Lecture Note #6A (Fall, 2022)

Liquid Interfaces

1. Surface energy and surface tension (5.2.1)
2. Liquid surfaces (5.2.2-)
3. Liquid films (5.3, 5.4, 5.5, 5.6)
4. Thermodynamics of liquid Interfaces (5.7)
5. Electrified and charged Interfaces (5.1, 5.8)

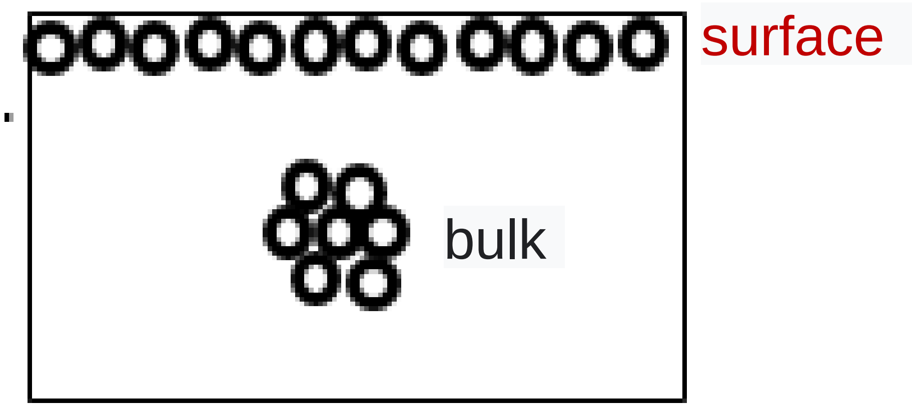
Reading: Kolasinski, ch.5,
Somorjai, ch.3, Shaw, ch. 4
Pashley

Surface energy and surface tension (5.2)

Water strider (소금쟁이)

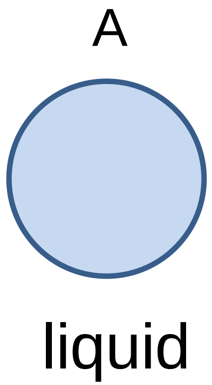
Molecules at surface vs. in the bulk

- 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.



Definition of surface thermodynamic functions

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



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

where

U^0 (or E^0) = internal energy per bulk atom,

A = surface area,

U^s (or E^s) = excess surface energy per unit area. $U^s > 0$

(specific surface energy (energy per unit area))

→ AU^s: excess energy due to the surface

- S^s and H^s, G^s, A^s can be similarly defined. Then,

  Surface free energy $G^s = H^s - TS^s$ (at const T, P),

  surface work content (Helmholtz free energy) $A^s = U^s - TS^s$

  (at const T, V)

- A homogeneous crystalline solid with N atoms & surface planes

$$E = NE^0 + AE^s$$

where E: total energy of the solid, A: surface area, E^0: energy in the bulk, E^s: specific surface energy (energy per unit area)

- Entropy

$$S = NS^b + AS^s$$

- Surface work content (energy per unit area)

$$A^s = E^s - TS^s$$

- Surface free energy (energy per unit area)

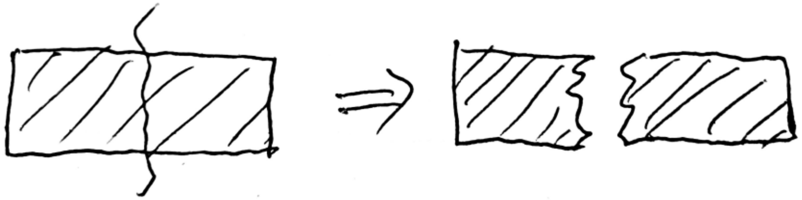
$$G^s = H^s - TS^s$$

- Total free energy

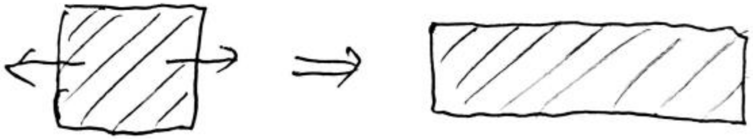
$$G = NG^0 + AG^s$$

Extension of surface

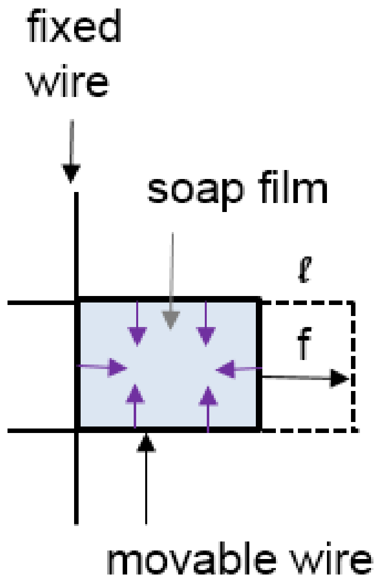
- Case I: bulk atom(or molecule) → surface
  -extension of a liquid film
  -breaking of a solid bar



- Case II: stretching (e.g., rubber mat): fixed number of surface atoms or molecules



Case I: extension of a soap film



- Extension brings more molecules from the bulk to the surface.
- Extension of the film requires work w
- $dG = dw_{rev} = f\, d\ell \rightarrow \Delta G = f\, \ell$
- 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.

