Nano Materials

김기범

서울대학교 재료공학부

Contents

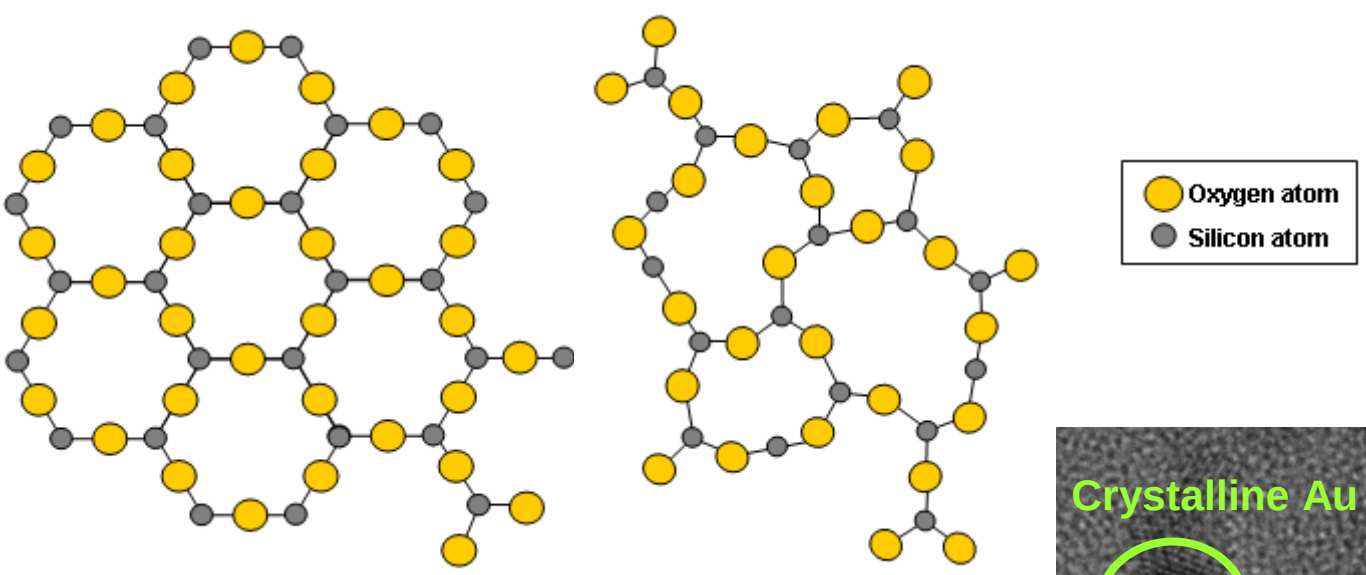
Basics

- Crystal structure
- Surface
- Kinetics
- Surface chemistry
- Consolidation
- Quantum confinement

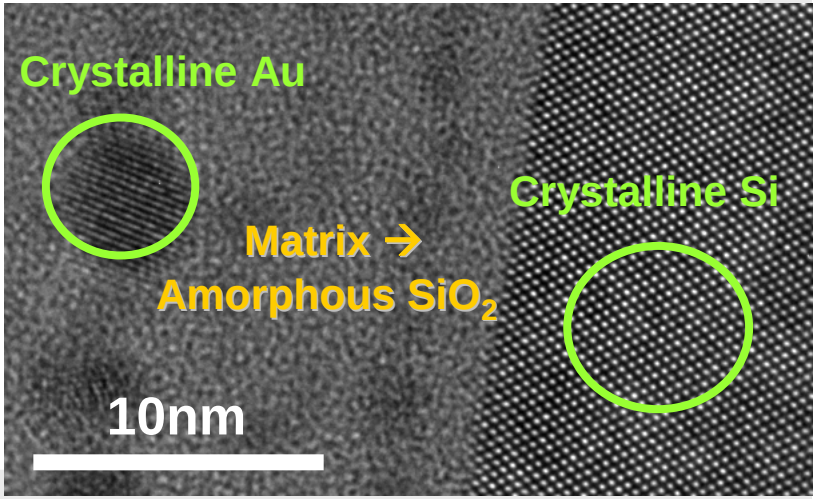
Basics- Crystal structure

❑ Crystalline vs. amorphous

Crystalline SiO_2 Amorphous SiO_2



Long range order **Short range order**



Basics- Crystal structure

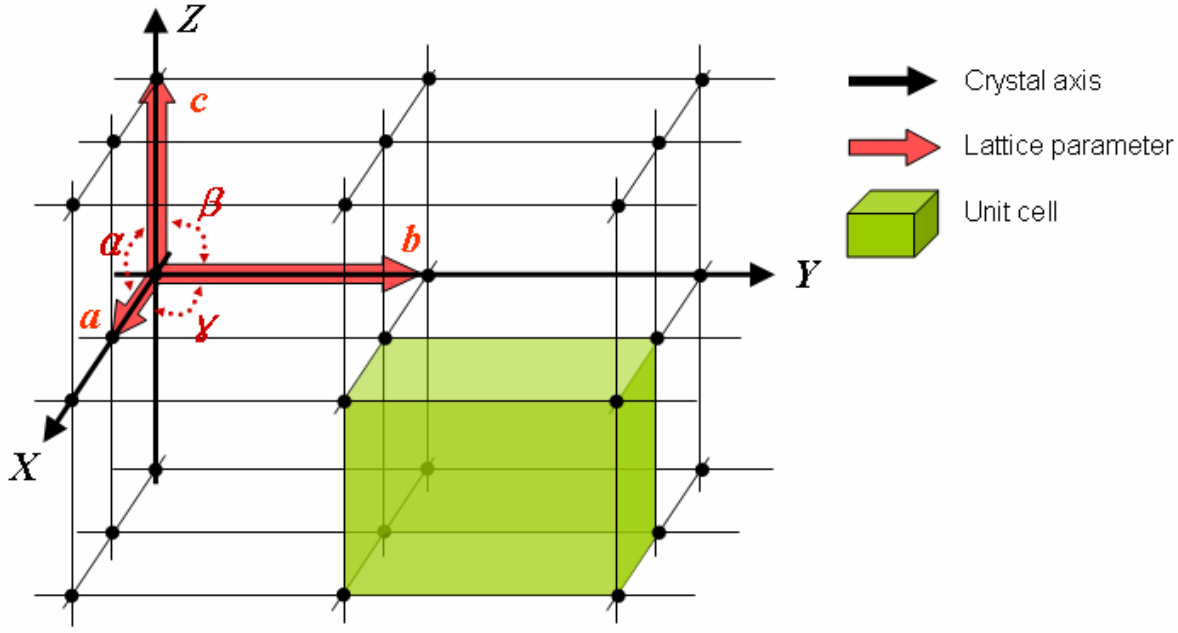
❑ Definition of Crystal

A crystal is an anisotropic, homogeneous body consisting of a three-dimensional periodic ordering of atoms, ions or molecules

❑ Definition of Lattice

A lattice means a three-dimensional array of points coinciding with atom positions (the space arrangement of equivalent sites in a crystal)

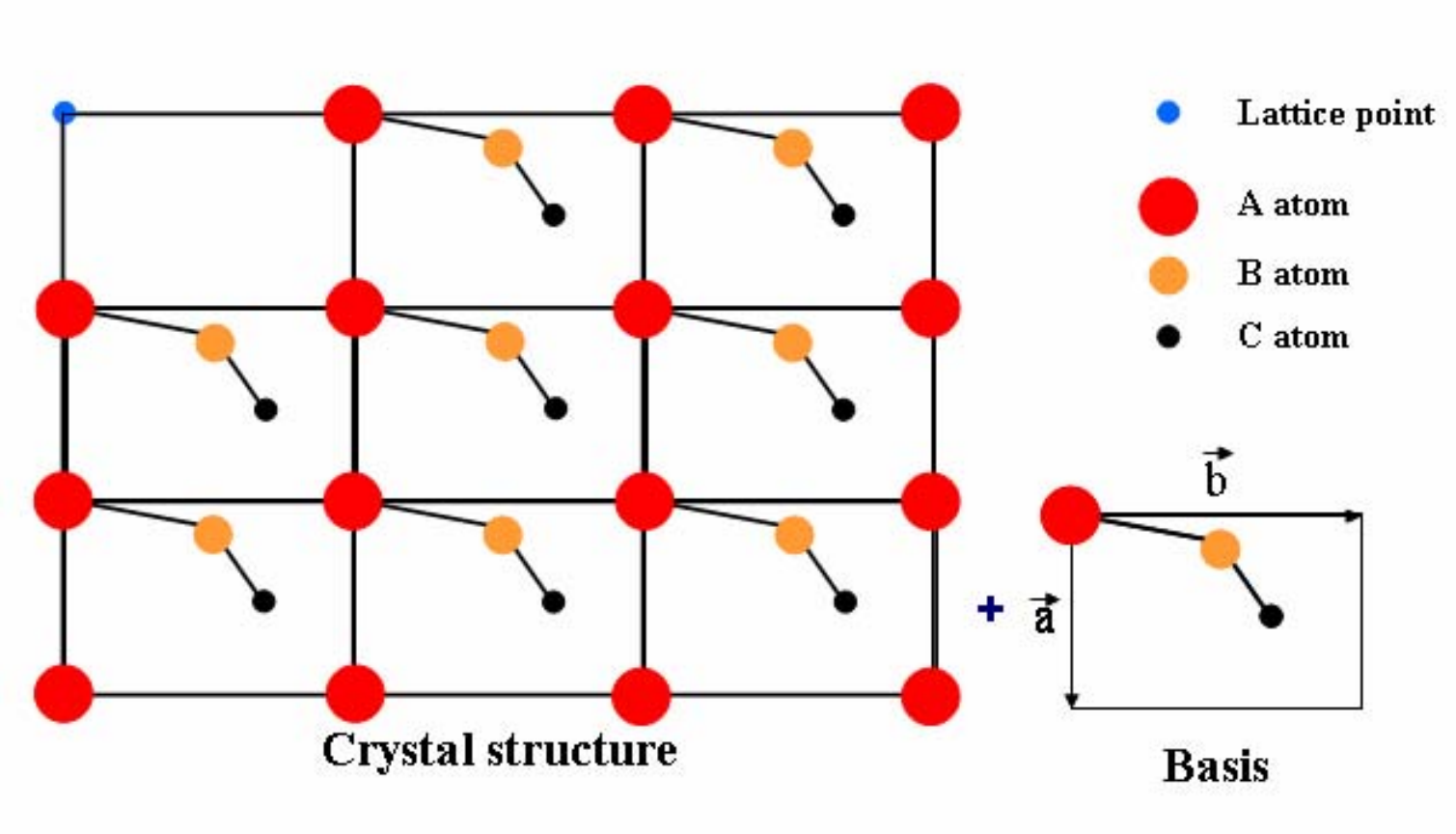
❑ Lattice Parameters



Basics- Crystal structure

❑ Crystal Structure

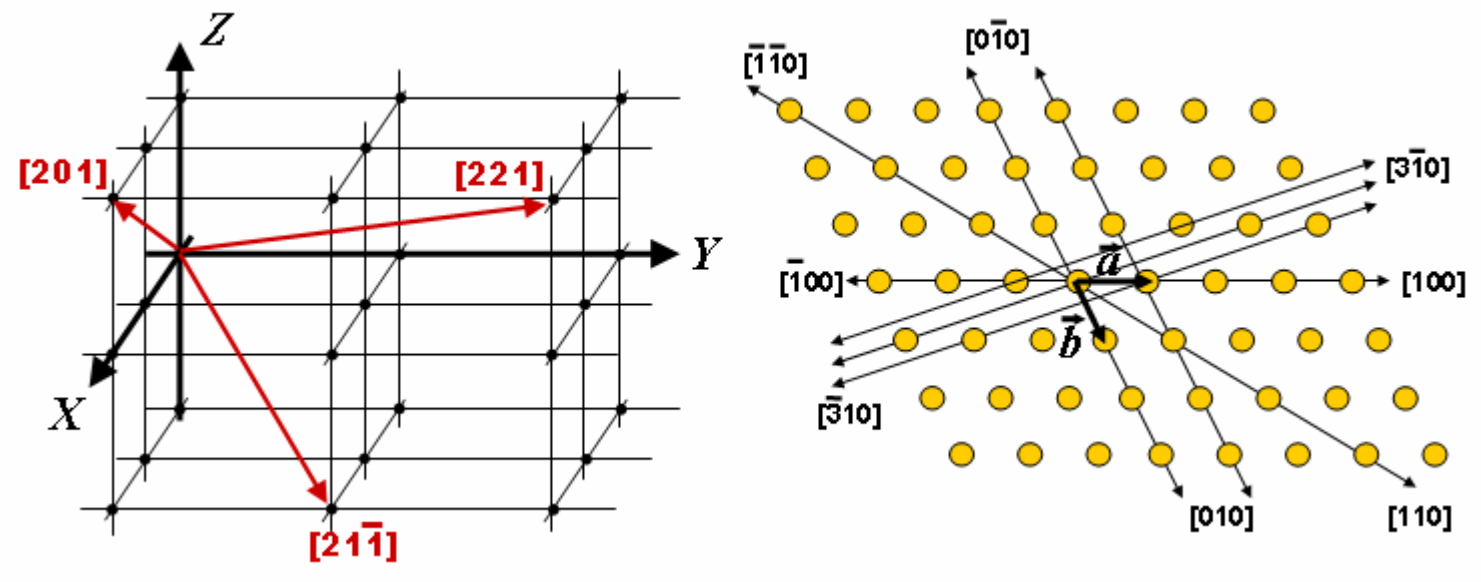
Crystal structure = Lattice + Basis



Basics- Crystal structure

❑ Definition of Crystallographic direction

Crystallographic direction is defined as a line between two points, or a vector.



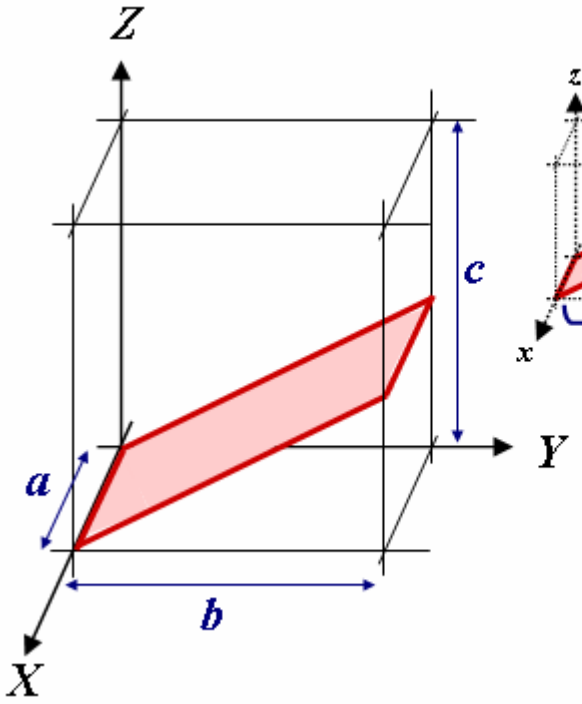
Note that the direction of [*uvw*] describes not only a line through the origin and the point *uvw*, but the infinite set of lines which are parallel to it.

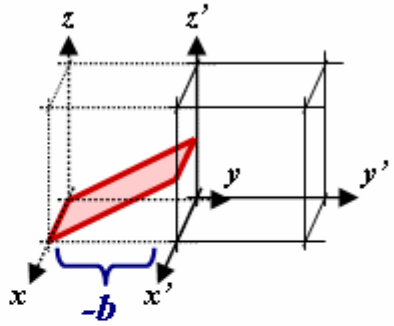
Basics- Crystal structure

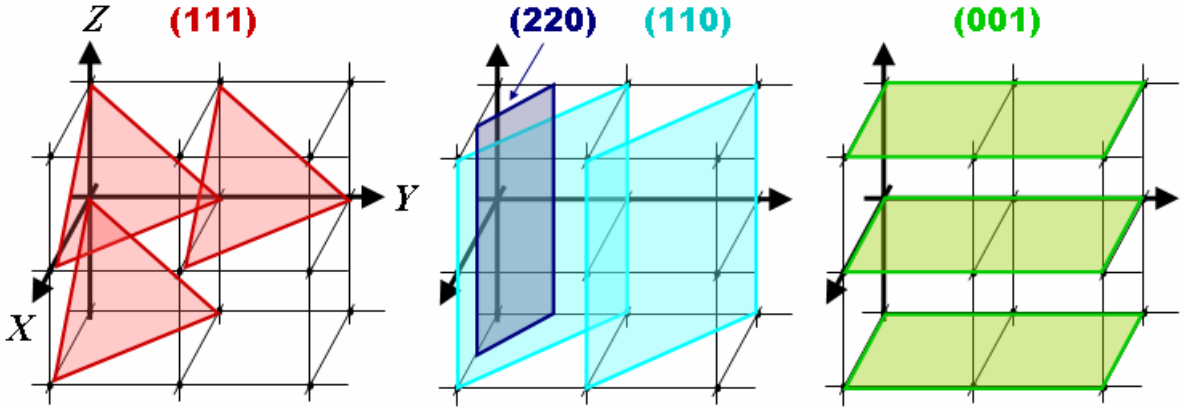
❑ Definition of Crystallographic plane

The values (*h k l*) are called Miller indices, and they are defined as the smallest integral multiples of the reciprocals of the plane intercepts of axis.

	x	*y*	*z*
Projections	*∞ a*	*- b*	*c/2*
Projections (in terms of *a*, *b*, and *c*)	*∞*	*- 1*	*1/2*
Reciprocal	*0*	*-1*	*2*
Reduction (unnecessary)			
Enclosure	[0 $\bar{1}$ 2]		



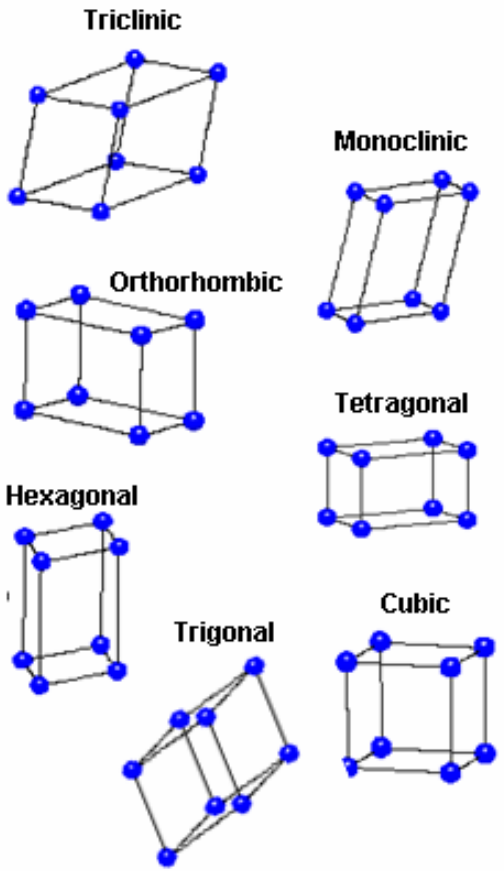




Basics- Crystal structure

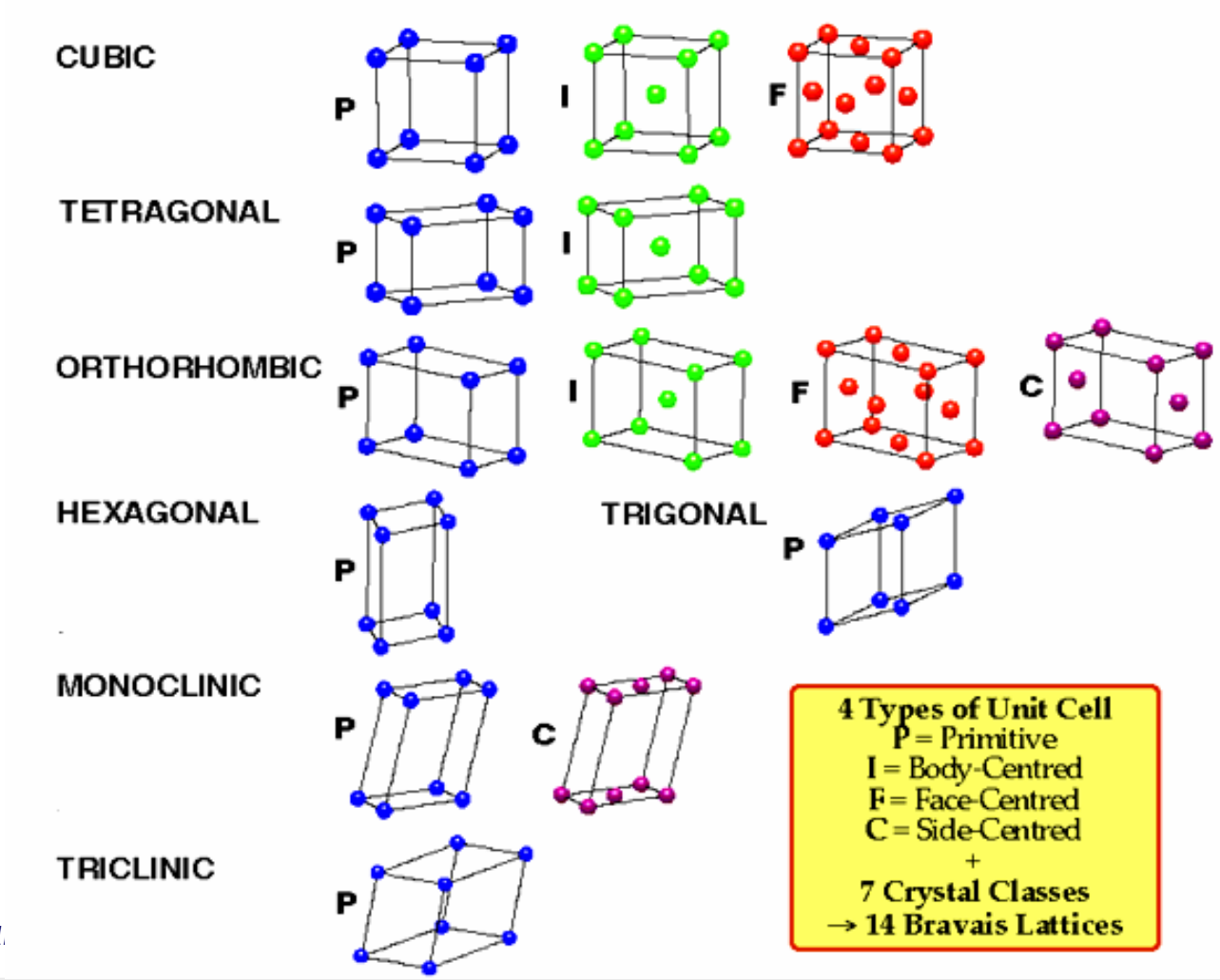
❑ Seven Crystal Systems

Crystal system	Restriction on the axial system
Triclinic	$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c \quad \alpha = \gamma = 90^\circ, \quad \beta > 90^\circ$
Orthorhombic	$a \neq b \neq c \quad \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c \quad \alpha = \beta = \gamma = 90^\circ$
Trigonal	$a = b = c \quad \alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c \quad \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ$
Cubic	$a = b = c \quad \alpha = \beta = \gamma = 90^\circ$



