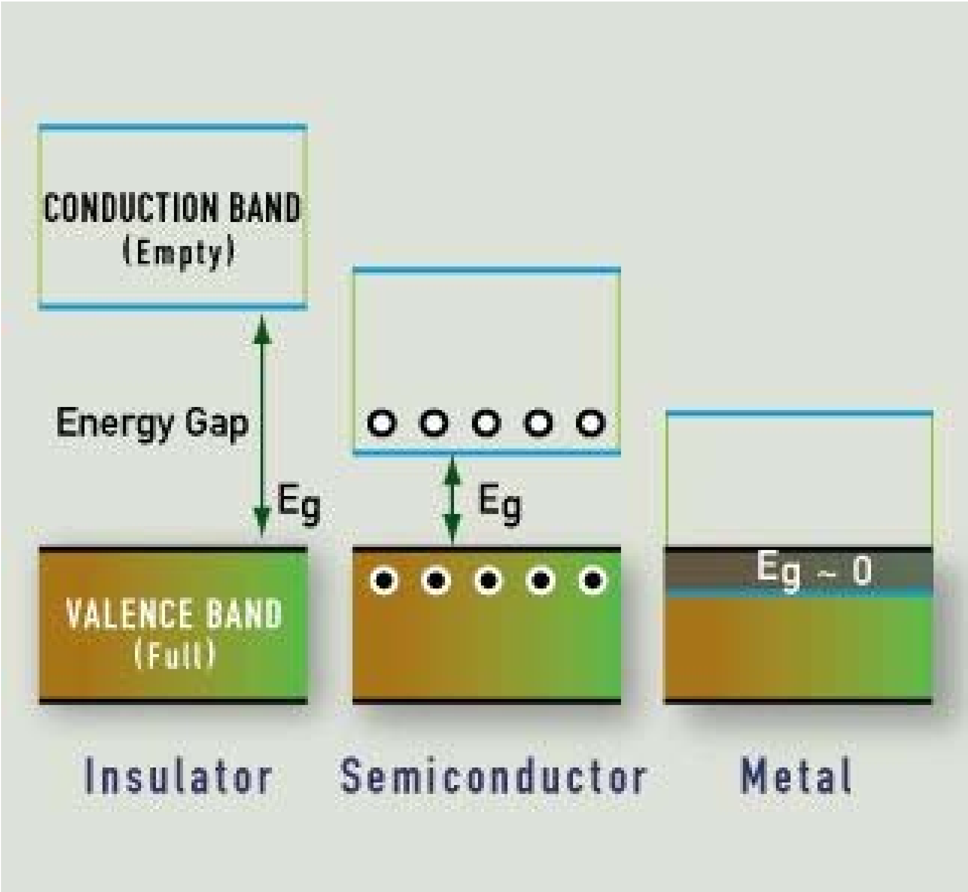
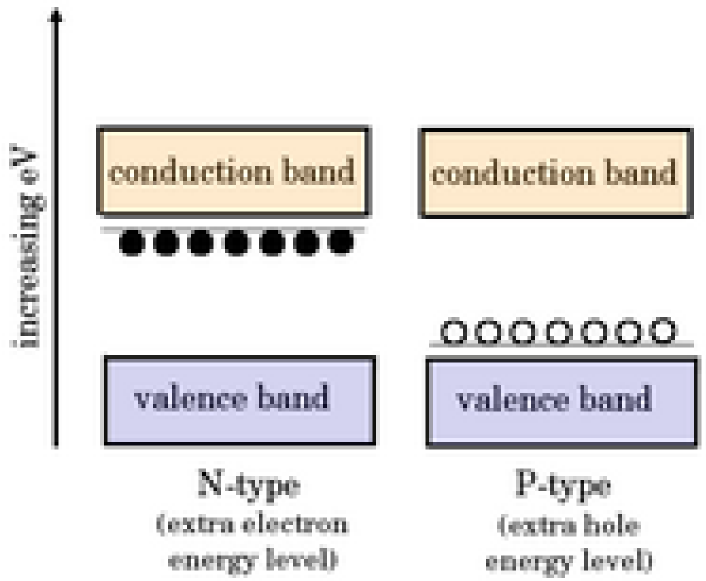
Nanomaterials

- Metals and Alloys
  - Fe, Al, Au
- Semiconductors
  - Band gap, CdS, TiO_2, ZnO
- Ceramic
  - Al_2O_3, Si_3N_4, MgO, , SiO_2, ZrO_2
- Carbon based
  - Diamond, graphite, nanotube, C60
- Polymers
  - Soft mater, block co-polymer
- Biological
  - Photonic, hydrophobic, adhesive,
- Composites

Bandgap

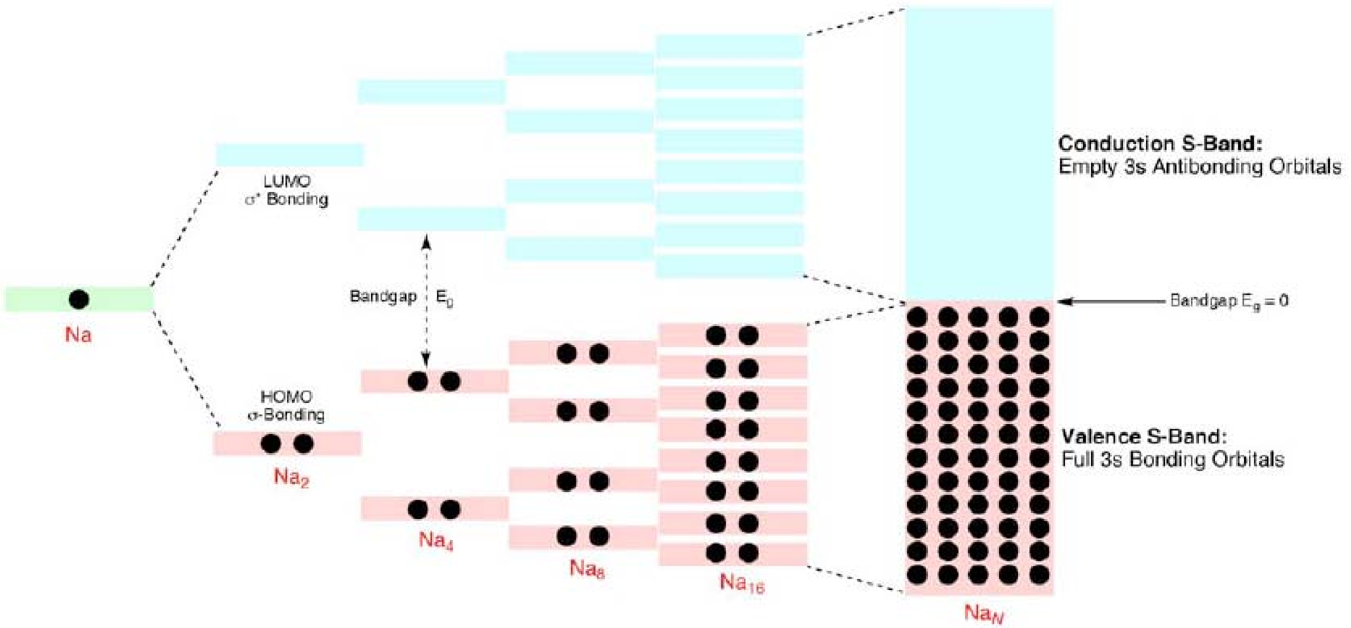


CONDUCTION BAND
(Empty)
Energy Gap
Eg
Eg
Eg ~ 0
VALENCE BAND
(Full)
Insulator
Semiconductor
Metal

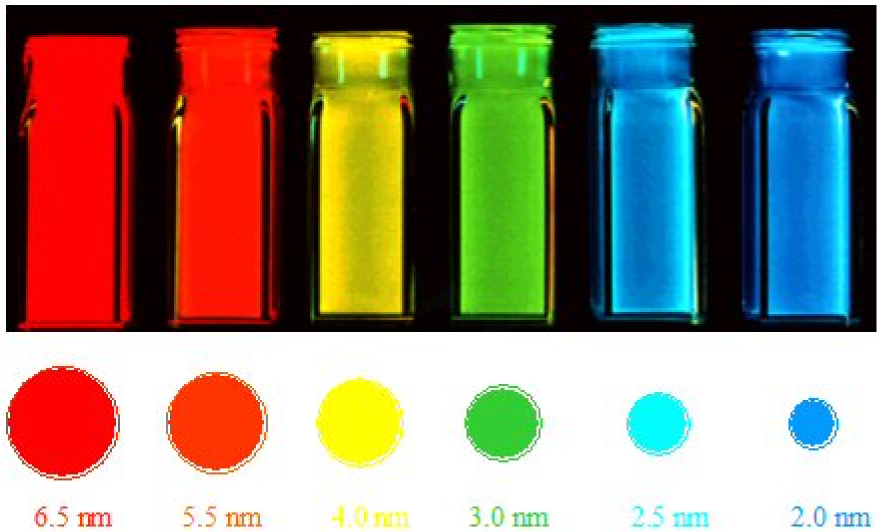


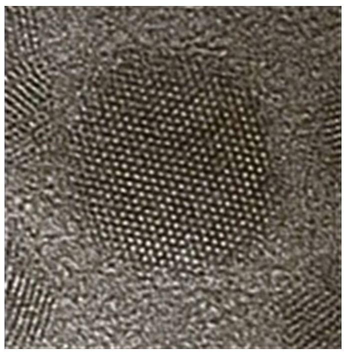
increasing eV
conduction band
conduction band
valence band
valence band
N-type
(extra electron energy level)
P-type
(extra hole energy level)

