Surfaces impact the free energy

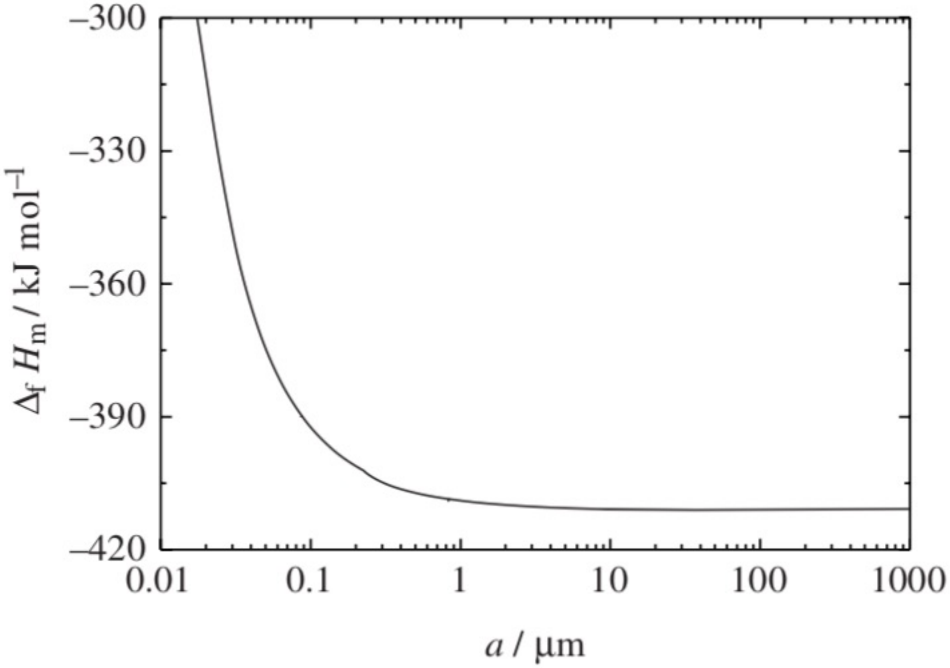

Figure 6.1 The molar enthalpy of formation of NaCl as a function of the cube edge *a* of the NaCl crystal cubes.

It takes energy to form surfaces

Small particles dissolve easier

There are limits to grinding, fine powdered sugar is about 50µm

$$\Delta H/r^3 = \Delta H_b r^3/r^3 + \sigma r^2/r^3$$
$$= \Delta H_b + \sigma/r$$

Surfaces impact the free energy

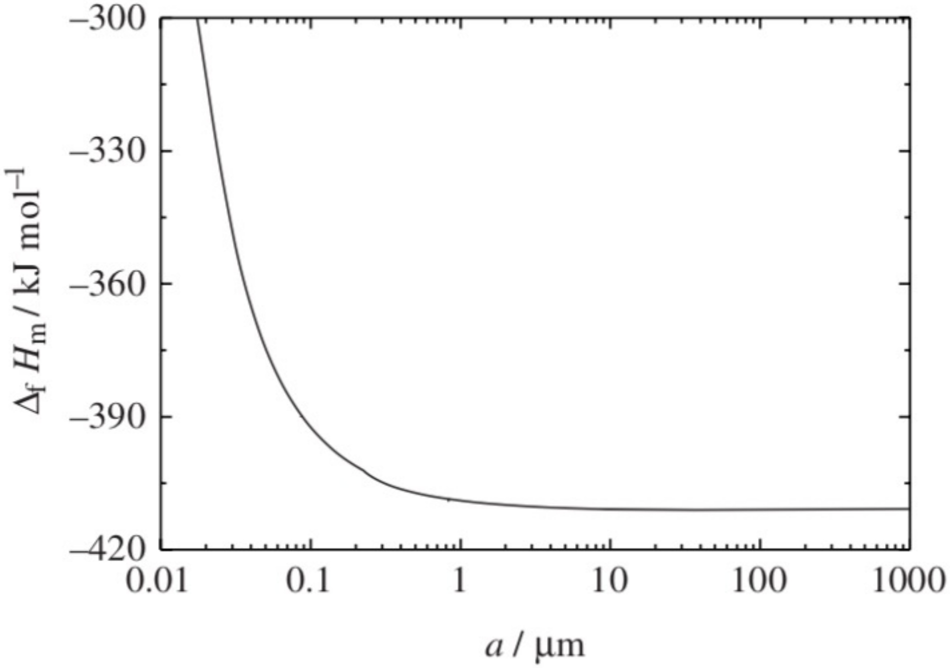

Figure 6.1 The molar enthalpy of formation of NaCl as a function of the cube edge *a* of the NaCl crystal cubes.

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There are limits to grinding, fine powdered sugar; about 50µm

Aggregates versus primary particles

C. Knieke et al. / Powder Technology 195 (2009) 25–30

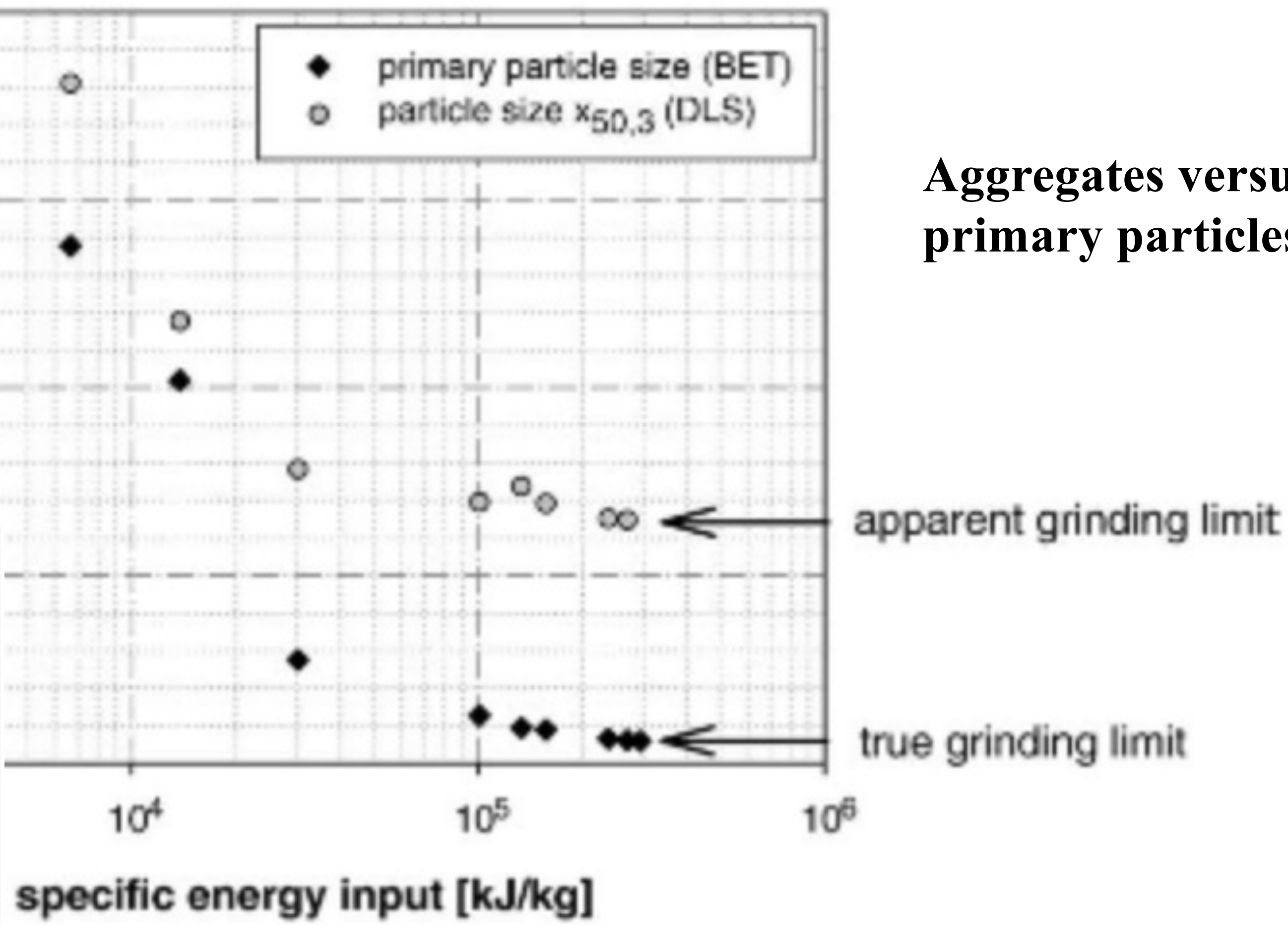


Fig. 2. Distinction between apparent and true grinding limit.

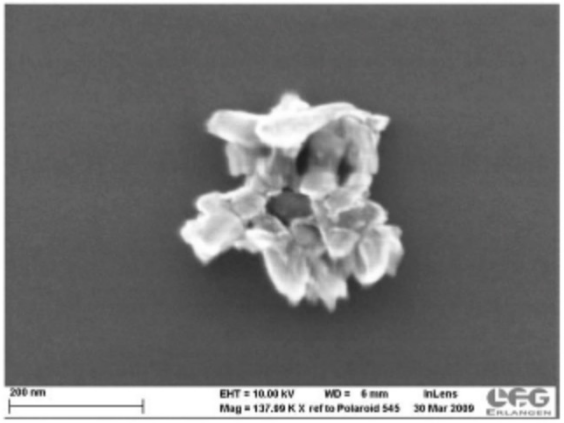
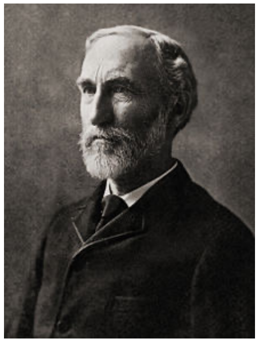


Fig. 3. SEM picture of quartz particles after grinding for 50 h.

Liquid-gas or solid-gas interface is called a **surface**
For surfaces we define a surface tension, σ, energy/area

Liquid/liquid or solid/liquid or solid/solid is just called an **interface**
For interfaces we define the interfacial energy, γ, energy/area



Gibbs Surface

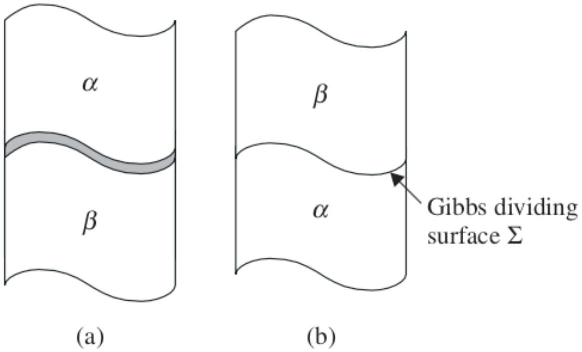
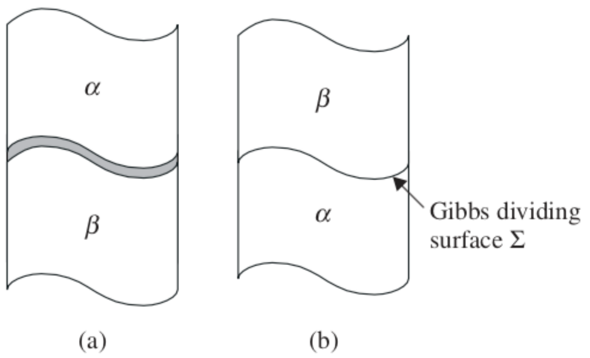


Figure 6.2 (a) Illustration of a real physical interface between two homogeneous phases α and β. (b) The hypothetical Gibbs dividing surface Σ.

Adsorption (not Absorption) *see video*

Surface Excess Moles

$$n_i^\sigma = n_i - n_i^\alpha - n_i^\beta$$



Adsorption of i $\Gamma_i = n_i^\sigma / A_\mathrm{s}$

The adsorption of “i”
There could be surface excess “i” or surface depletion of “i”
Γ_i can be positive or negative

Surface Excess Properties

$$U^\sigma = U - U^\alpha - U^\beta$$

$$S^\sigma = S - S^\alpha - S^\beta$$

$$V^\sigma = V - V^\alpha - V^\beta = 0$$

What is the change in internal energy by introduction of a surface?

-SUV
H A
-pGT

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

V doesn't change $$dU = TdS + \sum_i \mu_i dn_i$$

Surface excess $$dU^\sigma = dU - dU^\alpha - dU^\beta$$

$$dU^\alpha = TdS^\alpha + \sum^{C} \mu_i dn_i^\alpha$$

$$dU^\beta = TdS^\beta + \sum_{i=1}^{C} \mu_i dn_i^\beta$$

$$dU^\sigma = T(dS - dS^\alpha - dS^\beta) + \sum_{i=1}^{C} \mu_i (dn_i - dn_i^\alpha - dn_i^\beta)$$

$$dU^\sigma = TdS^\sigma + \sum_{i=1}^{C} \mu_i dn_i^\sigma$$

Surface Excess

Two additional contributions to the surface energy

1) Surface Area and 2) Curvature Energy Terms, $c_x = 1/r_x$, $c_y = 1/r_y$

If the thickness is much smaller than r you can ignore curvature

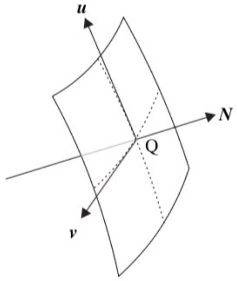


Figure 6.3 Illustration of the curvature of a geometrical surface.

$$dU^\sigma = TdS^\sigma + \sum_i \mu_i dn_i^\sigma + \sigma dA_s$$

$$dU^\alpha = TdS^\alpha + \sum_{i=1}^{C} \mu_i dn_i^\alpha - p^\alpha dV^\alpha$$

$$dU^\beta = TdS^\beta + \sum_{i=1}^{C} \mu_i dn_i^\beta - p^\beta dV^\beta$$

$$dU = T(dS^\sigma + dS^\alpha + dS^\beta) + \sum_{i=1}^{C} \mu_i (dn_i^\sigma + dn_i^\alpha + dn_i^\beta) - p^\alpha dV^\alpha - p^\beta dV^\beta + \sigma dA_s$$

For V/L or V/S

$$dU = TdS + \sum_{i=1}^{C} \mu_i dn_i - p^\alpha dV^\alpha - p^\beta dV^\beta + \sigma dA_s$$

Definition of Surface Tension

Surface Tension

$$\sigma = \left(\frac{\partial U}{\partial A_s} \right)_{S, V^\alpha, V^\beta, n_i}$$

Derive Laplace Equation

Curved Interface (Laplace Equation $p_{sat} \sim \sigma/r$)

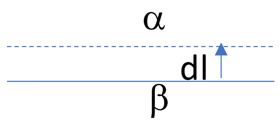
Force/Area x Distance = Energy/Area

$$T^{\alpha} = T^{\beta} = T^{\sigma} \qquad \mu_i^{\alpha} = \mu_i^{\beta} = \mu_i^{\sigma}$$

Pressure reaches equilibrium

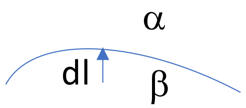
$$\mathrm{d}U = -p^{\alpha}\mathrm{d}V^{\alpha} - p^{\beta}\mathrm{d}V^{\beta} + \sigma\,\mathrm{d}A_{\mathrm{s}}$$

$$\mathrm{d}V^{\alpha} = A_{\mathrm{s}}\mathrm{d}l = -\mathrm{d}V^{\beta}$$



$dA_s = 0$ for flat surface

$$\mathrm{d}A_{\mathrm{s}} = (c_1 + c_2)A_{\mathrm{s}}\mathrm{d}l$$



For a sphere $A = 4\pi/3\ r^2$ :: $dA = 8\pi/3\ r\ dr$
$c = 1/r$ so $dA = 2A/r\ dr = 2Acdr$
if $dr = dl$ $dA = 2cAdl$

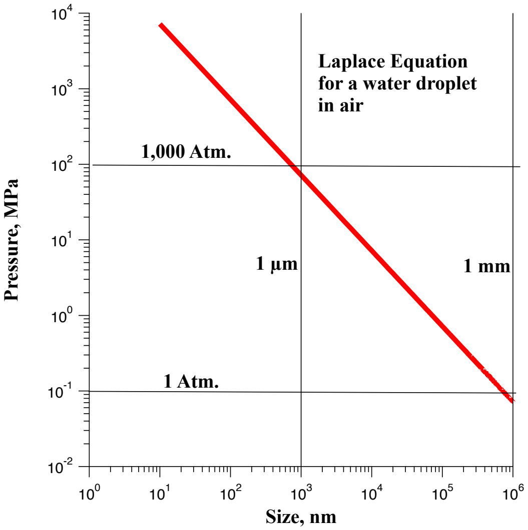
$$\mathrm{d}U = (p^{\beta} - p^{\alpha})A_{\mathrm{s}}\mathrm{d}l + \sigma(c_1 + c_2)A_{\mathrm{s}}\mathrm{d}l = [(p^{\beta} - p^{\alpha}) + \sigma(c_1 + c_2)]A_{\mathrm{s}}\mathrm{d}l$$

Change in internal energy is proportional to the change in interfacial width

$$\mathrm{d}U = [(p^{\beta} - p^{\alpha}) + \sigma(c_1 + c_2)]A_s \,\mathrm{d}l$$

$$\text{At equilibrium } (\mathrm{d}U)_{S,V,n_i} = 0$$

$$p^{\beta} - p^{\alpha} = \sigma(c_1 + c_2) = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$



Laplace Equation

For a 100 nm (1e^{-5} cm) droplet of water in air (72 e^{-7} J/cm^2 or 7.2 Pa-cm)
Pressure is 720 MPa (7,200 Atmospheres)

For S/S, S/L, L/L

Solid interface in a 1-component system

-SUV
 H   A
-pGT

$$dG = -SdT + Vdp + \gamma dA_s$$

$$dW_{T,p} = \gamma dA_s$$

Work to create the interface
Interfacial energy, γ

Surface creation always has an energy penalty.
γ is always positive
Nano-particles are unstable (increase in free energy with a surface)
Differences in surface energy for different crystal surfaces leads to fibrous or lamellar crystals

Crystal surface energy ~ number of bonds * bond energy
Density of bonds decreases with Miller Indices

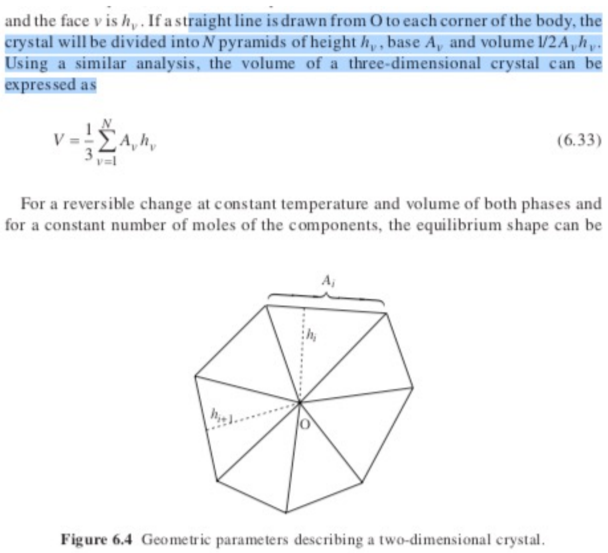
FCC	**Nearest Neighbors**	**Number of bonds** (Each pair share a bond)
[111]	6	3
[110]	12	6
[100]	8	4

Liquid droplets minimize surface area for a given volume
So, Spheres form

At high temperatures crystalline solids also form spheres
Because surface energy becomes less important

Consider a crystal with constant volume $V = \frac{1}{3}\sum_{\nu=1}^{N} A_\nu h_\nu$ with N facets.