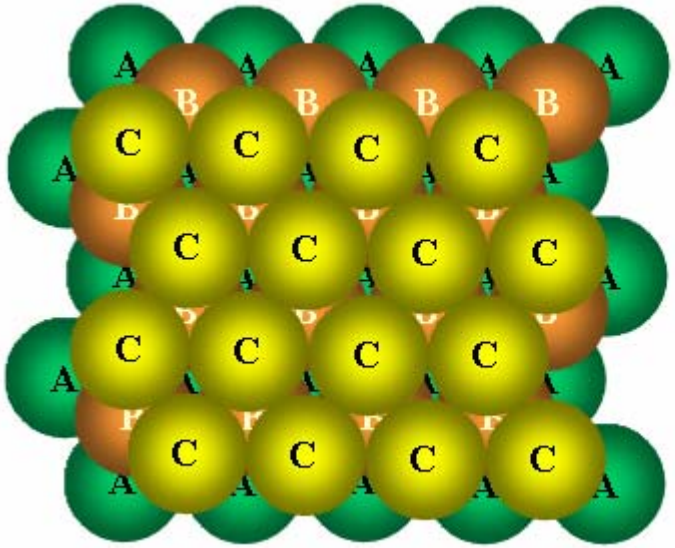
Basics- Crystal structure

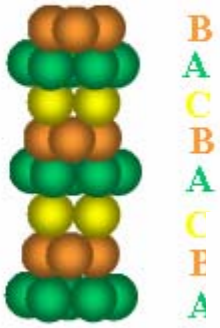
❑ 14 Bravais Lattice

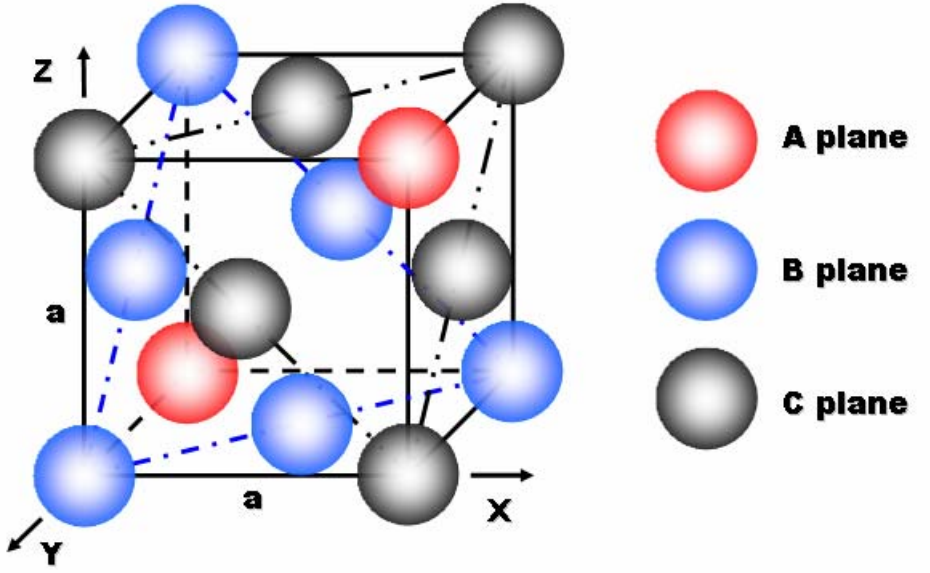


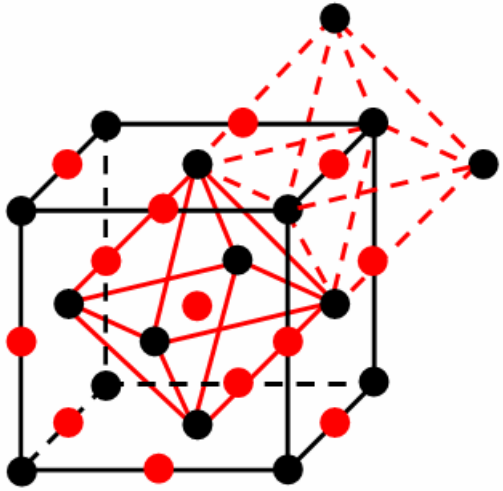
Basics- Crystal structure

❑ Close Packed Structure- FCC

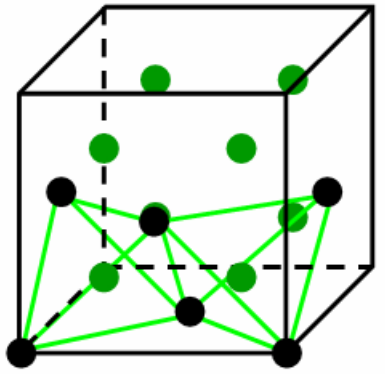








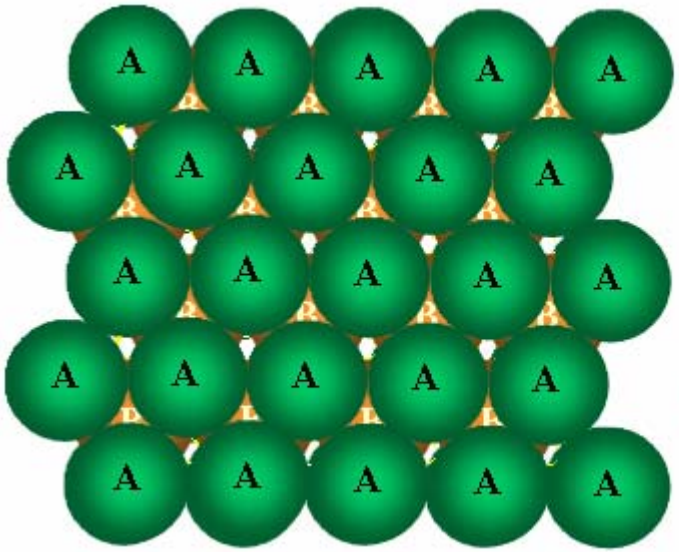
Octahedral sites ; 4

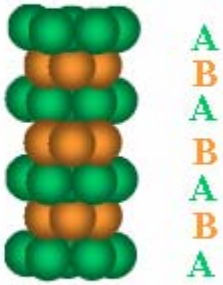


Tetrahedral sites ; 8

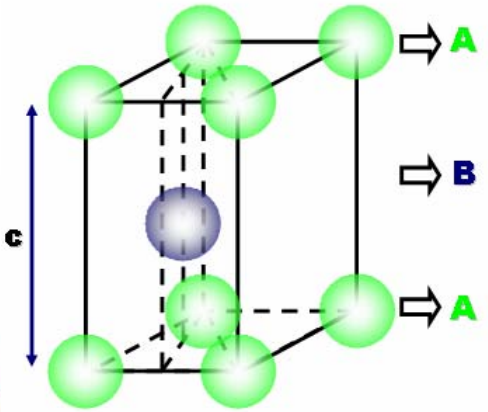
Basics- Crystal structure

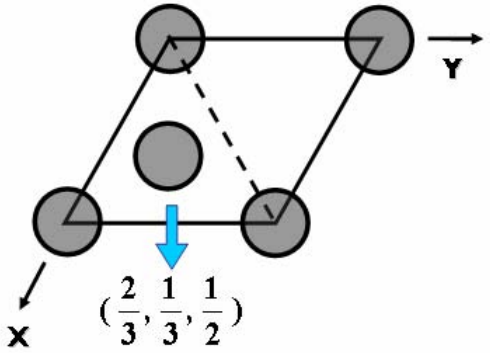
❑ Close Packed Structure- HCP

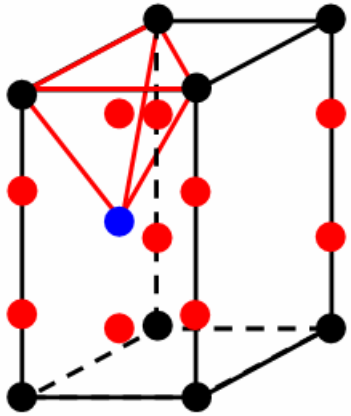


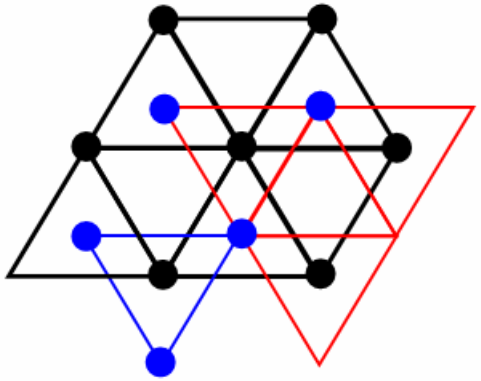


A
B
A
B
A
B
A







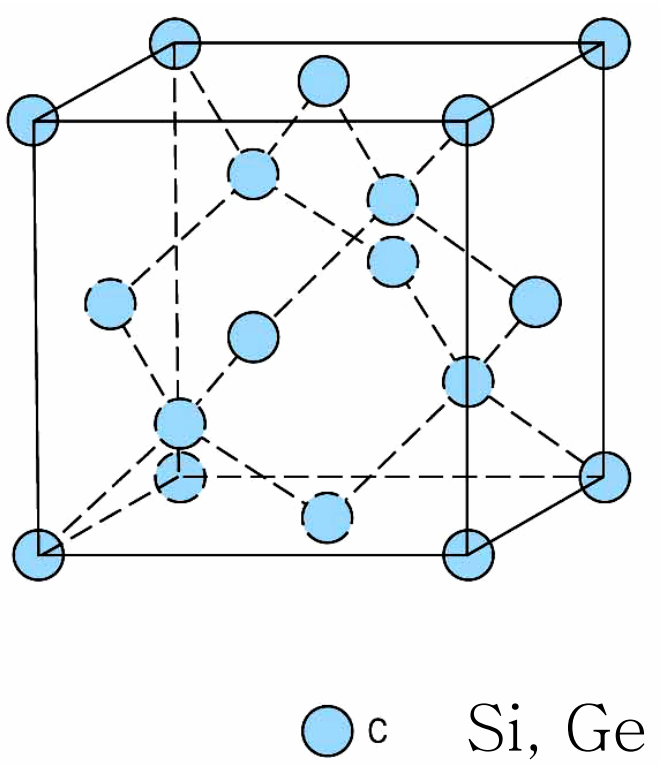


Tetrahedral sites ; 4

$(0,0,\frac{3}{8})$ $(0,0,\frac{5}{8})$ $(\frac{1}{3},\frac{2}{3},\frac{1}{8})$ $(\frac{1}{3},\frac{2}{3},\frac{7}{8})$

Basics- Crystal structure

❑ Diamond



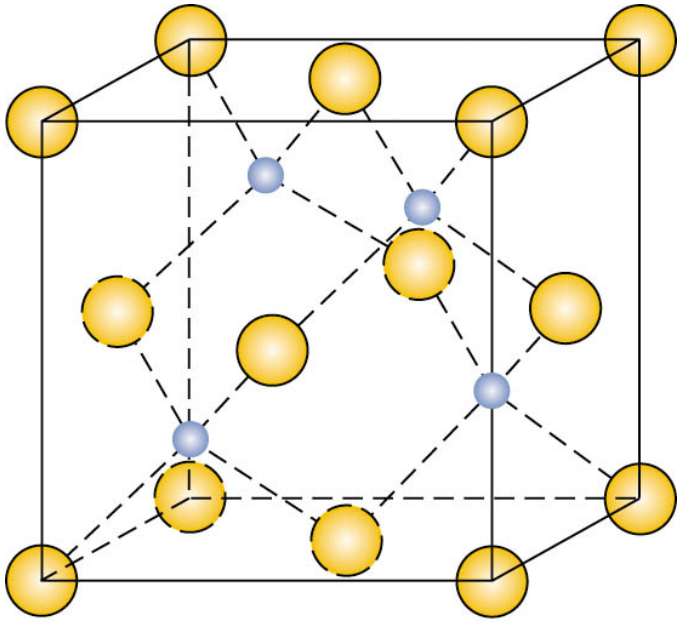
$\frac{1}{2}$ tet. sites

by cations

- 8 atoms/unit cell
- coordination #: 4:4
- FCC with two atoms per lattice point, (0,0,0) and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
- two interwoven FCC lattices

Basics- Crystal structure

❑ Zinc Blende



Zn S GaAs

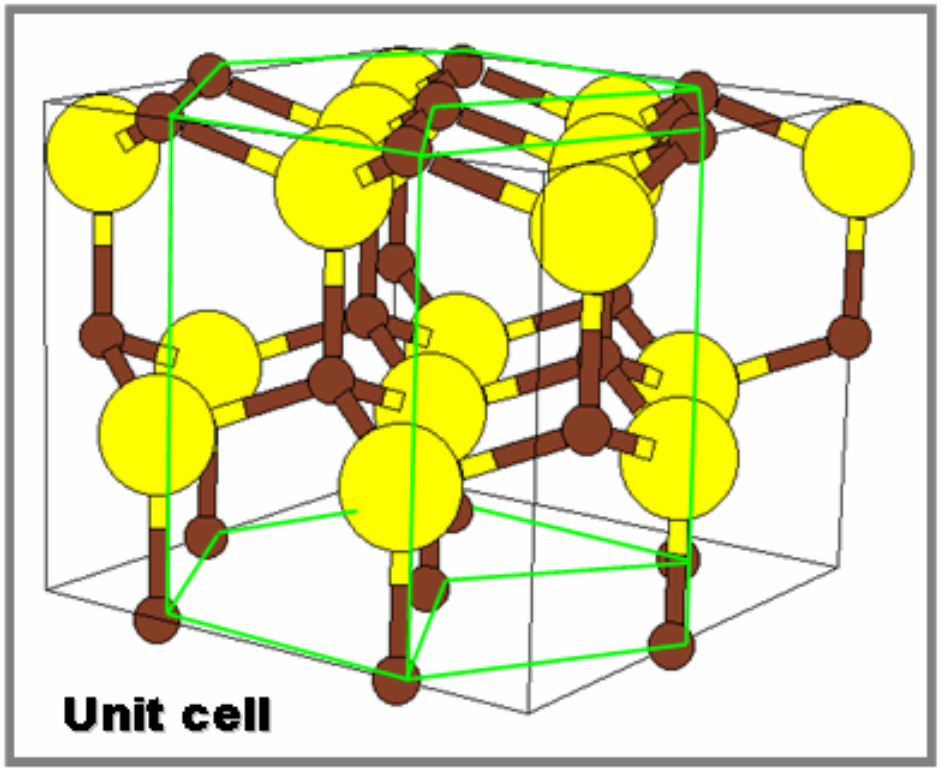
$\frac{1}{2}$ tet. sites

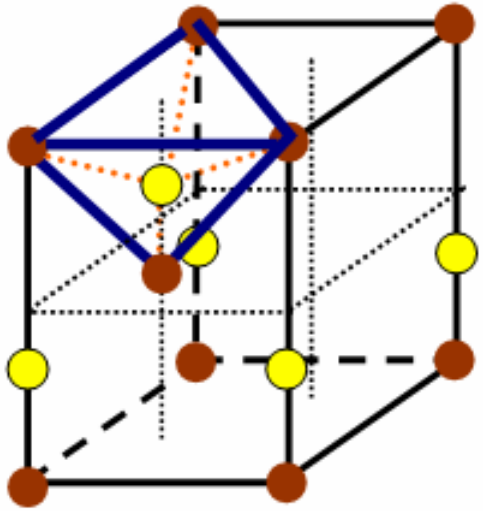
by cations

- 4 molecules/unit cell
- coordination #: 4:4
- FCC with two different atoms per lattice point, (0,0,0) $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
- two interwoven FCC lattices

Basics- Crystal structure

❑ Wutzite





HCP array of S &

Zn occupying of ½ tetrahedral sites

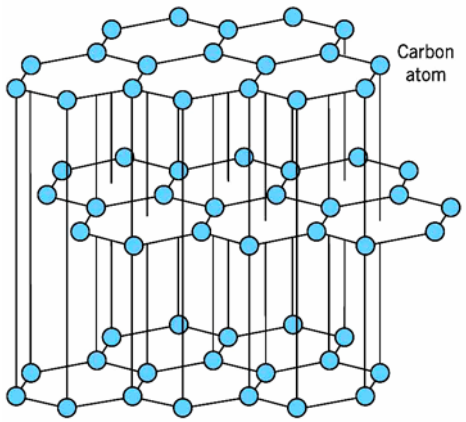
# of tetrahedral sites : 4

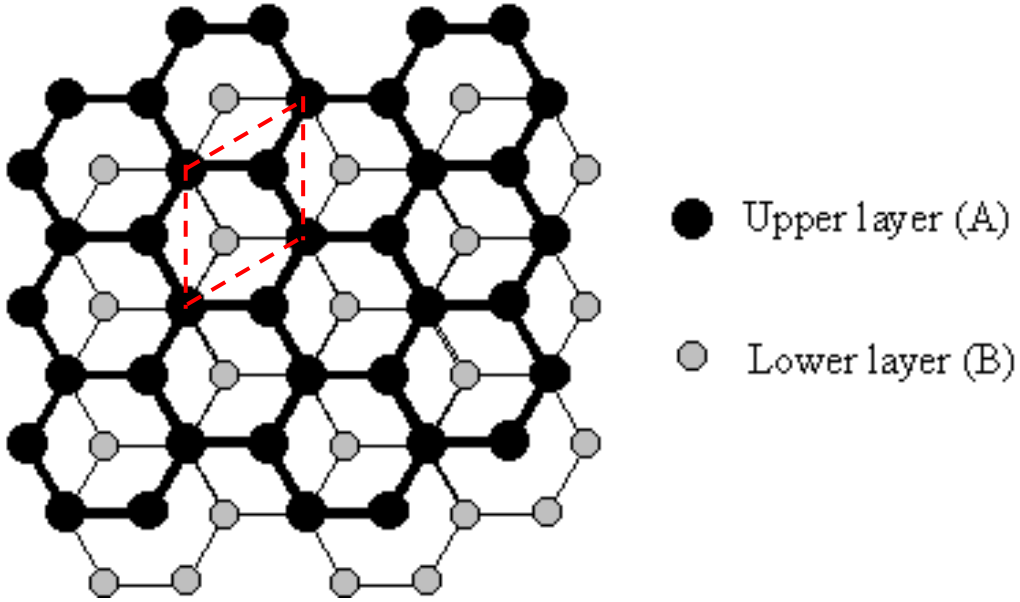
Upright 2 ; (2/3,1/3,1/8) (0,0,5/8) or
Inverted 2 ; (2/3,1/3,7/8) (0,0,3/8)

Basics- Crystal structure

❑ Carbon

- diamond
- graphite



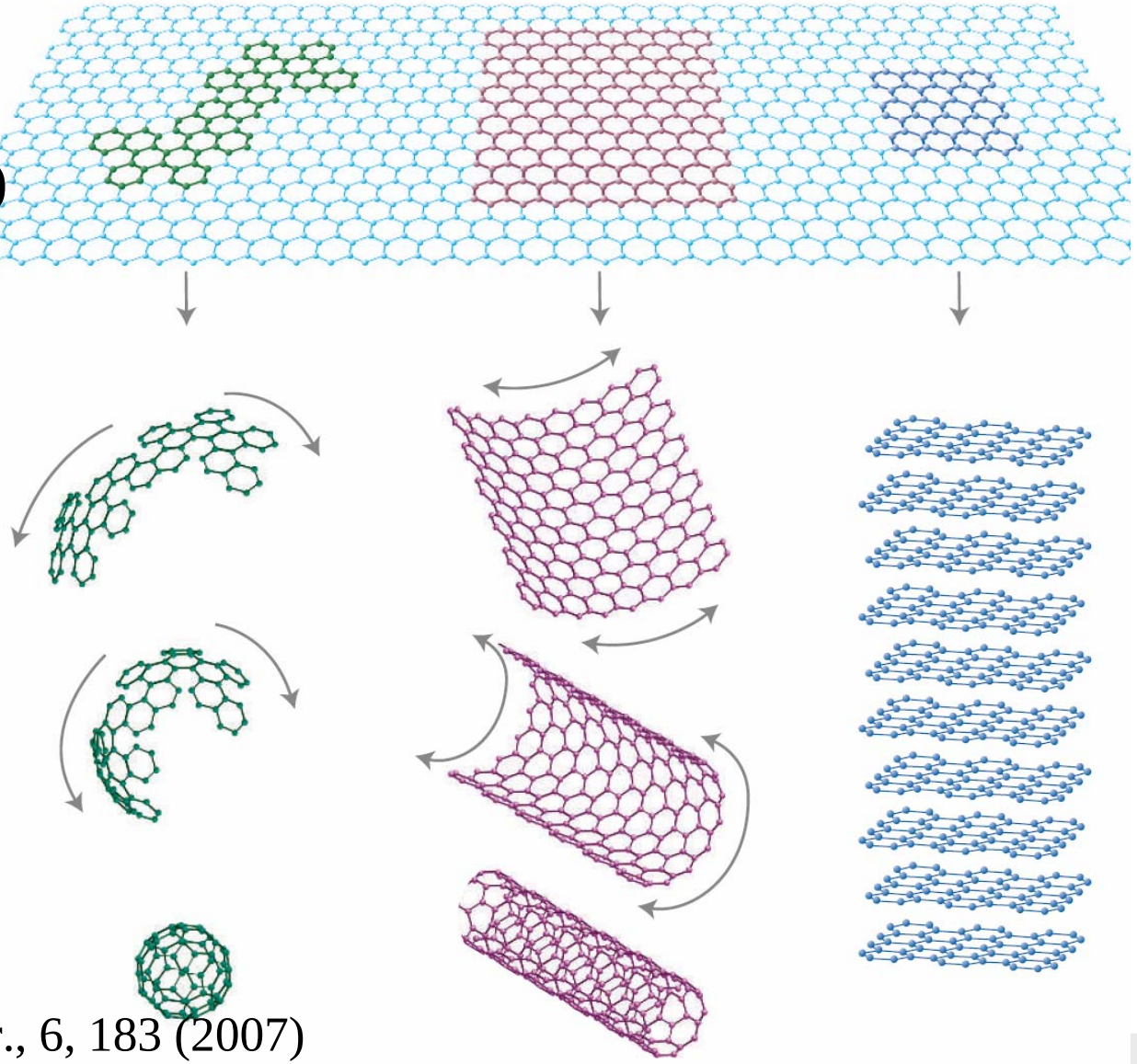


- covalent/van der Waals
- 1.48/3.4 Å
- 4 atoms/unit cell
- coordination #: 3

www.spmtips.com/products/hopg/

Basics- Crystal structure

- **Carbon**
  - **graphene**
  - **fullerenes (C_{60})**
  - **nanotube**

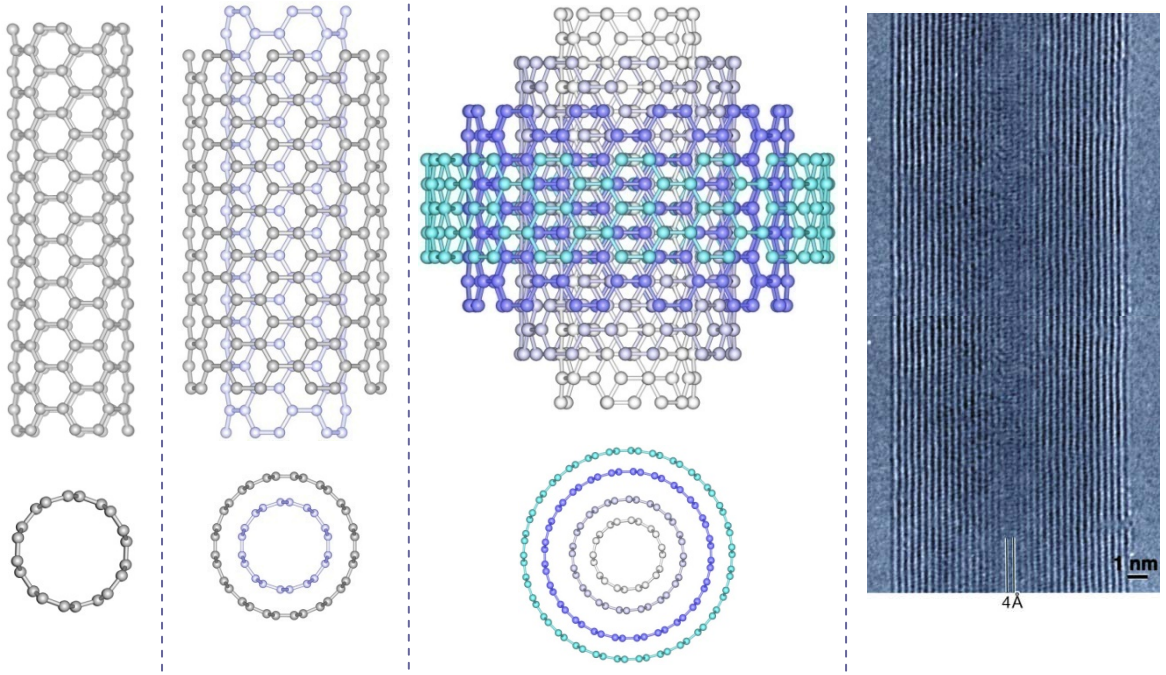


A.K.Geim, Nature Mater., 6, 183 (2007)

