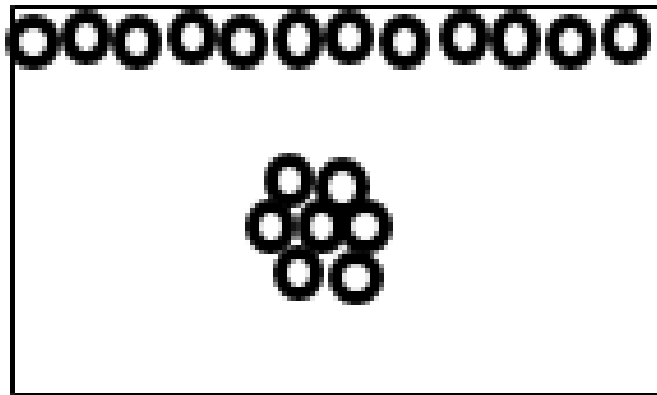


Thermodynamics of surfaces

1. Surface thermodynamic quantities
2. Surface tensions of liquids
3. Intermolecular interaction
4. Surface tensions of solids
5. Measurements of surface tension

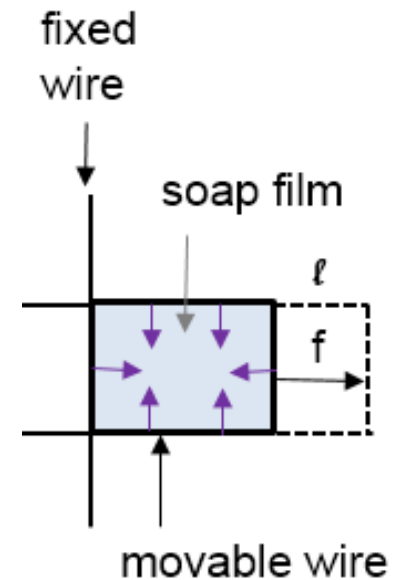
Molecules at surface vs. in the bulk

- Molecules (or atoms) at the surface are in a quite **different chemical environment** compared to those in the bulk **in terms of intermolecular interactions**.
- The surface molecules have less number of neighbors to interact with compared to those in the bulk.
- The interactions are attractive in liquids and solids.
- Therefore, the surface molecules are in a unstable state with a **higher free energy**.



Extension of a soap film

- Extension brings more molecules from the bulk to the surface.
- Extension of the film requires work w
- $dG = dw_{\text{rev}} = f d\ell \rightarrow \Delta G = f \ell$
- If the movable wire is freed, the soap film will contract to reduce the surface area with a force $-f$.
- The contracting force acts at every point on the surface in the direction perpendicular to the boundary: **negative 2D pressure**.
- The origin of the contraction force is due to the attractive force acting on the surface molecules by all the molecules below the surface.



Note: Surface does not mean only the outmost layer and it also includes the 2nd, 3rd, ... layers for which the intermolecular interactions with neighbors are not symmetrical. However, the contributions to E^s by the 2nd, 3rd, ... layers decrease rapidly.

Definition of surface thermodynamic functions

- Consider a liquid droplet consisting of N molecules (Figure).
- The total energy of the system can be written as

$$E_{\text{total}} = NU^0 + AU^s$$

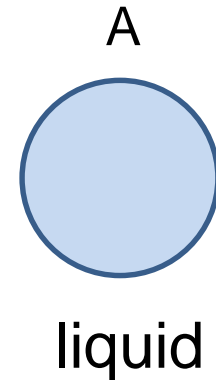
where

U^0 = internal energy per bulk atom,

A = surface area,

U^s = **excess** surface energy/ area. $U^s > 0$.

- S^s and H^s , G^s , A^s can be similarly defined. Then,
- $G^s = H^s - TS^s$, $A^s = U^s - TS^s$

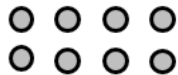


Surface Free Energy (Surface Tension), γ

- $G_{\text{total}} = NG^0 + AG^s = NG^0 + A\gamma$; $\gamma \equiv G^s$
- Since, G^0 is fixed at fixed P and T conditions,
- $dG = d(A\gamma) = \gamma dA + A(\partial\gamma/\partial A)_{P,T}$
- **Case I:** $(\partial\gamma/\partial A)_{P,T} = 0$; A-independent $\gamma \rightarrow$ **unstrained surface** \rightarrow the case for **liquids**.
 $dG = dw = \gamma dA$ as seen for a soap film
- **Case II:** $(\partial\gamma/\partial A)_{P,T} \neq 0$; A-dependent $\gamma \rightarrow$ **strained surface** \rightarrow the case for unannealed solids.
 e.g., a cold-rolled metal sheet



unstrained
(ideal)
surface



elongated
Surface (tensile
stress)



compressed
surface
(compressive stress)

