Contents of Today

Review previous

Surface energy / surface tension

Effect of surface curvature

Vapor pressure

Solubility of small particles

Wetting of surfaces

Gibbs Adsorption Isotherm

Microcanonical ensemble

An isolated system with N particals in a volume, V, with a fixed energy, E

Premise: all microstates are equally probable

Boltzmann hypothesis

The entropy of a system is linearly related to the logarithm of Ω

$$S = k \ln \Omega$$

Ω：thermodynamic probability

the number of different ways that macro-configuration can be achieved.

$$\Omega = \frac{N!}{N_{\mathrm{I}}! N_{\mathrm{II}}!}$$

Entropy of mixing of two components

Distribution of balls

$$Z_{xyz} = Z_x Z_y Z_z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} L^3 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

$$\underline{F} = -N_A kT \left(\ln \frac{Z}{N_A} + 1 \right)$$

$$P = -\left(\frac{\partial \underline{F}}{\partial \underline{V}} \right)_T$$

$$P = \left(\frac{\partial \left[N_A kT \left(\ln \frac{Z}{N_A} + 1 \right) \right]}{\partial \underline{V}} \right)_T = N_A kT \left(\frac{\partial \ln Z}{\partial \underline{V}} \right)_T$$

$$\boxed{P = \frac{N_A kT}{\underline{V}} = \frac{RT}{\underline{V}}}$$

- Surface energy / surface tension

- Effect of surface curvature

- Vapor pressure

- Solubility of small particles

- Wetting of surfaces

- Gibbs absorption isotherm

Surfaces and Interfaces

Everything is made of something and has to end somewhere.

An atom at a free surface of a solid has greater energy than an atom in the interior of a crystal because it is less tightly bound.

Surface energy

The sum of all the excess energies of the surface atoms

Can be defined in terms of energy, enthalpy, Helmholtz free energy, or Gibbs free energy, depending on the physical constraints placed on the definition

(a) 由劈开晶体形成的自由键

本来应该担任"配角"的界面比本当是"主角"的构成相扮演更重要的"演出角色"！
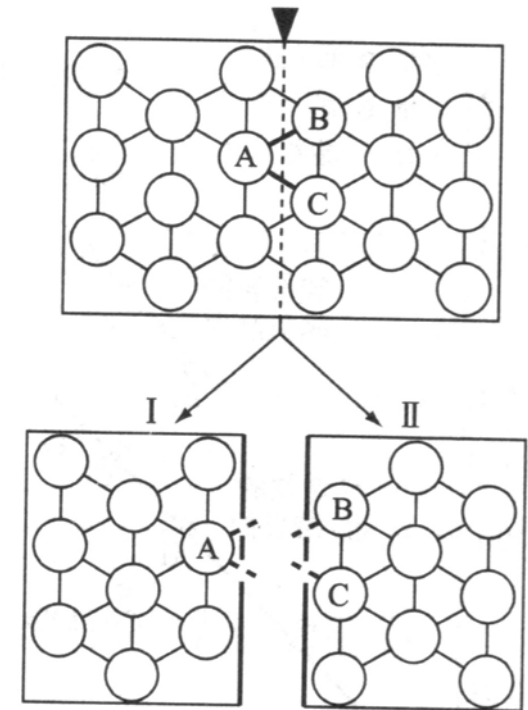
Surface energy based on Gibbs free energy

$$dG = -SdT + VdP + \gamma dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P}$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P} = \left(\frac{\partial U}{\partial A}\right)_{S,V} = \left(\frac{\partial H}{\partial A}\right)_{S,P} = \left(\frac{\partial F}{\partial A}\right)_{T,V}$$

Commonly observed manifestations

A liquid droplet tries to minimize its free energy, it assumes a spherical shape
Small droplets tend to agglomerate into larger droplets, minimizing their combined surface-to-volume ratios
Small particles of metals or ceramics, when pressed into a shape and heated at high temperatures, will "sinter" into a solid mass.

Image a film of liquid stretched on a frame

$$2l\gamma dx = Fdx$$

$$\gamma = F / 2l$$

$$\rightarrow dx \leftarrow$$

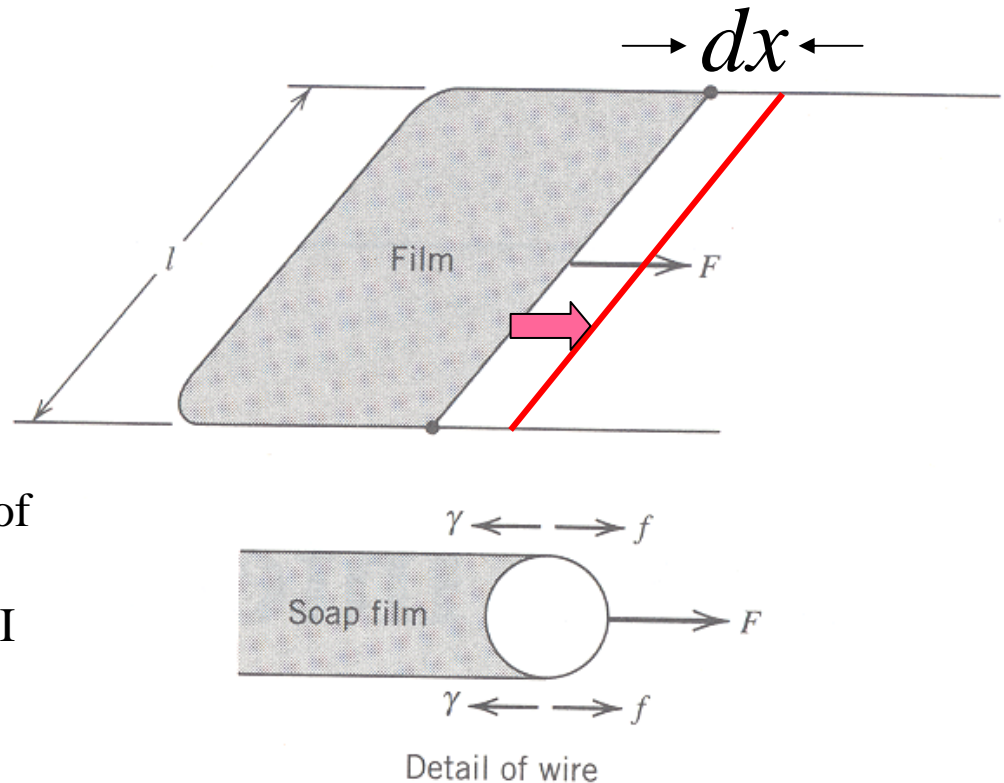γ — Surface energy with units of dynes per centimeter, or newtons per meter in the SI system.

Figure 4.1 Stretching a film—increasing area.

γ Surface energy with units of dynes per centimeter, or newtons per meter in the SI system.

	[界面张力]	[界面能]
SI 单位制	N(牛顿)·m^{-1}	= J(焦耳)·m^{-2}
cgs 单位制	dyn(达因)·cm^{-1}	= erg(尔格)·cm^{-2}

Surface Energy / Surface Tension (1)

