C8888 Nanochemistry

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Au nanoparticles

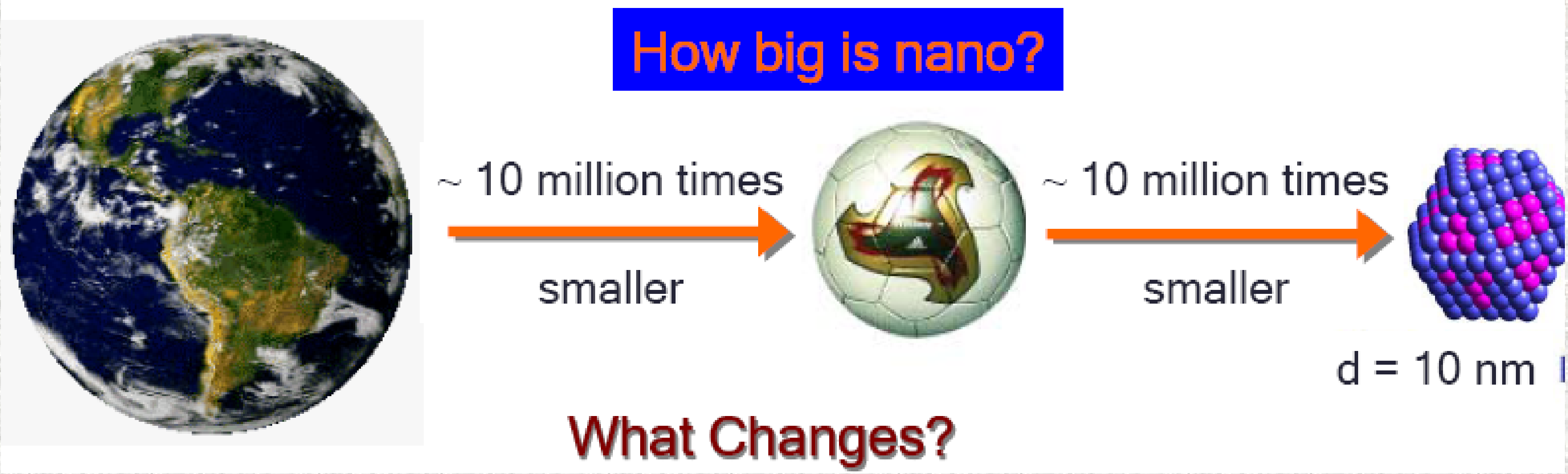
Ph.D. level course
Prerequsite C7780 Inorganic Materials Chemistry

Course grading:
Select a topic concerning nanochemistry and prepare:
Presentation - 30 min (20 %)
Written term paper - min 5 pages (80 %)

C8888 Nanochemistry
Time Plan for Spring 2019

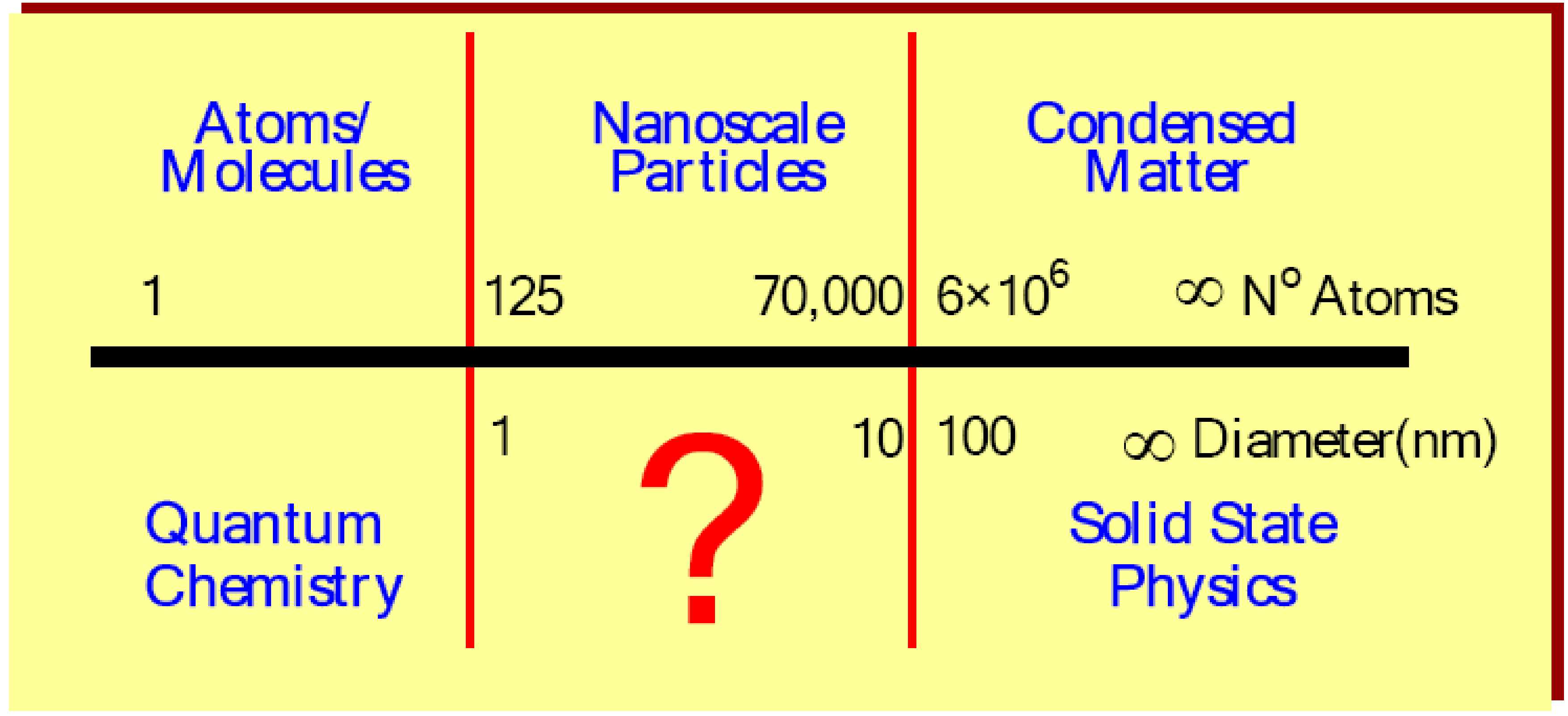
Feb 18	- Lecture 1
Feb 26	- **no lecture**
Mar 5	- Lecture 2
Mar 12	- Lecture 3
Mar 19	- Lecture 4 - Think of a topic for your paper
Mar 26	- Lecture 5 - Send me a 1-page abstract of your paper
Apr 2	- Lecture 6 - Final topic approval
Apr 9	- work on a paper
Apr 16	- work on a paper
Apr 23	- work on a paper
Apr 30	- 3 presentations
May 7	- 3 presentations
May 14	- no lecture - Hand in your term paper

Nanoscopic Materials



- **Chemical methods to change physical and chemical properties – composition, substituents,….**
- **Size is another variable to change physical and chemical properties for constant chemical composition**
- **Each physical property or fenomenon has a characteristic length**
- **When particle size is comparable to the characteristic length, property start to depend on the size**

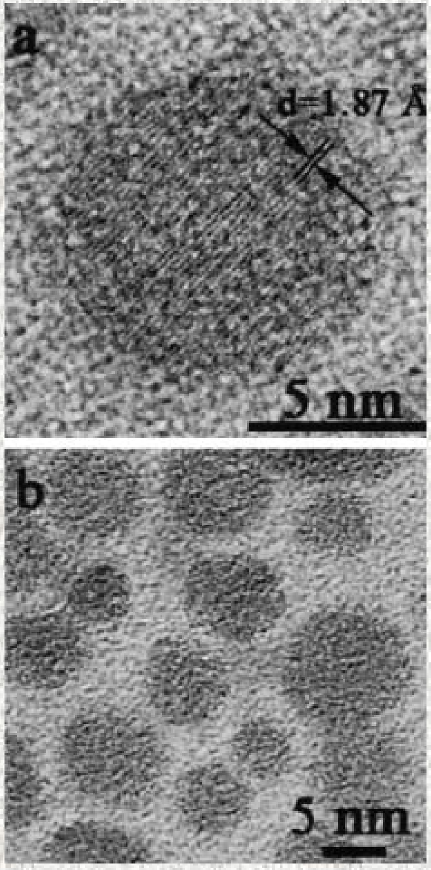
Nanoscopic Scales



Atoms/ Molecules	Nanoscale Particles	Condensed Matter	
1	125 70,000	6×10^{6} ∞	N° Atoms
	1 10	100 ∞	Diameter(nm)
Quantum Chemistry	?	Solid State Physics	

Nanoscopic Materials

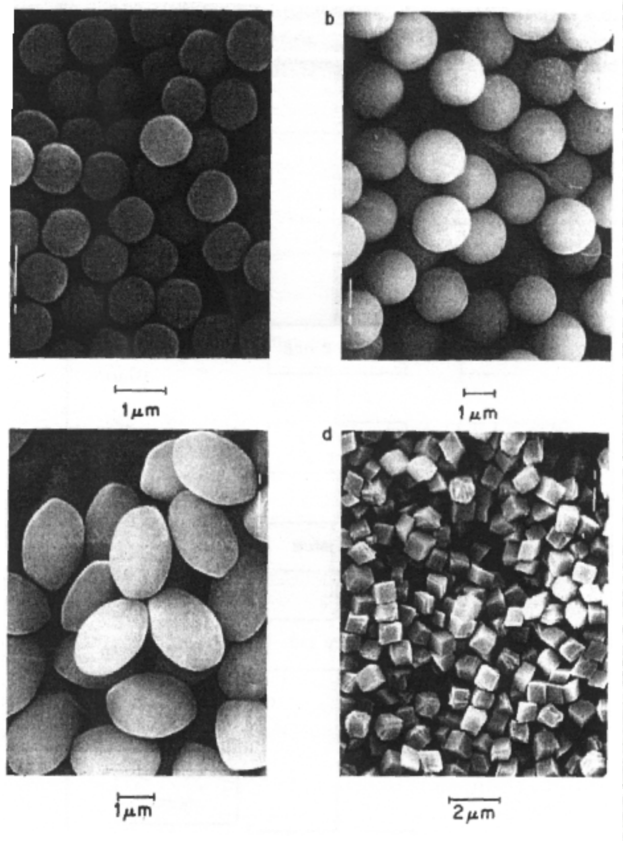
Nanoparticles 1 – 100 nm



1 nm = 10^{-9} m

1 nm = 10 Å

Traditional materials > 1 μm



Nanoscopic Materials

EU definition (2011):

Size 1 – 100 nm

A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm.

http://ec.europa.eu/environment/chemicals/nanotech/faq/definition_en.htm

Nanoscopic Materials

Nanoscale regime
Size 1 – 100 nm (traditional materials > 1 μm)

Physical and chemical properties depend on the size !!

Natural examples:
- ☯ **Human teeth, 1-2 nm fibrils of hydroxyapatite $Ca_5(PO_4)_3(OH)$ + collagen**
- ☯ **Asbestos, opals, calcedon**
- ☯ **Primitive meteorites, 5 nm C or SiC, early age of the Solar system**

Nanoscale objects have been around us, but only now we can observe them, manipulate and synthesize them.

Nanostructural Materials

“Prey”, the latest novel by Michael Crichton, author of “Jurassic Park”.

The horrible beasties threatening humanity in this new thriller are not giant dinosaurs, but swarms of minute “nanobots” that can invade and take control of human bodies.

Last summer, a report issued by a Canadian environmental body called the action group on erosion, technology and concentration took a swipe at nanotechnology. It urged a ban on the manufacture of new nanomaterials until their environmental impact had been assessed. The group is better known for successfully campaigning against biotechnology, and especially against genetically modified crops.

The research, led by a group at the National Aeronautics and Space Administration's Johnson Space Centre in Houston, has found in preliminary studies that inhaling vast amounts of nanotubes is dangerous. Since they are, in essence, a form of soot, this is not surprising. But as most applications embed nanotubes in other materials, they pose little risk in reality.

Room at the Bottom

What I want to talk about is the problem of manipulating and controlling things on a small scale …

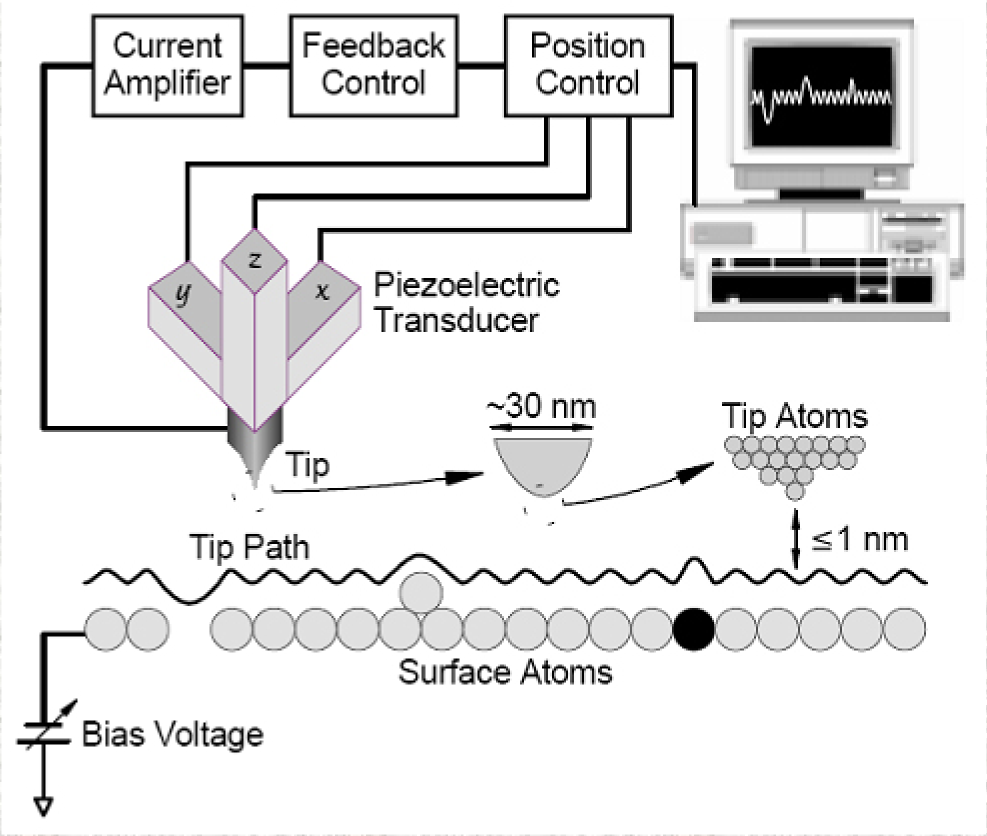
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It's a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction……

Prof. Richard Feynman in "There's plenty of room at the bottom", lecture delivered at the annual meeting of the APS, Caltech, 29 December, 1959.

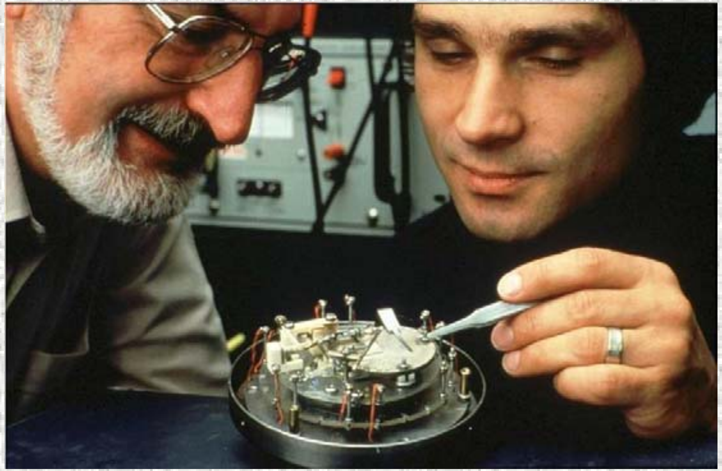
Manipulation atom-by-atom

STM

Scanning Tunelling Microscopy 1982



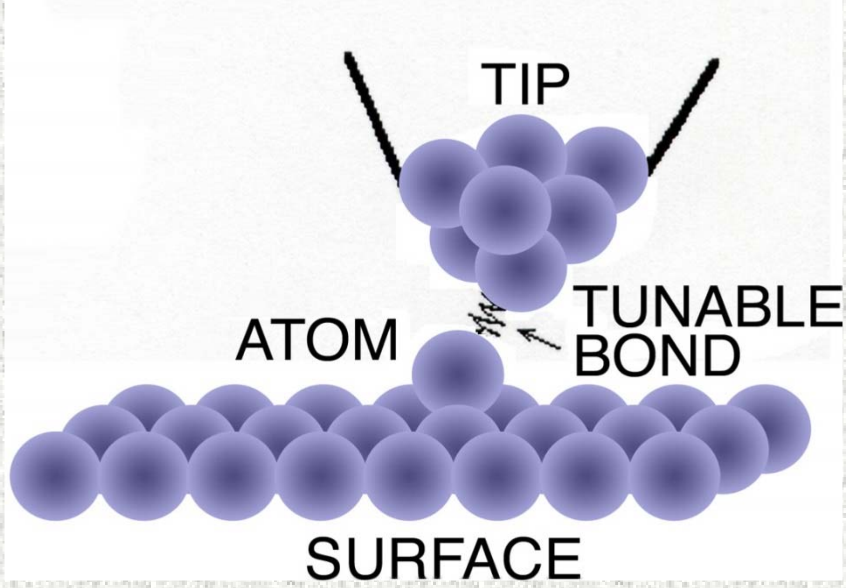
Binning and Rohrer
Nobel Prize 1986

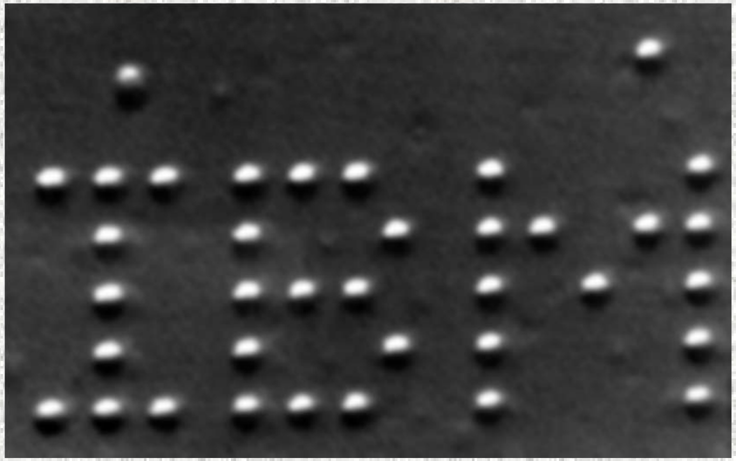


Nanoscale Writing

Manipulation atom-by-atom

STM positioned Xe atoms on Ni crystal, 5 nm letters





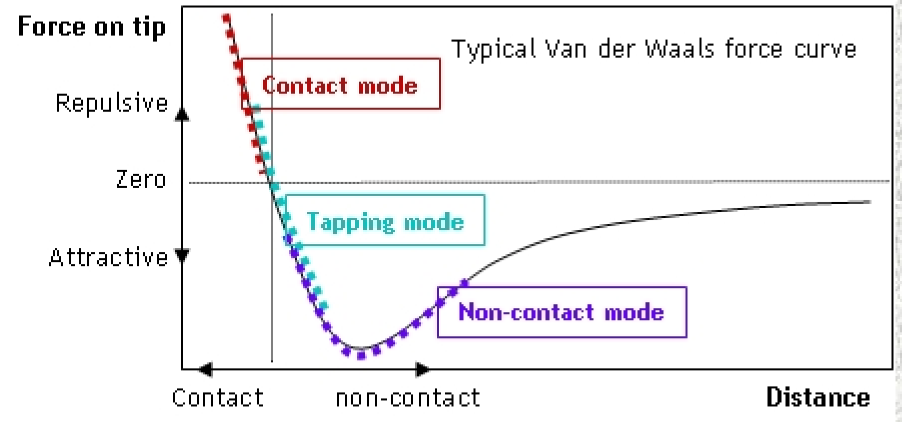
AFM

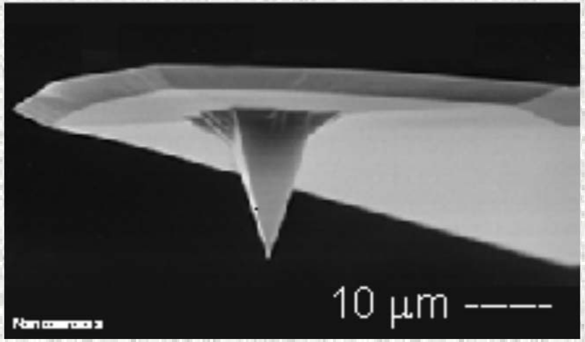
Atomic Force Microscopy 1986

Binnig, Quate, and Gerber

a method allowing a variety of non-conducting surfaces to be imaged and characterized at the atomic level

the detection of forces between an observed sample surface and a sharp tip located at the end of a cantilever