Surface Free Energy (Surface Tension), γ

- $G_{total} = NG^0 + AG^s = NG^0 + A\gamma$; $\gamma \equiv G^s$
  work needed to create a surface
- Since, G^0 is fixed at fixed P and T conditions,
- $dG = d(A\gamma) = \gamma\, dA + A(\partial\gamma/\partial A)_{P,T}$

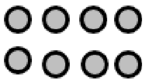
- Case I: $(\partial\gamma/\partial A)_{P,T} = 0$; A-independent γ
  -surface free energy is independent of the size of surface area
  -A new surface is created by bringing molecules in the bulk to the surface
  -specific surface free energy G^s is independent of surface area

→ unstrained surface → the case for liquids

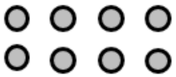
$dG = dw = G^s dA = \gamma\, dA$ as seen for a soap film

Exception: $\gamma \neq G^s$

- **Case II**: $(\partial\gamma/\partial A)_{P,T} \neq 0$; A-dependent γ → strained surface → 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), ⊥ to the wall, gas collisions
- 2D: liquid, contraction P, negative (inward), // to the surface, intermolecular force

- Surface tension, γ
  2D analogue of pressure, 2D analogue of PdV work

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

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

γ as a pressure along the surface plane that opposes the creation of more surface

Rough estimation of 2D (surface) pressure

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

→ atoms in a metal surfaces are subject to very large compressive forces

γ in liquid: low → lower energy required to make new surface
liquid: minimize surface area → curved structure

e.g. metal, $\gamma \sim 1\mathrm{N/m}$

$\rightarrow P = \gamma /d = 1\ \mathrm{Nm^{-1}}/10^{-9}\ \mathrm{m} = 10^{9}\ \mathrm{N/m^2} = 10^{9}\ \mathrm{Pa} \sim 10^{4}\ \mathrm{atm}$

→ atoms in a metal surfaces are subjected to very large compressive forces

***Table 5.1** Selected values of surface tension taken from Adamson and Gast [27]*

	Temperature/°C	γ/mN m^{-1}
Liquid-Vapour Interface		
Perfluoropentane	20	9.89
Heptane	20	20.14
Ethanol	20	22.39
Methanol	20	22.50
Benzene	30	27.56
	20	28.88
Water	25	72.13
	20	72.94
Hg	25	485.5
	20	486.5
Ag	1100	878.5
Cu	1357 (T_f)	1300
Pt	1772 (T_f)	1880