Bandgap


LUMO
σ* Bonding
Na
Bandgap E0
HOMO
σ-Bonding
Na2
Na4
Na8
Na16
NaN
Conduction S-Band:
Empty 3s Antibonding Orbitals
Bandgap Eg = 0
Valence S-Band:
Full 3s Bonding Orbitals

CdSe





TiO_2

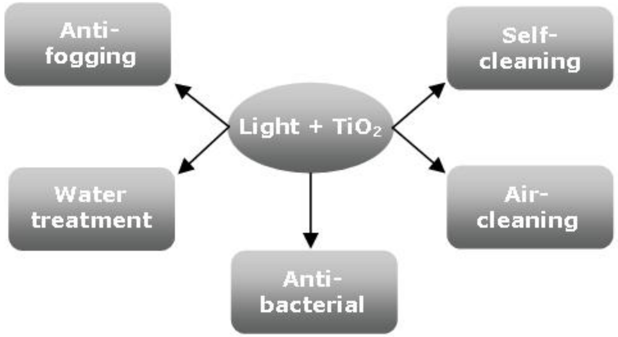
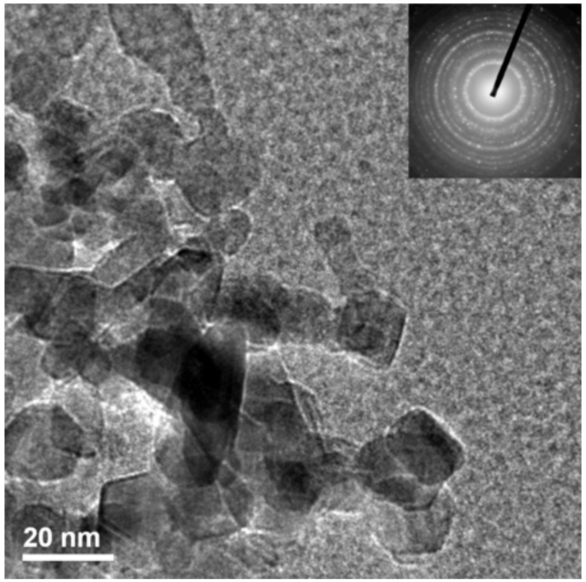
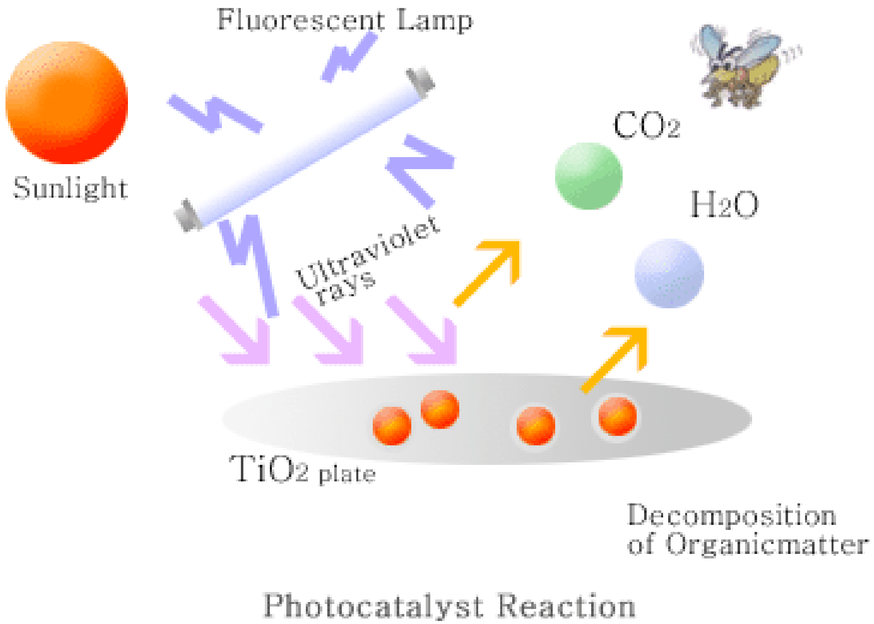
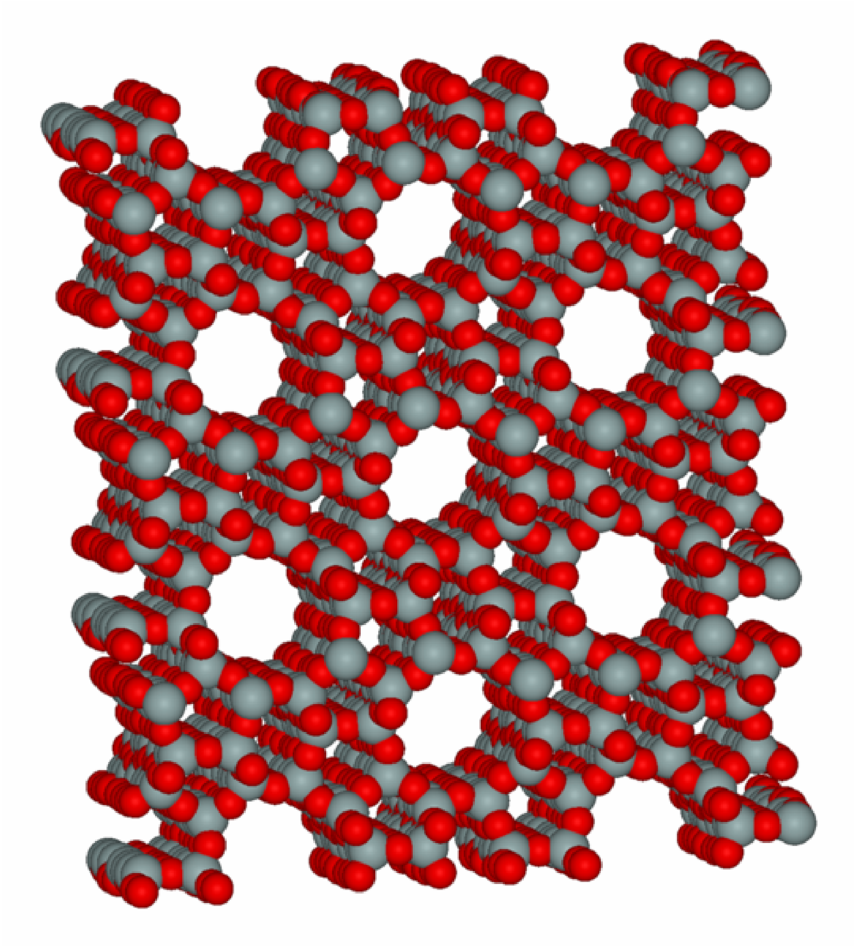


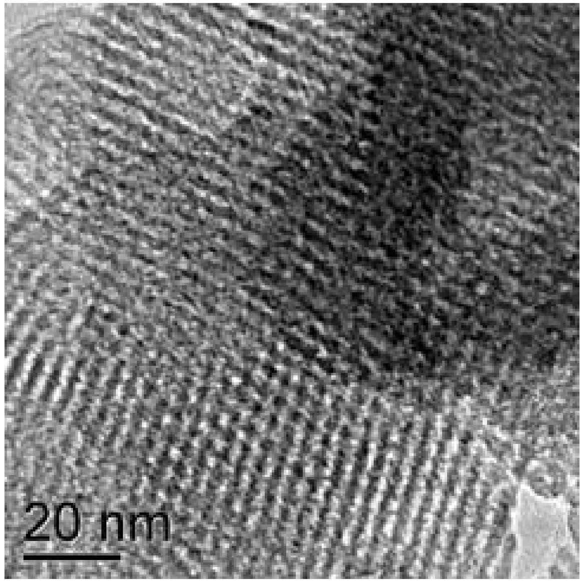
Figure 1. Major areas of activity in titanium dioxide photocatalysis