Surface tension or surface energy

Liquid

Isotropic

Surface energy does not change as the surface is stretched

Solids

Function of the crystallographic plane that is expected

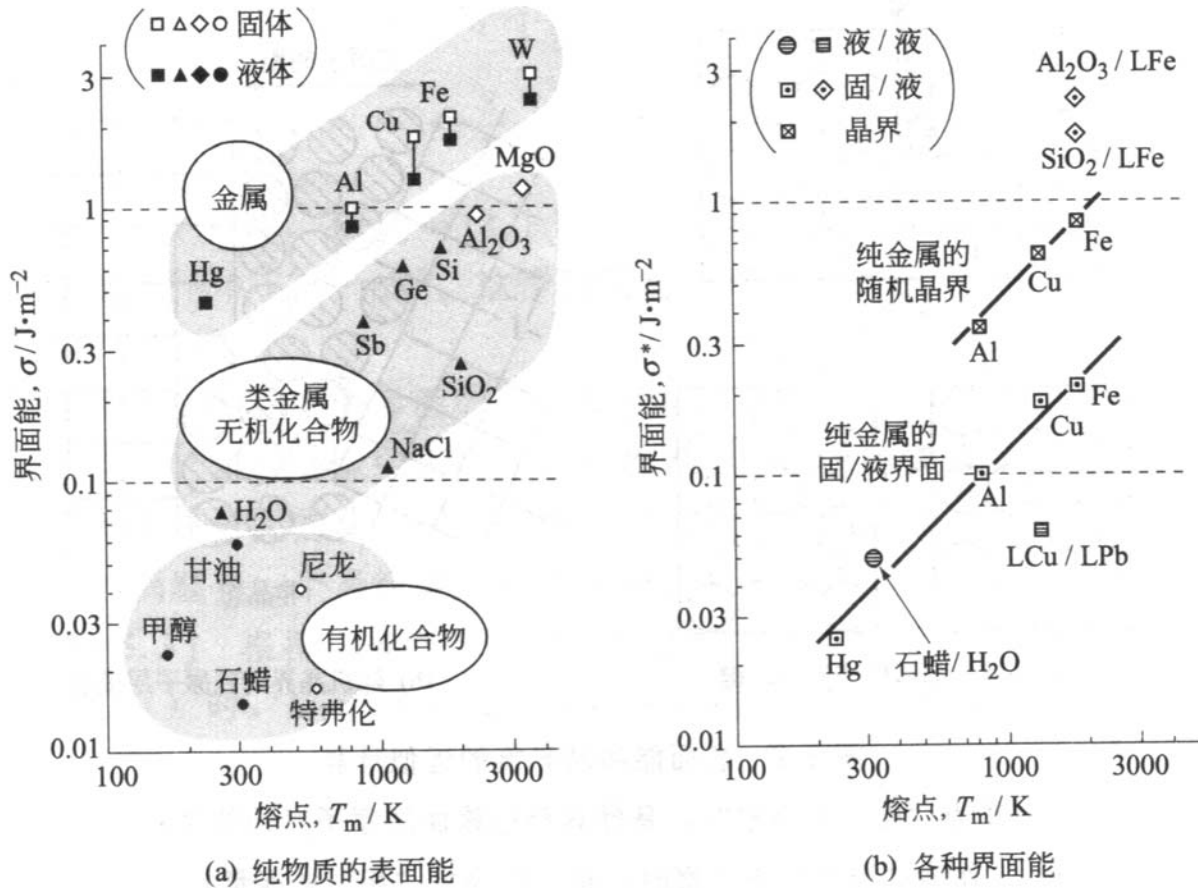The nature of a solid surface changes as the material is deformed.

纯物质的表面能和各种界面能

图 5.1　(a) 固体或液体的表面能（金属最大，塑料最小）；(b) 固/液或

液/液界面能和随机晶界能（因物质组合的不同而变得多种多样）

From T. Nishizawa　　SJTU Thermodynamics of Materials　　　　Spring 2008　　© X. J. Jin　　Lecture 20 surface

Approximate Calculation of Solid Surface Energy

The binding energy of an atom to a solid is the result of discrete bonds to its nearest neighbors, then the energy of one bond, ε, can be written as follows:

$$\varepsilon = \frac{\Delta \underline{H}_S}{0.5 Z N_A}$$

$\Delta \underline{H}_S$ The molar enthalpy of sublimation (breaking all the bonds)

Z The coordination number

N_A Avogadro's number

There are $0.5 Z N_A$ bonds per mole.

If we cleave a face-centered cubic crystal along a (111) plane, three bonds per atom will be broken. Two surfaces formed, the work required to form the surfaces will be 3ε/2 per surface atom.

$$w = \frac{3}{2}\varepsilon = \frac{\Delta \underline{H}_S}{4N_A} \quad (for \ Z = 12)$$

$$\gamma = \frac{\Delta \underline{H}_S}{4N_A}\left(\frac{N}{A}\right)$$

N/A is the number of atoms per unit area. For fcc structure:
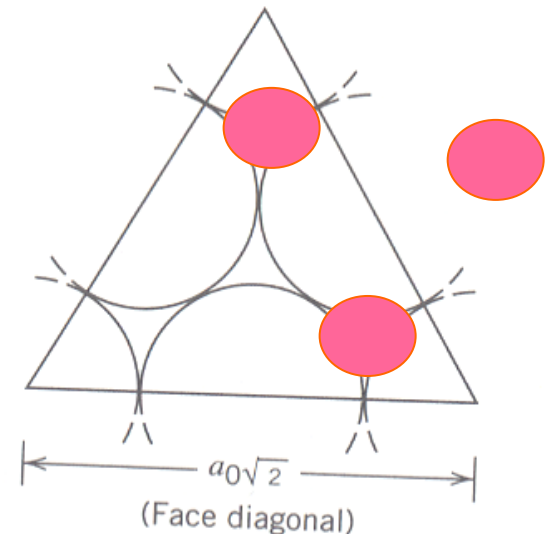
$$\frac{N}{A} = \frac{4}{\sqrt{3}a_0^2}$$

$a_0\sqrt{2}$
(Face diagonal)

Figure 4.2 Atomic packing on the (111) face of a face-centered cubic crystal.

For copper, the enthalpy of sublimation: 170000 J/(g.mol)
Lattice spacing, 3.615 A

Calculated. 1400 erg/cm^2
Measured, 1600 erg/cm^2

The surface energy of a solid depends on the crystallographic plane.
The work required to create the surface γ depends on the number of bonds broken per atom when the surface is created, and the number of atoms per area of surface. (N/A)
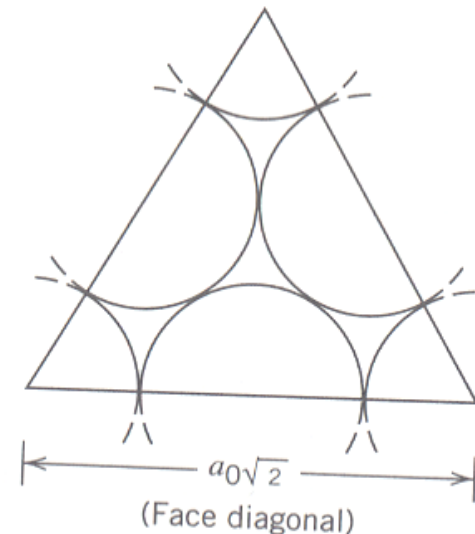

$a_0\sqrt{2}$
(Face diagonal)

Figure 4.2 Atomic packing on the (111) face of a face-centered cubic crystal.

For a (100) plane there are four broken bonds per atom, and the number of atoms per unit area:

$$\left(\frac{N}{A}\right)_{(100)} = \frac{2}{a_0^2}$$

The ratio of the two surface energies:

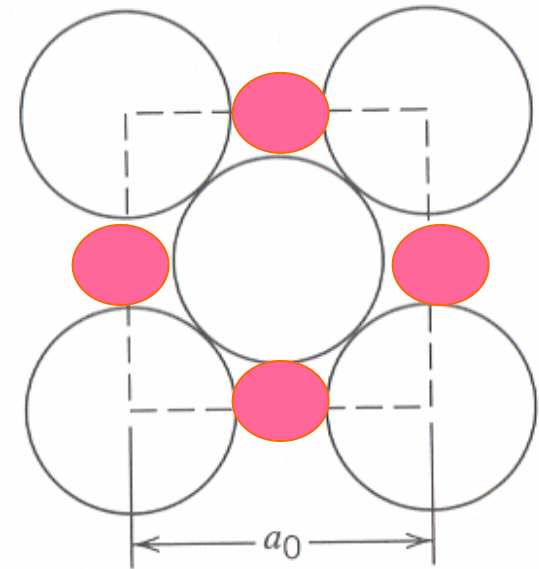$$\frac{\gamma_{(111)}}{\gamma_{(100)}} = \frac{2}{\sqrt{3}} = 1.15$$

