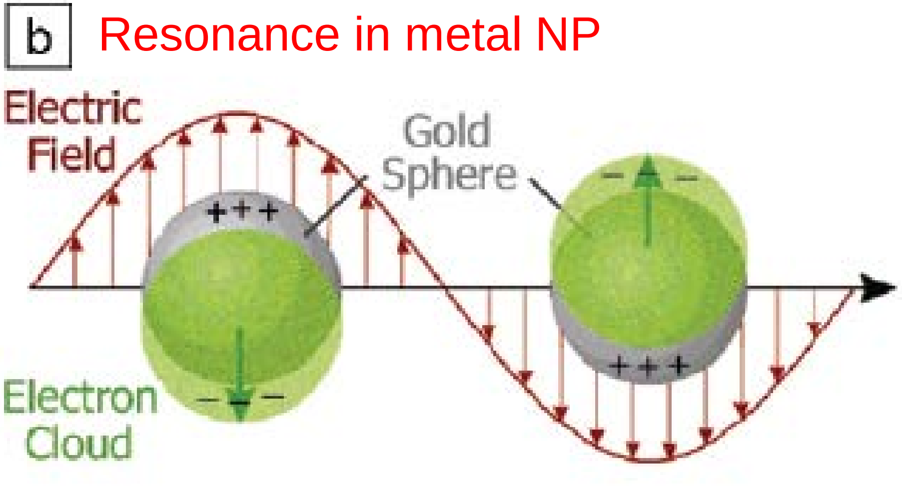
Surface Plasmons

- If the electric field is oscillating (like a photon), then the sea of electrons will oscillate too. These oscillations are quantized and resonate at a specific frequency. Such oscillations are called **plasmons**.

Resonance at a metal surface



Resonance in metal NP



Source: MRS Bulletin 2005, 30(5), 338.

OPTICAL PROPERTIES

- Surface Plasmons
  - Formal definition: Plasmons are the coherent excitation of *free electrons* in a metal.
  - The plasmon resonance frequency (f) depends on particle size, shape, and material type. It is related to the plasmon energy (E) by Planck's constant. E=h*f
  - Surface plasmons are confined to the surface of the material.
  - The optical properties of metal nanoparticles are dominated by the interaction of surface plasmons with incident photons.

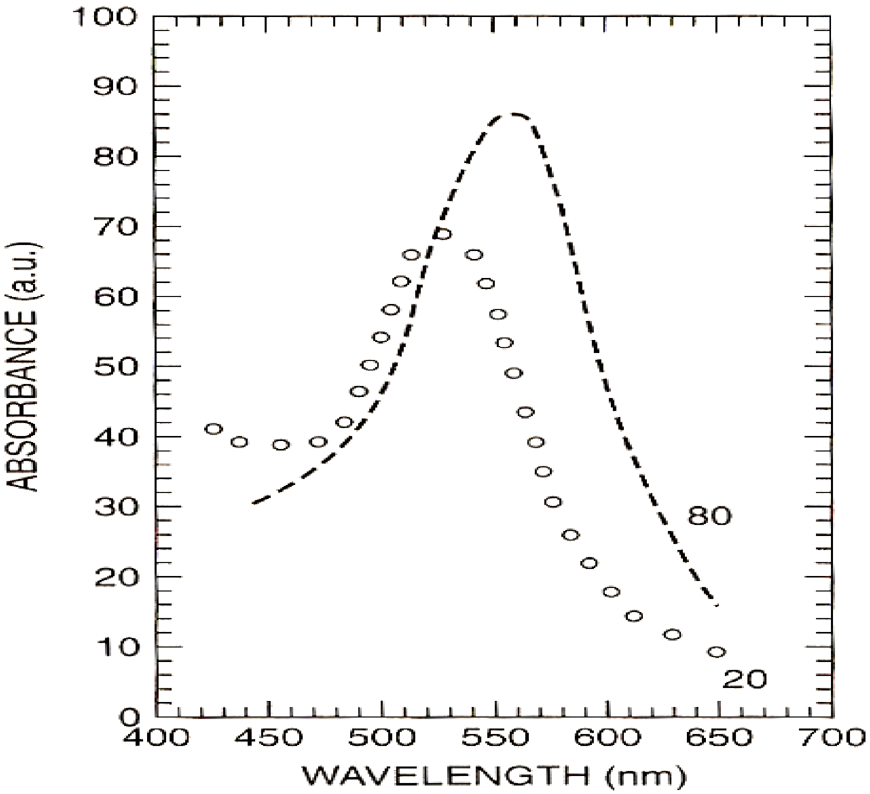
OPTICAL PROPERTIES

Surface Plasmons

- Metal nanoparticles like gold and silver have plasmon frequencies in the visible range.
- When white light impinges on metal nanoparticles the wavelength corresponding to the plasmon frequency is absorbed.
- The spectral locations, strengths, and number of plasmon resonances for a given particle depend on the particle's shape and size.

OPTICAL PROPERTIES

- Absorption spectra of spherical Au nanoparticles



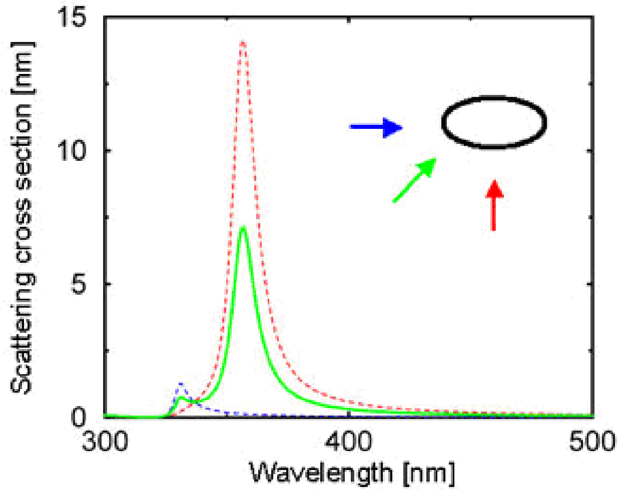
Optical absorption spectrum of 20- and 80-nm gold nanoparticles embedded in glass.
[Adapted from F. Gonella et al., in *Handbook of Nanostructured Material and Nanotechnology*, H. S. Nalwa, ed., Academic Press, San Diego, 2000, Vol. 4, Chapter 2, p.85.]

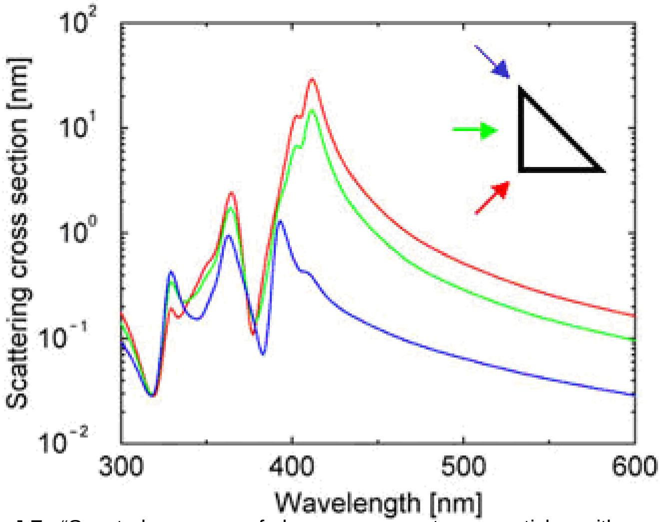
OPTICAL PROPERTIES

Surface Plasmons: Shape dependence of absorption spectra

•The amount of light that is scattered into the far field is described by the scattering cross section (SCS). The SCS is plotted against the wavelength of light used to illuminate a particle from a specific angle.

•The arrows indicate the illumination angle, and their colors correspond to the different plot lines.



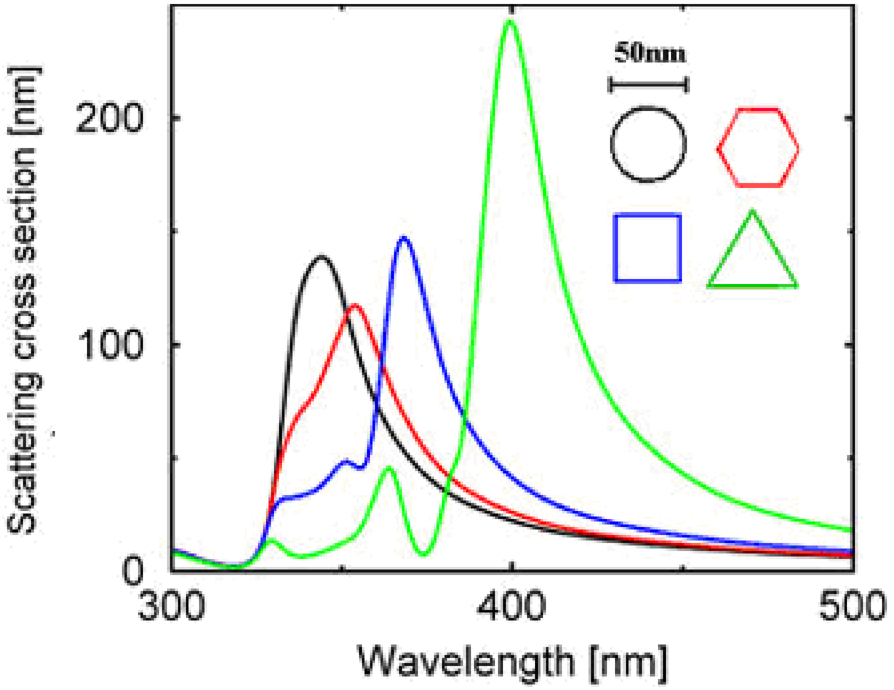


Martin, Olivier J.F. "Spectral response of plasmon resonant nanoparticles with non-regular shape". Optics Express Col. 6. No. 11 May 2000

OPTICAL PROPERTIES

Surface Plasmons: Shape dependence of absorption spectra

- Triangular shaped nanoparticles produce plasmons with altered frequency and magnitude



Martin, Olivier J.F. "Plasmons". Plasmons. 22 Mar. 2006. Ecole Polytechnique Fédérale de Lausanne. 26 Jan. 2003.

ELECTRICAL PROPERTIES

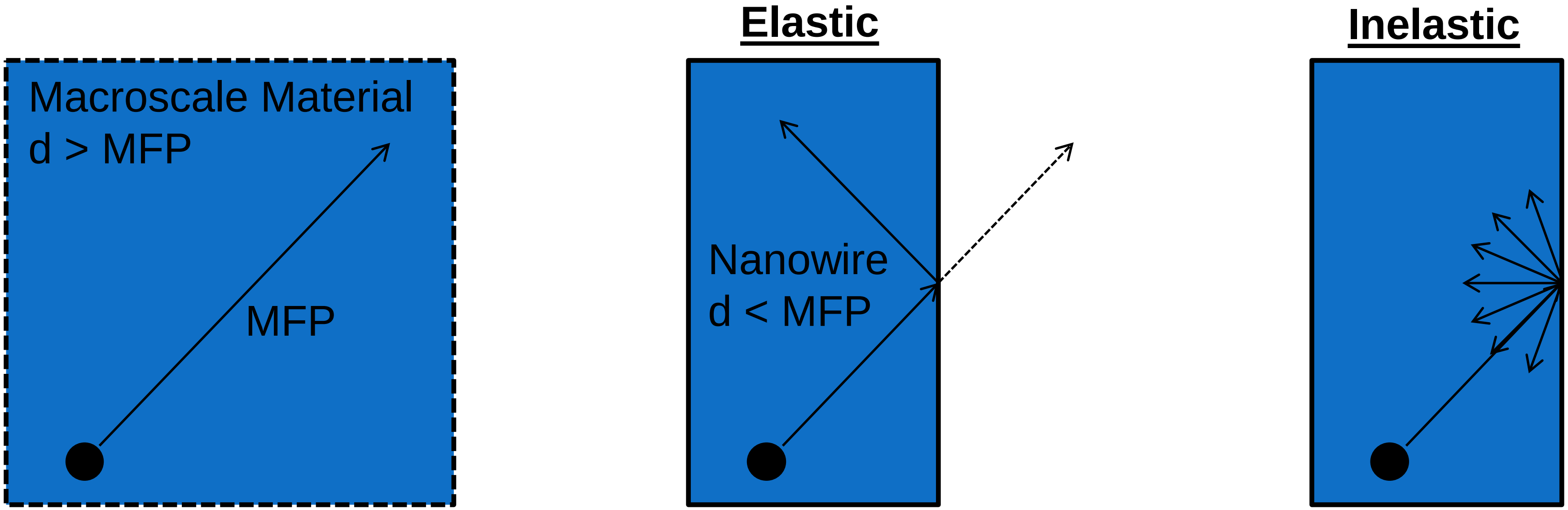
- Effect of structure on conduction
  - If nanostructures have fewer defects, one would expect increased conductivity vs macroscale
- Other electrical effects on the nanoscale:
  - Surface Scattering
  - Change in Electronic Structure
  - Ballistic Conduction
  - Discrete Charging
  - Tunneling Conduction
  - Microstructural Effects

SURFACE SCATTERING

- Electrons have a mean-free-path (MFP) in solid state materials.
- MFP is the distance between scattering events as charge carriers move through the material.
- In metals, the MFP is on the order of 10's of nanometers.
- If the dimensions of a nanostructure are smaller than the electron MFP, then surface scattering becomes a factor.

SURFACE SCATTERING

- There are two types of surface scattering: elastic and inelastic.
- Elastic scattering does not affect conductivity, while inelastic scattering decreases conductivity.