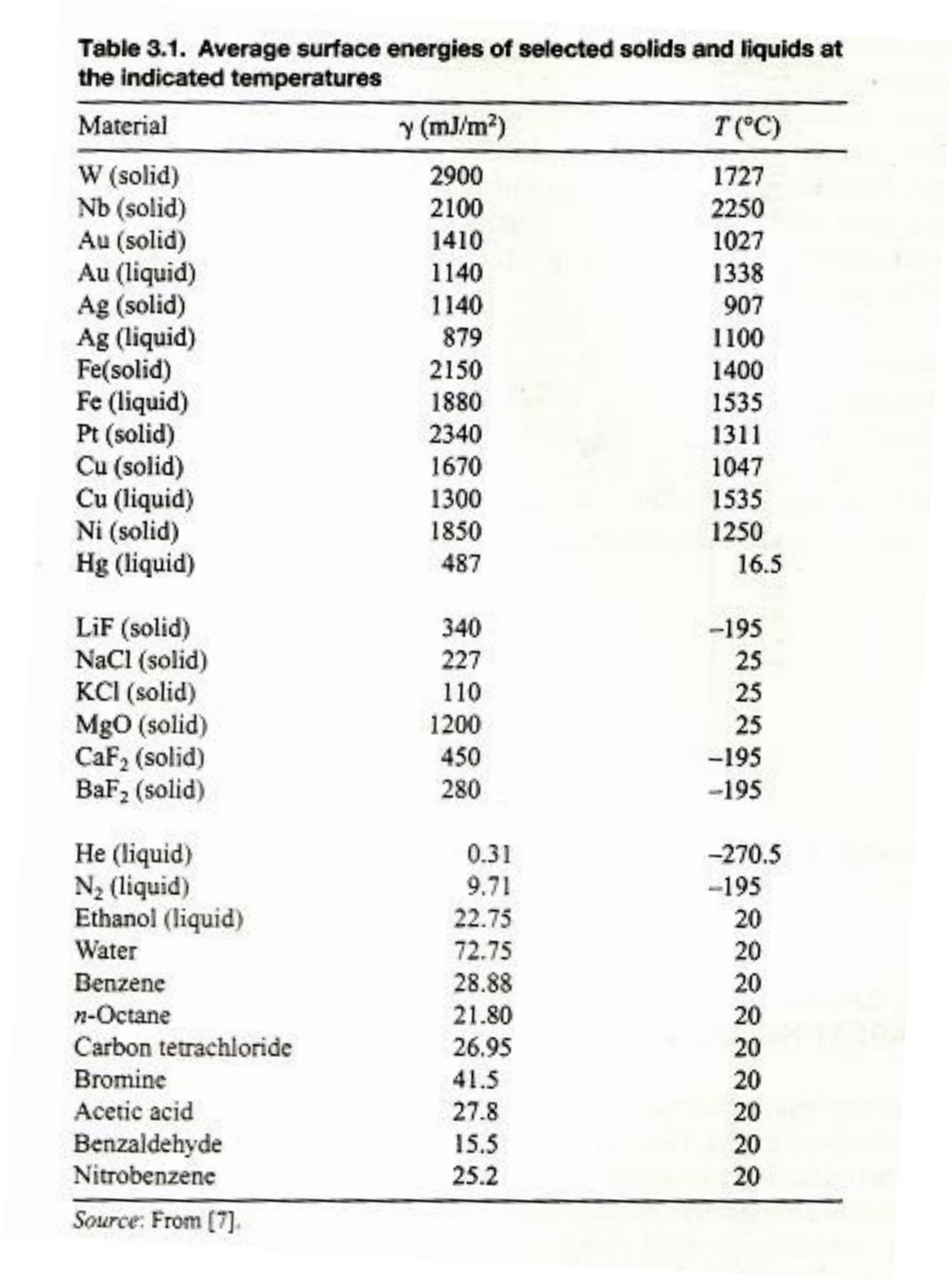


Table 3.1. Average surface energies of selected solids and liquids at the indicated temperatures

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
n-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].

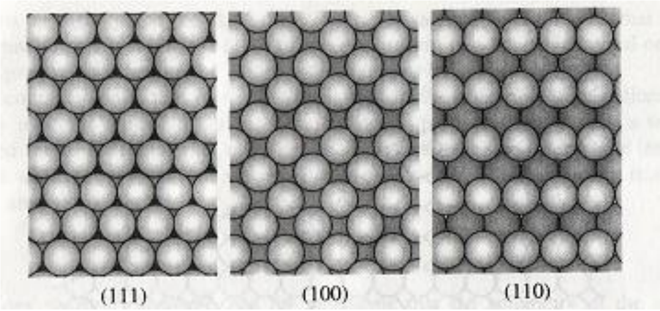
γ :
Vary 3 order magnitude
Low in liquid

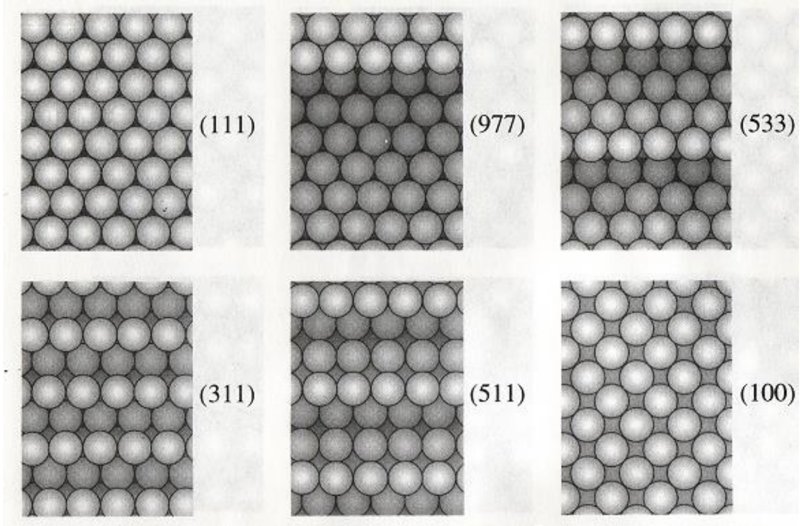
1 J = 10^7 ergs
J/m^2 = 10^3 ergs/cm^2

1 J/m^2 =1 N/m
= 10^3 ergs/cm^2 = 10^3 dyn/cm

γ dependence on crystal face

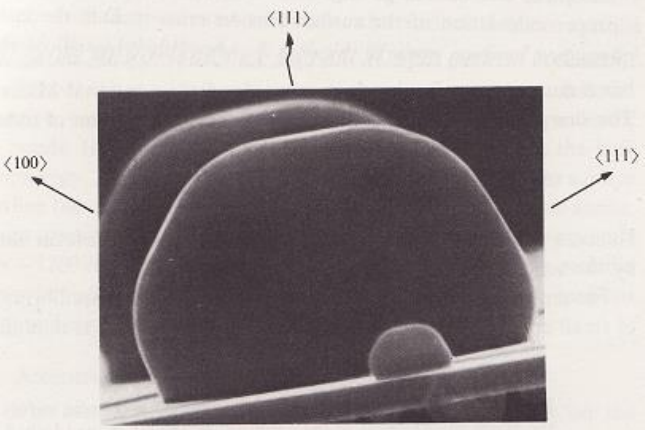
FCC (Ar, Ni, Pd, Cu, Ag, Au)





In solid, lowest specific surface energy(γ) by closed packing(compressed)

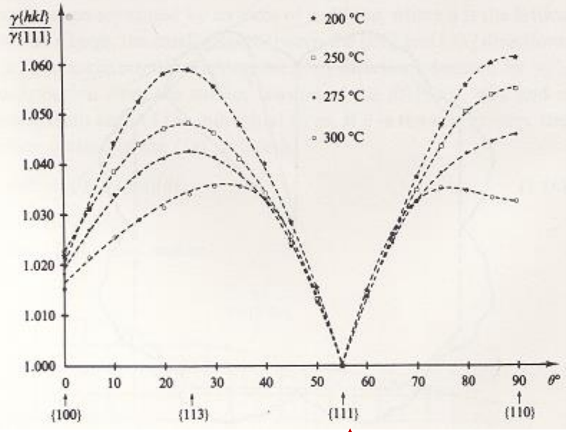
Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).