Basics- Crystal structure

❑ Carbon-Classification of carbon nanotubes

- Single-wall CNT, double-wall CNT, multi-wall CNTs
- Zigzag and armchair nanotubes, achiral nanotube

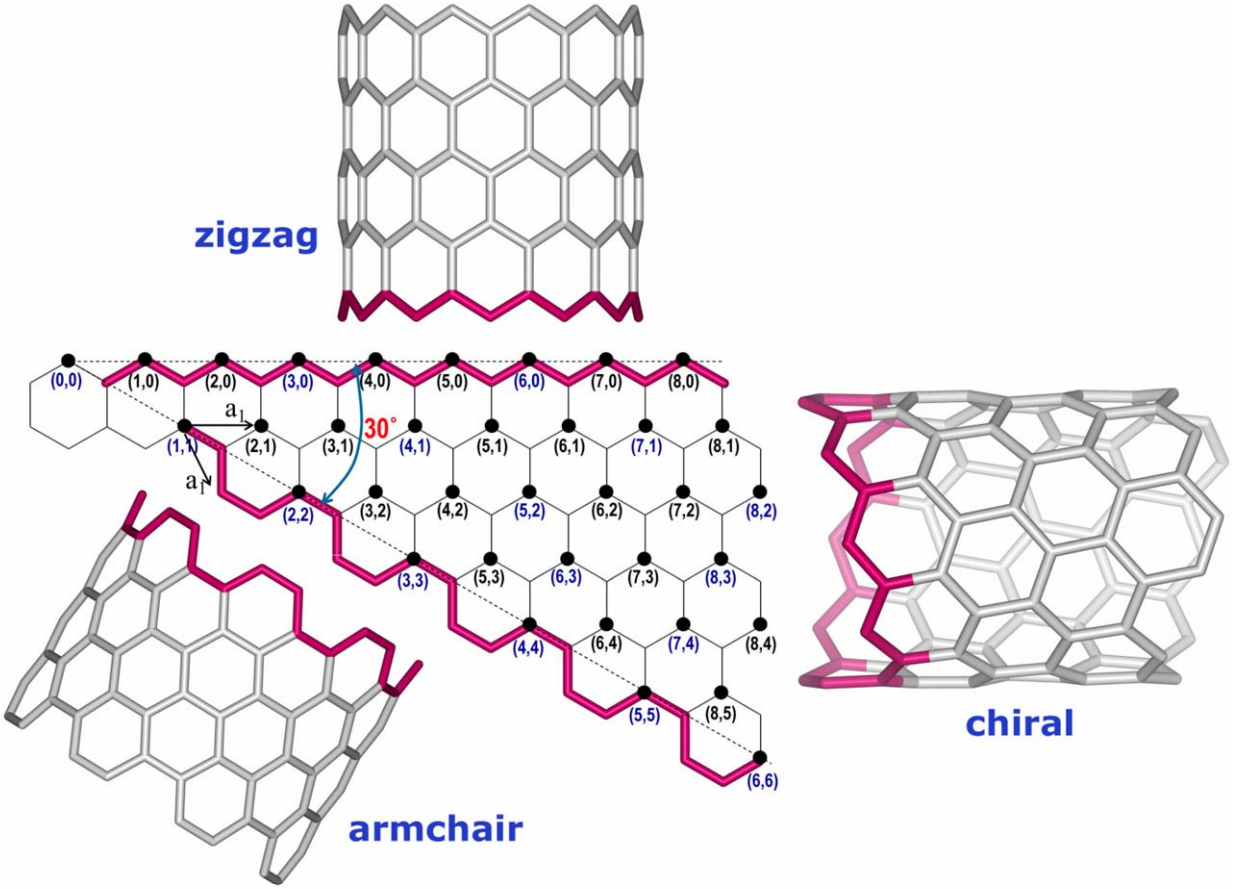


SWCNT | DWCNT | Thin-MWCNT | MWNCT

Basics- Crystal structure

❑ Carbon-Classification of carbon nanotubes

- Zigzag and armchair nanotubes, achiral nanotube



Basics- Defects

❑ Point Defect

- Vacancy
- Interstitial
- Impurities (Dopants)

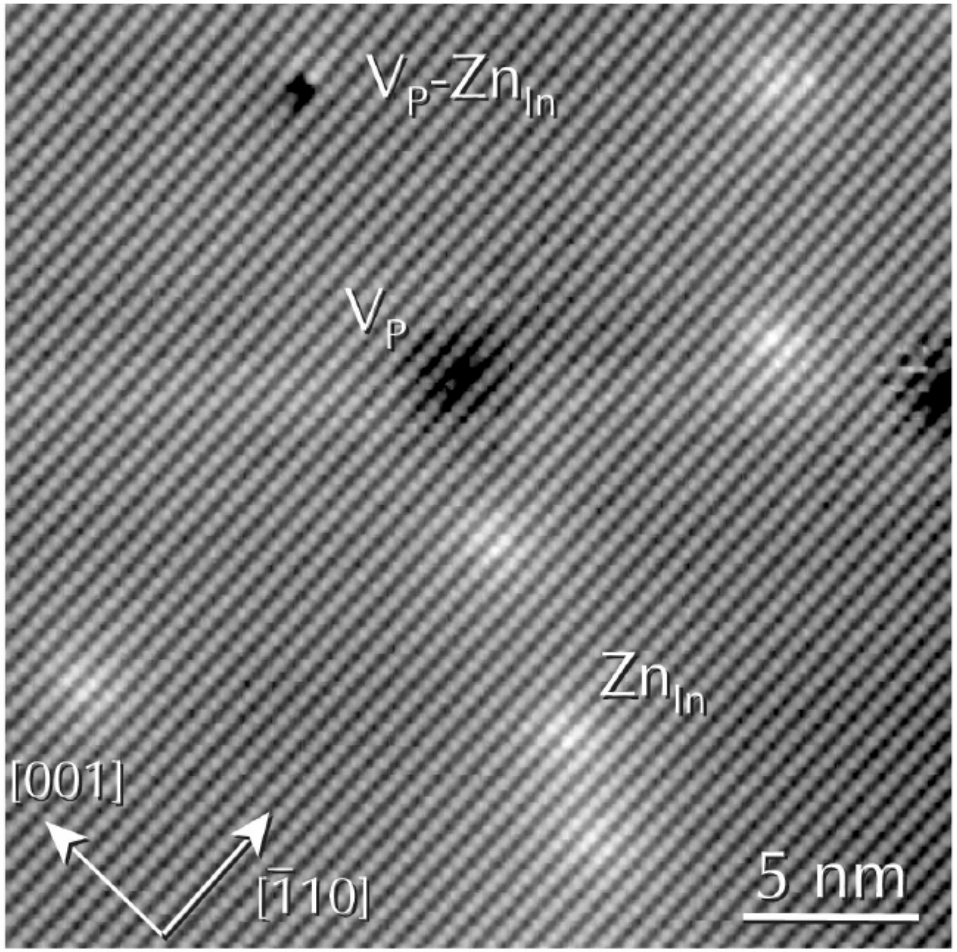


Fig. 1 Constant-current STM images of a p-doped InP(110) surface. Six Zn_{In} dopant atoms in different subsurface layers, one P vacancy (V_P), and one vacancy-dopant complex (V_P-Zn_{In}) are visible. The image shows the occupied states at -2.2 V sample voltage. (Adapted with permission from[6]. © 1996 American Physical Society.)

P. Ebert, Materials Today, 6, 36 (2003)

Basics- Defects

The value of seeing nothing

Jochen Mannhart and Darrell G. Schlom

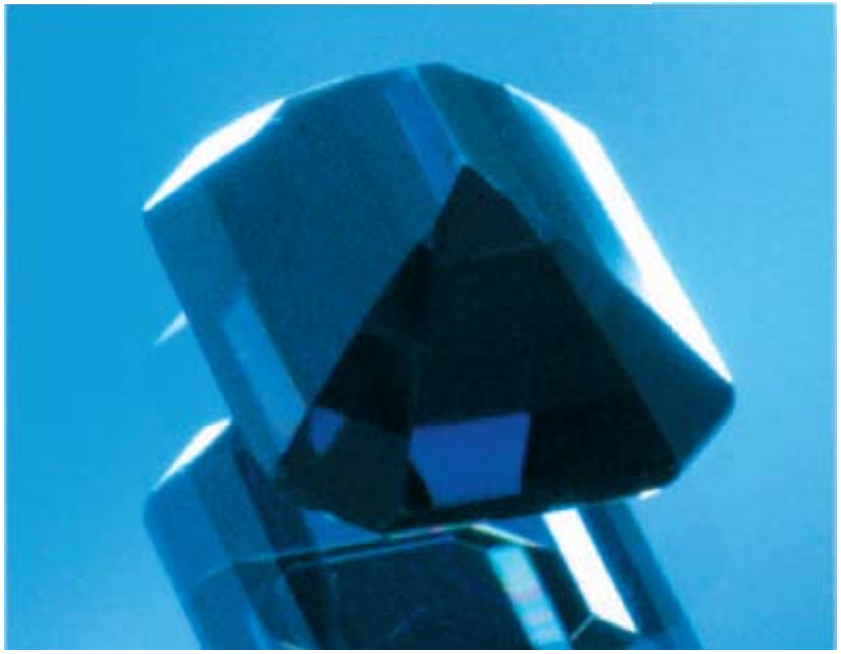


Figure 1 **Now you see it, now you don't. These micrographs of a $SrTiO_3$ crystal show the effect of removing oxygen atoms, leaving vacancies in the crystal lattice: the glistening oxidized gem (top) is transformed into a dull blue, conductive crystal (bottom).**

oxygen vacancy: $V_O^{\square\square} + 2e'$

Basics- Defects

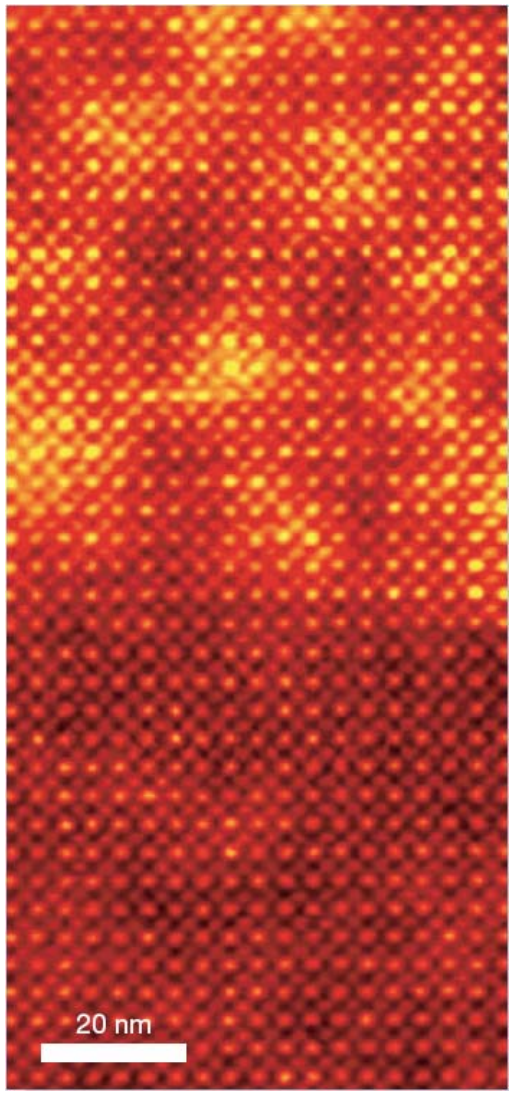
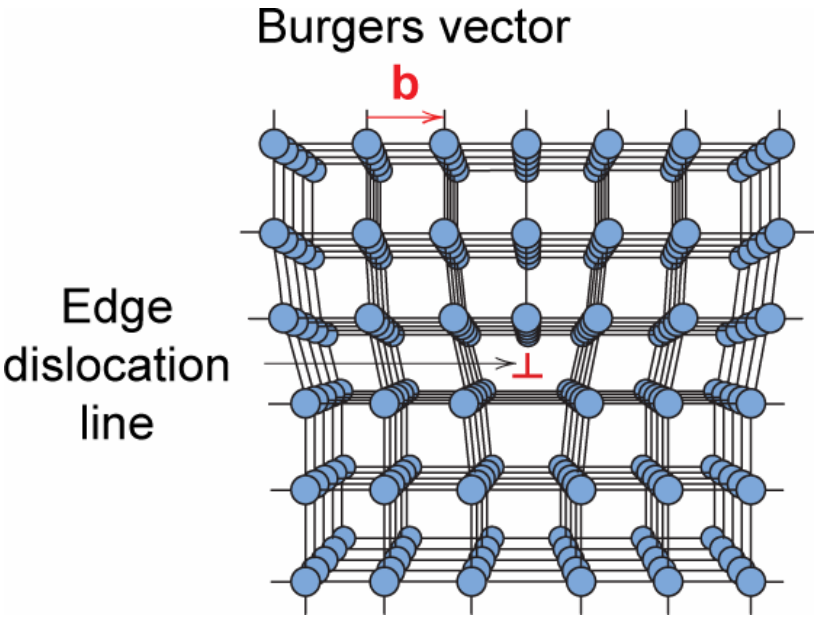


Figure 2 What a difference a layer makes. The abrupt junction between layers of $SrTiO_3$ (bottom) and $SrTiO_{3-\delta}$ (top) is clear in this image created by Muller *et al.*[3] using a scanning transmission electron microscope. Each bright-orange blob is a cluster of oxygen vacancies.

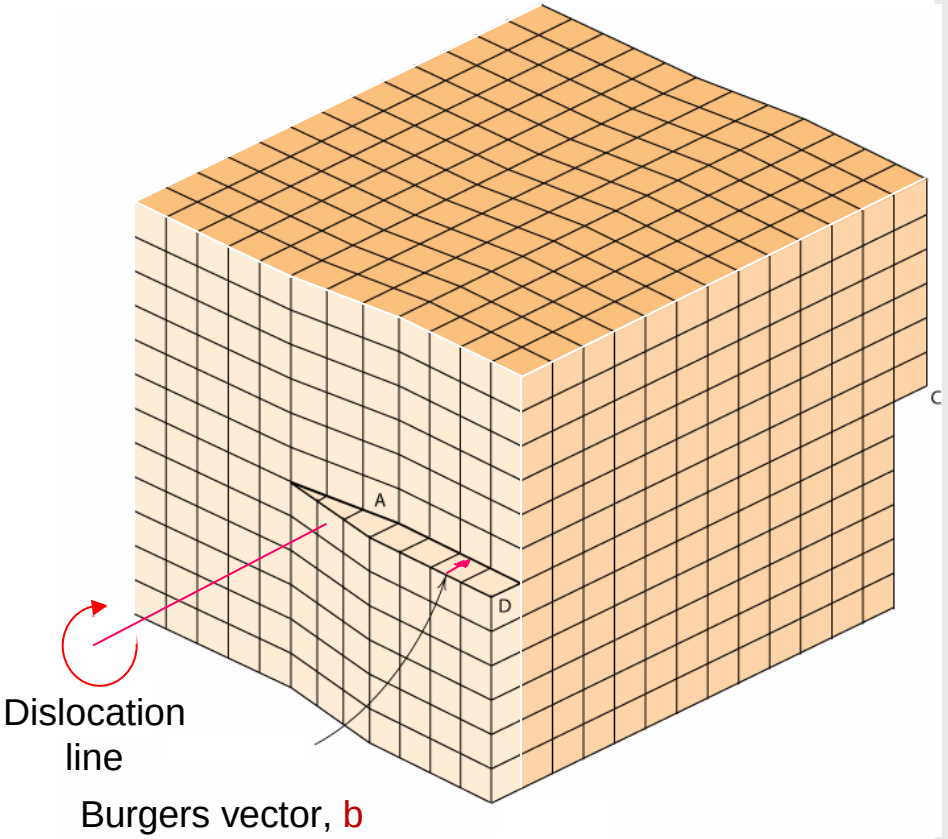
Basics- Defects

❑ Line Defect (dislocation)

- edge



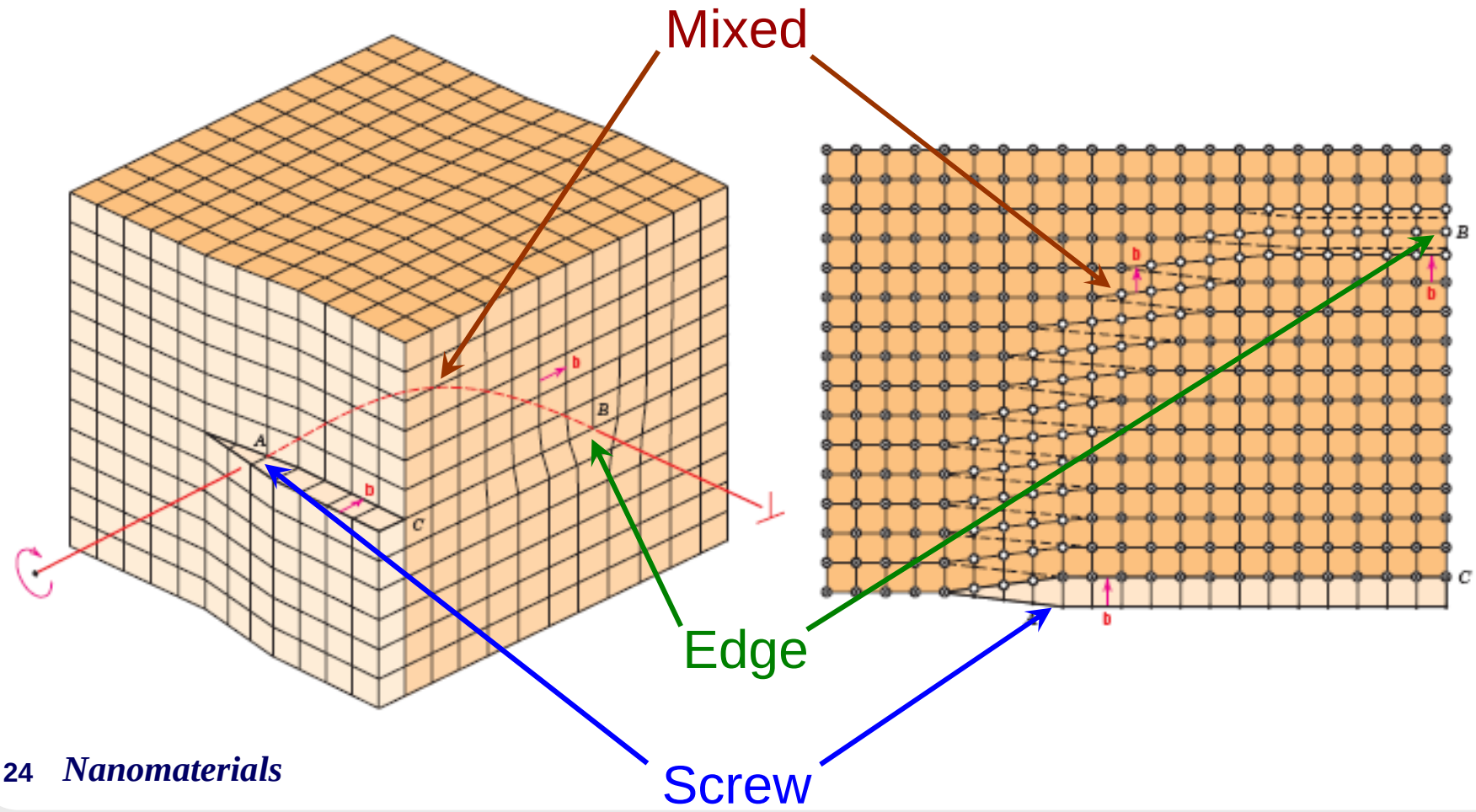
- screw



Basics- Defects

❑ Line Defect (dislocation)

- mixed

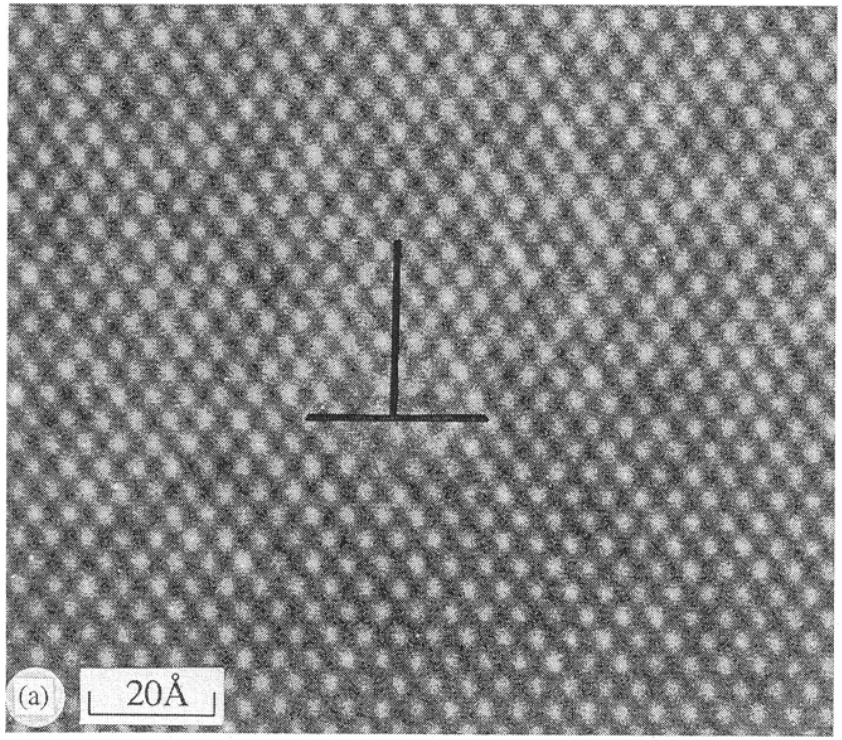


Basics- Defects

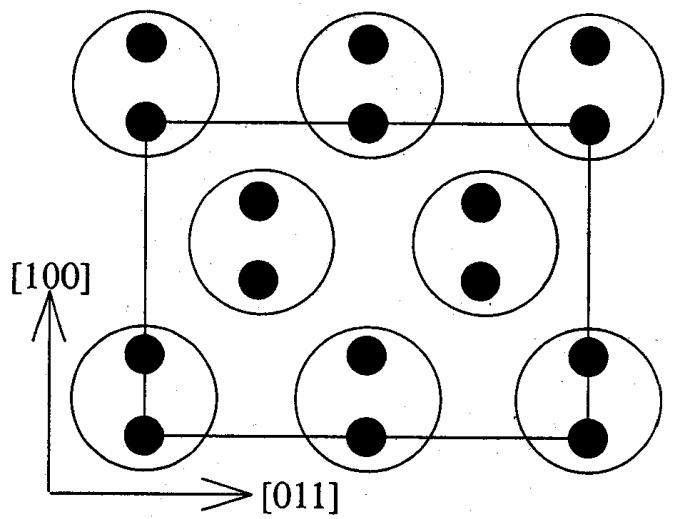
❑ Line Defect (dislocation)