Essential difference between 3D and 2D pressure

- 3D: gas in a container, expansion P , positive(outward), \perp to the wall, gas collisions
- 2D: liquid, contraction P , negative (inward), $//$ to the surface, intermolecular force

- Surface tension, γ

$\text{J/m}^2 \rightarrow \text{N}\cdot\text{m/m}^2 = \text{N/m}$, 2D surface pressure = force per unit length
pressure)

cf) pressure: force per unit area (N/m^2 or dynes/cm^2)

Rough estimation of 2D (surface) pressure

- Roughly assume that the surface pressure exists within 3 outmost molecular layers of $d \sim 1\text{ nm}$.
- $P = \text{force/area} = \gamma / d$.
- If the liquid is water ($\gamma = 72\text{ mN/m}$),
 $P = \gamma / d = (72\text{ mN/m}) / 10^{-9}\text{ m} = 7.2 \times 10^7\text{ Pa} \sim 720\text{ atm}$

Temperature dependence of γ

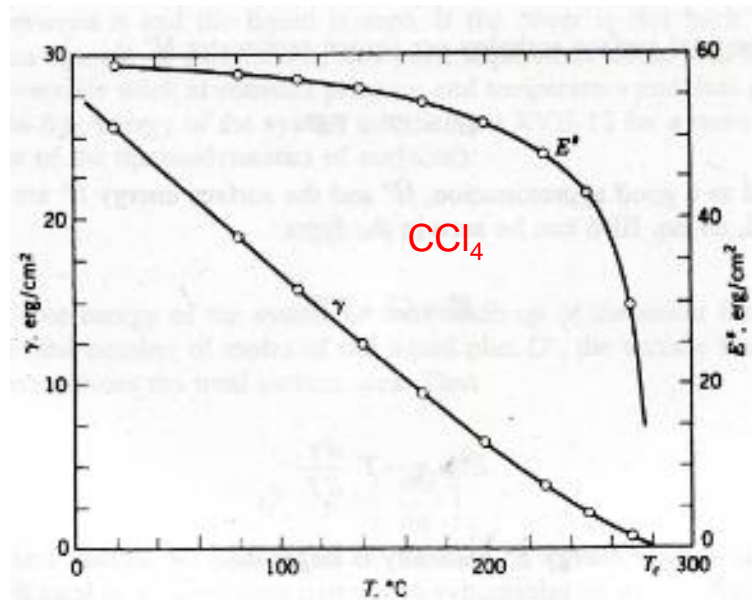
- For an unstrained surface

$$(\partial\gamma/\partial T)_P = (\partial G^s/\partial T)_P = -S^s < 0 \leftarrow dG = VdP - SdT$$

- S^s can be experimentally obtained from the T-dependence of γ .
- $H^s = G^s + TS^s = \gamma - T(\partial\gamma/\partial T)_P$
- $H^s = U^s + PV = U^s$; the surface does not have any volume.
- ΔH^s is the heat absorbed in a surface process, if no volume change is involved.
- $H^s = U^s = \gamma - T(\partial\gamma/\partial T)_P = (+) + (+) > 0$, $G^s = \gamma > 0$.
- Thus, all the surface thermodynamic quantities can be known.

Semiempirical equation for $\gamma(T)$

- $\gamma = \gamma^0 (1 - T/T_c)^n$, where γ^0 is the surface tension at 0 K and T_c is the critical temperature. So, $\gamma(0) = 0$
- $n \sim 1$ for metal and $n = 11/9$ for many organic liquids.
- A more satisfactory equation by Ramsay and Shields is $\gamma V_m^{2/3} = k (T_c - T - 6)$, where V_m is the molar volume and $k = 2.1 \times 10^{-7}$ J/K for most liquids.



Surface Heat Capacity

- $C_p^s = (\partial H^s / \partial T)_p = (\partial / \partial T)_p [\gamma - (\partial \gamma / \partial T)_p] = -T (\partial^2 \gamma / \partial T^2)_p$
- Estimation based on the Debye model for solid.
- For bulk $U_{T \rightarrow 0} \propto T^4 \rightarrow C_p \propto T^3$ at low T.
- For surface $U_{T \rightarrow 0} \propto T^3 \rightarrow C_p^s \propto T^2$ at low T.