T_m(Pb) = 601 K, fcc metal

Crystallographic orientation dependence of **γ**

Fig. 1.8. Anisotropy of γ relative to ⟨111⟩ for lead as a function of temperature (Heyraud & Metois, 1983).



lower energy needed to form

Correlation between γ and ΔH_{sub}

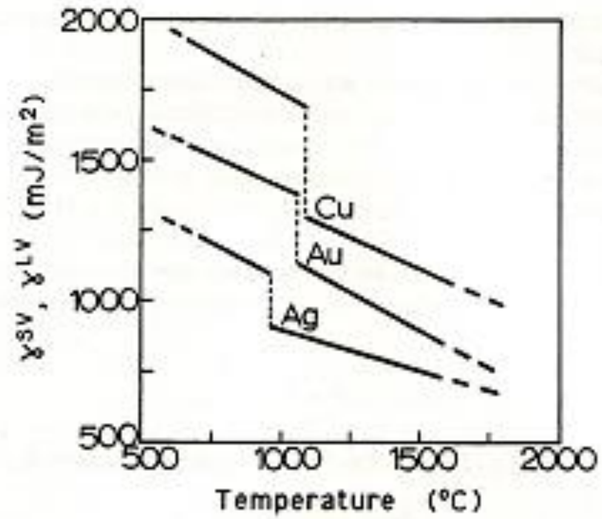
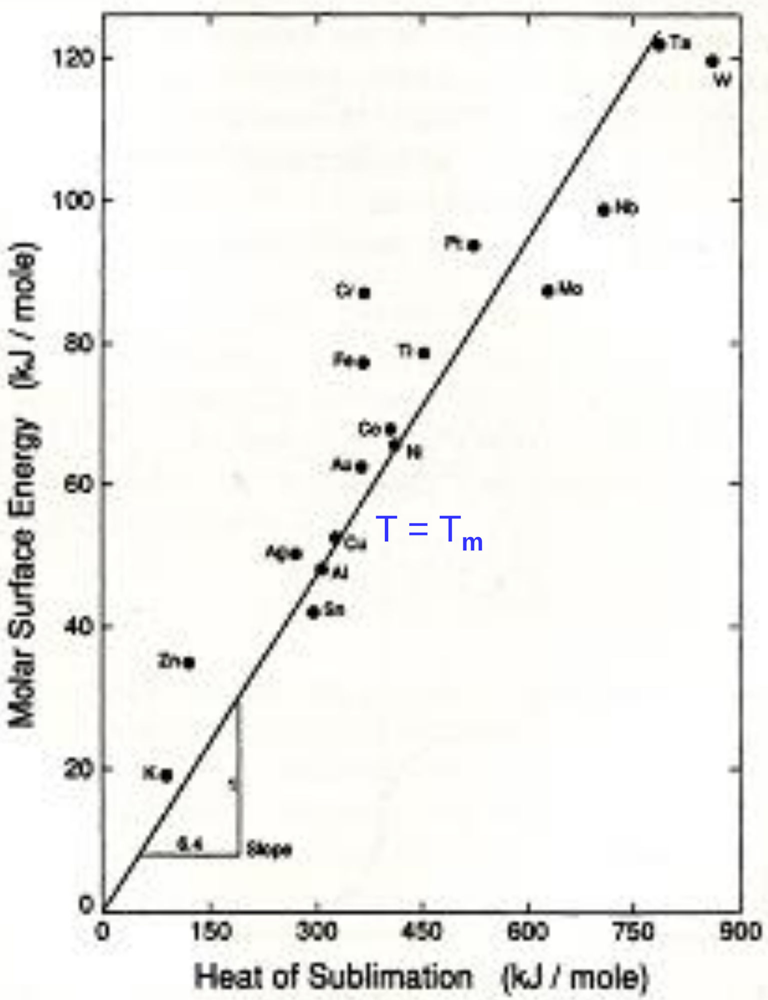


Figure 3.2. Temperature dependence of the surface energy and the solid–liquid phase transition for three f.c.c. metals. From [12].

$$\gamma^{SV} \cong 1.2(\gamma^{LV})_m + 0.45(T_m - T),$$

where $(\gamma^{LV})_m$ 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.

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



$T = T_m$

- Rough estimate of the magnitude of γ
- Surface work is same magnitude as the heat of sublimation continually creates a new surface