- observation of dislocation

high resolution transmission electron microscope image electron beam incident along an <011> zone of Si



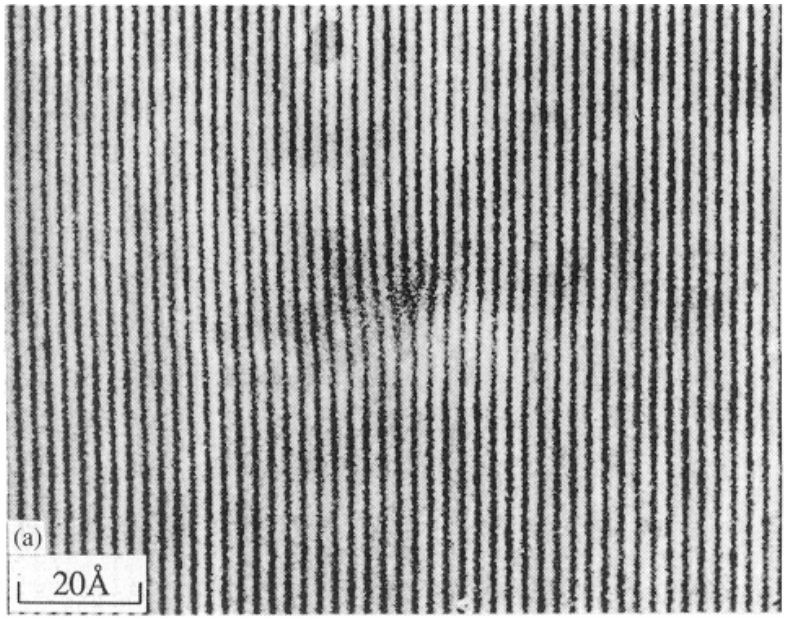
$\vec{b} = \frac{1}{2}[011]$



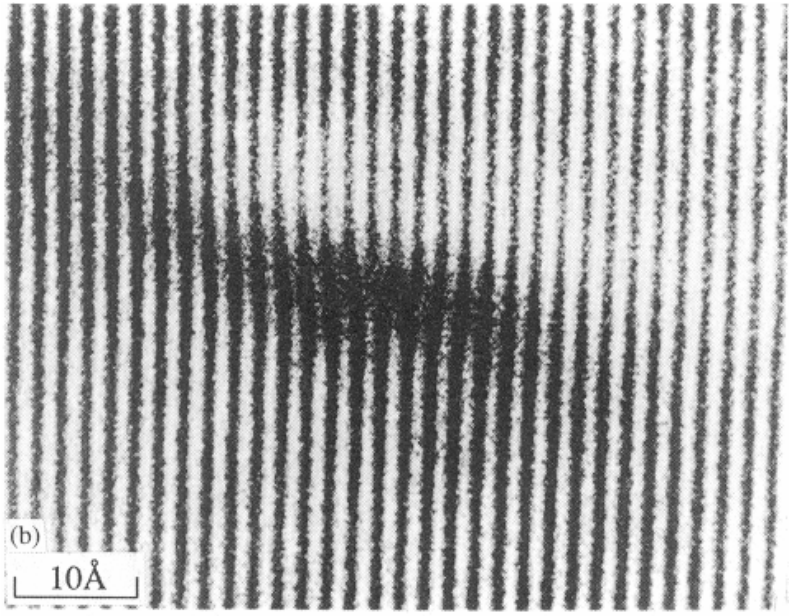
Basics- Defects

❑ Line Defect (dislocation)

- lattice fringe image of dislocation



narrow edge dislocation

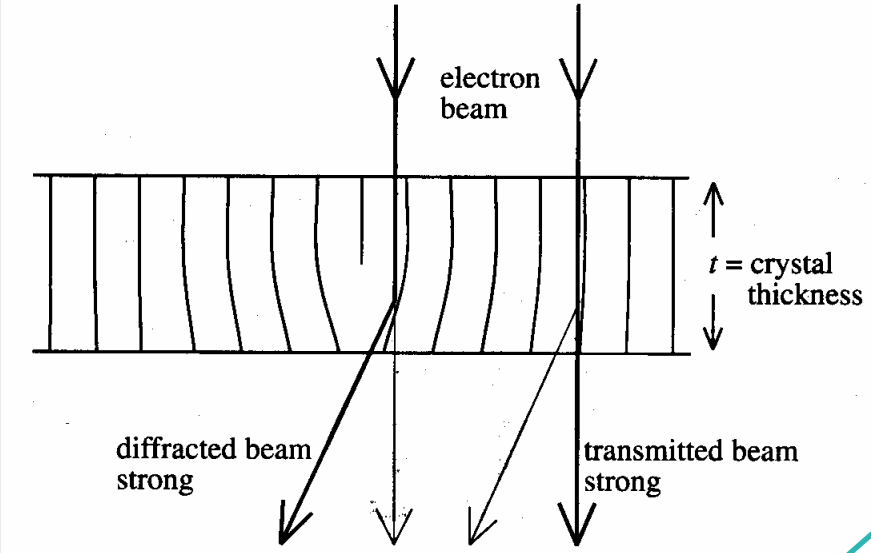


wide edge dislocation

Basics- Defects

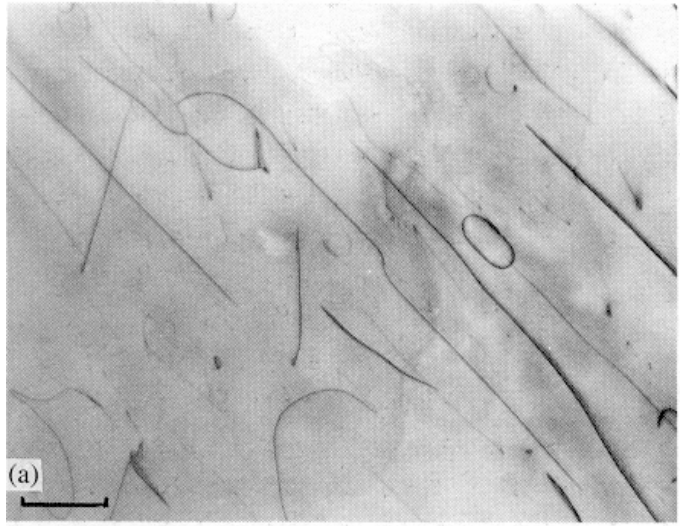
❑ Line Defect (dislocation)

- diffraction contrast



transmitted beam-bright field image-dislocation-dark

diffracted beam-dark field image -dislocation-bright



Basics- Surface

❑ Surface Energy

$$dG = -SdT + VdP + \sum_i \mu_i dn_i + \gamma dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{P,T,n_i} \quad : \text{ surface energy } [\mathrm{Jm}^{-2}]$$

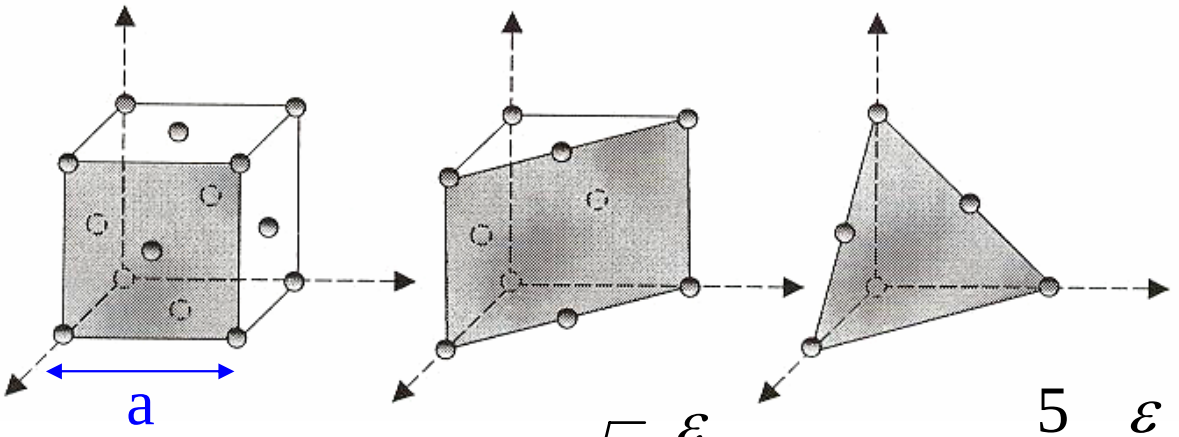
❑ Estimation of surface energy

$\gamma = \frac{1}{2} N_b \varepsilon \rho_a$ N_b : # of broken bonds, ρ_a : surface atomic density

❑ Anisotropy

FCC

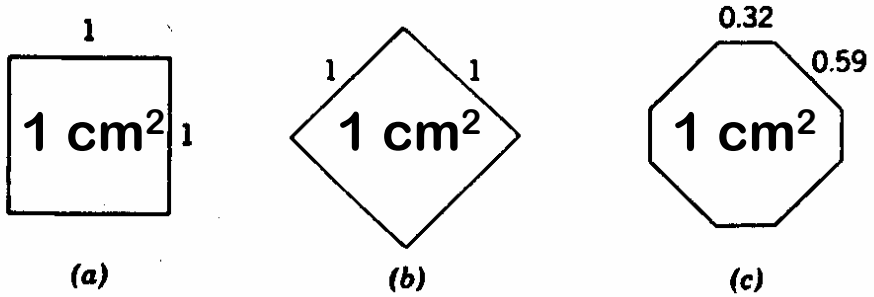
$$\gamma_{\{100\}} = \frac{1}{2}\frac{2}{a^2}4\varepsilon = \frac{4\varepsilon}{a^2}$$



$$\gamma_{\{111\}} = 2\sqrt{3}\frac{\varepsilon}{a^2} \qquad \gamma_{\{110\}} = \frac{5}{\sqrt{2}}\frac{\varepsilon}{a^2}$$

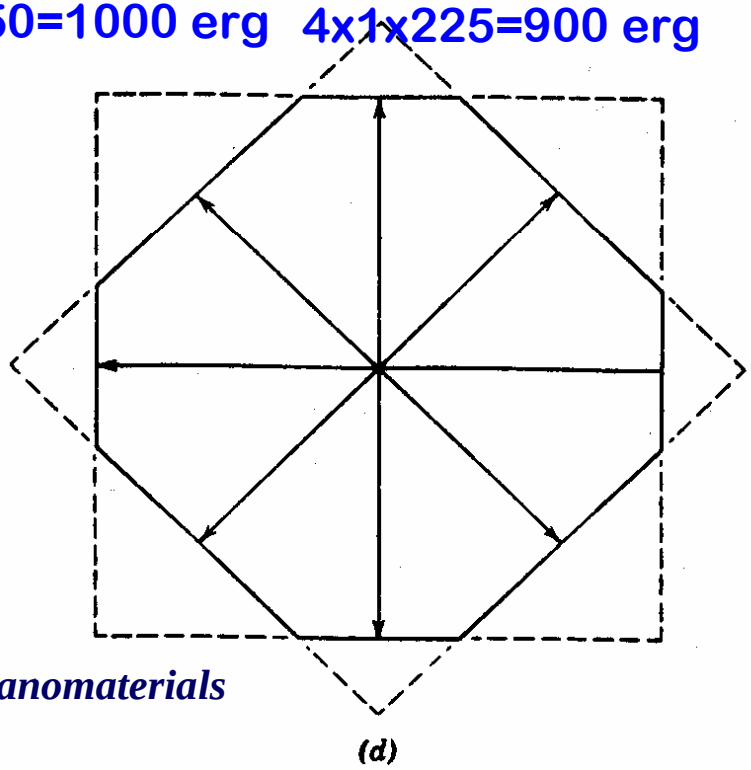
Basics- Surface

❑ Anisotropy of Surface Energy



4x1x250=1000 erg 4x1x225=900 erg

(4x0.32x250)+(4x0.59x225)
=851 erg



❑ Equilibrium shape

- total surface energy minimization

A.W. Adamson, Physical Chemistry of Surfaces (1982)

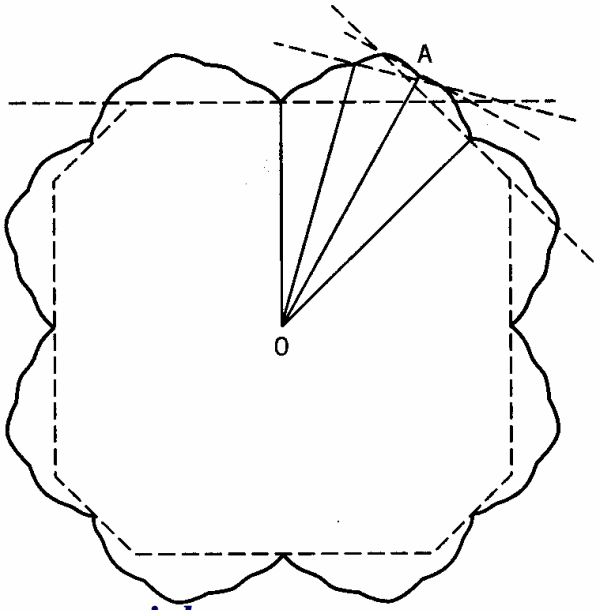
Basics- Surface

❑ Wulff plot

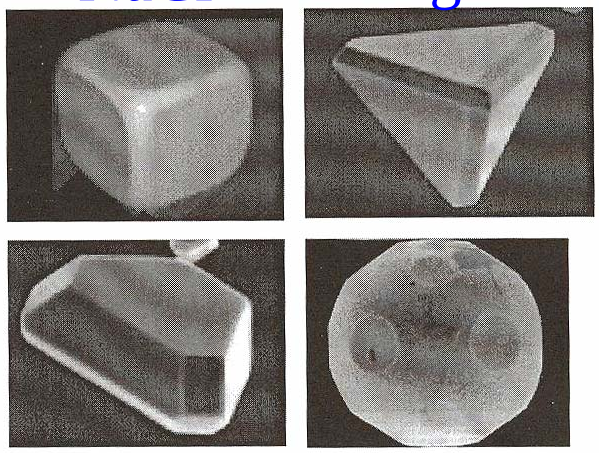
- γ-plot- curved outer line

$$\gamma_i = Ch_i$$

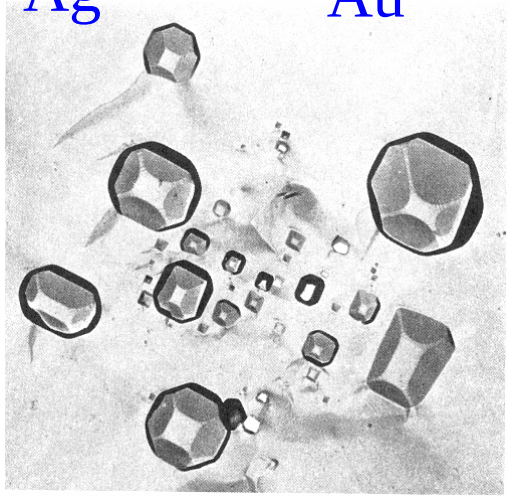
- crystal shape- inner envelope



NaCl Ag



Ag Au



Negative crystal UO_2

G. CaO, Nanostructures & Nanomaterials (2004)

Y.-M Chiang, Physical Ceramics (1997)

Basics- Surface

❑ Surface Energy

Table 5.2 Measured Surface Energies of Various Materials in Vacuum or Inert Atmospheres

	Temperature (°C)	Surface Energy (ergs/cm²)
Solids		
Copper	1080	1430
Silver	750	1140
Iron (γ phase)	1350	2100
Platinum	1300	2200
Al_2O_3	1850	905
TiC	1100	1190
0.20 Na_2O–0.80 SiO_2	1350	280
NaCl (100)	25	300
LiF (100)	−196 (77 K)	340
CaF_2 (111)	−196 (77 K)	500
BaF_2 (111)	−196 (77 K)	280
$CaCO_3$ (1010)	25	230
MgO (100)	−196 (77 K)	1500
Al_2O_3 $(10\bar{1}2)$	25	6000
$(10\bar{1}0)$	25	7300
(0001)	25	>40,000
$MgAl_2O_4$ (100)	25	3000
(111)	25	5000
SiC $(11\bar{2}0)$	25	20,000
Si (111)	—	1230
Ge (111)	—	1060

❑ Surface Energy vs. size

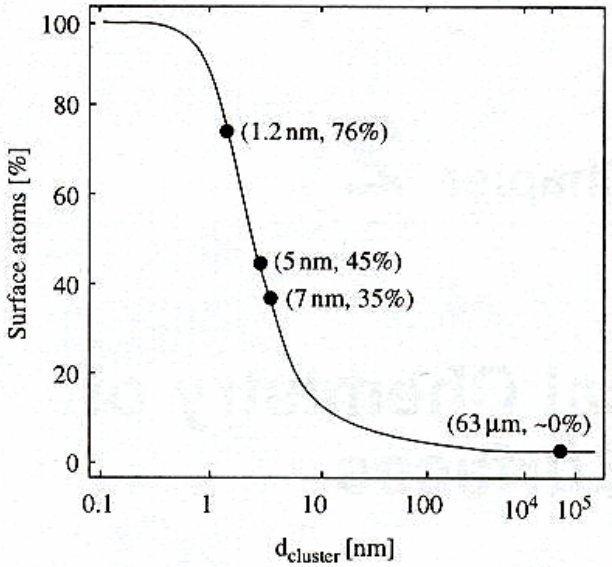


Table 2.1. Variation of surface energy with particle size.[22]

Side (cm)	*Total surface area* (cm²)	*Total edge* (cm)	*Surface energy* (J/g)	*Edge energy* (J/g)
0.77	3.6	9.3	7.2×10^{-5}	2.8×10^{-12}
0.1	28	550	5.6×10^{-4}	1.7×10^{-10}
0.01	280	5.5×10^{4}	5.6×10^{-3}	1.7×10^{-8}
0.001	2.8×10^{3}	5.5×10^{6}	5.6×10^{-2}	1.7×10^{-6}
10^{-4} (1 μm)	2.8×10^{4}	5.5×10^{8}	0.56	1.7×10^{-4}
10^{-7} (1 nm)	2.8×10^{7}	5.5×10^{14}	560	170

Y.-M Chiang, Physical Ceramics (1997) G. CaO, Nanostructures & Nanomaterials (2004)

Basics- Surface

❑ Curved Surface

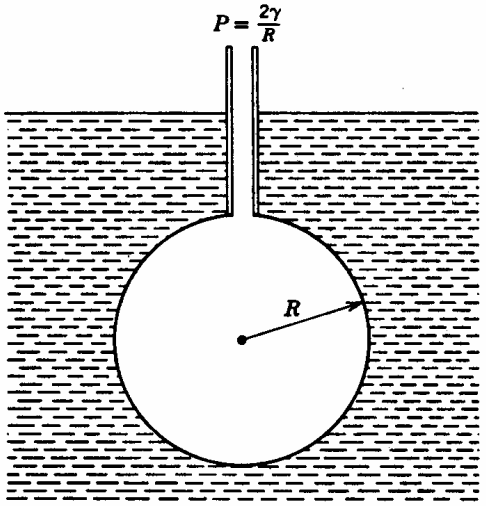
$$\Delta P dV = \gamma dA$$

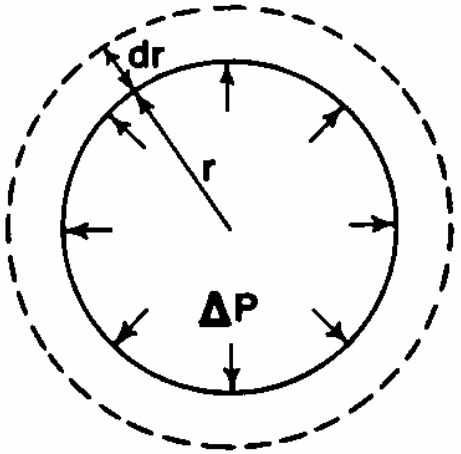
$dV = 4\pi r^2 dr \quad dA = 8\pi r dr$ for sphere

$$\Delta P = \gamma \frac{dA}{dV} = \frac{2\gamma}{r}$$

Laplace equation $\Delta P = \gamma(\frac{1}{r_1} + \frac{1}{r_2})$

r_1, r_2: principal radii of curvature





Basics- Surface

❑ Curved Surface

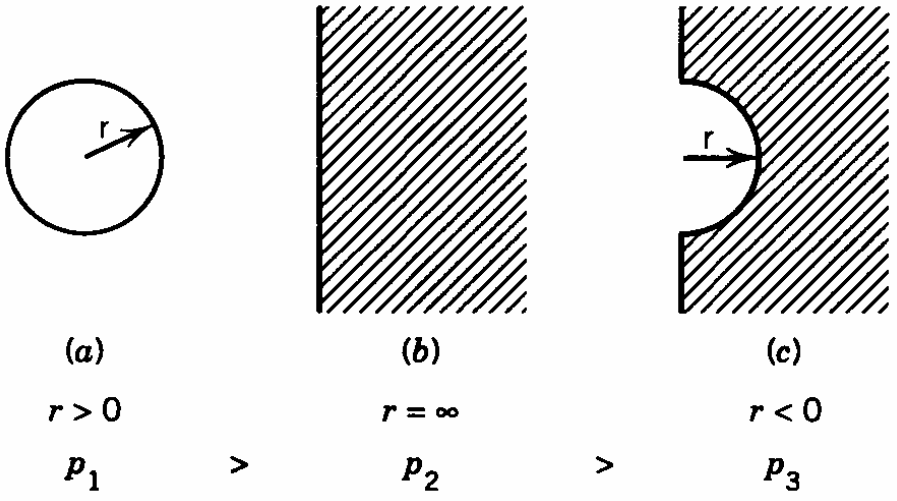
- pressure difference across a curved surface → a change in solubility or vapor pressure
- at constant T, P, n_i, transfer one mole from plat to curved

$$\mu = \mu_o + RT \ln a = \mu_o + RT \ln c = \mu_o + RT \ln P$$

$$\Delta\mu = RT \ln \frac{P(r)}{P(r=\infty)} = \gamma dA = \gamma 8\pi r dr,\ V_m = \frac{4}{3}\pi r^3$$

$$P(r) = P(r=\infty) \exp[\frac{2\gamma V_m}{RT}(\frac{1}{r})]$$

: Kelvin equation



Basics- Surface

❑ Solubility

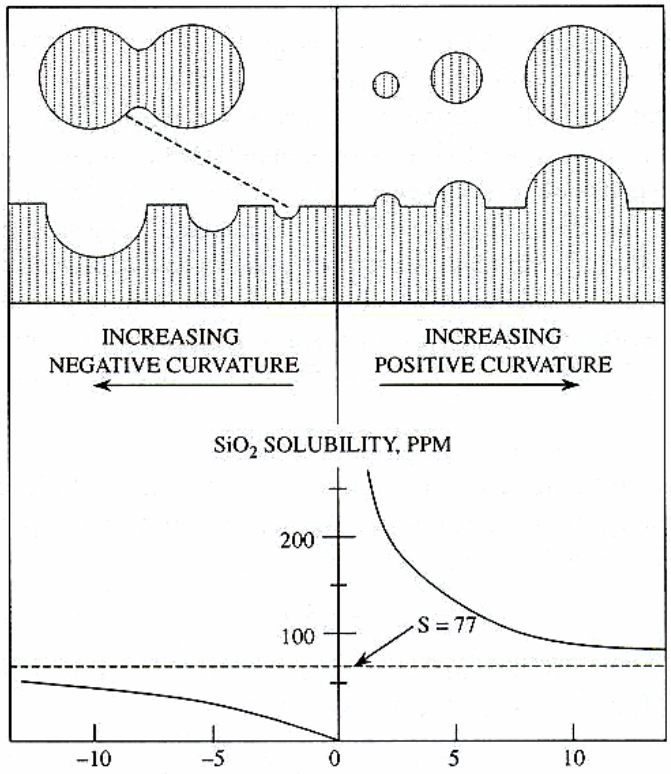


Fig. 2.11. Variation in solubility of silica with radius of curvature of surface. The positive radii of curvature are shown in cross-section as particles and projections from a planar surface; negative radii are shown as depressions or holes in the surface, and in the crevice between two particles. [R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.]