Draw a vector from the center of a crystal to a face, h_ν.



and the face v is h_ν. If a straight line is drawn from O to each corner of the body, the crystal will be divided into N pyramids of height h_ν, base A_ν and volume $1/2 A_\nu h_\nu$. Using a similar analysis, the volume of a three-dimensional crystal can be expressed as

$$V = \frac{1}{3}\sum_{\nu=1}^{N} A_\nu h_\nu \tag{6.33}$$

For a reversible change at constant temperature and volume of both phases and for a constant number of moles of the components, the equilibrium shape can be

Figure 6.4 Geometric parameters describing a two-dimensional crystal.

Wulff Construction

Surface excess energy $\Delta G_i = \sum_j \gamma_j O_j$

O is area
γ surface energy

Draw a vector from the center of a crystal to a face.
Gibbs-Wulff Theorem states that the length of the vector is proportional to the surface energy

$h_j = \lambda \gamma_j$ **Higher energy surfaces grow preferentially (λ is a constant)**

Minimization to find the lowest free energy $\delta\left(\sum_j \gamma_j O_j\right)_{V_c} = \sum_j \gamma_j \delta(O_j)_{V_c} = 0$

h_j O_j is proportional to the volume of a facet so for constant volume: $\delta(V_c)_{V_c} = \frac{1}{3}\delta\left(\sum_j h_j O_j\right)_{V_c} = 0$

$\sum_j h_j \delta(O_j)_{V_c} + \sum_j O_j \delta(h_j)_{V_c} = 0.$ And for constant volume: $O_1\delta(h_1)_{V_c} + O_2\delta(h_2)_{V_c} + \ldots = 0$

$\sum_j h_j \delta(O_j)_{V_c} = 0$ And $\sum_j \gamma_j \delta(O_j)_{V_c} = 0$

So: $\sum_j (h_i - \lambda\gamma_j)\delta(O_j)_{V_c} = 0$ And $h_j = \lambda\gamma_j$

R. F. Strickland-Constable: *Kinetics and Mechanism of Crystallization*, page 77, Academic Press, 1968.

Diffusion rates and twinning can alter the crystal shape for large crystals

Pressure difference for solid crystal facets

$$p^{\alpha} - p^{\beta} = 2\frac{\gamma_1}{h_1} = 2\frac{\gamma_v}{h_v} = \ldots = 2\frac{\gamma_N}{h_N}$$

(Force/length)/length = Force/Area

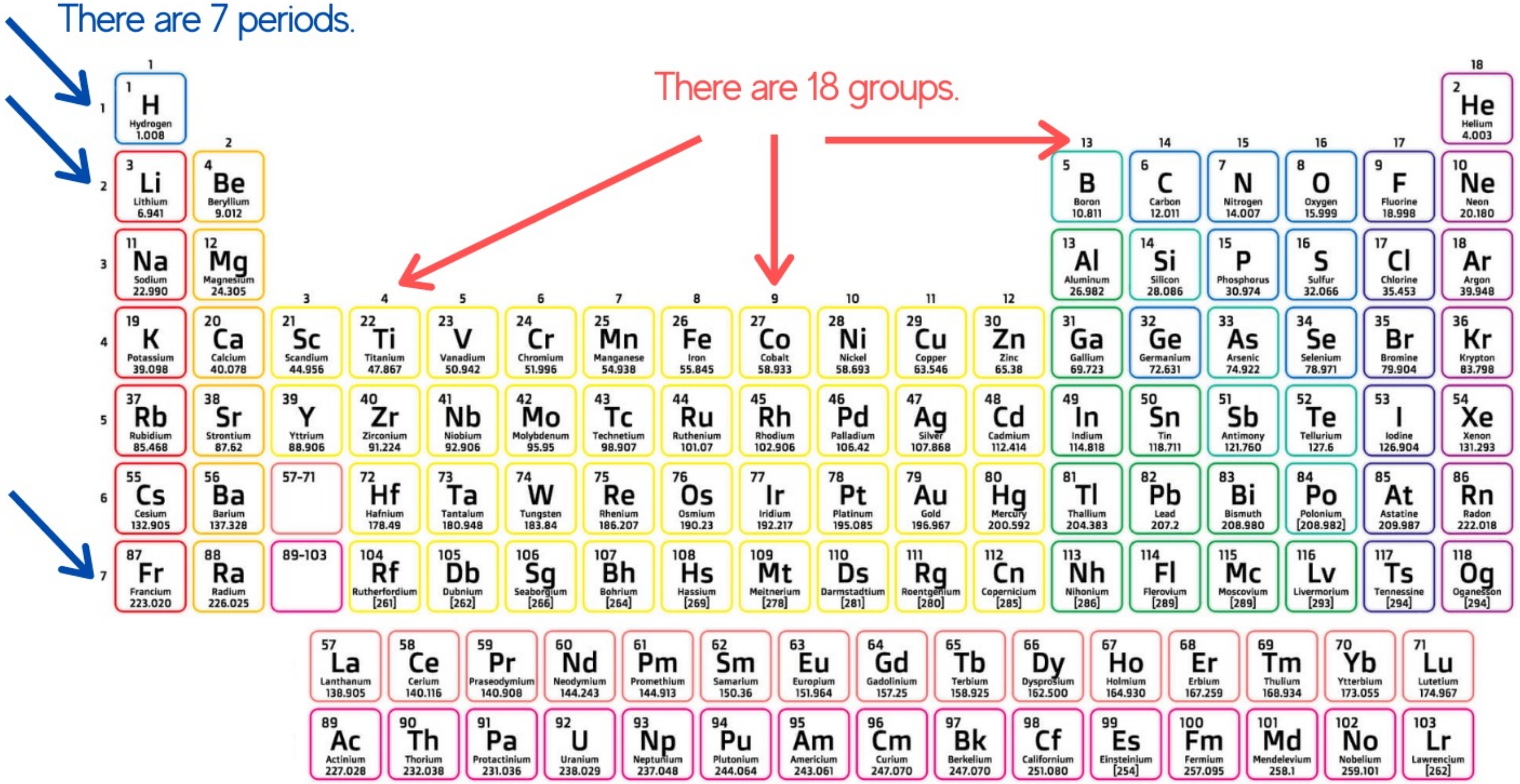
replace γ_v/h_v with γ/r for near-spherical crystals

Laplace Equation

$$p^{\beta} - p^{\alpha} = \sigma(c_1 + c_2) = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Periodic Table Groups and Periods

A group is a column on the periodic table. Elements have the same number of valence electrons.
A period is a row on the periodic table. Elements have the same number of electron shells.



There are 7 periods.

There are 18 groups.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H Hydrogen 1.008																	2 He Helium 4.003
2	3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.293
6	55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
7	87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]
			57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967	
			89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]	

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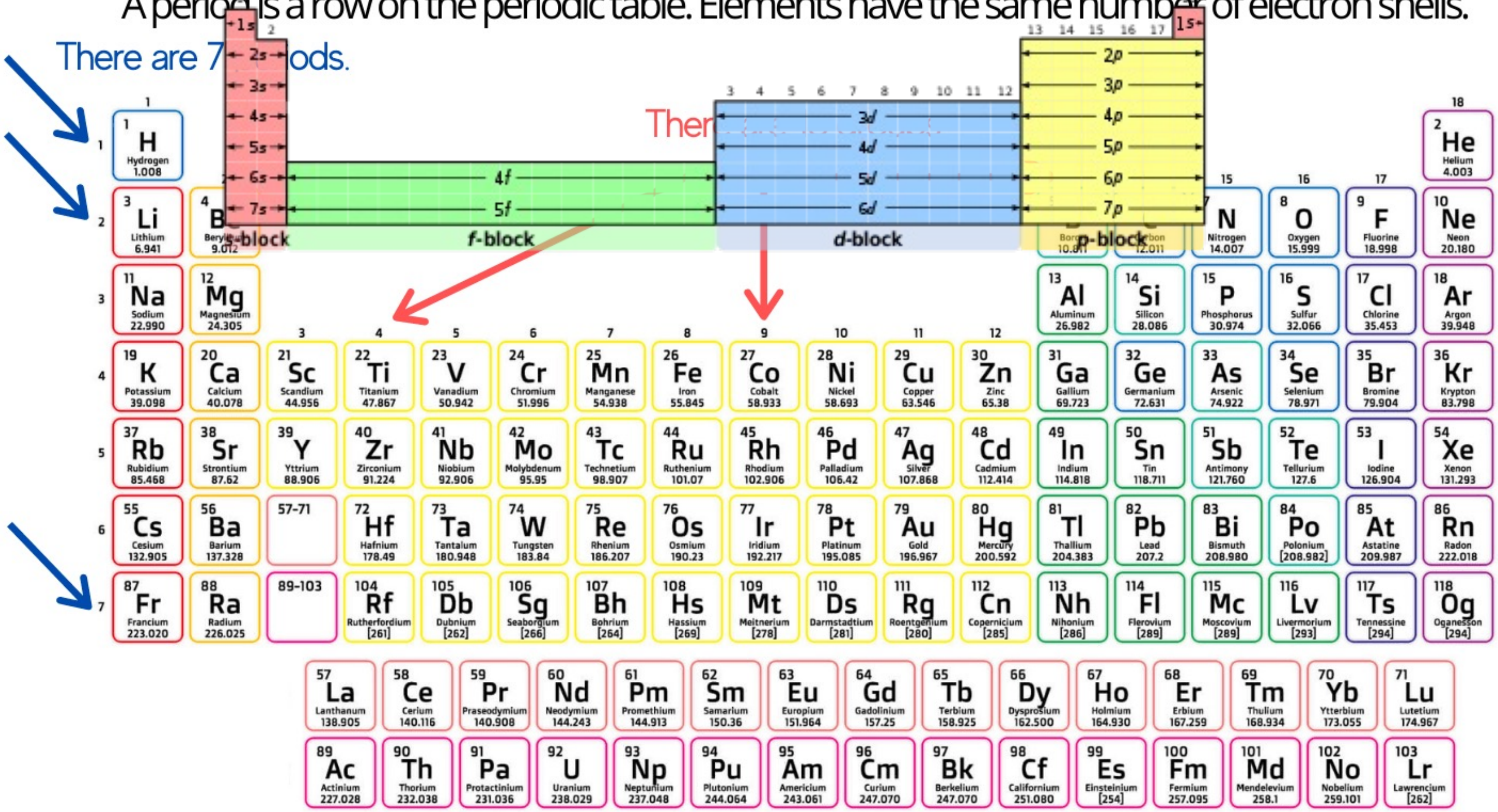

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5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.293
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7	87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

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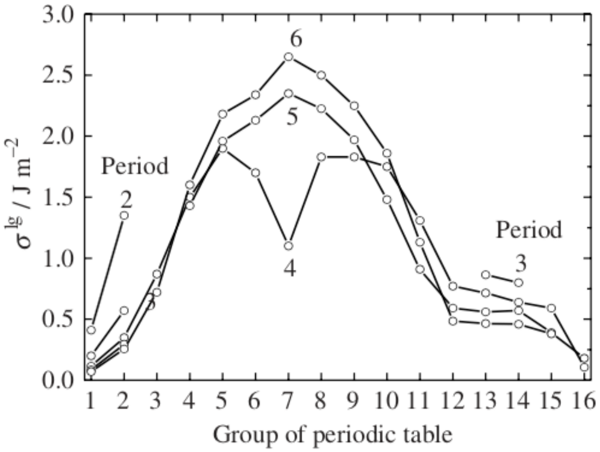
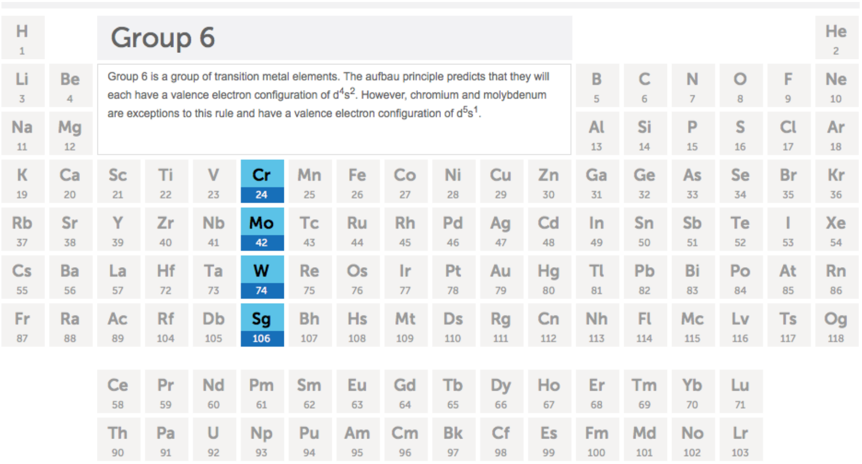


Figure 6.5 Periodic trends in the surface tension of selected liquid elements in periods 2–6 at their melting temperature [8].



Group 6

Group 6 is a group of transition metal elements. The aufbau principle predicts that they will each have a valence electron configuration of d^4s^2. However, chromium and molybdenum are exceptions to this rule and have a valence electron configuration of d^5s^1.

H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	Rf 104	Db 105	Sg 106	Bh 107	Hs 108	Mt 109	Ds 110	Rg 111	Cn 112	Nh 113	Fl 114	Mc 115	Lv 116	Ts 117	Og 118
		Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71		
		Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103		

Strength of bonding impacts surface tension
d-block transition metals have strong bonds

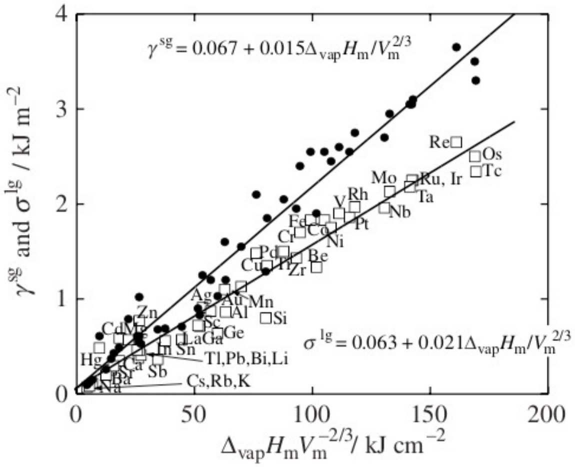


Figure 6.6 Surface tension of the liquid elements at T_{fus}, σ^{lg} (open squares), and surface energy of the solid elements at 0 K, γ^{sg} (filled circles), versus $\Delta_{fus}H_mV_m^{-2/3}$ [8].

Table 6.1 Surface tension or average surface energy of some solid and liquid substances [12, 13].

Substance	σ^{lg} /J m^{-2}
NaCl(l) (1000 °C)	0.098
Al_2O_3(l) (2050 °C)	0.69
SiO_2(l) (1800 °C)	0.307
P_2O_5(l) (100 °C)	0.06
Cu_2S(l) (1200 °C)	0.4
NiS(l) (1200 °C)	0.577
PbS(l)(1200 °C)	0.2
Sb_2S_3(l) (1200 °C)	0.094
H_2O(l) (25 °C)	0.072
	γ^{sg}/J m^{-2}
LiF(s) (25 °C)	0.34
CaF_2(s) (25 °C)	0.45
NaCl(s) (25 °C)	0.227
MgO(s) (25 °C)	1.2

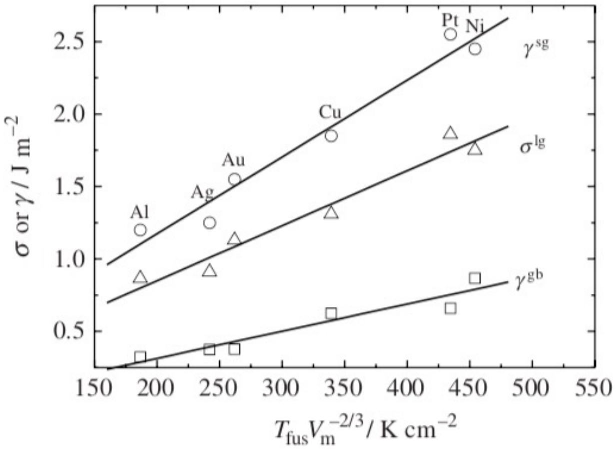


Figure 6.7 Average grain boundary energy, γ^{gb}, surface energy of crystals at 0 K, γ^{sg}, and surface tension σ^{lg} of liquid Al, Ag, Au, Ni and Pt as a function of melting temperature $T_{fus}V_m^{-2/3}$ [8, 11].

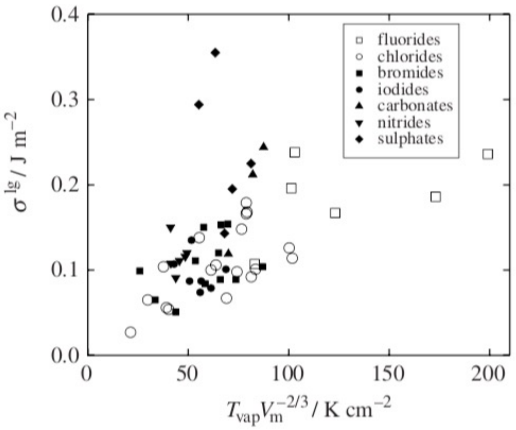


Figure 6.8 Surface tension of fused salts as a function of melting temperature normalized with the molar volume $T_{vap}V_m^{-2/3}$ [14, 15].