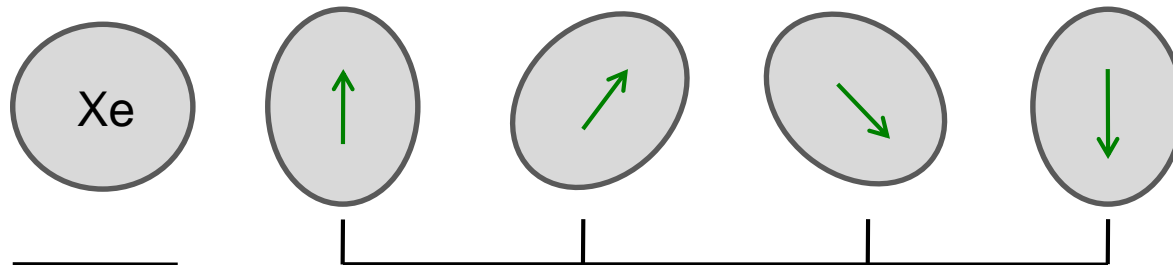
Origin of γ : attractive interatomic (solid) or intermolecular (liquid) force

Origin of van der Waals

1) Fluctuating dipole

- Consider Xe-Xe interaction
- Xe is an atom with a spherically symmetric electron distribution around the nucleus, so it poses no permanent electrical dipole moment
- The probability of finding an electron at a given time, which is given by the solution of the Schrödinger equation, $|\Psi|^2$, is spherically symmetric.
- However, the above does not mean that the actual electron distribution at a given time is not necessarily spherically symmetric.
- In fact, it can be aspherical as shown, for example in the figure below;

electron distribution in Xe atom



time average
with $p = 0$

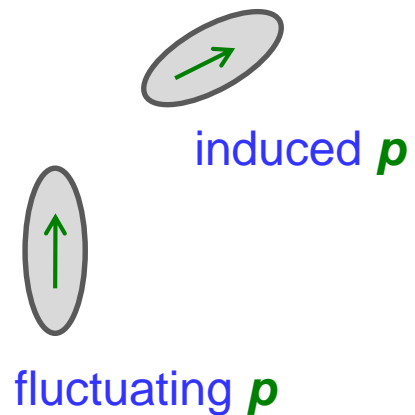
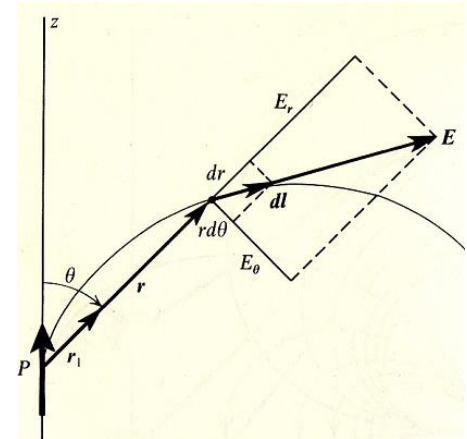
fluctuating dipole at various instants
with $p \neq 0$

2) Induced dipole

- Fluctuating (instantaneous) dipole produces an electric field \mathbf{E} in space, which induces a dipole moment in another Xe atom given by
- $\mathbf{p}_{\text{ind}} = \alpha \mathbf{E}$, α is the electric **polarizability**.
- The interaction energy

$$V = - \int_0. E \mathbf{p}_{\text{ind}} \cdot d\mathbf{E} = \alpha E^2/2$$
- The magnitude of the fluctuating dipole is also proportional to α , the tendency of forming an aspherical electron distribution.
- The angle θ between the two dipole can be varied from $0 \leq \theta \leq 2\pi$ at a given distance r .
- When averaged over all orientations,

$$\mathbf{V}(\mathbf{r}) = - a \alpha^2/r^6 = - \mathbf{A}/r^6$$
, where $A (>0)$ is a atom or molecule-dependent constant.
- $\mathbf{V}(\mathbf{r})$ is always negative (**attraction**).
- α' (polarizability volume) = $\alpha'/4\pi\epsilon_0$ is the volume of the electron cloud in atom(molecule).
- A larger molecule has a larger α , hence a larger attractive interaction, resulting in a higher boiling and melting points.



cf.

E field by a *static* electric dipole

dipole moment $\mathbf{p} = Q\mathbf{s}$

\mathbf{p} is a vector quantity whose direction is from (-) to (+) charge.