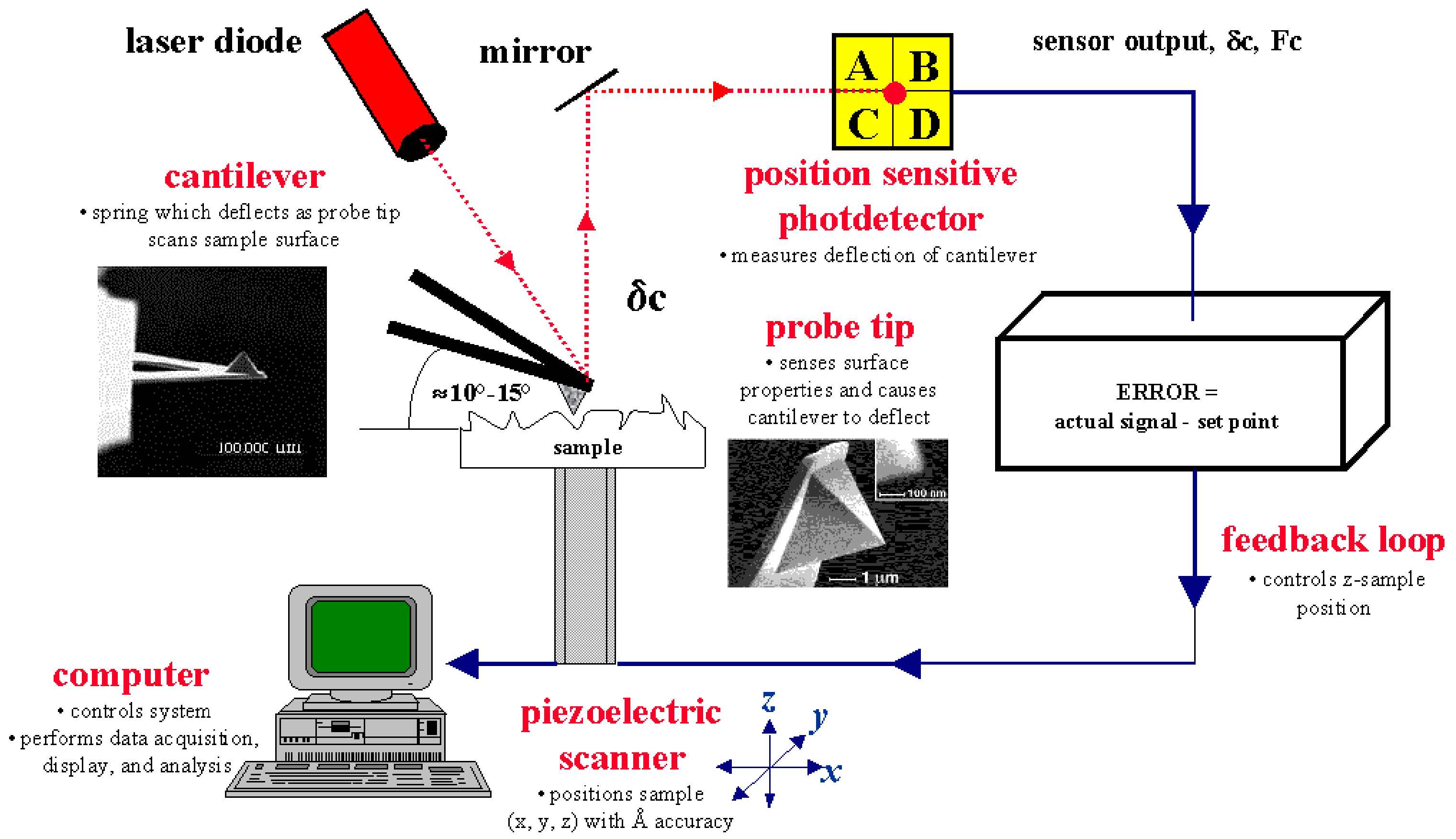




AFM

Atomic Force Microscopy (AFM) :

General Components and Their Functions



cantilever
- spring which deflects as probe tip scans sample surface

position sensitive photdetector
- measures deflection of cantilever

probe tip
- senses surface properties and causes cantilever to deflect

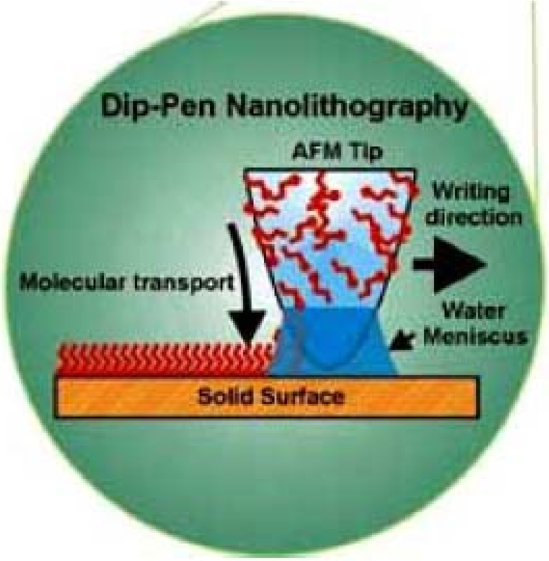
ERROR =
actual signal - set point

feedback loop
- controls z-sample position

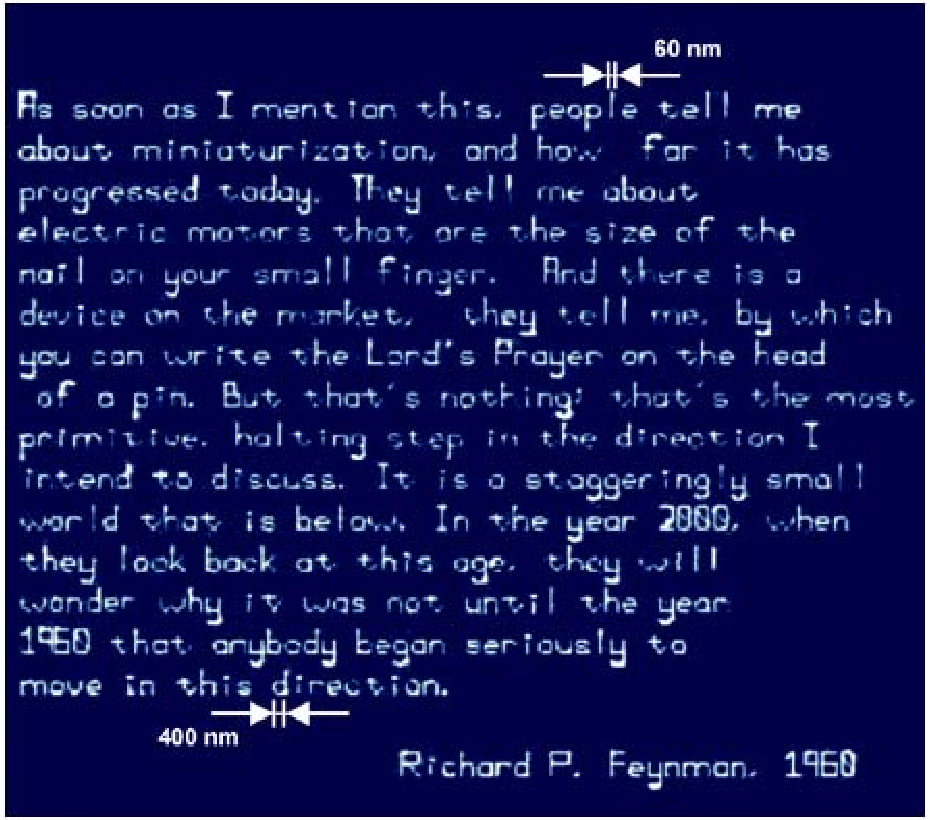
computer
- controls system
- performs data acquisition, display, and analysis

piezoelectric scanner
- positions sample (x, y, z) with Å accuracy

Nanoscale Writing



Nanoscale writing with an AFM (Mirkin et al.)



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1960 that anybody began seriously to
move in this direction.

Richard P. Feynman, 1960

Nanoscopic Materials

Negligible light scattering - New optics

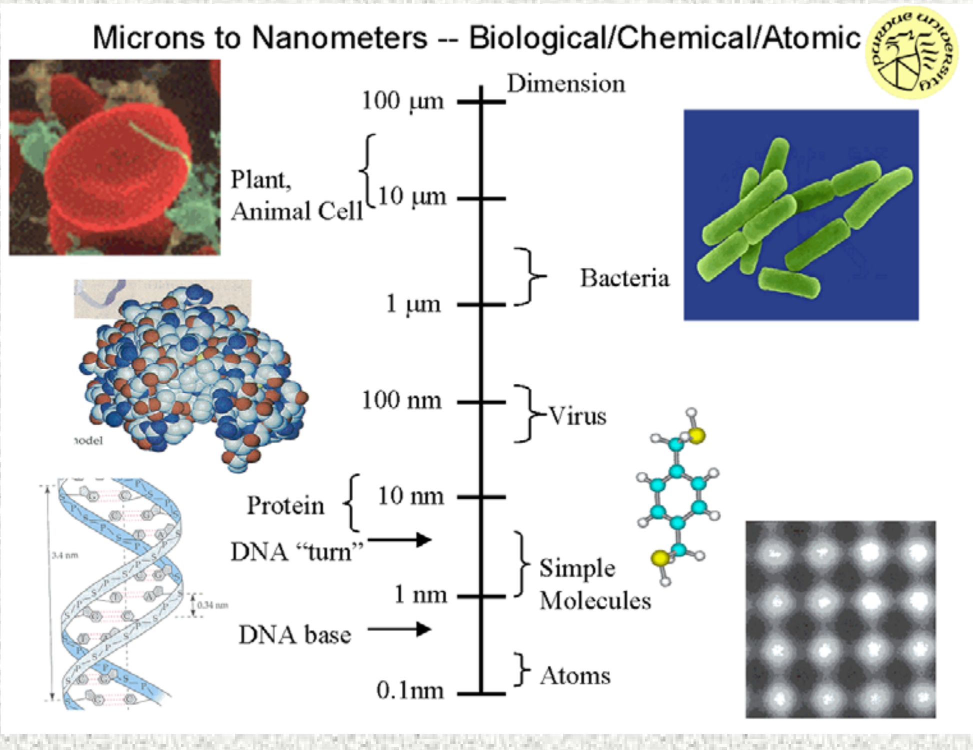
Quantum size effects - Information technology, Storage media

High surface area - Catalysts, Adsorbents

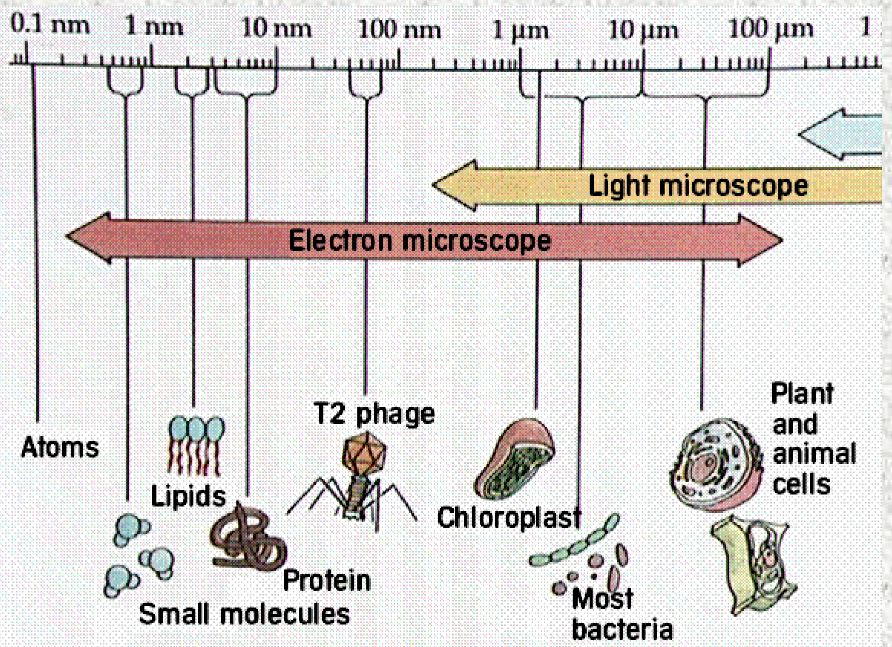
Large interfacial area - New composites

Surface modifications - Targeted drug delivery

Nanoscopic Size



1 – 100 nm



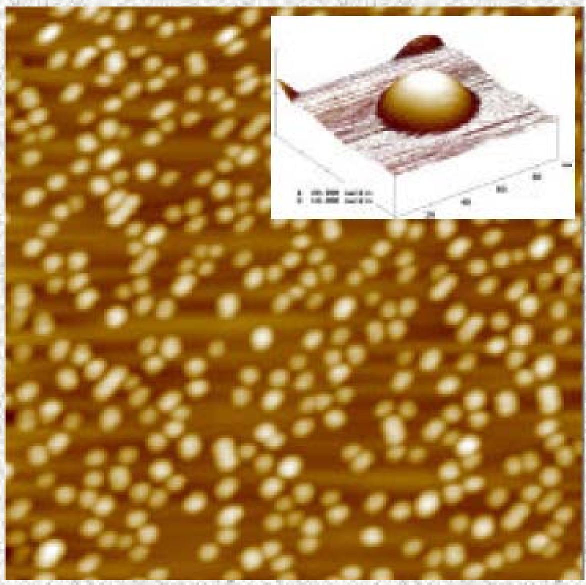
The largest known bacterium -
Thiomargarita namibiensis - 100-750 microns

The Nano-Family

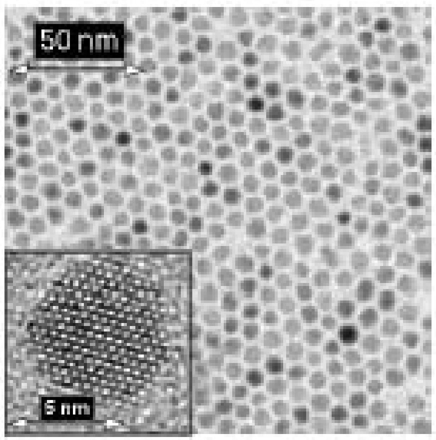
At least one dimension is between 1 - 100 nm

0-D structures (3-D confinement):

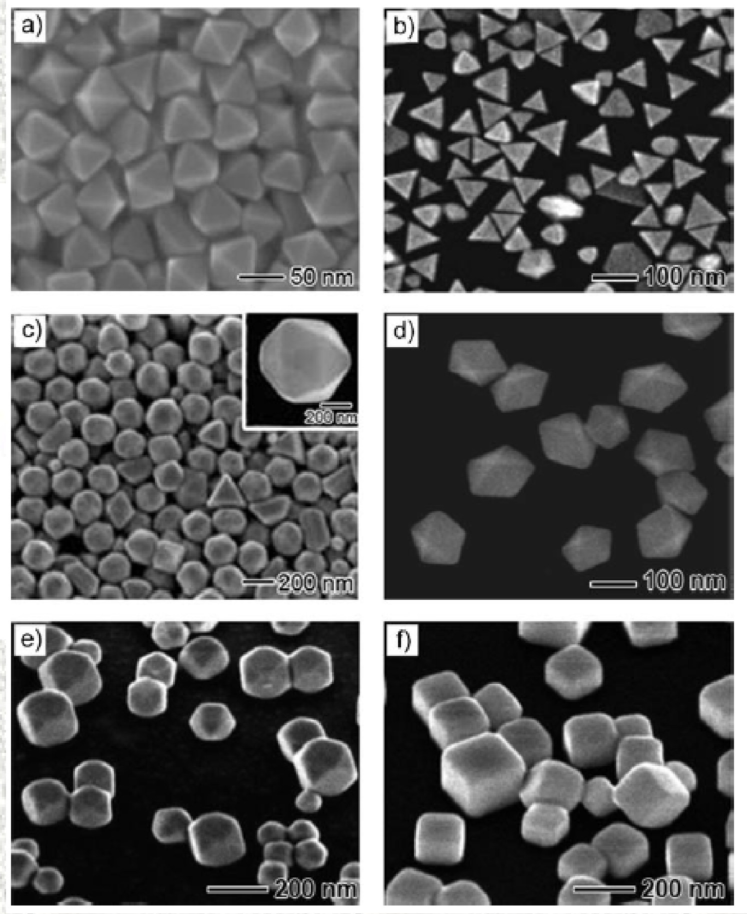
- **Quantum dots**
- **Nanoparticles**



AFM 1 μm x 1 μm
InAs on GaAs/InP



CdTe nanoparticles

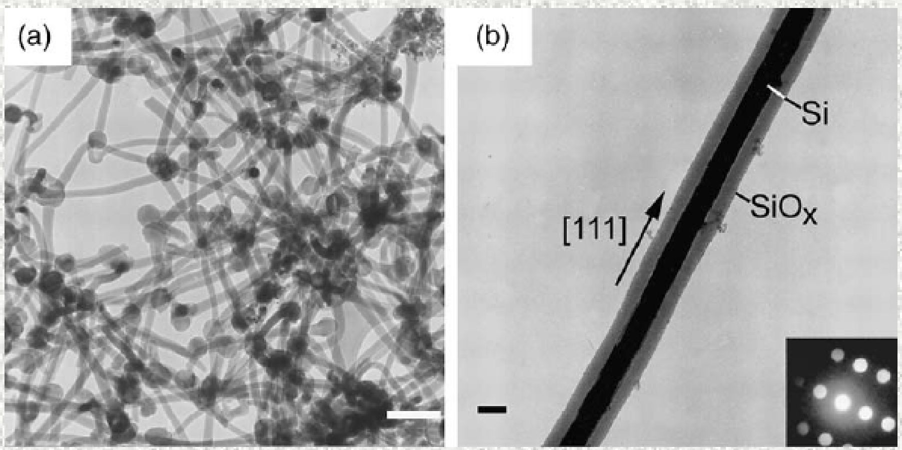


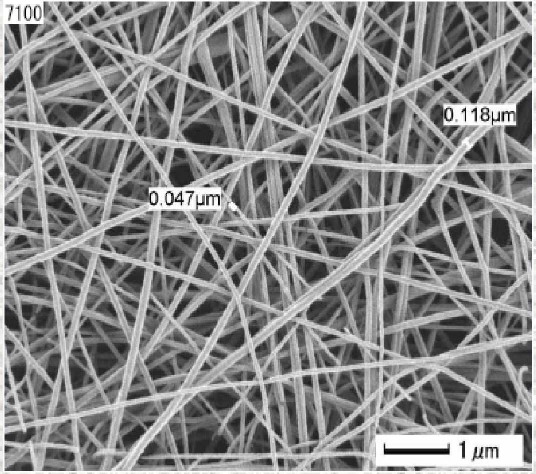
Au nanoparticles

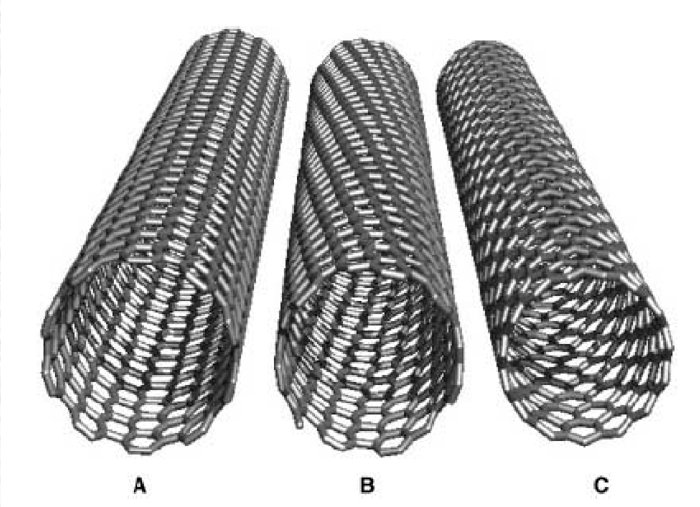
The Nano-Family

1-D structures (2-D confinement):