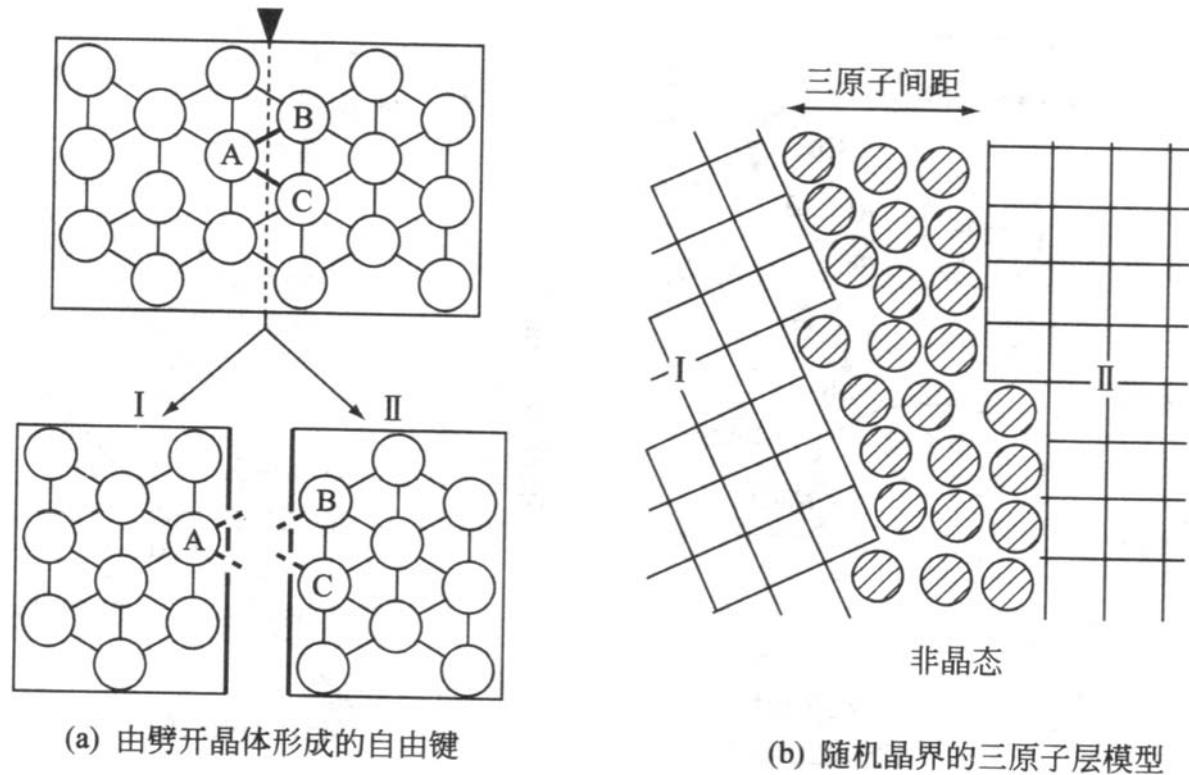**Figure 4.3** Atomic packing on the (100) face of a face-centered cubic crystal.

表面能和晶界能的近似计算

(a) 由劈开晶体形成的自由键

(b) 随机晶界的三原子层模型

图 5.2 表面能和晶界能的近似计算

（作为"面"来考察时，是计算穿过该面的原子对的能量；

作为"薄膜"来考察时，是计算膜状"相"的能量）

From T. Nishizawa

Effect of Surface Curvature

We can locate a geometrical surface between two phases in a way that assigns no mass to the surface.

$$dG = \underline{G}_I dm_I + \underline{G}_{II} dm_{II} + \gamma dA = \delta w_{rev}$$

At equilibrium the reversible work is ZERO.

$$\boxed{\overline{G} = \mu = \underline{G}}$$

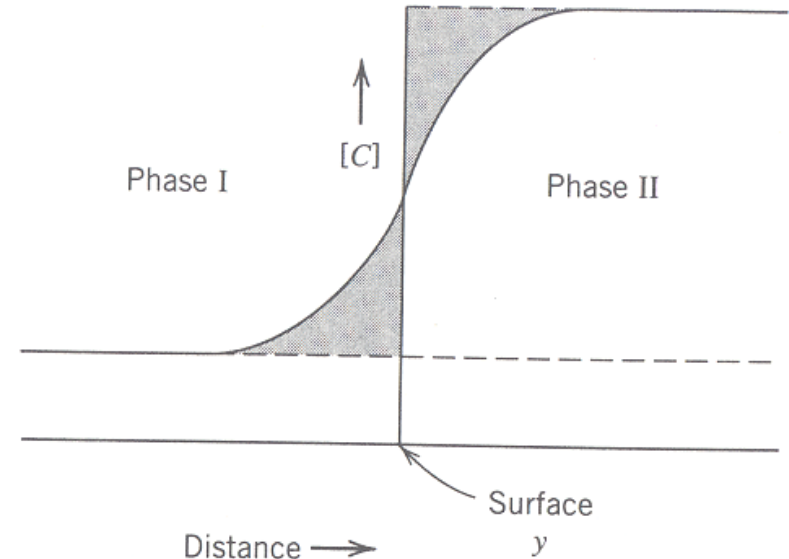$$\mu_I dm_I + \mu_{II} dm_{II} + \gamma dA = 0$$

Figure 4.4 Concentration of component C as a function of distance. Surface is assumed to be at location where shaded areas are equal.

$$\mu_I dm_I + \mu_{II} dm_{II} + \gamma dA = 0$$

$$\boxed{dm_I = -dm_{II} = dm}$$

$$\mu_I - \mu_{II} = \gamma \frac{dA}{dm}$$

If the surface is flat, dA/dm=0

$$\mu_I = \mu_{II} = \mu_\infty$$

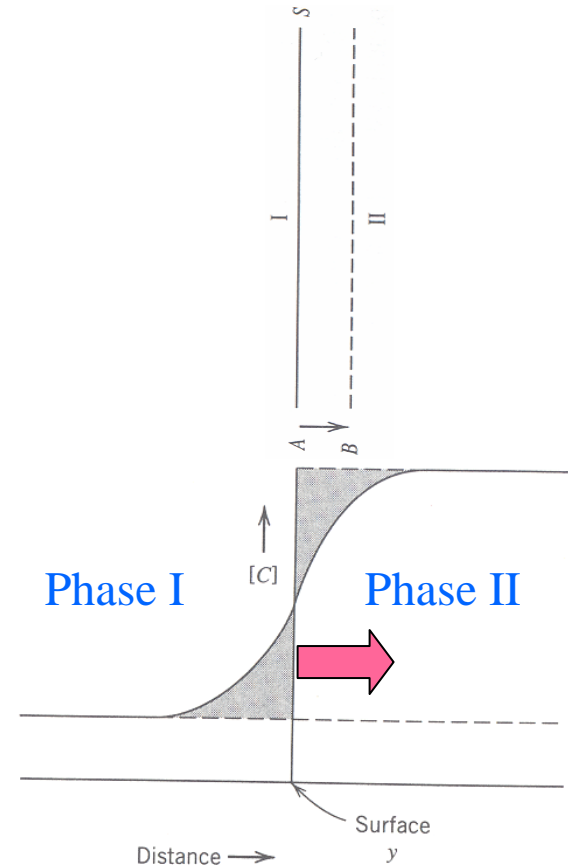The chemical potential of a material with an infinite radius of curvature.

Phase I   Phase II

Figure 4.4 Concentration of component C as a function of distance. Surface is assumed to be at location where shaded areas are equal.