❑ Vapor Pressure

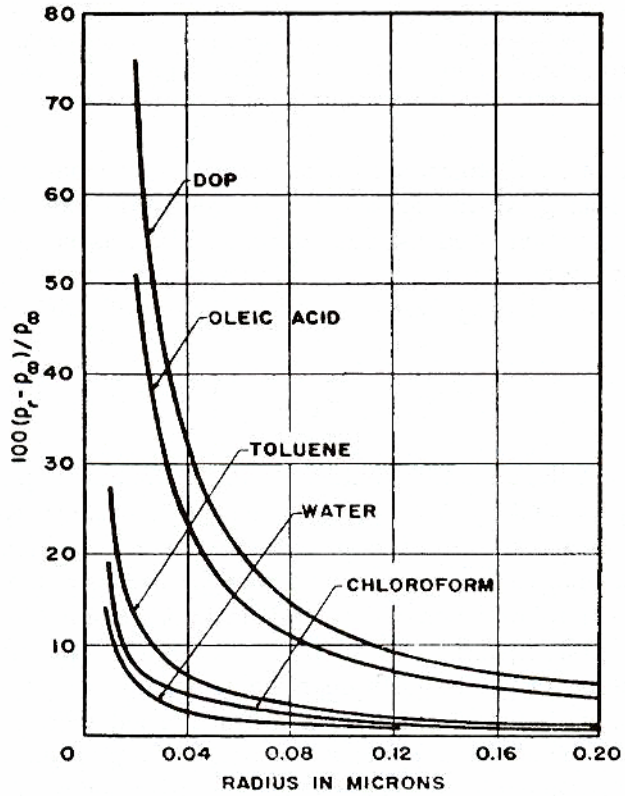


Fig. 2.12. Vapor pressure of a number of liquids as a function of droplet radius. [V.K. La Mer and R. Gruen, *Trans. Faraday Soc.* **48**, 410 (1952).]

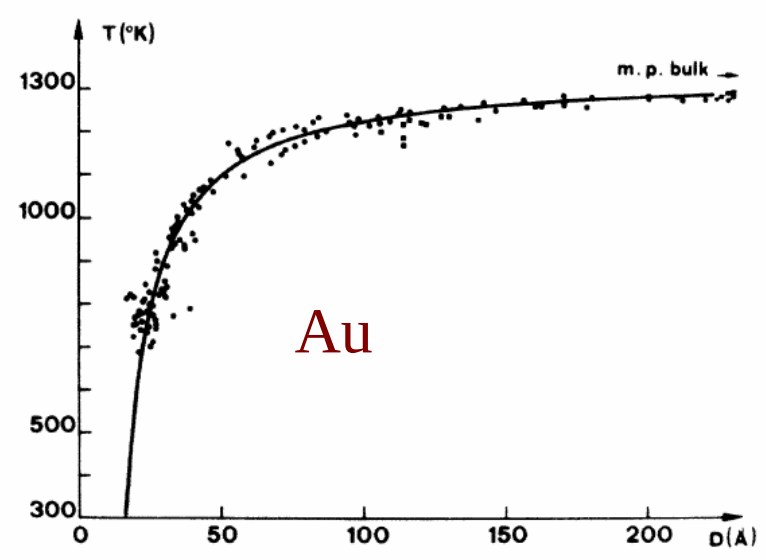
G. CaO, Nanostructures & Nanomaterials (2004)

Basics- Surface

❑ Melting Point

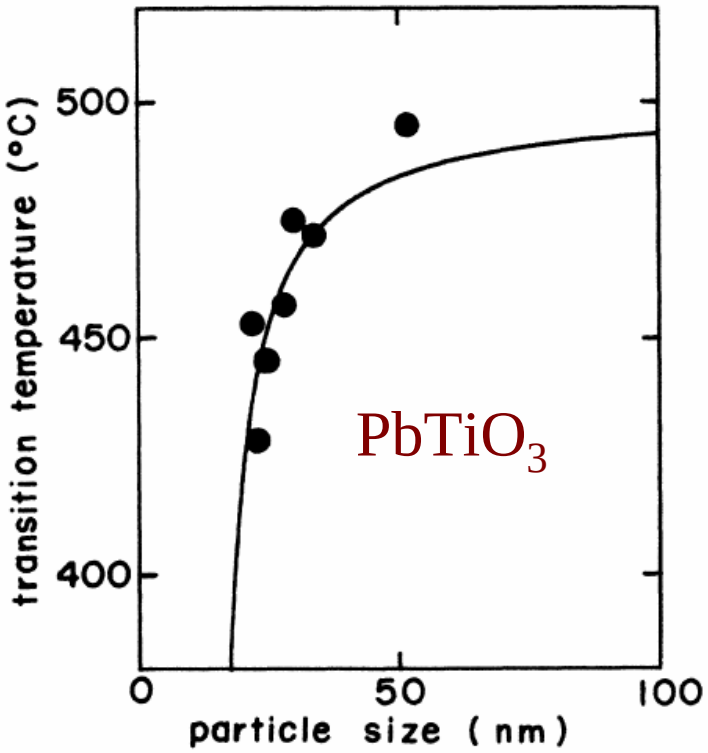
- melting point ↓ ⇔ particle size ↓

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



❑ Transition Temperature

$$T_c = 500 - 588.5/(D - 12.6)\ (°C)$$



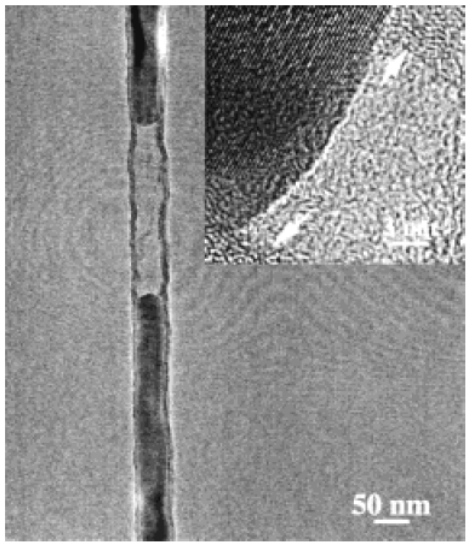
Ph. Buffat, Phys. Rew., A13 (1976) 2287

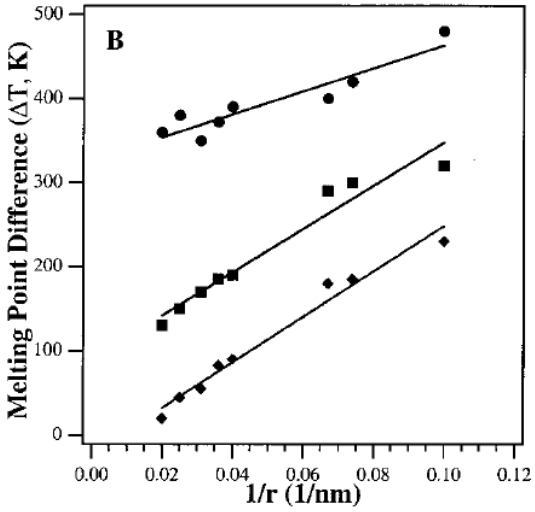
K. Ishikawa, Phys. Rew., B37 (1976) 5852

Basics- Surface

❑ Melting Point of nano-wire

- Ge nano-wire





- Rayleigh instability

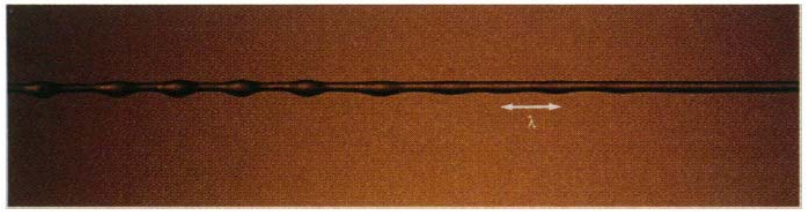


Fig. 1. Film of honey on a fishing line of radius b = 140 μm. The film is made by drawing the thread horizontally out of a large drop of honey. The instability is fully developed on the left, but still not on the right where the optimal wavelength λ has not yet been selected.

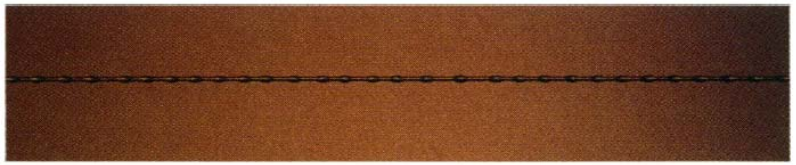


Fig. 2. Drops resulting from a thin film of silicone oil coating a nylon fiber (radius b = 80 μm). The spacing between the droplets is regular and is about $10b$ (as shown by Rayleigh) for thin films on fibers.

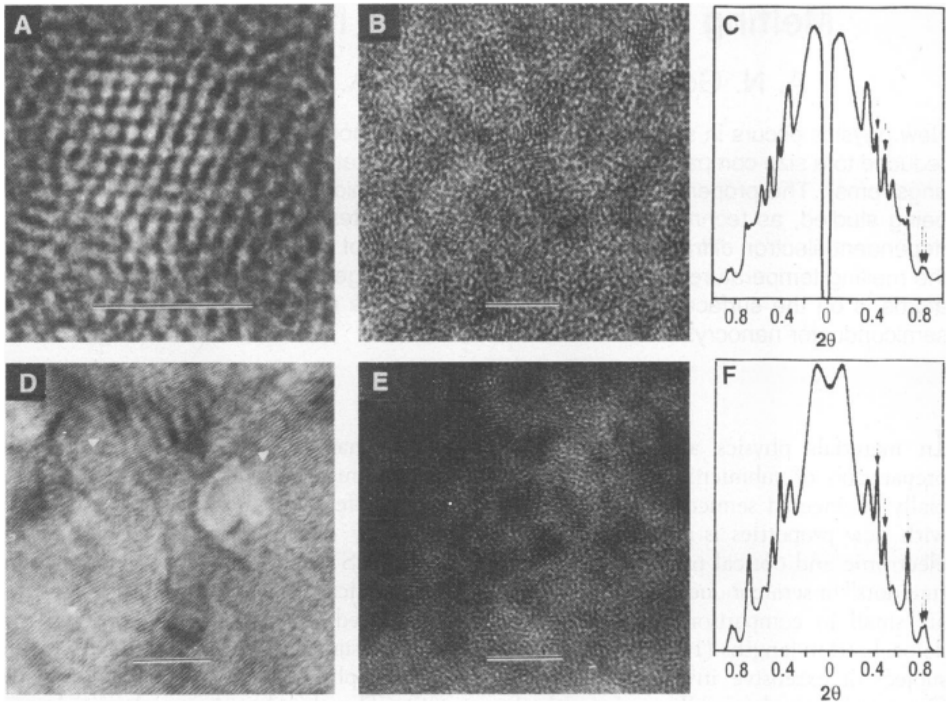
Y. Wu, Adv. Mater., 13 (2001) 520

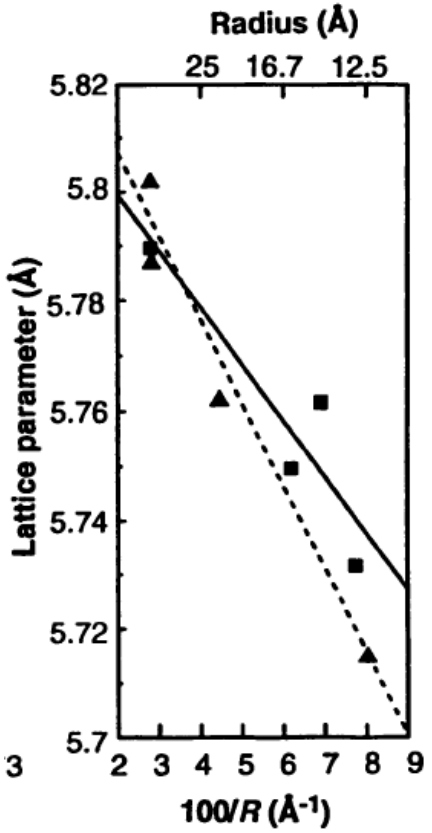
D. Quere, Science, 249 (1990)1256.

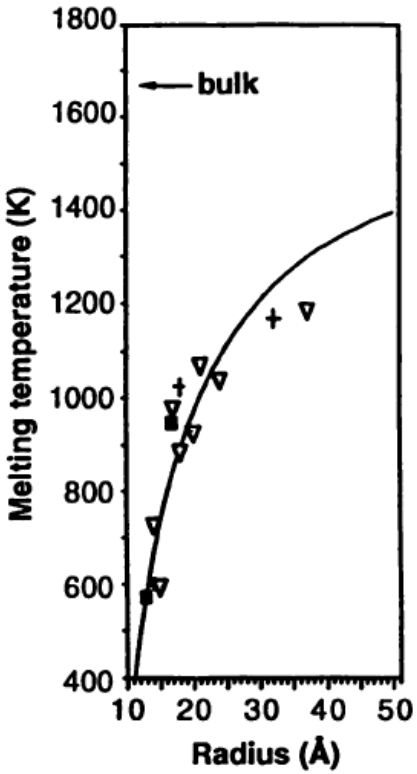
Basics- Surface

❑ Melting Point & Lattice Parameter

- CdS nanocrystal





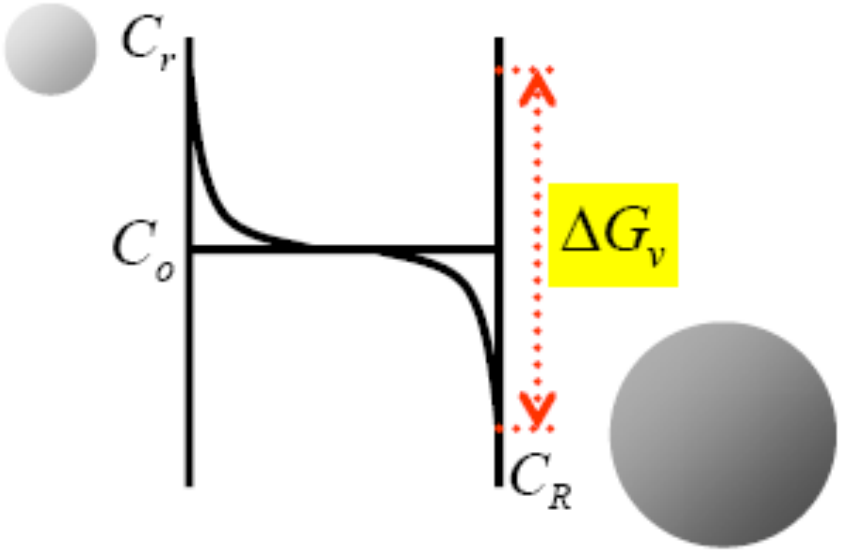


A.N.Goldenstein, Science, 256 (1992)1425.

Basics- Surface

❑ Ostwald Ripening

$$C_r = C_o\left(1+\frac{2\sigma V_m}{RT}\frac{1}{r}\right)$$



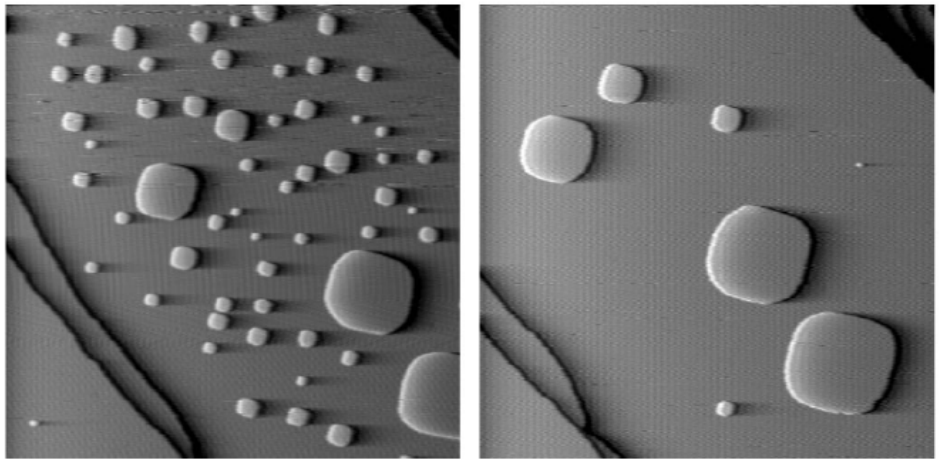


FIG. 2. Two 300 nm × 300 nm STM images, separated in time by 20 000 s, showing island ripening on Cu(001) at 343 K.

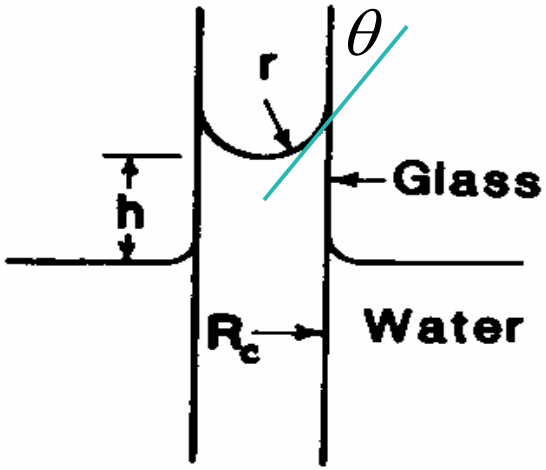
J. B. Hannon, Phys. Rev. Lett., 79 (1997) 2506

Basics- Surface

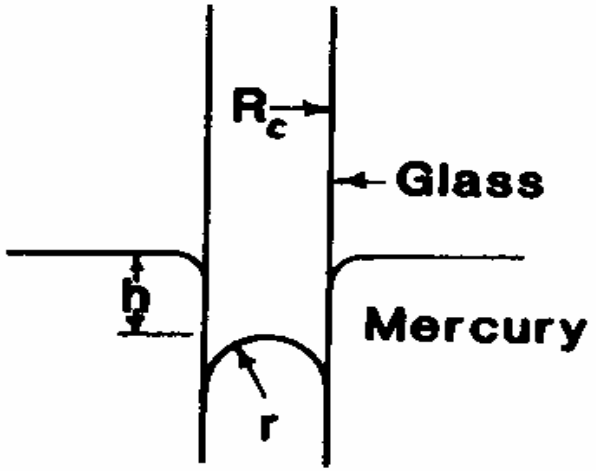
❑ Capillary Rise

$$\Delta P = \gamma\left(\frac{2}{r}\right) = \gamma\left(\frac{2\cos\theta}{R_c}\right) = \rho g h \qquad \gamma = \frac{R\rho g h}{2\cos\theta}$$

$0 < \theta < 90$



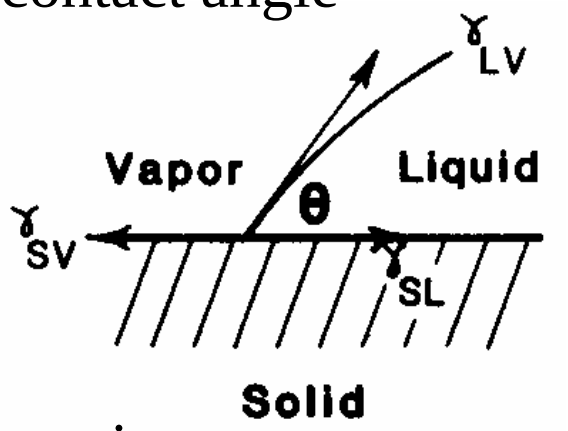
$90 < \theta < 180$



Basics- Surface

❑ Wetting & Spreading

- contact angle

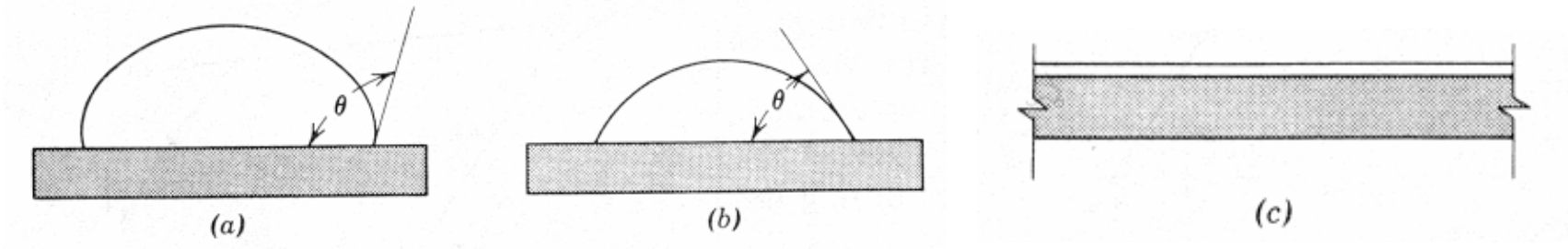


$\gamma_{SV}=\gamma_{SL}+\gamma_{LV}\cos\theta$

θ: contact angle

Young equation

- wetting



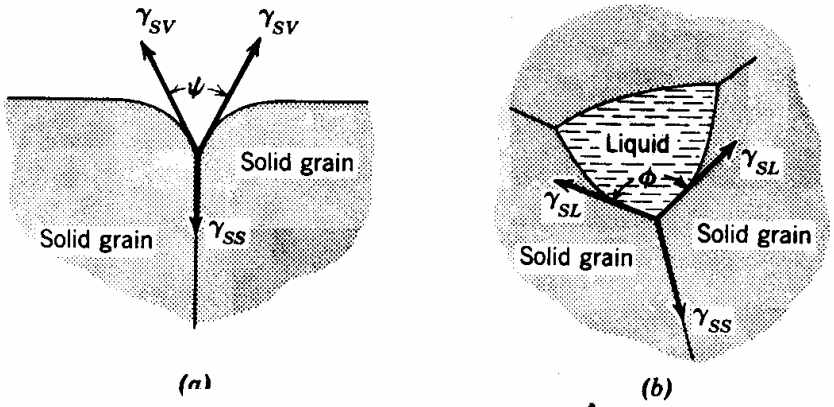
nonwetting θ > 90 wetting θ < 90 spreading θ = 90