Macroscale Material
d > MFP

MFP

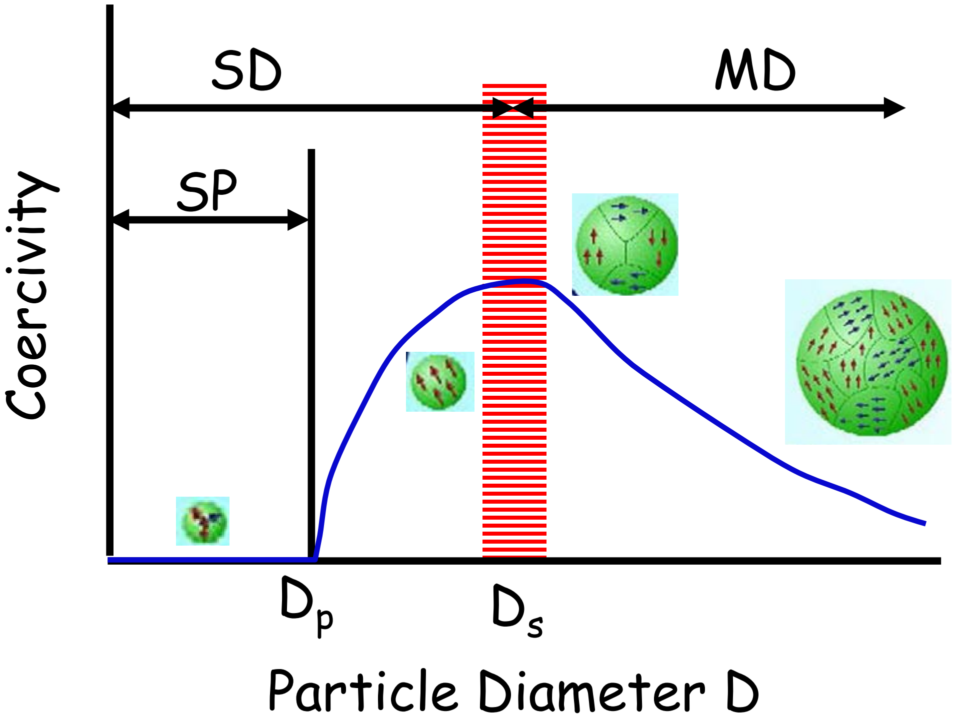
Elastic

Nanowire
d < MFP

Inelastic

F. Magnetic properties

Coercivity of nanomagnet:



- SP→ Superparamagnetic Regime
- SD → Single Domain Regie
- MD →Multiple Domain Regime
- D_s → Critical Diameter
- D_p → Diameter below which SP

- ✓ The particle size is reduced, the coercivity increases to a maximum and then decreases toward zero.
- ✓ When the size of single-domain particles further decreases below a critical diameter, the coercivity becomes zero, and such particles become superparamagnetic.
- ✓ Superparamagnetism is caused by thermal effects. In superparamagnetic particles, thermal fluctuations are strong enough to spontaneously demagnetize a previously saturated assembly; therefore, these particles have zero coercivity and have no hysteresis.

F. Magnetic properties

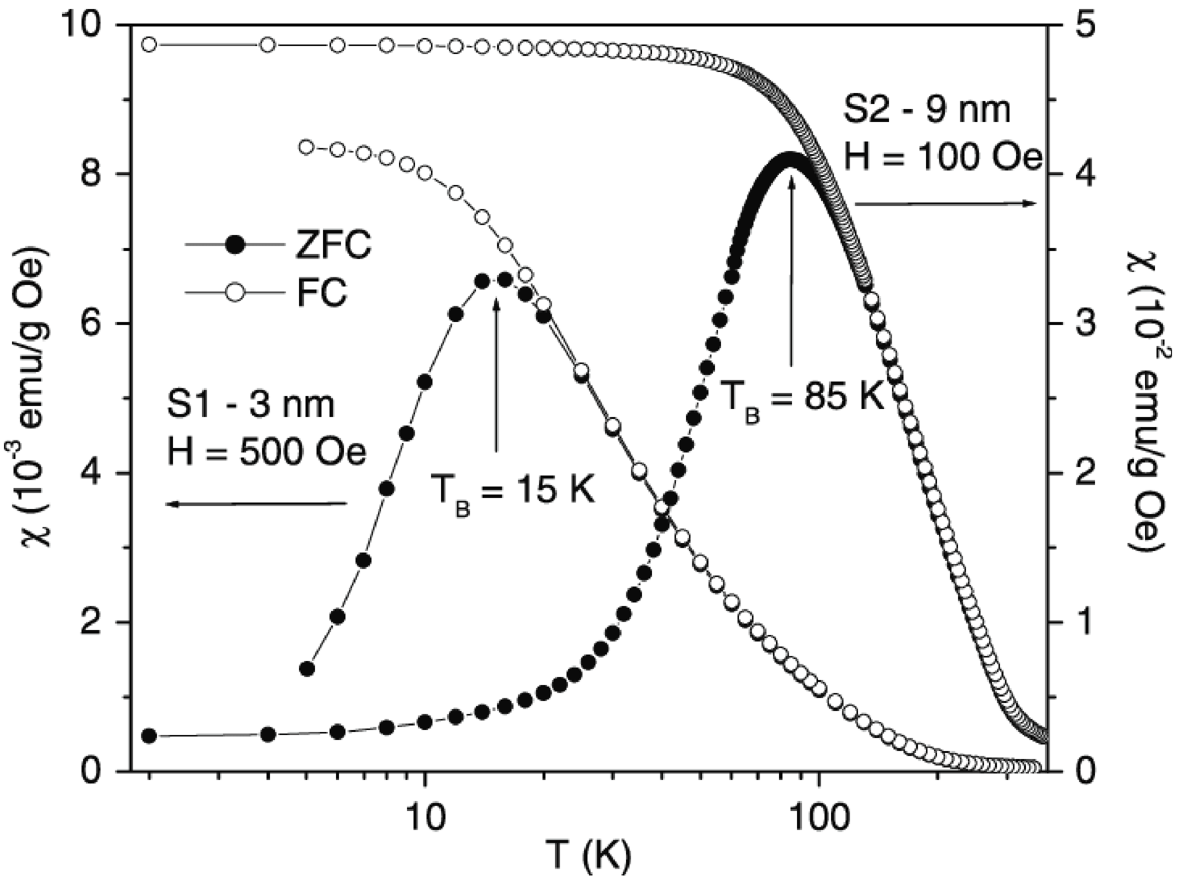
- ☐ Why does the coercivity increase when decrease in size?
  - Working with large magnetic NP sizes implies that there exist several magnetic domains within the particle, making the inversion of magnetization happen through the movement of the walls of the domains rather than spin rotation, resulting in low values of coercive field, H_c.
- ☐ Why is maximum coercivity for single domain particle?
  - When the NPs size is reduced they become single domain, and thus the inversion of magnetization happens via coherent rotation, which has a high energetic cost and leads to an increase of the coercive field.

F. Magnetic properties

- ❑ Why does coercivity decrease when size is less than SD ?
  - – If the size of the NPs is too small, thermal agitation is non-negligible and provokes fluctuations and, therefore, H_c decreases again becoming eventually zero (i.e., transition from ferromagnetic to superparamagnetic).
- ❑ What causes the superparamagnetism?
  - – Superparamagnetism is caused by thermal effects. In superparamagnetic particles, thermal fluctuations are strong enough to spontaneously demagnetize a previously saturated assembly; therefore, these particles have zero coercivity and have no hysteresis.

F. Magnetic properties

Superparamagnetic behavior is caused by thermal flipping of the anisotropic barrier to magnetization reversal. Below a certain temperature, called the blocking temperature, temperature-induced flipping or relaxation can be arrested and the nanocrystals acquire a finite coercivity.



F. Magnetic properties

Why is maximum coercivity for single domain particle?

F. Chemical properties

D-1 Bohr exciton radius and confinement

$$a_e = \frac{4\pi\epsilon\epsilon_0\hbar^2}{m_e q^2},$$

$$a_h = \frac{4\pi\epsilon\epsilon_0\hbar^2}{m_h q^2},$$

$$a_B = \frac{4\pi\epsilon\epsilon_0\hbar^2}{\mu q^2} = a_e + a_h,$$

where one often sees a_B written in terms of a_0,

$$a_B = \frac{\epsilon m_0}{\mu} a_0.$$

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_0 q^2}.$$

$$r_B^{ex} = \frac{\varepsilon m_0}{\varepsilon_0 \mu}\frac{4\pi\varepsilon_0\hbar^2}{m_0 q^2} = \frac{4\pi\varepsilon\hbar^2}{\mu q^2}$$

$$r_B^{ex} = \frac{4\pi\varepsilon_r\varepsilon_0\hbar^2}{\mu q^2} = \frac{\varepsilon_r m_0}{\mu} a_B$$

- Exciton→ Bound state of electron and hole

$$r_B^{ex} = \frac{\varepsilon r_B m_0}{\varepsilon_0 \mu} \quad \text{where} \left[\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h}\right]$$

$$F_c = -\frac{e^2}{4\pi\varepsilon_0 r^2} \;\&\; E_g = E_g^{bulk} - \frac{e^2}{4\pi\varepsilon_0 r^2}$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \Longrightarrow \varepsilon = \varepsilon_r \varepsilon_0$$

- For bulk material: $F_c \ll kT$, less likely to formation of exciton at RT

Quantum dot

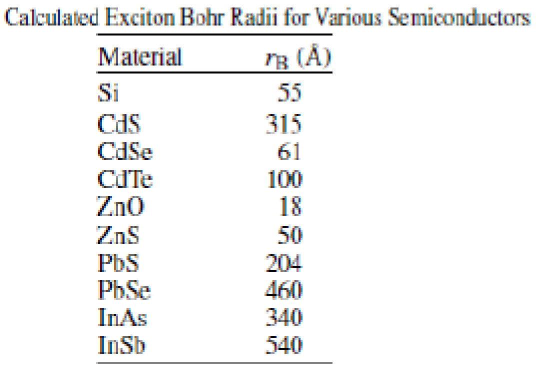
when an electron is promoted from the valence to conduction bands, an electron–hole pair known as an *exciton* is created in the bulk lattice. The physical separation between the electron and hole is referred to as the *exciton Bohr radius* (r_B) that varies depending on the semiconductor composition.

In a bulk semiconductor crystal, r_B is significantly smaller than the overall size of the crystal; hence, the exciton is free to migrate throughout the lattice

However, in a quantum dot, r_B is of the same order of magnitude as the diameter (*D*) of the nanocrystal, giving rise to *quantum confinement* of the exciton. Empirically, this translates to the strongest exciton confinement when $D < 2r$

Analogous to the "particle-in-a-box" model from introductory physical chemistry, exciton quantum confinement results in discrete energy levels rather than the continuous bands of a bulk semiconductor crystal. Since the gap between adjacent energy levels is infinitesimally small for a bulk semiconductor, the bandgap is considered as a fixed value. In contrast, since the dimensions of a quantum dot are extremely small, the addition/subtraction of a single atom will significantly change the nanocrystal dimensions and bandgap.

Table lists the *r*B values for common semiconductor crystals whose bandgap may be easily fine-tuned by simply changing the diameter of the quantum dot, as long as the dimensions are smaller than *r*B.



Calculated Exciton Bohr Radii for Various Semiconductors

Material	r_B (Å)
Si	55
CdS	315
CdSe	61
CdTe	100
ZnO	18
ZnS	50
PbS	204
PbSe	460
InAs	340
InSb	540

In the early 1980s, Efros described the size-dependent electronic properties of quantum dots, first delineating that the bandgap, *E*n, will increase from the bulk value based on a 1/*R*2 confinement energy term (Eq. 1). According to quantum confinement theory, electrons in the conduction band and holes in the valence band are spatially confined by the potential barrier of the surface. Due to confinement of both electrons and holes, the lowest energy optical transition from the valence to conduction band will increase in energy, effectively increasing the bandgap.

$$(1) \qquad E_{\mathrm{n}} = E_{\mathrm{g}} + \frac{h^2\pi^2}{2\mu R^2},$$

where *Eg* is the bandgap of the bulk semiconductor; *h*, Planck's constant; *R*, the radius of the quantum dot; and *μ* is mass of the exciton given by $m_e m_h/(m_e + m_h)$. Here *me* and m_h are masses of the electron and hole, respectively

$$(2) \qquad E_{\mathrm{n}} = E_{\mathrm{g}} + \frac{h^2\pi^2}{2\mu R^2} - \frac{1.786\,\mathrm{e}^2}{\varepsilon R} + 0.284\,E_{\mathrm{R}},$$

where E_R is the Rydberg (spatial correlation) energy of bulk semiconductor:

$$E_{\mathrm{R}} = \frac{\mu\,\mathrm{e}^4}{2\varepsilon^2\varepsilon_0^2 h^2} = 13.56\frac{\mu}{\varepsilon^2 m_{\mathrm{e}}},$$

where ε_0 is the permittivity of free space; ε, the dielectric constant of the bulk semiconductor; and m_e is the mass of the electron. Hence, the absorption energy of quantum dots will shift to higher frequency with decreasing diameter of the dots, with a dependence of $1/R^2$.

(D-1). QUANTUM SIZE EFFECTS

● When the size of a nanocrystal (i.e. a single crystal nanoparticle) is smaller than the de Broglie wavelength, electrons and holes are spatially confined and electric dipoles are formed, and discrete electronic energy level would be formed in all materials. Similar to a particle in a box, the energy separation between adjacent levels increases with decreasing dimenaions.

F8.22

Nano5-7

Nano5-8

- These changes arise through systematic transformations in the density of electronic energy levels as a function of the size, and these changes result in strong variations in the optical and electrical properties with size.

F8.22

- In the case of metals, where the Fermi level lies in the center of a band and the relevant energy level spacing is very small, the electronic and optical properties more closely resemble those of continuum, even in relatively small sizes (tens or hundreds of atoms). In semiconductors, the Fermi level lies between two bands, so that the edges of the bands are dominating the low-energy optical and electrical behavior. Optical excitations across the gap depend strongly on the size, even for crystallites as large as 10,000 atoms. For insulators, the band gap between two bands is already too big in bulk form.