Empirical relationship for the temperature dependence, entropy at interface is high, n ~ 1.2 for metals.

$$\sigma^{lg} = \sigma_o^{lg}\left(1 - \frac{T}{T_c}\right)^n$$

For a liquid with its own vapor
Reminiscent of $\Delta G = \Delta H(1 - T/T^*)$

Liquid/Vapor surface

From Hiemenz’s Book

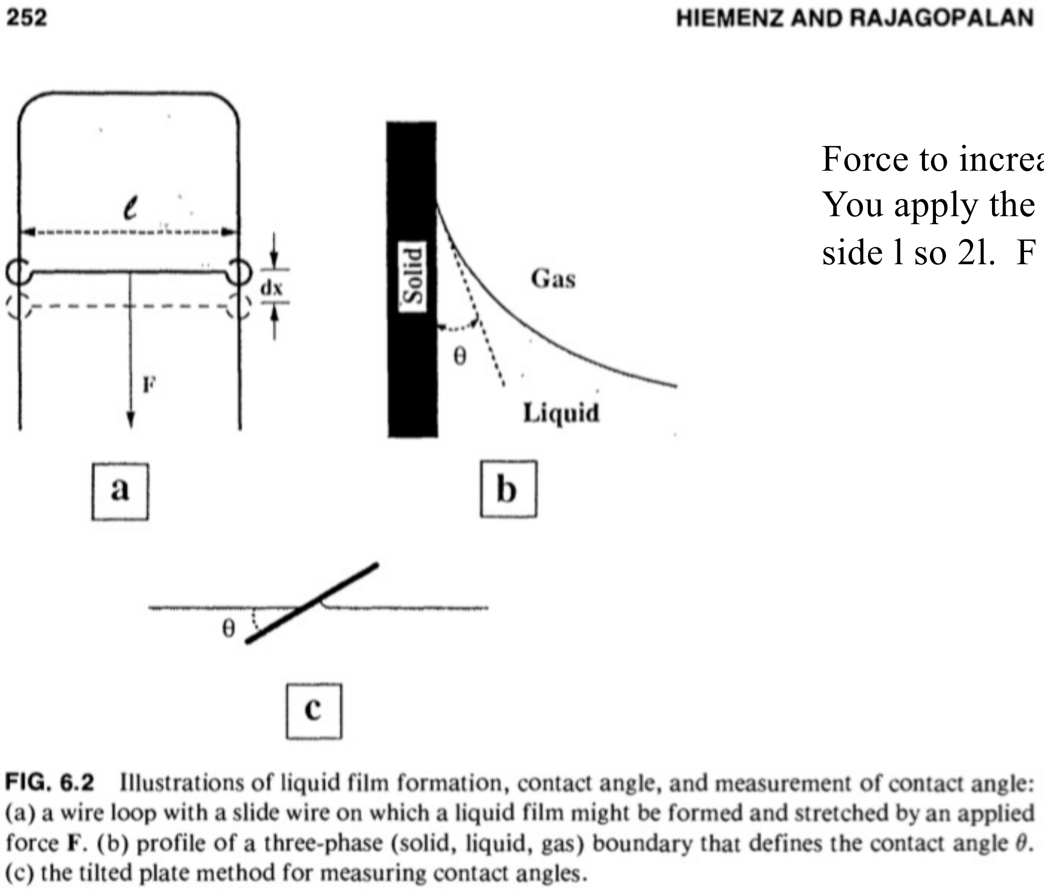

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FIG. 6.2 Illustrations of liquid film formation, contact angle, and measurement of contact angle: (a) a wire loop with a slide wire on which a liquid film might be formed and stretched by an applied force **F**. (b) profile of a three-phase (solid, liquid, gas) boundary that defines the contact angle θ. (c) the tilted plate method for measuring contact angles.

Force to increase a 2d film area
You apply the force to the the side *l* and the opposite side l so 2l. $F \sim 2l$ or $F/(2l) = \gamma$

$$w = P\gamma \cos\theta$$

w = Force
P = Wetted Perimeter
t = Thickness
l = Plate Length

$$P = 2(\ell + t)$$

$$2\pi R_C \gamma \cos\theta \approx \pi R_c^2 h \Delta\rho g$$

Perimeter gamma cosθ= mgh

$$\frac{R_c h}{\cos\theta} \approx \frac{2\gamma}{\Delta\rho g}$$

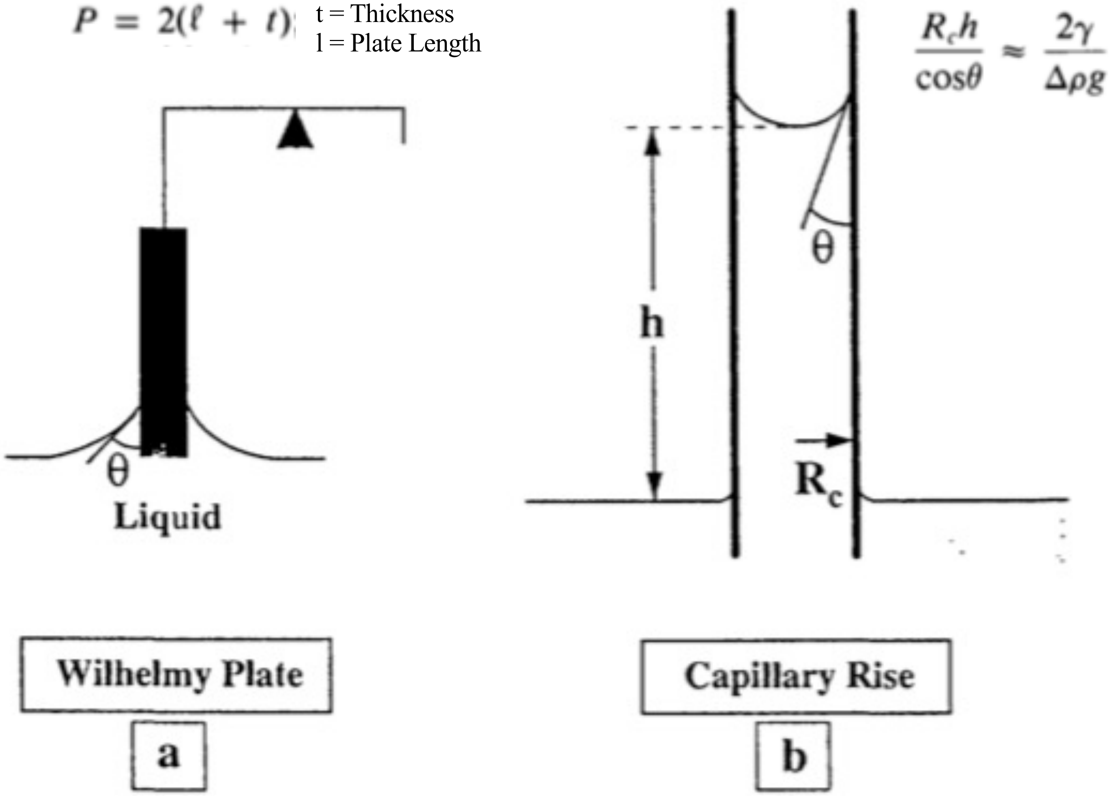


FIG. 6.3 Surface tension and capillary rise: (a) the Wilhelmy plate method for measuring γ; (b) schematic illustration of capillary rise in a cylindrical tube of radius R_c.

sions as forces acting along the perimeter of the drop enables us to write immediately an equation that describes the equilibrium force balance in the horizontal direction:

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (44)$$

Young-Dupré Equation

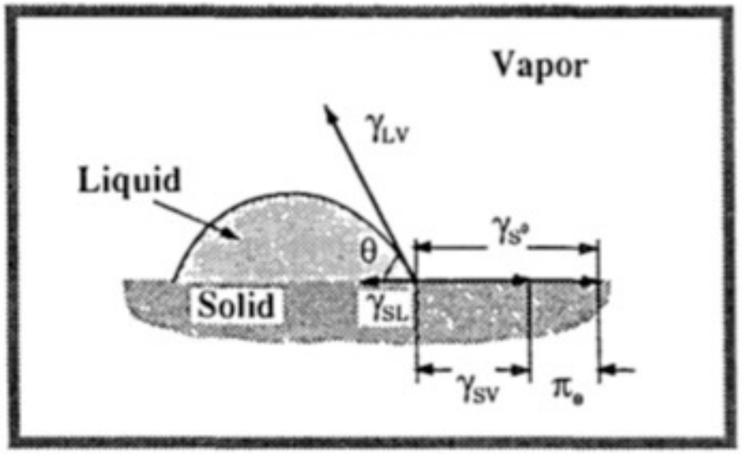


FIG. 6.6 Components of interfacial tension needed to derive Young's equation.

Equation (6.39) was first derived by Young, and is often referred to as the **Young–Dupré** equation. We usually distinguish between full $(\theta < 90^\circ)$ and partial wetting $(\theta > 90^\circ)$ and an alternative measure of the same property is given by the **wetting coefficient**:

$$k = \frac{\gamma^{\mathrm{sg}} - \gamma^{\mathrm{sl}}}{\sigma^{\mathrm{lg}}} = \cos\theta \qquad (6.40)$$

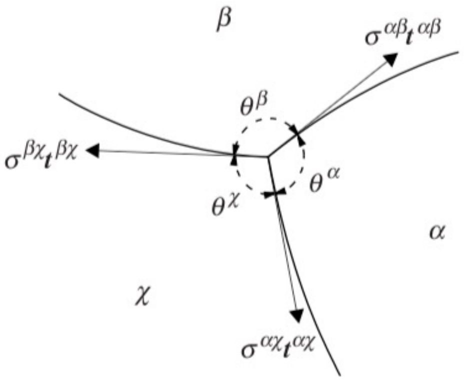


Figure 6.9 Two-dimensional projection of equilibrium at a plane of contact between three phases α, β and χ where the angles between the three two-phase boundaries meeting in a line of contact are denoted θ^{α}, θ^{β} and θ^{χ}.

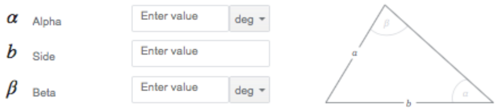
t is the tangent vector along the surface at the point of contact, tσ is a force in the tangent direction

$$\sigma^{\alpha\beta}t^{\alpha\beta}+\sigma^{\beta\chi}t^{\beta\chi}+\sigma^{\alpha\chi}t^{\alpha\chi}=0$$

Larger angle means smaller displacement t, t ~ 1/sin(θ)

$$\frac{\sigma^{\alpha\beta}}{\sin\theta^{\chi}}=\frac{\sigma^{\beta\chi}}{\sin\theta^{\alpha}}=\frac{\sigma^{\alpha\chi}}{\sin\theta^{\beta}}=0$$

$$a=b\frac{\sin\alpha}{\sin\beta}$$


α Alpha Enter value deg
b Side Enter value
β Beta Enter value deg

$$\frac{\sin A}{a}=\frac{\sin B}{b}=\frac{\sin C}{c}$$

This defines the observed angles in a micrograph in terms of the surface tension for the various phases

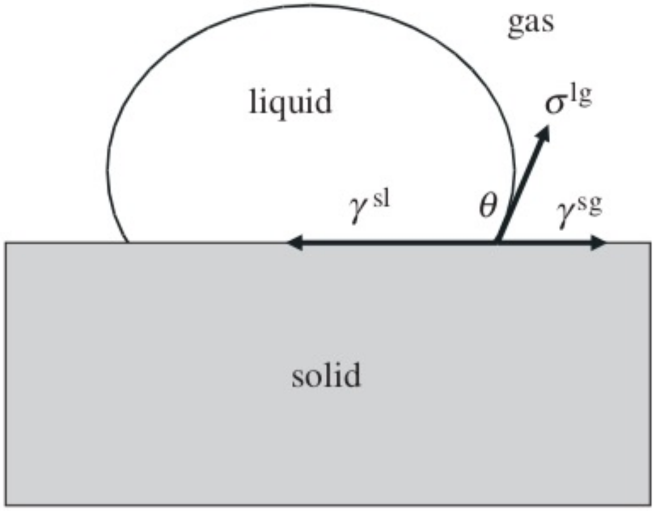


Figure 6.10 Contact angle θ of a liquid drop resting on a solid surface. The definition of the forces used in the figure eliminates the contribution from gravity.

$$\gamma^{sg} = \gamma^{sl} + \sigma^{lg} \cos\theta = 0$$

Young-Dupre Equation

Figure 3: Coexistence of three fluid phases in mutual contact; here, α, β, and θ each indicate both a phase and its contact angle.

Three phases and three angles
Define the phase by the angle

Take the α, θ line as the vector direction then

$\gamma^{\alpha\theta} + \gamma^{\theta\beta}\cos(\theta) + \gamma^{\beta\alpha}\cos(\alpha) = 0$ using the dot product of the vectors

For the θ, β line as the vector direction then

$\gamma^{\alpha\theta}\cos(\theta) + \gamma^{\theta\beta} + \gamma^{\alpha\beta}\cos(\beta) = 0$ using the dot product of the vectors

For the α, β line as the vector direction then

$\gamma^{\alpha\theta}\cos(\alpha) + \gamma^{\theta\beta}\cos(\beta) + \gamma^{\alpha\beta} = 0$ using the dot product of the vectors

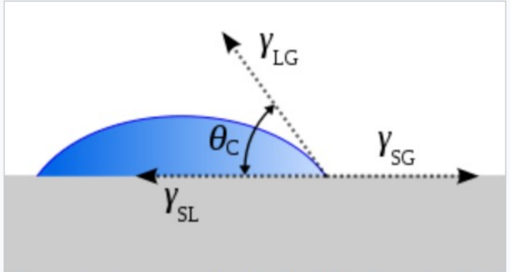


Figure 5: Contact angle of a liquid droplet wetted to a rigid solid surface

β is a flat rigid surface, $\beta = \pi$

$\gamma^{\alpha\theta}\cos(\theta) + \gamma^{\theta\beta} + \gamma^{\alpha\beta}\cos(\beta) = 0$

$\gamma^{gl}\cos(\theta) + \gamma^{ls} - \gamma^{gs} = 0$

$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$ Spreading Parameter: S>0 wets; S<0 partially wets

$S = \gamma_{LG}\left(\cos(\theta) - 1\right)$ For S<0

Dihedral Angle

$$\gamma^{\alpha\alpha} - 2\gamma^{\alpha\beta}\cos\left(\frac{\phi}{2}\right) = 0$$

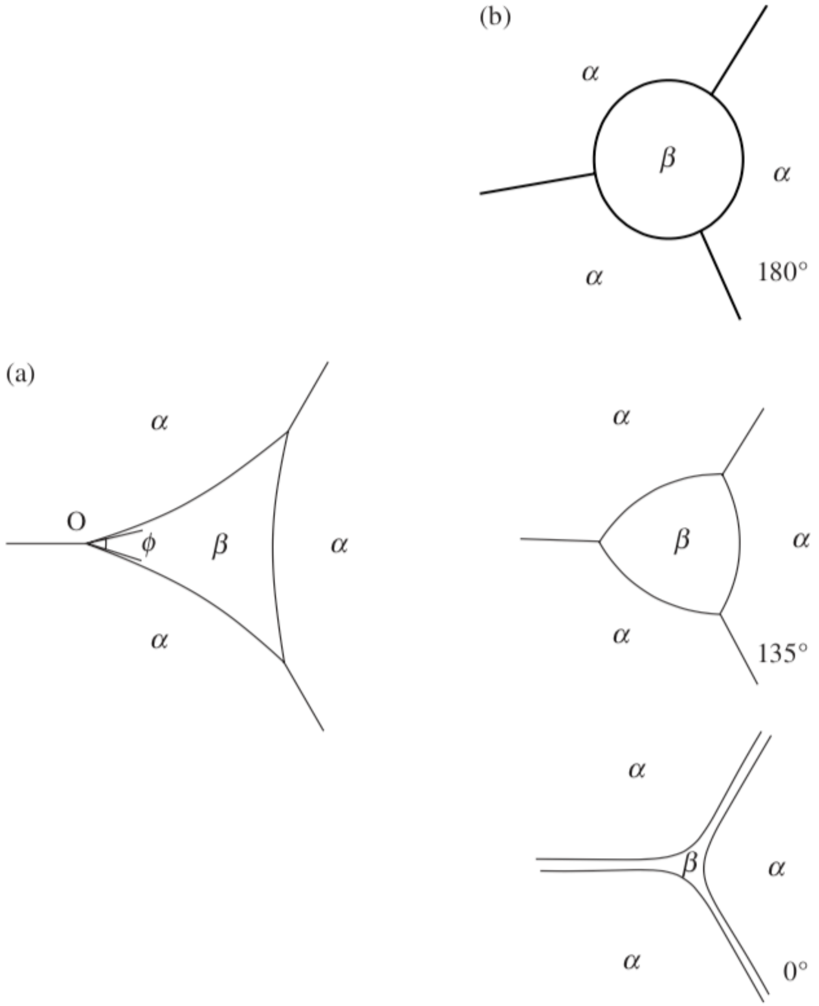


Figure 6.11 (a) Definition of the dihedral angle, ϕ, at a junction of three grain boundaries in a polycrystalline solid. (b) Schematic illustration of the shape of an inclusion phase for different dihedral angles.

Dihedral Angle in Microscopy

$$\gamma^{\alpha\alpha} - 2\gamma^{\alpha\beta}\cos\left(\frac{\phi}{2}\right) = 0$$

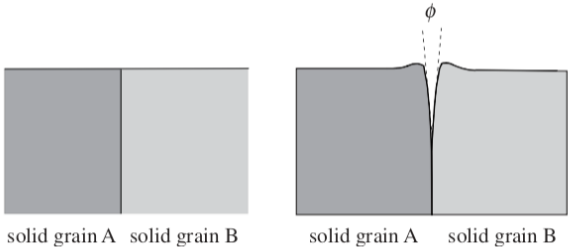


Figure 6.12 Grain boundary after polishing (a) and after the subsequent thermal etching (b).

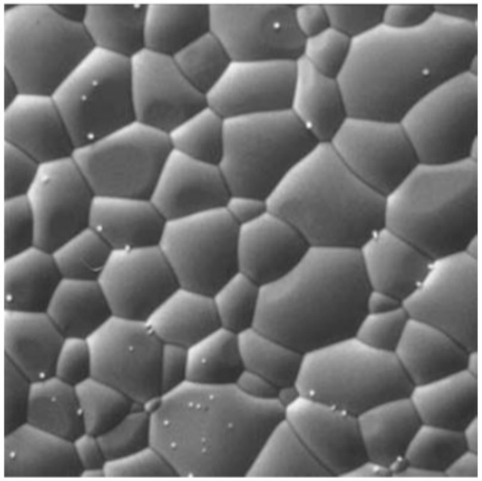


Figure 6.13 Surface of thermally etched $La_{0.5}Sr_{0.5}Fe_{0.5}Co_{0.5}O_3$, a polycrystalline ceramic material .

Thomson's (or Kelvin's) **equation**

$$\ln \frac{p^{\mathrm{g}}}{p^{\mathrm{g}}_{r=\infty}} = \frac{V^{\mathrm{l}}}{RT}\frac{2\sigma^{\mathrm{lg}}}{r}$$

Pressure for equilibrium of a liquid droplet of size ”r”

$\mathrm{d}\mu^{\mathrm{l}} = \mathrm{d}\mu^{\mathrm{g}}$ Reversible equilibrium

$V^{\mathrm{g}}\mathrm{d}p^{\mathrm{g}} = V^{\mathrm{l}}\mathrm{d}p^{\mathrm{l}}$ At constant temperature

$\mathrm{d}p^{\mathrm{l}} = V^{\mathrm{g}}/V^{\mathrm{l}}\,\mathrm{d}p^{\mathrm{g}}$

$\mathrm{d}(p^{\mathrm{g}} - p^{\mathrm{l}}) = \mathrm{d}\left(\frac{2\sigma^{\mathrm{lg}}}{r}\right)$ Differential Laplace equation

$$\frac{V^{\mathrm{g}} - V^{\mathrm{l}}}{V^{\mathrm{l}}}\mathrm{d}p^{\mathrm{g}} = \mathrm{d}\left(\frac{2\sigma^{\mathrm{lg}}}{r}\right)$$

$V^{\mathrm{g}} = RT/p^{\mathrm{g}} \qquad V^{\mathrm{g}} - V^{\mathrm{l}} \approx V^{\mathrm{g}}$

$$\frac{RT}{V^{\mathrm{l}}}\frac{\mathrm{d}p^{\mathrm{g}}}{p^{\mathrm{g}}} = \mathrm{d}\left(\frac{2\sigma^{\mathrm{lg}}}{r}\right)$$

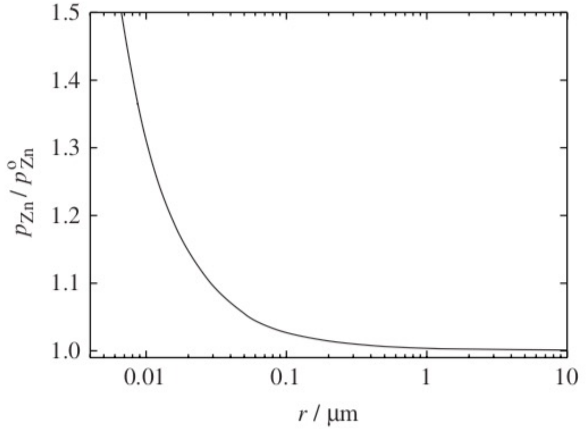


Figure 6.14 The vapour pressure of Zn over a spherical droplet of molten Zn at the melting temperature as a function of the droplet radius. $p^{\mathrm{o}}_{\mathrm{Zn}} = 2\cdot10^{-4}$ bar, $\sigma^{\mathrm{lg}} = 0.78$ J m^{-2} and $\rho = 6.58$ g cm^{-3} [8].