Distance ⟶   Surface
y

$$\mu_I - \mu_{II} = \gamma \frac{dA}{dm} = \underline{V}\gamma \frac{dA}{dV}$$

For a spherical surface

$$V = \frac{\pi r^3}{3} \quad and \quad A = \pi r^2$$
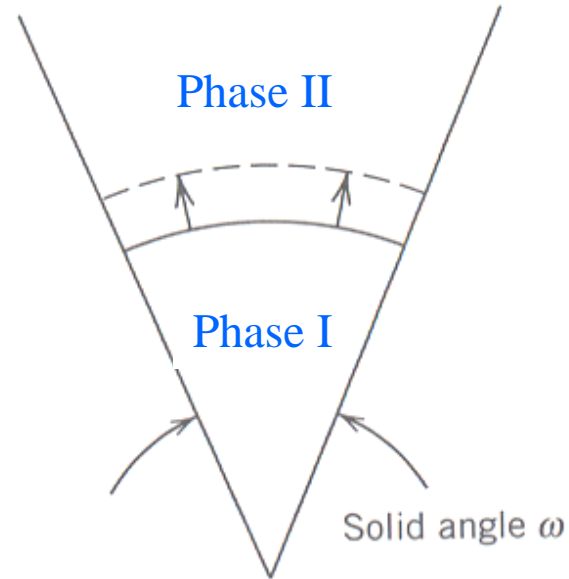
$$\frac{dA}{dV} = \frac{2}{r}$$

Phase II

Phase I

Solid angle ω

Figure 4.6 Movement of a spherical surface with finite radius of curvature.

$$\boxed{\mu_I - \mu_{II} = \gamma \frac{dA}{dm} = \underline{V}\gamma \frac{dA}{dV} = \underline{V}\frac{2\gamma}{r}}$$

S. J. T. U.
Phase Transformation and Applications

$$\mu_I - \mu_\infty = \underline{V}\frac{2\gamma}{r}$$

The chemical potential of a material with a radius of curvature r is greater than the chemical potential for that same material with an infinite radius of curvature.

For a non-spherical, curved surface with principal radii of curvature r_1 and r_2, the difference in chemical potential is:

$$\mu_{r_1,r_2} - \mu_\infty = \underline{V}\gamma(\frac{1}{r_1} + \frac{2}{r_2})$$

表面张力造成的内压和两个肥皂泡的实验

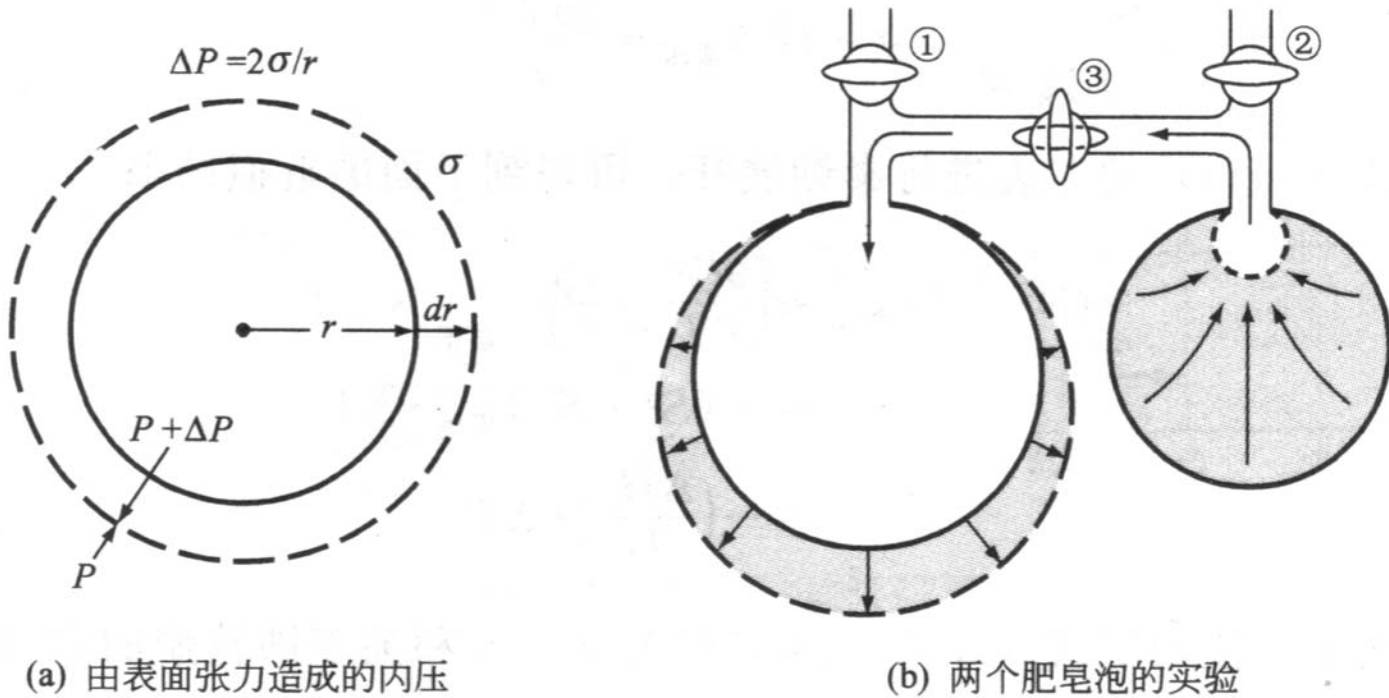$$\Delta P = 2\sigma/r$$

$P + \Delta P$

P

σ

r dr

(a) 由表面张力造成的内压

(b) 两个肥皂泡的实验

图 5.4　(a) 拉普拉斯公式的图解；(b) 小肥皂泡收缩而大肥皂泡膨胀

From T. Nishizawa

S. J. T. U.
Phase Transformation and Applications

The surface as a membrane surrounding the condensed phase, and the surface tension as the stress in the membrane, we can establish the pressure difference across the curved surface through a force balance.

The force tending to push the two halves of the sphere apart is the product of the cross-sectional area of the sphere at its mid-point
The difference in pressure between the inside and the outside of the sphere

$$\pi r^2 \Delta P = 2\pi r \gamma$$

$$\Delta P = 2\gamma / r$$

$$d\mu = \underline{V} dP$$

$$\int_{\mu_0}^{\mu_i} d\mu = \underline{V} \int_{P_0}^{P_i} dP = \underline{V}(P_i - P_0) = \underline{V}\Delta P$$
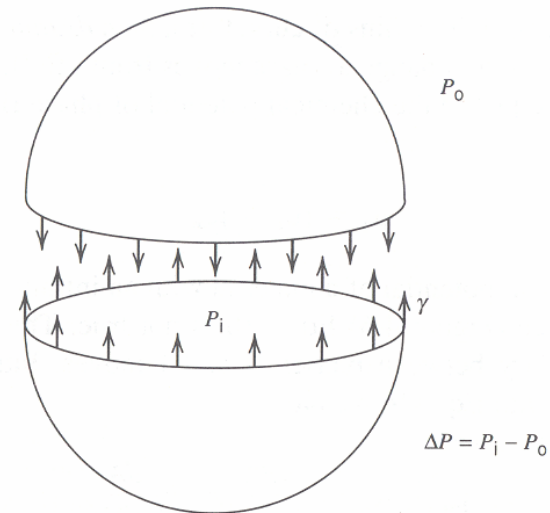
$$\mu_r - \mu_\infty = \underline{V}\frac{2\gamma}{r}$$

Figure 4.7 Force holding two hemispheres together is $2\pi r\gamma$; force pushing them apart is $\pi r^2 \Delta P$, where $\Delta P = 2\gamma/r$.

The chemical potential of the condensed material μ_C is equal to the chemical potential μ_V of its vapor

$$\mu_C = \mu_V$$

$$\mu_{C,r} = \mu_{V,r}$$

$$\mu_{C,\infty} = \mu_{V,\infty}$$

$$\mu_{C,r} - \mu_{C,\infty} = \underline{V}\frac{2\gamma}{r}$$

$$\mu_{V,r} = \mu_{V,r}^0 + RT\ln P_r^0$$

$$\mu_{V,r} - \mu_{V,\infty} = RT\ln\frac{P_r^0}{P_\infty^0}$$

Ideal gas

$$\ln\frac{P_r^0}{P_\infty^0} = \frac{\underline{V}}{RT}\frac{2\gamma}{r}$$

Smaller particles have higher vapor pressures. The smaller particles will tend to shrink.

The gas molecules will diffuse from the vicinity of the smaller particles to the larger ones.

Melting Temperature of Small Particles

The curved surface of a particle influences its vapor pressure and its solubility.