- Nanowires
- Nanorods
- Nanotubes
- Nanofibers

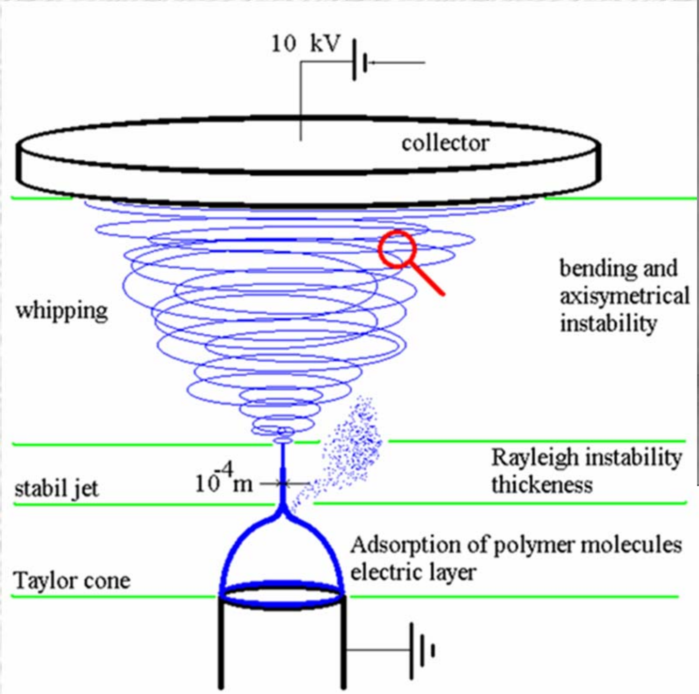


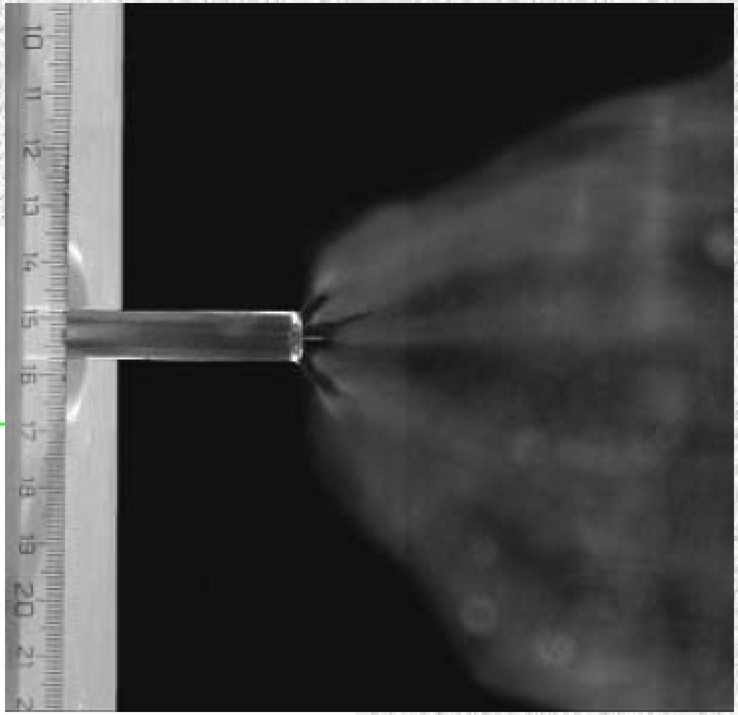




Electrospinning

Nanofibers

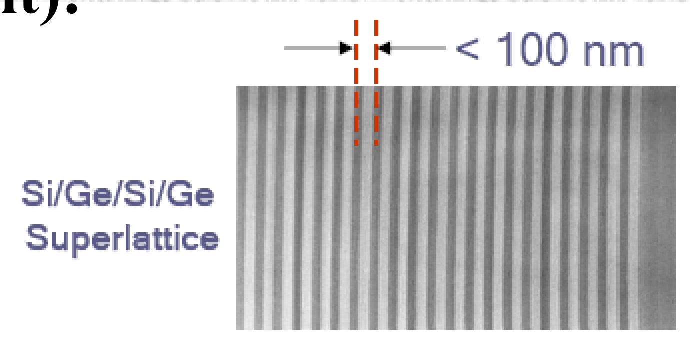


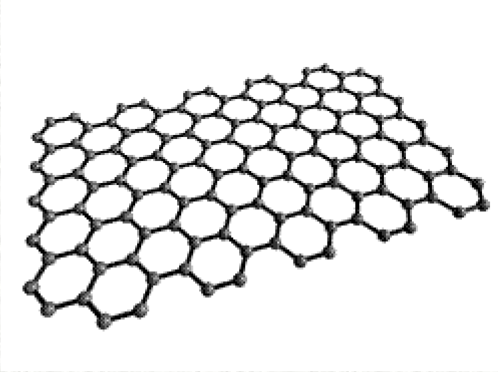


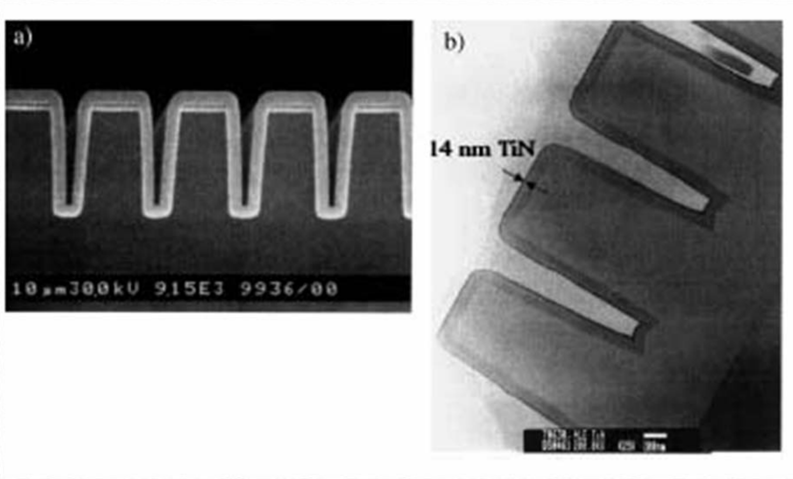
The Nano-Family

2-D structures (1-D confinement):

- **Thin films - CVD, ALD**
- **Planar quantum wells**
- **Superlattices**
- **Graphene**
- **SAM**







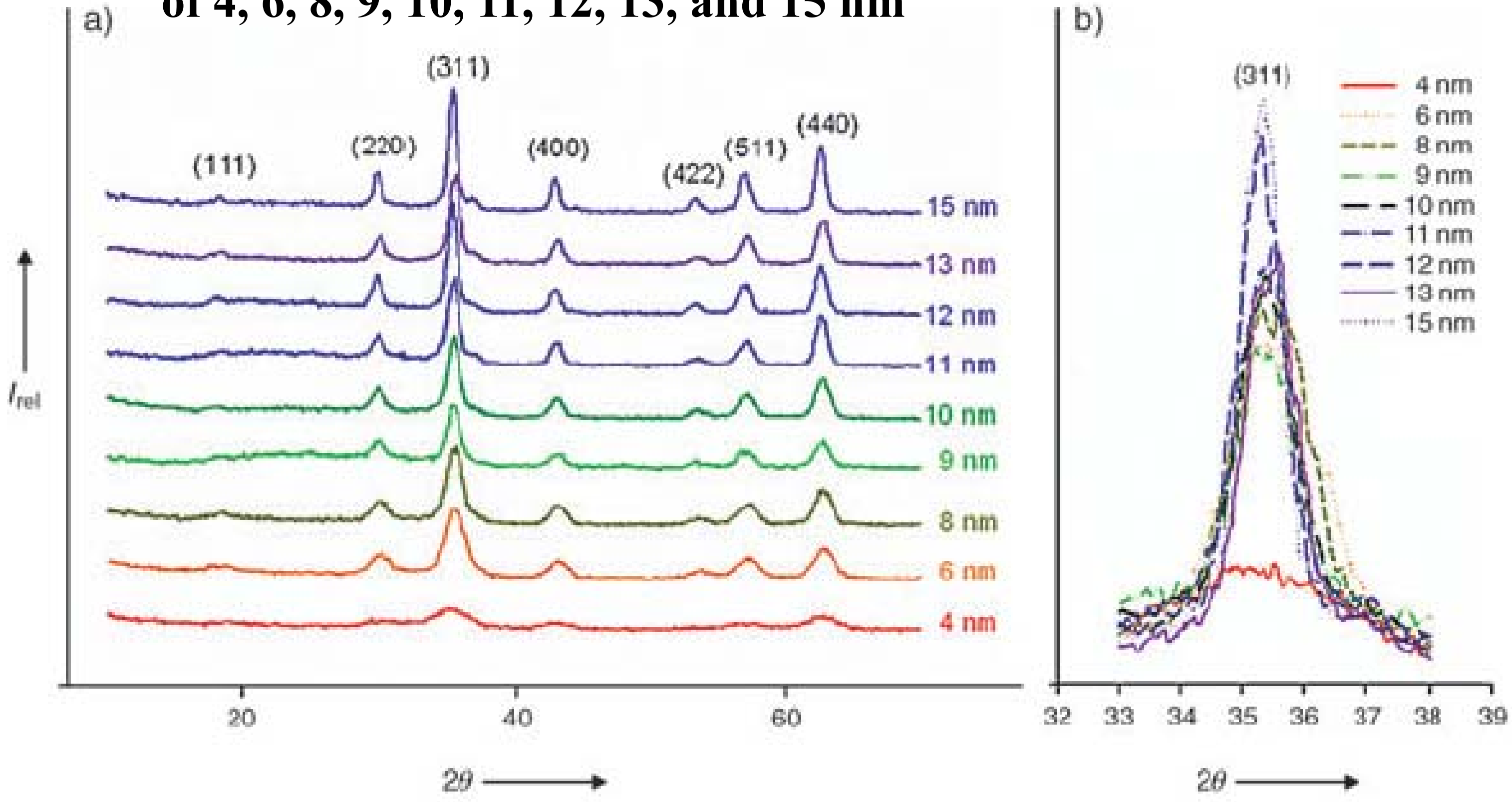
Coherence Length, *d*

Scherrer equation

$$d = \frac{k\lambda}{\beta \cos\theta}$$

k = 0.89, λ = wavelength,
β = full width at half-maximum of a standard (Si)

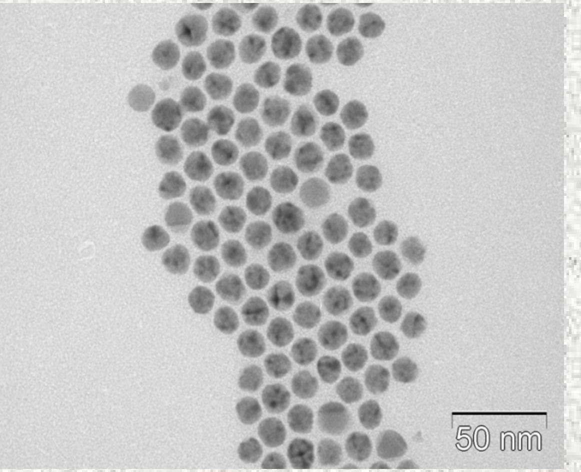
XRD patterns of iron oxide nanocrystals of 4, 6, 8, 9, 10, 11, 12, 13, and 15 nm



Nanoscopic Behavior of Materials

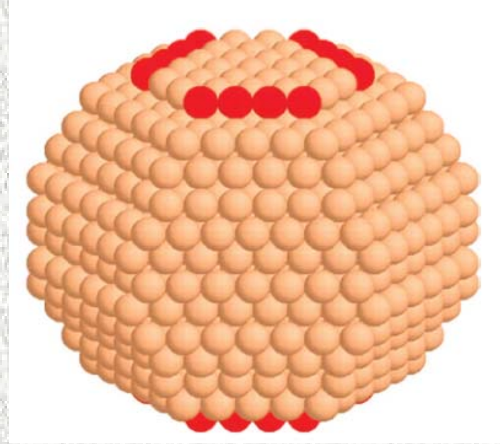
Differences between bulk and nanoscale materials

- **Surface Effects**
- **Quantum Confinement Effects**

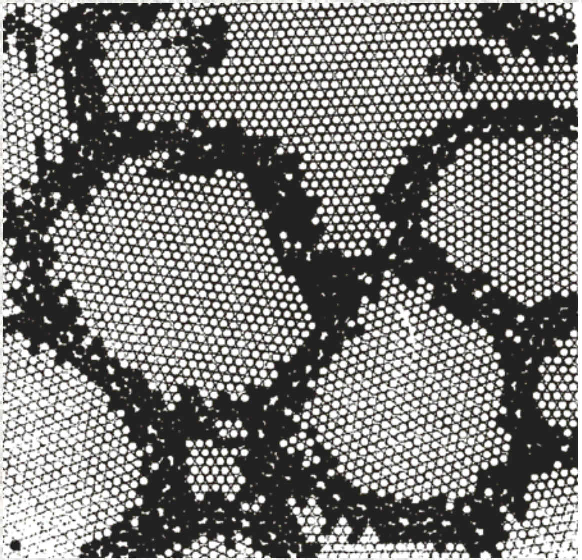


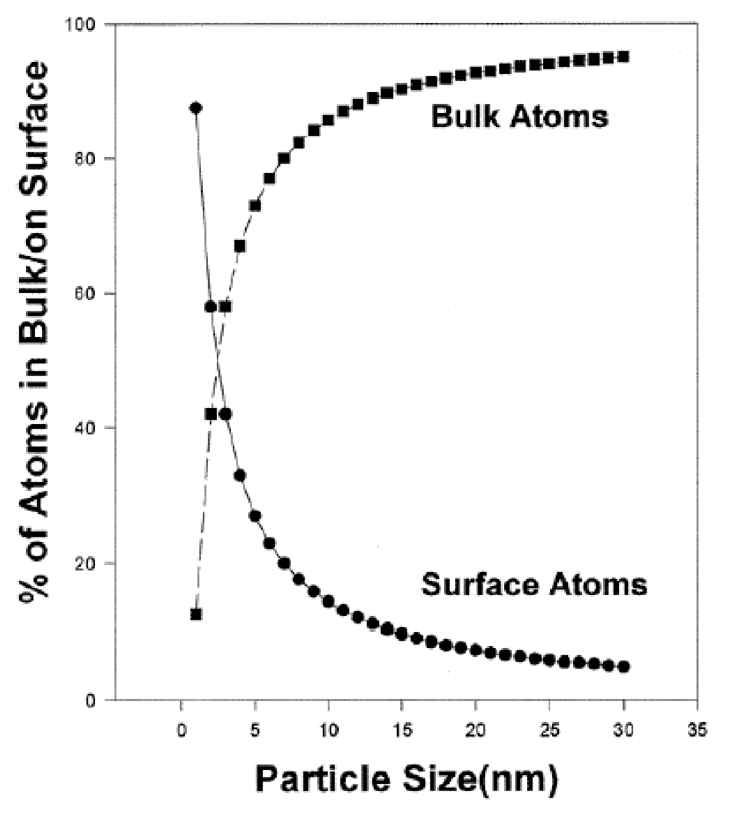
Surface Effects

Decreasing grain size = Increasing volume fraction of grain boundaries (50% for 3 nm particles)



Ru particle diameter 2.9 nm





Surface Effects

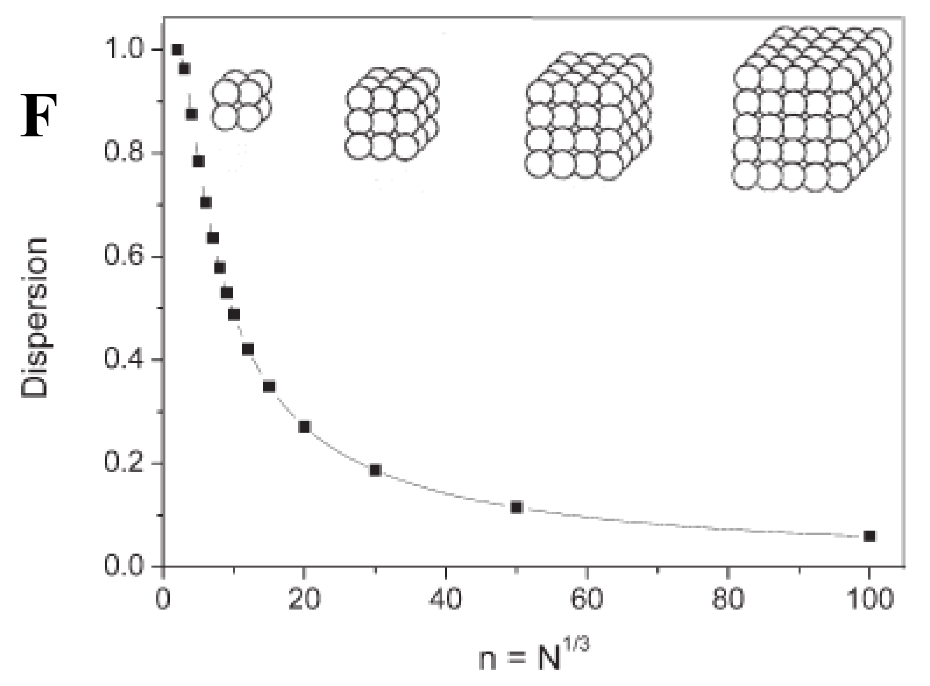
Dispersion F = the fraction of atoms at the surface

F is proportional to surface area divided by volume

N = total number of atoms

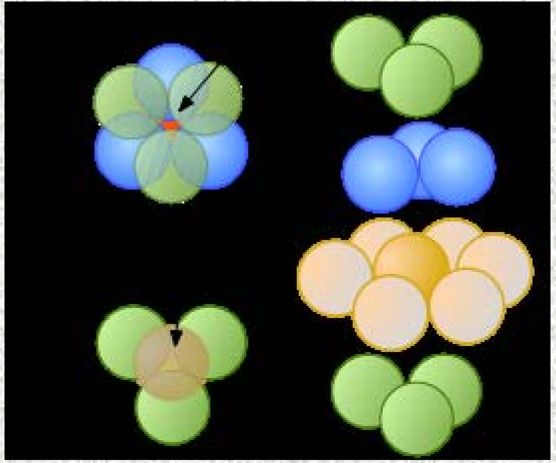
$V \sim r^3 \sim N$

$$F \approx \frac{r^2}{r^3} \approx \frac{1}{r} \approx \frac{1}{\sqrt[3]{N}}$$



n = number of atoms at the cube edge

Surface Effects



Properties of grain boundaries

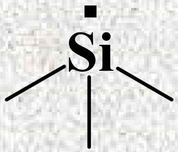
- **Lower coordination number of atoms**
- **Reduced atomic density (by 10 – 30 %)**
- **Broad spectrum of interatomic distances**

Experimental evidence

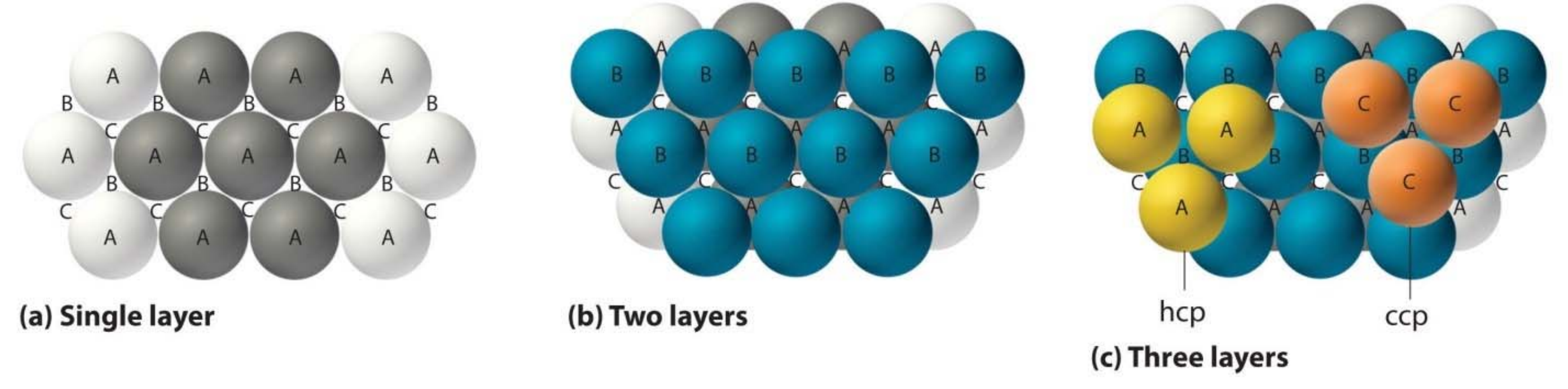
- **HREM**
- **EXAFS, reduced number of nearest and next-nearest neighbors**
- **Raman spectroscopy**
- **Mössbauer spectroscopy, quadrupole splitting distribution broadened**
- **Diffusivity enhanced by up to 20 orders of magnitude !!**
- **Solute solubility in the boundary region**

Ag (fcc) and Fe (bcc) immiscible in (s) or (l), but do form solid solution as nanocrystalline alloy