(A) Semiconductor

- The quantum size effect is most pronounced for semiconductor nanoparticles, where the band gap increases with a decreasing size, resulting in the interband transition shifting to higher frequencies.
- In a semiconductor, the energy separation is of the order of a few electrovolts and increases rapidly with a decreasing size. Figure 8.23 : both the absorption edge and the luminescence peak position shift to a higher energy as the particle size reduces. Such a size dependence of absorption peak has been widely used in determining the size of nanocrystals.

(B) Metal nanoparticles

Ceram

metals

- For metal nanoparticles, to observe the localization of the energy levels, the size must be well below 2 nm, (as the level spacing has to exceed the thermal energy (~26 meV.)) (made up of~100 atoms)
- The spacing, δ, depends on the Fermi energy of the metal, E_F, and on the number of electrons in the metal, N
- The discrete electronic energy level has been observed in far-infrared absorption measurements of gold nanoparticle

$$\delta = \frac{4E_F}{3N} \qquad (8.21)$$

Nano05-8

- In addition to the size confinement, light emitted from nanowires is highly polarized along their longitudinal directions.
- Quantum dots are used to describe small particles that exhibit quantum size effects.
- Quantum wires are referred to as quantum wires when exhibiting quantum effects.

F8.25

(D-2). SURFACE PLASMON RESONANCE

- Surface plasmon resonance is the coherent excitiation of all the “free” electrons within the conduction band leading to an in-phase oscillation.
- When the size of a metal nanocrystal is smaller than the wave-length of incident radiation, a surface plasmon resonance is generated
- The electric field of an incoming light induces a polarization of the free electrons relative to the cationic lattice.
- A dipolar oscillation of electrons is created with a certain frequency.

F8.20

- Mie was the first to explain the red color of gold nanopaticle colloidal in 1908 by solving Max well's equation ：

$$\sigma_{ext} = \left[\frac{2\pi}{|\kappa|^2}\right]\Sigma(2L+1)\mathrm{Re}(a_L + b_L) \tag{8.15}$$

$$\sigma_{sca} = \left[\frac{2\pi}{|\kappa|^2}\right]\Sigma(2L+1)(|a_L|^2 + |b_L|^2) \tag{8.16}$$

$$a_L = \frac{m\psi_L(mx)\,\psi_L'(x) - \psi_L'(mx)\,\psi_L(x)}{m\psi_L(mx)\,\eta_L'(x) - \psi_L'(mx)\,\eta_L(x)} \tag{8.17}$$

$$b_L = \frac{\psi_L(mx)\,\psi_L'(x) - m\psi_L'(mx)\,\psi_L(x)}{\psi_L(mx)\,\eta_L'(x) - m\psi_L'(mx)\,\eta_L(x)} \tag{8.18}$$

- The larger the particles, the more important the higher-order modes as the light can no longer polarize the nanoparticles homogeneously. These higher-order modes peak at lower energies. Therefore, the plasmon band red shifts with increasing particle size. At the same time, the plasmon bandwidth increases with increasing particle size.
- The increase of both absorption wavelength and peak width with increasing particle size：extrinsic size effects.

- More complicated for smaller nanoparticles：only the dipole term is important
  - For nanoparticles much smaller than the wavelength of incident light ($2r<<\lambda$, or roughly $2r< \lambda_{max}/10$), only the dipole oscillation contributes to the extinction cross-section.

- The Mie theory can be simplified to the following relationship (diopole approximation) ：

$$\sigma_{ext}(\omega) \cong \frac{9\omega\varepsilon_m^{3/2}\,V\,\varepsilon_2(\omega)}{c\,\{[\varepsilon_1(\omega)+2\varepsilon_m]^2+\varepsilon_2(\omega)^2\}} \qquad (8.19)$$

- Equation (8.19)shows that the extinction coefficient does not depend on the particle sizes ; however, a size dependence is observed experimentally. This discrepancy arises obviously from the assumption in Mie theory, that the electronic structure and dielectric constant of nanoparticles are the same as those of its bulk form, which becomes no longer valid when the particle size becomes very small. Therefore, the Mie theory needs to be modified by introducing the quantum size effect.

- In small particles, electron surface scattering becomes significant. For example, conduction electrons in silver and gold have a mean free path of 40-50 nm and will be limited by the particle surfaces in particles of 20 nm. If the electrons scatter with the surface in an elastic but totally random way, the coherence of the overall plasmon oscillation is lost.
- The smaller the particles, the faster the electrons can scatter and lose the coherence more quickly. As a result, the plasmon bandwidth increases with decreasing particle size.

F 8.21

- In this region, the absorption wave length increases, but the peak width decreases with increasing particle size ：Intrinsic size effect
- Extinction coefficient＝1×10⁹ $M^{-1}cm^{-1}$ for 20 nm gold nanoparticles, increases linearly with increasing volume of the particles, and three to four orders of magnitude higher than those for the very strong absorbing organic dye molecules.
- The coloration of nanoparticles renders practical applications. For example, the color of gold ruby glass results from an absorption band at about 0.53μm.

- The spherical boundary condition of the particles shifts the resonance oscillation to lower frequencies or longer wavelength.
- The size of the gold particles influences the absorption. For particle larger than about 20 nm in diameter, the band shifts to longer wavelength as the oscillation becomes more complex. For smaller particles, the bandwidth progressively increases because the mean free path of the free electrons in the particles is about 40nm, and is effectively reduced.
- Silver particles in glass color it yellow, resulting from a similar absorption band at 0.41µm.
- Copper has a plasma absorption band at 0.565µm for copper particles in glass.

- Metal nanowires also have surface plasmon resonance properties.
- Metal nanorods exhibited two surface plasmon resomance modes： transverse and longitudinal excitations.
  - Transverse mode is essentially fixed around 520 nm for Au and 410 nm for Ag
  - Longitudinal modes can be easily tuned to span across the spectral region from visible to near infrared by controlling their aspect ratios.
  - Gold nanorods with an aspect ratio of 2-5.4 could fluoresce with a quantum yield more than one million times that of the bulk metal.

E. ELECTRICAL CONDUCTIVITY

Mechanisms for the effects of size on electrical conductivity of nanostructures and nanomaterials can be generally grouped into four categories:

- Surface scattering
- quantized conduction
- coulomb charging and tunneling
- widening and discrete of band gap

Other factors:

- Change of microstructures
- Increased perfection

(E-1). SURFACE SCATTERING

- Electrical conduction in metals or (Ohmic conduction) can be described by the various electron scattering, the total resistivity, ρ_{T}, is a combination of individual and independent scattering, known as Matthiessen's rule□

$$\rho_{T} \square \ \rho_{Th} \square \ \rho_{D}$$

ρ_{Th}□ the thermal resistivity□ andρ_{D}□ the defect resistivity

Thermal or phonon contribution, increases linearly with temperature.

#2 #3 MPS13-5 F18.7 F18.8

- Considering individual electrical resistivity inversely proportional to the respective mean free path (λ) between collisions, the Mattienssen's rule can be written as□

$$\frac{1}{\lambda_T} = \frac{1}{\lambda_{Th}} + \frac{1}{\lambda_D} \qquad \left(\rho \propto \frac{1}{\lambda} \right) \qquad (8.23)$$

- λ_T ranges from several tens to hundreds of nano-meters.
- Reduction in material's dimensions would have two different effects on electrical resistivity:
- One is an increase in crystal perfection thus a reduction in resistivity. However, the defect scattering makes a minor contribution, and thus has a very small influence on the electrical resistivity.
- The other is to create an additional contribution to the total resistivity due to surface scattering, which plays a very important role.
- If the mean free electron path, λ_s, is the smallest, then it will dominate the total electrical resistivity□

$$\frac{1}{\lambda_T} = \frac{1}{\lambda_{Th}} + \frac{1}{\lambda_D} + \frac{1}{\lambda_S} \qquad (8.24)$$

- The electrons undergo either elastic or inelastic scattering. In elastic, also known as specular, scattering, the electron does not lose its energy and its momentum or velocity along the direction parallel to the surface the electrical conductivity remains the same.
- When scattering is totally inelastic, or nonspecular or diffuse, the scattered electron loses its velocity along the direction parallel to the surface or the conduction direction, and the electrical conductivity decrease. There will be a size effect on electrical conduction.

F8.26

- Figure 8.26 depicts the Tomposon model for inelastic scattering of electrons from film surface with film thickness, d, less than the bulk free mean electron path, λ_o. The mean value of λ_f is given by

$$\lambda = \frac{1}{2}d\int_0^d dz\int_0^\pi \lambda \sin\theta \, d\theta \qquad (8.25)$$

After integration, we have

$$\lambda_f = \frac{d}{2}\left(\ln\left(\frac{\lambda_0}{d}\right) + \frac{3}{2}\right) \qquad (8.26)$$

- Finally the film resistivity, ρ_f, relative to bulk values, ρ_o, are given by□

$$\frac{\rho_0}{\rho_f} = \frac{d}{2\lambda_0}\left(\ln\left(\frac{\lambda_0}{d}\right) + \frac{3}{2}\right) \qquad (8.27)$$

- It is clear that as d shrinks, λ_f decreases and ρ_f increases, and there is an obvious size dependence. The above model is based on an assumption that all surface scattering is inelastic and in terms of classical physics.
- A more accurate quantum theory, known as Fuchs-Sondheimer (F-S) theory, was also developed.

- With P being the fraction of elastic surface scattering, an approximate formula for thin films. Where $\lambda_o >> d$, is obtained□

$$\frac{\rho_0}{\rho_f} = \frac{3d}{4\lambda_0}(1+2P)\left(\ln\left(\frac{\lambda_0}{d}\right)+0.423\right) \qquad (8.28)$$

- The fraction of elastic scattering on a surface is very difficult to determine experimentally□ it is known that surface impurity and roughness favor inelastic scattering.

F8.27

- An increased surface scattering would result in reduced electron mobility and, thus, an increased electrical resistivity. Increased electrical resistivity of metallic nanowires with reduced diameters due to surface scattering has been widely reported.

- In a polycrystalline material, as the crystallite size becomes smaller than the electron mean-free path, a contribution to electrical resistivity from grain boundary scattering arises□ grain boundary scattering.
- The surface inelastic scattering of electrons and phonons would result in a reduced thermal conductivity of nanostructures and nanomaterials.
- Theoretical studies suggest that thermal conductivity of silicon nanowires with a diameter less than 20nm would be significantly smaller than the bulk value.

F8.28

(E-2). CHANGE OF ELECTRONIC STRUCTURE

- A reduction in characteristic dimension below a critical, i.e. the electron de Broglie wavelength, would result in a change of electronic structure, leading to widening and discrete band gap (changing optical properties and a reduced electrical conductivity)

#7	Nano5-8	F18.4	F18.5	F18.6	F8.22

- Some metal nanowires may undergo a transition to become semiconducting and semiconductor nanowires may become insulators. (qiantum size effects)
- For example, single crystalline Bi nanowires undergo a metal-to-semiconductor transition at a diameter of~52nm. Si nanowires of ~15 nm became insulating.

(E-3). QUANTUM TRANSPORT

(A). Ballistic Conduction

- Ballistic conduction occurs when the length of conductor is smaller than the electron mean-free path. In this case,
  - Each transverse waveguide mode or conducting channel contributes $G_0 \square\ 2e^2/h \square\ 12.9k\Omega^{-1}$ to the total conductance.
  - No energy is dissipated in the conduction,
  - There exist no elastic scattering. (This requires the absence of impurity and defects. When elastic scattering occurs, the transmission coefficients, and thus the electrical conductance will be reduced)
  - The conductance of arc-produced multi-wall carbon nanotubes is one unit of the conductance quantum G_0, and no heat dissipation is observed. Extremely high stable current densities, $J \square\ 10^7$ A/cm^2 have been attained.

F8.29

(B). Coulomb blockade

- Coulomb blockade (or Coulomb charging or Coulombic staircase) occurs when the contact resistance is larger than the resistance of nanostructures in question and when the total capacitance of the object is so small that adding a single electron requires significant charging energy.

- A discrete electron configuration permits one to pick up the electric charge one electron at a time, at specific voltage values.

- Nanoparticles with diameters below 2-3nm: Single electron transistors (SETs)

#46 #75 #56

- For a nanoparticle surrounded by a dielectric with a dielectric constant of ε_r, the capacitance of the nanoparticle is dependent on its size as□

$$C(r) = 4\pi r \varepsilon_0 \varepsilon_r \qquad (8.29)$$

r□ radius of the nanoparticle,

ε_o□ permittivity of vacuum

Energy required to add a single charge to the particle is given by the charging energy□

$$E_c = \frac{e^2}{2C(r)} \qquad (8.30)$$

#56

- Tunneling of single charges can be seen at temperatures of $k_B T$□ E_c, Eqs. (8.29) and (8.30) indicate that the charging energy is independent of materials.

F8.30

(C). TUNNELING CONDUCTION

- Tunneling conduction□ charge transport through an insulating medium separating two conductors that are extremely closely spaced.
- The electrical conductivity decreases exponentially with increasing thickness of insulting layer.
- Electrons are able #99 un #90 through the dielectric material when an electric is applied.
- Tunneling conduction is not a material property, but is a system property depending on the characteristic dimension.

F8.31

(D). EFFECT OF MICROSTRUCTURE

- Electrical conductivity may change due to the formation of ordered microstructure, when the size is reduced to a nanometer scale.
- For example, polymer fibers within nanometer fibris, polymers are aligned parallel to the axis of the fibris, which results in increased contribution of intramolecular conduction and reduced contribution of intermolecular conduction.
- Since intermolecular conduction is far smaller than intramolecular conduction, ordered arrangement of polymers with polymer chains aligned result in an increased electrical conduction.
- A lower synthesis temperature also favors a better alignment and thus a higher electrical conductivity.