The melting temperature depends on their radii.
The melting temperature of the point of a needle is different from the melting point of the body of the needle. Concept of solidification.

$$\mu_S = \mu_l$$

$$P_S = P_l + \frac{2\gamma_{l-S}}{r}$$

$$(\underline{S}_l - \underline{S}_S)dT - (\underline{V}_l - \underline{V}_S)dP_l - 2\underline{V}_S\gamma_{l-S}\frac{dr}{r^2} = 0$$

$$d\mu_l = -\underline{S}_l dT + \underline{V}_l dP_l$$

$$d\mu_S = -\underline{S}_S dT + \underline{V}_S dP_S = -\underline{S}_S dT + \underline{V}_S d(P_l + \frac{2\gamma_{l-S}}{r})$$

Melting Temperature of Small Particles (2)

$$(\underline{S}_l - \underline{S}_S)dT - (\underline{V}_l - \underline{V}_S)dP_l - 2\underline{V}_S\gamma_{l-S}\frac{dr}{r^2} = 0$$

$$dP_l = 0 \quad \text{Atmosphere pressure constant}$$

$$\underline{S}_l - \underline{S}_S = \Delta\underline{S}_m$$

$$\Delta\underline{S}_m dT = 2\underline{V}_S\gamma_{l-S}\frac{dr}{r^2}$$

$$\Delta\underline{S}_m\int_{T_\infty}^{T_r} dT = 2\underline{V}_S\gamma_{l-S}\int_{r=\infty}^{r}\frac{dr}{r^2}$$

$$\Delta T = -2\frac{\underline{V}_S\gamma_{l-S}}{\Delta\underline{S}_m}\frac{1}{r}$$

$$\Delta T = -2\frac{\underline{V}_S\gamma_{l-S}T_m}{\Delta\underline{H}_m}\frac{1}{r}$$

Melting Temperature of Small Particles (3)

Melting point of very fine particles of gold, with radius 100 A

$$\Delta T = -2\frac{V_S \gamma_{l-S} T_m}{\Delta H_m}\frac{1}{r} = -\frac{2 \times 0.132 \times 10.2 \times 10^{-6} \times 1336}{12360}\frac{1}{10^{-8}}$$

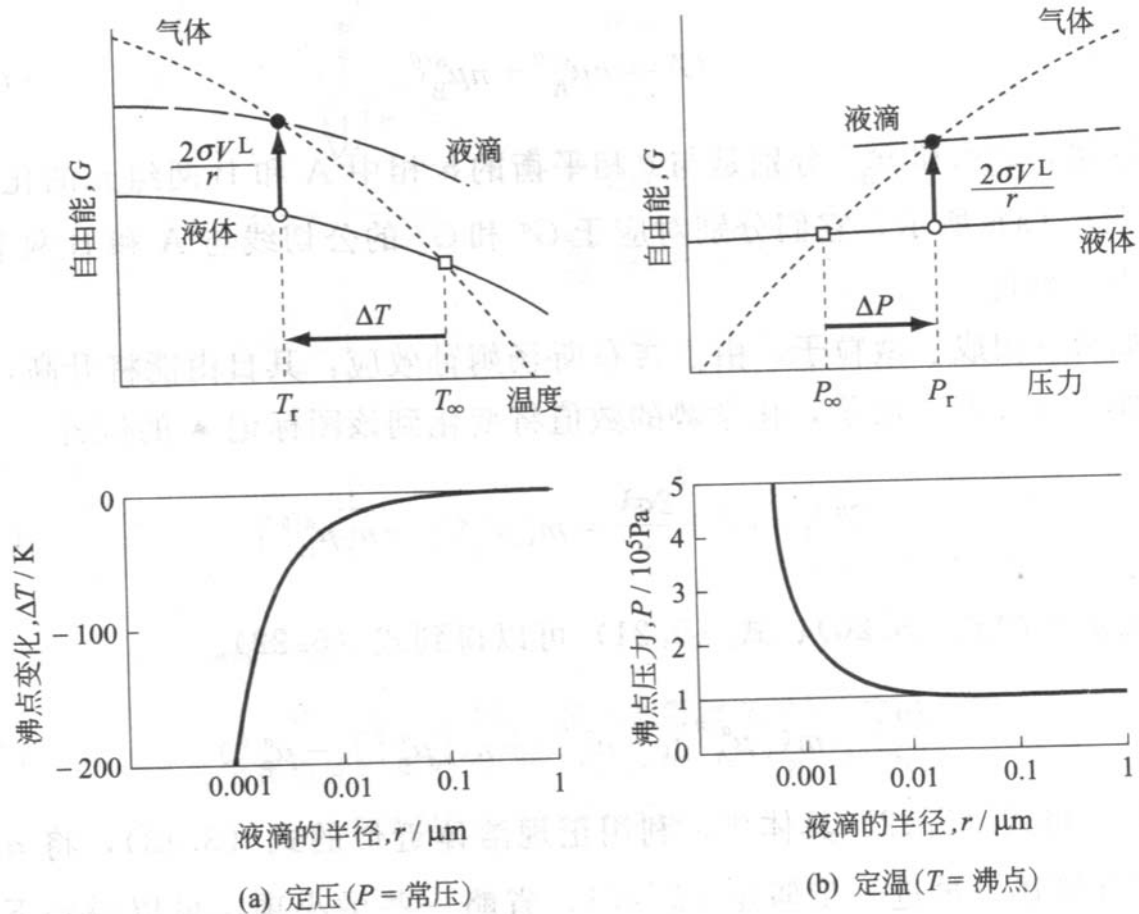$$\Delta T = T_r - T_\infty = -29.1\ K$$

由微粒化带来的沸腾温度下降和沸腾压力上升

From T. Nishizawa

图 5.5 由微粒化带来的沸腾温度下降和沸腾压力上升

Solubility of Small Particles

If material B exists as small spherical particles

$$\mu_{B,r} - \mu_{B,\infty} = \frac{2V\gamma_{\alpha-\beta}}{r}$$

The surface energy in this equation is the interfacial energy between pure B and phase α

Define the standard state for B as pure B with an infinite radius of curvature.

$$\mu_{B,r} = \mu_{B,\infty} + RT \ln a_B$$

$$\mu_{B,r} - \mu_{B,\infty} = RT \ln \frac{x_{B,r}}{x_{B,\infty}}$$

$$\ln \frac{x_{B,r}}{x_{B,\infty}} = \frac{V}{RT} \frac{2\gamma_{\alpha-\beta}}{r}$$

Henry law

$$a_B = kx_B$$

$$1 = kx_{B,\infty}$$

$$k = \frac{1}{x_{B,\infty}}$$
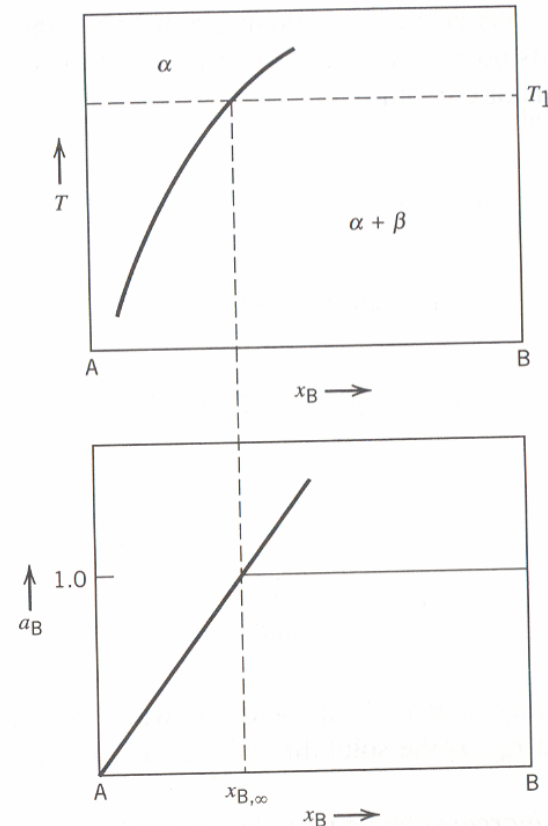
Figure 4.8 Activity of B in an A–B system with no solubility of A in B.

$$\ln \frac{x_{B,r}}{x_{B,\infty}} = \frac{V}{RT} \frac{2\gamma_{\alpha-\beta}}{r}$$

The solubility of B increases as its particle size (radius of curvature) decrease.