- **EPR, nano-Si gives a sharp signal**



Close Packed Atoms



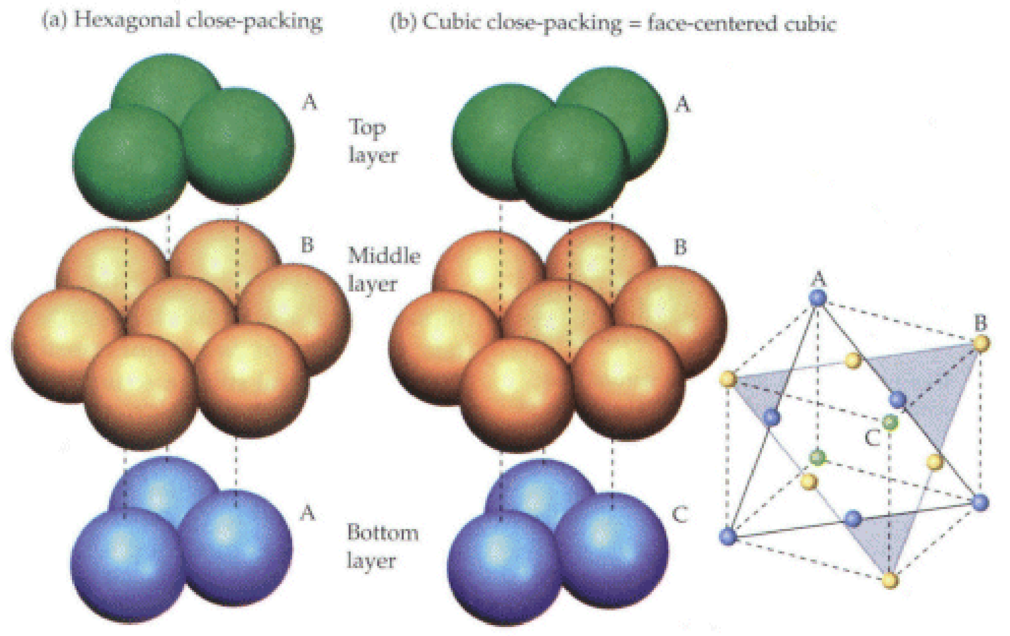
(a) Single layer

(b) Two layers

hcp

ccp

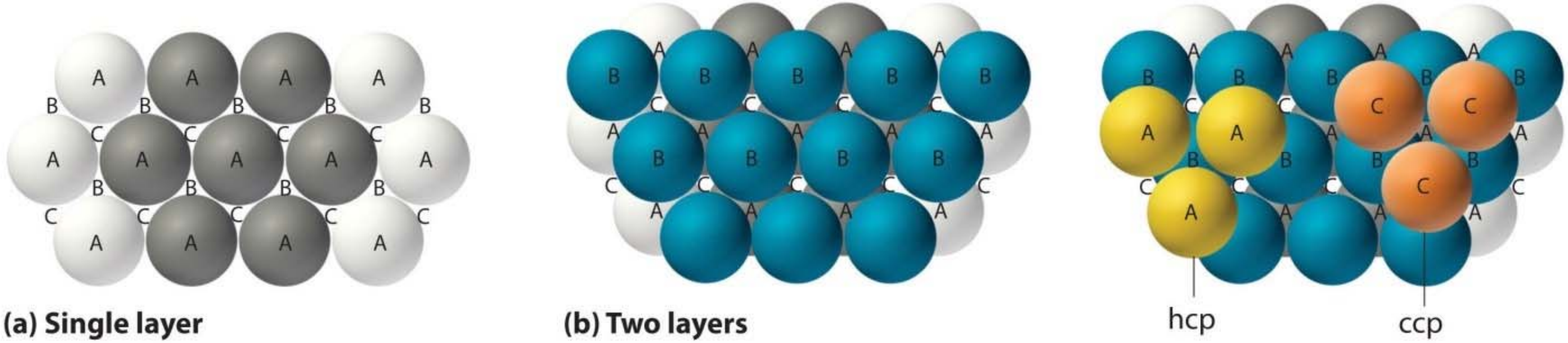
(c) Three layers



(a) Hexagonal close-packing

(b) Cubic close-packing = face-centered cubic

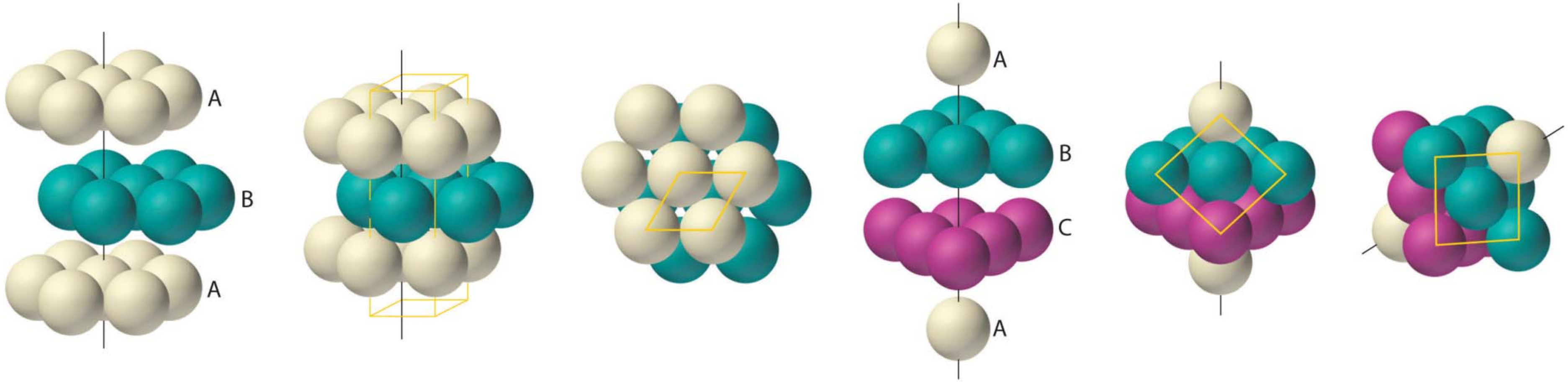
Close Packed Atoms



(a) Single layer

(b) Two layers

(c) Three layers



(a) Hexagonal close-packed (hcp)

(b) Cubic close-packed (ccp)

Surface Effects

Atoms at surfaces

- fewer neighbors than atoms in the bulk = lower coordination number
- stronger and shorter bonds
- unsatisfied bonds - dangling bonds
- surface atoms are less stabilized than bulk atoms

The smaller a particle the larger the fraction of atoms at the surface, and the higher the average binding energy per atom

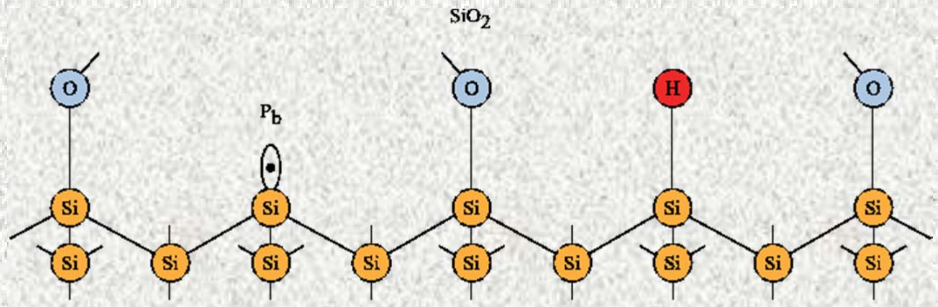
The melting and other phase transition temperatures scale with surface-to-volume ratio and with the inverse size

Example: the melting point depression in nanocrystals

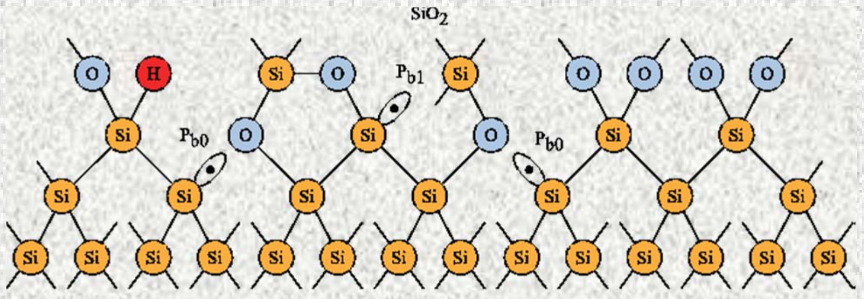
2.5 nm Au particles 930 K **bulk Au 1336 K**

Dangling Bonds

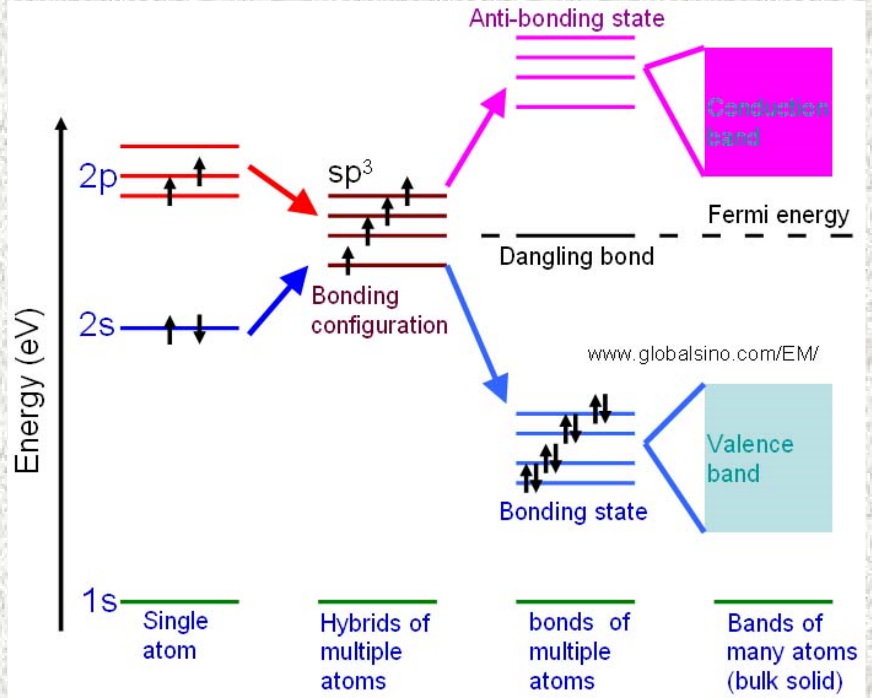
- Empty orbital
- 1-e orbital
- 2-e orbital



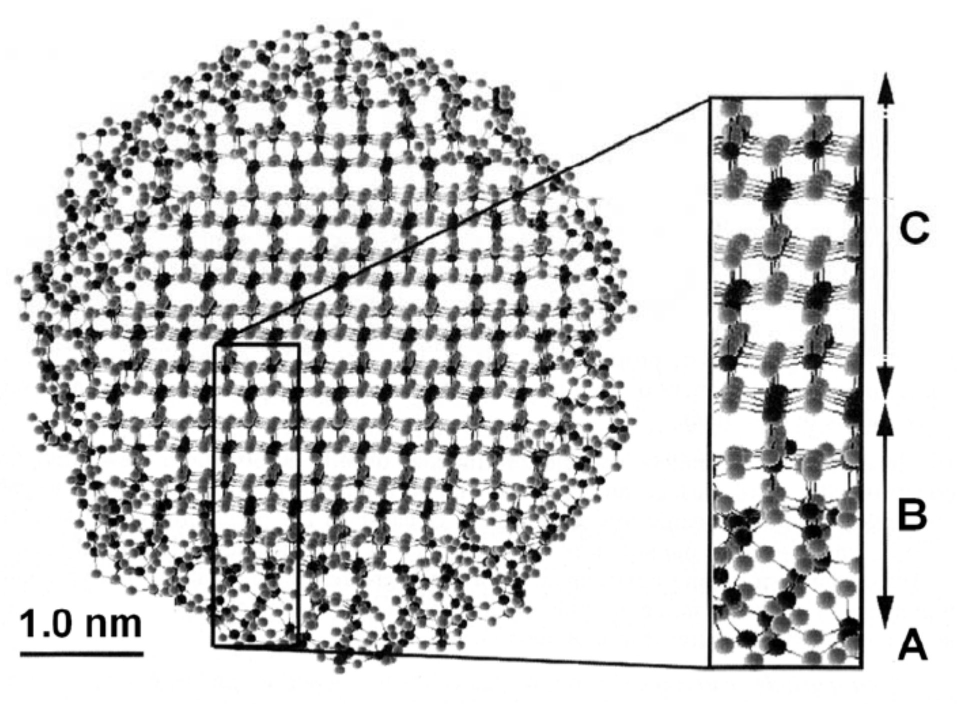
Silicon (111)



Silicon (100)



Surface Effects



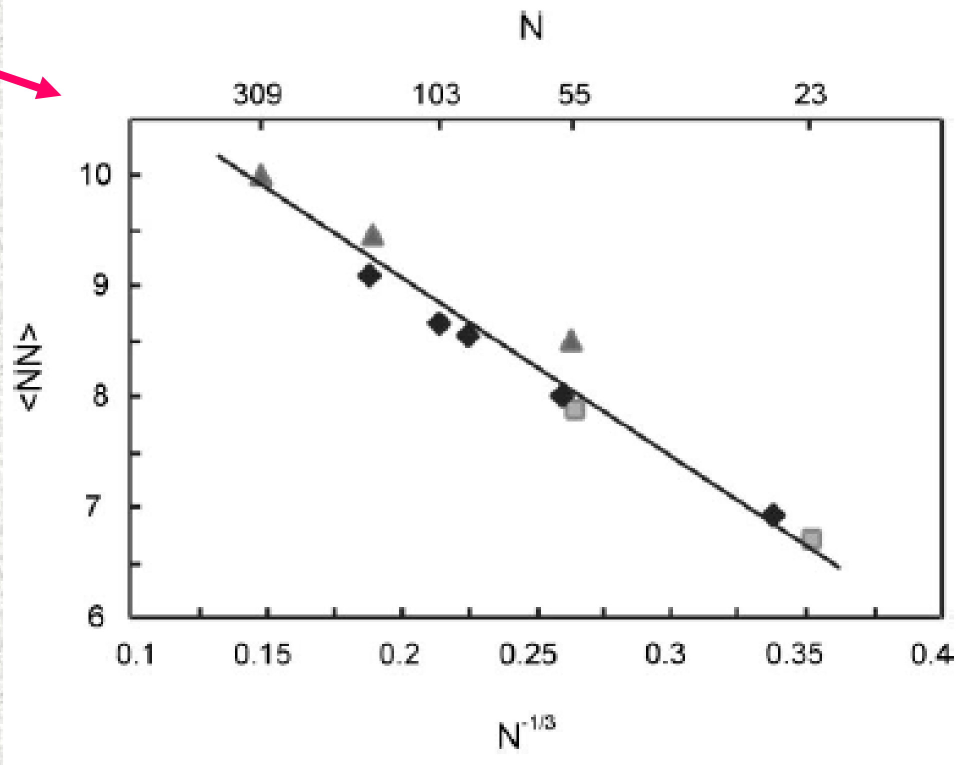
A = Atoms at surfaces (one layer) – fewer neighbors, lower coordination, unsatisfied (dangling) bonds
B = Atoms close to surface (several layers) – deformation of coordination sphere, distorted bond distances and angles
C = Bulk atoms, regular ordering – not present in particles below 2 nm

Graphite shells

What is the bulk value?

Surface Effects

Mean coordination number

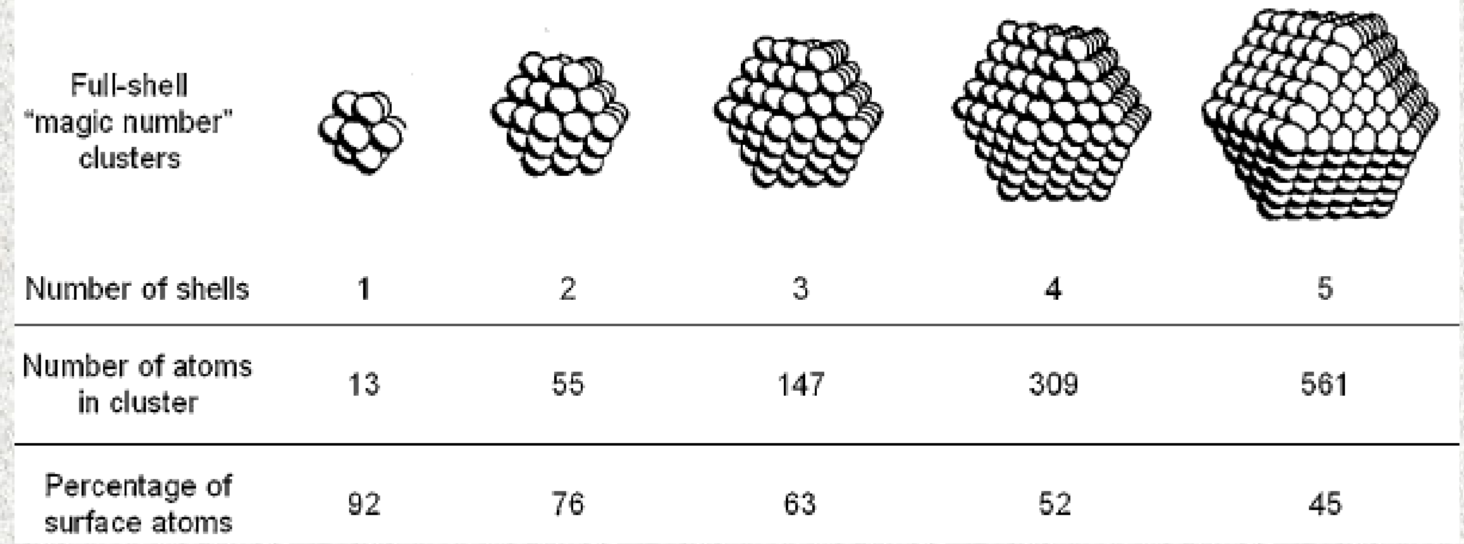


Calculated mean coordination number <NN> as a function of inverse radius, represented by $N^{-1/3}$ for Mg clusters (triangles = icosahedra, squares = decahedra, diamonds = hcp

Surface Effects

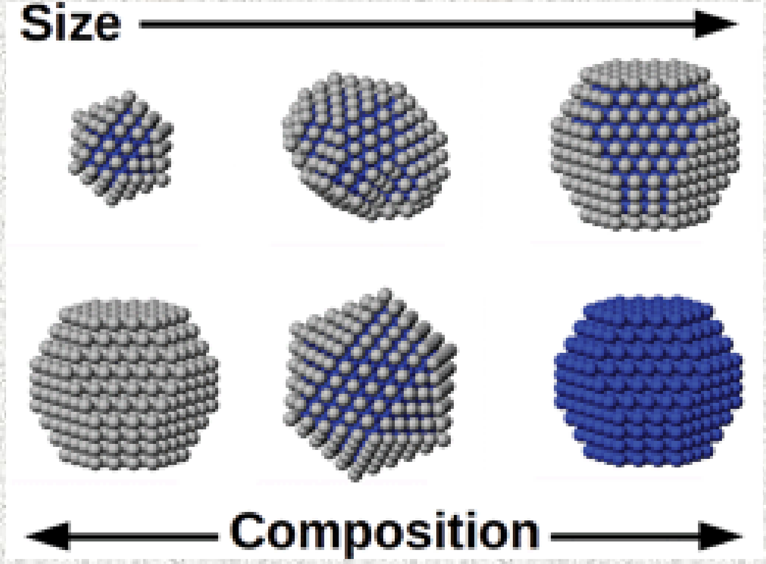
Atom binding (vaporization) energies lower in nanoparticles, fewer neighbors to keep atoms from escaping

Plasticity of nanocrystalline ceramics

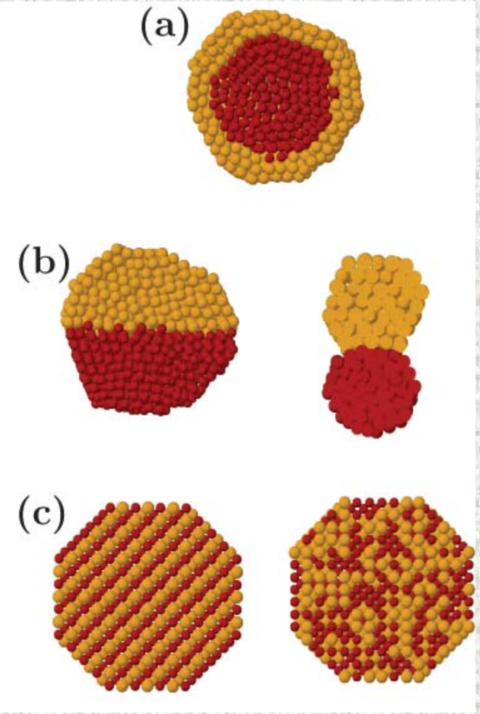


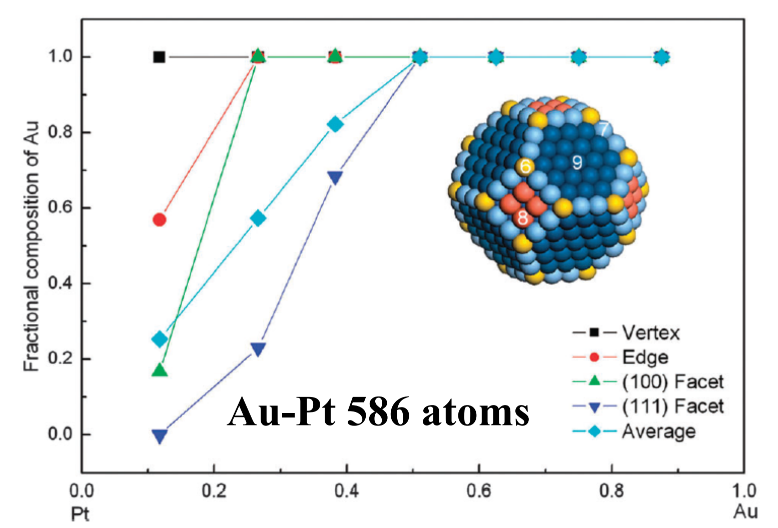
Full-shell “magic number” clusters					
Number of shells	1	2	3	4	5
Number of atoms in cluster	13	55	147	309	561
Percentage of surface atoms	92	76	63	52	45