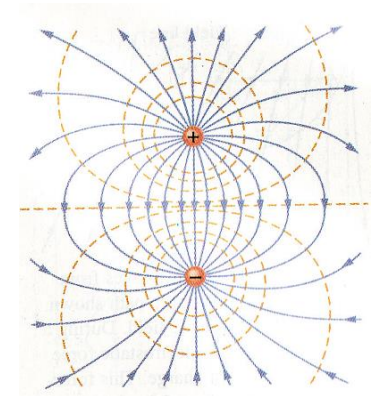
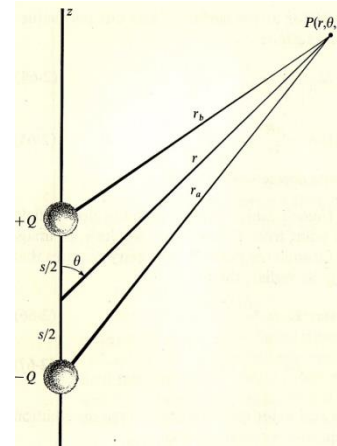
$$V = \frac{\mathbf{p} \cdot \mathbf{r}_1}{4\pi\epsilon_0 r^2}$$

$$V = \frac{Q}{4\pi\epsilon_0} \left(\frac{1}{r_b} - \frac{1}{r_a} \right),$$

$$r_a^2 = r^2 + \left(\frac{s}{2} \right)^2 + rs \cos \theta,$$

$$\frac{r}{r_a} = \left[1 + \left(\frac{s}{2r} \right)^2 + \frac{s}{r} \cos \theta \right]^{-1/2},$$

$$= 1 - \frac{1}{2} \left(\frac{s^2}{4r^2} + \frac{s}{r} \cos \theta \right) + \frac{3}{8} \left(\frac{s^2}{4r^2} + \frac{s}{r} \cos \theta \right)^2 -$$



$$\frac{r}{r_a} = 1 - \frac{s}{2r} \cos \theta + \frac{s^2}{4r^2} \frac{3 \cos^2 \theta - 1}{2}.$$

$$\frac{r}{r_b} = 1 + \frac{s}{2r} \cos \theta + \frac{s^2}{4r^2} \frac{3 \cos^2 \theta - 1}{2},$$

$$V = \frac{Qs}{4\pi\epsilon_0 r^2} \cos \theta \quad (r^3 \gg s^3).$$

$$E_r = -\frac{\partial V}{\partial r} = \frac{1}{4\pi\epsilon_0} \frac{2p}{r^3} \cos \theta,$$

$$E_\theta = -\frac{1}{r} \frac{\partial V}{\partial \theta} = \frac{1}{4\pi\epsilon_0} \frac{p}{r^3} \sin \theta,$$

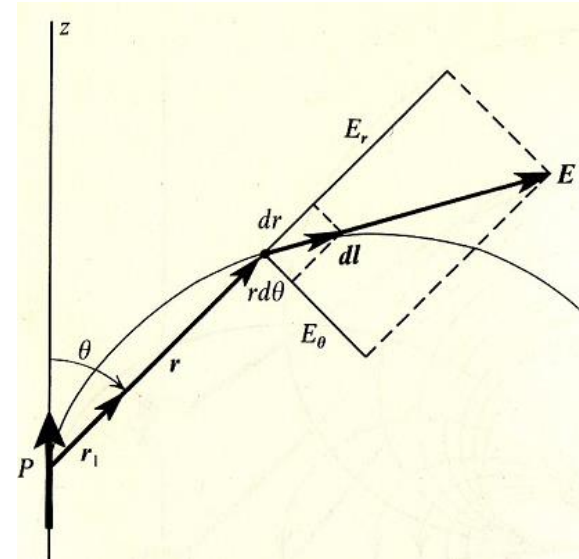
$$E_\phi = -\frac{1}{r \sin \theta} \frac{\partial V}{\partial \phi} = 0.$$

$$\mathbf{E} = \frac{p_0}{4\pi\epsilon_0 r^3} (2 \cos \theta \mathbf{r}_1 + \sin \theta \boldsymbol{\theta}_1)$$

$$\frac{r d\theta}{dr} = \frac{E_\theta}{E_r} = \frac{\sin \theta}{2 \cos \theta},$$

$$\frac{dr}{r} = \frac{2d(\sin \theta)}{\sin \theta},$$

$$r = A \sin^2 \theta.$$



Intermolecular interactions

1. van der Waals (Dispersion force)

$$V(r) = -A/r^6$$

2. dipole-induced dipole

3. dipole-dipole

4. Hydrogen bonding

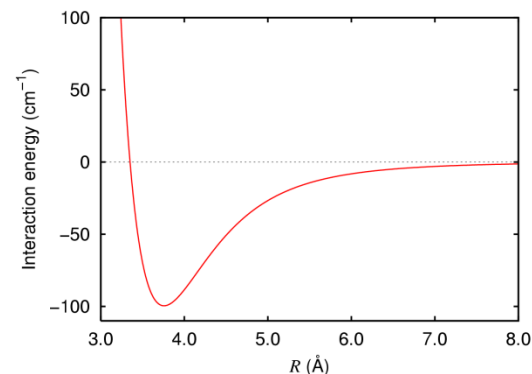
Relative magnitude

$$1 < 2 < 3 < 4$$

T_b of gases (K)