  e.g. for many metals,

  → the heat of sublimation $\sim 10^5$ cal·mol^{-1} = 6.94 x 10^{-19} J/atom

  = 6.94 x10^{-12} erg/atom

  typical surface concentration ~ 10^{15} atoms/cm^2 = 10^{19} atoms/m^2

  → estimated surface tension ~ 6.94 x 10^{-19} J/atom x 10^{19} atoms/m^2

  ~ 7 J/m^2 = 7000 erg/cm^2

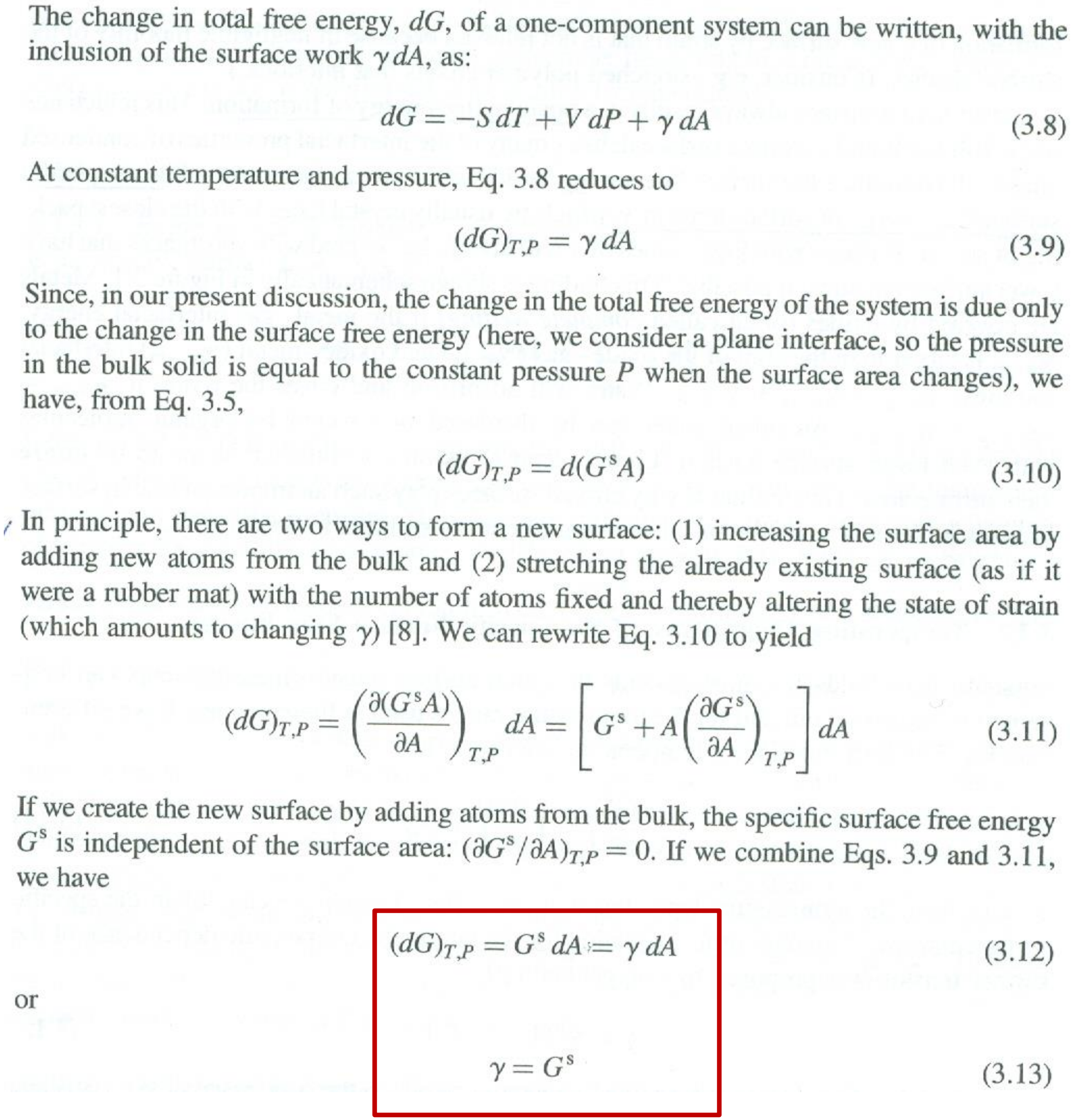
- Experimentally (in practice), $\gamma \sim 0.16\ \Delta H_{sub}$

  → not necessary to break all the metal-metal bonds in the bulk to create a new surface

  &

  considering relaxation: relaxation lowers the surface tension appreciably (contract toward to the bulk to maximize their bonding with the remaining neighbors)

The surface free energy is always positive



The change in total free energy, dG, of a one-component system can be written, with the inclusion of the surface work $\gamma\, dA$, as:

$$dG = -S\,dT + V\,dP + \gamma\, dA \tag{3.8}$$

At constant temperature and pressure, Eq. 3.8 reduces to

$$(dG)_{T,P} = \gamma\, dA \tag{3.9}$$

Since, in our present discussion, the change in the total free energy of the system is due only to the change in the surface free energy (here, we consider a plane interface, so the pressure in the bulk solid is equal to the constant pressure P when the surface area changes), we have, from Eq. 3.5,

$$(dG)_{T,P} = d(G^{s}A) \tag{3.10}$$

In principle, there are two ways to form a new surface: (1) increasing the surface area by adding new atoms from the bulk and (2) stretching the already existing surface (as if it were a rubber mat) with the number of atoms fixed and thereby altering the state of strain (which amounts to changing γ) [8]. We can rewrite Eq. 3.10 to yield

$$(dG)_{T,P} = \left(\frac{\partial(G^{s}A)}{\partial A}\right)_{T,P} dA = \left[G^{s} + A\left(\frac{\partial G^{s}}{\partial A}\right)_{T,P}\right] dA \tag{3.11}$$

If we create the new surface by adding atoms from the bulk, the specific surface free energy G^{s} is independent of the surface area: $(\partial G^{s}/\partial A)_{T,P} = 0$. If we combine Eqs. 3.9 and 3.11, we have

$$\boxed{(dG)_{T,P} = G^{s}\, dA = \gamma\, dA} \tag{3.12}$$

or

$$\boxed{\gamma = G^{s}} \tag{3.13}$$

- Creation of surface always results in a positive free energy of formation → to minimize the surface free energy, solids will form surfaces of the lowest specific surface free energy or surface tension γ, which are usually crystal faces with the closest packing of atoms