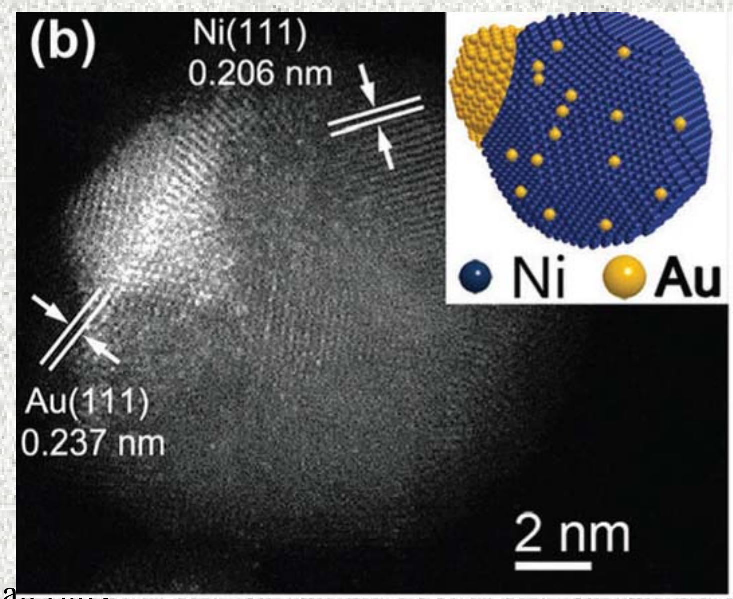
Surface Effects in Alloys



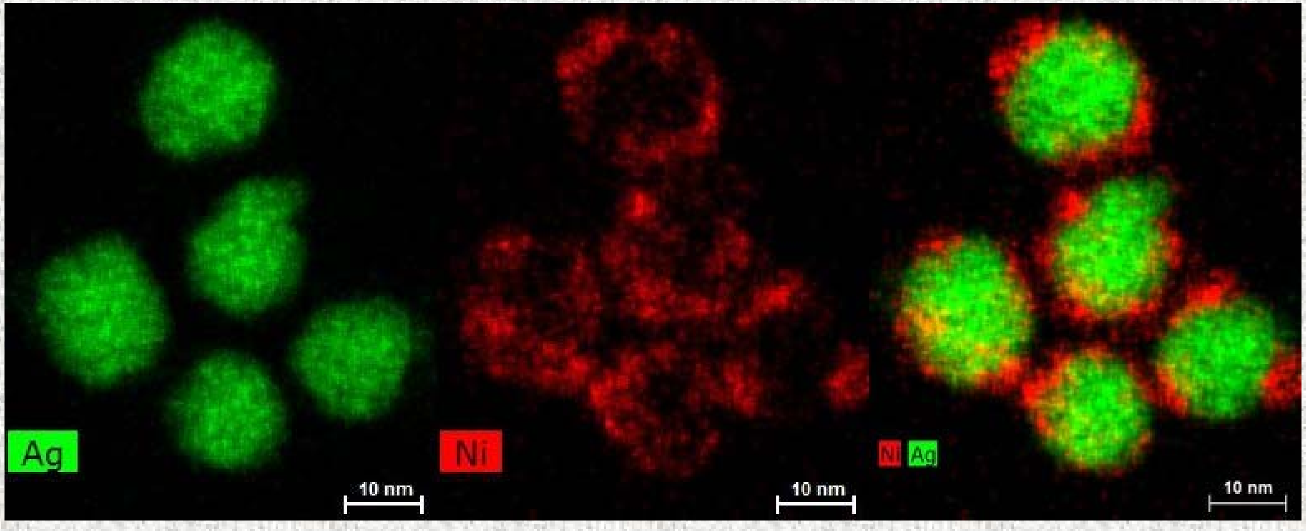
Alloys:
Core-shell
Janus
Random mixture



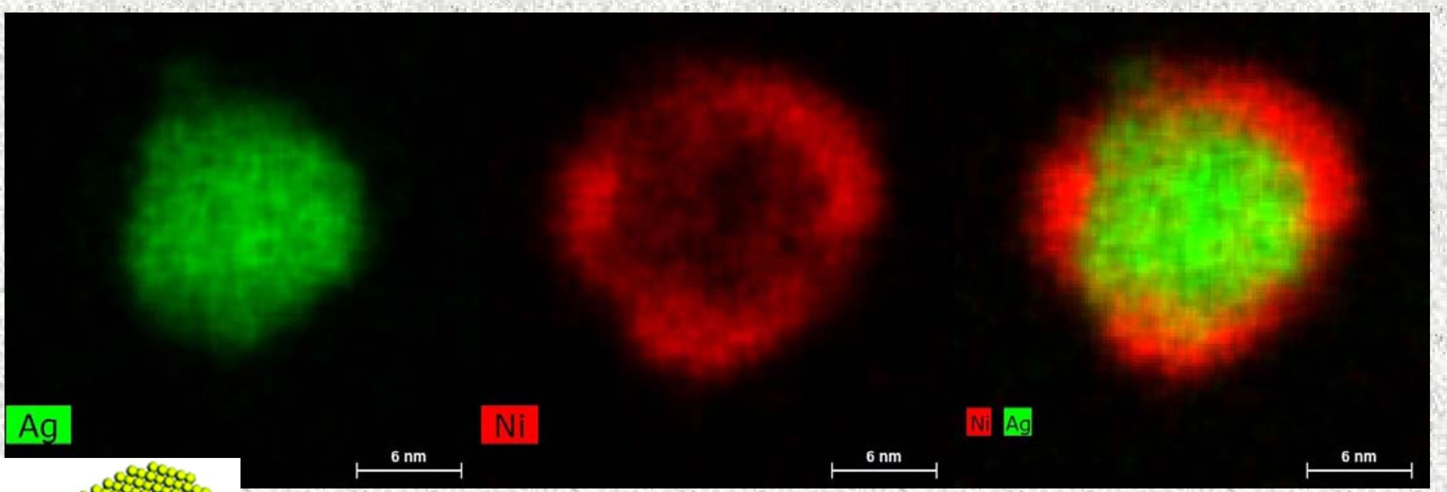




Transmission Electron Microscopy Energy Dispersive X-ray Spectroscopy

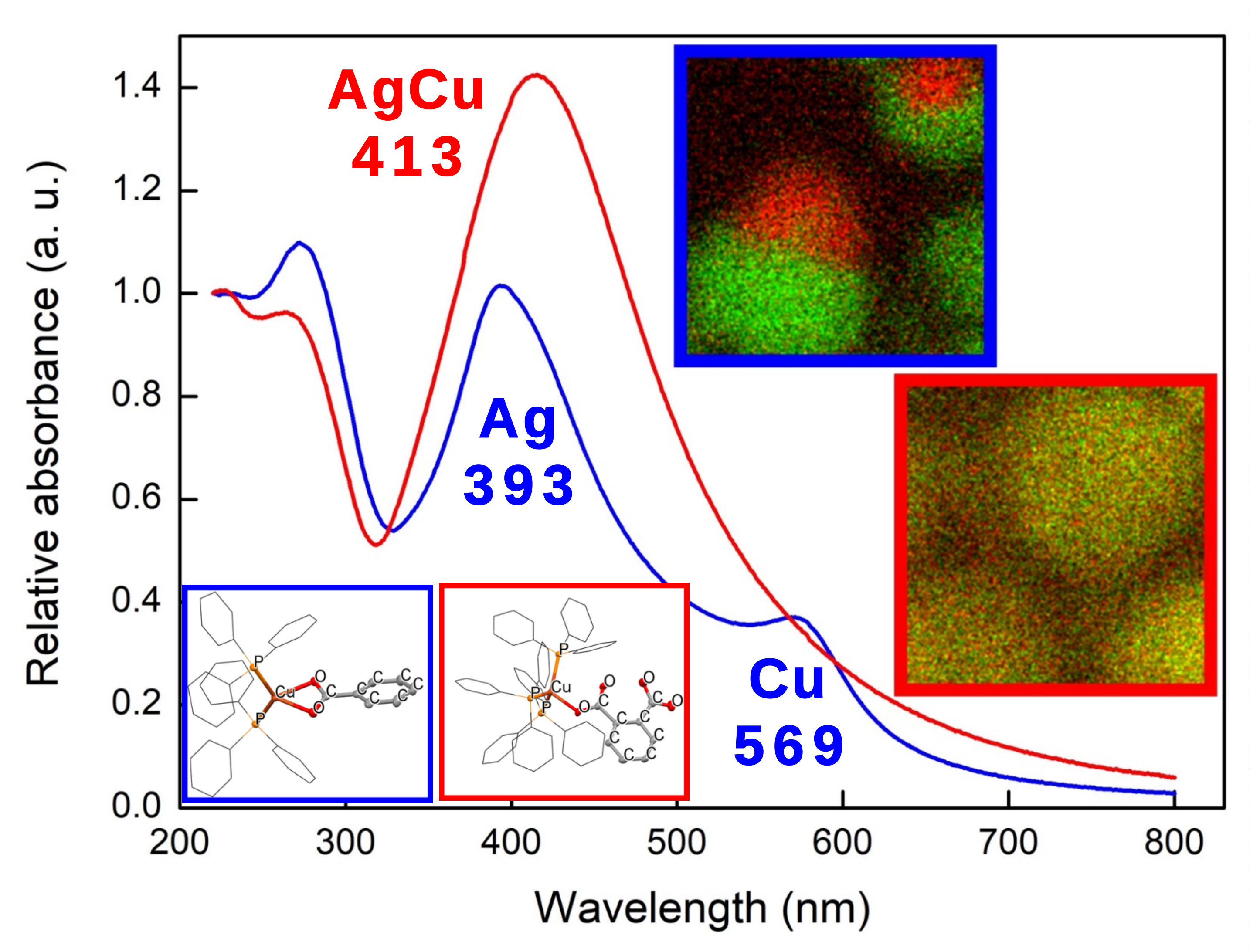


ICP-OES: Ag 68.8 mol%, EDS: Ag 84.2 mol%

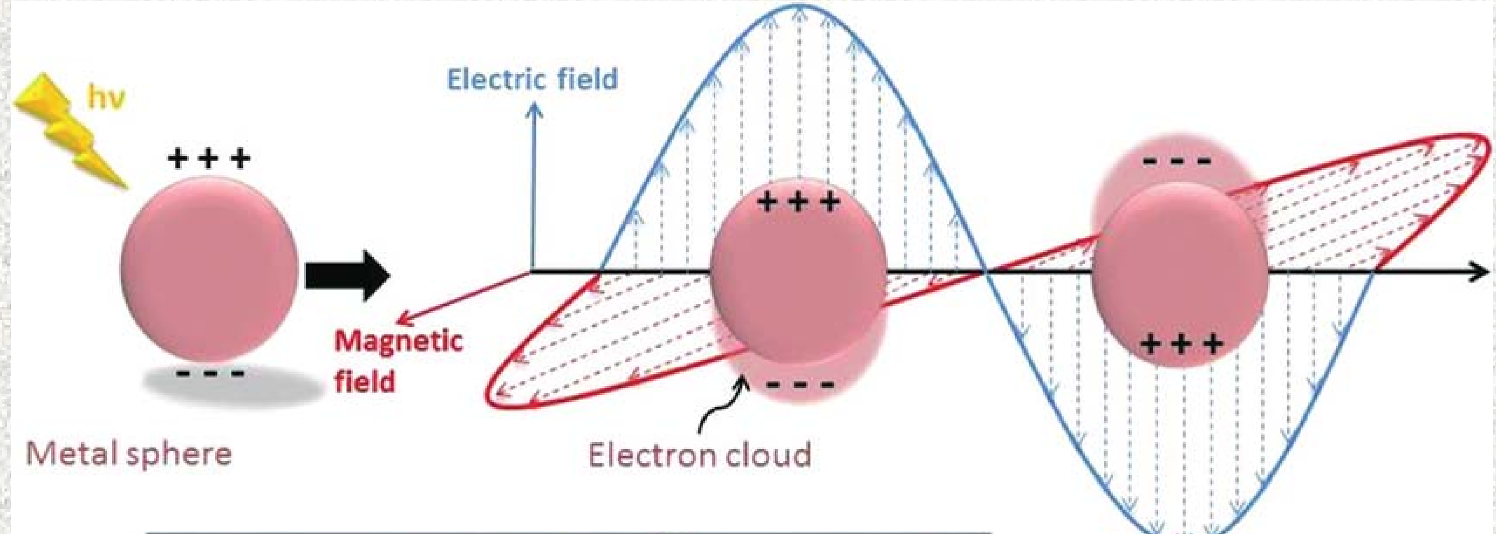


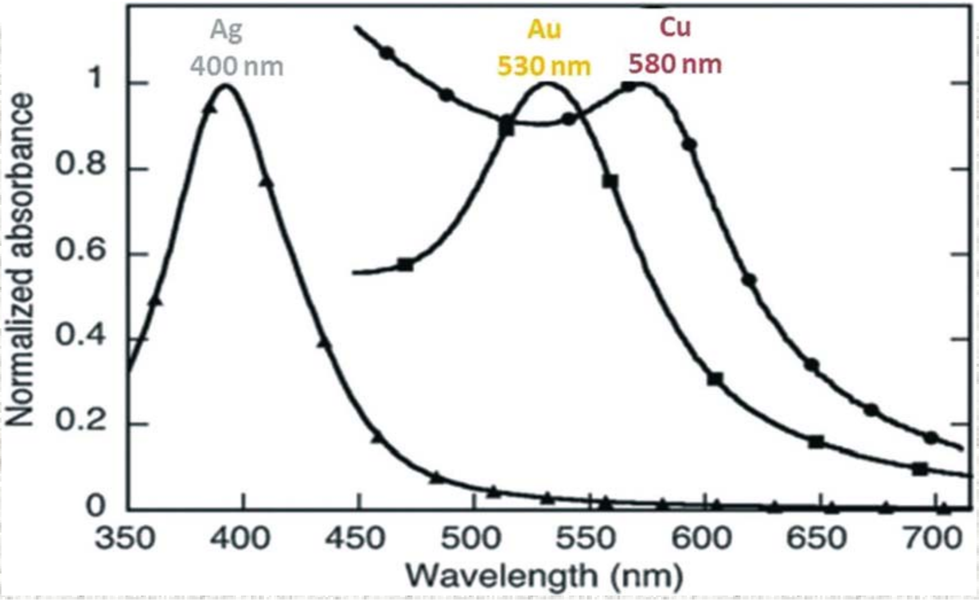
ICP-OES: Ag 50.3 mol%, EDS: Ag 62.5 mol%

Effects of Synthesis



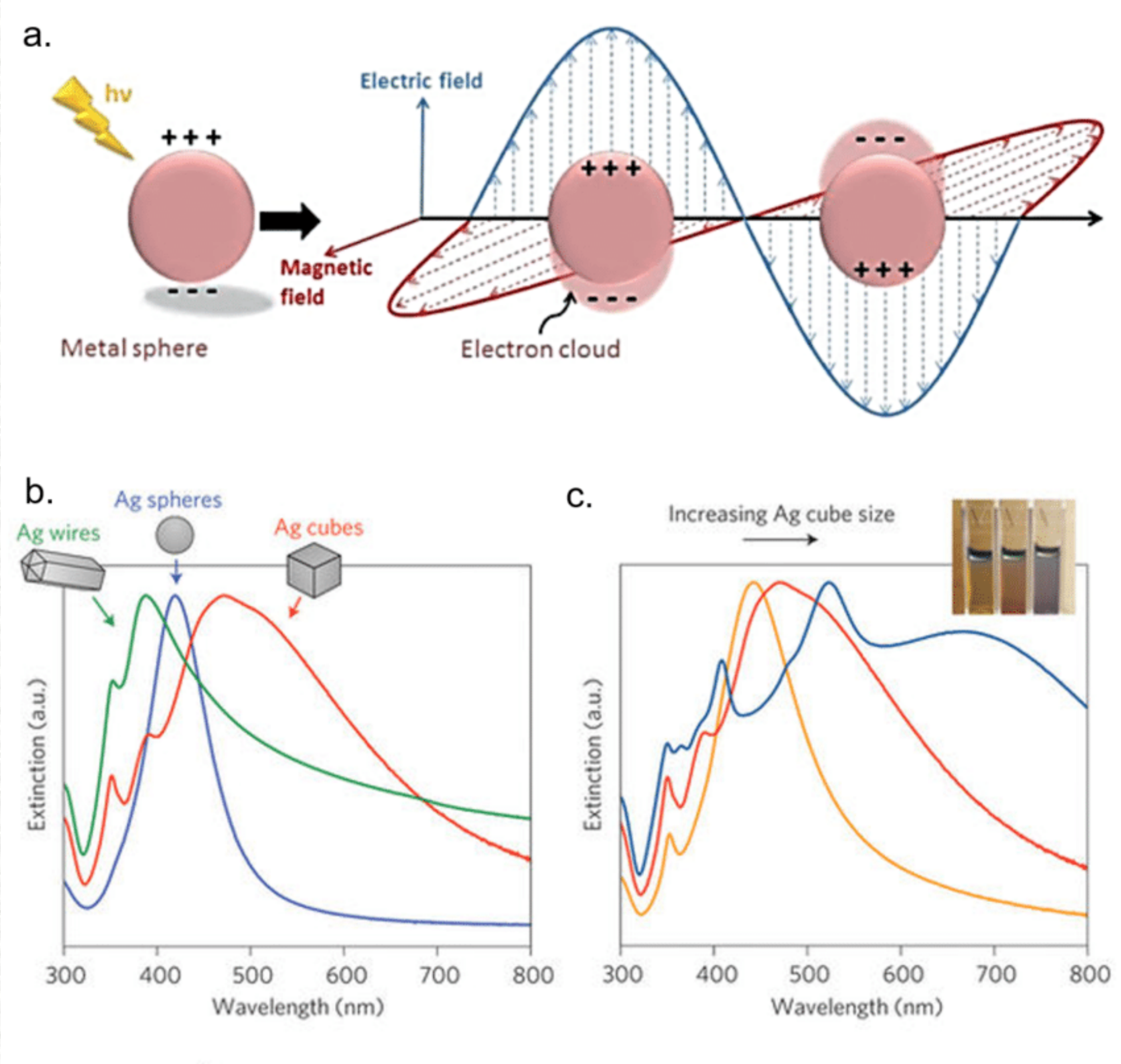
Localized Surface Plasmon Resonance (LSPR)





Faraday's colloidal solution of gold

Localized Surface Plasmon Resonance (LSPR)

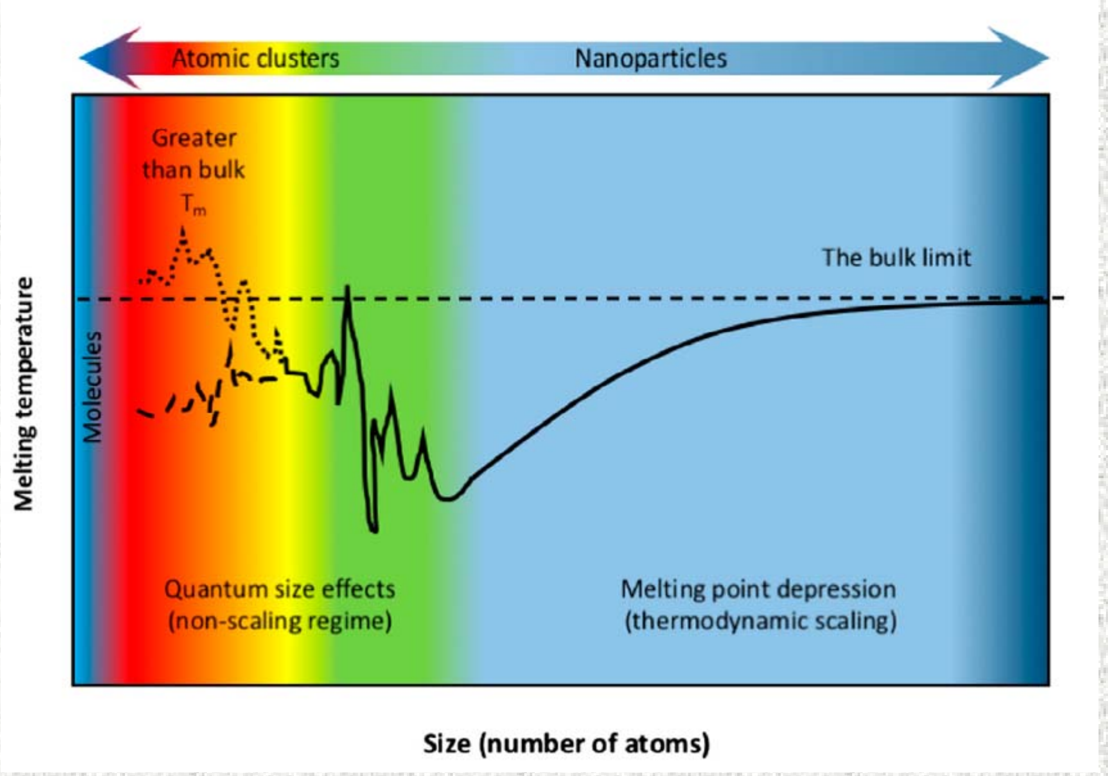


Melting Point Depression

Surface atoms in solids are bound by a lower number of shorter and stronger bonds
Nanoparticles with a large fraction of surface atoms

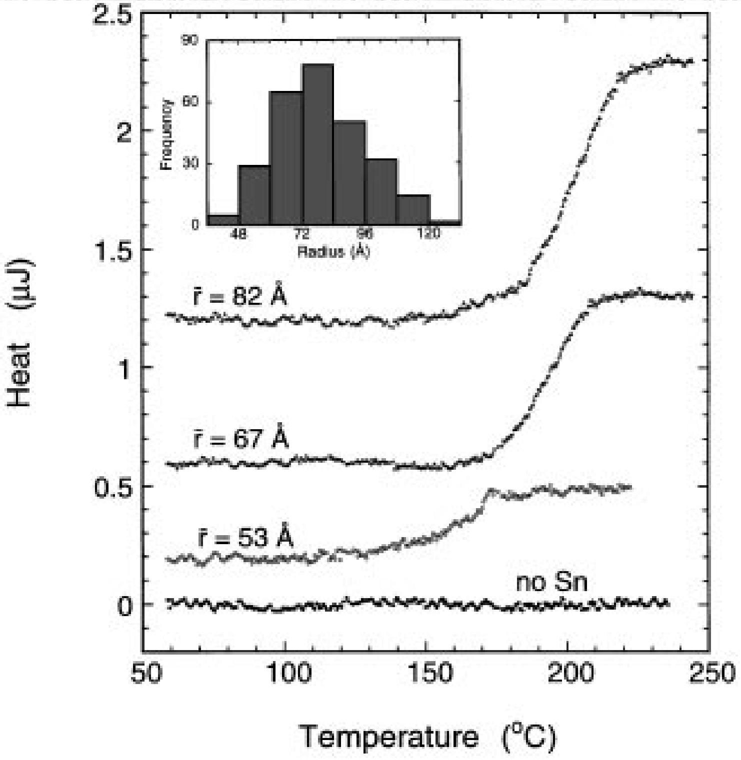
- **Lowering of average cohesion energy**
- **Increasing average amplitude of thermal**
- **Increasing internal pressure**

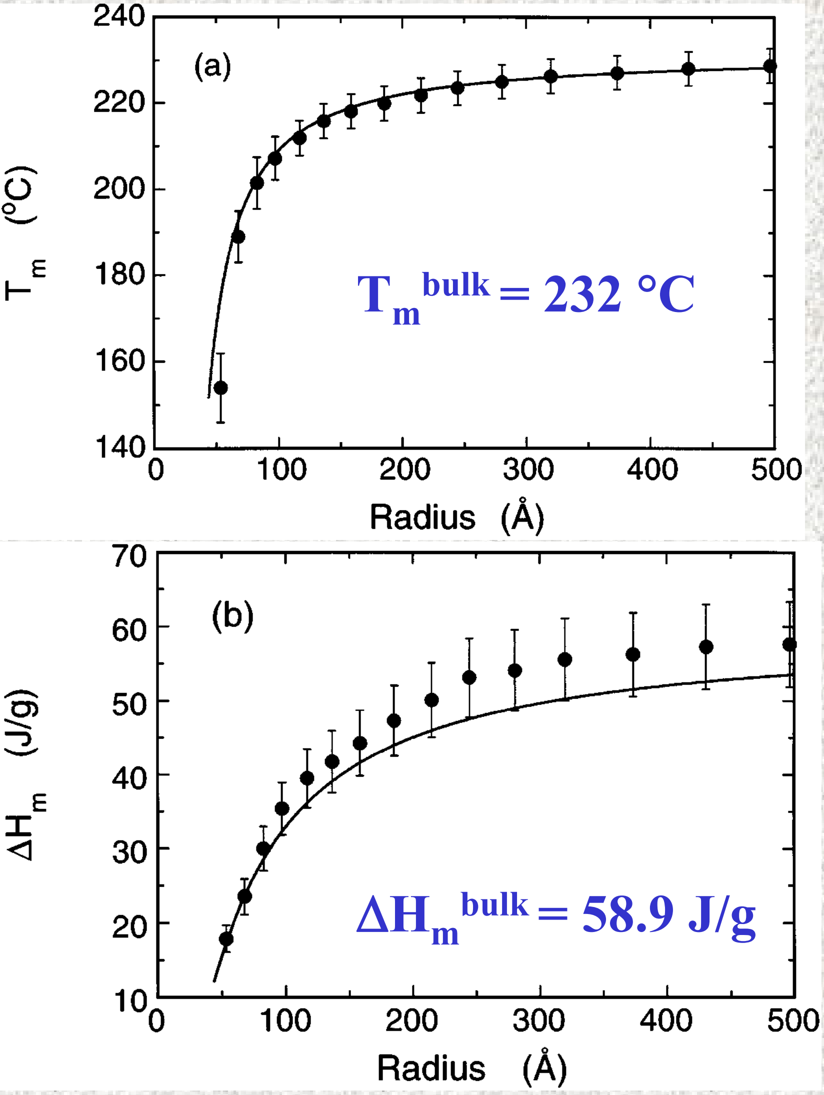
Result = depression of melting point of nanoparticles.