Small drops evaporate, large drops grow

In the absence of nuclei, the initial bubbles on boiling can be very small
These bubbles are unstable due to high pressure so boiling can be prevented leading to a superheated fluid

$$-S^{\mathrm{g}}\mathrm{d}T + V^{\mathrm{g}}\mathrm{d}p^{\mathrm{g}} = -S^{\mathrm{l}}\mathrm{d}T$$

Equilibrium

$$V^{\mathrm{g}}\mathrm{d}p^{\mathrm{g}} = (S^{\mathrm{g}} - S^{\mathrm{l}})\mathrm{d}T = (H^{\mathrm{g}} - H^{\mathrm{l}})\frac{\mathrm{d}T}{T}$$

$$\frac{\mathrm{d}T}{T^2} = \frac{R}{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}\frac{\mathrm{d}p^{\mathrm{g}}}{p^{\mathrm{g}}}$$

Ideal gas

$$\frac{\mathrm{d}T}{T^2} = \frac{R}{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}\frac{\mathrm{d}(2\sigma^{\mathrm{lg}}/r)}{(p^{\mathrm{l}} + [2\sigma^{\mathrm{lg}}/r])}$$

Laplace equation for pressure

$$\left(\frac{1}{T}\right)_{r=\infty} - \left(\frac{1}{T}\right)_{r} = \frac{R}{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}\ln\left(1 + \frac{2\sigma^{\mathrm{lg}}/r}{p^{\mathrm{l}}}\right)$$

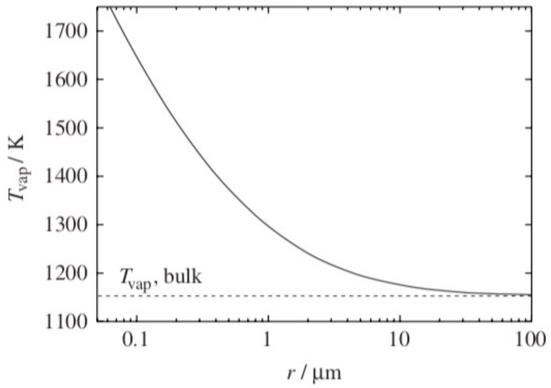


Figure 6.15 The boiling temperature of Na as a function of the radius of a vapour bubble surrounded by molten Na. $\Delta_{\mathrm{vap}}H_{\mathrm{m}} = 101.3$ kJ mol^{-1} and $\sigma^{\mathrm{lg}} = 0.19$ J m^{-2} [8].

Smaller bubbles at higher temperatures

Solubility and Size, r

Consider a particle of size r_i in a solution of concentration x_i with activity a_i

-SUV
 H A
-pGT

$$\mathrm{d}(p^{\mathrm{s}} - p^{\mathrm{l}}) = \mathrm{d}\left(\frac{2\gamma^{\mathrm{sl}}}{r}\right)$$

Derivative form of the Laplace equation $p^{\beta} - p^{\alpha} = \sigma(c_1 + c_2) = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$

$$\mathrm{d}\mu_i^{\mathrm{l}} = \mathrm{d}\mu_i^{\mathrm{s}} = V_i^{\mathrm{s}}\mathrm{d}p^{\mathrm{s}} = V_i^{\mathrm{s}}\mathrm{d}\left(\frac{2\gamma^{\mathrm{sl}}}{r}\right)$$

Dynamic equilibrium

$$(\mu_i^{\mathrm{l}})_r - (\mu_i^{\mathrm{l}})_{r=\infty} = V_i^{\mathrm{s}}\frac{2\gamma^{\mathrm{sl}}}{r}$$

For an incompressible solid phase

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{*} + RT\ln a_{\mathrm{A}}$$

Definition of activity

$$\ln\frac{(x_i^{\mathrm{l}})_r}{(x_i^{\mathrm{l}})_{r=\infty}} = \frac{V_i^{\mathrm{s}}}{RT}\frac{2\gamma^{\mathrm{sl}}}{r}$$

Solubility increases exponentially with reduction in size, r

$$(x_i^{l})_r = (x_i^{l})_{r=\infty}\exp(2\gamma^{sl}/(\rho RT\, r))$$

Small particles dissolve to build large particles with lower solubility

-To obtain nanoparticles you need to supersaturate to a high concentration (far from equilibrium).
-Low surface energy favors nanoparticles. (Such as at high temperatures)
-High temperature and high solid density favor nanoparticles.

Supersaturation is required for any nucleation

One form of the Gibbs-Thompson Equation

Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

Bulk decreases free energy

$$\Delta_{\mathrm{l-s}}G = -\frac{4}{3}\pi r^3\left(\frac{\rho}{M}\right)\Delta_{\mathrm{fus}}G_{\mathrm{m}} + 4\pi r^2\gamma^{\mathrm{sl}}$$

Surface increases free energy

(M/ρ) is molar volume

$$\frac{\mathrm{d}\Delta_{\mathrm{l-s}}G}{\mathrm{d}r} = -4\pi r^2\left(\frac{\rho}{M}\right)\Delta_{\mathrm{fus}}G_{\mathrm{m}} + 8\pi r\gamma^{\mathrm{sl}}$$

maximum $\mathrm{d}\Delta_{\mathrm{l-s}}G/\mathrm{d}r = 0$

Barrier energy for nucleation at the critical nucleus size beyond which growth is spontaneous

$$r^* = [2(M/\rho)\gamma^{\mathrm{sl}}]/\Delta_{\mathrm{fus}}G_{\mathrm{m}}$$

$$\Delta_{\mathrm{l-s}}G^* = \frac{16\pi(\gamma^{\mathrm{sl}})^3M^2}{3\rho^2\Delta_{\mathrm{fus}}G_{\mathrm{m}}^2}$$

Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

Homogeneous (assume a sphere of radius r)

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

$$\frac{\mathrm{d}\Delta G_{homo}}{dr} = 0 = 4\pi r^{*2} \Delta G_V + 8\pi r^* \gamma$$

$$r^*_{homo} = \frac{2\gamma}{\Delta G_V}$$

$$\Delta G^*_{homo} = \frac{4\pi 8\gamma^3}{3\Delta G_V{}^2} + \frac{4\pi 4\gamma^3}{\Delta G_V{}^2} = \frac{80\pi\gamma^3}{3\Delta G_V{}^2} = \frac{20\pi\gamma r^{*2}_{homo}}{3}$$

Heterogeneous (assume a disk of radius r, thickness t nucleating on the same material)

$$\Delta G_{hetero} = \pi t r^2 \Delta G_V + 2\pi r t \gamma$$

$$\frac{\mathrm{d}\Delta G_{hetero}}{dr} = 0 = 2\pi t r^* \Delta G_V + 2\pi t \gamma$$

$$r^*_{hetero} = \frac{\gamma}{\Delta G_V} = \frac{r^*_{homo}}{2}$$

$$\Delta G^*_{hetero} = \frac{\pi t \gamma^2}{\Delta G_V} + \frac{2\pi t \gamma^2}{\Delta G_V} = \frac{3\pi t \gamma^2}{\Delta G_V} = \frac{9\mathrm{t}\Delta G_V \Delta G^*_{homo}}{80\gamma} = \frac{3\pi t \gamma r^*_{homo}}{2} = \frac{9t}{40 r^*_{homo}} \Delta G^*_{homo}$$

$$\Delta G^*_{hetero} = \frac{9t}{80 r^*_{hetero}} \Delta G^*_{homo}$$

$\frac{t}{r^*_{hetero}} \ll 1 \; and \; \frac{9}{80} < 1$ so $\Delta G^*_{hetero} \ll \Delta G^*_{homo}$

Critical Nucleus and Activation Energy for Crystalline Nucleation (Gibbs)

$$r^* = [2(M/\rho)\gamma^{\mathrm{sl}}]/\Delta_{\mathrm{fus}}G_{\mathrm{m}}$$

$$\Delta_{\mathrm{l-s}}G^* = \frac{16\pi(\gamma^{\mathrm{sl}})^3 M^2}{3\rho^2 \Delta_{\mathrm{fus}}G_{\mathrm{m}}^2}$$

$\Delta_{\mathrm{fus}}G_{\mathrm{m}} = \Delta_{\mathrm{fus}}H_{\mathrm{m}} - T\Delta_{\mathrm{fus}}S_{\mathrm{m}}$

Lower T leads to larger $\Delta_{\mathrm{fus}}G_{\mathrm{m}}$ (Driving force for crystallization) smaller r* and smaller $\Delta_{\mathrm{l-s}}G^*$

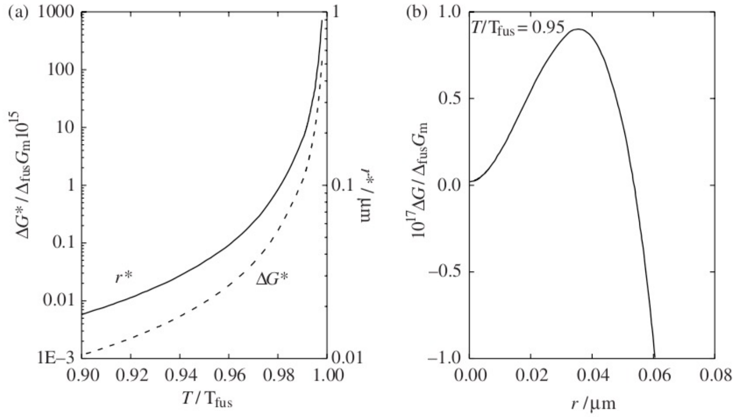


Figure 6.16 (a) The critical radius (r^*) and thermodynamic barrier for nucleation of Al (ΔG^*) versus degree of supercooling T/T_{fus}. (b) The Gibbs energy of a spherical Al crystal relative to the supercooled Al(l) as a function of its radius. $\Delta_{\mathrm{fus}}H_{\mathrm{m}} = 10.794$ kJ mol^{-1}, $T_{\mathrm{fus}} = 933.47$ K and $\rho = 2.55$ g cm^{-3} [8].

Deep quench, far from equilibrium leads to nanoparticles

$$\Delta_{\mathrm{l-s}}G = -\frac{4}{3}\pi r^3\left(\frac{\rho}{M}\right)\Delta_{\mathrm{fus}}G_{\mathrm{m}} + 4\pi r^2\gamma^{\mathrm{sl}}$$

One form of the Gibbs-Thompson Equation

Ostwald Ripening

$$p^{\beta} - p^{\alpha} = \sigma(c_1 + c_2) = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

PV = μ

Dissolution/precipitation mechanism for grain growth
Consider small and large grains in contact with a solution

$$(\mu_i^{\mathrm{s}})_{r'} - (\mu_i^{\mathrm{s}})_{r''} = 2V_i^{\mathrm{s}}\gamma^{\mathrm{sl}}\left(\frac{1}{r'} - \frac{1}{r''}\right)$$

Grain Growth and Elimination of Pores

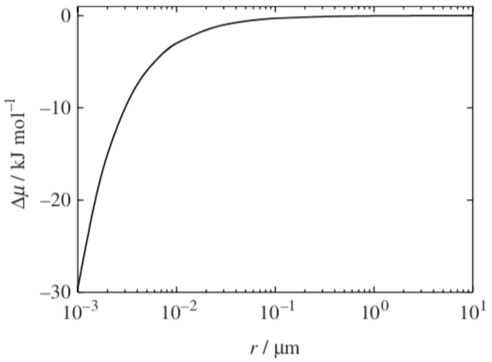
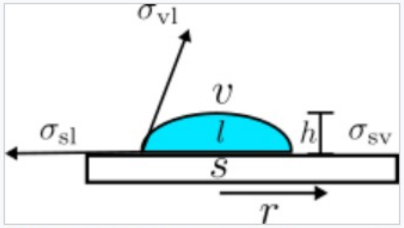
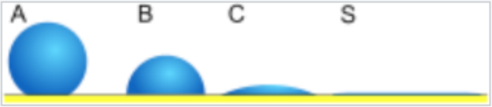


Figure 6.17 The difference in the chemical potential of Au(s) between a spherical particle with radius 10 μm and a smaller particle with radius r. $\rho = 18.4$ g cm^{-3} and $\gamma^{\mathrm{sl}} = 1.38$ J m^{-2} [21].

Heterogeneous versus Homogeneous Nucleation

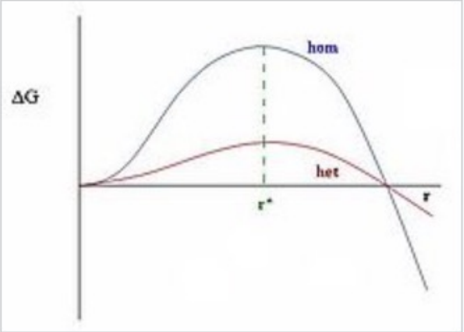


A diagram featuring all of the factors that affect heterogeneous nucleation



Three droplets on a surface, illustrating decreasing contact angles. The contact angle the droplet surface makes with the solid horizontal surface decreases from left to right.

$$\Delta G^{het} = f(\theta)\Delta G^{hom}, \qquad f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$



Difference in energy barriers

Formation of a surface nucleus versus a bulk nucleus from n monomers

Homogeneous

$$\Delta G_n = -n\phi + \psi_n \qquad \phi = \mu - \mu_\infty = kT\ln\left(\frac{x}{x_\infty}\right)$$

$$\psi_n = \mu_n^{v} - n\mu_0 \qquad \psi_n = a_n\gamma = \gamma\left(\frac{27\beta v_1^2}{4}\right)^{\frac{1}{3}} n^{\frac{2}{3}} = \psi n^{\frac{2}{3}}$$

Bulk vs n-mer
So, surface excess chemical potential

$$\Delta G_n = -\phi n + \psi n^{\frac{2}{3}}$$

$$n^* = \left(\frac{2\psi}{3\phi}\right)^3$$

$$\Delta G^* = \frac{4\psi^3}{27\phi^2} = \frac{\psi n^{*\frac{2}{3}}}{3} = \frac{\phi n^*}{2}$$

Heterogeneous (Surface Patch)

$$\Delta G'_{n'} = -\phi n' + \psi'_{n'}$$

$$\psi'_{n'} = 2\pi r h\gamma = 2\gamma\sqrt{\pi h v_1 n'} = \psi' n'^{\frac{1}{2}}$$

Surface energy from the sides of the patch

$$\Delta G'_{n'} = -\phi n' + \psi' n'^{\frac{1}{2}}$$

$$n'^* = \left(\frac{\psi'}{2\phi}\right)^2$$

$$\Delta G'^* = \frac{\psi'^2}{4\phi} = \frac{\psi'\sqrt{n'^*}}{2} = \phi n'^* = \frac{\pi h v_1 \gamma^2}{\phi}$$

Barrier is half the height for surface nucleation
Stable size is half the size

$$\Delta G^* = \frac{4\psi^3}{27\phi^2} = \frac{\psi n^{*\frac{2}{3}}}{3} = \frac{\phi n^*}{2} \qquad \Delta G'^* = \frac{\psi'^2}{4\phi} = \frac{\psi'\sqrt{n'^*}}{2} = \phi n'^* = \frac{\pi h v_1 \gamma^2}{\phi}$$

$$r^* = \frac{2\gamma v_1}{\phi} = 2r'^* \qquad r'^* = \sqrt{\frac{n'^* v_1}{\pi h}} = \frac{\gamma v_1}{\phi}$$

Adamson Physical Chemistry of Surfaces pp. 328 Classical Nucleation Theory

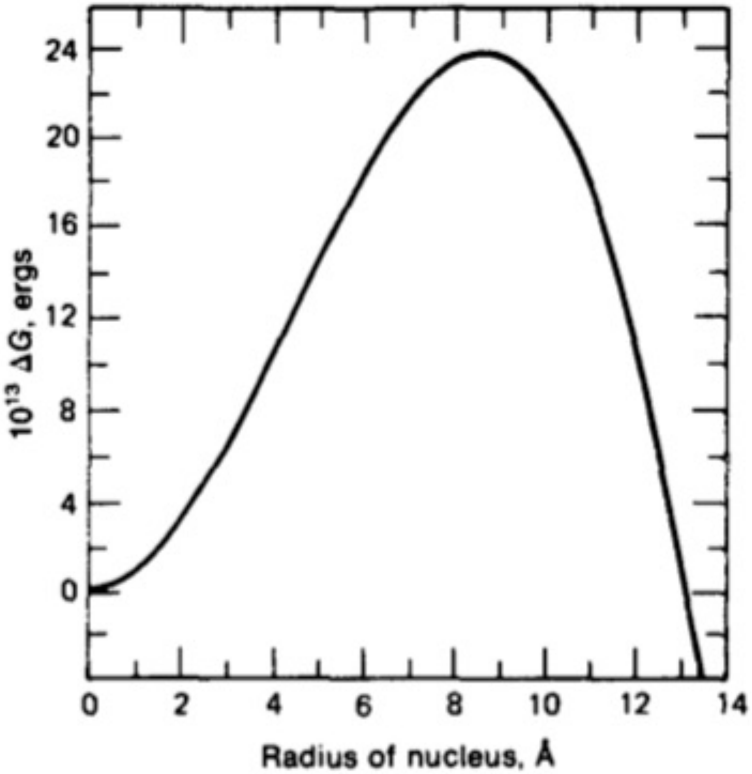


Fig. IX-1. Variation of ΔG with droplet size for water vapor at 0°C at four times the saturation pressure. (From Ref. 2.)

$$\Delta G = -n\,\Delta\mu + 4\pi r^2 \gamma \qquad \text{(IX-1)}$$

condensation

$$\Delta G_{\text{cond}} = -n\Delta\mu = -nkT \ln \frac{P}{P^0} = -nkT \ln x \qquad \text{(IX-2)}$$