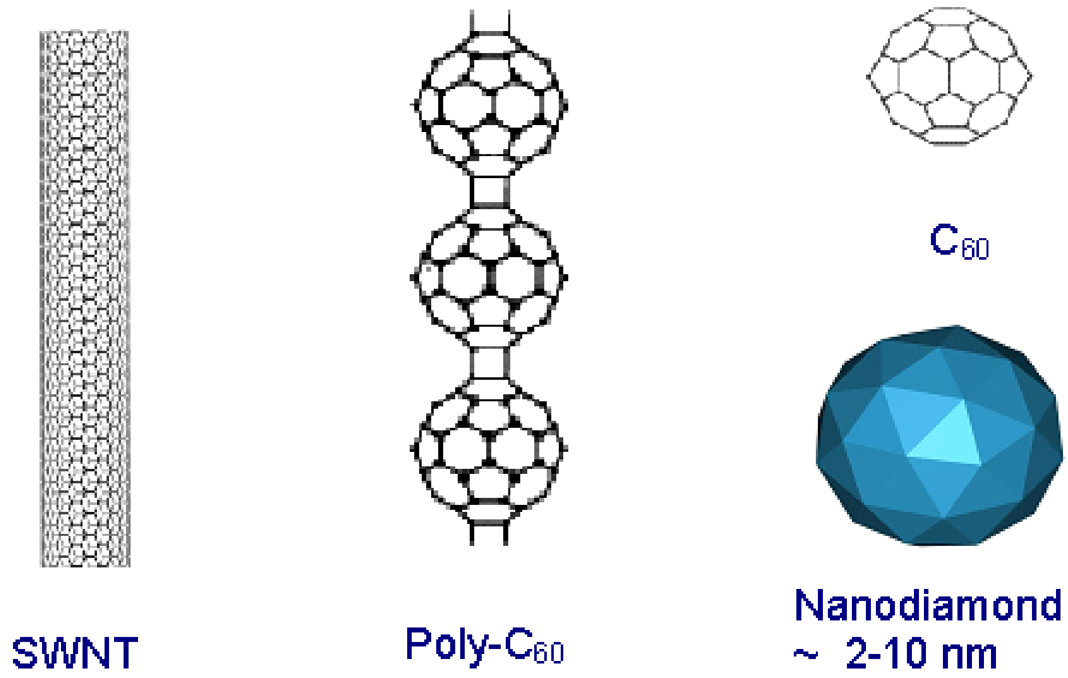


Zeolite

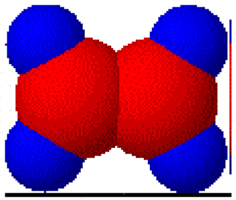




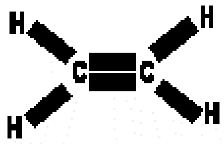
Carbon



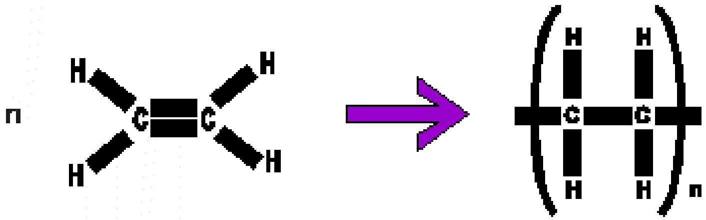
Polymer

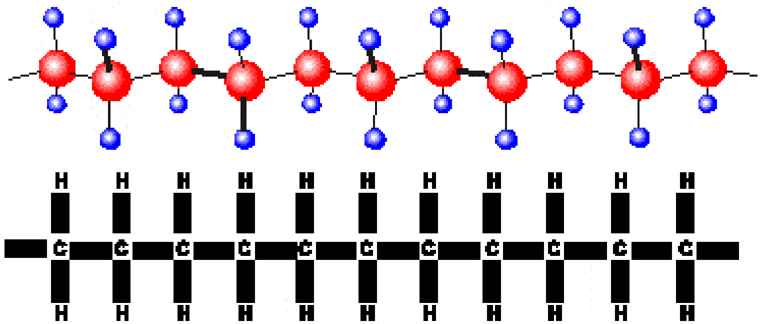


a monomer ethene

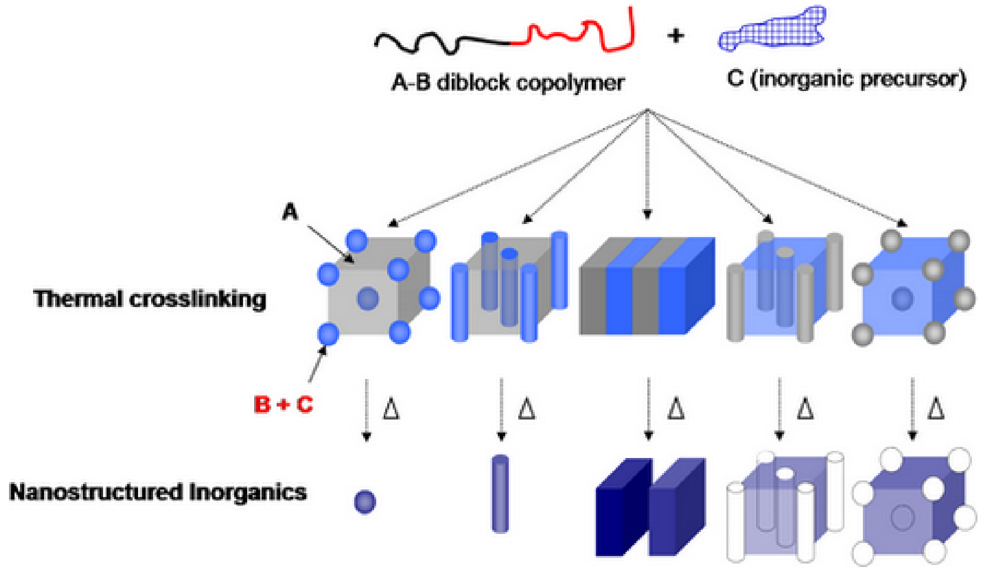


C_2H_4

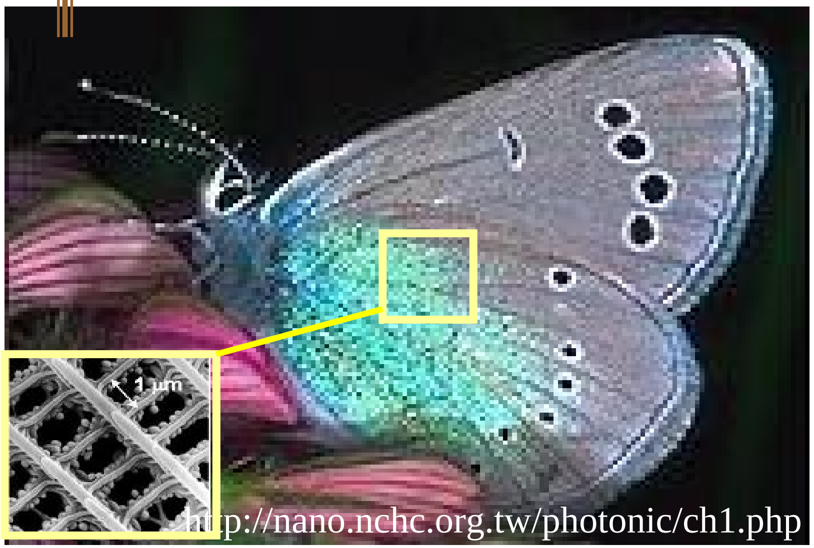


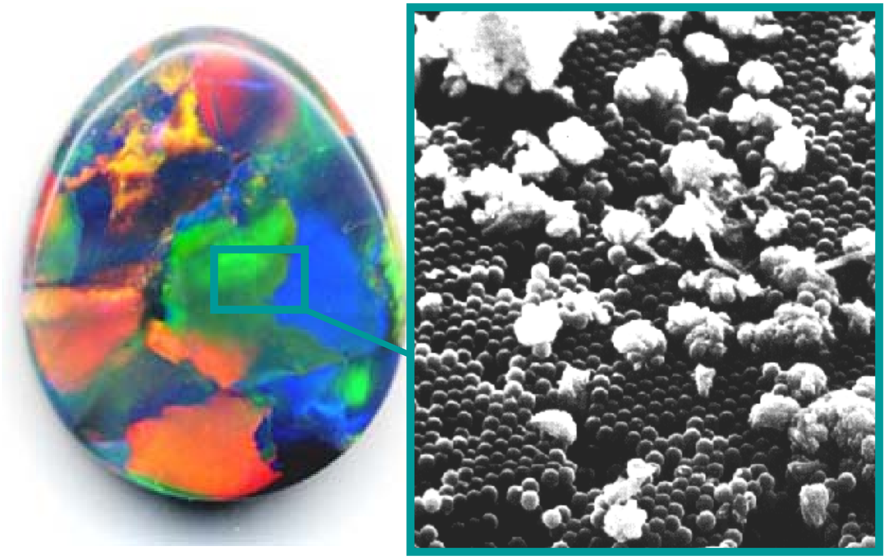


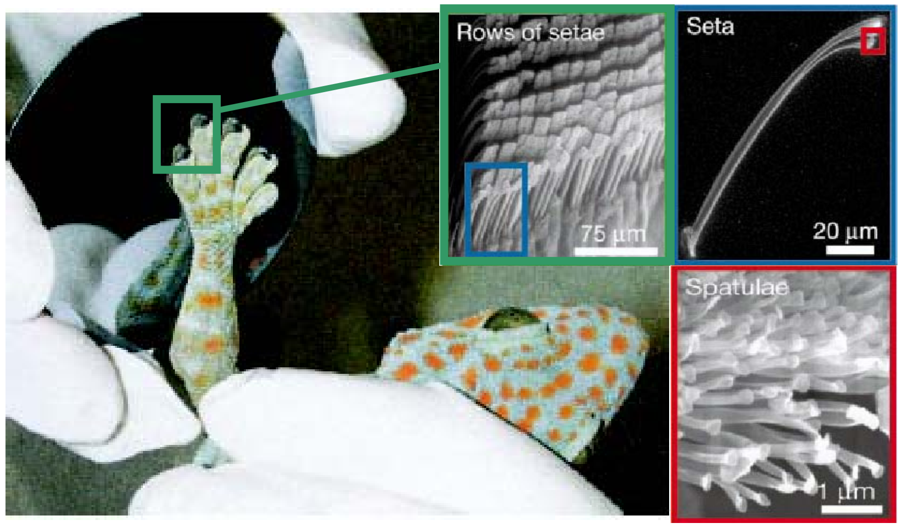
a polymer poly(ethene)



Nature Materials



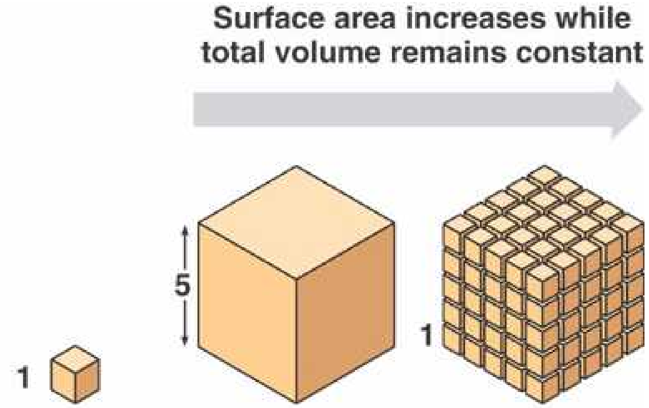




Surfaces

- Collective surface area of nanocube 1 nm
- Porous materials
  - Micropore (<2 nm)
  - Mesopore (2 nm ~ 50 nm)
  - Marcopore (> 50nm)
- Void volume
  - $V_{pore}/V_{material}$