Melting Point and Enthalpy Depression

Nanocalorimetry of Sn nanoparticles



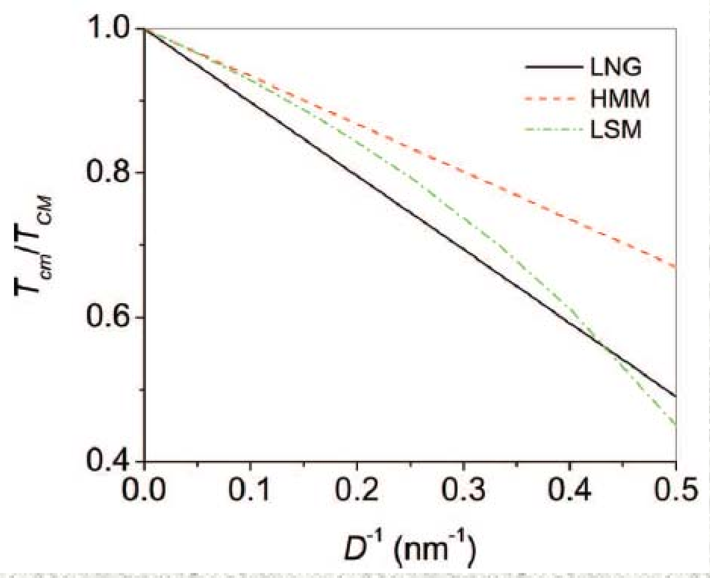


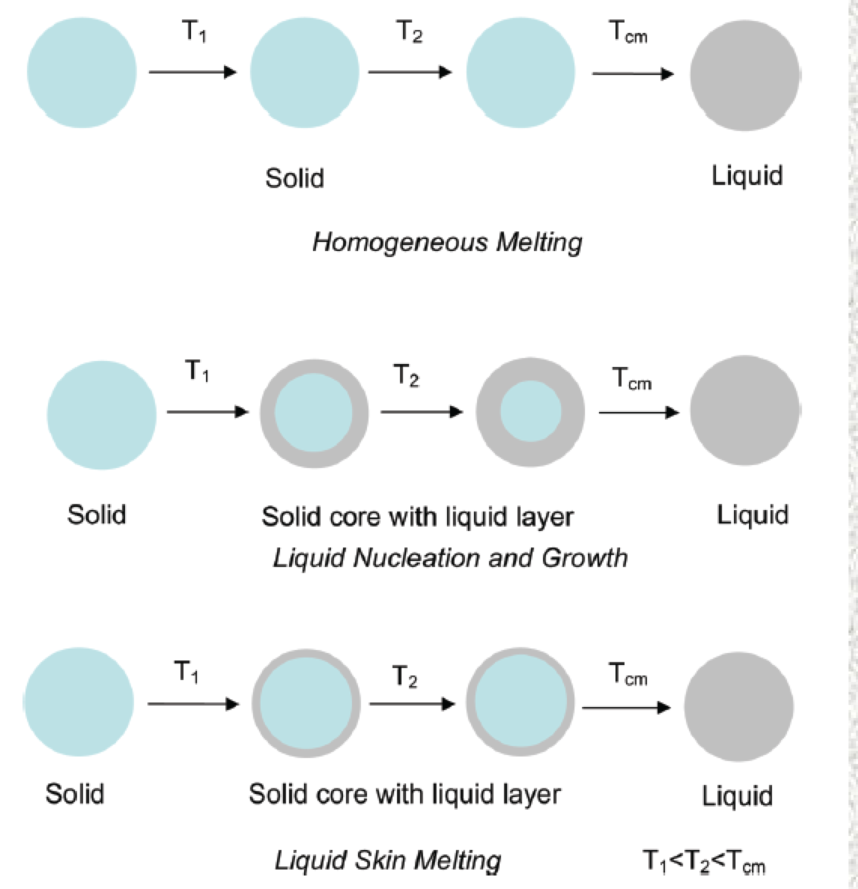
$T_m^{bulk} = 232$ °C

$\Delta H_m^{bulk} = 58.9$ J/g

Melting Point and Enthalpy Depression

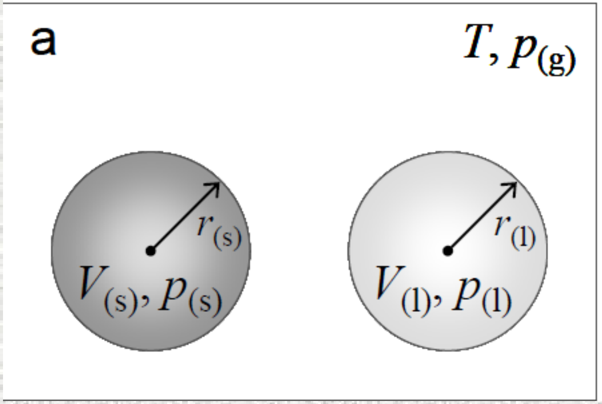
Nanocalorimetry of Sn nanoparticles





Melting Point Depression

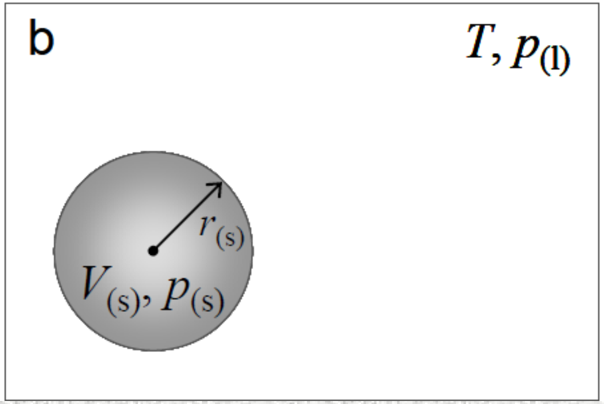
Homogeneous melting model



Triple point of coexisting solid and liquid nanoparticles of the same mass surrounded by vapor

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}} \left[\gamma_{(\mathrm{sg})} - \gamma_{(\mathrm{lg})} \left(\frac{\rho_{(\mathrm{s})}}{\rho_{(\mathrm{l})}} \right)^{2/3} \right]$$

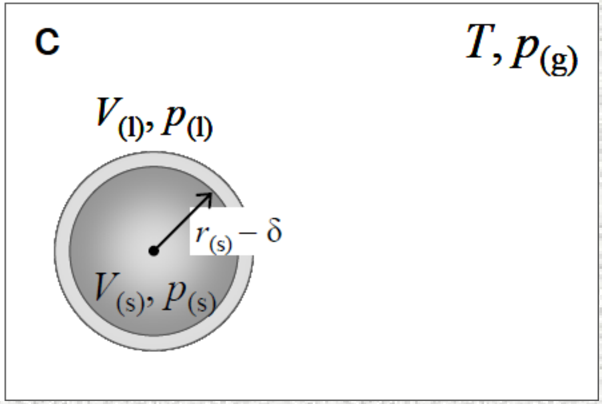
Continuous Liquid Meling



Melting particle is surrounded by liquid

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}} \gamma_{(\mathrm{sl})}$$

Liquid Skin Melting



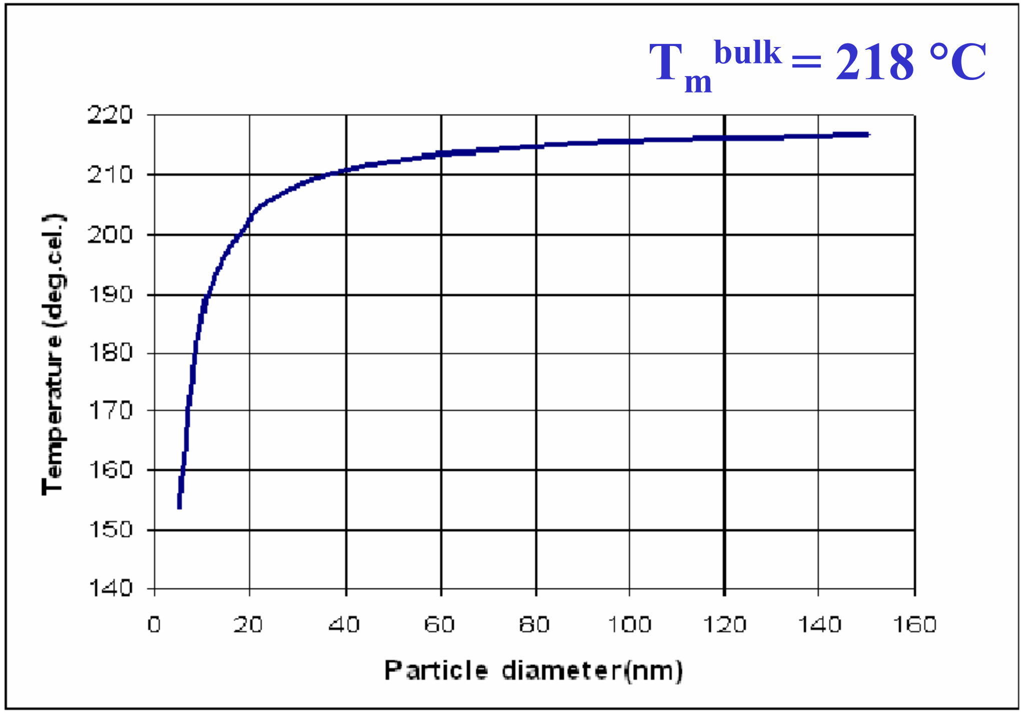
Thin melted layer of a constant thickness δ coexisting with solid core and vapor

$$\frac{T_r^{\mathrm{F}}}{T_\infty^{\mathrm{F}}} = 1 - \frac{2M}{\Delta H_{\mathrm{m}}^{\mathrm{F}} \rho_{(\mathrm{s})} r_{(\mathrm{s})}} \left[\frac{\gamma_{(\mathrm{sl})}}{1 - \delta / r_{(\mathrm{s})}} + \gamma_{(\mathrm{lg})} \left(1 - \frac{\rho_{(\mathrm{s})}}{\rho_{(\mathrm{l})}} \right) \right]$$

Melting Point Depression

$$T_m(r) = T_m(\text{bulk}) - \frac{2T_m(\text{bulk})M}{\Delta H_m^{bulk}\rho_s r}\left[\gamma_{sg} - \gamma_{lg}\left(\frac{\rho_s}{\rho_l}\right)^{\frac{2}{3}}\right]$$

Sn – 4wt%**Ag –** 0.5wt%**Cu** Nano alloy particles



T_m^{bulk} = 218 °C

Homogeneous melting model:

$T_m(r)$ = mp of the cluster with radius r

T_m^{bulk} = mp of the bulk material

γ_{sg} = the interfacial energies between the s and g phases

γ_{lg} = the interfacial energies between the l and g phases

ρ_s and ρ_l = solid and liquid phase densities

M = molar mass

ΔH_m^{bulk} = the bulk latent heat of melting

Gibbs–Thomson Equation

for $\rho_s \sim \rho_l$

$\gamma_{sl} = \gamma_{sg} - \gamma_{lg}$ **Continuous Liquid Meling**

$$\frac{T_m(r)-T_m^{bulk}}{T_m^{bulk}} = -\frac{2V_{mol}^{l}\gamma_{sl}}{\Delta H_m r}$$

$T_m(r)$ = mp of the nanoparticle with radius r

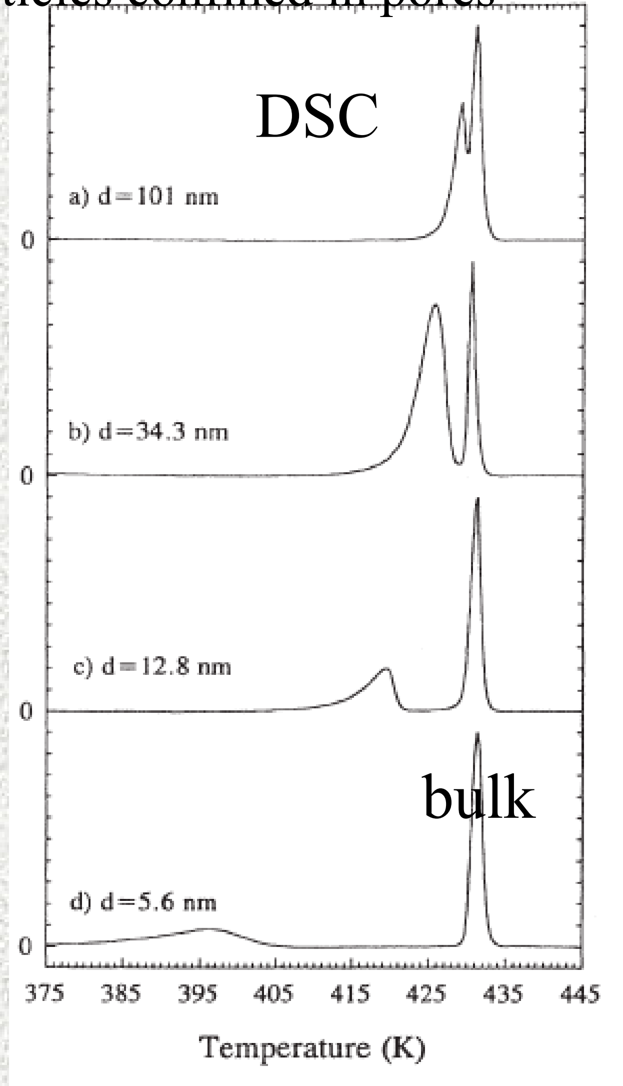
T_m^{bulk} = mp of the bulk material

V_{mol}^{l} = the molar volume of the liquid = M/ρ_s solid?

γ_{sl} = the interfacial tension between the s and l surface

ΔH_m^{bulk} = the bulk molar enthalpy of melting, endothermic

In nanoparticles confined in pores

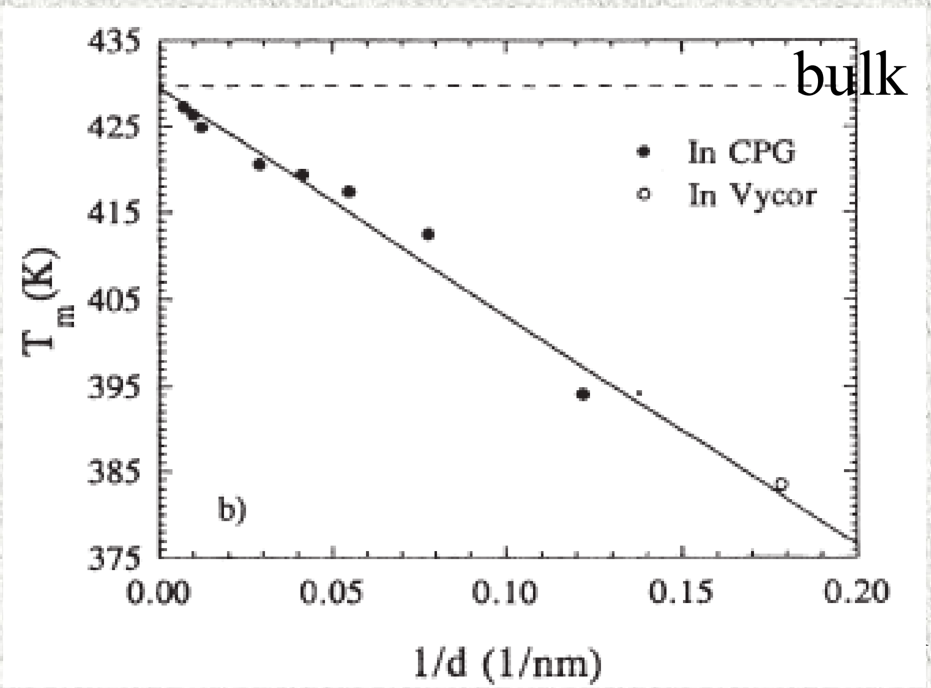


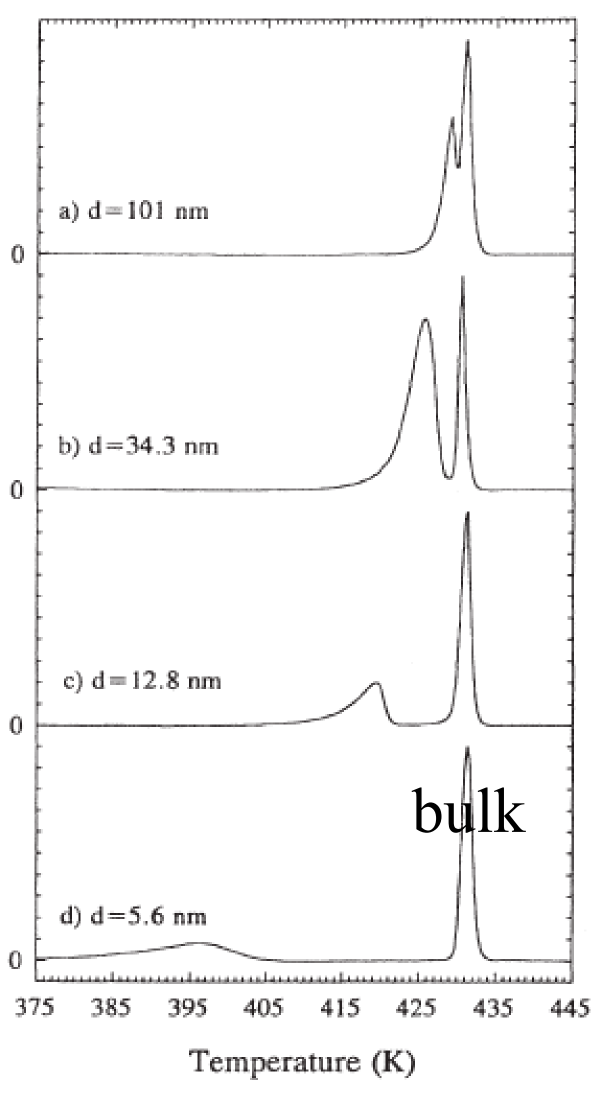
Phase Transitions

Phase transitions = collective phenomena

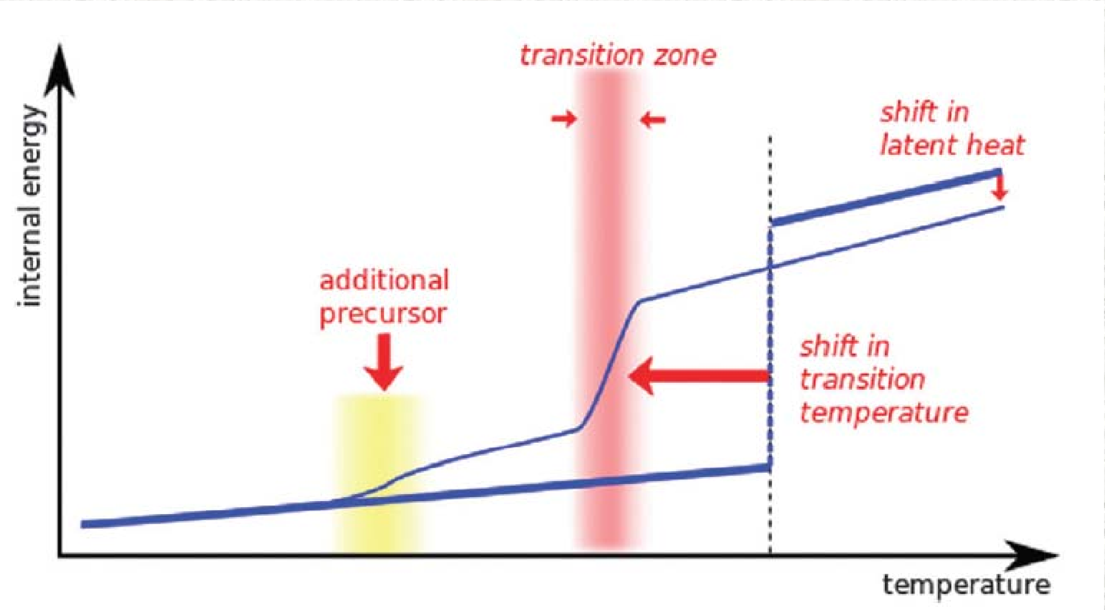
With a lower number of atoms in a cluster a phase transition is less well defined and broadened