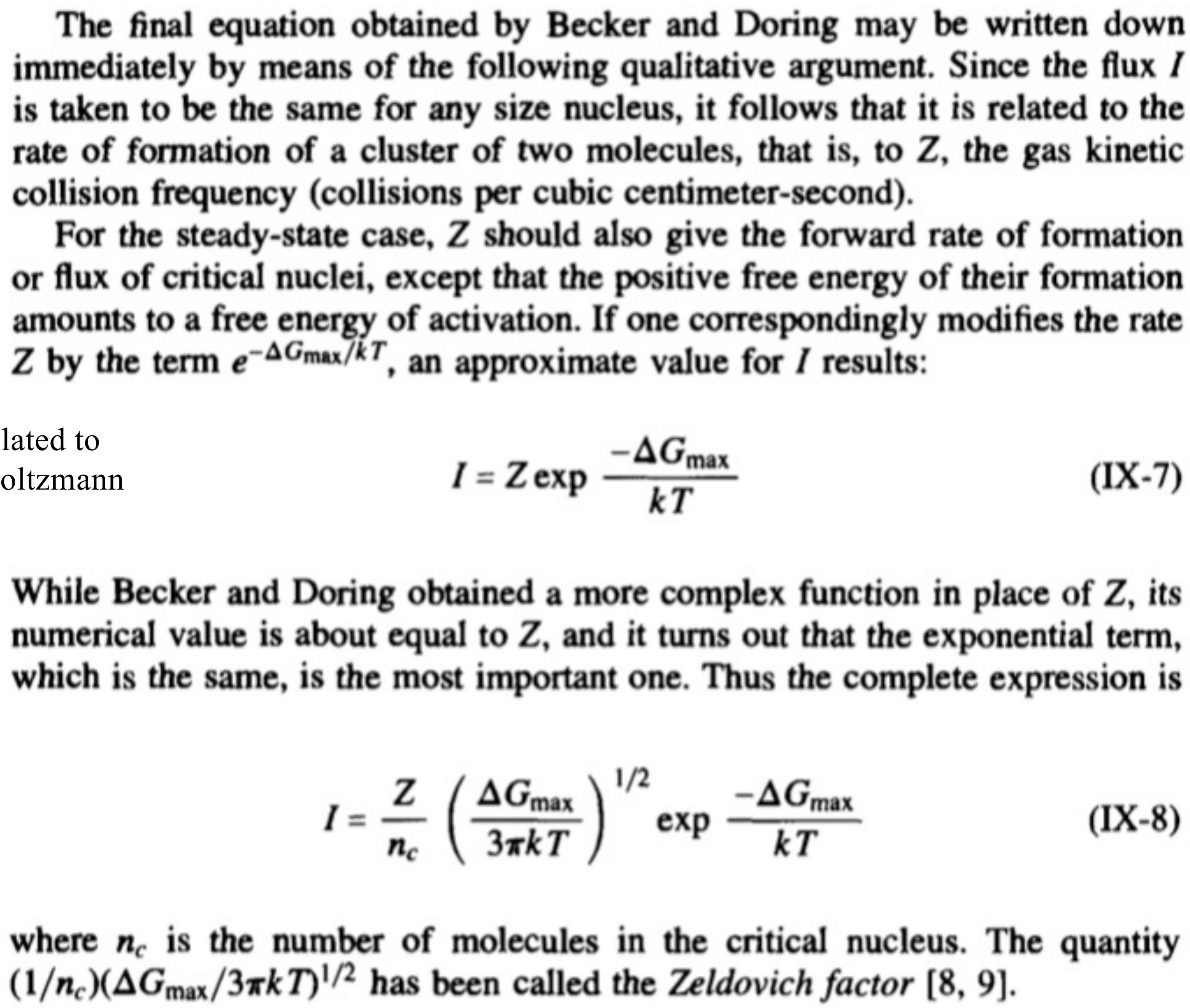
where P^0 is the pressure or activity of the liquid phase. The number of molecules in the cluster is related to its size

$$n = \frac{4\pi}{3} r^3 \hat{\rho} \qquad \text{(IX-3)}$$

$$n_c = \frac{32\pi\gamma^3}{3\hat{\rho}^2\,\Delta\mu^3} \qquad \text{(IX-4)}$$

$$\Delta G_{\max} = \frac{16\pi\gamma^3}{3\hat{\rho}^2\,\Delta\mu^2} = \frac{4\pi r_c^2 \gamma}{3} \qquad \text{(IX-6)}$$

$$r_c = \frac{2\gamma}{\hat{\rho}\,\Delta\mu} \qquad \text{(IX-5)}$$



The final equation obtained by Becker and Doring may be written down immediately by means of the following qualitative argument. Since the flux I is taken to be the same for any size nucleus, it follows that it is related to the rate of formation of a cluster of two molecules, that is, to Z, the gas kinetic collision frequency (collisions per cubic centimeter-second).

For the steady-state case, Z should also give the forward rate of formation or flux of critical nuclei, except that the positive free energy of their formation amounts to a free energy of activation. If one correspondingly modifies the rate Z by the term $e^{-\Delta G_{\max}/kT}$, an approximate value for I results:

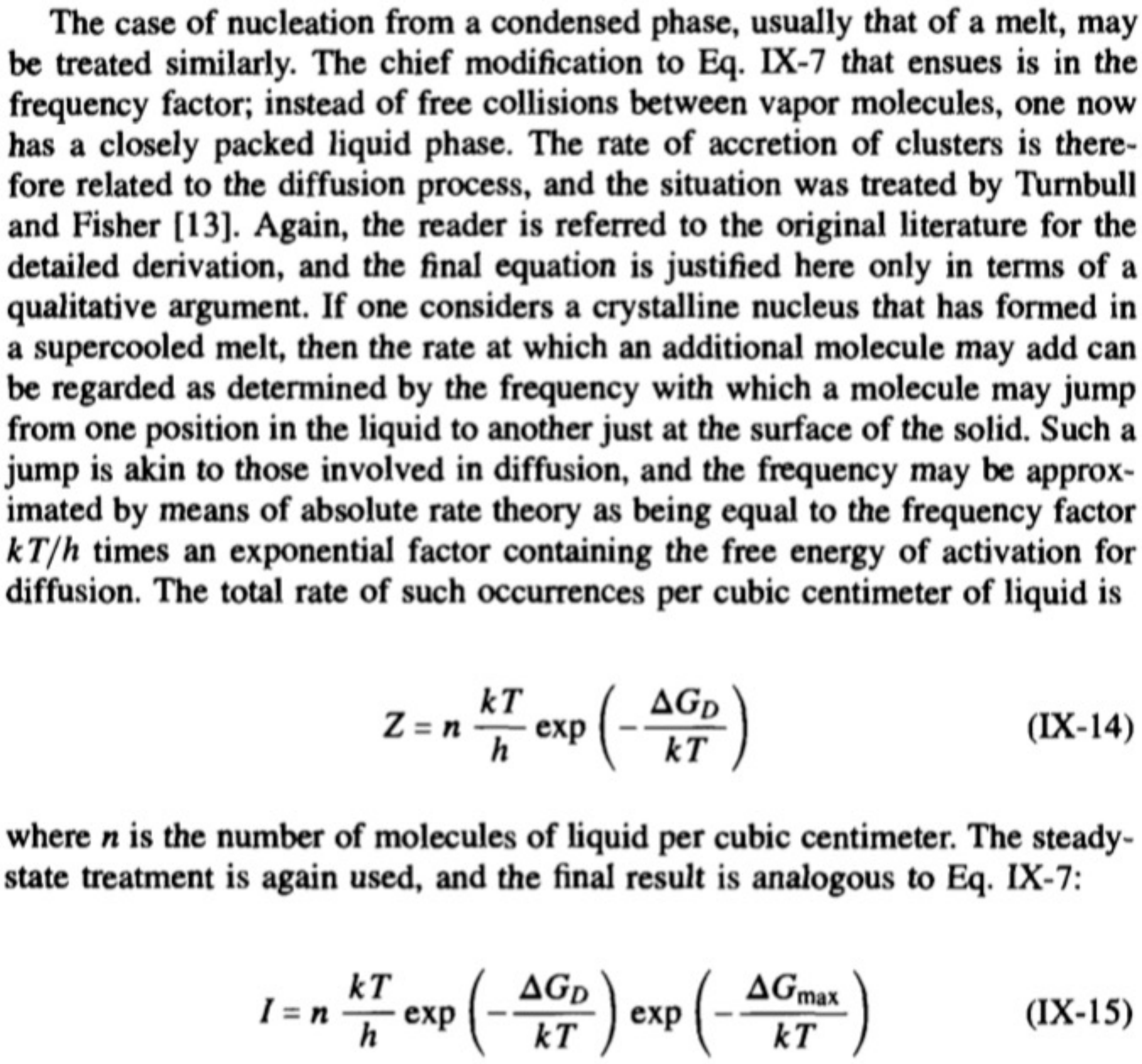
$$I = Z \exp \frac{-\Delta G_{\max}}{kT} \qquad \text{(IX-7)}$$

While Becker and Doring obtained a more complex function in place of Z, its numerical value is about equal to Z, and it turns out that the exponential term, which is the same, is the most important one. Thus the complete expression is

$$I = \frac{Z}{n_c} \left(\frac{\Delta G_{\max}}{3\pi kT} \right)^{1/2} \exp \frac{-\Delta G_{\max}}{kT} \qquad \text{(IX-8)}$$

where n_c is the number of molecules in the critical nucleus. The quantity $(1/n_c)(\Delta G_{\max}/3\pi kT)^{1/2}$ has been called the *Zeldovich factor* [8, 9].

Growth rate I is related to collisions Z and Boltzmann probability



The case of nucleation from a condensed phase, usually that of a melt, may be treated similarly. The chief modification to Eq. IX-7 that ensues is in the frequency factor; instead of free collisions between vapor molecules, one now has a closely packed liquid phase. The rate of accretion of clusters is therefore related to the diffusion process, and the situation was treated by Turnbull and Fisher [13]. Again, the reader is referred to the original literature for the detailed derivation, and the final equation is justified here only in terms of a qualitative argument. If one considers a crystalline nucleus that has formed in a supercooled melt, then the rate at which an additional molecule may add can be regarded as determined by the frequency with which a molecule may jump from one position in the liquid to another just at the surface of the solid. Such a jump is akin to those involved in diffusion, and the frequency may be approximated by means of absolute rate theory as being equal to the frequency factor kT/h times an exponential factor containing the free energy of activation for diffusion. The total rate of such occurrences per cubic centimeter of liquid is

$$Z = n\,\frac{kT}{h}\exp\left(-\frac{\Delta G_D}{kT}\right) \qquad \text{(IX-14)}$$

where n is the number of molecules of liquid per cubic centimeter. The steady-state treatment is again used, and the final result is analogous to Eq. IX-7:

$$I = n\,\frac{kT}{h}\exp\left(-\frac{\Delta G_D}{kT}\right)\exp\left(-\frac{\Delta G_{\max}}{kT}\right) \qquad \text{(IX-15)}$$

Three forms of the Gibbs-Thompson Equation

Ostwald-Freundlich Equation

$$x = x_{\infty} \exp\left(\frac{2v_1\gamma}{rkT}\right)$$

x = supersaturated mole fraction
x_{∞} = equilibrium mole fraction
ν_1 = the molar volume

$$\Delta G = -n\phi + \gamma A$$

Free energy of formation for an n-mer nanoparticle from a supersaturated solution at T

$$\phi = \mu - \mu_{\infty} = kT\ln\left(\frac{x}{x_{\infty}}\right)$$

Difference in chemical potential between a monomer in supersaturated conditions and equilibrium with the particle of size r

$$\frac{d(\Delta G)}{dn} = 0 = -\phi + \gamma v_1 \frac{dA}{dV}$$

At equilibrium

For a sphere

$$\mathrm{A} = 4\pi \mathrm{r}^2 = (4\pi)^{\frac{1}{3}} 3^{\frac{2}{3}} V^{\frac{2}{3}} \qquad \frac{dA}{dV} \sim \frac{2}{r}$$

Three forms of the Gibbs-Thompson Equation

Ostwald-Freundlich Equation

$$x = x_\infty \exp\left(\frac{2v_1\gamma}{rkT}\right)$$

Areas of sharp curvature nucleate and grow to fill in. Curvature $\kappa = 1/r$

$$x = x_\infty \exp\left(\frac{2(\kappa_1 + \kappa_2)v_1\gamma}{kT}\right)$$

Second Form of GT Equation

Three forms of the Gibbs-Thompson Equation

$$r = \frac{B\gamma T_\infty}{\Delta H_f (T_\infty - T)}$$

Third form of GT Equation/ Hoffman-Lauritzen Equation
B is a geometric factor from 2 to 6

$$\Delta S = \frac{\Delta H}{T_\infty}$$

Crystallize from a melt, so supersaturate by a deep quench

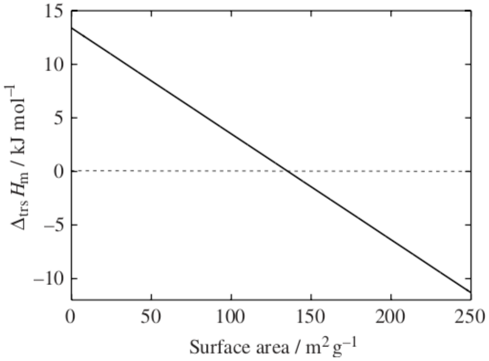
$$\Delta f = 0 \sim r^3\left(\Delta H_f - \frac{T}{T_\infty}\Delta H_f\right) - Br^2\gamma = r^3\,\frac{\Delta H_f}{T_\infty}(T_\infty - T) - Br^2\gamma$$

Free energy of a
crystal formed at
supercooled
temperature T

$$\frac{T}{T_\infty} = 1 - \frac{B\gamma}{r\Delta H_f} \sim \exp\left(\frac{-B\gamma}{r\Delta H_f}\right) \qquad x = x_\infty \exp\left(\frac{2(\kappa_1 + \kappa_2)v_1\gamma}{kT}\right) \qquad x = x_\infty \exp\left(\frac{2v_1\gamma}{rkT}\right)$$

For fine grain particles at times a high Gibbs free energy polymorph forms

α-Al_2O_3 is the stable form but γ-Al_2O_3 forms for small particles
γ-Al_2O_3 has a lower surface energy



135 m^2/g ~ 12 nm particles

S/V ~ 1/r

Figure 6.19 The enthalpy of transition of γ-Al_2O_3 to α-Al_2O_3 as a function of the surface area of the nanocrystalline particles [25].

Adsorption (Adherence to surface, can be chemical or physical)

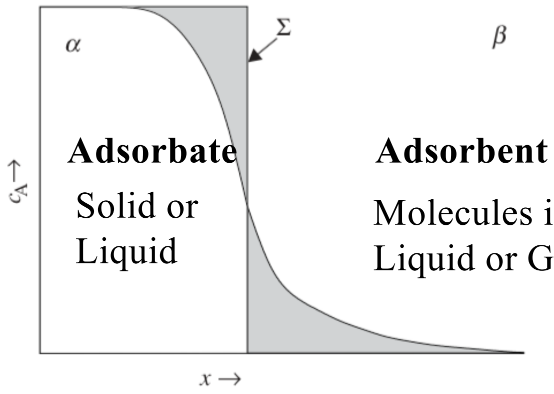


Figure 6.21 Schematic illustration of the concentration of component A across an interface. The Gibbs dividing surface is positioned such that it gives zero adsorption of component A since the algebraic sum of the two shaded areas with opposite sign is zero.

Adsorbate

Solid or Liquid

Adsorbent

Molecules in a Liquid or Gas

The adsorption

$$\Gamma_i = n_i^{\sigma} / A_s$$

Surface Excess Moles

Physical adsorption: Low enthalpy of adsorption; **reversible adsorption isotherm**

Chemical adsorption: Large enthalpy of adsorption; **irreversible**; chemical change to surface
Hysteresis in adsorption isotherm

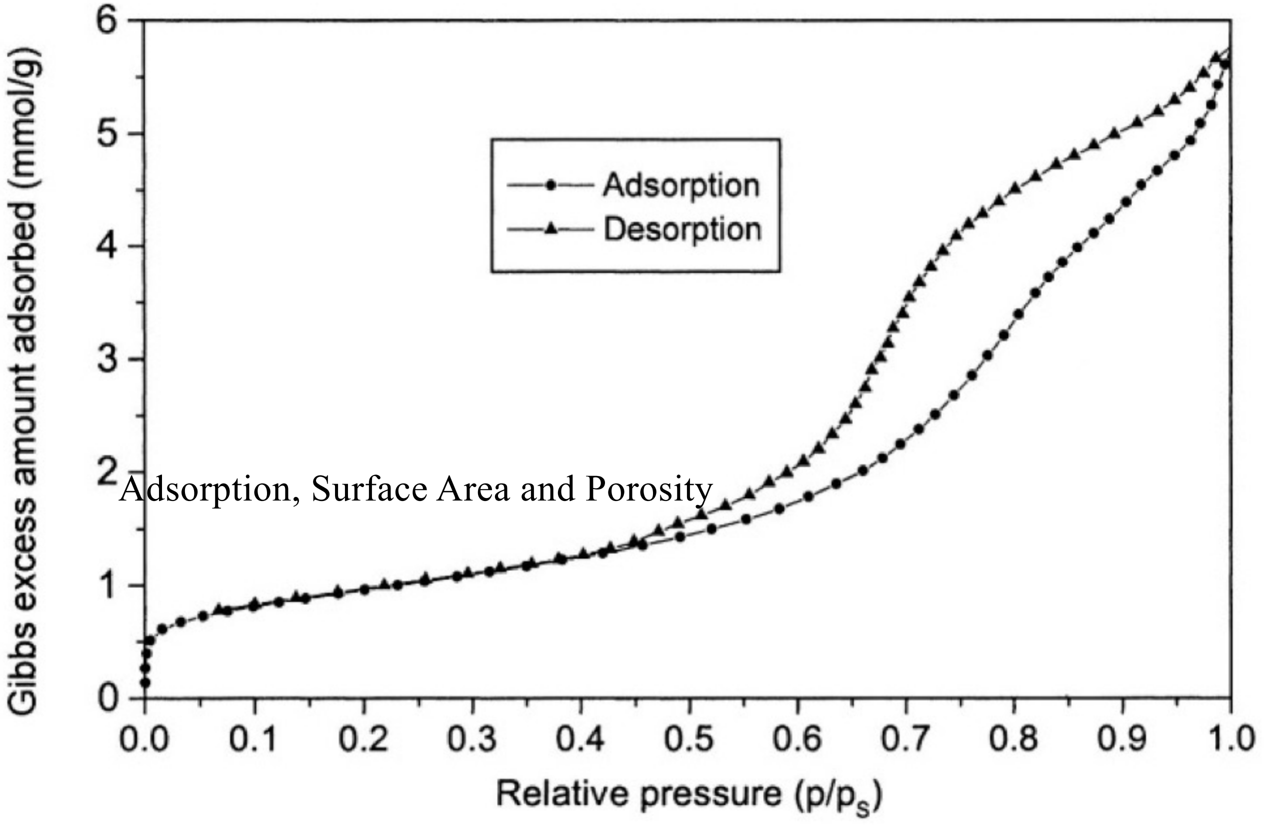
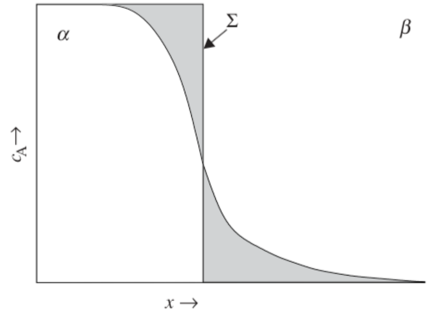


Figure 1.12. Adsorption- and desorption isotherm of N_2 (5.0) on standardized material CRMBAM-PM-104 at 77.3 K, p_0 = 1 atm, [1.36].