Coarsening or Ostwald ripening : The material immediately surrounding the small particles, the concentration of B will be higher. If the sample is held at a high temperature where B atoms are mobile, the small particles will tend to dissolve and the larger particles will grow.
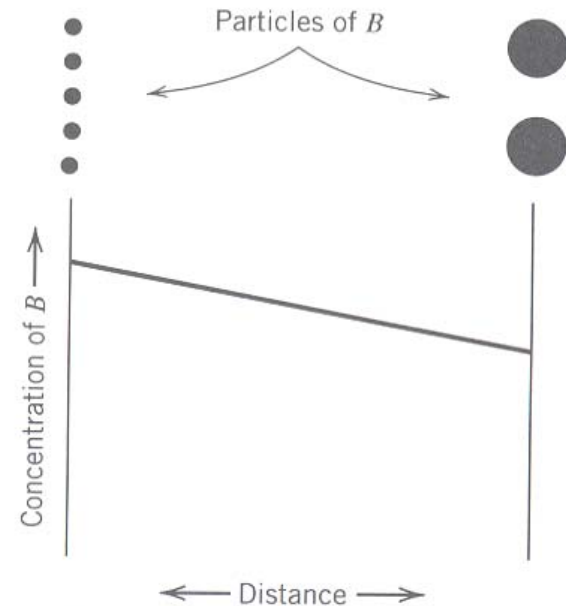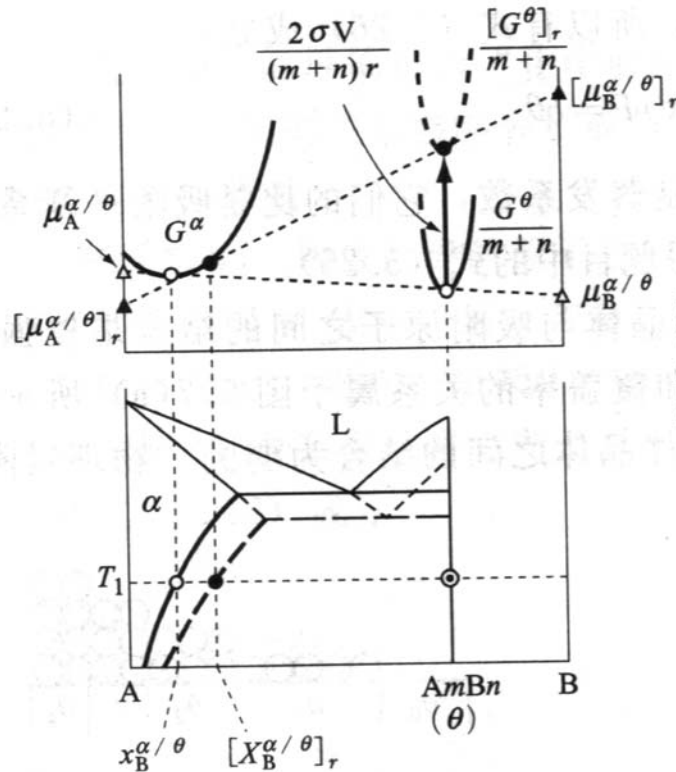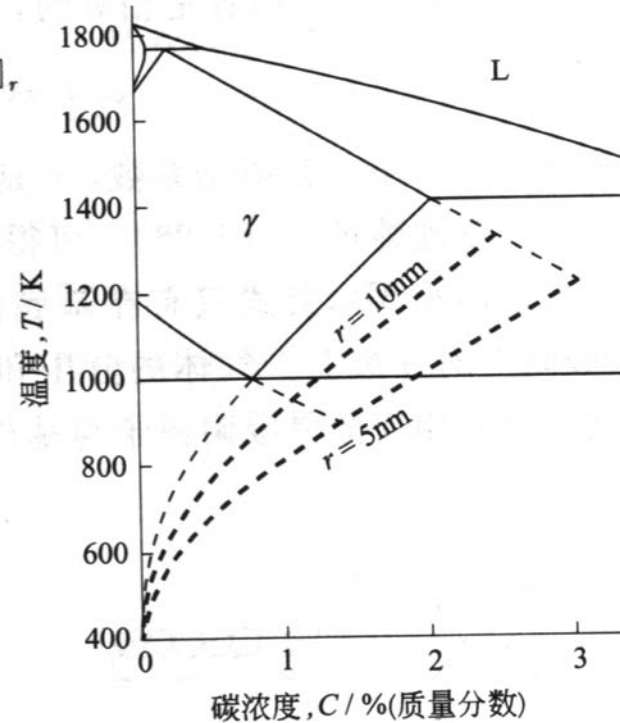
Particles of B

Concentration of B

Distance

Figure 4.9 Solubility as a function of particle size.

微粒化带来的溶解度增加

(a) 自由能图与相图

(b) Fe₃C在Fe-C系奥氏体中的溶解度曲线

图 5.6　由微粒化带来的溶解度增加

From T. Nishizawa

Measurement of surface energy

$$\Delta P = P_i - P_o = \frac{2\gamma}{r}$$

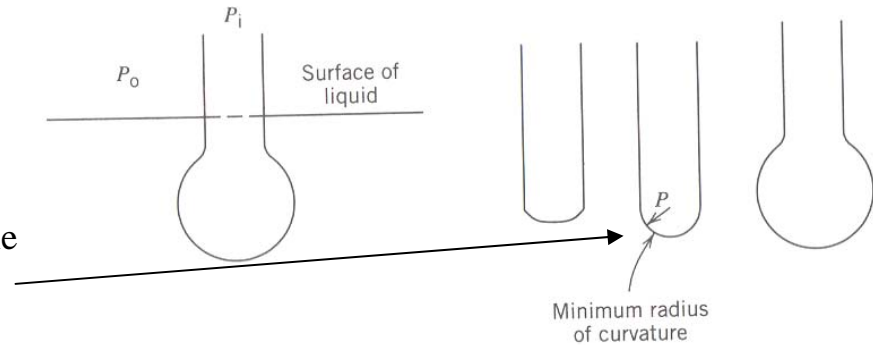Maximum pressure   minimum radius: bubble

Figure 4.10 Bubble method for surface energy determination.

$$\Delta P = \rho g h = \frac{(2\cos\theta)\gamma}{R}$$
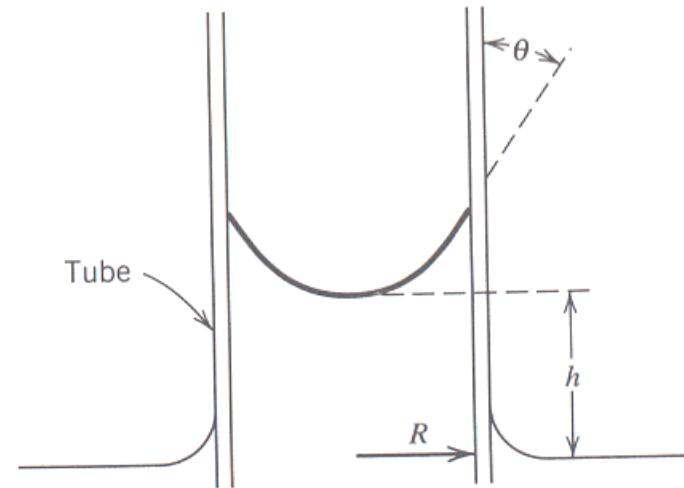
$$\gamma = \frac{R\rho g h}{\cos\theta}$$

Figure 4.11 Capillary rise method for surface energy measurement.