F8.32

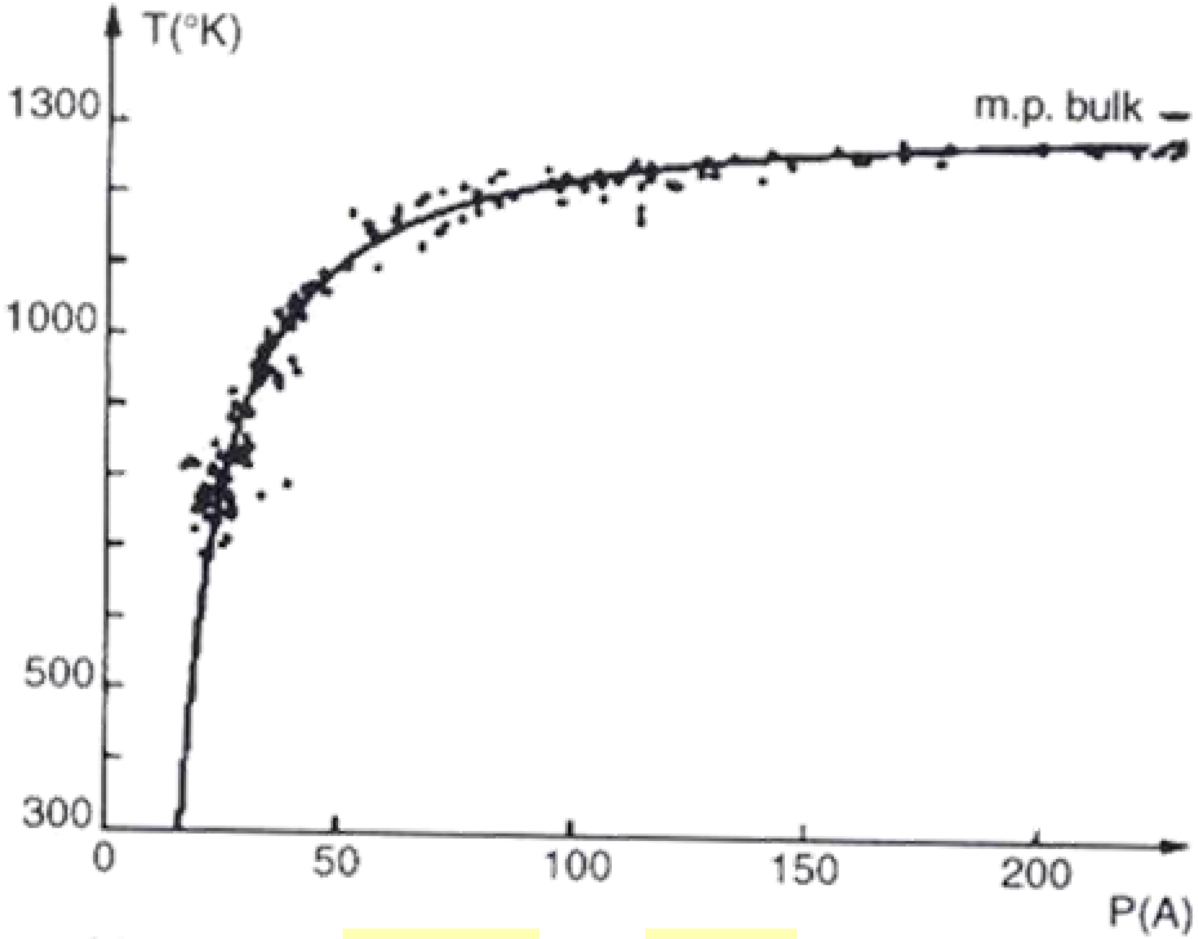


Fig. 8.13. The melting point of bulk gold is of 1337 K and decreases rapidly for nanoparticles with diameters below 5 nm. Both experimental data (the dots) and the results of a least-squares fits to Eq. (8.1) (the solid line) are included. [Ph. Buffat and J.-P. Borel, *Phys. Rev.* **A13**, 2287 (1976).]

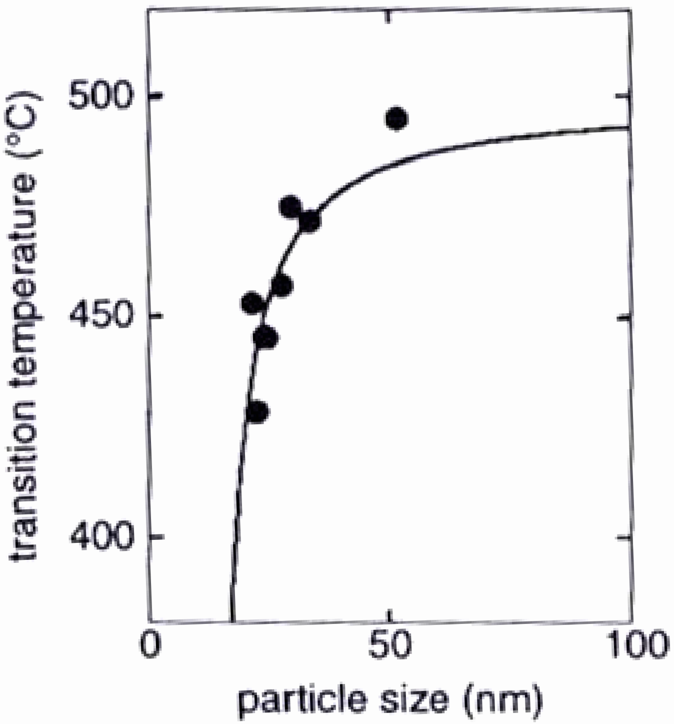


Fig. 8.14. The transition temperature as a function of lead titanate particle size. Experimental data are denoted by full circles and the solid curve is obtained by an empirical expression $Tc = 500 - 588.5/(D - 12.6)$, where D is the particle diameter in nm. [K. Ishikawa, K. Yoshikawa, and N. Okada, *Phys. Rev.* **B37**, 5852 (1988).]

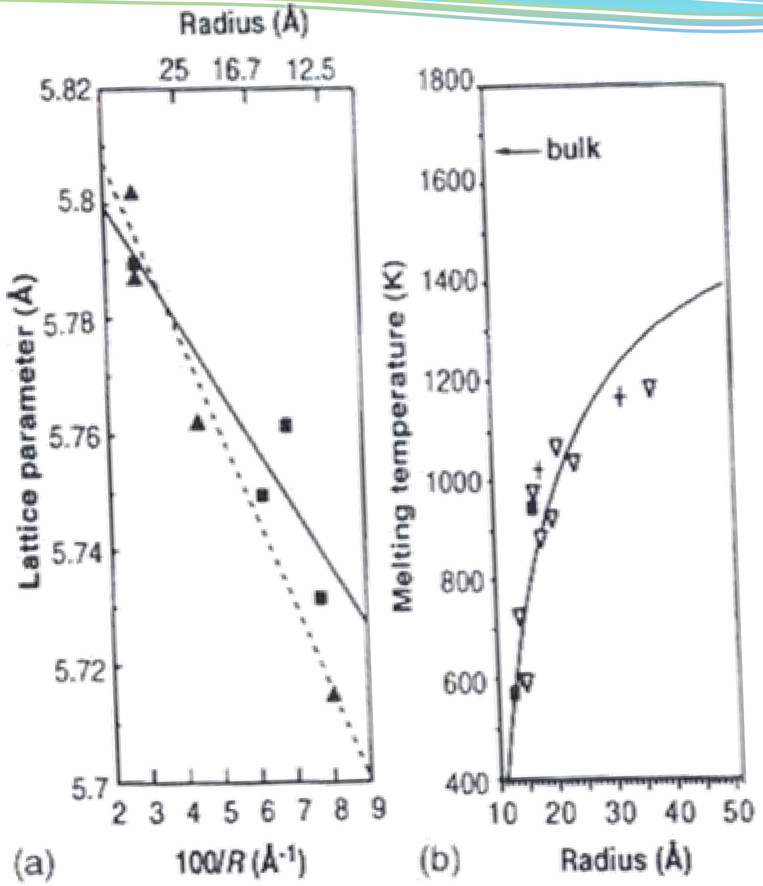


Fig. 8.15. (a) Lattice parameter of CdS nanocrystals as a function of the reciprocal particle radius, *R*. Δ: points from bare nanocrystals, the dashed line for bare nanocrystals yields a surface tension of 2.50 N.m., points from mercaptoacetic acid-capped nanocrystals, the solid line fit yields a surface tension of 1.74 N/m. (b) Size dependence of the melting point of CdS nanocrystals, and +: thiophenol or mercaptoacetic acid-capped nanocrystals determined by the disappearance of electron diffraction. ∇: determined by observing the change in dark field of a single CdS particle. [A.N. Goldstein, C.M. Echer, and A.P. Alivisatos, *Science* **256**, 1425 (1992).]

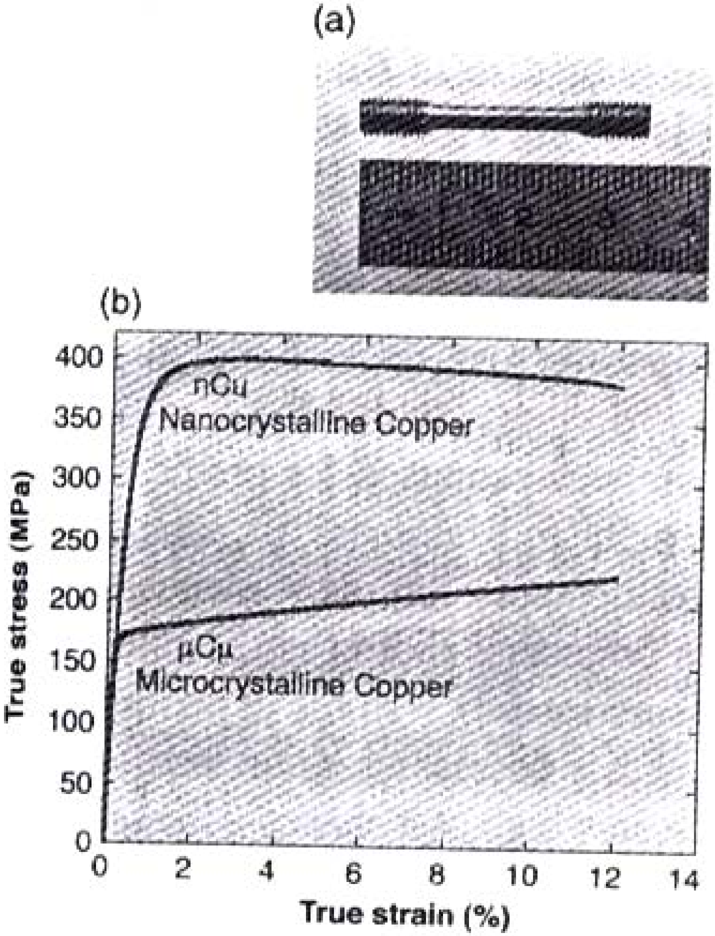


Fig. 8.19. (a) Tensile test specimens are machine cut from the nanocrystalline metal, prepared by powder metallurgy. (b) Comparison of stress and strain for nanocrystalline and microcrystalline copper. The tensile tests are carried out at room temperature and at the low strain rate of $5 \times 10^{-6}\ \mathrm{s}^{-1}$. [Y. Champion, C. Langlois, S. Guérin-Mailly, P. Langlois, J. Bonnentien, and M.J. Hÿtch, *Science* **300**, 310 (2003).]

particle size ↓ (μm → nm)

polarization of free electrons

dipolar oscillation

oscillation frequency
↕ match
visible light frequency

⇒visible light absorption (plasmon resonance absorption)

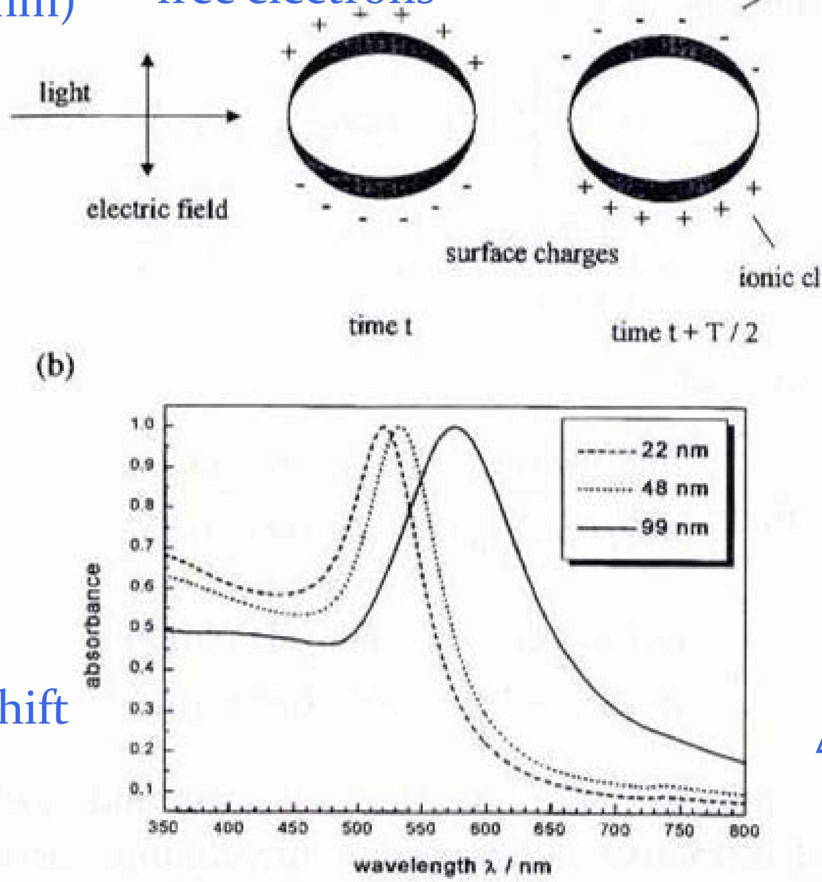
period of oscillation: T

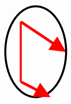
frequency of absorption: ϒ

surface scattering

absorption warelength: λ

band width: Δ λ

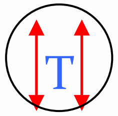




λ

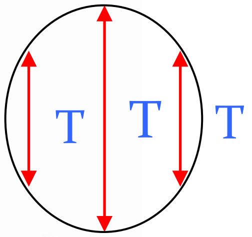
blue shift

Δλ



λ

Δλ



λ

red shift

Δλ

Fig. 8.20. Surface plasmon absorption of spherical nanoparticles and its size dependence. (a) A schematic illustrating the excitation of the dipole surface plasmon oscillation. The electric field of an incoming light wave induces a polarization of the (free) conduction electrons with respect to the much heavier ionic core of a spherical metal nanoparticle. A net charge difference is only felt at the nanoparticle surfaces, which in turn acts as a restoring force. In this way a dipolar oscillation of the electrons is created with period *T*. (b) Optical absorption spectra of 22, 48 and 99 nm spherical gold nanoparticles. The broad absorption band corresponds to the surface plasmon resonance. [S. Link and M.A. El-Sayed, *Int. Rev. Phys. Chem.* **19**, 409 (2000).]