W. D. Kingery, Introduction to Ceramics (1976)

Basics- Surface

❑ Wetting

- grain boundary



$$\gamma_{SS} = 2\gamma_{SV}\cos\frac{\psi}{2}$$

$$\gamma_{SS} = 2\gamma_{SL}\cos\frac{\phi}{2}$$

$$\cos\frac{\phi}{2} = \frac{1}{2}\frac{\gamma_{SS}}{\gamma_{SL}}$$

ϕ: dihedral angle

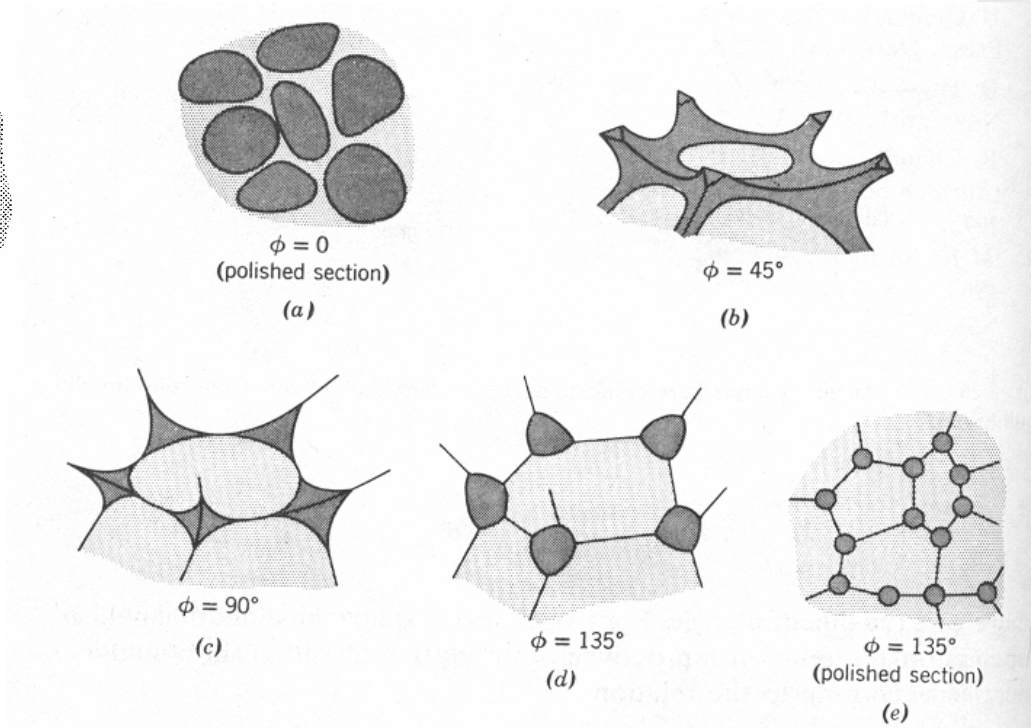


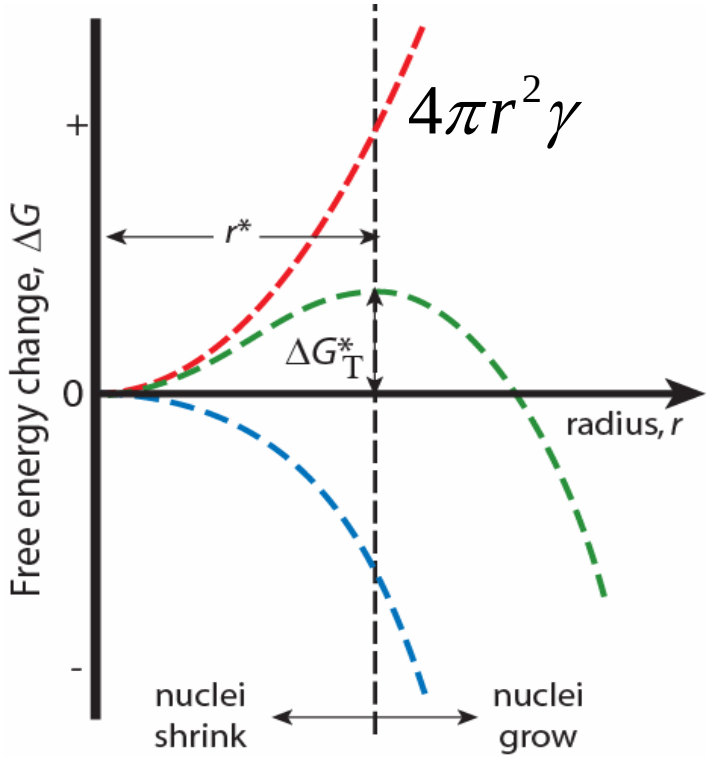
Fig. 5.27. Second-phase distribution for different values of the dihedral angle.

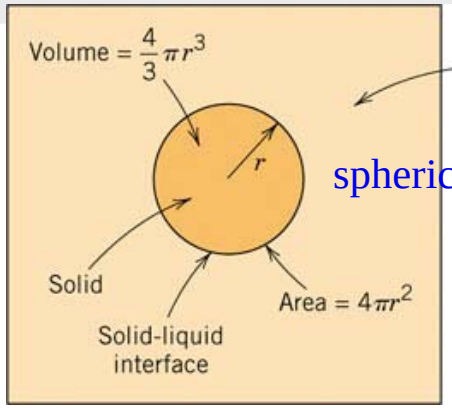
W. D. Kingery, Introduction to Ceramics (1976)

Basics- Kinetics

❑ Homogeneous Nucleation

- supersaturation (ΔGv)
- surface





spherical nuclei

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma$$

critical radius r^*

$$\left(\frac{d(\Delta G)}{dr}\right)_{r=r^*} = 0 \rightarrow r^* = \frac{-2\gamma}{\Delta G_V}$$

barrier height ΔG^*

$$\Delta G^* = \frac{16\pi r^3}{3\Delta G_V}$$

W. D. Callister, Materials Science and Engineering

Basics- Kinetics

❑ Homogeneous Nucleation

ex) supersaturated solution

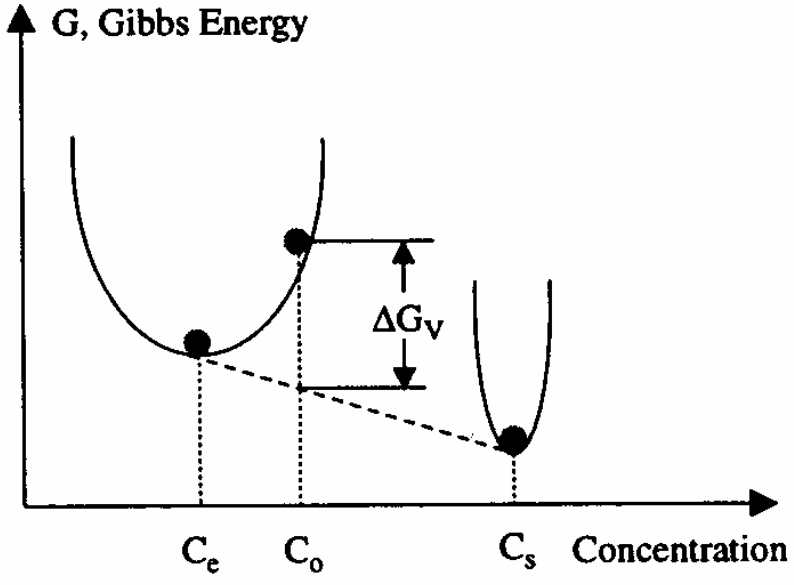
$$\Delta G_v = -\frac{kT}{\Omega}\ln(C/C_o) = -\frac{kT}{\Omega}\ln(1+\sigma)$$

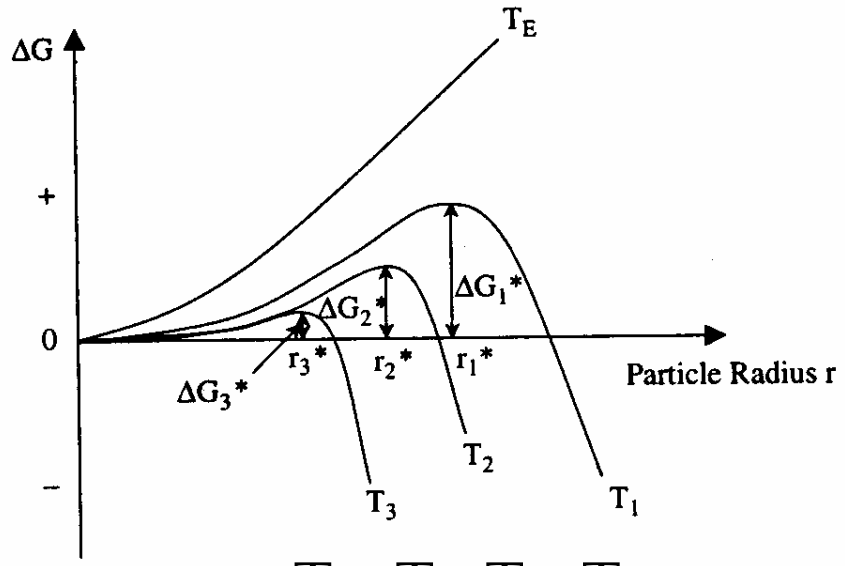
$$\sigma = (C - C_o)/C_o$$

- For nanoparticles

$$-\Delta G_v \Uparrow \leftarrow \sigma \Uparrow \leftarrow T \Downarrow$$

$$-\gamma \Downarrow$$





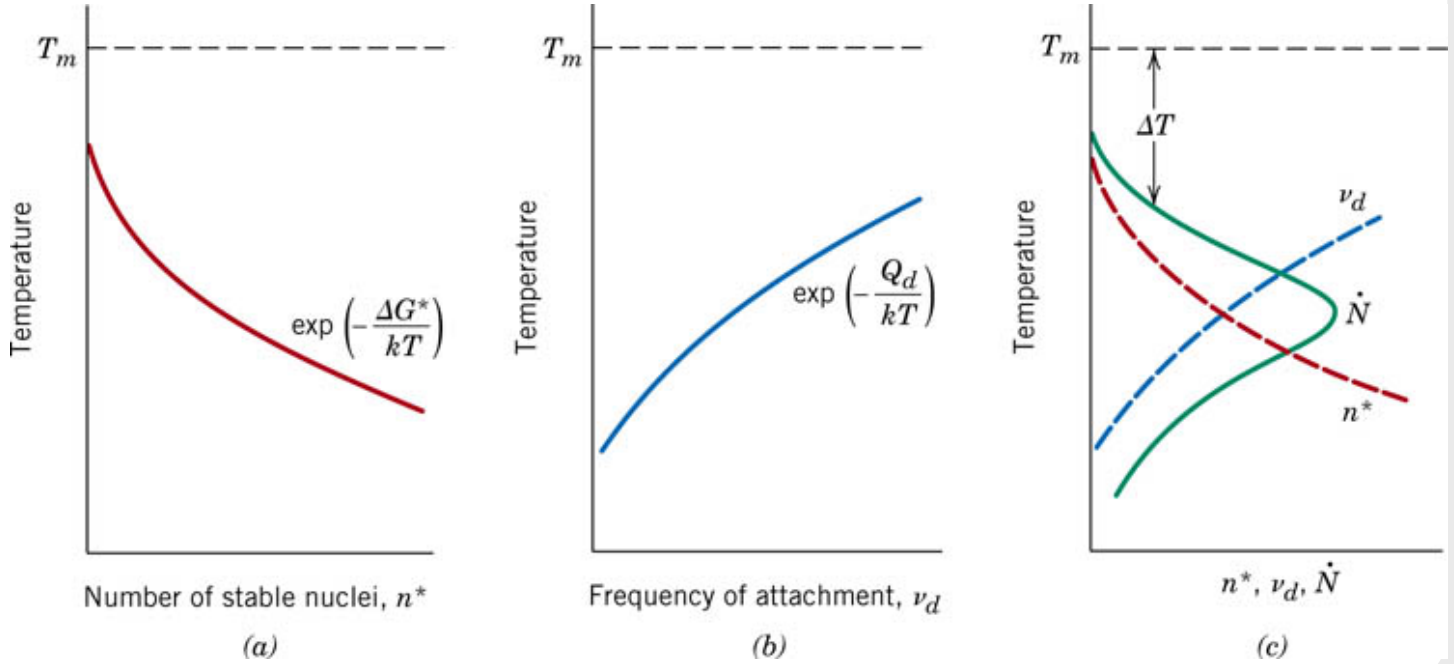
$$T_E > T_1 > T_2 > T_3$$

Basics- Kinetics

Nucleation Rate

$$\dot{N} \sim n^{*}(\#\text{ of stable nuclei}) \times \nu_d \ (\text{collision frequency})$$

$$\sim K_1 \exp(-\frac{\Delta G^{*}}{kT}) K_2 \exp(-\frac{Q_d}{kT})$$



W. D. Callister, Materials Science and Engineering

Basics- Kinetics

How to achieve the uniformity in size?

1. **High rate of nucleation**
2. **Quick down to the minimum concentration.**
   → prevent further nucleation

❑ Mono-dispersed Particle

- Lamar diagram

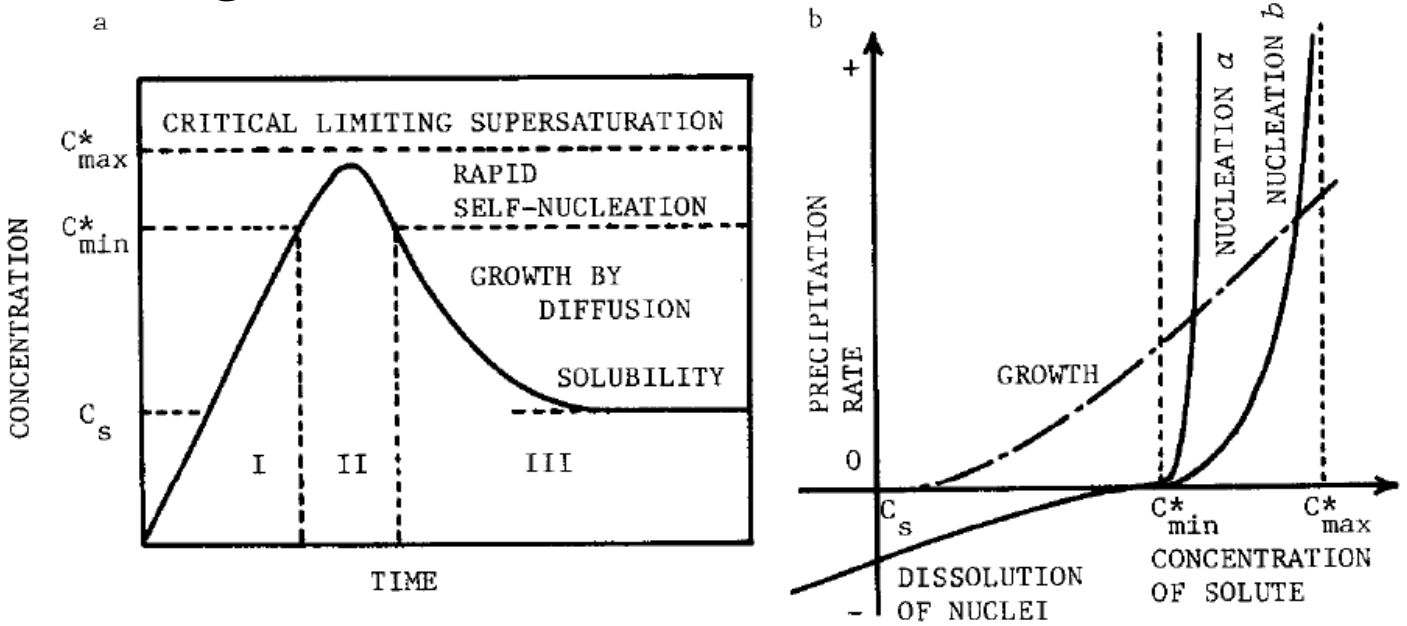
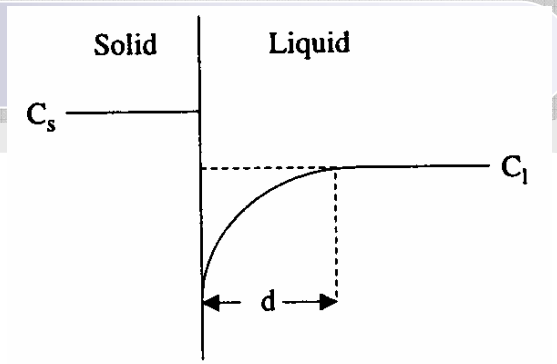


Fig. 1. (a) The LaMer model for monodispersed particle formation (C_s: solubility; C^*_{min}: minimum concentration for nucleation; C^*_{max}: maximum concentration for nucleation; I: prenucleation period; II: nucleation period; III: growth period) (ref. 15). (b) Precipitation rate for nucleation and growth as a function of solute concentration, where the growth curve is the one for a given amount of seed particles.

T. Sugimoto, Adv. Colloid Interface Sci., 28 (1987) 65

Basics- Kinetics



❑ Homogeneous Nucleation

- subsequent growth

(1) diffusion controlled

$$\frac{dr}{dt} = D(C - C_S)\frac{V_m}{r}$$

$$r^2 = 2D(C - C_S)V_m t + r_o^{\,2}$$

$$r^2 = k_D t + r_o^{\,2}$$

$$\delta r = \frac{r_o(\delta r_o)}{r} = \frac{r_o(\delta r_o)}{\sqrt{k_D t + r_o^{\,2}}}$$

(2) interface controlled

(2-1) monolayer growth

$$dr/dt = k_m r^2; \frac{1}{r} = \frac{1}{r_o} - k_m t$$

$$\delta r = r^2\left(\frac{\delta r_o}{r_o^{\,2}}\right)$$

(2-2) multilayer growth

$$\frac{dr}{dt} = k_p; r = k_p t + r_o$$

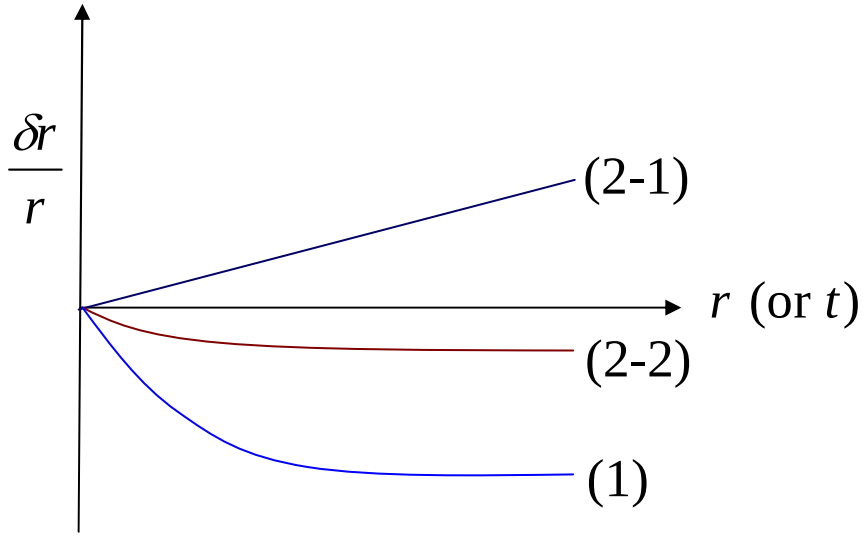
$$\delta r = \delta r_o$$

Basics- Kinetics

❑ Homogeneous Nucleation

- for the uniformity in size

→ diffusion controlled process is desired



- how to achieve it

→ extremely low concentration of growth species

high viscosity, diffusion barrier, controlled supply of growth species

Basics- Kinetics

❑ Homogeneous Nucleation

ex) ZnS

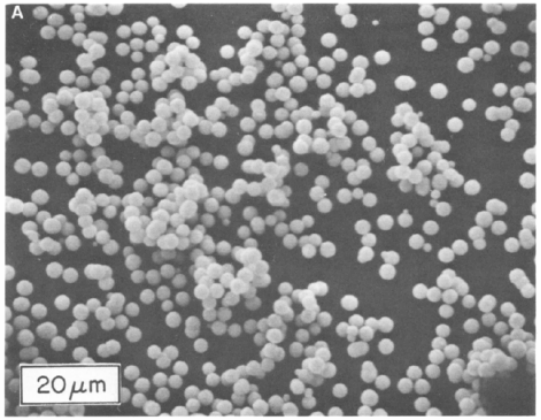
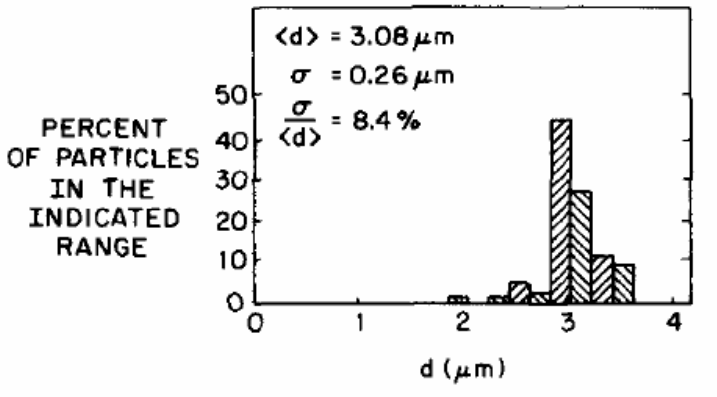
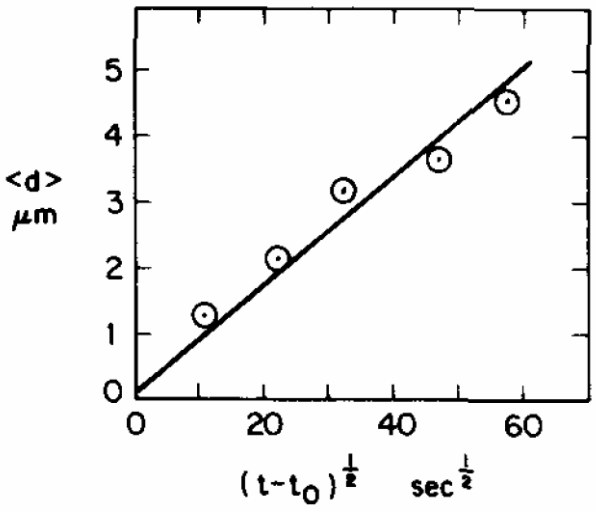


FIG. 1. (A) Particles of ZnS growth under conditions that minimize stirring and convection. Zn^{2+} initial concentration = 0.05 mole/liter. Thioacetamide initial concentration = 0.21 mole/liter. H_2SO_4 initial concentration = 0.15 mole/liter. Scanning electron microscope photo taken at 1000× magnification. Temperature = 80°C.





- diffusion of the HS- ion to the growing particle is the rate-limiting process

R.Williams et al., J. Colloid Interface Sci. 106, 388 (1985).