Surface Energy of Solids

0.9 Tm

Surfaces have a liquid-like quality

Elongate: weights

Shrink: surface force

$$\delta w_{rev} = mgdl = \gamma dA$$

Surface area changes:

$$A = 2\pi r l$$
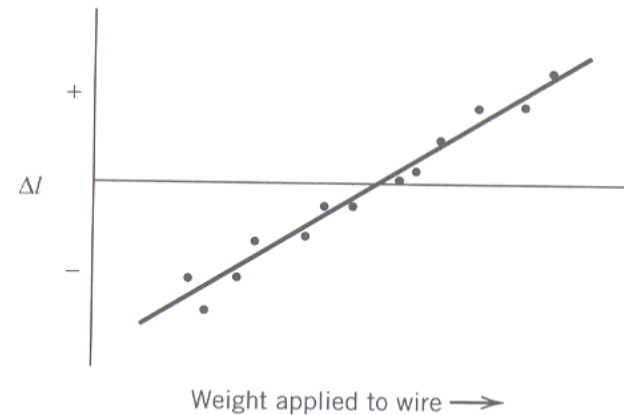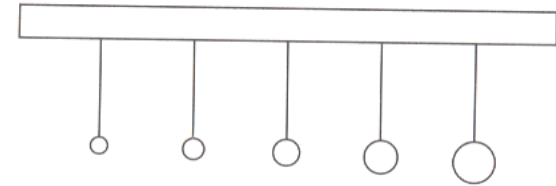
$$dA = 2\pi (rdl + ldr)$$

The volume is constant:

Figure 4.12 Elongation method for measurement of surface energy of solids.

$$\delta w_{rev} = mgdl = \gamma dA$$

$$dA = 2\pi(rdl + ldr)$$
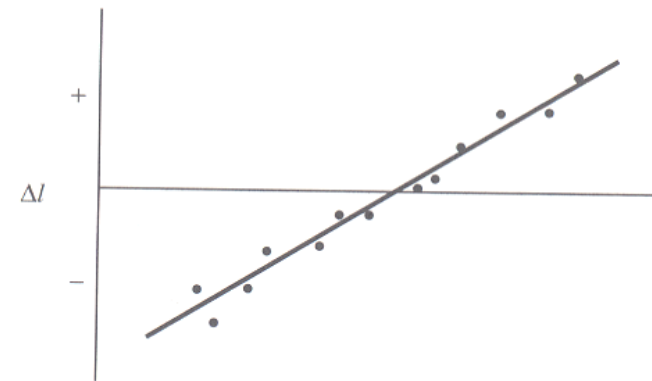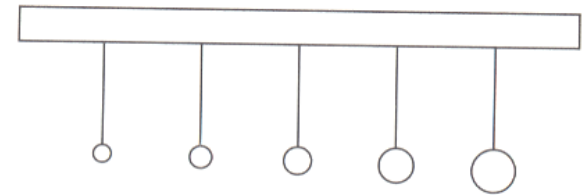
The volume is constant:

$$V = \pi r^2 l$$

$$dV = 2\pi l r dr + \pi r^2 dl = 0$$

$$dr = -\frac{1}{2}\frac{r}{l}dl$$

At the balance point: no elongation

$$\boxed{\gamma = \frac{mg}{\pi r}}$$

Figure 4.12 Elongation method for measurement of surface energy of solids.

Surface Energy of Solids (3)

Solids: internal surfaces such as GB

$$\delta w_{rev} = mgdl = dG_S$$

$$mg = \frac{\partial G_S}{\partial l} \qquad G_S = \gamma \cdot 2\pi rl + \gamma_{gb} \cdot n\pi r^2$$

Grain boundaries

Stress

Figure 4.13 Location of grain boundaries in elongation method.

Volume constant: $\frac{\partial V}{\partial l} = 0$

n is the number of grain boundaries per unit length

The surface energy against a variety of gases.

$$mg = \pi \gamma r - \pi r^2 \frac{n}{l} \gamma_{gb}$$

• Conducted at temperatures high enough for atoms to be mobile.
• Average values for the surface energy of solids.

Relative Surface Energies

Measuring the angles among them after the phases have been allowed to equilibrate. The surface were free to move, the force balance at equilibrium:
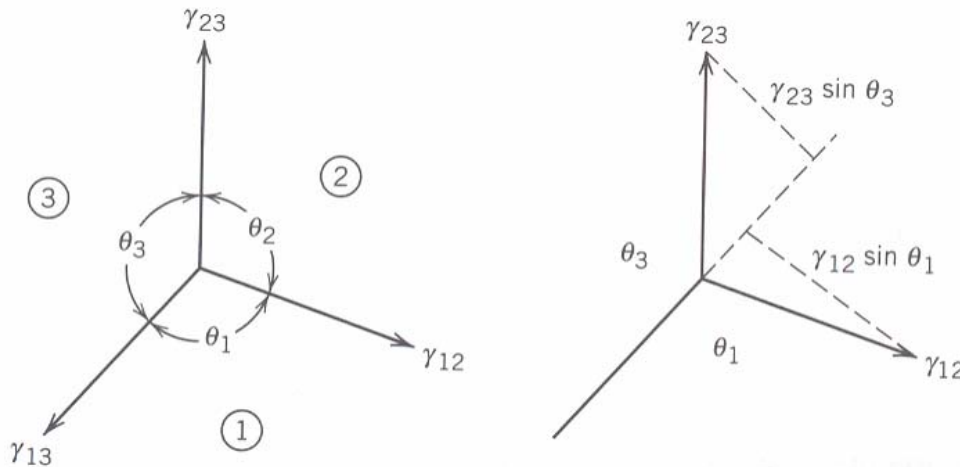
$$\gamma_{23} \sin \theta_3 = \gamma_{12} \sin \theta_1$$

$$\frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{12}}{\sin \theta_3} = \frac{\gamma_{31}}{\sin \theta_2}$$

Figure 4.14 Three-phase equilibrium.

Relative Surface Energies (2)

Two of the phases are identical, then

$$\gamma_{11} = 2\gamma_{12} \cos\left(\frac{\theta}{2}\right)$$

Determination of grain boundary energies
through thermal etching or grooving.

Figure 4.15 Two-phase equilibrium.

γ_{11} The grain boundary energy

γ_{12} The surface energy of the solid/vapor

θ The groove angle
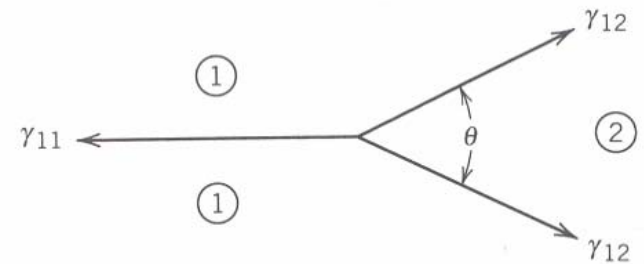
Wetting of Surfaces

Sessile drop technique: heated to the temperature in a furnace with one clear end.

$$\gamma_{l,s} = \gamma_{s,v} - \gamma_{l,v} \cos\theta$$

Wet: angle less 90
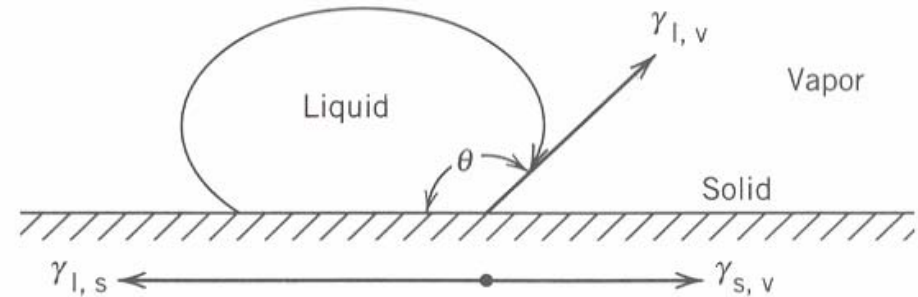Non-wetting: angle greater than 90

A glaze in ceramics, complete wetting

Figure 4.16 Liquid–solid–vapor equilibrium.