Small clusters behave more like molecules than as bulk matter





First-Order Phase Transitions



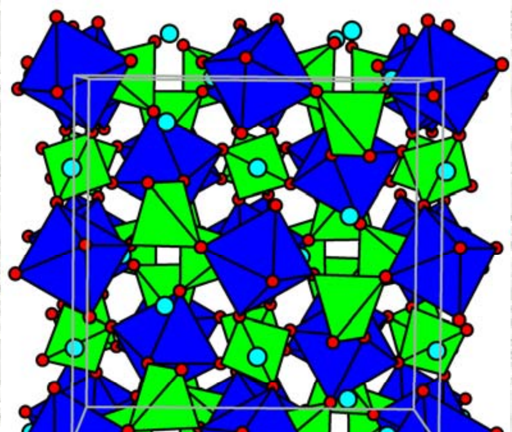
3 main consequences of a size decrease on caloric curve:

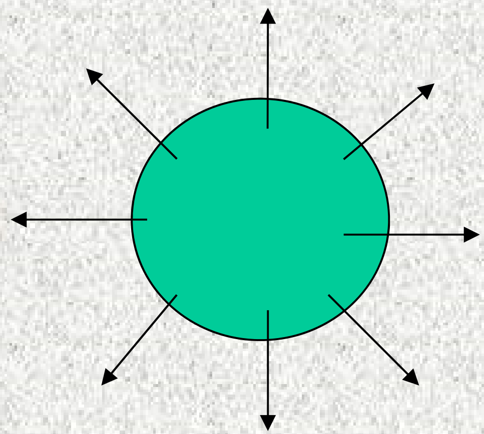
*** The transition is shifted, usually to a lower temperature (surface atoms are less coordinated and less bound than interior atoms)**
*** The transition temp. is no longer sharp but becomes smooth and takes place over a finite range (fluctuations in TD quantities)**
*** The latent heat is lower than in the bulk limit**

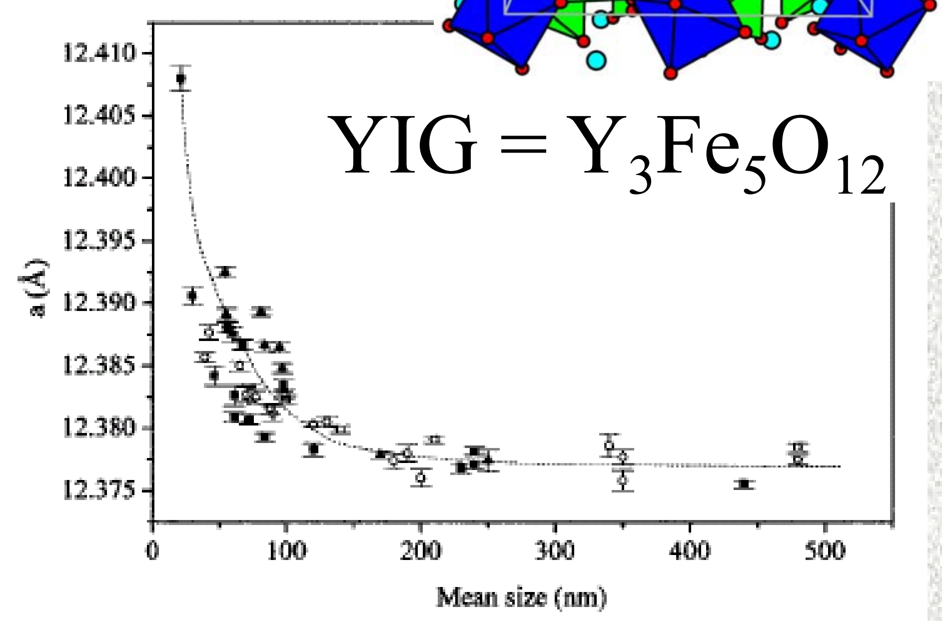
Surface Effects

Reduction in particle size

- Metal particles usually exhibit a lattice contraction
- Oxide particles exhibit a lattice expansion





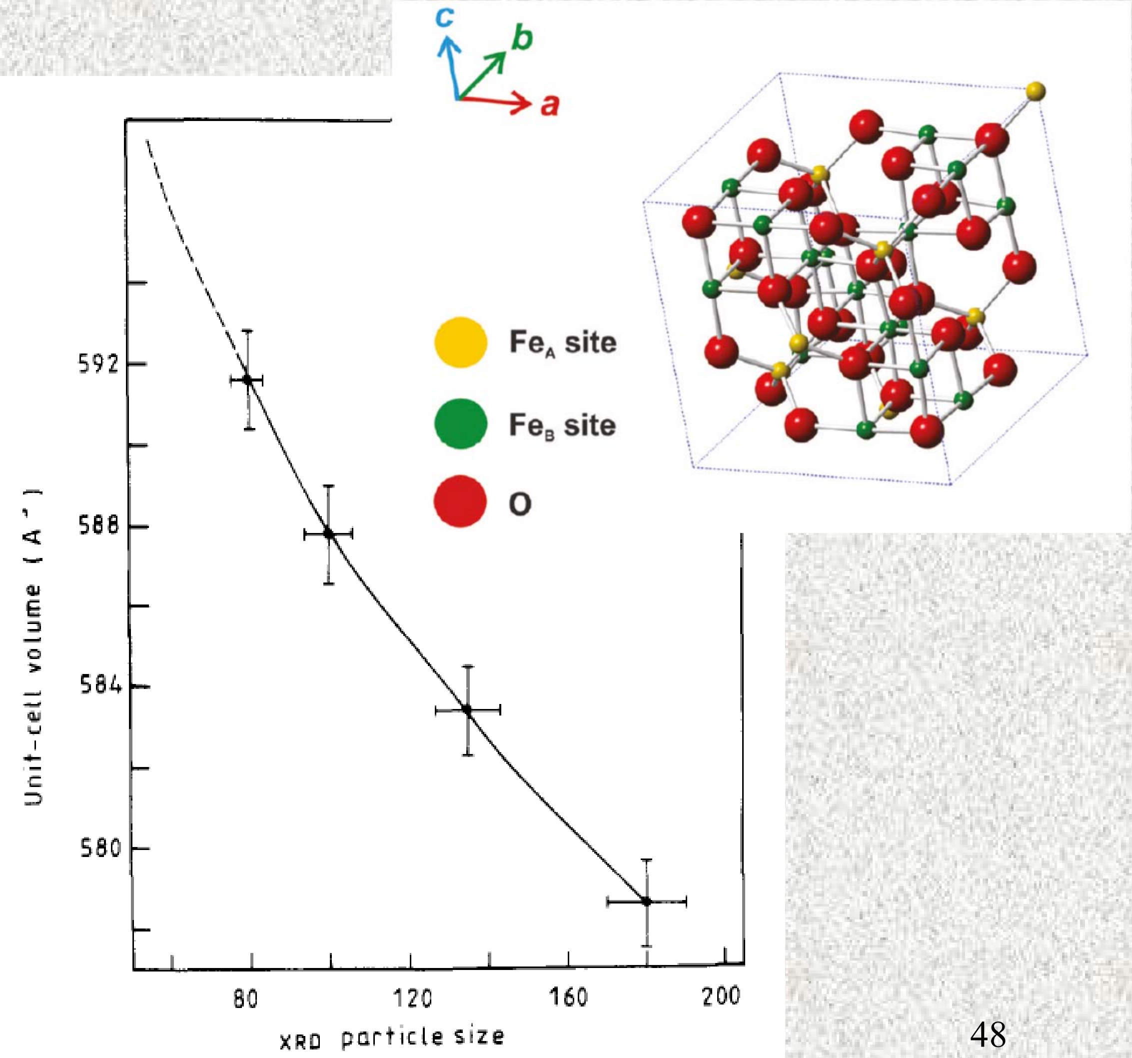


$\mathrm{YIG} = \mathrm{Y_3Fe_5O_{12}}$

Surface Effects

Correlation between the unit-cell volume (cubic) and the XRD particle size in γ-Fe_2O_3 nanoparticles

The smaller the particle size the larger the unit cell volume.



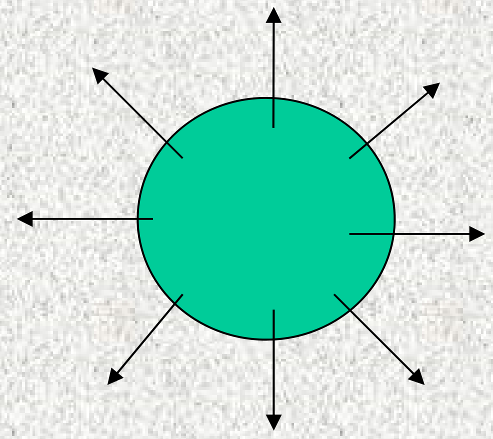
Surface Effects

The inter-ionic bonding in nanoparticles has a directional character

Ions in the outermost layer of unit cells possess unpaired electronic orbitals

Associated electric dipole moments, aligned roughly parallel to each other point outwards from the surface

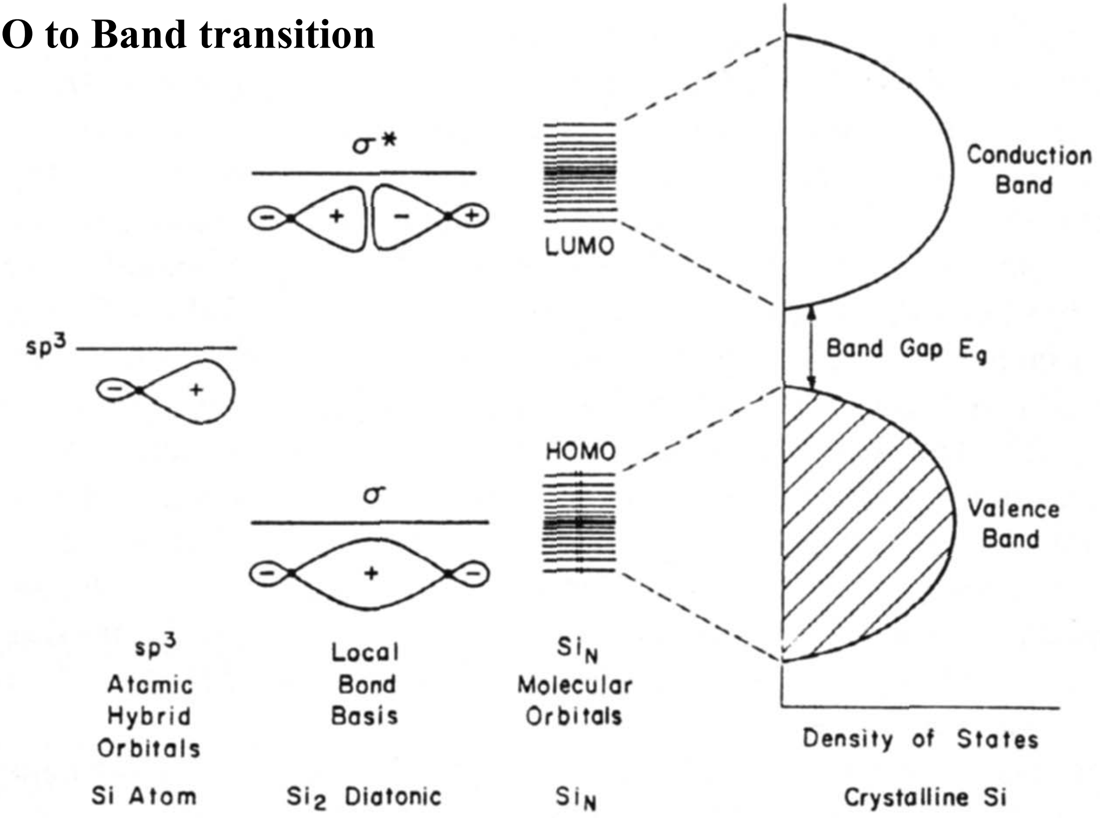
The repulsive dipolar interactions increase in smaller particles reduced by allowing unit cell volume to increase



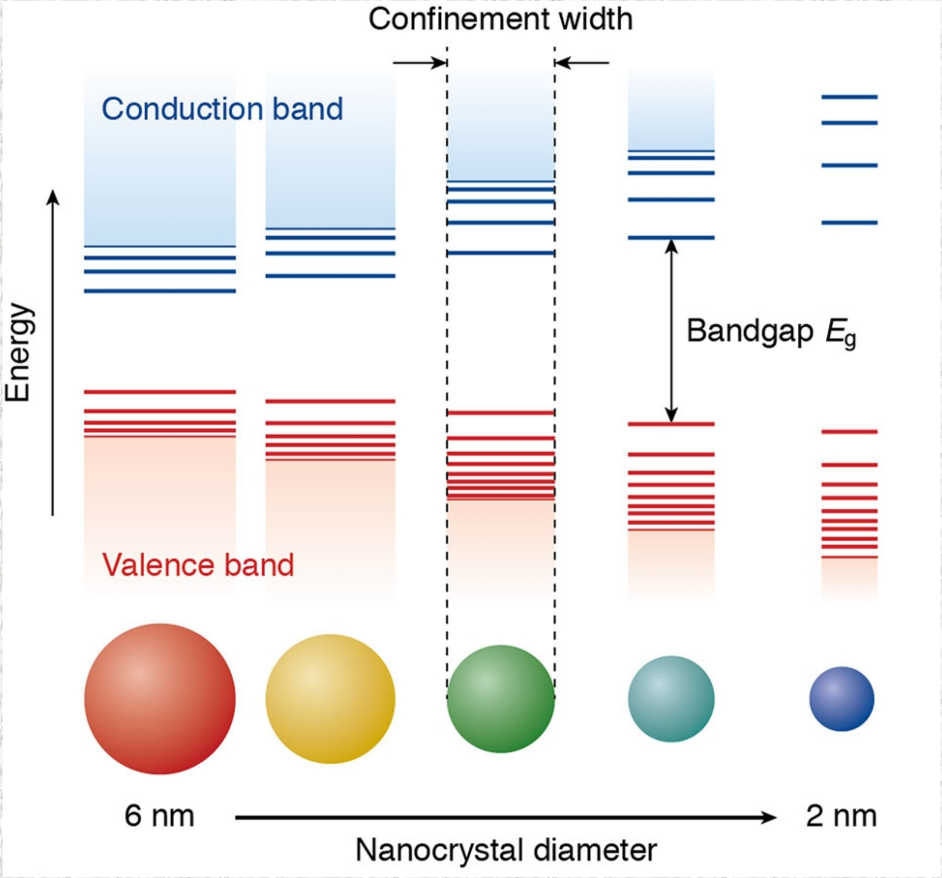
Quantum Confinement Effects

Physical and chemical properties depend on the size !!