Surface to Volume Ratio



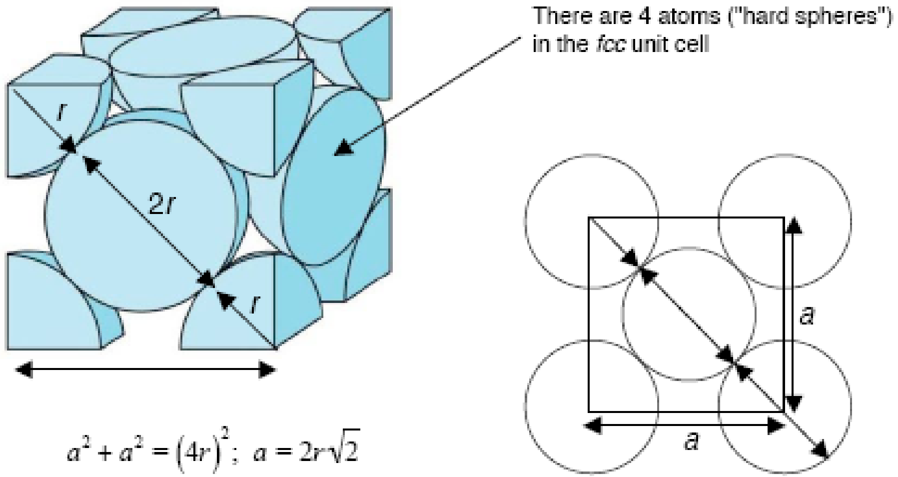
Total surface area (height × width × number of sides × number of boxes)	6	150	750
Total volume (height × width × length × number of boxes)	1	125	125
Surface-to-volume ratio (surface area / volume)	6	1.2	6

Surface to Volume Ratio

Au: AAA
Atomic mass: 196.967
Density 19.31
Radii =0.144 nm

Number of Au atoms in 1 m	$3.4\ 10^{9}$
Volume of Au atom	$4.19\ 10^{28}$
Surface area Au atom	$7.22\ 10^{19}$
Surface/volume ratio	$1.72\ 10^{-9}$

fcc



$$a^2 + a^2 = (4r)^2;\ \ a = 2r\sqrt{2}$$

$$V_{unit\ \ cell} = a^3 = \left(2r\sqrt{2}\right)^3 = 16(r)^3\sqrt{2}$$

$$V_{unit\ \ cell} = a^3 = \left(2r\sqrt{2}\right)^3 = 16(0.5\text{nm})^3\sqrt{2} = \mathbf{2.828\ nm^3}$$

$$\frac{10^{27}\ \text{nm}^3}{2.828\ \text{nm}^3} = \mathbf{3.536x10^{26}\ nano\ \ unit\ cells}$$

$$\text{Collective Area} = 3.536x10^{26}\ \text{nano unit cells}\left(\frac{4\ \text{spheres}}{\text{unit cell}}\right)\left(\frac{4\pi r^2}{\text{sphere}}\right) = \mathbf{4.44x10^{27}\ \ nm^2}$$

$$\frac{S_{spheres}}{S_{unit\ \ cell}} = \frac{4.44x10^9\ \text{m}^2}{6.0x10^9\ \text{m}^2} = \mathbf{0.74}$$

Packing Fraction

$$\mathrm{APF} = \frac{N_{\mathrm{atoms}} V_{\mathrm{atom}}}{V_{\mathrm{crystal}}}$$

Unit Cell

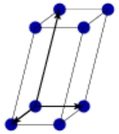
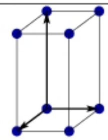
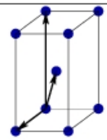
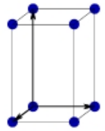
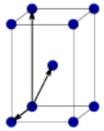
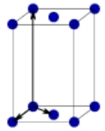
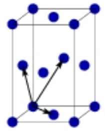
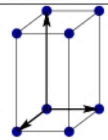
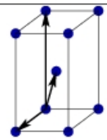
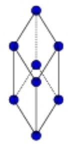
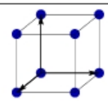
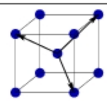
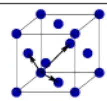
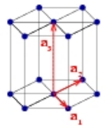
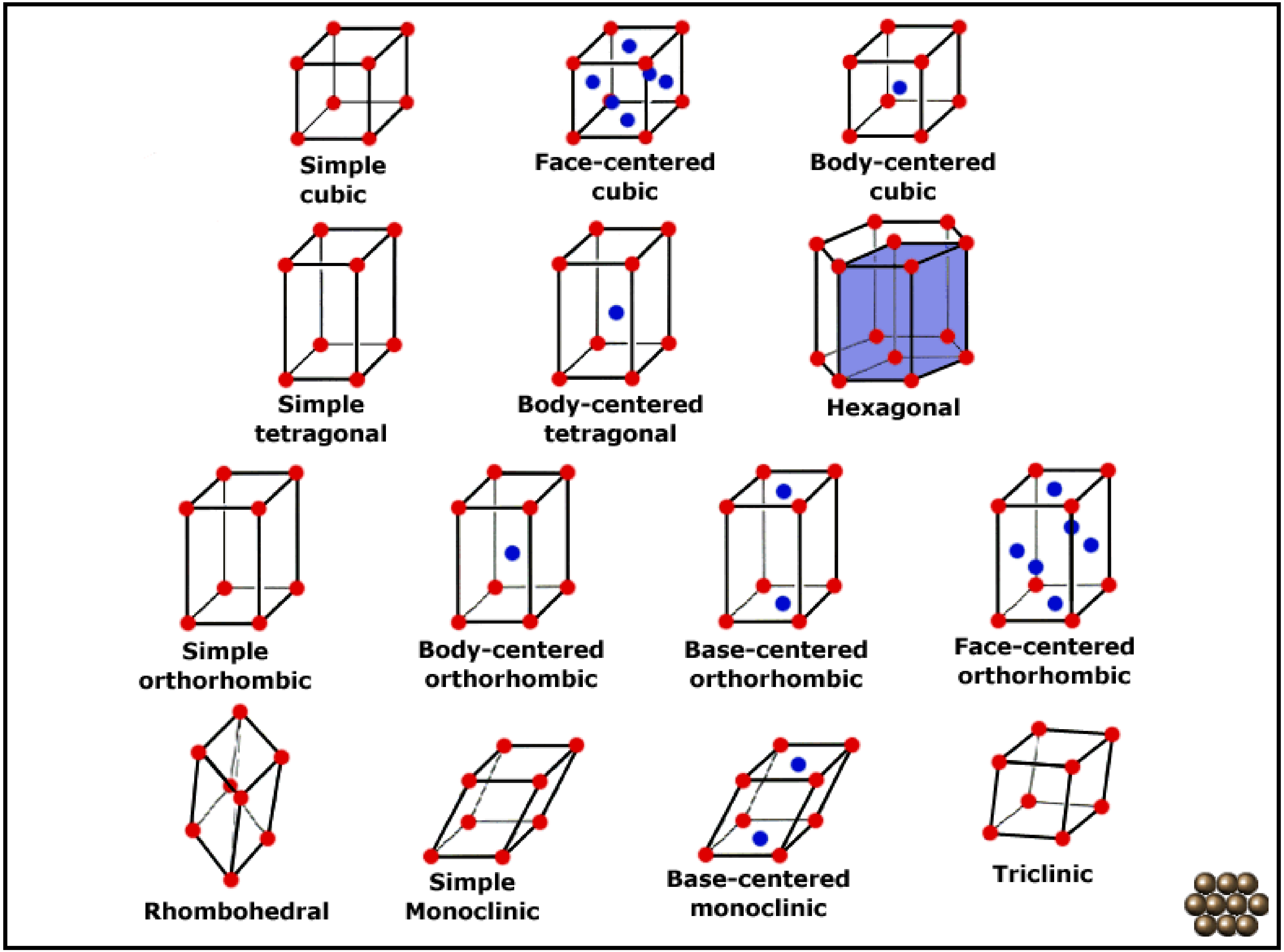
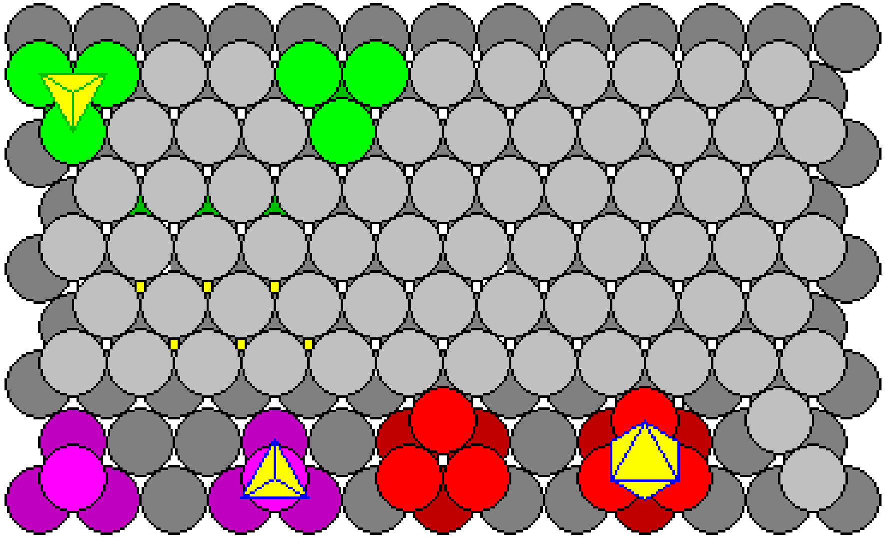
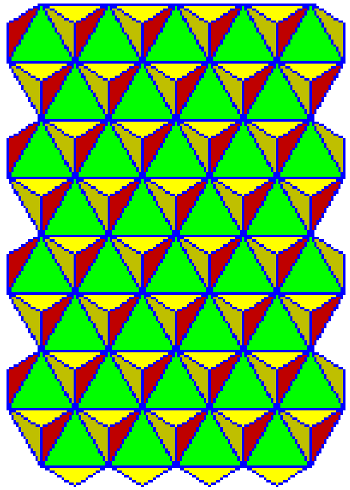
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Table 1.1: Bravais lattices in three-dimensions.