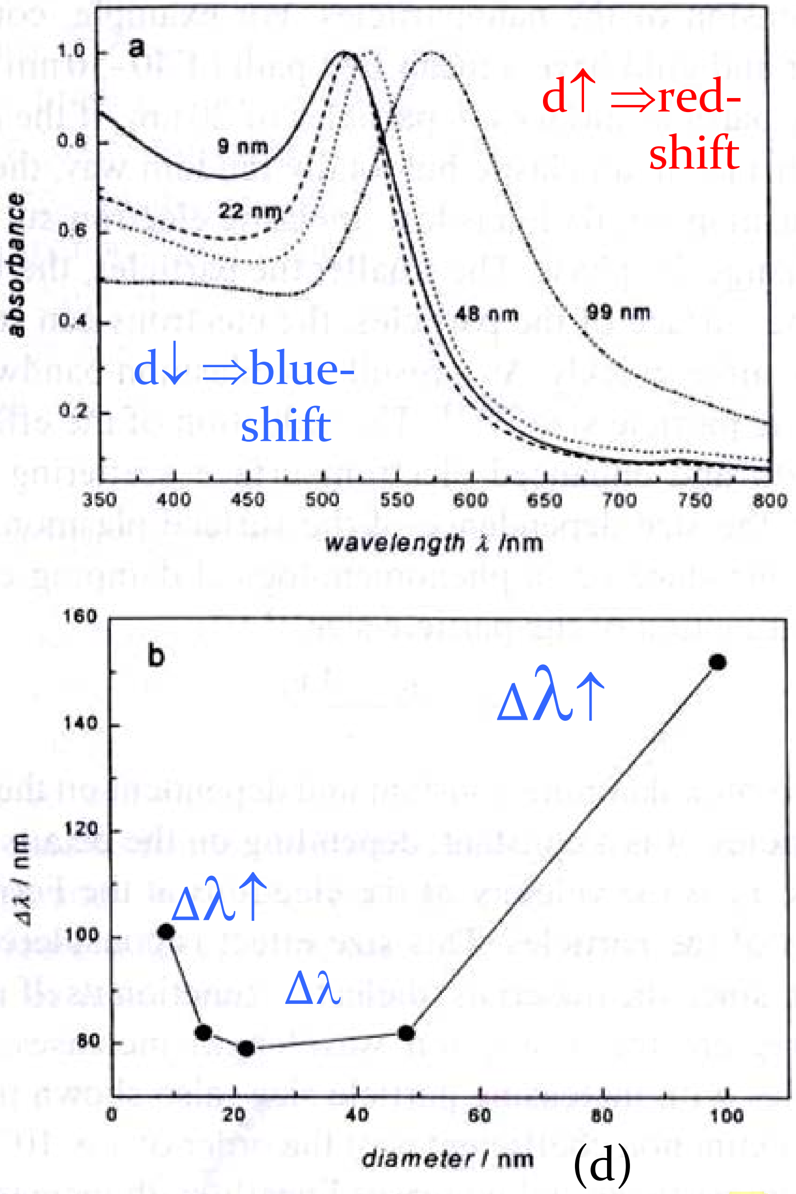
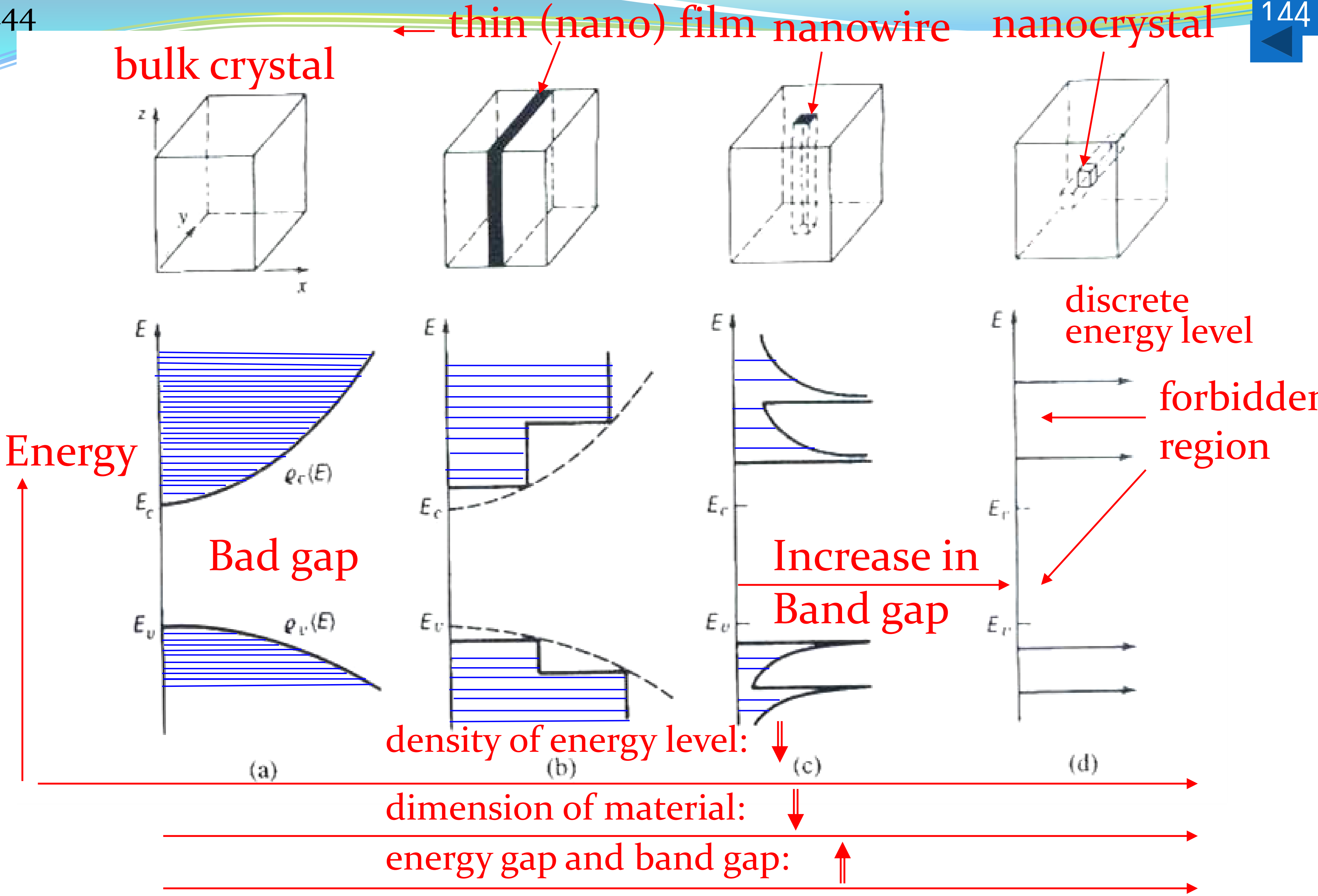


Fig. 8.21. (a) UV-Vis absorption spectra of 9, 22, 48 and 99 nm gold nanoparticles in water. All spectra are normalized at their absorption maxima, which are 517, 521, 533 and 575 nm, respectively. (b) The plasmon bandwidth Δλ as a function of particle diameter. [S. Link and M.A. El-Sayed, *J. Phys. Chem.* **B103**, 4212 (1999).]



bulk crystal ← thin (nano) film nanowire nanocrystal

Energy

Bad gap

discrete
energy level

forbidden
region

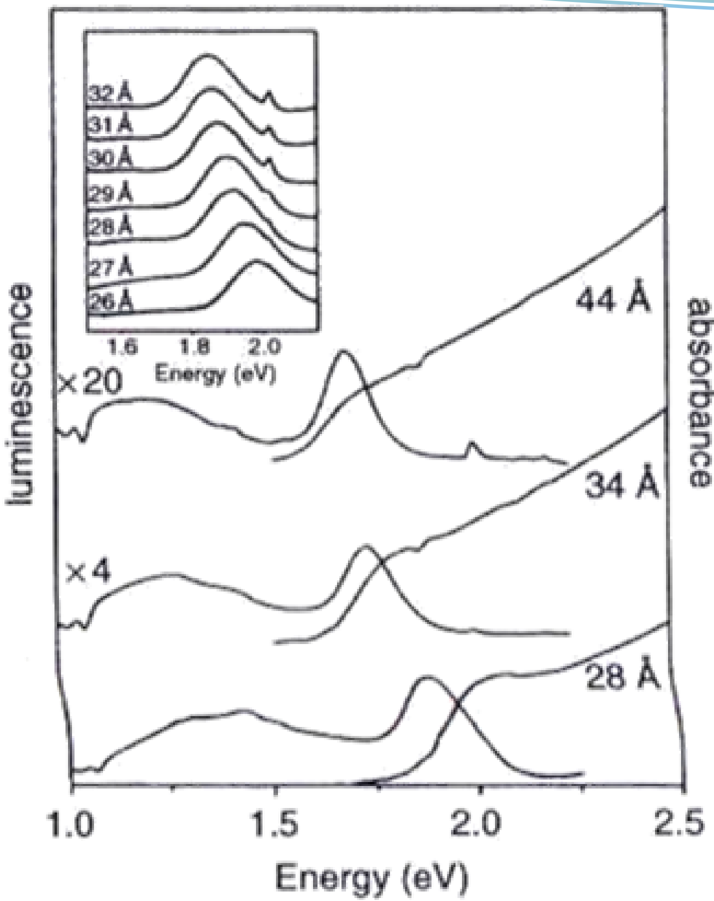
Increase in
Band gap

density of energy level: ⇓

dimension of material: ⇓

energy gap and band gap: ⇑

Fig. 8.22. Schematic illustrating discrete electronic configurations in nanocrystals, nanowires and thin films and enlarged band gap between valence band and conduction band.



particle size ↓

bond gap ↑

absorption edge, λ ↓
(blue shift)

Fig. 8.23. Optical absorption and PL spectra of InP nanocrystals as a function of particle size. The PL spectra are composed of a high-energy band edge emission band and a low-energy trapped emission band. The insert shows additional scaled PL spectra of a sequence of samples with decreasing sizes exhibiting a smooth blue shift of the band edge emission feature with decreasing nanocrystal size. The samples have been treated with decylamine and were exposed to air. [A.A. Guzelian, J.E.B. Katari, A.V. Kadavanich, U. Banin, K. Hamad, E. Juban, A.P. Alivisatos, R.H. Wolters, C.C. Arnold, and J.R. Heath, *J. Phys. Chem.* **100**, 7212 (1996).]

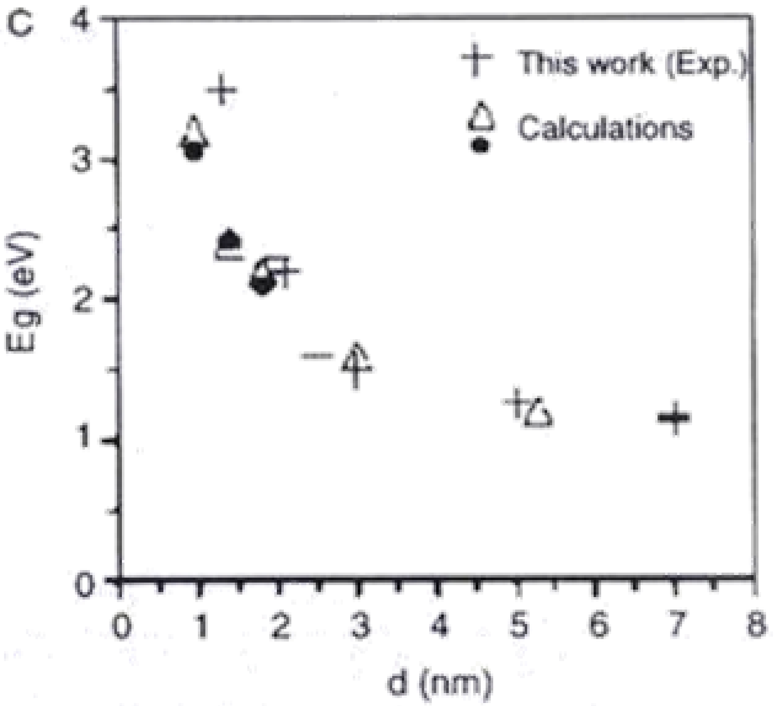


Fig. 8.24. The band gap of silicon nanowires as a function of the nanowire diameter, including both experimental results [D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, and S.T. Lee, *Science* **299**, 1874 (2003)] and calculated data. [A.J. Read, R.J. Needs, K.J. Nash, L.T. Canham, P.D.J. Calcott, and A. Qteish, *Phys. Rev. Lett.* **69**, 1232 (1992) and B. Delley and E.F. Steigmeier, *Appl. Phys. Lett.* **67**, 2370 (1995).]