ⓘ Finite-size effects
MO to Band transition



Quantum Size Effects

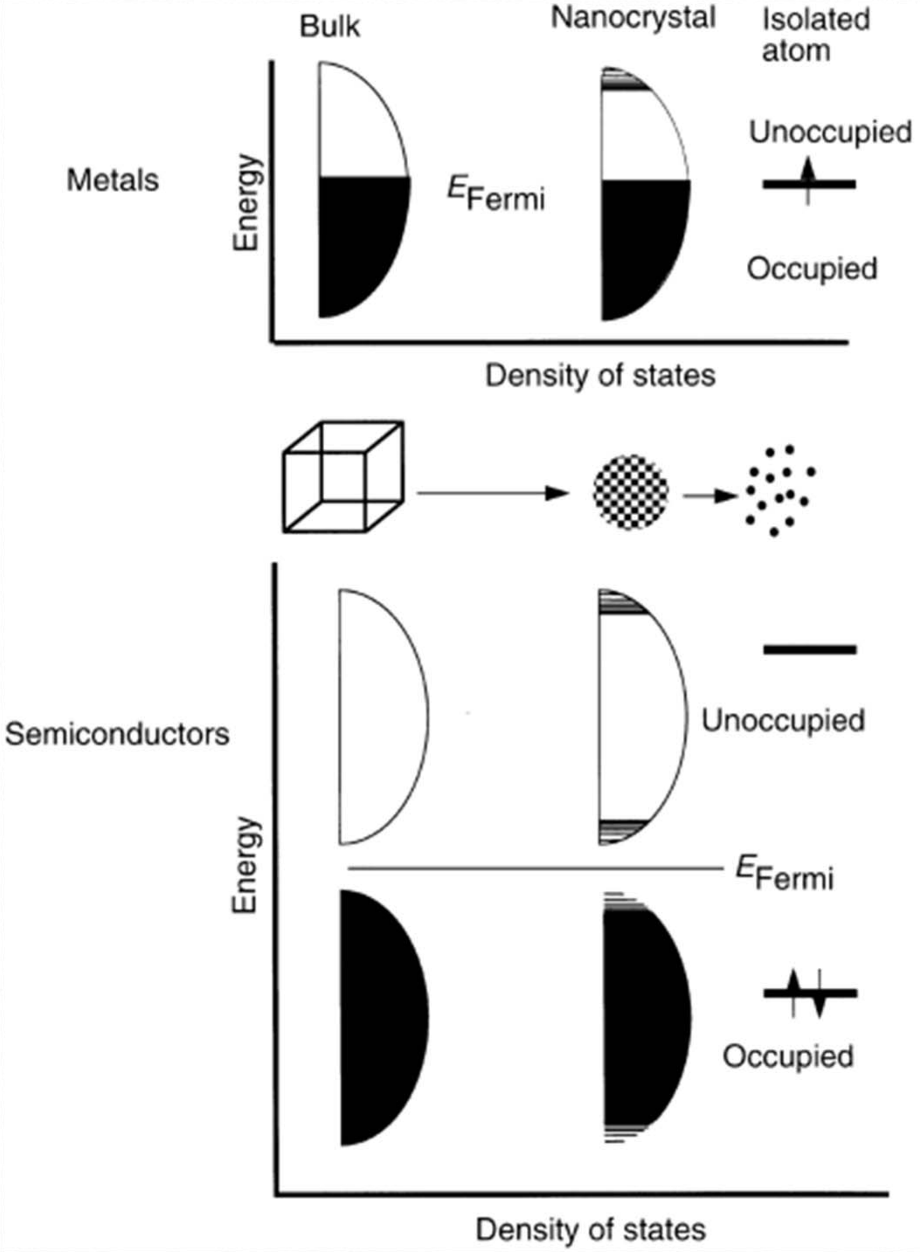


Band gap dependency on the nanoparticle size

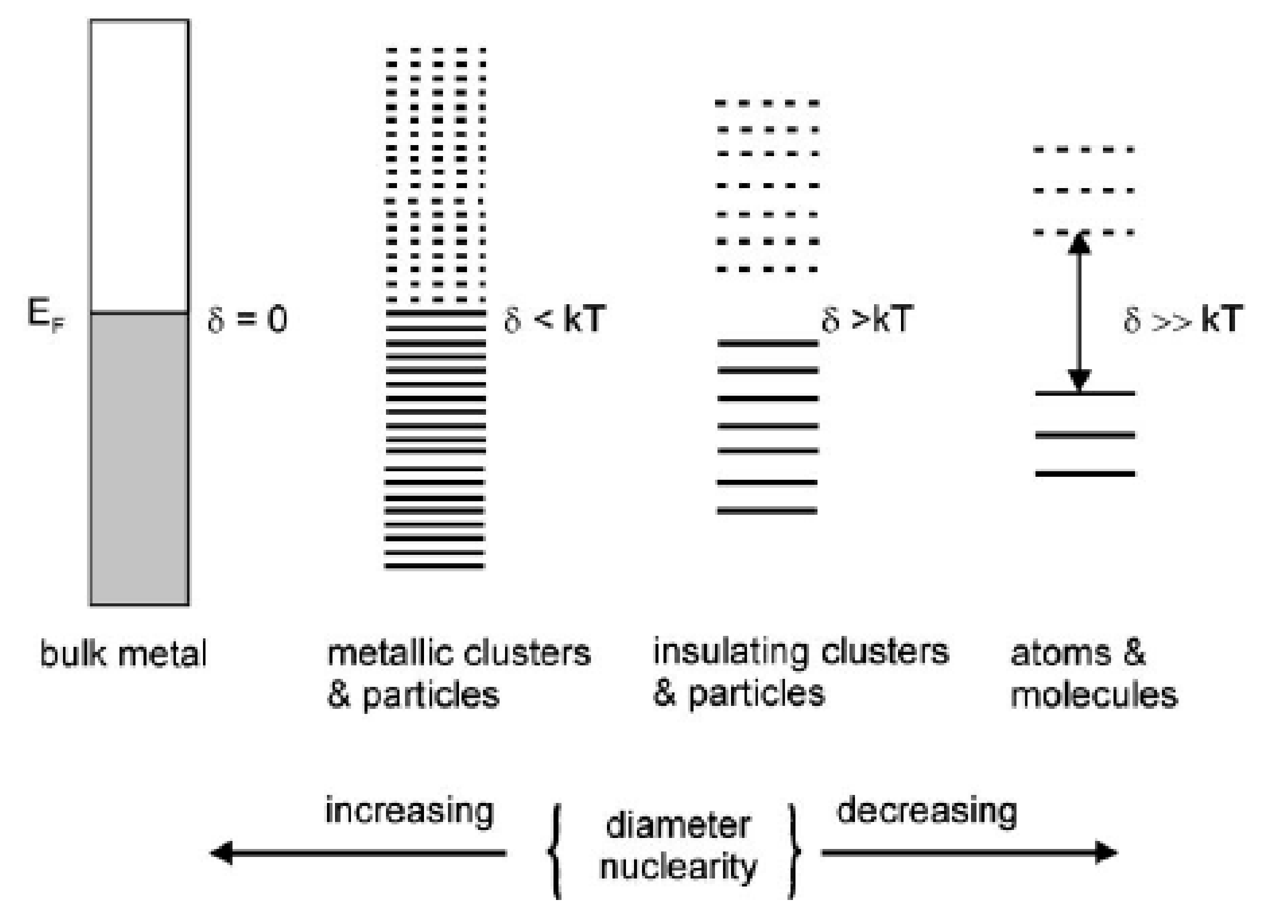
Quantum Size Effects

Metals

Semiconductors

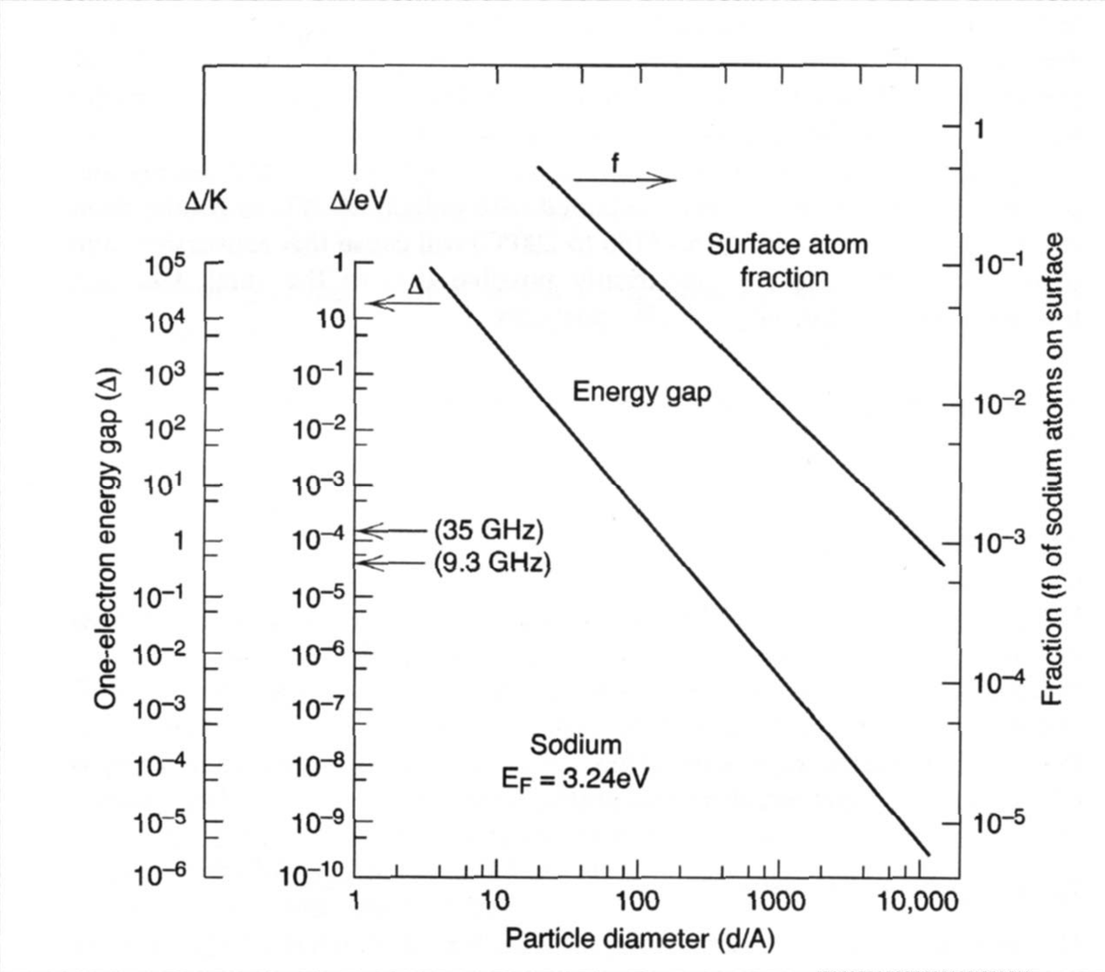


Metal-to-Insulator Transition



Metal-to-Insulator Transition

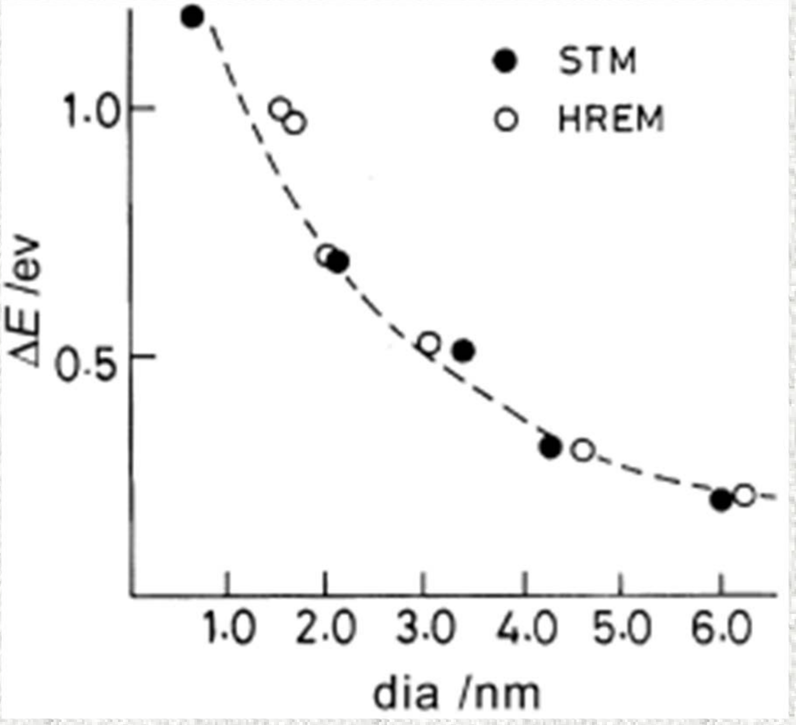
Band gap increases with decreasing size



Metallic behavior
Single atom cannot behave as a metal
nonmetal to metal transition
100-1000 atoms

Magnetic behavior
Single domain particles
large coercive field

Metal-to-Insulator Transition



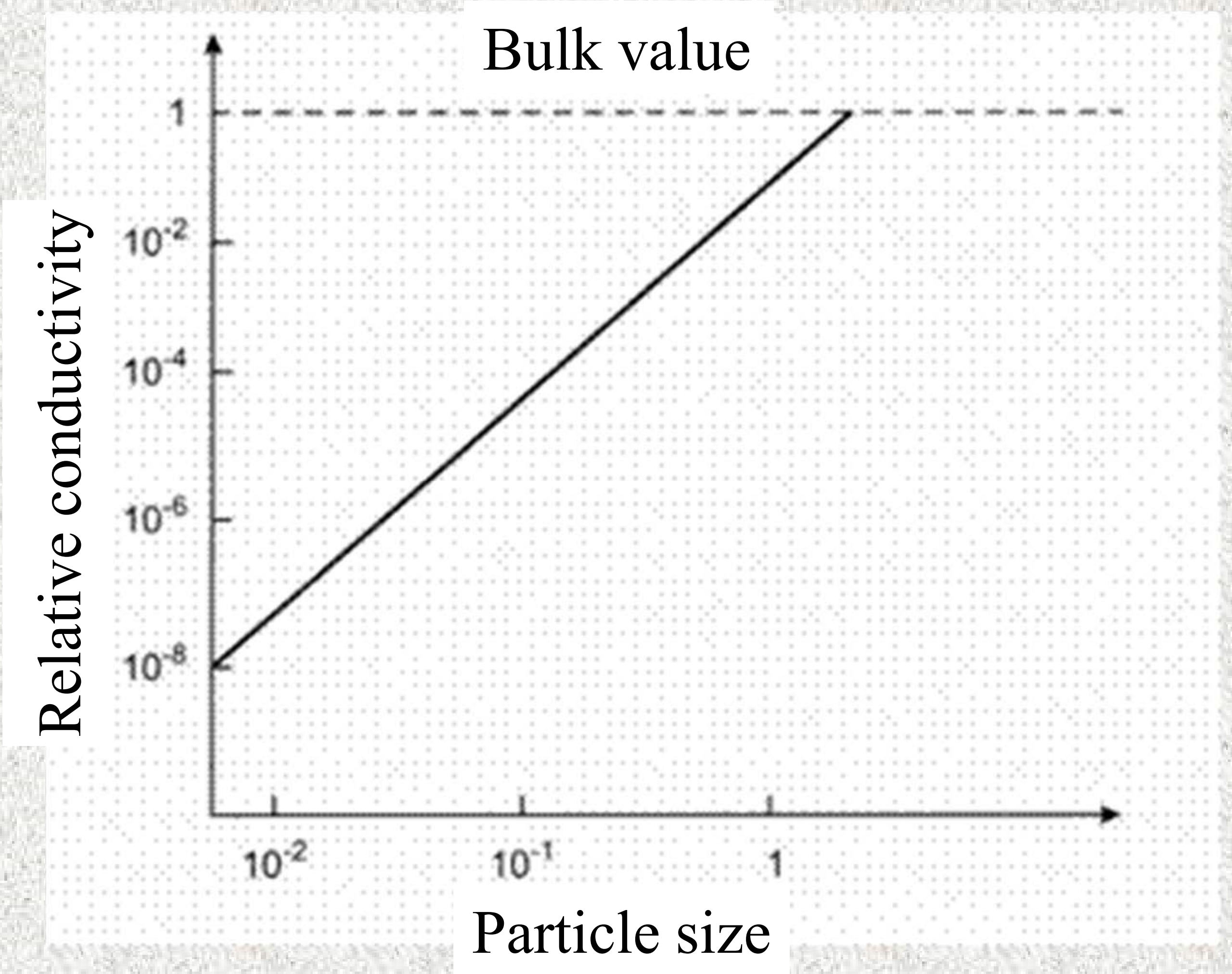
The increase in the core-level binding energy in small particles

poor screening of the core charge

the size-induced metal-nonmetal transition in nanocrystals

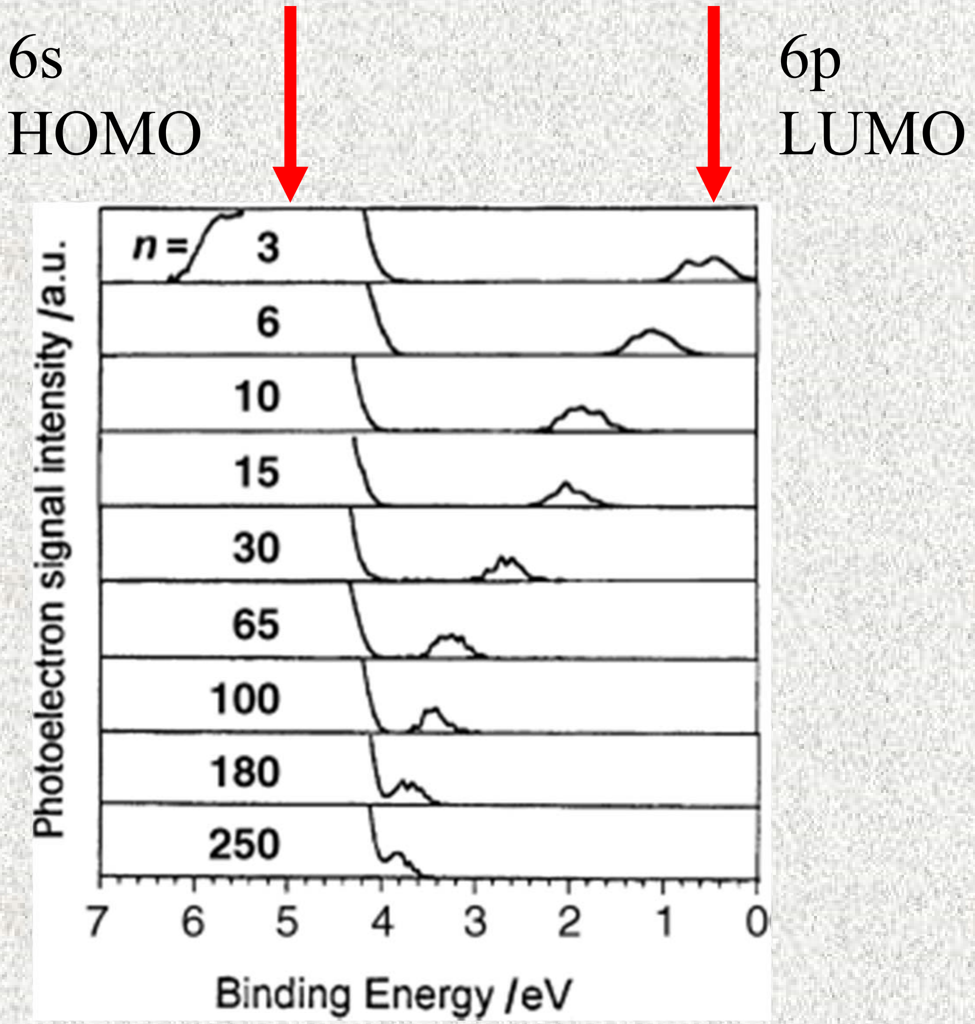
Variation of the shift, Δ*E*, in the core-level binding energy (relative to the bulk metal value) of Pd with the nanoparticle diameter

Electrical Conductivity



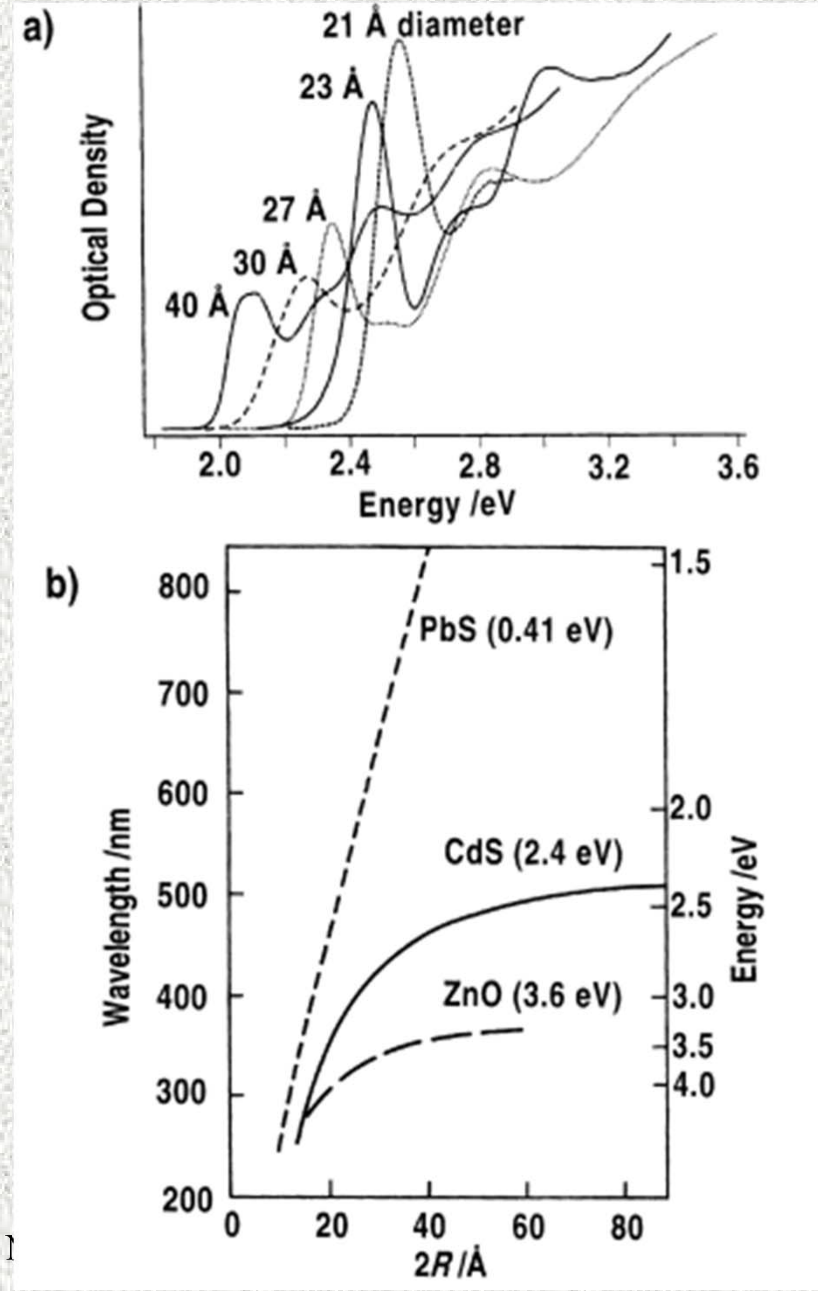
Hg

Valence electron configuration?



Photoelectron spectra of Hg clusters of nuclearity n
The 6p peak moves gradually towards the Fermi level
the band gap shrinks with increase in cluster size

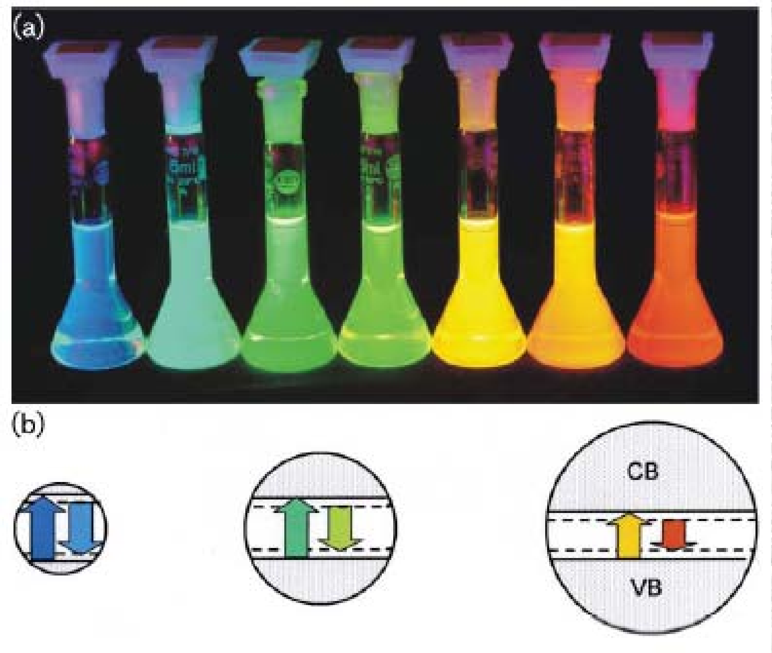
Quantum Size Effects In Semiconductors



a) Absorption spectra of CdSe nanocrystals (at 10 K) of various diameters

b) Wavelength of the absorption threshold and band gap as a function of the particle diameter for various semiconductors. The energy gap in the bulk state in parenthesis

Quantum Confinement Effects

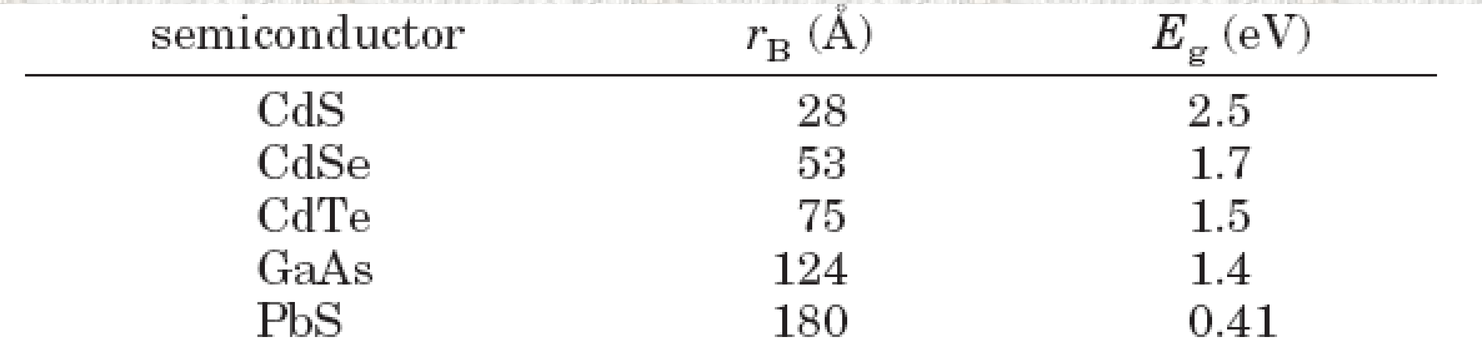


Fluorescence of CdSe–CdS core–shell nanoparticles with a diameter of 1.7 nm (blue) up to 6 nm (red)

Smaller particles have a wider band gap

Bohr Radii

Quantum confinement - particles must be smaller than the Bohr radius of the electron-hole pair



semiconductor	r_B (Å)	E_g (eV)
CdS	28	2.5
CdSe	53	1.7
CdTe	75	1.5
GaAs	124	1.4
PbS	180	0.41

Quantum Confinement Effects

Optical properties

nc-TiO_2 is transparent - applications?

Blue shift in optical spectra of TiO_2 nanoparticles