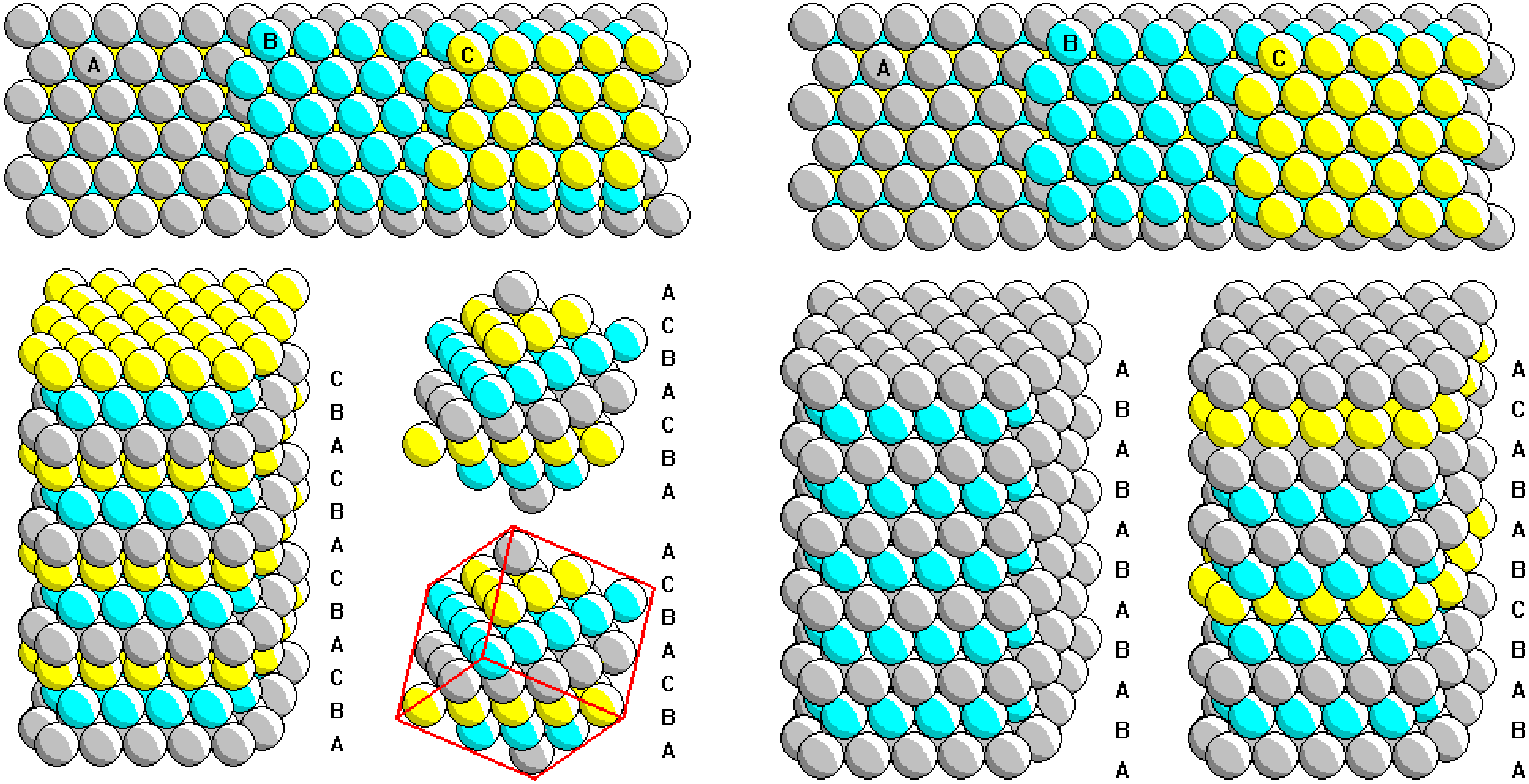

Simple cubic
Face-centered cubic
Body-centered cubic
Simple tetragonal
Body-centered tetragonal
Hexagonal
Simple orthorhombic
Body-centered orthorhombic
Base-centered orthorhombic
Face-centered orthorhombic
Rhombohedral
Simple Monoclinic
Base-centered monoclinic
Triclinic

Packing

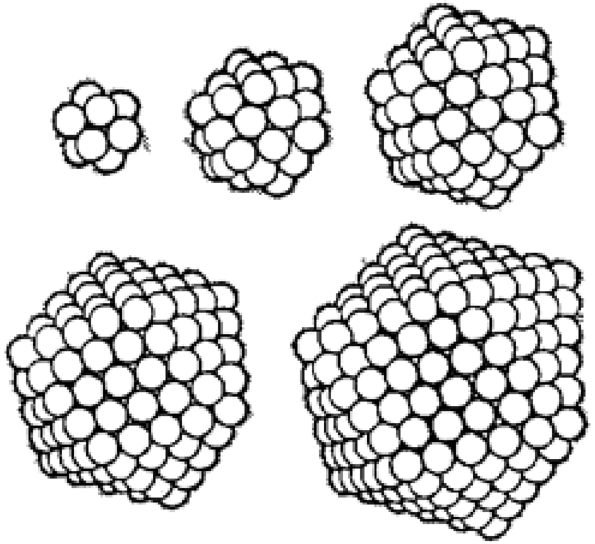


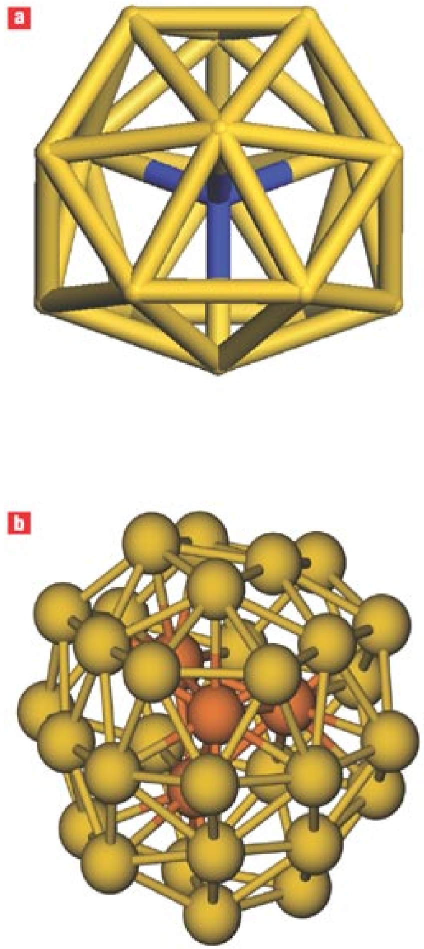


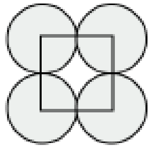
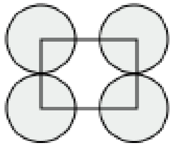
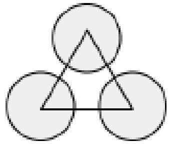
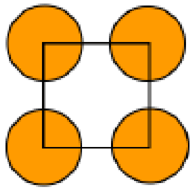
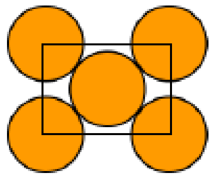
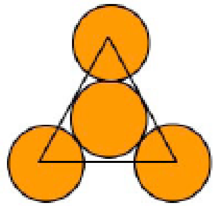
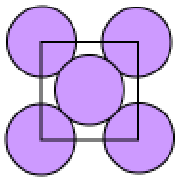
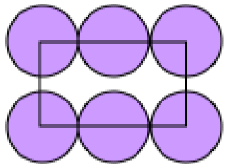
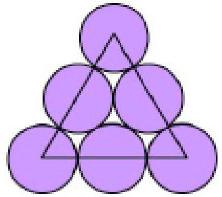
Packing