He	Ar	Xe	NH ₃	H ₂ O	C ₁₀ H ₈
4.2	87.3	165	230.7	373	491

Interaction energy of Ar-Ar



Contribution of the dispersion to the total intermolecular interaction energy

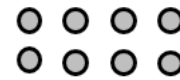
Molecule pair <input type="checkbox"/>	% of the total energy of interaction <input type="checkbox"/>
CH ₃ Cl-CH ₃ Cl	68
CH ₄ -CH ₄	100
H ₂ O-CH ₄	87
H ₂ O-H ₂ O	24
HBr-HBr	96
HCl-HCl	86
HCl-HI	96
HI-HI	99
Ne-Ne	100
NH ₃ -NH ₃	57

Surface free energy of solids

- The γ of two solids composed of the same material having the same surface area may differ depending on their surface strains; ex: a cold-rolled metal sheet



unstrained



Strained
tensile

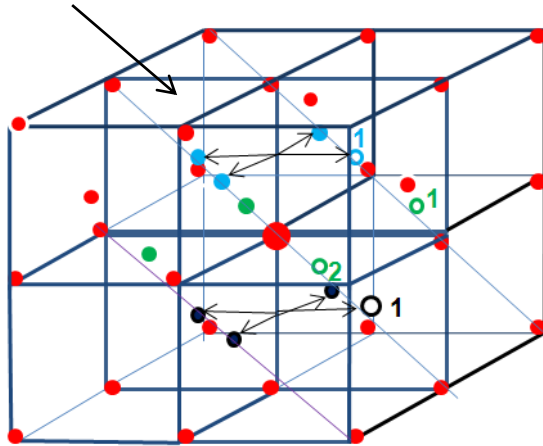


compressed

- For single crystals, which do not have a strain (all the atoms are in their equilibrium positions), their γ values can be estimated based on the **broken bond model**.
- Consider a single crystal metal consisting of a single element A with a A-A bond energy of E_b J/mol.
- If every surface atom has n broken bonds compare with a bulk atom, $U^s = n E_b N$, assuming the surface atom density is N atoms/m².
- $H^s = U^s + PV^s = U^s$
- H^s can be taken from the experimentally measured heat of sublimation ΔH_{sub}
- In a sublimation process $A_N(s) \rightarrow N A(g) + \Delta H_{\text{sub}}$ ($N = N_A$),
 $\Delta H_{\text{sub,m}} = \Delta U_{\text{sub,m}} + RT$ (assumed an ideal gas) $\sim \Delta U_{\text{sub,m}} = N_A N_c E_b / 2$ ($N_c =$ coordination #)
- $\gamma = G^s - TS^s$
- One can estimate γ , if one knows S^s , which can be obtained from
 $S^s = - (\partial \gamma / \partial T)_P$

γ of solid surface: broken bond model

fcc (110) plane



When viewed from the large red atom,
there are 3 groups of nearest neighbors.

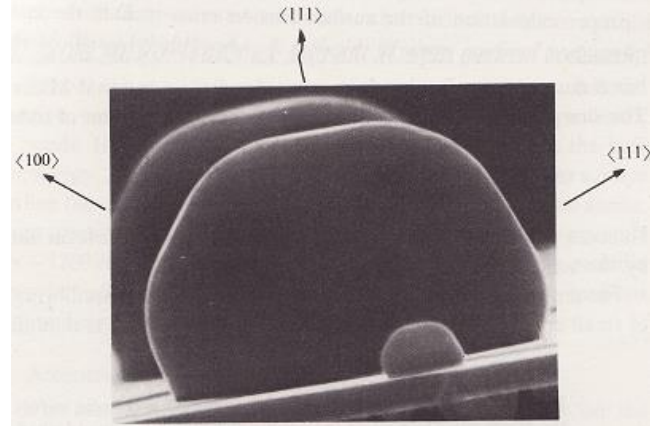
- 1) in the same plane (4●), among which 1 and 2(○) are above the (110) plane.
 - 2) in the plane $a/2$ above (4●), among which 1(○) is above the (110) plane.
 - 3) in the plane $a/2$ above (4●), among which 1(○) is above the (110) plane.
- So, each surface atom has 4 broken bonds.