→ Surfaces with high γ will always be covered with substances with lower γ

e.g. metals are covered by oxides if metal-gas interfacial energy,

$\gamma_{m\text{-}g} > \gamma_{ox\text{-}g} + \gamma_{ox\text{-}m}$

Water will cover on the oxide if $\gamma_{ox\text{-}g} > \gamma_{H2O\text{-}g} + \gamma_{H2O\text{-}ox}$

Organic molecules cover with even lower γ

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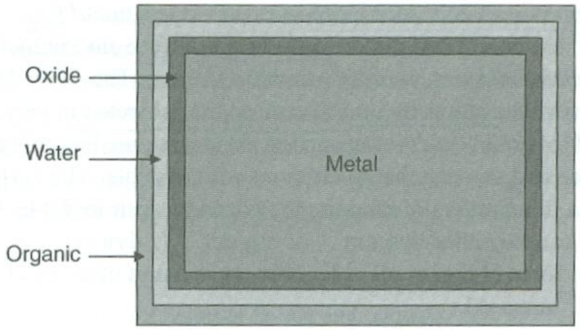


Figure 3.1. Representation of materials of lower surface energy coating materials of higher surface energy, leading to a net reduction of total surface energy ($\gamma_{\text{old surface}} > \gamma_{\text{new surface}} + \gamma_{\text{interface}}$).

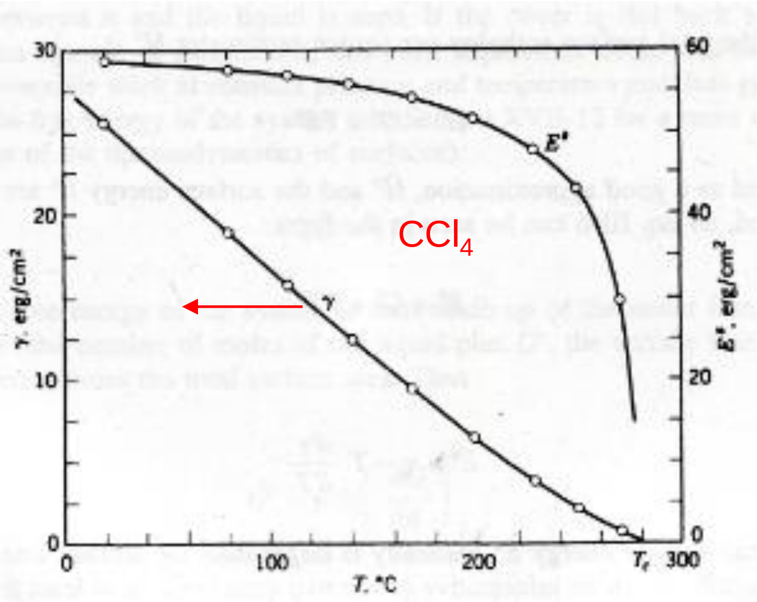
Temperature dependence of γ

- 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.
- $H^s = G^s + TS^s = \gamma - T(\partial\gamma/\partial T)_P$ >0 (surface formation: heat absorbed (at const P))
- $H^s = U^s + PV = U^s$; the surface does not have any volume (no volume change).
- 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.
- $\gamma\downarrow$ as $T\uparrow \rightarrow (\partial\gamma/\partial T)_P < 0$, U^s or $H^s > G^s$ $(=\gamma)$

c.f. adsorption: $\Delta H_{ads} < 0$

Semiempirical equation for $\gamma(T)$

- $\gamma = \gamma^o (1- T/T_c)^n$, where γ^o is the surface tension at 0 K and T_c is the critical temperature. So, $\gamma = \gamma^0$ at 0K,
  $\gamma = 0$ at T_c (no surface tension): no surface defined, condensed phase vanished
- $n \sim 1$ 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.



$\gamma\downarrow$ as $T\uparrow \rightarrow (\partial\gamma/\partial T)_P < 0$,
U^s or $H^s > G^s$ $(=\gamma)$

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

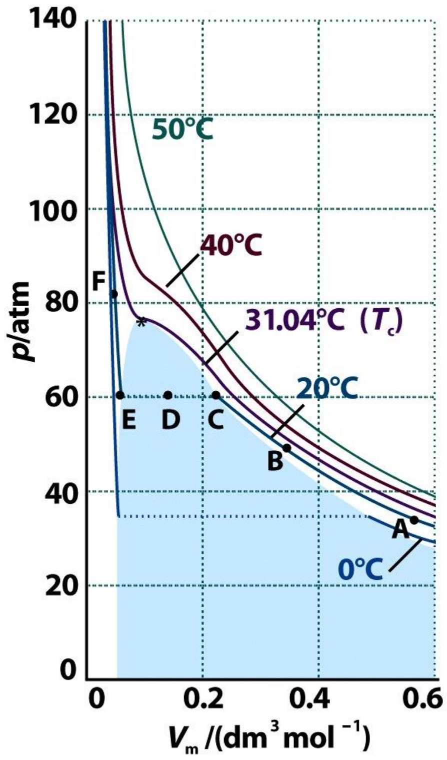


Figure 1-15
Atkins Physical Chemistry, Eighth Edition
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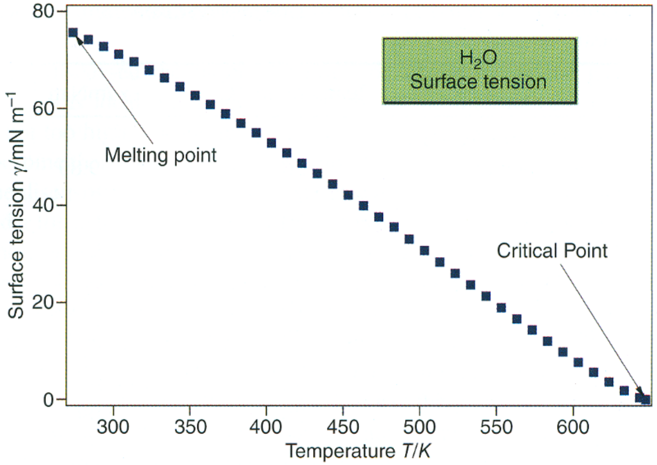