Gibbs Adsorption Equation

Internal Energy of System: $$U = TS - p^{\alpha}V^{\alpha} - p^{\beta}V^{\beta} + \sum_{i=1}^{C} n_i \mu_i + \sigma A_s$$

Surface Excess Internal Energy: $$U^{\sigma} = TS^{\sigma} + \sum_{i=1}^{C} n_i^{\sigma} \mu_i + \sigma A_s$$

-SUV
H A
-pGT

Differential Form with respect to the area: $$dU^{\sigma} = TdS^{\sigma} + \sum_{i} \mu_i dn_i^{\sigma} + \sigma dA_s$$

Subtract the total derivative from the differential form yields the Gibbs-Duhem for Surface Excess: $$S^{\sigma} dT + \sum_{i=1}^{C} n_i^{\sigma} d\mu_i + A_s d\sigma = 0$$

$$\Gamma_i = n_i^{\sigma} / A_s$$

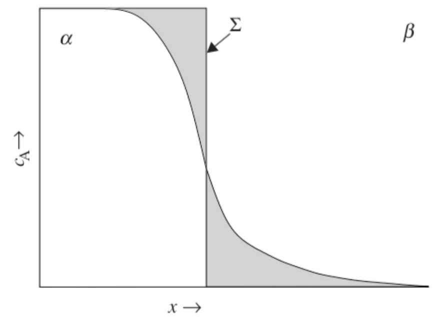
Gibbs Adsorption Equation $$d\sigma = -\frac{S^{\sigma}}{A_s} dT - \sum_{i=1}^{C} \Gamma_i d\mu_i$$

Gibbs Adsorption Equation $d\sigma = -\frac{S^{\sigma}}{A_s}dT - \sum_{i=1}^{C}\Gamma_i d\mu_i$

Gibbs-Duhem Equation: $\sum_i n_i d\mu_i = 0$ $\quad d\mu_A = -\frac{x_B}{x_A}d\mu_B$

$$-\left(\frac{d\sigma}{d\mu_B}\right)_T = \left[\Gamma_B - \left(\frac{x_A}{x_B}\right)\Gamma_A\right]$$

$$d\sigma/d\ln(x_B))_T = -RT[\Gamma_B - (x_A/x_B)\,\Gamma_A)$$



Adsorption, Γ, depends on the position of the "surface"

$$\Gamma_i = n_i^{\sigma} / A_\mathrm{s}$$

Relative Adsorption, doesn't

$$\Gamma_i - \Gamma_\mathrm{A}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_\mathrm{A}^{\alpha} - c_\mathrm{A}^{\beta}}\right)$$

$$\Gamma_i = \frac{n_i^{\sigma}}{A_\mathrm{s}} = \frac{1}{A_\mathrm{s}}(n_i - n_i^{\alpha} - n_i^{\beta}) = \frac{1}{A_\mathrm{s}}(n_i - c_i^{\alpha} V^{\alpha} - c_i^{\beta} V^{\beta})$$

V^{α} is the volume of the α-phase

$$\Gamma_\mathrm{A} = \frac{1}{A_\mathrm{s}}[n_\mathrm{A} - c_\mathrm{A}^{\alpha} V - (c_\mathrm{A}^{\beta} - c_\mathrm{A}^{\alpha}) V^{\beta}]$$

Relative Adsorption

$$\Gamma_i - \Gamma_\mathrm{A}\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_\mathrm{A}^{\alpha} - c_\mathrm{A}^{\beta}}\right) = \frac{1}{A_\mathrm{s}}\left[(n_i - c_i^{\alpha} V) - (n_\mathrm{A} - c_\mathrm{A}^{\alpha} V)\left(\frac{c_i^{\alpha} - c_i^{\beta}}{c_\mathrm{A}^{\alpha} - c_\mathrm{A}^{\beta}}\right)\right]$$

Multiply second equation by c ratio then subtract, it doesn't depend on the position of the surface.

Relative Adsorption

$$\Gamma_{\mathrm{B}}^{(\mathrm{A})} = \Gamma_{\mathrm{B}} - \Gamma_{\mathrm{A}} \left(\frac{c_{\mathrm{B}}^{\alpha} - c_{\mathrm{B}}^{\beta}}{c_{\mathrm{A}}^{\alpha} - c_{\mathrm{A}}^{\beta}} \right)$$

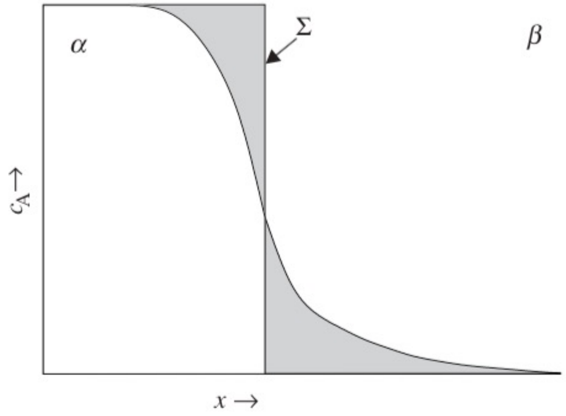


Figure 6.21 Schematic illustration of the concentration of component A across an interface. The Gibbs dividing surface is positioned such that it gives zero adsorption of component A since the algebraic sum of the two shaded areas with opposite sign is zero.

Gibbs Surface Σ is located where there is no net adsorption of A

$$-\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\mu_{\mathrm{B}}}\right)_T = \left[\Gamma_{\mathrm{B}} - \left(\frac{x_{\mathrm{A}}}{x_{\mathrm{B}}}\right)\Gamma_{\mathrm{A}}\right]$$

$$\Gamma_{\mathrm{B}}^{(\mathrm{A})} = \Gamma_{\mathrm{B}} - \Gamma_{\mathrm{A}}\left(\frac{c_{\mathrm{B}}^{\alpha} - c_{\mathrm{B}}^{\beta}}{c_{\mathrm{A}}^{\alpha} - c_{\mathrm{A}}^{\beta}}\right)$$

$$\Gamma_{\mathrm{B}} = \Gamma_{\mathrm{B}}^{(A)} = -\left(\frac{\partial\sigma}{\partial\mu_{\mathrm{B}}}\right)_T \qquad \text{for } \Gamma_{\mathrm{A}} = 0$$

Solutes that reduce the surface tension are adsorbed

Henry’s Law for Surfaces (surface impurities change surface tension)

$$\Gamma_{\mathrm{B}} = \Gamma_{\mathrm{B}}^{(A)} = -\left(\frac{\partial \sigma}{\partial \mu_{\mathrm{B}}}\right)_T \quad \text{for } \Gamma_{\mathrm{A}} = 0$$

For an ideal gas $\mu_B = RT\ln p_B$ where p_B is the partial pressure of B

$$\Gamma_{\mathrm{B}} = \Gamma_{\mathrm{B}}^{(A)} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln p_{\mathrm{B}}}\right)_T$$

Define j as the surface activity of an impurity

Surface Activity of B $$j_{\mathrm{B}} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial x_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1}$$

At infinite dilution so Henry’s Law Regime

$$p_i = x_i p_i^*$$

$$j_{\mathrm{B}} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial x_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \mu_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1}\left(\frac{\partial \mu_{\mathrm{B}}}{\partial x_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1} = +\frac{1}{RT}\Gamma_{\mathrm{B}}^{(\mathrm{A})}\left(\frac{\partial \mu_{\mathrm{B}}}{\partial x_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1}$$

$$= \Gamma_{\mathrm{B}}^{(\mathrm{A})}\left(\frac{\partial \ln a_{\mathrm{B}}}{\partial x_{\mathrm{B}}}\right)_{x_{\mathrm{A}} \to 1}$$

A small number of electronegative elements can have a large impact on surface energy of metals j_A ~1000 for oxygen and sulfur

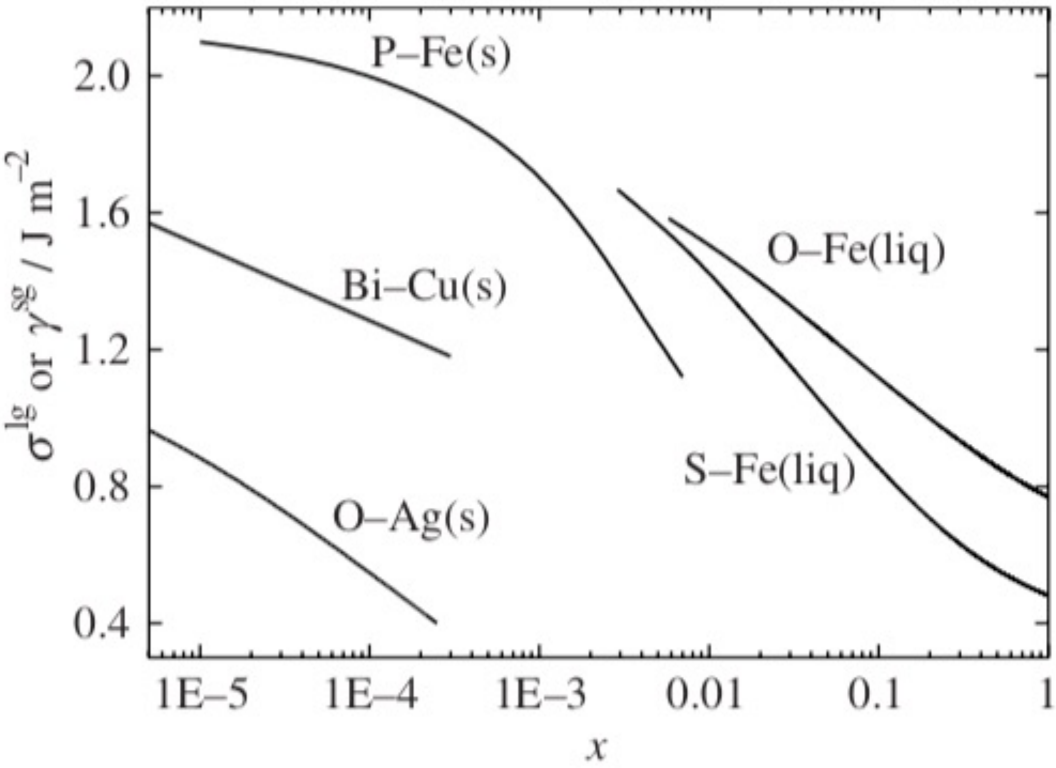


Figure 6.22 Surface tension as a function of the concentration for some surface-active species in solid Fe, Cu and Ag near their melting temperatures [27] and liquid Fe at 1550–1600 °C [28].

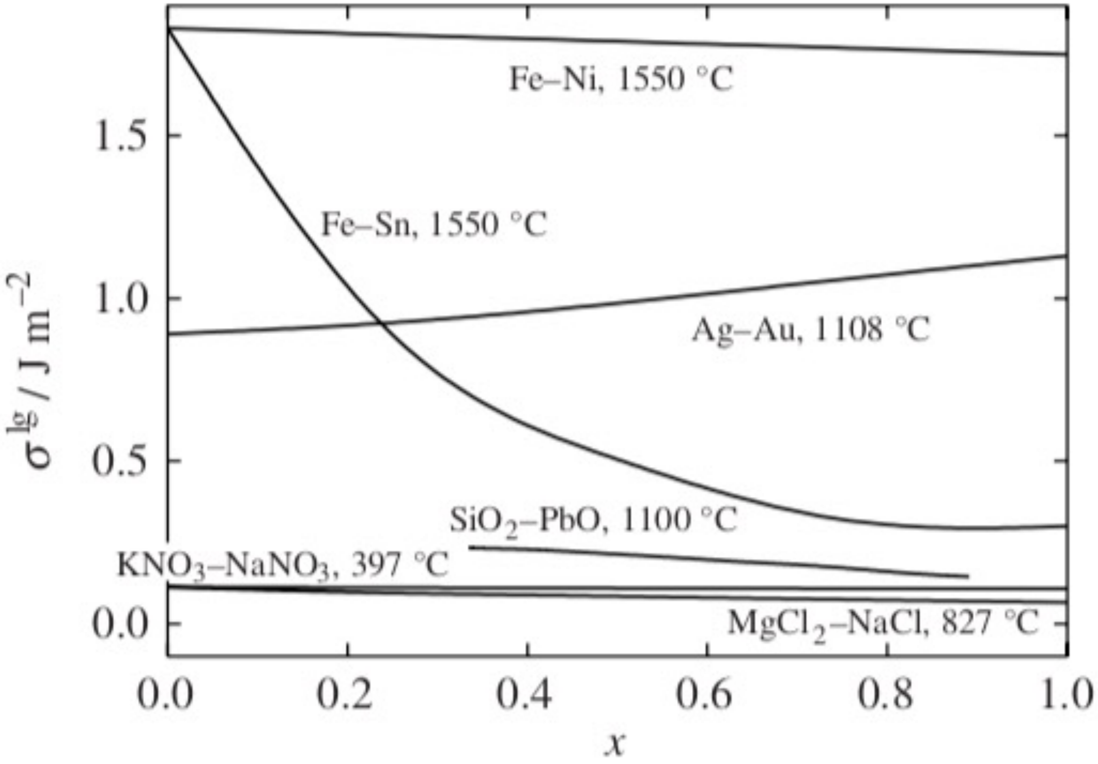


Figure 6.23 Isothermal surface tension versus composition of some binary metals [28], oxide [29] and salt systems [14, 15].

Nitrogen (or Argon) adsorption

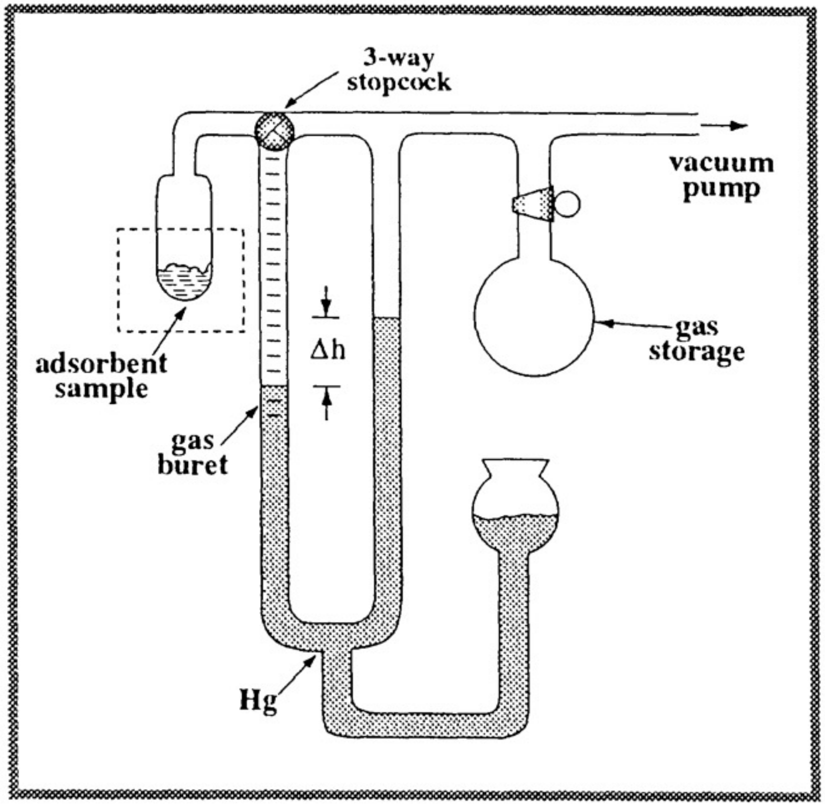


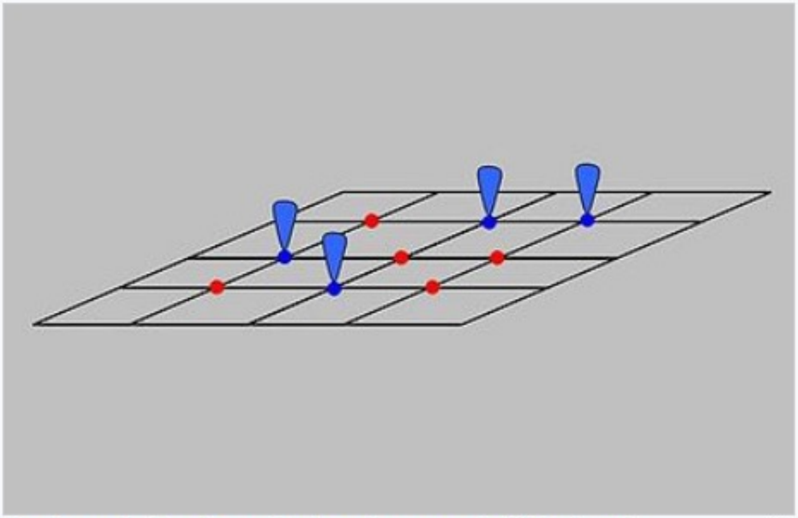
FIG. 9.3 Schematic illustration of a gas adsorption apparatus.

Langmuir Equation (Wikipedia)

Can be obtained using Equilibria or Kinetic Model

$$\mathrm{A_g + S \rightleftharpoons A_{ad}}$$

1) The surface containing the adsorbing sites is a perfectly flat plane with no corrugations (assume the surface is homogeneous). However, chemically heterogeneous surfaces can be considered to be homogeneous if the adsorbate is bound to only one type of functional groups on the surface.
2) The adsorbing gas adsorbs into an immobile state.
3) All sites are energetically equivalent and the energy of adsorption is equal for all sites.
4) Each site can hold at most one molecule of A (mono-layer coverage only).
5) No (or ideal) interactions between adsorbate molecules on adjacent sites. When the interactions are ideal, the energy of side-to-side interactions is equal for all sites regardless of the surface occupancy.



A schematic showing equivalent sites, occupied (blue) and unoccupied (red) clarifying the basic assumptions used in the model. The adsorption sites (heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface.

Langmuir Equation (Wikipedia)

Can be obtained using Equilibria or Kinetic Model

Equilibrium Reaction Model

Solvent (bound) + Solute (free) ↔ Solvent (free) + Solute (bound)

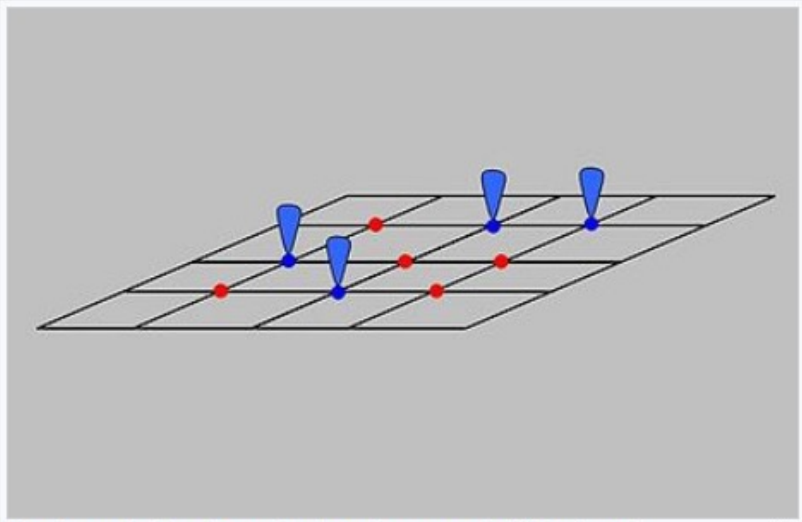
Solvent = 1; Solute = 2; s = surface bound; b = bulk solution free

$$K = \frac{a_1^b \times a_2^s}{a_2^b \times a_1^s}$$

$a_2^s = X_2^s = \theta$, $a_1^s = X_1^s$, and $X_1^s + X_2^s = 1$

$a_1^b \sim 1$

$$\theta = \frac{K.a_2^b}{1 + K.a_2^b}$$



A schematic showing equivalent sites, occupied (blue) and unoccupied (red) clarifying the basic assumptions used in the model. The adsorption sites (heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface.