Table 3.1. Average surface energies of selected solids and liquids at the indicated temperatures

Material	γ (mJ/m ²)	T (°C)
W (solid)	2900	1727
Nb (solid)	2100	2250
Au (solid)	1410	1027
Au (liquid)	1140	1338
Ag (solid)	1140	907
Ag (liquid)	879	1100
Fe(solid)	2150	1400
Fe (liquid)	1880	1535
Pt (solid)	2340	1311
Cu (solid)	1670	1047
Cu (liquid)	1300	1535
Ni (solid)	1850	1250
Hg (liquid)	487	16.5
LiF (solid)	340	-195
NaCl (solid)	227	25
KCl (solid)	110	25
MgO (solid)	1200	25
CaF ₂ (solid)	450	-195
BaF ₂ (solid)	280	-195
He (liquid)	0.31	-270.5
N ₂ (liquid)	9.71	-195
Ethanol (liquid)	22.75	20
Water	72.75	20
Benzene	28.88	20
<i>n</i> -Octane	21.80	20
Carbon tetrachloride	26.95	20
Bromine	41.5	20
Acetic acid	27.8	20
Benzaldehyde	15.5	20
Nitrobenzene	25.2	20

Source: From [7].

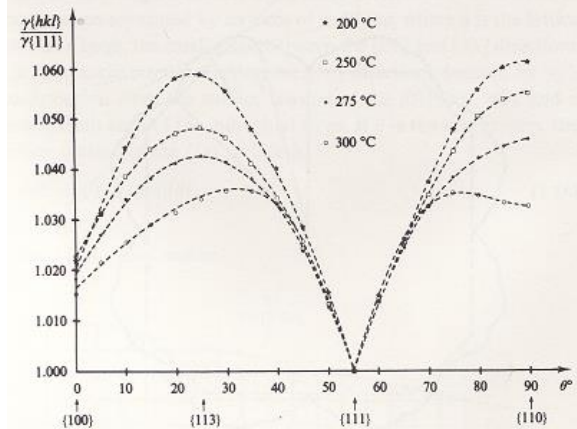
Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).



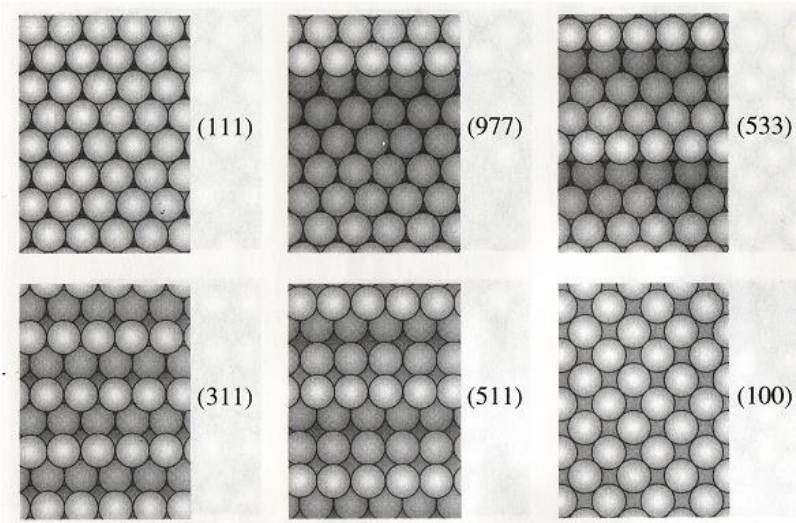
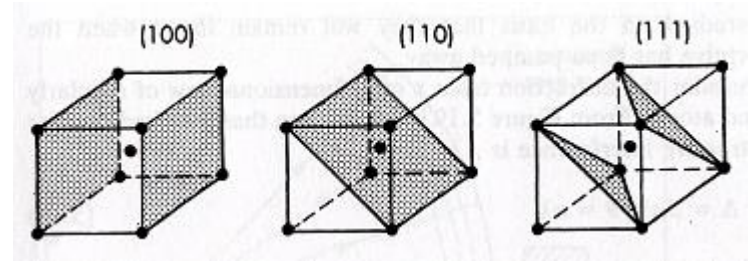
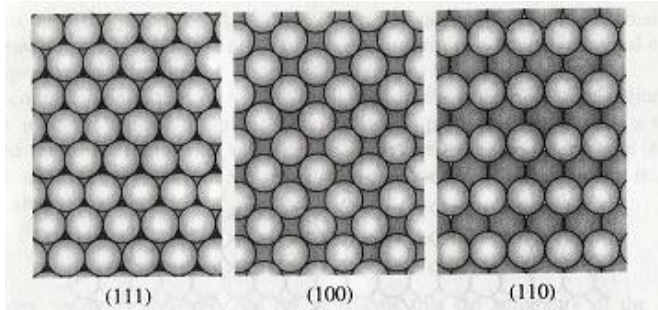
$T_m(\text{Pb}) = 601 \text{ K}$, fcc metal

Crystallographic orientation dependence of γ

Fig. 1.8. Anisotropy of γ relative to $\langle 111 \rangle$ for lead as a function of temperature (Heyraud & Metois, 1983).