Figure 5.3 *The surface tension of water plotted as a function of temperature over its normal existence range at standard pressure p° = 100 kPa. Source: Data taken from the Handbook of Chemistry and Physics, 96th Edition.*

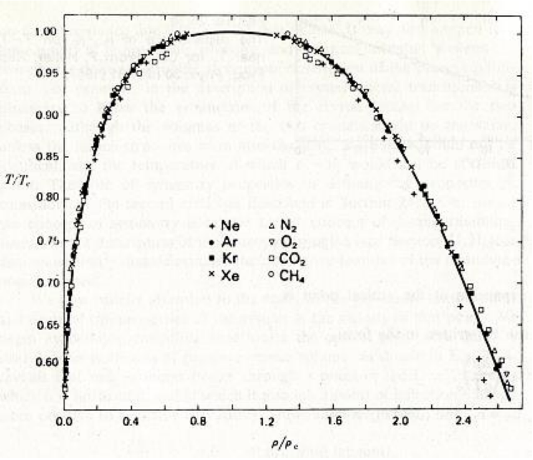


FIGURE 24.11
The liquid–gas coexistence curve for simple substances. The curve is a composite of data for Ne, Ar, Kr, Xe, N_2, O_2, CO_2, and CH_4. Note the use of the reduced variables T/T_c and ρ/ρ_c. From E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

Surface Heat Capacity

- $C_p^s = (\partial H^s/\partial T)_P = (\partial/\partial T)_P [\gamma - T(\partial\gamma/\partial T)_P] = (\partial\gamma/\partial T)_P - (\partial\gamma/\partial T)_P - T(\partial\gamma^2/\partial T^2)_P] = - T (\partial^2\gamma/\partial T^2)_P]$
- Heat capacity → temperature derivative of surface tension → measurement of surface tension → surface heat capacity!

- 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

- $C_v^s = (\partial U^s/\partial T)_v \sim 43.2\ Nk_B(T/\theta_D)^2$, θ_D : Debye temperature
- In surface, $U_s = H_s$, $C_p^s = C_v^s$

c.f. in Lecture Note #2, surface atom vibration “phonon”

→Debye frequency(v_D) & Debye temp(θ_D) “a measure of rigidity”

Additional notes on surface tension

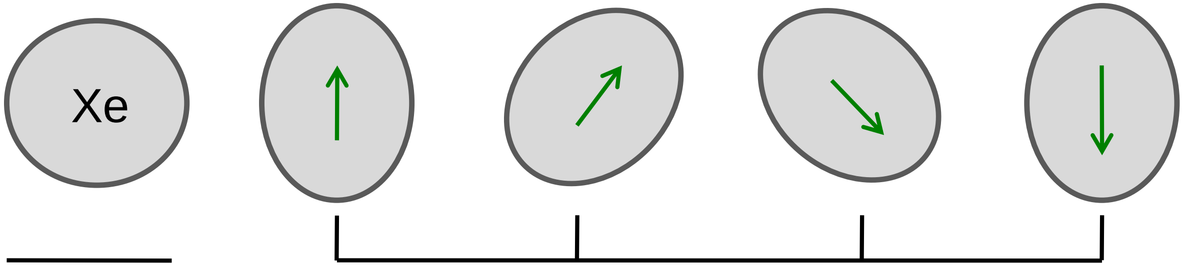
Origin of γ : attractive interatomic (solid) or intermolecular (liquid) force

Origin of van der Waals

1) Fluctuating dipole

- Conside Xe-Xe interation
- .Xe is an atom with a spherically symmetric electron distribution around the nucleus, so it possesses 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 give 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



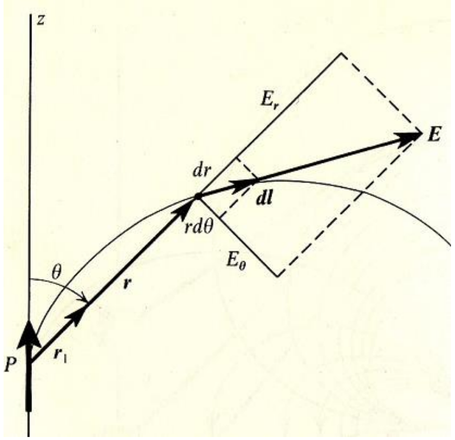
time average with $\rho = 0$

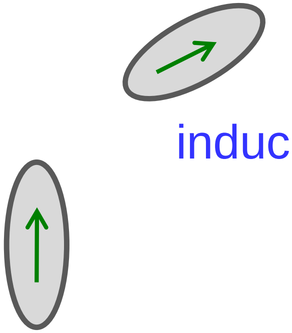
fluctuating dipole at various instants with $p \neq 0$