Concentrations of solute of the interface in excess of the concentration in the bulk α and β phases.

$$G^y = \gamma A + m_A^y \mu_A^y + m_B^y \mu_B^y$$

$$dG^y = \gamma dA + A d\gamma + m_A^y d\mu_A^y + \mu_A^y dm_A^y + m_B^y d\mu_B^y + \mu_B^y dm_B^y$$

Gibbs-Duhem equation,

$$\sum \mu_i dm_i + \gamma dA = 0$$

$$dG^y = \gamma dA + m_A^y d\mu_A^y + m_B^y d\mu_B^y$$

The mass balance for B,

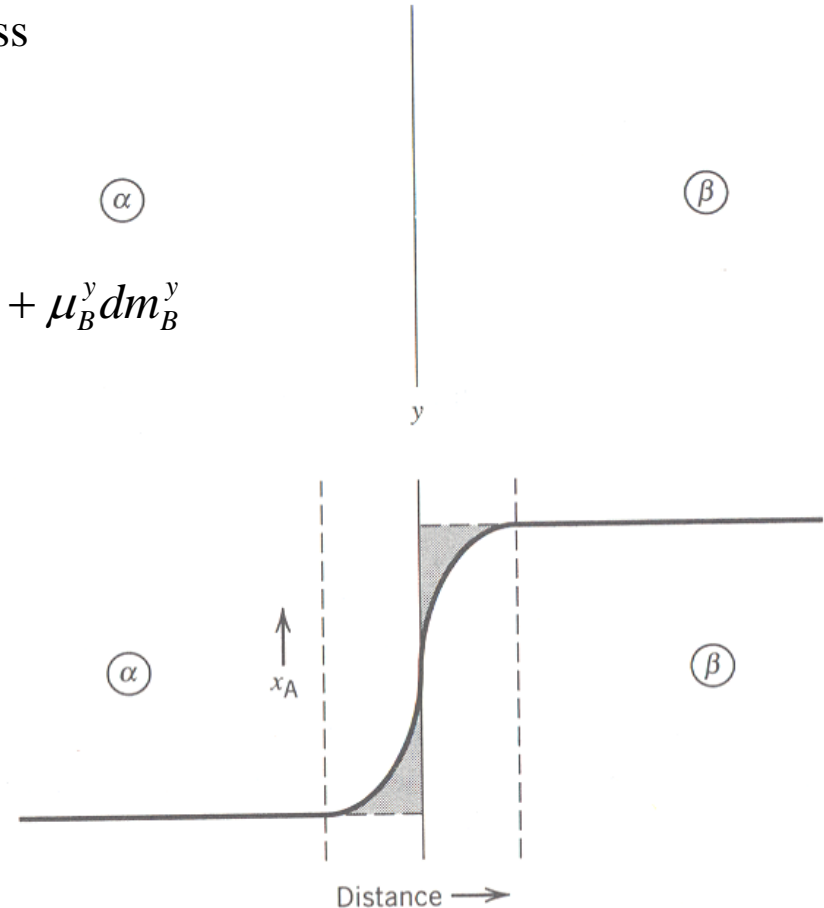$$m_B = x_B^\alpha m_\alpha + x_B^\beta m_\beta + m_B^y$$

α β

y

α β

x_A

Distance →

Figure 4.17 Concentrations at interface.

The surface excess concentration of B at y as:

$$\Gamma_B^y = \frac{m_B^y}{A}$$

$$m_B = x_B^\alpha m_\alpha + x_B^\beta m_\beta + \Gamma_B^y A$$

$$m_A = x_A^\alpha m_\alpha + x_A^\beta m_\beta + \Gamma_A^y A$$

The physical interface between phases α and β is not a sharp geometrical surface.

No excess surface concentration of A:

$$\Gamma_A^y = 0$$

$$m_A = x_A^\alpha m_\alpha + x_A^\beta m_\beta$$

$$d\gamma + \Gamma_A^y d\mu_A^y + \Gamma_B^y d\mu_B^y = 0$$

Definition, $\Gamma_A^y = 0$

$$d\gamma = -\Gamma_B^y d\mu_B$$

$$\Gamma_B^y = -\left(\frac{\partial\gamma}{\partial\mu_B}\right)_T$$

$$\mu_B = \mu_B^0 + RT \ln \alpha_B$$

$$d\mu_B = RTd \ln \alpha_B$$

$$d\mu_B = RTd \ln x_B$$

$$\Gamma_B^y = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial x_B}\right)_T$$

The activity coefficient of B is constant:

If the addition of B to a system lowers the surface energy of the interface, material B will segregate preferentially at the interface.
If one of the phases β is a vapor phase, material B will be adsorbed on the α surface.
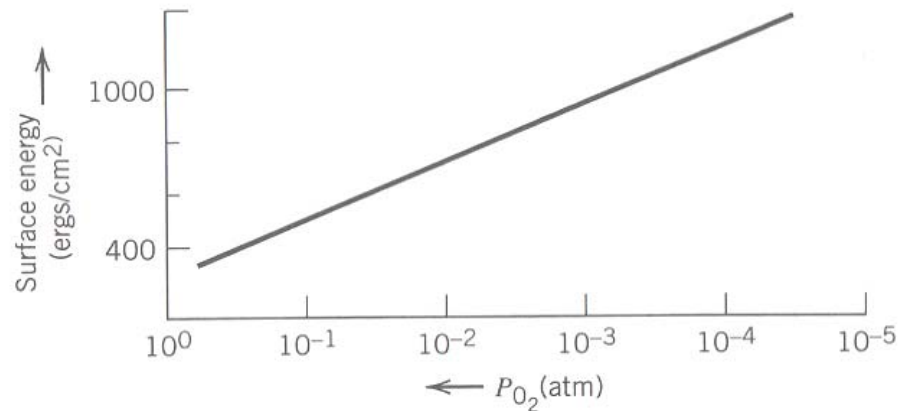

Figure 4.18 Surface energy as a function of activity (pressure) of oxygen.

Adsorption on Solids (Adsorption Isotherms)

Relation between the pressure of an adsorbing gas and the fraction of a solid surface occupied by the adsorbate.

Physical adsorption

Van der Waals forces, a few kJ/mol,
Multiple adsorption layers are possible

Chemisorption

The bonding between the gas and the solid, tens or hundreds of kJ/mol
Monolayers, very tightly bound to the solid.

Langmuir: degree of surface coverage Φ and the pressure of the adsorbing gas P

$$\dot{m}_d = k_d \Phi$$

$$\dot{m}_a = k_a P(1-\Phi)$$

$$k_d \Phi = k_a P(1-\Phi)$$

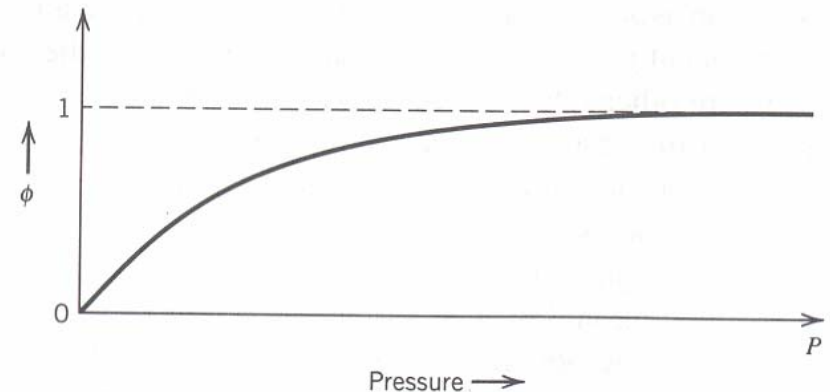$$\Phi = \frac{KP}{KP+1}$$

Figure 4.19 Langmuir adsorption isotherm: fraction of surface covered versus pressure of adsorbing gas.

Chemisorption / one adsorption

The surface atoms have fewer bonds to their nearest neighbors than atoms away from the surface.

Differ entropically from atoms in the bulk of the solid.

$$\left(\frac{\partial S}{\partial A}\right)_{T,P} = -\left(\frac{\partial \gamma}{\partial T}\right)_{A,P} = S_s$$

Homework

- Exercises in Chap 4 / Volume II

  P123, 4.1, 4.4