FCC (Ar, Ni, Pd, Cu, Ag, Au)



Correlation between γ and ΔH_{sub}

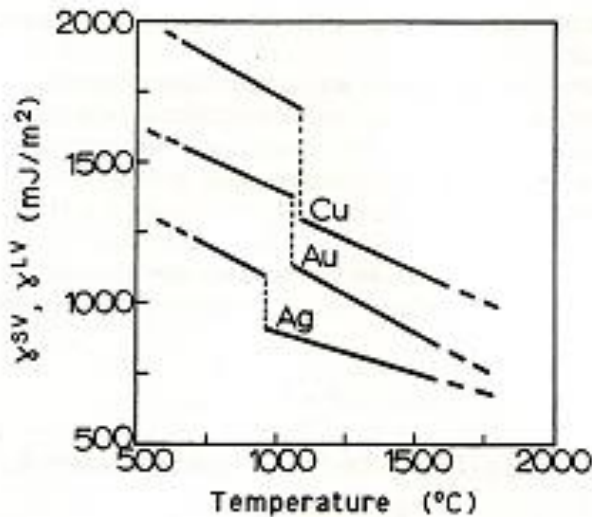
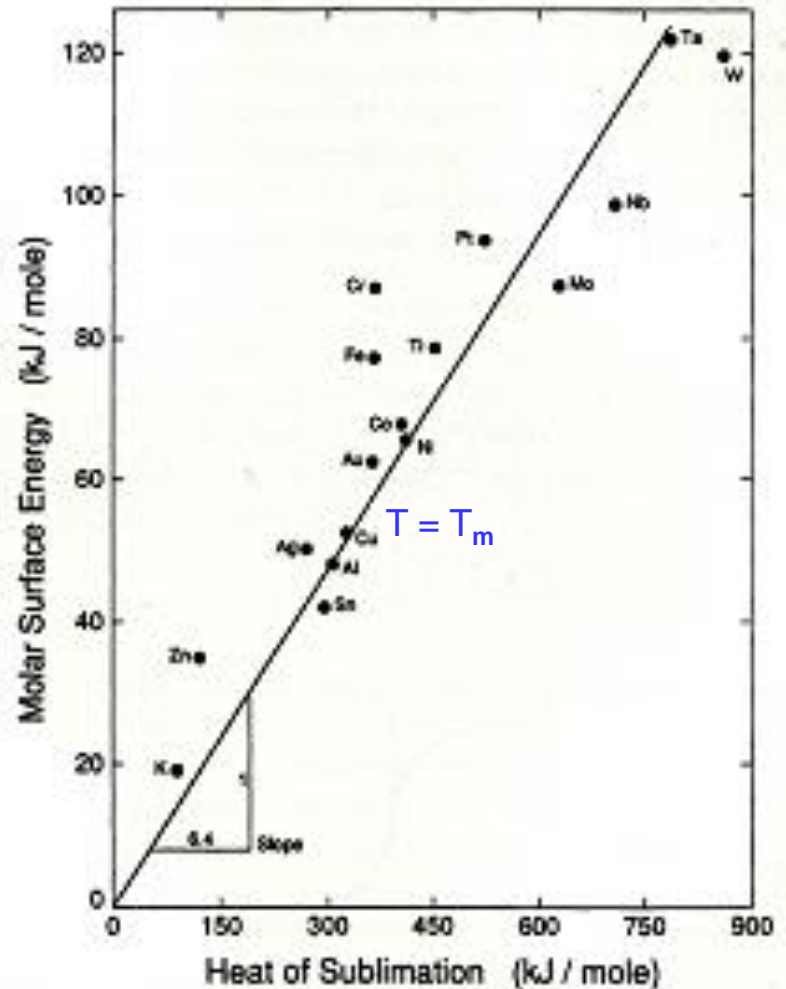


Figure 3.2. Temperature dependence of the surface energy and the solid-liquid phase transition for three f.c.c. metals. From [12].

$$\gamma^{\text{SV}} \cong 1.2(\gamma^{\text{LV}})_{\text{m}} + 0.45(T_{\text{m}} - T),$$

where $(\gamma^{\text{LV}})_{\text{m}}$ is the liquid surface energy at the melting point, T_{m} is the melting temperature, and T is the temperature below the melting point of the solid.