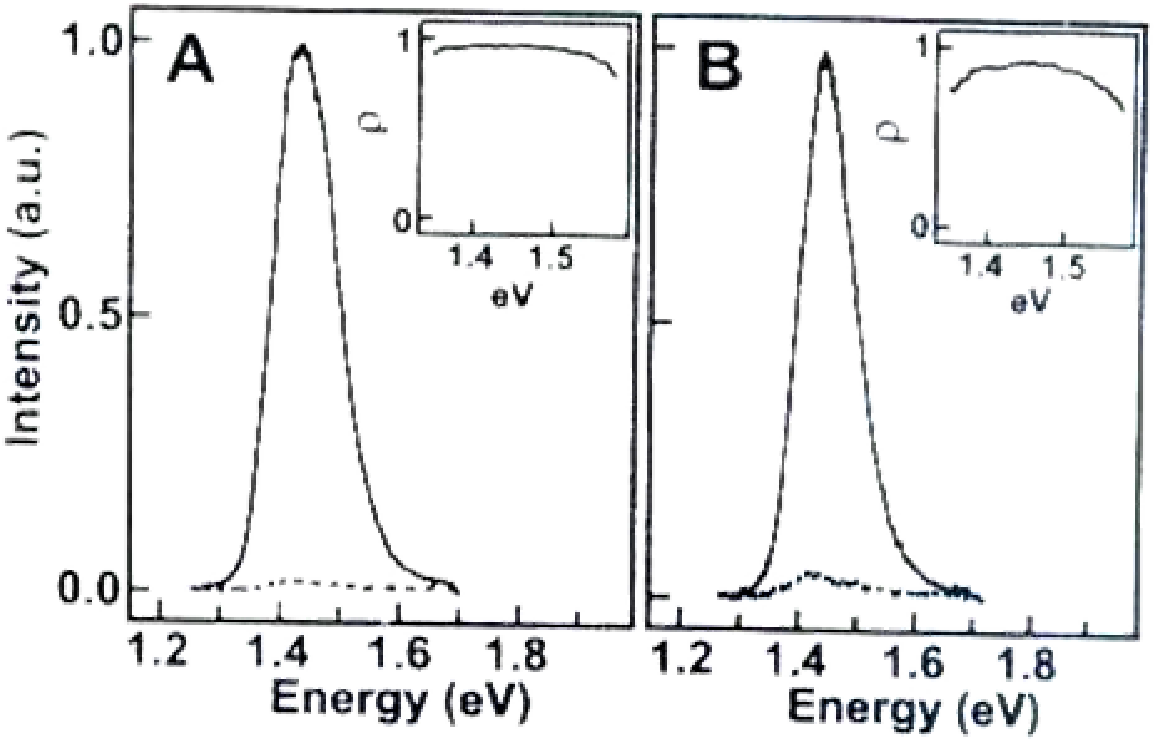


Fig. 8.25. (A) Excitation and (B) emission spectra recorded from an individual InP nanowires of 15 nm in diameter. The polarization of the exciting laser was aligned parallel (solid line) and perpendicular (dashed line) to the long axis of this nanowire, respectively. The inset plots the polarization ratio as a function of energy. [J.F. Wang, M.S. Gudiksen, X.F. Duan, Y. Cui, and C.M. Lieber, *Science* **293**, 1455 (2001).]

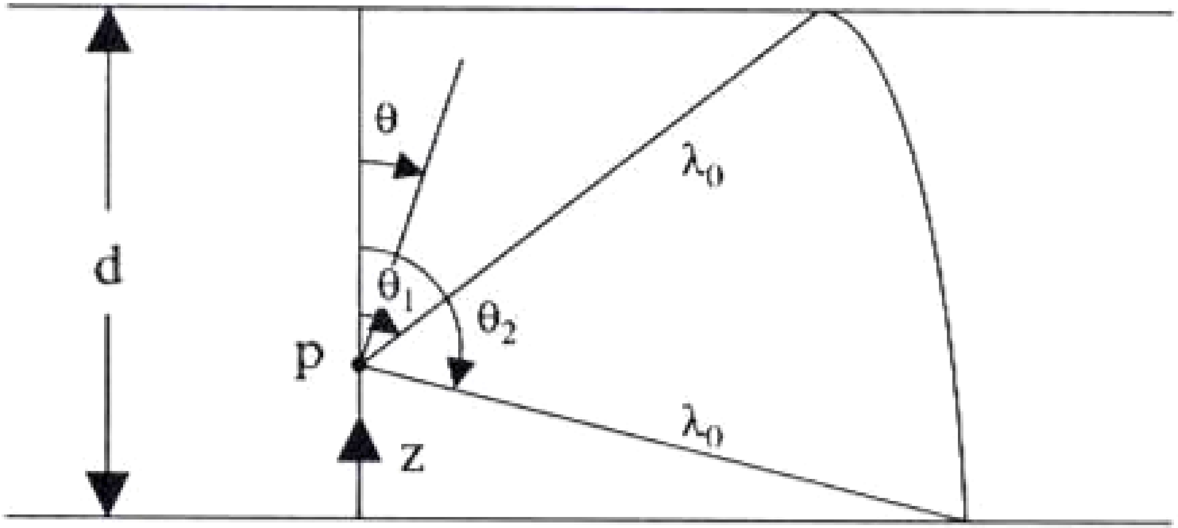


Fig. 8.26. Schematic illustrating the Thompson model for inelastic scattering of electrons from film surface with film thickness, *d*, less than the bulk free mean electron path, λ_0. [J.J. Thompson, *Proc. Cambridge Phil. Soc.* **11**, 120 (1901).]

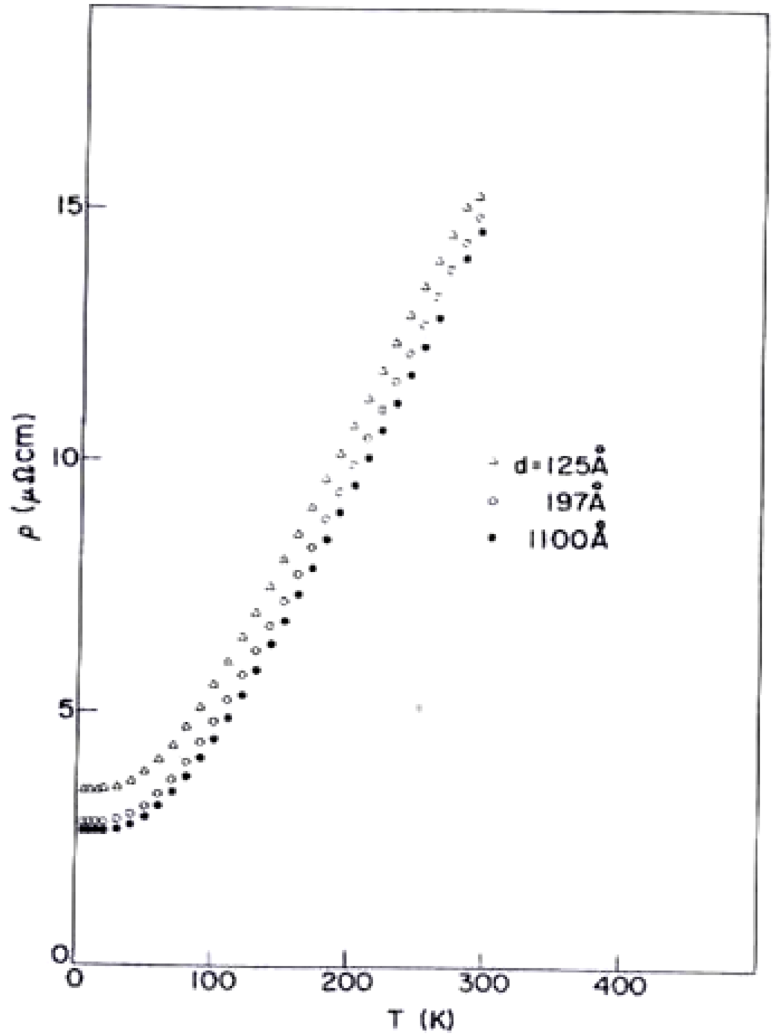


Fig. 8.27. The thickness dependence of electrical resistivities of thin films as a function of temperature. [J.C. Hensel, R.T. Tung, J.M. Poate, and F.C. Unterwald, *Phys. Rev. Lett.* **54**, 1840 (1985).]

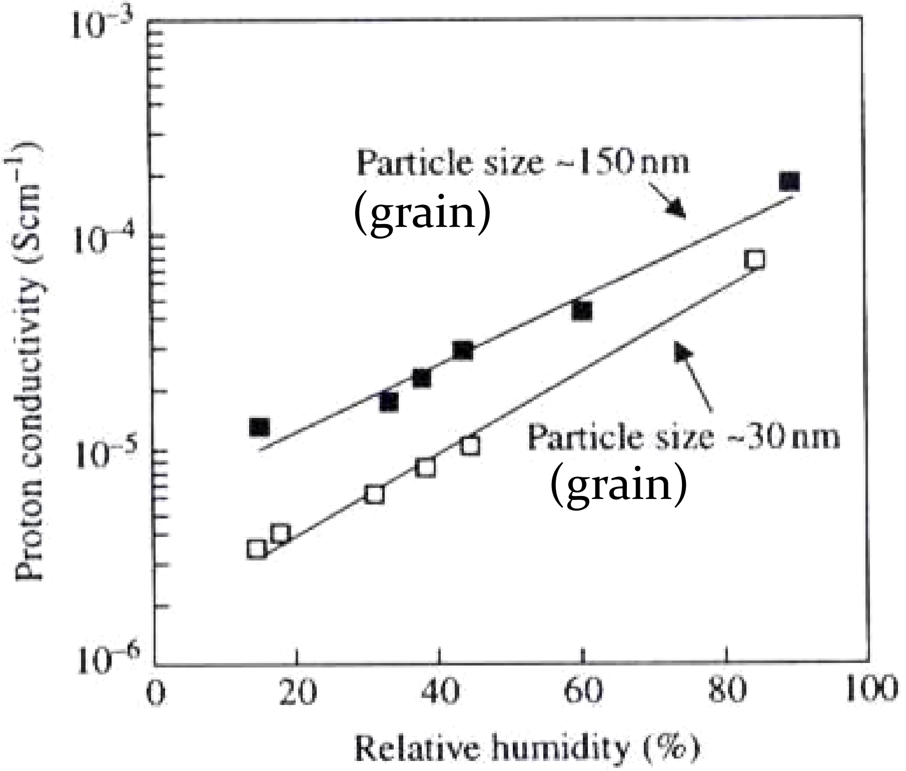


Fig. 8.28. The proton conductivity of polycrystalline hydrated antimony oxide discs at 19.5 °C as a function of relative humidity. Throughout the entire measurement region of humidity, the disc consisting of larger grains has a larger proton conductivity than of small grained sample, which was attributed to grain boundary scattering. [K. Ozawa, Y. Sakka, and M. Amano, *J. Sol-Gel Sci. Technol.* **19**, 595 (2000).]

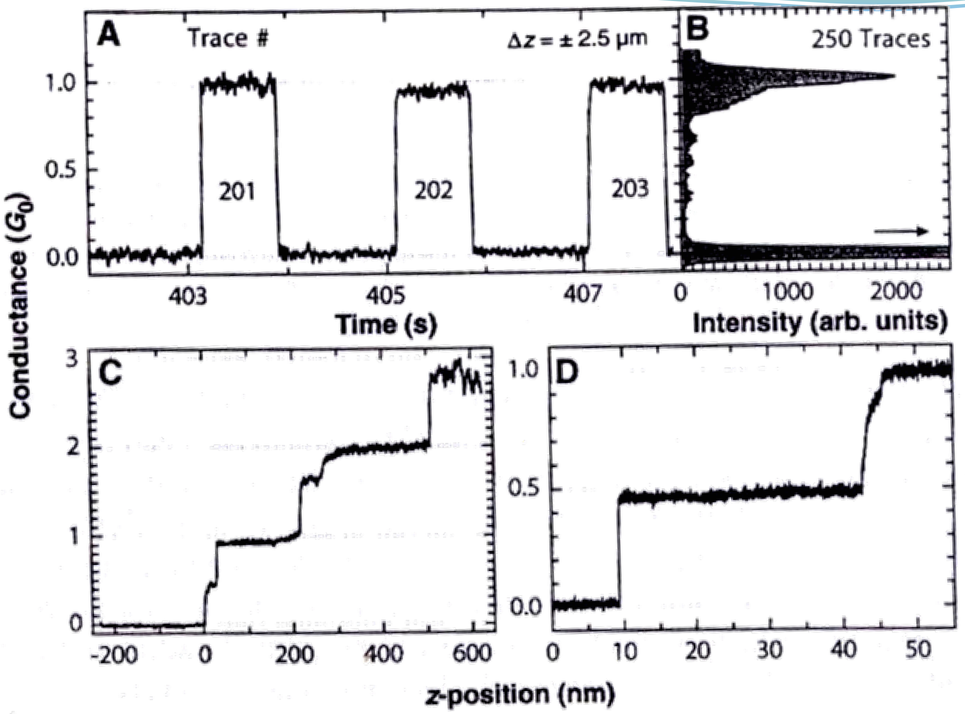


Fig. 8.29. (A) Conductance of a nanotube contact that is moved at constant speed into and out of the mercury contact as a function of time. The period of motion is 2 s and the displacement $\Delta z = \pm 2.5\ \mu\text{m}$. The conductance "jumps" to $\sim 1G_0$ and then remains constant for $\sim 2\ \mu\text{m}$ of its dipping depth. The direction of motion is then reversed and the contact is broken after 2 μm. The cycle is repeated to show its reproducibility; cycles 201 through 203 are displayed as an example. (B) Histogram of the conductance data of all 250 traces in the sequence. The plateaus at $1G_0$ and at 0 produce peaks in the histogram. The relative areas under the peaks correspond to the relative plateau lengths. Because the total displacement is known, the plateau lengths can be accurately determined; in this case, the $1G_0$ plateau corresponds to a displacement of 1880 nm. Plateau lengths thus determined are insensitive to random oscillations of the liquid level and hence are more accurate than measurements from individual traces. (C) A trace of a nanotube contact with two major plateaus, each with a minor pre-step. This trace is interpreted as resulting from a nanotube that is bundled with a second one (as in Fig. (A), inset). The second tube comes into contact with the metal ~200 nm after the first. Shorter plateaus (from ~10 to 50 nm long) with noninteger conductance are often seen and are interpreted to result from the nanotube tips. A clear example of this effect is shown in (D). [S. Frank, P. Poncharal, Z.L. Wang, and W.A. de Heer, *Science* **280**, 1744 (1998).]