A
B
C
A
B
C
C B A C B A C B A C B A
A C B A C B A
A C B A C B A
A B A B A B A B A B A
A C A B A B C B A B A

Magic Number



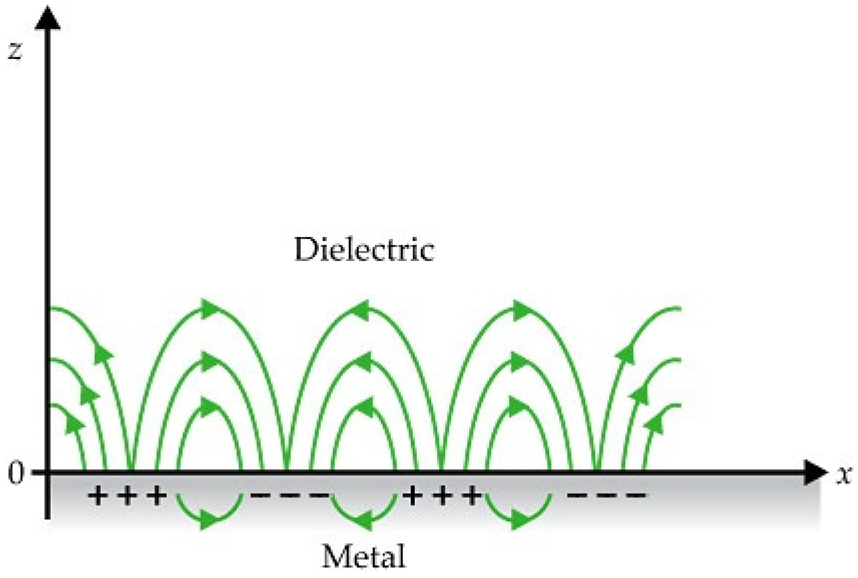


Crystal Type	Low Index Plane		
	100	110	111
Primitive Cubic *Lattice Parameter:* $a_o = 2R$ **Relative Size = 1.0** *Face Diagonal* @[110]: $a_o\sqrt{2} = 2R\cdot\sqrt{2}$ *Body Diagonal* @[111]: $a_o\sqrt{3} = 2R\sqrt{3}$			
Body-Centered Cubic Lattice Parameter: $a_o = 4R/\sqrt{3}$ **Relative Size = 1.156** Face Diagonal @[110]: $a_o\sqrt{2} = \left(4R/\sqrt{3}\right)\cdot\sqrt{2} = 4R.\sqrt{\frac{2}{3}}$ Body Diagonal @[111]: $a_o\sqrt{3} = 4R$			
Face-Centered Cubic *Lattice Parameter:* $a_o = 2R\sqrt{2} = 4R/\sqrt{2}$ **Relative Size = 1.415** *Face Diagonal* @[110]: $a_o\sqrt{2} = 2R\sqrt{2}\cdot\sqrt{2} = 4R$ *Body Diagonal* @[111]: $a_o\sqrt{3} = 4R/\sqrt{2}\cdot\sqrt{3} = 4R.\sqrt{\frac{3}{2}}$			

Property	Primitive	Body-Centered	Face-Centered
Lattice Parameter	$a_o = 2R$	$a_o = \frac{4R}{\sqrt{3}} = 2.31R$	$a_o = \frac{4R}{\sqrt{2}} = 2R\sqrt{2} = 2.83R$
Cell Volume	$V_{pc} = 8R^3$	$V_{bcc} = \frac{64R^3}{3\sqrt{3}} = 12.3R^3$	$V_{bcc} = \frac{64R^3}{2\sqrt{2}} = 22.6R^3$

	Planar Density		
(100)	$\frac{N_a}{A_{100}} = \frac{1}{4R^2}$	$\frac{N_a}{A_{110}} = \frac{1}{\left(\frac{4}{\sqrt{3}}R\right)^2} = \frac{1}{5.33R^2}$	$\frac{N_a}{A_{11}} = \frac{2}{\left(\frac{4}{\sqrt{2}}R\right)^2} = \frac{2}{8R^2} = \frac{1}{4R^2}$
(110)	$\frac{N_a}{a_o \cdot a_o\sqrt{2}} = \frac{1}{\sqrt{2}\left(2R\right)^2} = \frac{1}{5.66R^2}$	$\frac{N_a}{a_o \cdot a_o\sqrt{2}} = \frac{2}{\sqrt{2}\left(\frac{4}{\sqrt{3}}R\right)^2} = \frac{2}{7.54R^2}$	$\frac{N_a}{a_o \cdot a_o\sqrt{2}} = \frac{2}{\sqrt{2}\left(\frac{4}{\sqrt{2}}R\right)^2} = \frac{2}{11.31R^2}$
(111)	**Extra Problem:** **X-5.15.1**	**Extra Problem:** **X-5.15.2**	$\frac{N_a}{\frac{1}{2}b \cdot h = \frac{1}{2}a_o\sqrt{2} \cdot a_o\sqrt{\frac{3}{2}}} = \frac{2}{4R^2\sqrt{3}} = \frac{2}{6.93R^2}$

Surface Plasmonon



$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2}$$

Surface Energy

One face surface energy: γ

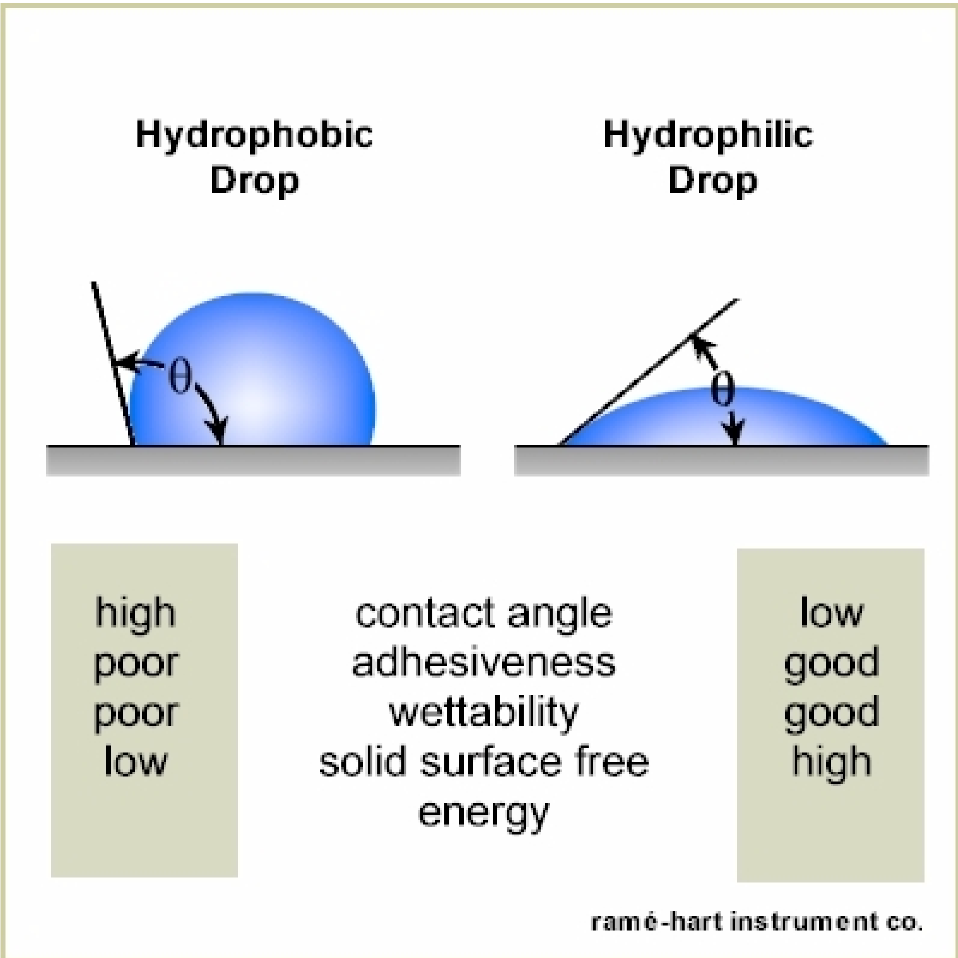
27 cube: 27 x 6 γ

3 x 9 cube line: 114 γ

3 x (3x3) square: 90 γ

3 x 3 x 3 cube: 54 γ

Contact Angle

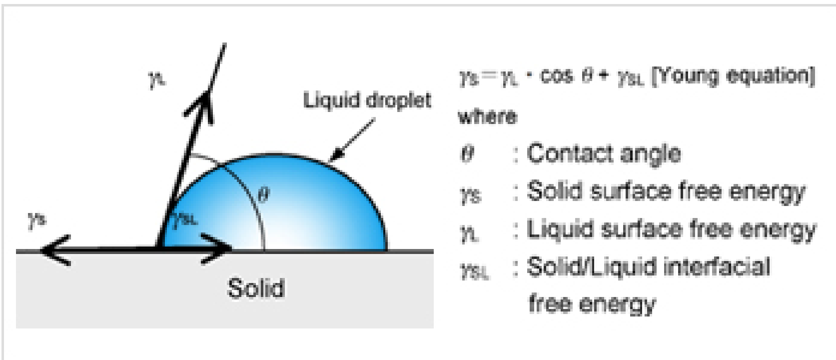


Kelvin Equation

$$\ln \frac{p}{p_0} = \frac{2\gamma V_m}{rRT}$$

Young’s Equation

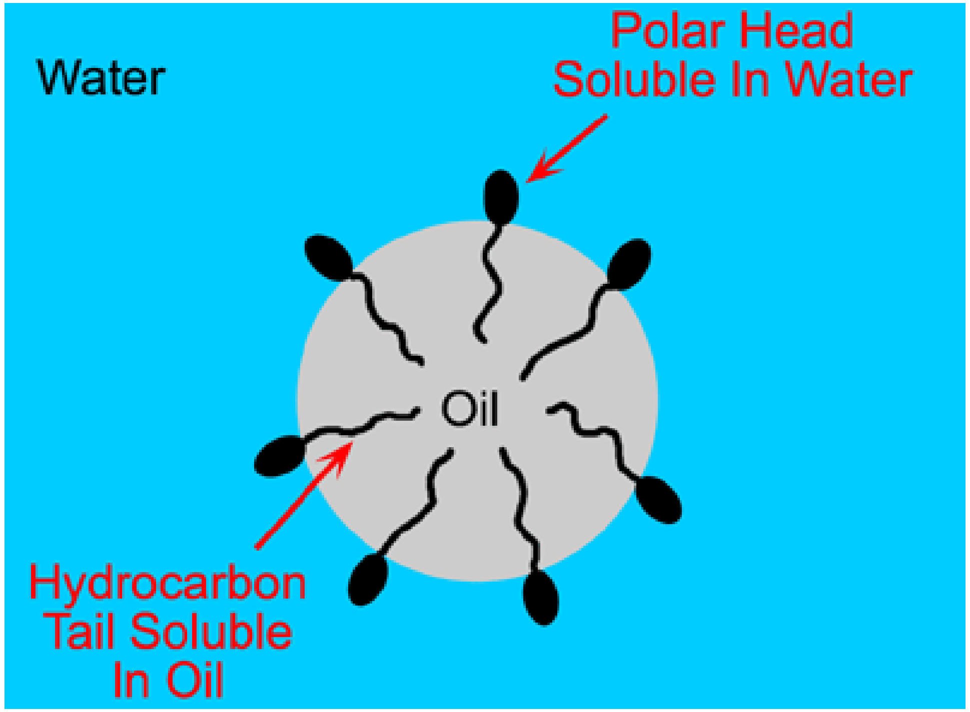
$$\gamma_{SL} + \gamma_{LV} \cos\theta_c = \gamma_{SV}$$