- $\gamma \propto \Delta H_{\text{sub}} \sim 0.16 \Delta H_{\text{sub}}$



Critical point

At $T = T_c$

- Not a liquid, not a vapor
- Condensation and vaporization occur rapidly.
- Local fluctuation of density
- No surface tension at $T = T_c$

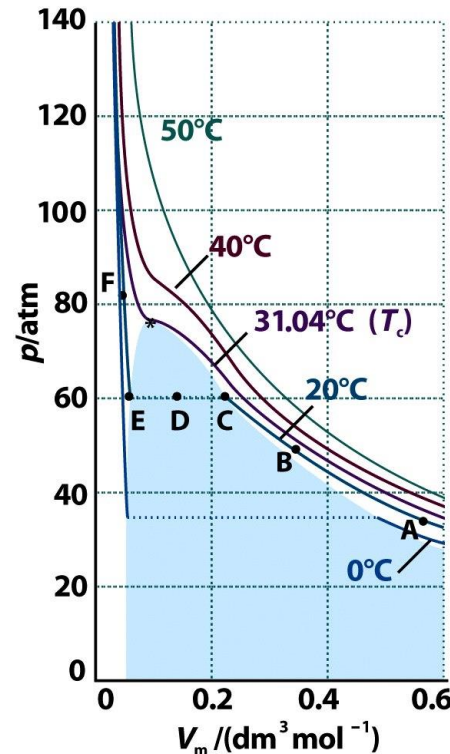


Figure 1-15
Atkins Physical Chemistry, Eighth Edition
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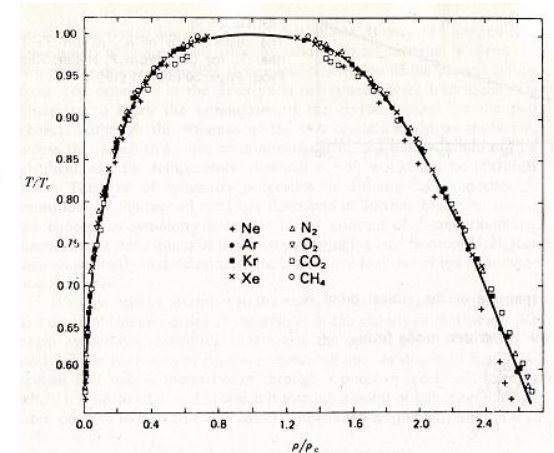
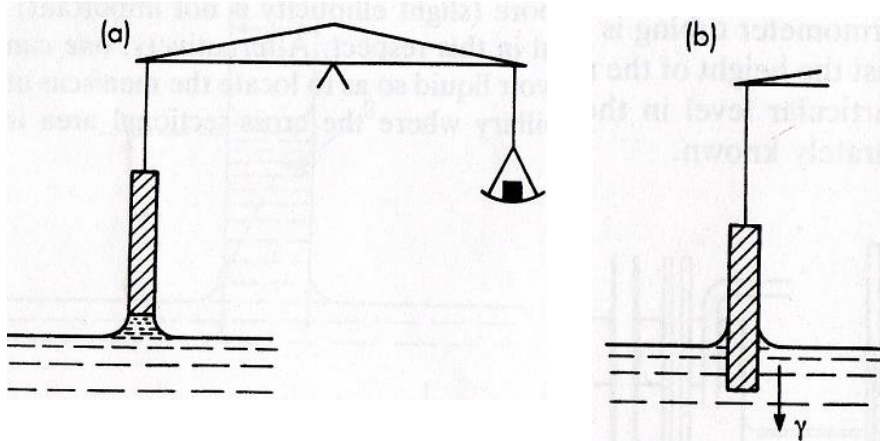


FIGURE 24.11

The liquid–gas coexistence curve for simple substances. The curve is a composite of data for Ne, Ar, Kr, Xe, N₂, O₂, CO₂, and CH₄. Note the use of the reduced variables T/T_c and ρ/ρ_c . From E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

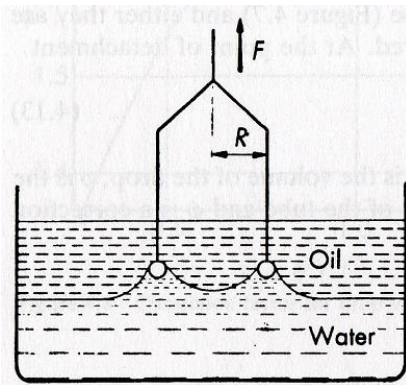
Measurements of surface tension

Measurement of interfacial tension by the ring method



$$W_{\text{det.}} - W = 2(x + y)\gamma$$

Wilhelmy plate methods: (a) detachment; (b) static



$$\gamma = \frac{\beta F}{4\pi R}$$

$$(\beta - a)^2 = \frac{4b}{\pi^2} \cdot \frac{1}{R^2} \cdot \frac{F}{4\pi R(\rho_1 - \rho_2)} + c$$

Correction factor β