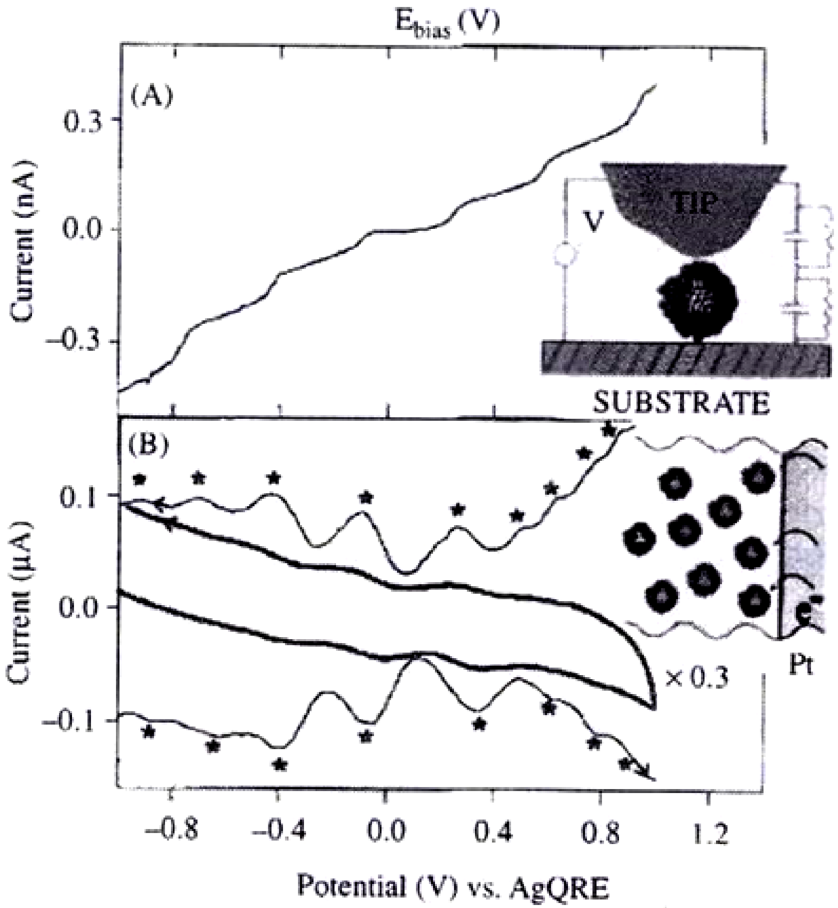


Fig. 8.30. (A) Au STM tip addressing a single cluster adsorbed on an Au-on-mica substrate (inset) and Coulomb staircase I–V curve at 83 K; potential is tip-substrate bias; equivalent circuit of the double tunnel junction gives capacitances $C_{upper} = 0.59$ aF and $C_{lower} = 0.48$ aF. (B) voltammetry (CV -, 100 mV/s; DPV _, ★ are current peaks, 20 mV/s, 25 mV pulse, top and bottom are negative and positive scans, respectively) of a 0.1 mM 28 kDa cluster solution in 2 : 1 toluene: acetonitrile/0.05 M Hx_4NClO_4 at a 7.9×10^{-3} cm^2 Pt electrode, 298 K, Ag wire pseudoreference electrode. [R.S. Ingram, M.J. Hostetler, R.W. Murray, T.G. Schaaff, J.T. Khoury, R.L. Whetten, T.P. Bigioni, D.K. Guthrie, and P.N. First, *J. Am. Chem. Soc.* **119**, 9279 (1997).]

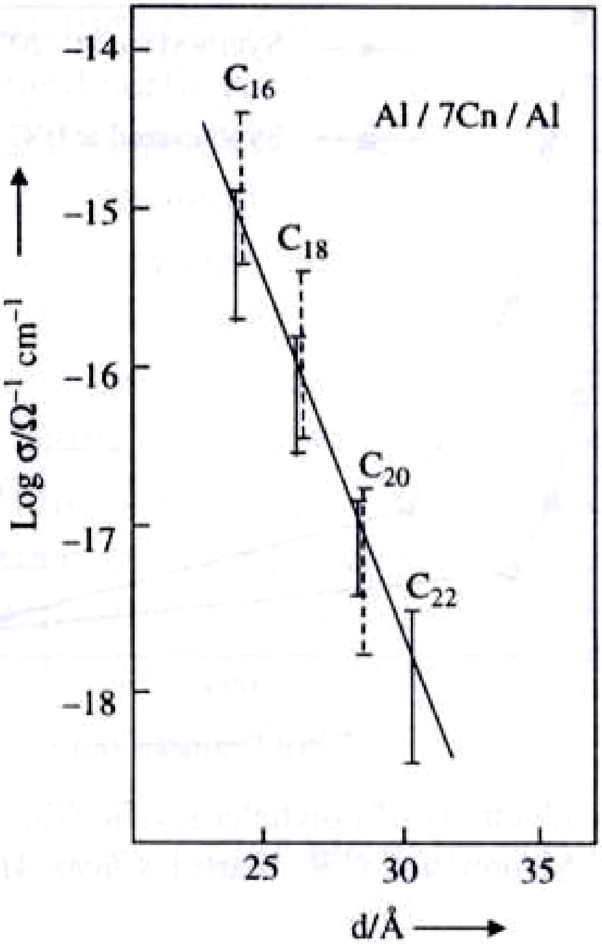


Fig. 8.31. The tunneling conductivity of a self-assembled monolayer as a function of molecular length or film thickness, when changing from C_{14} to C_{23} fatty acid monolayers, demonstrating that the electrical conductivity decreases exponentially with increasing thickness of insulating layer. [H. Kuhn, J. *Photochem.* **10**, 111 (1979).]

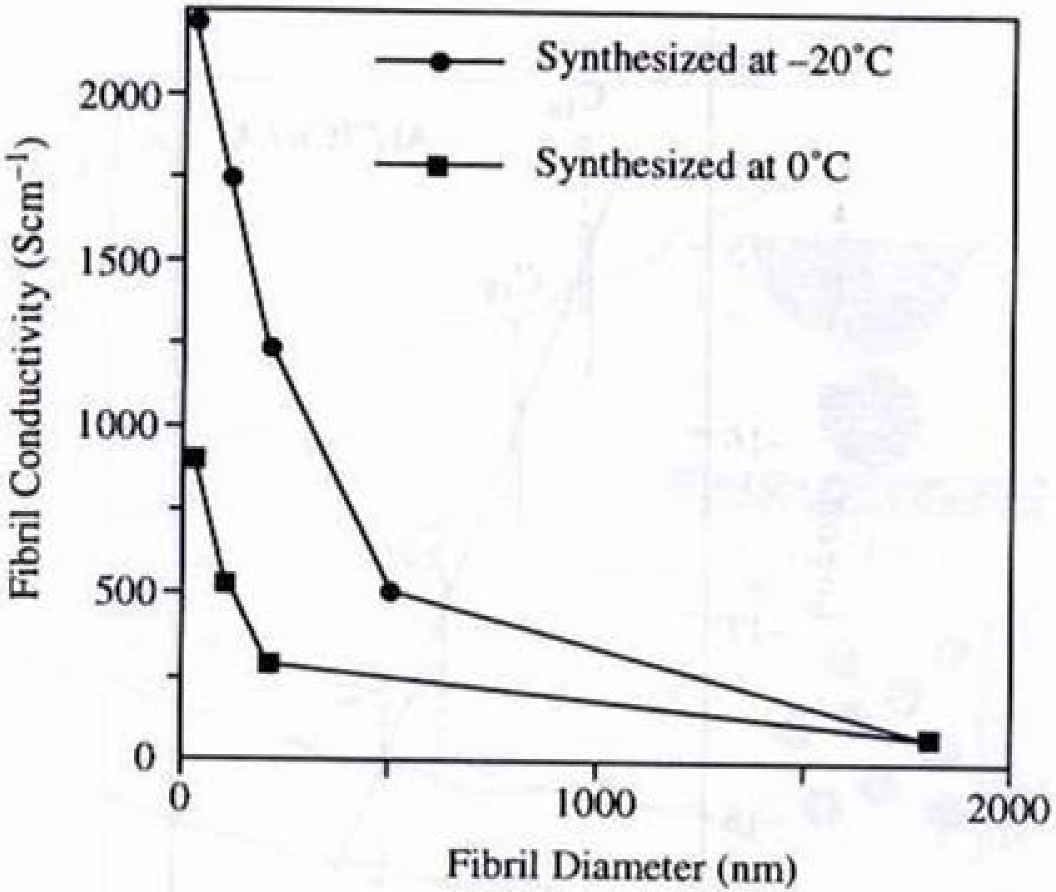


Fig. 8.32. The electrical conductivity of polyheterocyclic fibris as a function of diameter. [Z. Cai, J. Lei, W. Liang, V. Menon, and C.R. Martin, *Chem. Mater.* **3**, 960 (1991).]

B. Surface Energy

B-1. Interpretation of surface energy

Atoms or molecules on a solid surface possess fewer nearest neighbors or coordination numbers, and are under an inwardly directed force and the bond distance between the surface atoms or molecules and the sub-surface atoms or molecules, is smaller than that between interior atoms or molecules.

When solid particles are very small, the lattice constants show an appreciable reduction.

2.4

Surface energy, surface free energy or surface tension, by definition, is the energy required to create a unit area of “new” surface:

A. Basic Concepts

- two fundamental dislocation types□
  edge dislocation, screw dislocation

- Plastic deformation□
  motion of large numbers of dislocations

- plastic deformation produced by dislocation motion□
  - **slip**
  - *slip plane*
  - Direction of Motion
  - a screw dislocation : direction of movement is perpendicular to the stress direction.
  - an edge dislocation : parallel to the shear stress.

K. THE TEMPERATURE DEPENDENCE OF CARRIER CONCENTRATION

F18.15

Intrinsic carrier concentration (electrons and holes) increase with temperature because, with rising temperature, more thermal energy is available to excite electrons from the valence to the conduction band. $P \propto \exp(-Eg/RT)$ $n \propto \exp(-Eg/RT)$

P	n	Eg	T
↑	↑	□	↑
↑	↑	↓	□

“□ ” □ remains cm changed

Carrier concentration in Ge is greater than for Si due to germanium’s smaller band gap (0.67 versus 1.11 eV, Table 18.2).

One particle in one – dimensional box
What is the energy ?

$$\alpha = \pm n\pi / a = \sqrt{2mE/\hbar^2}$$

$$2mE/\hbar^2 = n^2\pi^2/a^2 \, , \quad \hbar^2 = 4\pi^2$$

$E_n = n^2 h^2 / 8ma^2$ n= 1,2,3,… (11.149)

n (Quantum Number)	E_n	E_n ($h^2/8ma^2$)	ψ_n
4	$16\ h^2/8ma^2$	16	$(2/a)^2 \sin(4\pi/a)$ X
3	$9\ h^2/8ma^2$	9	$(2/a)^2 \sin(3\pi/a)$ X
2 (Excited States)	$4\ h^2/8ma^2$	4	$(2/a)^2 \sin(2\pi/a)$ X
1 (ground State)	$h^2/8ma^2$	1	$(2/a)^2 \sin(\pi/a)$ X

ΔE

$$7\frac{h^2}{8ma^2}$$

$$5\frac{h^2}{8ma^2}$$

$$3\frac{h^2}{8ma^2}$$

One particle in one – dimensional box

$$\Delta E_{n+1\rightarrow n} = \left[(n+1)^2 - n^2\right]\frac{h^2}{8ma^2} = (2n+1)\frac{h^2}{8ma^2}$$

$$\Delta E = h\gamma = \frac{hc}{\lambda}$$

$m\downarrow$ or/and $a\downarrow \Rightarrow \Delta E\uparrow$ and $\gamma\uparrow(\lambda\downarrow)$

$m\uparrow$ or/and $a\uparrow \Rightarrow \Delta E\downarrow$ and $\gamma\downarrow(\lambda\uparrow)$

$m\rightarrow 0$ or $a\rightarrow\infty \Rightarrow \Delta E\rightarrow 0$

☐ $a\rightarrow\infty$ ☐ free particle $\Rightarrow$ energy is not quantized

(but contineous)

no energy gap

(B) CERAMICS

Forward bias: Large numbers of charge carriers flow across the semiconductor as evidenced by an appreciable current and a low resistivity.

$$\text{Electron} + \text{hole} \xrightarrow{\qquad\qquad\qquad} \text{energy} \quad (18.18)$$

Reverse bias: The junction region is relatively free of mobile charge carriers, the junction is highly insulative.

At high reverse bias voltages, order of several hundred volts, large numbers of charge carriers (electrons and holes) are generated. A very abrupt increase in current: breakdown.