Langmuir Equation (Wikipedia)

Can be obtained using Equilibria or Kinetic Model

Kinetic Reaction Model

$$r_{\mathrm{ad}} = k_{\mathrm{ad}}\, p_A\, [S],$$

p_A is the partial pressure of A over the surface

$$r_{\mathrm{d}} = k_d\, [A_{\mathrm{ad}}],$$

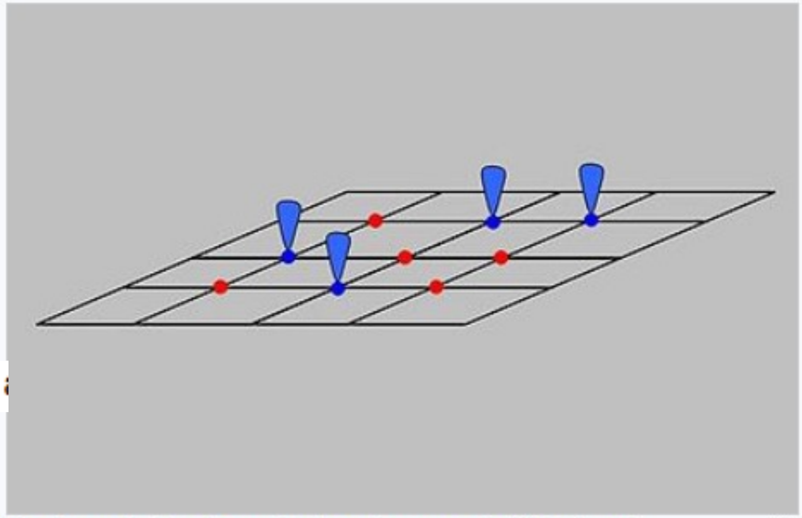
$[S]$ is the concentration of free sites in number/m^2,

$[A_{\mathrm{ad}}]$ is the surface concentration of A in molecules/m^2 (concentration of occupied sites)

k_{ad} and k_{d} are constants of forward adsorption reaction and backward desorption reaction

Setting $r_{\mathrm{ad}} = r_{\mathrm{d}}$

$$\frac{[A_{\mathrm{ad}}]}{p_A[S]} = \frac{k_{\mathrm{ad}}}{k_{\mathrm{d}}} = K^A_{\mathrm{eq}}$$

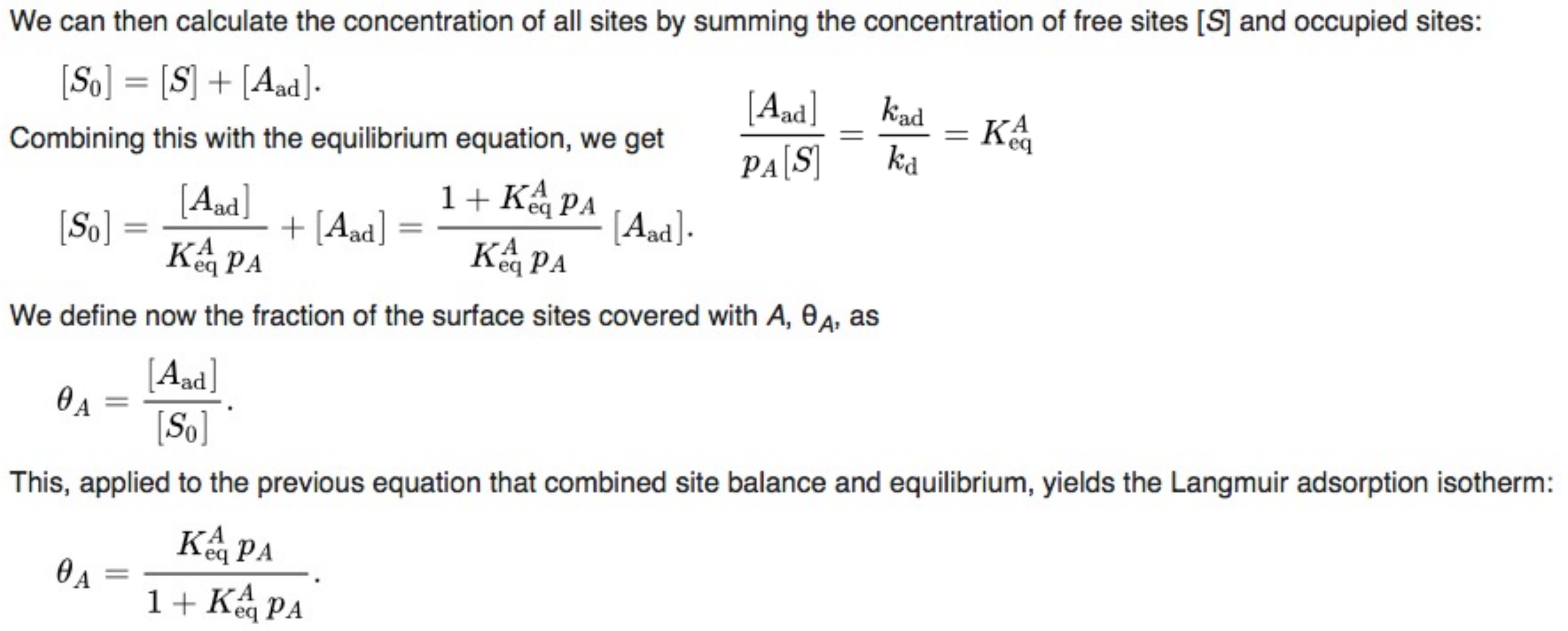


A schematic showing equivalent sites, occupied (blue) and unoccupied (red) clarifying the basic assumptions used in the model. The adsorption sites (heavy dots) are equivalent and can have unit occupancy. Also, the adsorbates are immobile on the surface.

Langmuir Equation (Wikipedia)

Can be obtained using Equilibria or Kinetic Model

Kinetic Reaction Model



We can then calculate the concentration of all sites by summing the concentration of free sites [*S*] and occupied sites:

$$[S_0] = [S] + [A_{\mathrm{ad}}].$$

$$\frac{[A_{\mathrm{ad}}]}{p_A[S]} = \frac{k_{\mathrm{ad}}}{k_{\mathrm{d}}} = K^A_{\mathrm{eq}}$$

Combining this with the equilibrium equation, we get

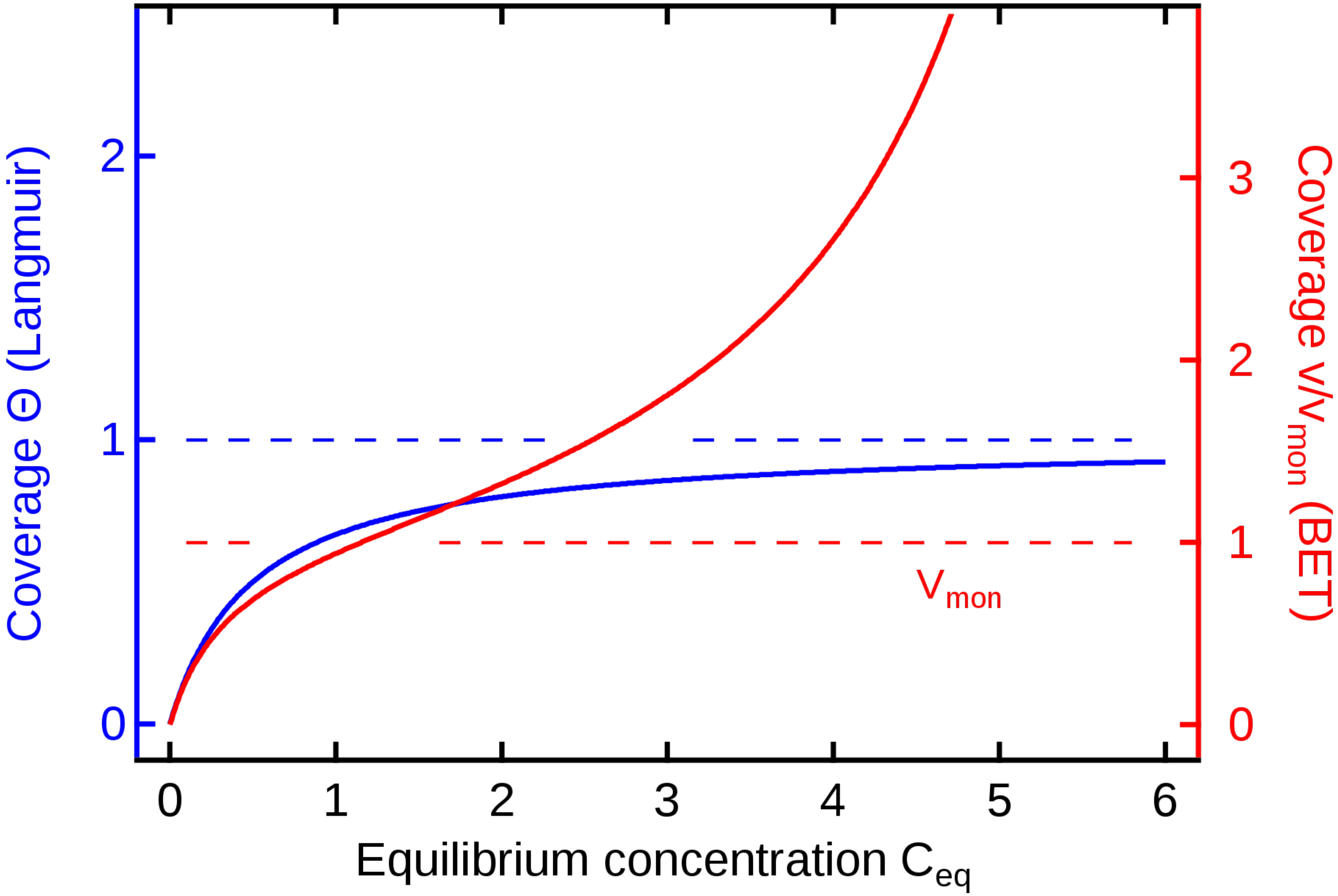
$$[S_0] = \frac{[A_{\mathrm{ad}}]}{K^A_{\mathrm{eq}}\, p_A} + [A_{\mathrm{ad}}] = \frac{1 + K^A_{\mathrm{eq}}\, p_A}{K^A_{\mathrm{eq}}\, p_A}\, [A_{\mathrm{ad}}].$$

We define now the fraction of the surface sites covered with *A*, θ_A, as

$$\theta_A = \frac{[A_{\mathrm{ad}}]}{[S_0]}.$$

This, applied to the previous equation that combined site balance and equilibrium, yields the Langmuir adsorption isotherm:

$$\theta_A = \frac{K^A_{\mathrm{eq}}\, p_A}{1 + K^A_{\mathrm{eq}}\, p_A}.$$


Coverage Θ (Langmuir)
0
1
2
Coverage v/v$_{mon}$ (BET)
0
1
2
3
V$_{mon}$
0
1
2
3
4
5
6
Equilibrium concentration C$_{eq}$

$A_{(g)} + S \rightleftharpoons AS,$

$A_{(g)} + AS \rightleftharpoons A_2S,$

$A_{(g)} + A_2S \rightleftharpoons A_3S$ and so on.

1938 Stephen Brunauer, Paul Emmett, and Edward Teller

$$(P/P_0)/(v_{ads}(1-P/P_0)) = 1/(K_{eq}v_{mono\ ads}) + (P/P_0)(K_{eq} - 1)/(K_{eq}v_{mono\ ads})$$

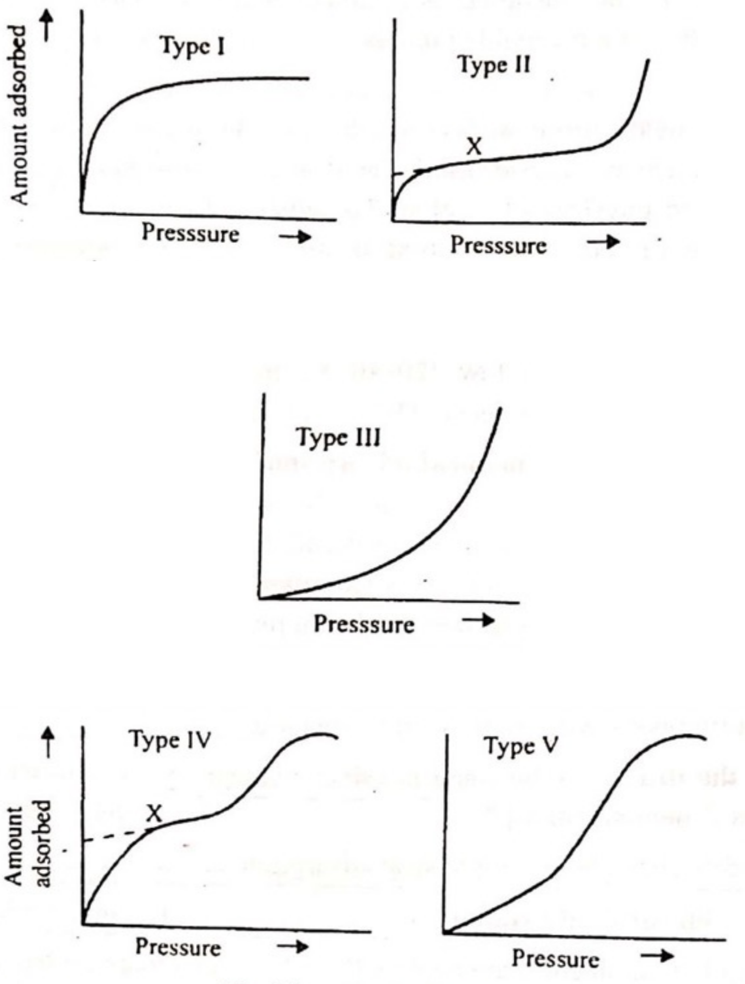


Fig. Adsorption isotherms

Type I adsorption isotherm

Type I isotherms are those in which the pore size is not substantially larger than the molecular diameter of the sorbate molecules. This isotherm shows that the extent of adsorption increases with pressure until it reaches saturation, at which point no further adsorption occurs.

Type II adsorption Isotherm

Isotherms of type II are generally observed in adsorbents that have a wide range of pore sizes i.e. macroporous. It is obtained when the bilayer is formed only after the monolayer has been fully formed, and the trilayer is formed only after the bilayer has been fully formed.

Type III adsorption Isotherm

It is obtained when the formation of monolayers, bilayers, trilayers, and other layers all take place at the same time, resulting in an almost exponential increase in the amount of adsorption.

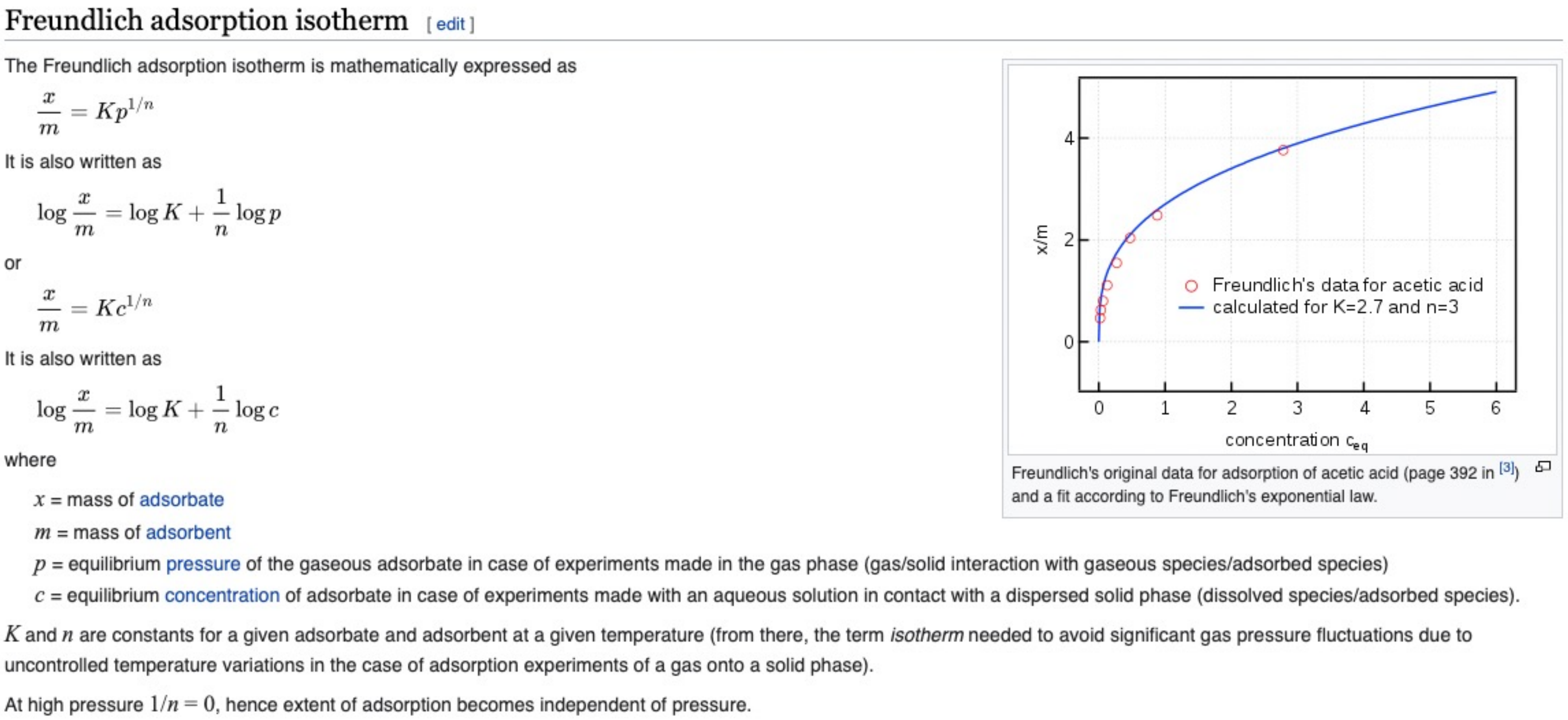
Type IV adsorption isotherm

Type IV isotherm predicts the formation of two surface layers on the plane surface or on the wall of a pore much wider than the sorbate's molecular diameter i.e.e mesoporous.

Type V adsorption isotherm

This type of adsorption isotherm is obtained only when intermolecular attraction effects are large, and adsorption takes place in pores and capillaries.

Empirical power-law equation for adsorption



Freundlich adsorption isotherm

The Freundlich adsorption isotherm is mathematically expressed as

$$\frac{x}{m} = Kp^{1/n}$$

It is also written as

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log p$$

or

$$\frac{x}{m} = Kc^{1/n}$$

It is also written as

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log c$$

where

x = mass of adsorbate

m = mass of adsorbent

p = equilibrium pressure of the gaseous adsorbate in case of experiments made in the gas phase (gas/solid interaction with gaseous species/adsorbed species)

c = equilibrium concentration of adsorbate in case of experiments made with an aqueous solution in contact with a dispersed solid phase (dissolved species/adsorbed species).

K and n are constants for a given adsorbate and adsorbent at a given temperature (from there, the term *isotherm* needed to avoid significant gas pressure fluctuations due to uncontrolled temperature variations in the case of adsorption experiments of a gas onto a solid phase).

At high pressure $1/n = 0$, hence extent of adsorption becomes independent of pressure.

Freundlich's original data for adsorption of acetic acid (page 392 in [3]) and a fit according to Freundlich's exponential law.