Surface Energy Minimization

- Surfactants
- DLVO
- Polymeric
- Nucleation
- Ostwald Ripening
- Sintering
- Restructure

Surfactant


Water
Polar Head
Soluble In Water
Oil
Hydrocarbon
Tail Soluble
In Oil

DLVO Theory

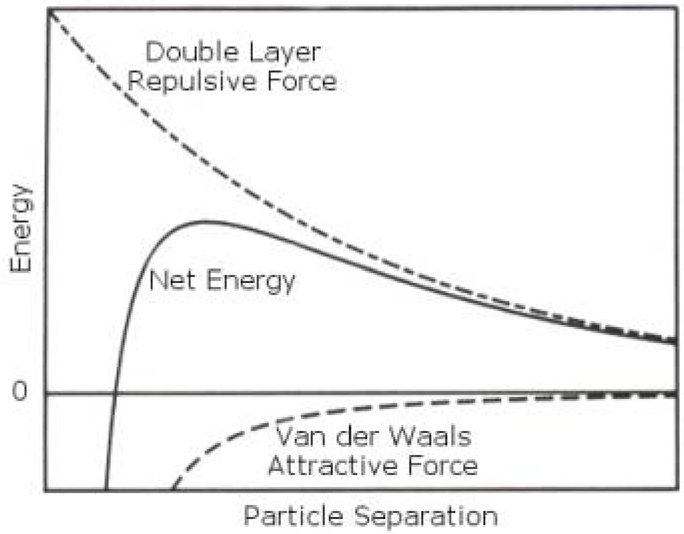
$$V_T = V_A + V_R + V_S$$

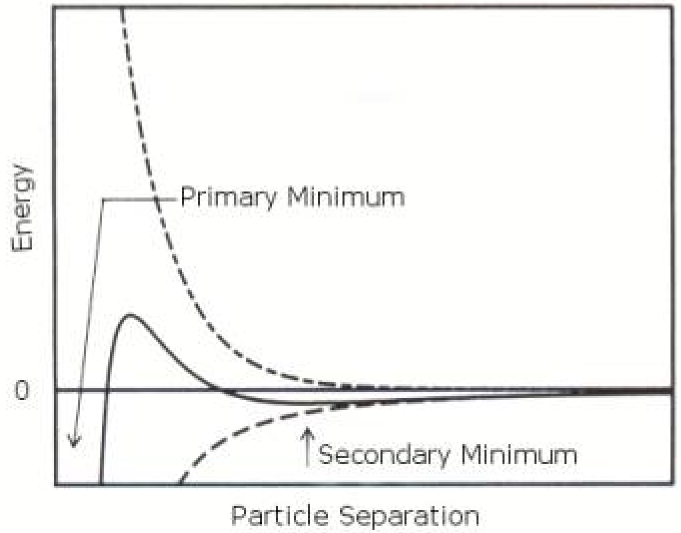
$$V_A = -A/(12\ \pi\ D^2)$$

A is the Hamaker constant and D is the particle separation

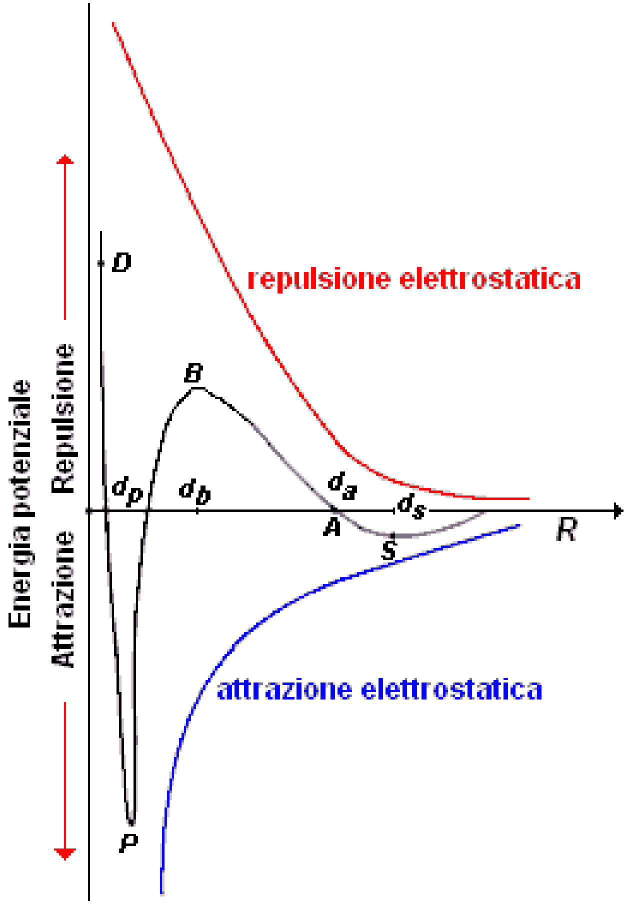
$$V_R = 2\ \pi\ \varepsilon\ a\ \xi^2 \exp(-\ \kappa D)$$

a is the particle radius, π is the solvent permeability,
κ is a function of the ionic composition and ξ is the zeta potential

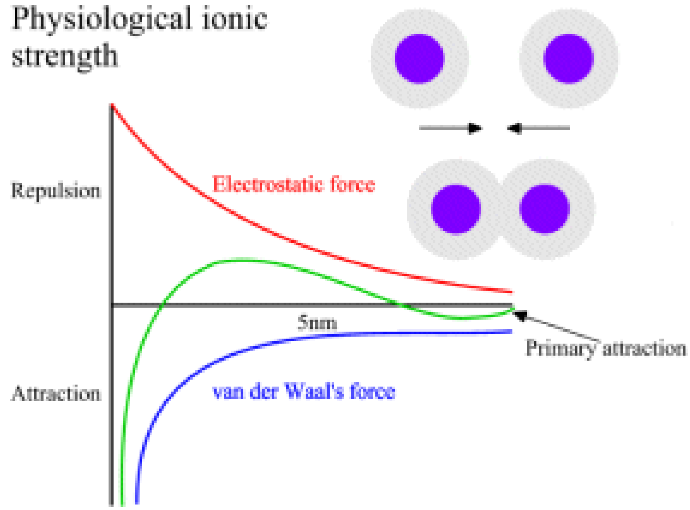

Double Layer
Repulsive Force
Energy
Net Energy
0
Van der Waals
Attractive Force
Particle Separation


Energy
Primary Minimum
0
Secondary Minimum
Particle Separation

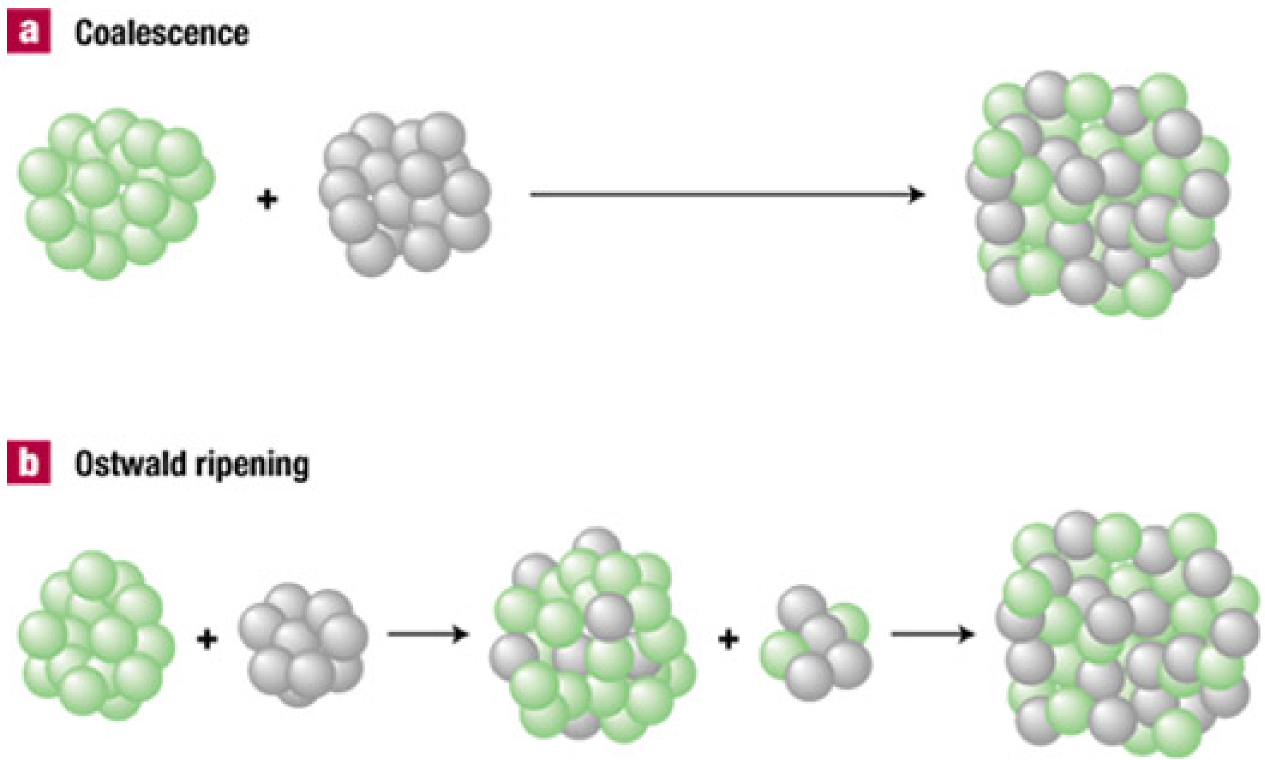
DLVO Theory



repulsione elettrostatica
attrazione elettrostatica
Energia potenziale
Repulsione
Attrazione
D
B
P
A
S
d_p
d_b
d_a
d_s
R