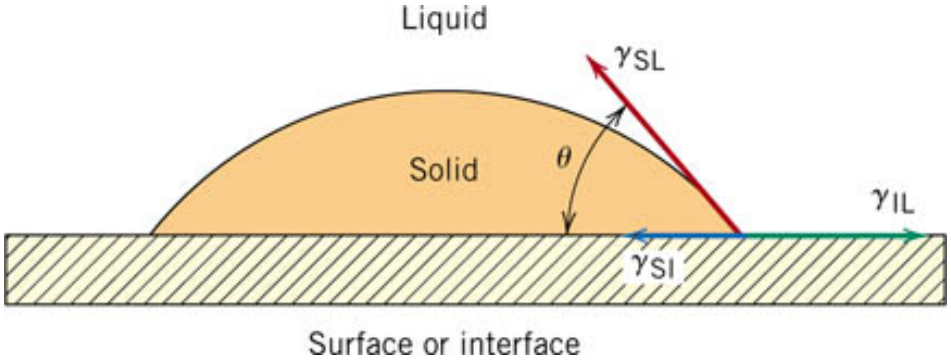
Basics- Kinetics

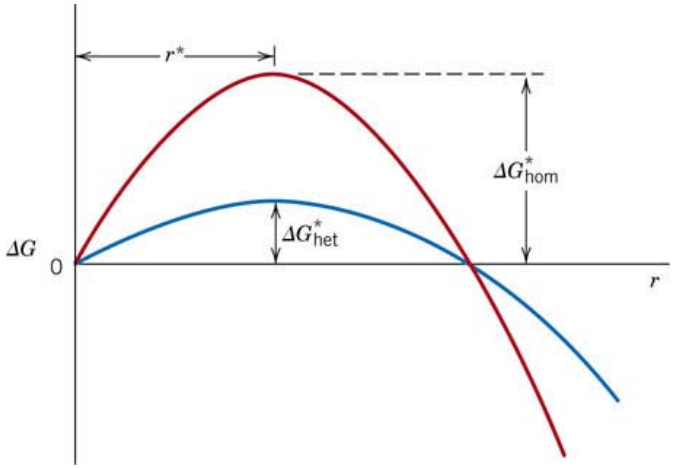
❑ Heterogeneous Nucleation

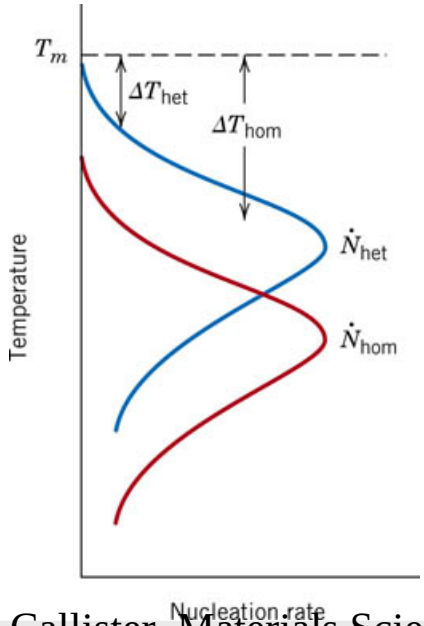
$$r^*_{heter} = r^*_{\text{homo}} \frac{\sin^2\theta\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}$$

$$\Delta G^*_{heter} = \Delta G^*_{\text{homo}} f(\theta)$$

$$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$







W. D. Callister, Materials Science and Engineering

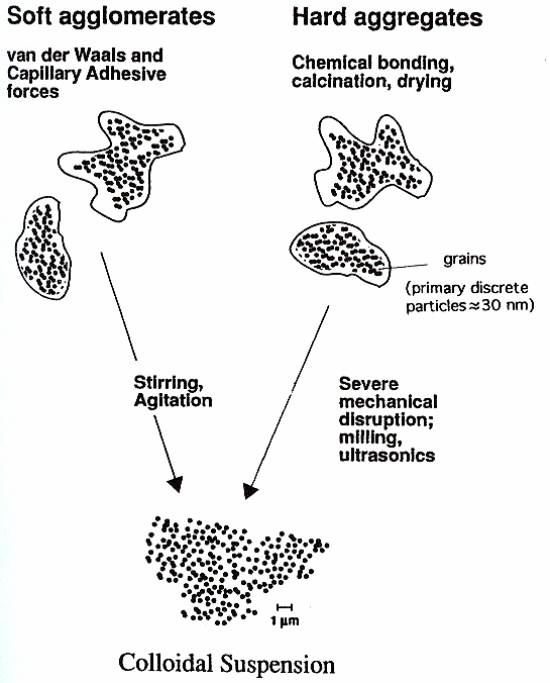
Basics- Surface chemistry

❑ Dispersion

- a high solids homogeneous suspension with a well-defined rheological behavior

❑ Dispersion in liquid

- wetting - interparticle interaction



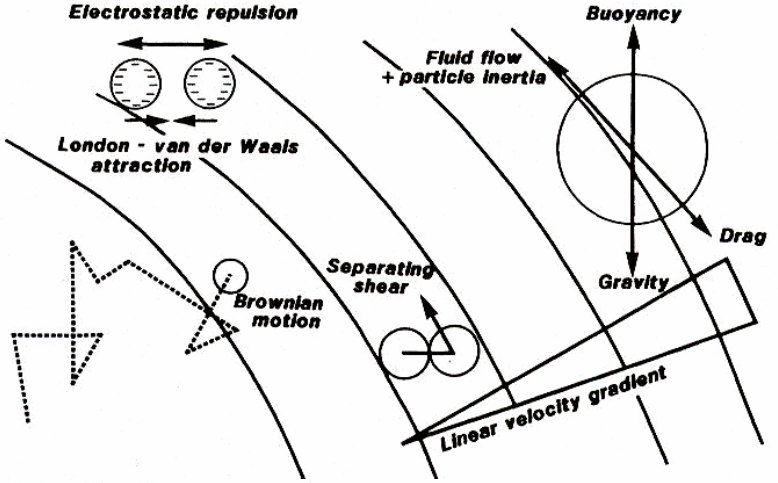


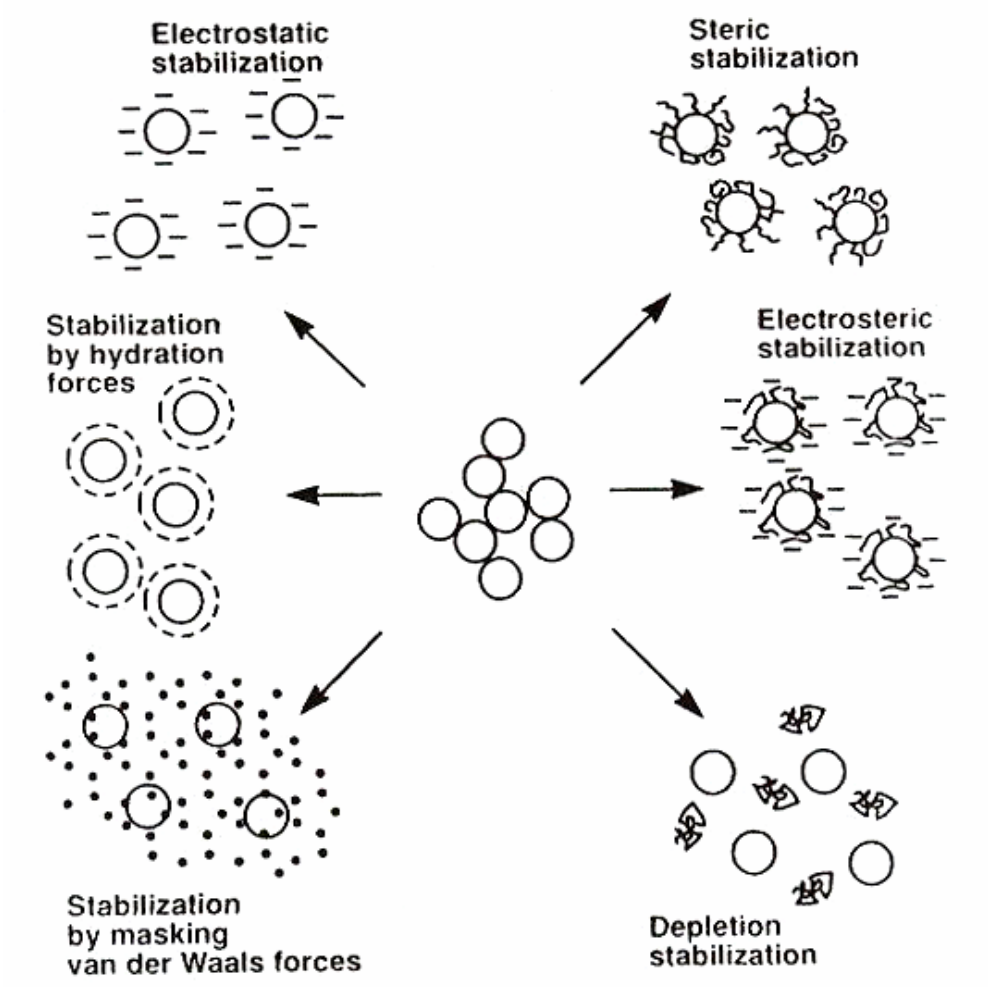
TABLE 2 Energies of Particles in Suspension due to Various Interactions

Type of interaction	Energy (in units of kT) for particles of given size		
	0.1 μm	1 μm	10 μm
van der Waals attraction	10	100	1000
Electrostatic repulsion	0–100	0–1000	0–10,000
Brownian motion	1	1	1
Kinetic energy of sedimentation	10^{-13}	10^{-6}	10
Kinetic energy of stirring	1	1000	10^{6}

R. J. Pugh, Surface and Colloid Chemistry in Advanced Ceramic Processing

Basics- Surface chemistry

❑ Stabilization



R. J. Pugh, Surface and Colloid Chemistry in Advanced Ceramic Processing

Basics- Surface chemistry

❑ Electrostatic Stabilization

electrical repulsion

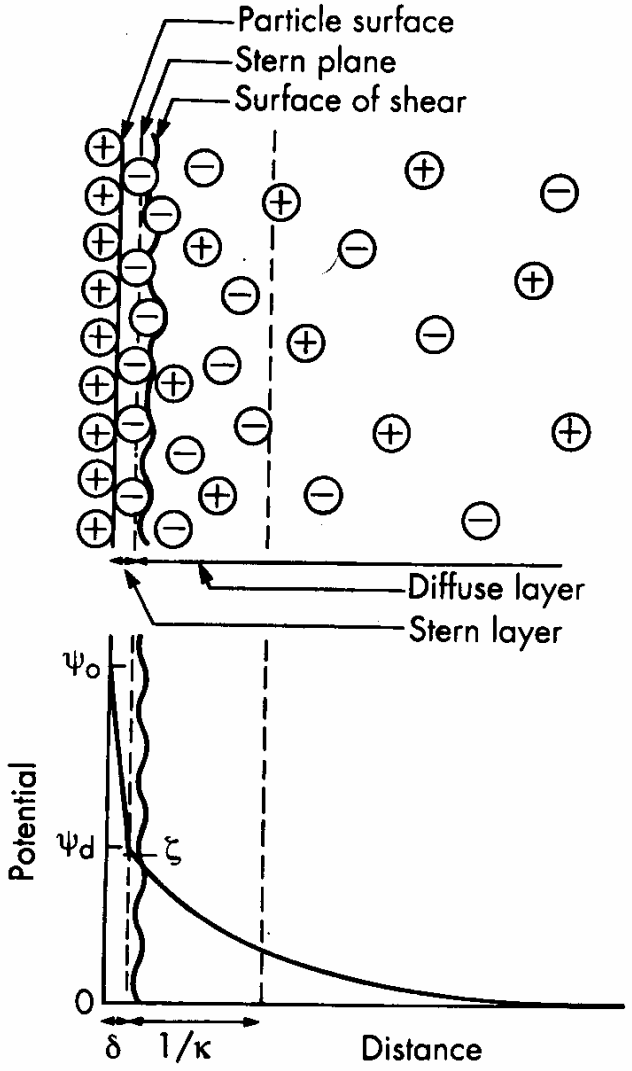
van der waals attraction

❑ Electrical double layer

- surface charge (Ψ_o)
- stern potential (Ψ_d)
  specific adsorption of counter-ion
- electrockinetic or ζ(zeta) potential
  at plane of shear (slipping plane)
- double layer thickness (κ^{-1})

$$\kappa = \left(\frac{1000 e^2 N_A}{\varepsilon k T} \sum_i z_i^2 M_i \right)^{1/2}$$

M_i : molar concentration



D.J.Shaw, Introduction to colloid and surface chemistry, 1992

Basics- Surface chemistry

- **Van der Waals attraction**

  induced dipole- induced dipole (London) ~ x^{-6}

  permanent dipole- induced dipole (Debye) ~ x^{-6}

  permanent dipole- permanent dipole (Keesom) ~ x^{-6}

- **Attraction between two spheres**

$$\Phi_A = \frac{-Ar}{12S}$$ A: Hamaker constant

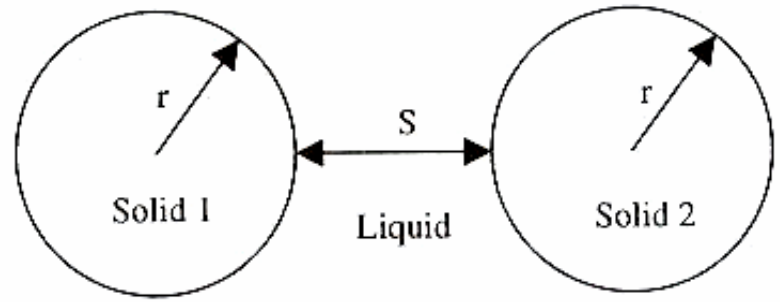


Table 2.3. Hamaker constants for some common materials.[45]

Materials	$A_i(10^{-20}\,J)$
Metals	16.2–45.5
Gold	45.3
Oxides	10.5–15.5
Al_2O_3	15.4
MgO	10.5
SiO_2 (fused)	6.5
SiO_2 (quartz)	8.8
Ionic crystals	6.3–15.3
CaF_2	7.2
Calcite	10.1
Polymers	6.15–6.6
Polyvinyl chloride	10.82
Polyethylene oxide	7.51
Water	4.35
Acetone	4.20
Carbon tetrachloride	4.78
Chlorobenzene	5.89
Ethyl acetate	4.17
Hexane	4.32
Toluene	5.40

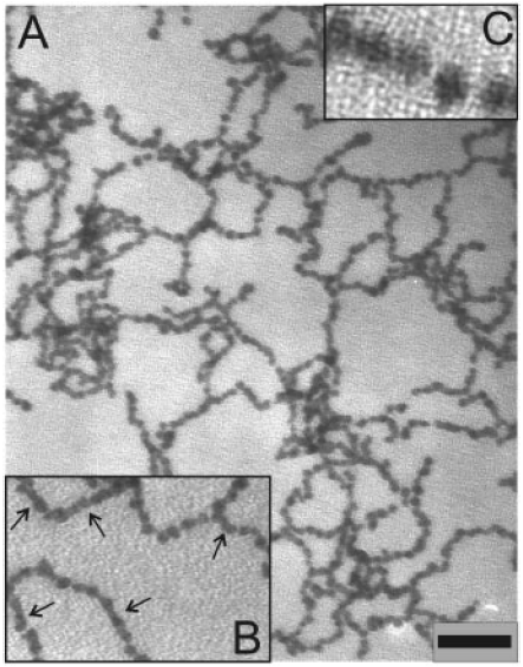
G. CaO, Nanostructures & Nanomaterials (2004)

Basics- Surface chemistry

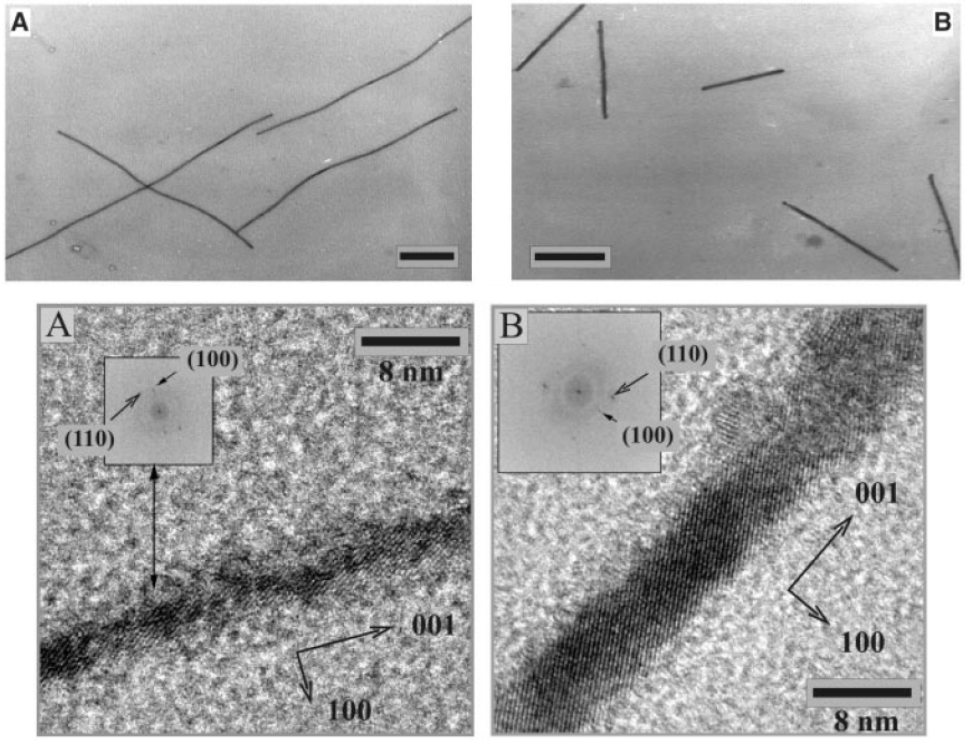
❑ Example- CdTe nanowire

dipole-dipole interaction between nano-particles produce nano-wires with self assembling modes

intermediate stage



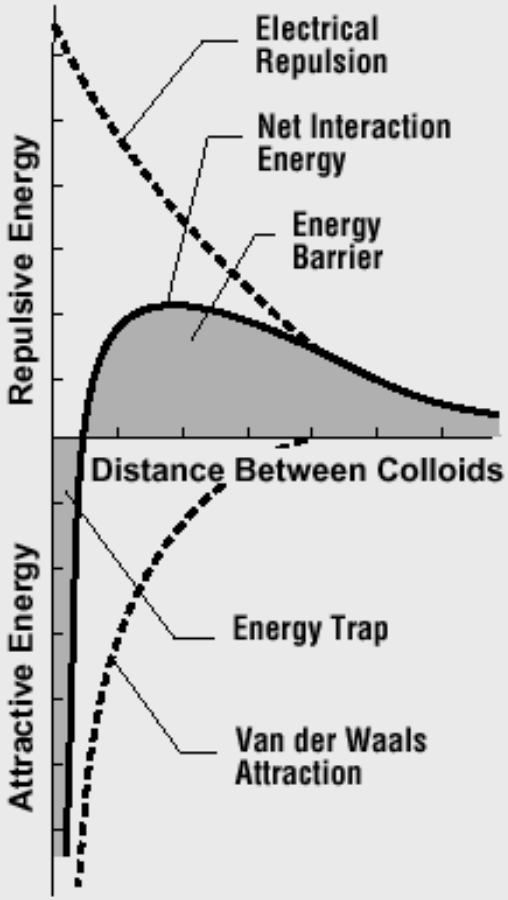
nano-wire



Z. Tang, Science, 297 (2002)237

Basics- Surface chemistry

❑ DLVO theory



$$\Phi = \Phi_R + \Phi_A$$

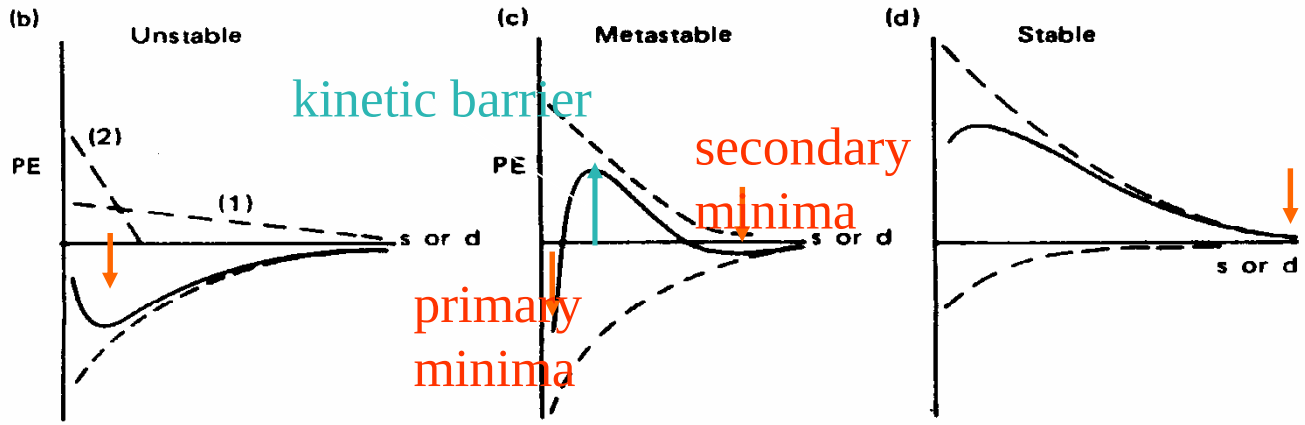


Figure 11.1 Potential energy curves for the interaction of two colloidal particles. Negative values correspond to attraction, and positive values to repulsion. (a) Definition of variables. (b) Repulsion less than attraction in magnitude and/or range. (c) Repulsion and attraction comparable in magnitude and range. (d) Attraction less than repulsion.

http://www.zeta-meter.com/

P. C. Hiemenz, Principles of colloid and surface chemistry (1986)

Basics- Surface chemistry

❑ DLVO theory

- effect of

Hamaker constant surface potential electrolyte conc.

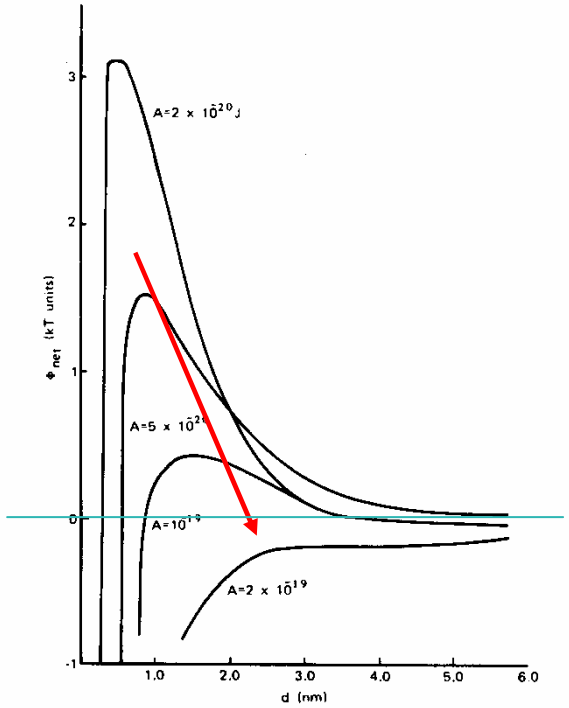


Figure 12.7 Plot of Φ_{net} versus d according to Eq. (83) for flat blocks. Cur are drawn for different values of A_{212} with constant values of κ (10^9 m^{-1}) and (103 mV). Units of ordinate: multiples of kT at 25°C for an interaction area of nm^2.