Dipole moment, ρ or μ

2) Induced dipole

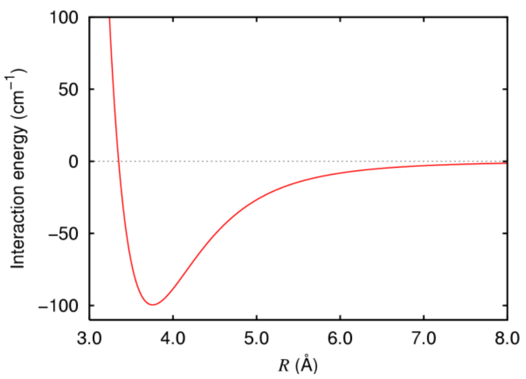
- Fluctuating (instantaneous) dipole produces an electric field ***E*** in space, which induces a dipole moment in another Xe atom given by
- $\boldsymbol{p}_{\mathrm{ind}} = \alpha \boldsymbol{E}$, α is the electric polarizability.
- The interaction energy
  $V = - \int_{0,\,E} \boldsymbol{p}_{\mathrm{ind}} \cdot d\boldsymbol{E} = \alpha E^2/2$
- 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 $0 \le \theta \le 2\pi$ at a given distance r.
- When averaged over all orientations,
  $\mathbf{V(r) = - a\, \alpha^2/r^6 = - A/r^6}$, where A (>0) is a atom or molecule-dependent constant.
- **V(r)** is always negative (attraction).
- α' (polarizability volume) = $\alpha/4\pi\varepsilon_0$ 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.





Intermolecular interactions

Interaction energy of Ar-Ar



1. van der Waals (Dispersion force)
   $V(r) = -A/r^6$ Induced dipole-induced dipole
2. (permanent) 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_2O	$C_{10}H_8$
4.2	87.3	165	230.7	373	491

- Dipole : molecular interactions

electric dipole : two electric changes (−) → (+) direction

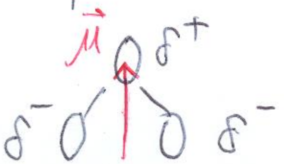
$-q \xrightarrow{r} +q$ magnitude $\mu = q \cdot r$ 1 Debye $= 3.333564 \times 10^{-30}$ C·m

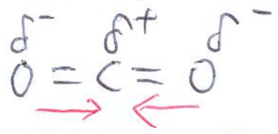
$\overrightarrow{\mu}$ (or $\overrightarrow{e}$)

e.g.) $+e \underset{100\,\mathrm{pm}}{—} -e \Rightarrow 1.6 \times 10^{-19}\,\mathrm{C} \cdot 100 \times 10^{-12}\,\mathrm{m}$

$= 1.6 \times 10^{-29}\,\mathrm{C \cdot m} = \underline{4.8\,\mathrm{D}}$

- Polar molecules : permanent electric dipole moment





- Induced dipole moment : applied electric field can distort as well as align its permanent electric dipole moment

→ polarizability ($C^2 \cdot m^2 \cdot J^{-1}$)

μ^* (or e_{ind}) $= \alpha E$ → field strength

$\alpha\uparrow \rightarrow \mu^*\uparrow$

$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$: polarizability volume

	α' (10^{-30} m^3)
CCl_4	10.5
H_2	0.819

- polarization P : electric dipole moment density

$P = \langle\mu\rangle N$ → number density

$\langle\mu\rangle$ ↓ mean dipole moment

- q_1, q_2 two charge separation, r, in vacuum

→ Coulomb potential energy of the interaction, $V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$ in vacuum

in a medium (e.g. air or liquid), $V = \frac{q_1 q_2}{4\pi\varepsilon r}$, ε: permittivity

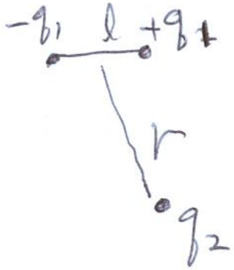
→ $\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$, ε_r: relative permittivity ≡ dielectric constant

e.g.) H_2O at 25°c, $\varepsilon_r = 78$ → Coulomb interaction $\frac{1}{78}$ vs. vaccum

→ weaken interaction

highly polarizable molecule → $\varepsilon_r \uparrow$

- Interaction between molecules
  - interaction between dipoles

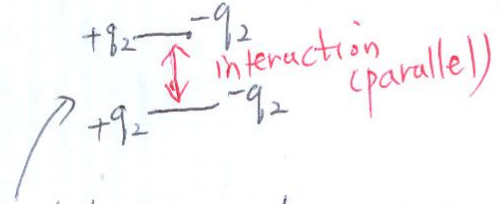


$\Rightarrow \mu_1 = q_1 l$

Coulomb potential energy of the interaction

ion-dipole interaction $V = -\frac{\mu_1 q_2}{4\pi\varepsilon_0 r^2}$

Interaction type	distance dependence of potential energy (−: attractive)	typical enegy (kJ/mol)	
ion-ion	$-\frac{1}{r}$	250	
ion-dipole	$-\frac{1}{r^2}$	15	
dipole-dipole	$-\frac{1}{r^3}$	2	between stationary polar molecules (non-rotating)
	$-\frac{1}{r^6}$	0.6	between rotating polar molecules
London (dispersion)	$-\frac{1}{r^6}$	2	between all types of molecules
Hydrogen bond		20	A−H····B



- Van der Waals interactions : the attractive molecules between closed-~~sche~~ shell molecules
  ($\frac{1}{r^6}$ interactions)