Adsorption, Surface Area and Porosity

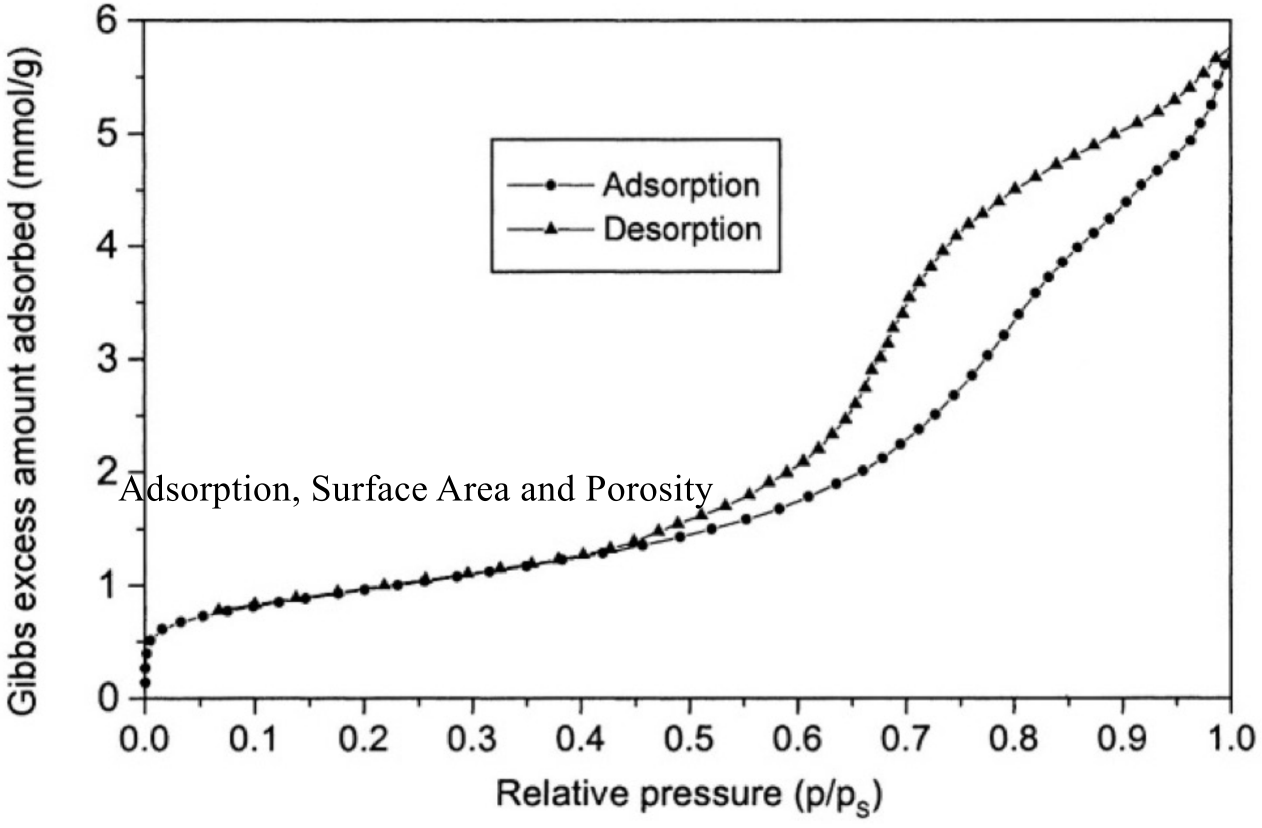


Figure 1.12. Adsorption- and desorption isotherm of N_2 (5.0) on standardized material CRMBAM-PM-104 at 77.3 K, p_0 = 1 atm, [1.36].

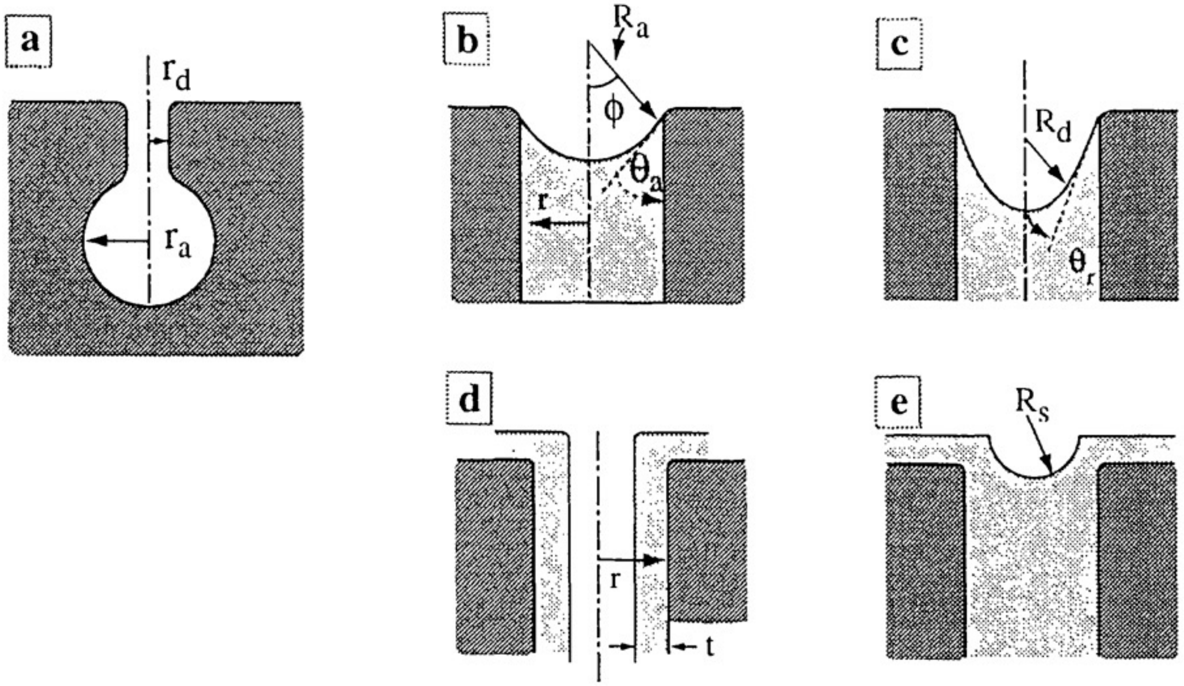


FIG. 9.12 Five models for capillary condensation. The radius of the pore equals r, the radius of curvature of the spherical meniscus is R_s, and t is the thickness of the adsorbed layer. The subscripts a and d refer to adsorption and desorption.

Surface Energy Term and Block Co-Polymers

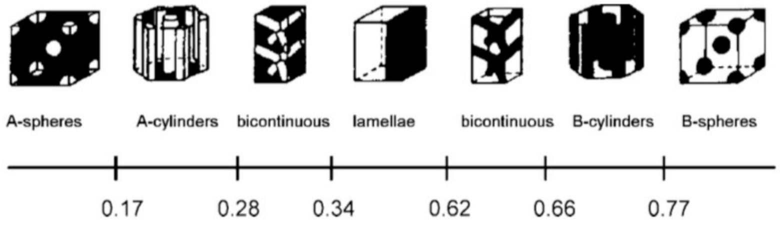
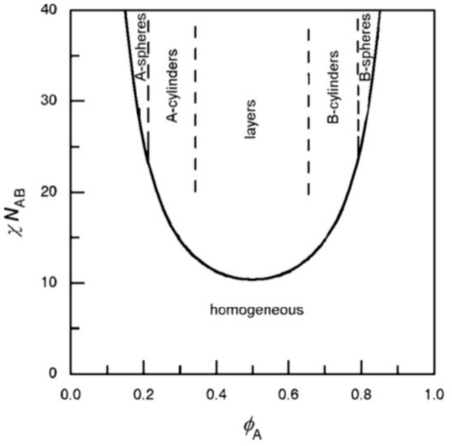


Fig. 4.27. Different classes of microphase separated structures in block copolymers, as exemplified by PS-*block*-PI. The *numbers* give the phase boundaries in terms of the volume fraction of the PS blocks. Figure taken from a review article by Bates and Frederickson [29]



$$\phi_{\mathrm{A}} = \frac{N_{\mathrm{A}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}$$

Fig. 4.29. Phase diagram of a di-block copolymer in a schematic representation. The curve describes the points of transition between the homogeneous phase and the microphase separated states. The ordered states are split into different classes as indicated by the *dashed boundary lines*. They are only shown here for the region of higher values of χN_{AB} away from the phase transition line

Micro-Phase Separation

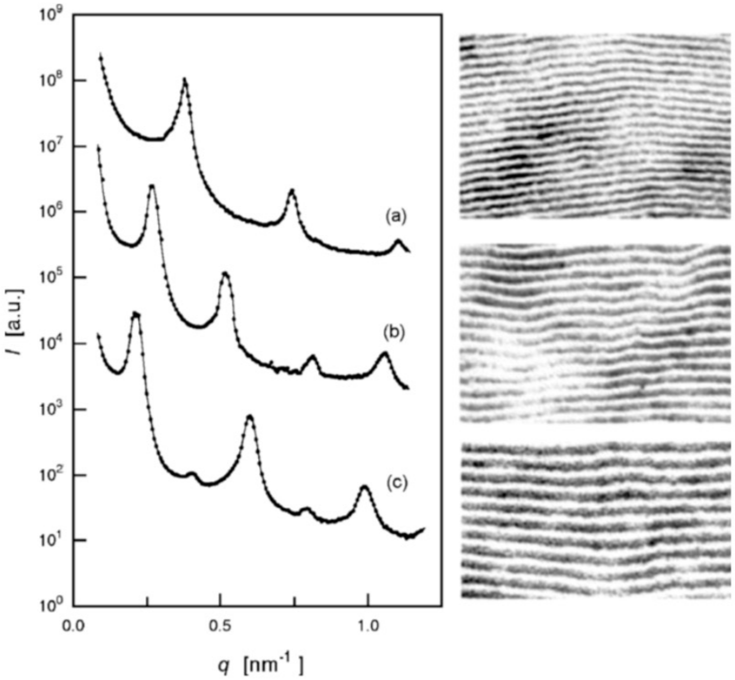


Fig. 4.28. SAXS curves measured for a series of PS-*block*-PI with different molar masses in the microphase separated state: (a) $M = 2.1 \times 10^4\,\mathrm{g\,mol^{-1}}$, $\phi(\mathrm{PS}) = 0.53$; (b) $M = 3.1 \times 10^4\,\mathrm{g\,mol^{-1}}$, $\phi(\mathrm{PS}) = 0.40$; (c) $M = 4.9 \times 10^4\,\mathrm{g\,mol^{-1}}$, $\phi(\mathrm{PS}) = 0.45$ (*left*). Transmission electron micrographs obtained using ultra-thin sections of specimen stained with $\mathrm{OsO_4}$ (*right*). Structures belong to the layer regime. Data from Hashimoto et al. [30]

How can you predict the phase size? (Meier and Helfand Theory)
Consider lamellar micro-phase separation.

For a symmetric binary blend of polymers, the FH theory predicts a critical point at $\chi N = 2$.
If the same two polymers are bonded, they microphase separate at $\chi N = 10.5$, the bonding makes the polymers more miscible.

$$\Delta g_{\mathrm{p}} = \Delta h_{\mathrm{p}} - T\Delta s_{\mathrm{p,if}} - T\Delta s_{\mathrm{p,conf}}$$

Enthalpy associated with phase segregation
Entropy associated with locating the junction points at the phase interface
Entropy associated with stretching the chains

$\chi > 0$ Drives a positive enthalpic contribution that favors micro-phase separation

$$\Delta h_{\mathrm{p}} = -kT\chi N_{\mathrm{AB}}\phi_{\mathrm{A}}(1-\phi_{\mathrm{A}}) + \Delta h_{\mathrm{p,if}}$$

Assume transition from perfectly mixed to perfectly demixed

$$\Delta h_{\mathrm{p,if}} \simeq kT\chi \frac{o_{\mathrm{p}} d_{\mathrm{t}}}{v_{\mathrm{c}}}$$

An interfacial layer of thickness d_t,
Area per polymer chain o_p

How can you predict the phase size? (Meier and Helfand Theory)
Consider lamellar micro-phase separation.

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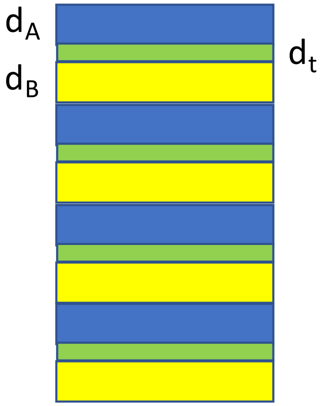
$$\Delta s_{\mathrm{p,if}} \simeq k \ln \frac{d_{\mathrm{t}}}{d_{\mathrm{A}} + d_{\mathrm{B}}}$$

$$\Delta s_{\mathrm{p,conf}} \simeq -k \left(\frac{R}{R_0}\right)^2$$

$$\Delta s_{\mathrm{p,conf}} \simeq -k\beta^2 \left(\frac{d_{\mathrm{AB}}}{R_0}\right)^2$$

$R_0^2 = Nl^2$
$R = \beta\, d_{AB} = \beta(d_A + d_B)$



$$o_{\mathrm{p}} d_{\mathrm{AB}} = N_{\mathrm{AB}} v_{\mathrm{c}}$$

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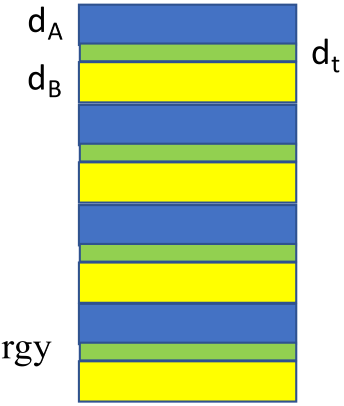
$$\Delta g_\mathrm{p} = \Delta h_\mathrm{p} - T\Delta s_\mathrm{p,if} - T\Delta s_\mathrm{p,conf}$$

There is only one free parameter, for instance o_p,
the cross-sectional area per polymer chain (Tom Witten, U Chicago)



$$\frac{1}{kT}\Delta g_\mathrm{p} = -\chi N_\mathrm{AB}\phi_\mathrm{A}(1-\phi_\mathrm{A}) + \chi o_\mathrm{p} d_\mathrm{t} v_\mathrm{c}^{-1} + \ln\frac{d_\mathrm{t}}{d_\mathrm{AB}} + \beta^2\left(\frac{d_\mathrm{AB}}{R_0}\right)^2$$

$$o_\mathrm{p} d_\mathrm{AB} = N_\mathrm{AB} v_\mathrm{c}$$

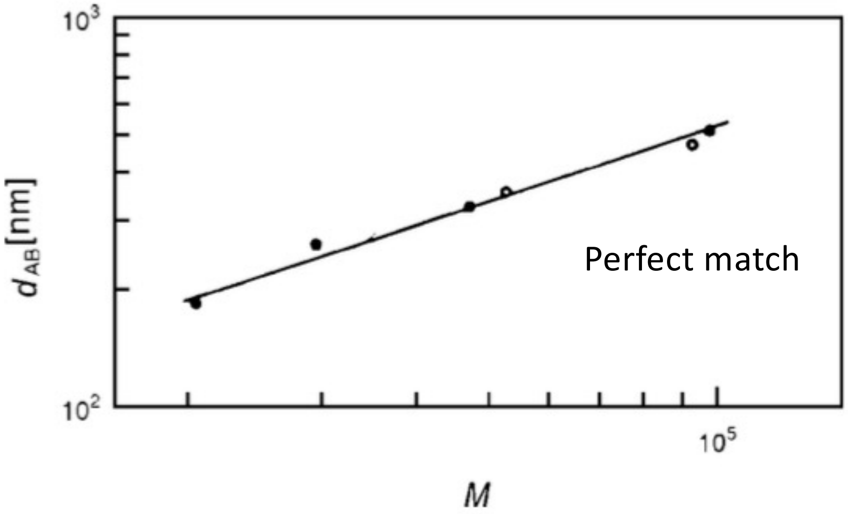
$$\frac{1}{kT}\frac{\mathrm{d}\Delta g_\mathrm{p}}{\mathrm{d}o_\mathrm{p}} = \chi\frac{d_\mathrm{t}}{v_\mathrm{c}} - 2\beta^2\frac{N_\mathrm{AB}^2 v_\mathrm{c}^2}{R_0^2}\frac{1}{o_\mathrm{p}^3}$$

Find the minimum in the free energy
by varying o_p
Ignoring “ln” term that varies slowly

$$o_\mathrm{p}^3 \propto 2\frac{v_\mathrm{c}^3}{R_0^2 d_\mathrm{t}\chi}N_\mathrm{AB}^2 \qquad R_0^2 \propto v_\mathrm{c}^{2/3} N_\mathrm{AB} \qquad o_\mathrm{p}^3 \propto \frac{v_\mathrm{c}^{7/3}}{d_\mathrm{t}\chi}N_\mathrm{AB} \qquad d_\mathrm{AB}^3 = \frac{N_\mathrm{AB}^3 v_\mathrm{c}^3}{o_\mathrm{p}^3} \propto \chi d_\mathrm{t} v_\mathrm{c}^{2/3} N_\mathrm{AB}^2$$

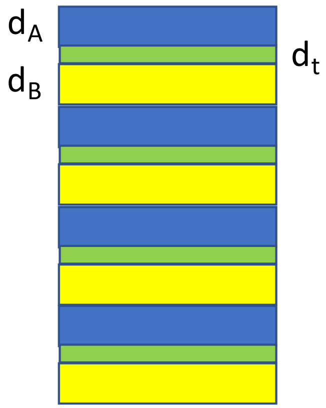
How can you predict the phase size? (Meier and Helfand Theory) Consider lamellar micro-phase separation.

$$d_{\mathrm{AB}}^3 = \frac{N_{\mathrm{AB}}^3 v_{\mathrm{c}}^3}{o_{\mathrm{p}}^3} \propto \chi d_{\mathrm{t}} v_{\mathrm{c}}^{2/3} N_{\mathrm{AB}}^2$$



Perfect match

Fig. 4.30. Set of samples of Fig. 4.28. Molecular weight dependence of the layer spacing d_{AB}



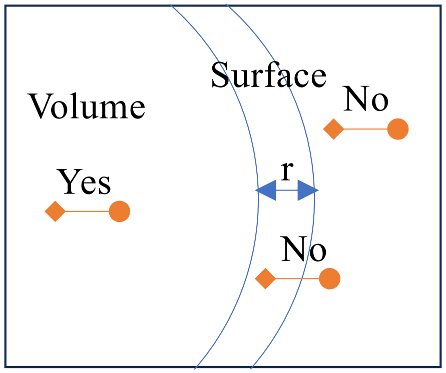
Binary Correlation Function (Radial Distribution Function) and S/V ratio

g(r) is the probability of finding a point “x” (diamond) in a phase and
of finding a point “y” (circle) a distance “r” from “x” also in the phase

Consider small “r” compared to the particle size for a smooth/sharp interface (not a spinodal or diffuse interface)

Probability of “x” being in the phase is the volume fraction “ϕ” of the particle phase.

There are three possibilities:



Yes for “x” = ϕ
g(r) = Yes for “x” and for “y” = ϕ (1 – (S/V) r)
So, this is a straight line that decays with (S/V)
For small “r” where the curvature of the phase doesn’t matter and
For smooth sharp interfaces, **not diffuse and not rough interfaces**

The Fourier transform of the correlation function is the X-ray or neutron scattering and small sizes are at large angles in the small angle regime for nanoparticles. The transform of this linear decay is a power-law decay of -4 slope, $I(q) \sim S/V\ q^{-4}$ *Porod’s Law*