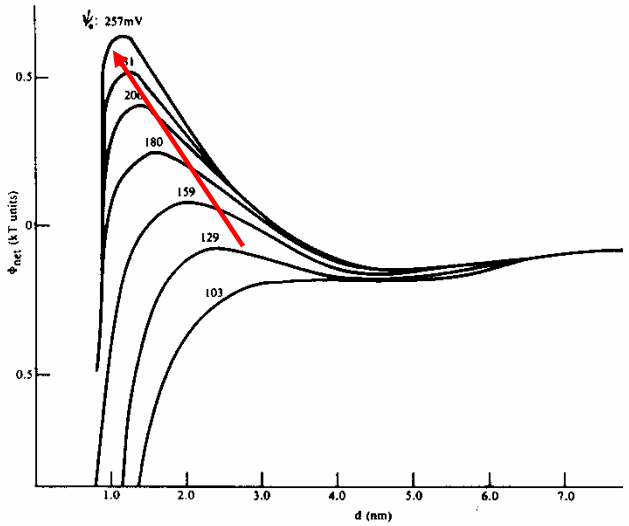


Figure 12.8 Plot of Φ_{net} versus d according to Eq. (83) for flat blocks. Curves are drawn for different values of ψ_0 with constant values of κ (10^9 m^{-1}) and A (2×10^{-19} J). Units of ordinate: multiples of kT at 25°C for an interaction area of 4.0 nm^2.

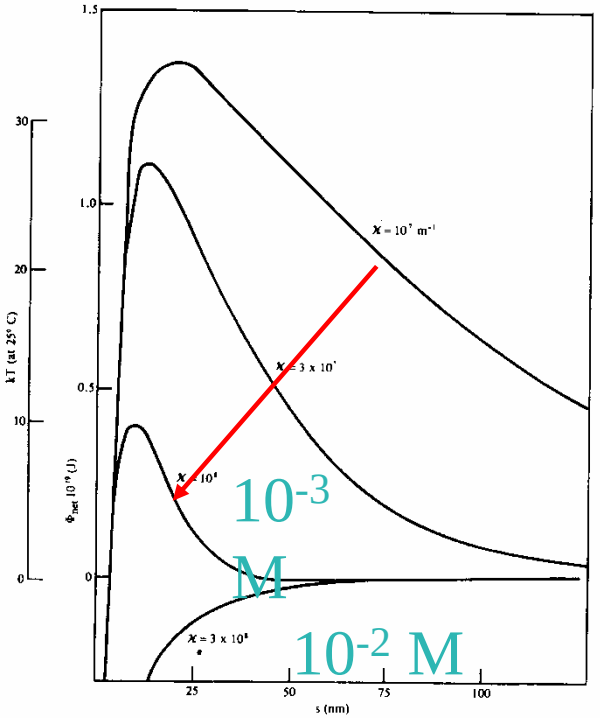


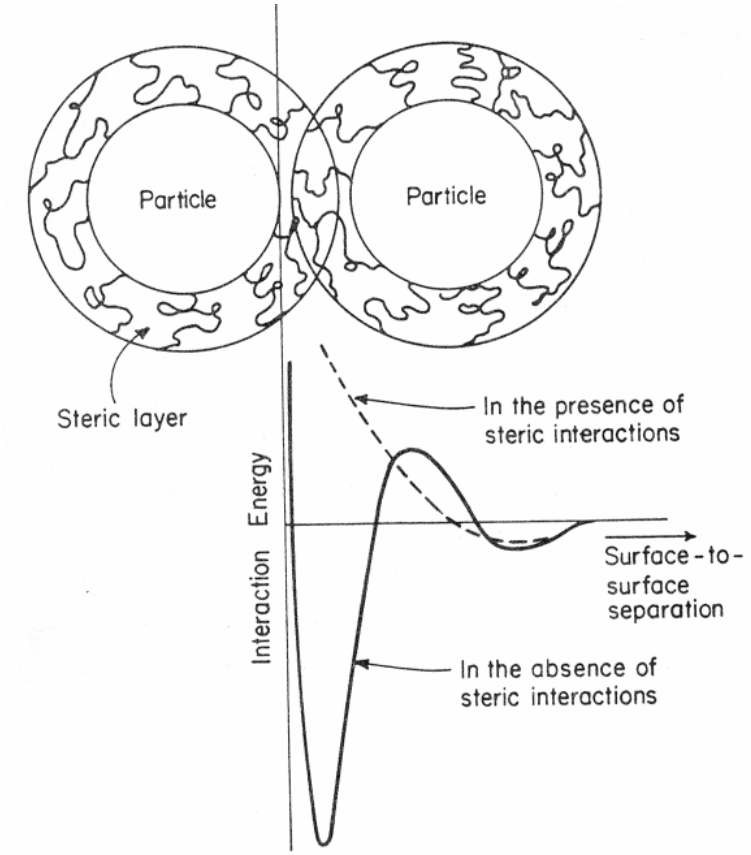
Figure 12.9 Plot of Φ_{net} versus s, the separation of surfaces, for two spheres of equal radius (100 nm). Curves are drawn for different values of κ with constant values of A (10^{-19} J) and ψ_0 (25.7 mV). (From Ref. 8, used with permission.)

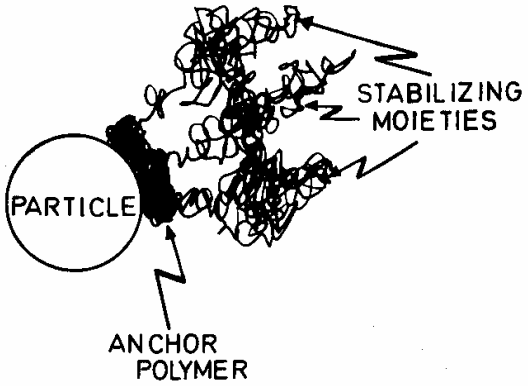
P. C. Hiemenz, Principles of colloid and surface chemistry (1986)

Basics- Surface chemistry

❑ Steric Stabilization

Steric stabilizer : amphipathic block or graft copolymer





Typical stabilizing moieties and anchor polymers for sterically stabilized dispersions

Aqueous dispersions	
Anchor polymer	Stabilizing moieties
polystyrene	poly(oxyethylene)
poly(vinyl acetate)	poly(vinyl alcohol)
poly(methyl methacrylate)	poly(acrylic acid)
poly(acrylonitrile)	poly(methacrylic acid)
poly(dimethylsiloxane)	poly(acrylamide)
poly(vinyl chloride)	poly(vinyl pyrrolidone)
poly(ethylene)	poly(ethylene imine)
poly(propylene)	poly(vinyl methyl ether)
poly(lauryl methacrylate)	poly(4-vinylpyridine)

D. H. Napper, Polymeric Stabilization of Colloidal Dispersions (1983)

Basics- Stability of Nanoparticle

❑ Metal oxide nanoparticles in aqueous suspensions

- kinetic stability- energy barrier (DLVO theory)
  - dispersion, aggregation, flocculation
- thermodyamic stability- surface energy minimization
  - Ostwald ripening (dissolution-reprecipitation)

* Is it possible to avoid the ripening of nanoparticles in suspension and to control their dimension by monitoring the precipitation conditions?

ex) thermodynamically stable dispersed system- microemulsion

answer) possible

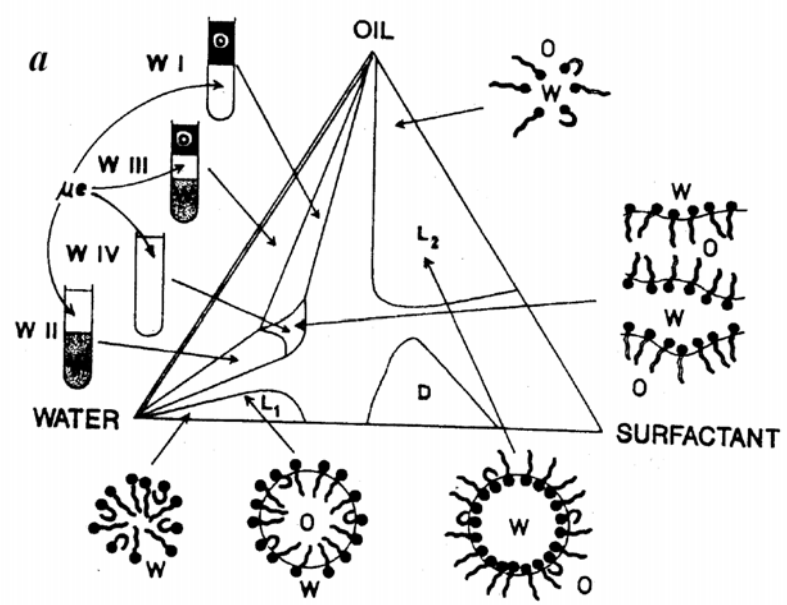
When the pH of precipitation is sufficiently far from the point of zero charge and the ionic strength sufficiently high, the ripening of nanoparticles is avoided. The stability condition, defined by a 'zero' interfacial tension, corresponds to the chemical and electrostatic saturation of the water-oxide interface. In such a condition, the density of charged surface groups reaches its maximum, the interfacial tension its minimum and further adsorption forces the surface area to expand and consequently, the size of nanoparticles to decrease.

L. Vayssieres, Int. J. Nanotech. 2, 411 (2005)

Basics- Stability of Nanoparticle

❑ Microemulsion

- clear, stable, isotropic liquid mixtures of oil, water, and surfactant, frequently in combination with a co-surfactant.
- aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins.
- thermodynamically stable
- interfacial tension is very low (10^{-2}~10^{-3} mN/m)



E. Ruckenstein, Chem. Phys. Lett. 57, 517 (1978)

B.K. Paul, Current Science 80, 990 (2001)

Basics- Stability of Nanoparticle

❑ Metal oxide nanoparticles in aqueous suspensions

	Domain of Precipitation	
	Unstable	Stable
Experimental condition	$PZC \leq pH < PZIT$	$pH \geq PZIT$
Surface charge	$\sigma < \sigma_{max}$	$\sigma = \sigma_{max}$
Interfacial tension	$\gamma > 0$	$\gamma \approx 0$

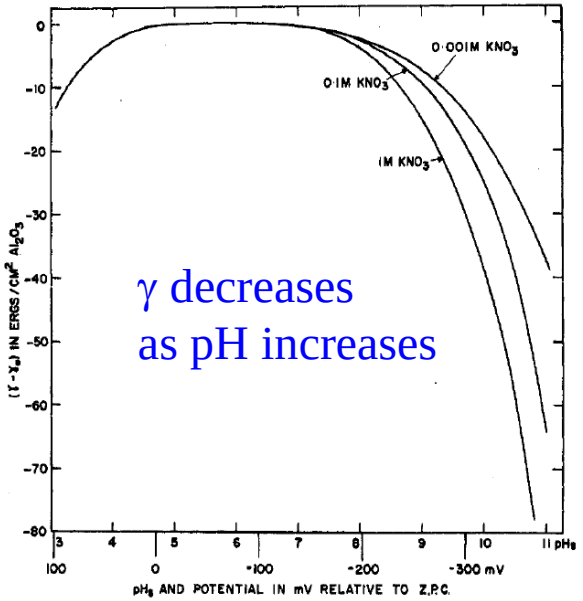


Figure 5. Variation in $(\gamma - \gamma_0)$ at the Al_2O_3–solution interface with final pH_s and potential difference relative to the zpc.

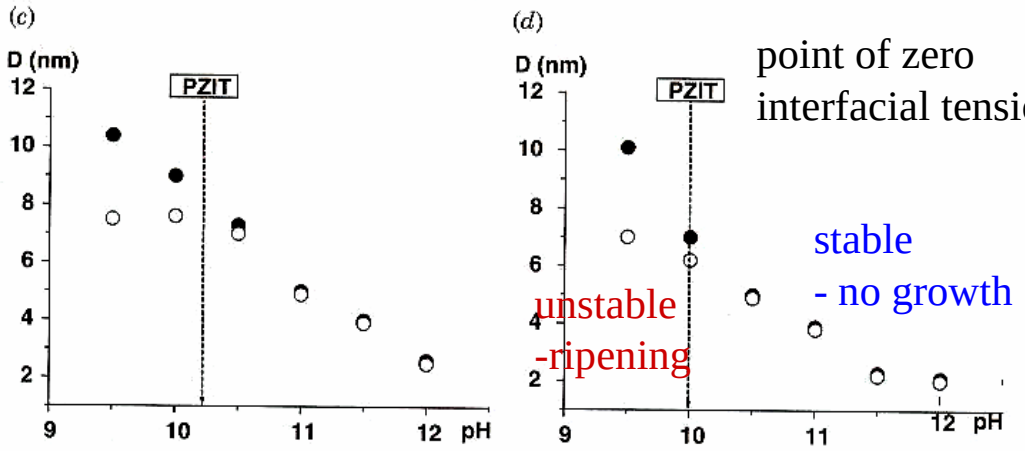


Figure 2.5. Influence of the precipitation medium on the average particle size of magnetite nanoparticles observed by TEM immediately after the synthesis (○) and after 8 days of ageing in suspension (●) for precipitations performed at pH 12.0 and (*a*) I = 0.5 M, (*b*) I = 1.0 M, (*c*) I = 1.5 M, and (*d*) I = 3.0 M. The PZIT is displayed as dotted lines and indicates the limit between the stable and unstable domains as calculated from Eq. 2.16 with PZC = 8.1 and $\sigma_{max} = 0.84\,C/m^2$ (such values were obtained by titration methods) from Ref. 100 with permission.

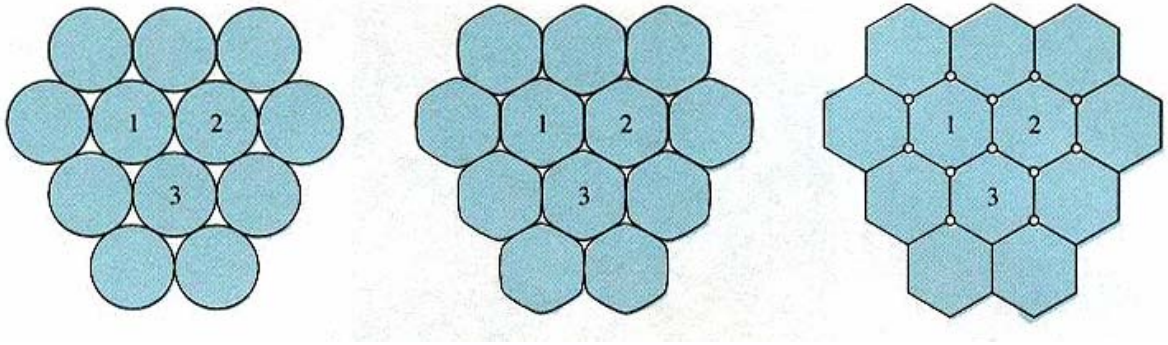
S.M.Ahmed, J. Phys. Chem. 73, 3546 (1969) L. Vayssieres, Int. J. Nanotech. 2, 411 (2005)

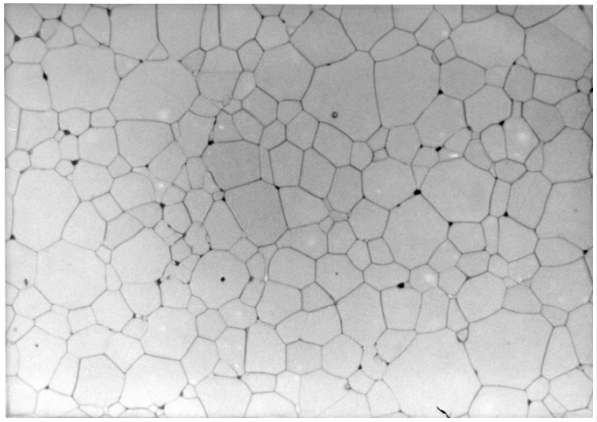
Basics- Consolidation

❑ Consolidation (sintering)

processes involved in the heat treatment of powder compacts at elevated temperatures, usually at $T > 0.5Tm$ [K], in the temperature range where diffusional mass transport is appreciable resulting in a dense polycrystalline solid.

- pore removal
  densification



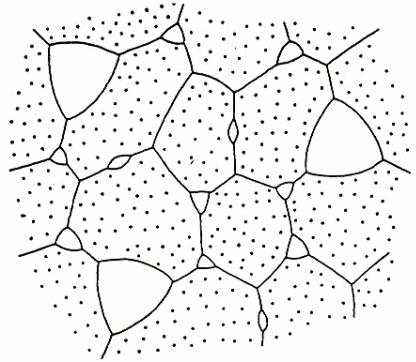


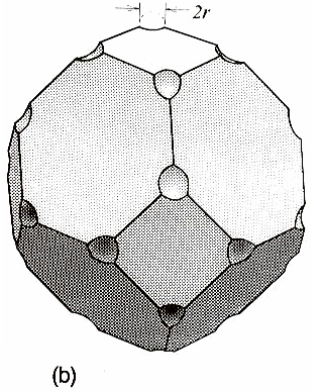
MgO-doped Al_2O_3

J. P. Schaffer et al, The Science and Design of Engineering Materials

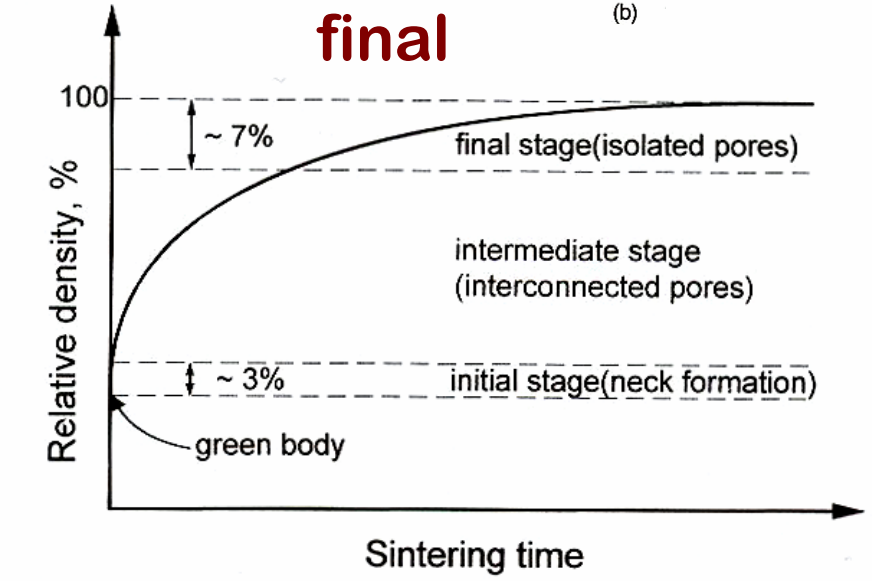
Basics- Consolidation

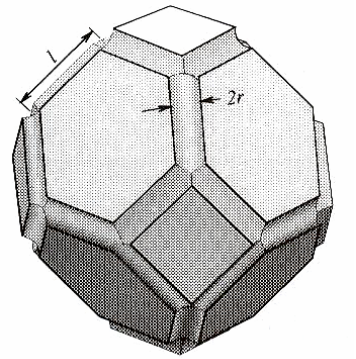
❑ Solid state sintering



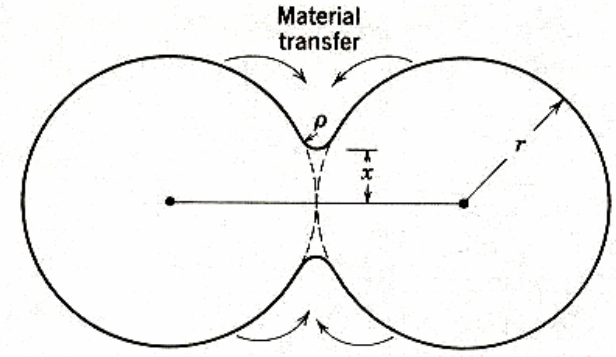


final





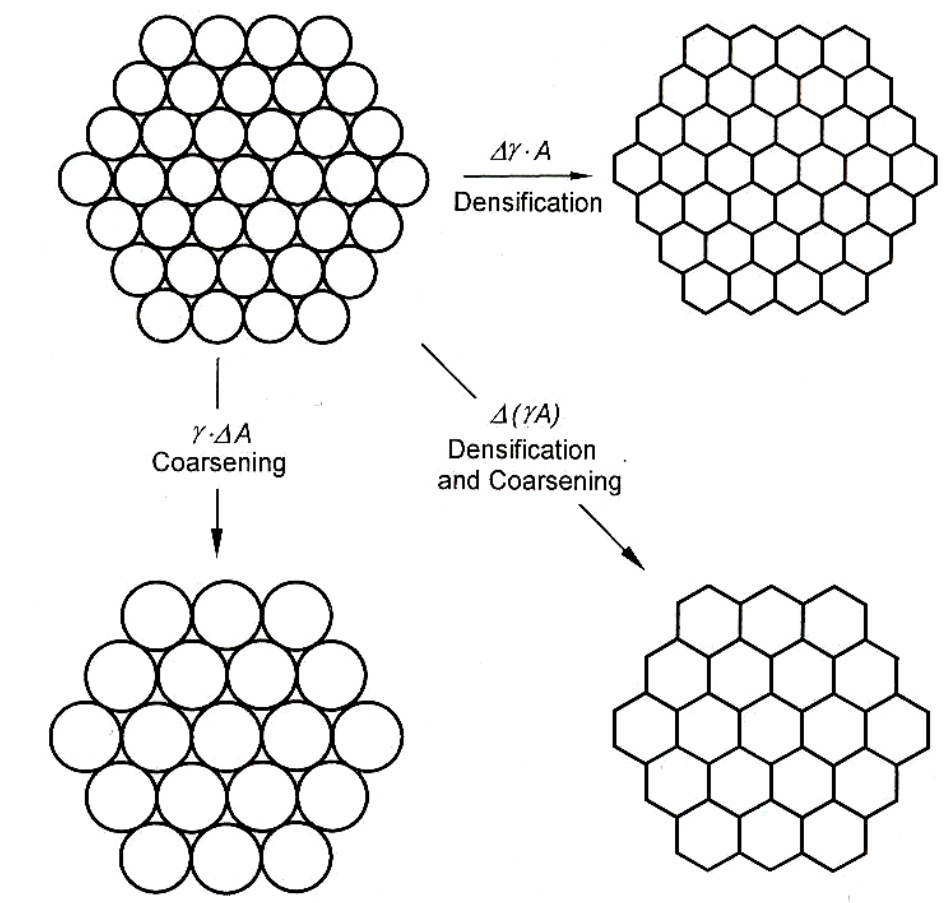
intermediate

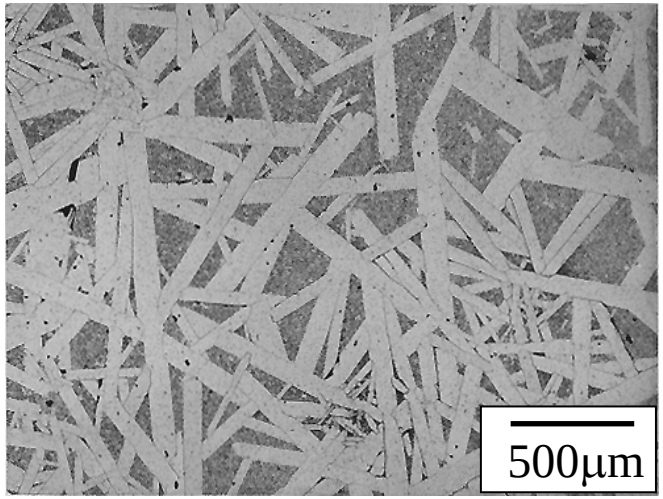


initial

Basics- Consolidation

❑ Densification vs. Grain Growth





TiO_2 & SiO_2-doped Al_2O_3

O. S. Kwon, Acta Mater., 50 (2002) 4865-4872