G. ELECTRICAL RESISTIVITY OF MTALS

T8-1

Most metals are extremely good conductors: because of the large numbers of free electrons that have been excited into empty states above the Fermi energy (n has a large value)

Crystalline defects serve as scattering centers for conduction electrons it has been observed experimentally that the total resistivity ρ_{total} of a metal is the sum of the cotributions from thermal vibrations ρ_t impurities ρ_i, and platic deformation (ρ_d, cold work): (scattering mechanisms act independently)

$$\rho_{total} = \rho_t + \rho_i + \rho_d \quad (18.9)$$

$$\rho = \frac{1}{\sigma}$$

Matthiessen’s rule

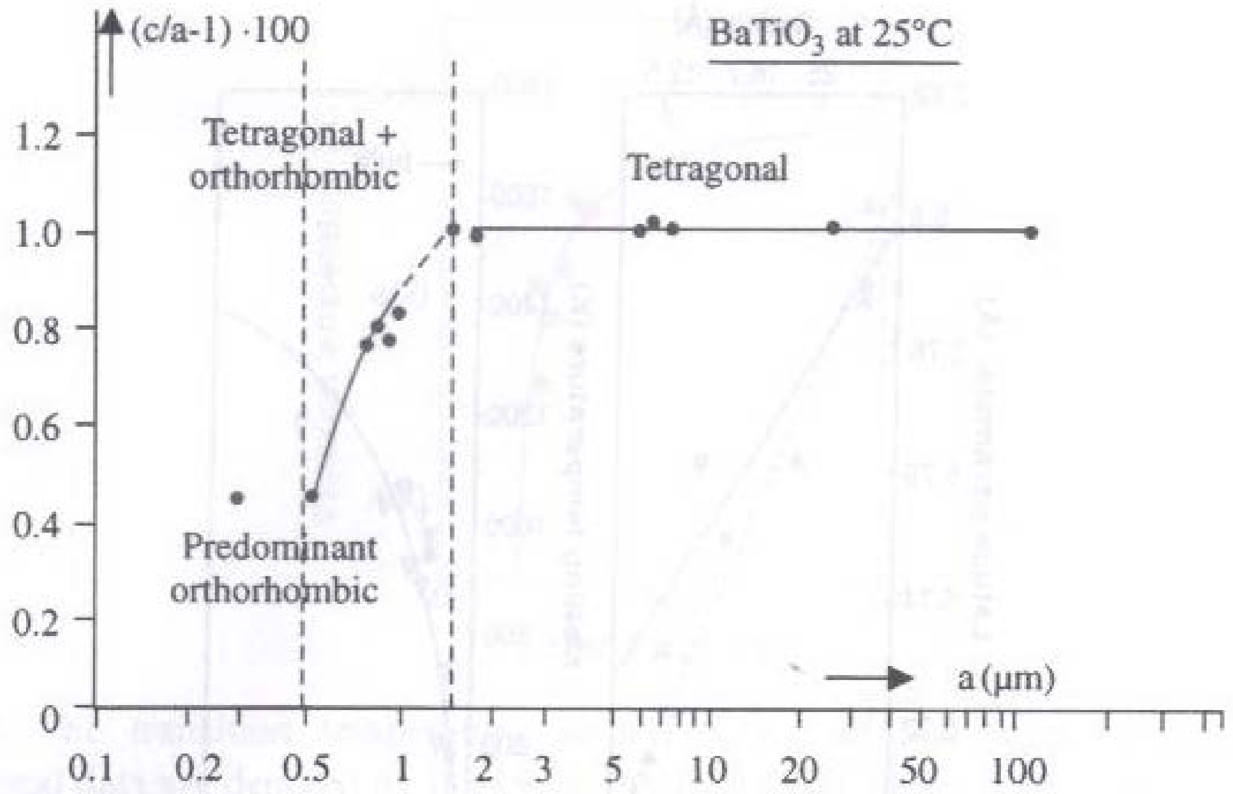


Fig. 8.16. The dependence of the lattice constant ratio of tetragonal BaTiO$_3$ on the average particle size. [G. Arlt, D. Hennings, and G. de With, *J. Appl. Phys.* **58**, 1619 (1985).]

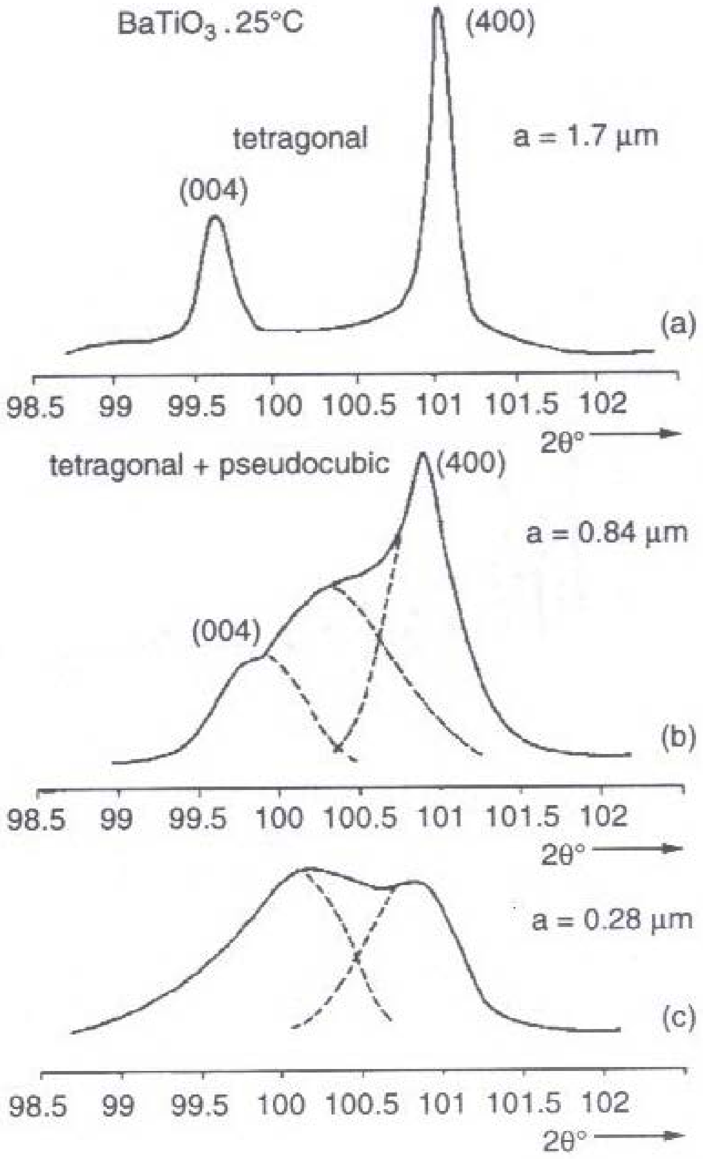


Fig. 8.17. A gradual phase transition from tetragonal structure of large sized BaTiO$_3$ particles of 1.7 µm in diameter to pseudocubic or orthorhombic structure of small size BaTiO$_3$ particles of 0.28 µm in diameter. [G. Arlt, D. Hennings, and G. de With, *J. Appl. Phys.* **58**, 1619 (1985).]

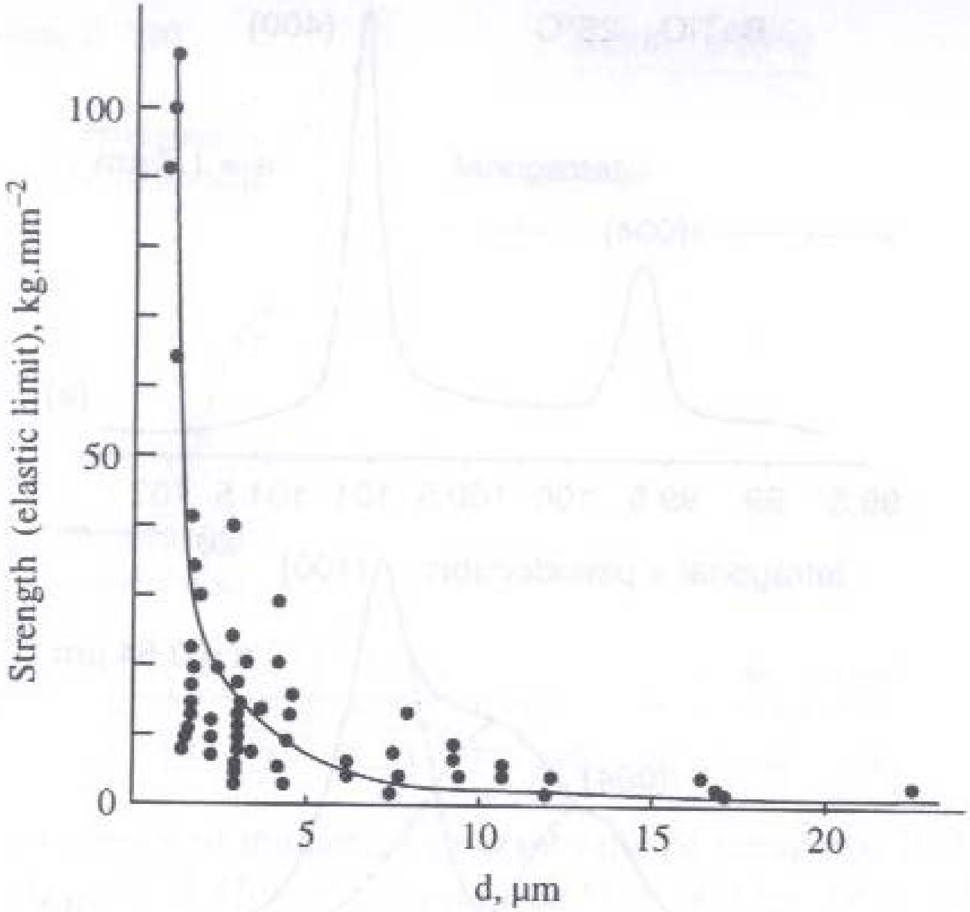


Fig. 8.18. The mechanical strength of NaCl whiskers increases significantly and approaches the theoretical strength as the diameters decrease below ~1 μm due to an increased bulk and surface perfections. [Z. Gyulai, *Z. Phys.* **138**, 317 (1954).]

13-I. ELECTRICAL CONDUCTION

A. OHM'S LAW

The ease with which a solid material transmits an electric current

$$V = IR \qquad (18.1)$$

F18.1

V, I, and R: voltage in volts (J/C), current in amperes (C/s), and resistance in ohms (V/A). R is influenced by specimen configuration, resistivity ρ is independent of specimen geometry

$$R \propto \ell, R \propto \ell/A$$

$$\rho = \frac{RA}{\ell} \qquad (18.2)$$

ρ: ohm-meters (Ω-m)

$$\rho = \frac{\mathrm{VA}}{\mathrm{I}\ell} \qquad (18.3)$$

B. ELECTRICAL CONDUCTIVITY

$$\sigma = \frac{1}{\rho} \qquad (18.4) \qquad\qquad \sigma = \frac{I\ell}{VA} = \frac{I}{A}\left(\frac{1}{\frac{V}{\ell}}\right)$$

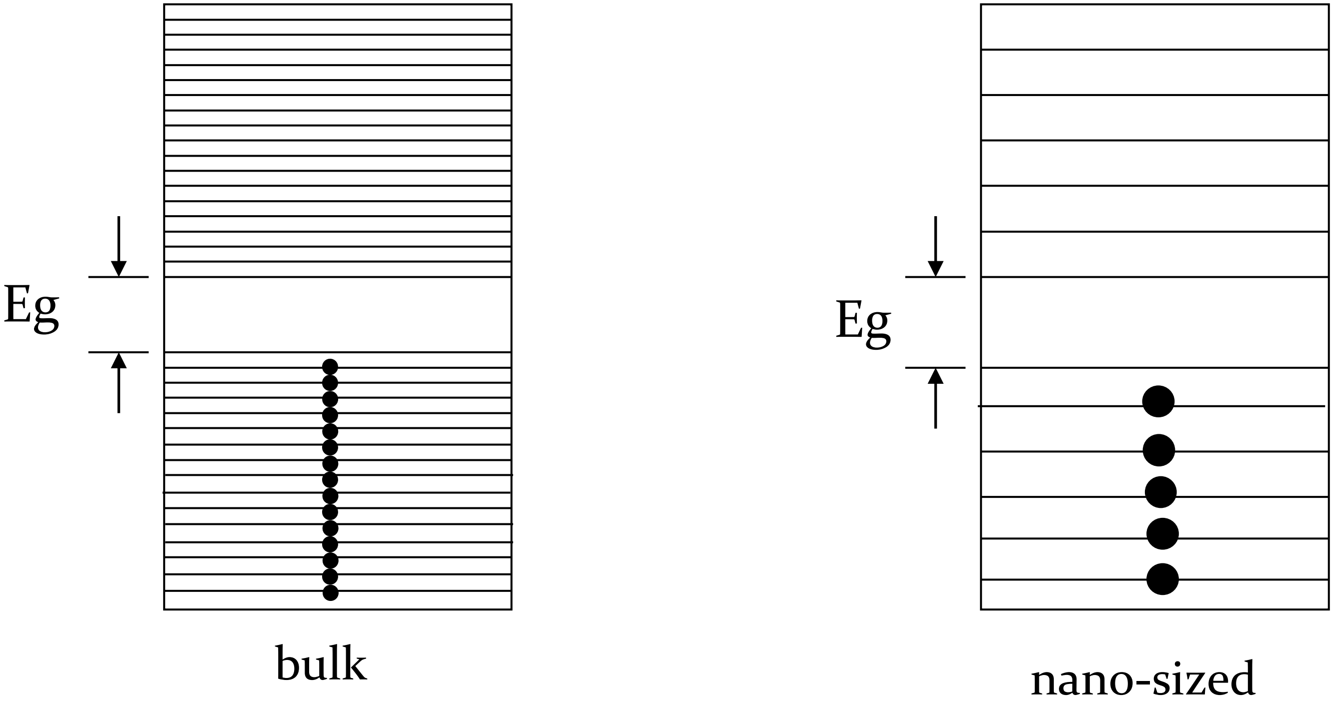
Capability of conductiong an eletric current,

σ: [(Ω-m)$^{-1}$, or mho/m], Ohm's law may be expressed as

$$J = \sigma\varepsilon \qquad (18.5)$$

- For Solid□
- The electrical properties are a consequence of its electron band structure: the arrangement of the outermost electron bands and the way in which they are filled with electrons.(Eletrical conduction occurs only when there are available positions(empty states or holes) for electrons to move.)
- Four different types of band structures are possible at 0 k:
  - The first : partially filled(valence)band: conductor (Eg=0, i.e., no band gap), e.g., copper, one 4s electron(per atom), only half the available electorn positions within this 4S band are filled.

Semiconductors



Eg <1.8 ev (opaque) ⇒ 1.8 < Eg < 3.1

(partial absorption of visible: colorful)

partial absorption of visible:

1.8< Eg <3.1 ev (colorful) ⇒ 3.1 ev < Eg

(electrically insulative: transparent to visible light)