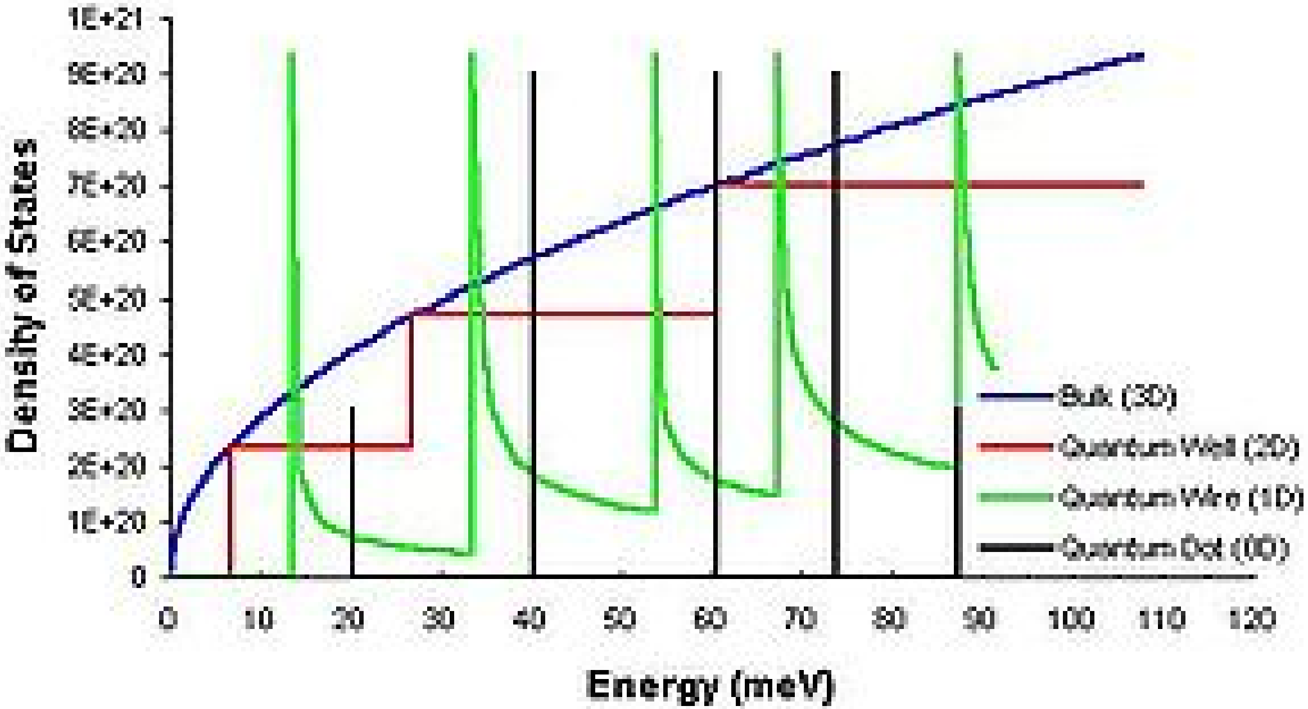


Physiological ionic strength
Repulsion
Attraction
Electrostatic force
van der Waal's force
5nm
Primary attraction



Two main mechanisms are shown here: **a**, coalescence sintering, and **b**, Ostwald ripening sintering. Coalescence sintering occurs when two clusters touch or collide and merge to form one bigger cluster. In contrast, Ostwald ripening sintering occurs by evaporation of atoms from one cluster, which then transfer to another. This is a dynamic process — both clusters exchange atoms, but the rate of loss from the smaller cluster is higher, because of the lower average coordination of atoms at the surface and their relative ease of removal. Thus big clusters get bigger at the expense of smaller clusters, which shrink and eventually disappear. The latter process is the usual form of sintering for metal clusters on a supported surface that are well spaced apart, although coalescence can occur for a high density of clusters. In general, the presence of the surface results in SMORS (surface-mediated Ostwald ripening sintering) in which material is transferred from one cluster to another by diffusion across the surface, and not through the gas phase.

Density of State

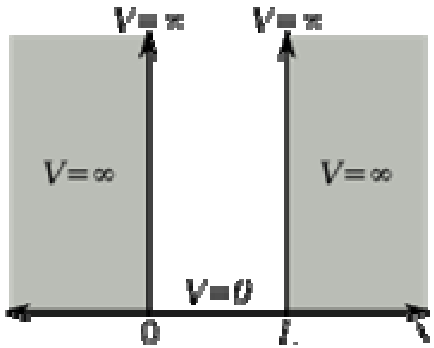


Particle in a Box

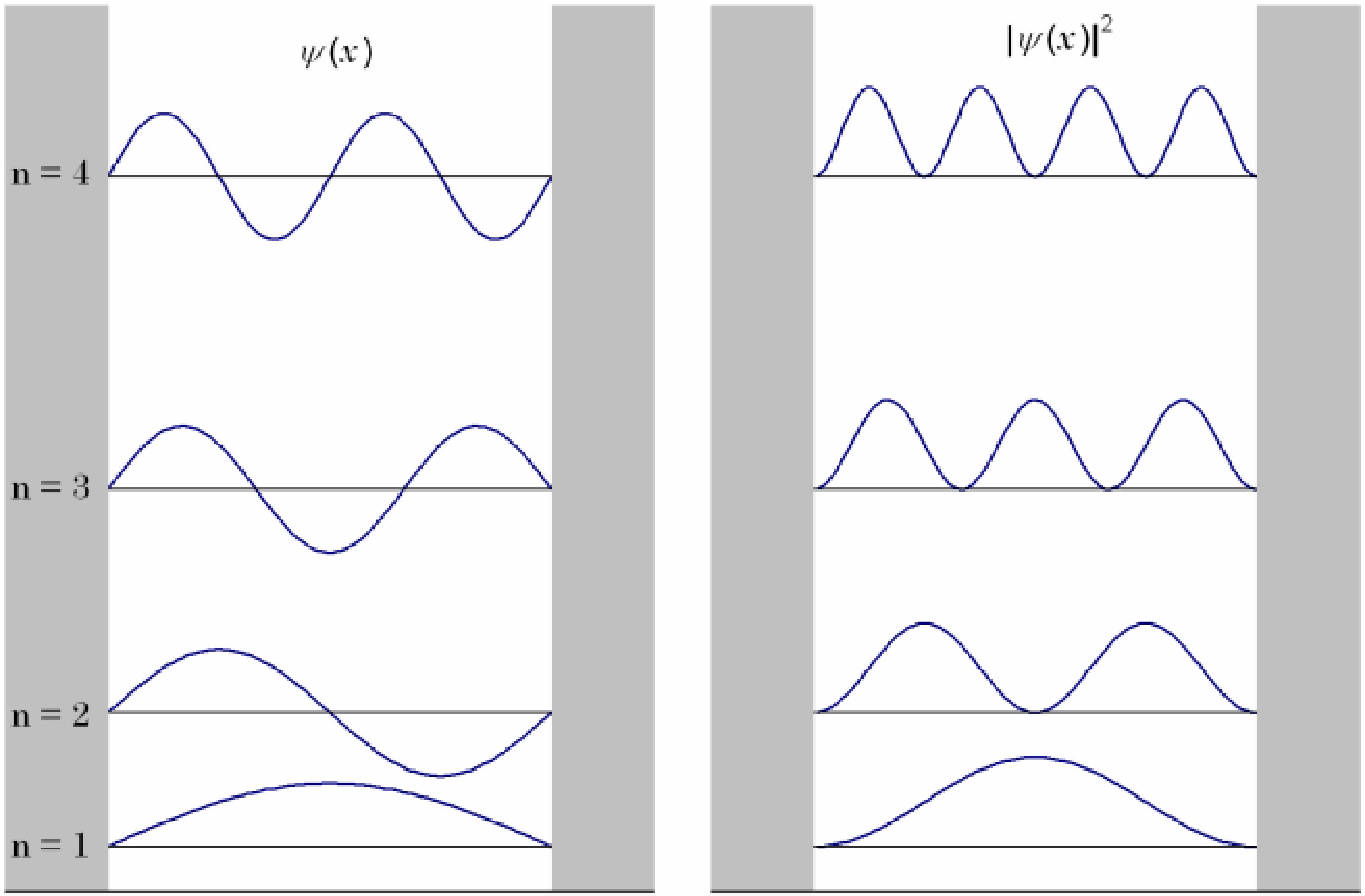
$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2}+V(x)\psi(x)=E\psi(x) \quad (1)$$

$$\psi_n=\sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$

$$E_n=\frac{\hbar^2\pi^2}{2mL^2}n^2$$



Particle in a Box



$$\psi_{n_x,n_y} = \sqrt{\frac{4}{L_x L_y}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

$$E_{n_x,n_y} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 \right]$$

$$\psi_{n_x,n_y,n_z} = \sqrt{\frac{8}{L_x L_y L_z}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right) \sin\left(\frac{n_z \pi z}{L_z}\right) \quad (22)$$

$$E_{n_x,n_y,n_z} = \frac{\hbar^2 \pi^2}{2m} \left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2 \right] \quad (23)$$

Bohr Exciton Radius