

Lecture Note #6B (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

Liquid surfaces (curved) (5.2.2)

Phenomena at curved surfaces

Pressure difference across a surface

- Liquid drop suspended in air → The equilibrium shape is a sphere
→ Minimization of surface area for a given volume. (smallest A/V)
- Can you prove it using the calculus of variation?
- The free energy change dG in contraction from $r \rightarrow r-dr$ is

$$dG = -\gamma 8\pi r dr + \Delta P \cdot 4\pi r^2 dr$$

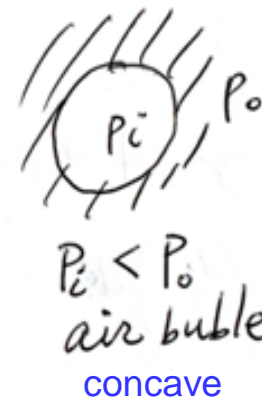
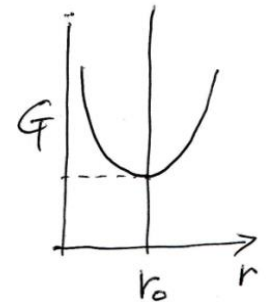
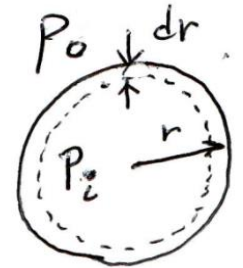
at equilibrium $dG = 0$.

$$\Delta P = \frac{8\pi r \gamma}{4\pi r^2} = \frac{2\gamma}{r} \quad \text{Young-Laplace eq.}$$

In general, a surface has two principal curvatures of radii r_1 and r_2

$$\Delta P = \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \gamma$$

$$\Delta P = P_i - P_o$$



- $dW = PdV = \gamma dA \rightarrow P[\frac{3}{4}\pi(r + dr)^3 - \frac{3}{4}\pi r^3] = \gamma[4\pi(r + dr)^2 - 4\pi r^2]$
- smallest surface to volume ratio
volume $V = \frac{3}{4}\pi r^3$, $dV = 4\pi r^2 dr$
- Opposite sign: i) PV : expanding force, ii) γA : contracting force
i) $4\pi r^2(P_i - P_o)dr$
ii) $dA \rightarrow [4\pi(r + dr)^2 - 4\pi r^2] = 8\pi r dr$

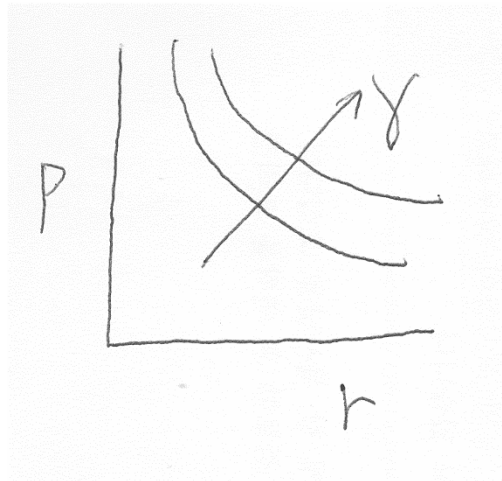
$$\rightarrow \gamma dA = 8\pi r \gamma dr$$

Young-Laplace equation

$$P_{in} = P_{out} + 2\gamma/r \rightarrow \Delta P = 2\gamma/r$$

$$r \downarrow (\text{droplet} \downarrow) \rightarrow \Delta P \uparrow$$

$$r = \infty \rightarrow \Delta P = 0$$



Equilibrium vapor pressure of a liquid drop

A Liquid drop is in a compressed state

→ The inner pressure is higher than that of liquid with a flat surface by ΔP

→ in a higher free energy state → higher vapor pressure.

Chemical potential change in the processes 1 and 2

$$d\mu = -SdT + VdP$$

$$\begin{aligned}\mu_l^{(c)} - \mu_l^{(f)} &= \int V dp \sim V_m \Delta P \\ \mu_g^{(c)} - \mu_g^{(f)} &= RT \ln(P_2/P_1)\end{aligned}$$

where V_m is the molar volume of the liquid, which is assumed to be constant.

$$(V_m = M/\rho, \rho: \text{density})$$

The two quantities should be the same, and therefore

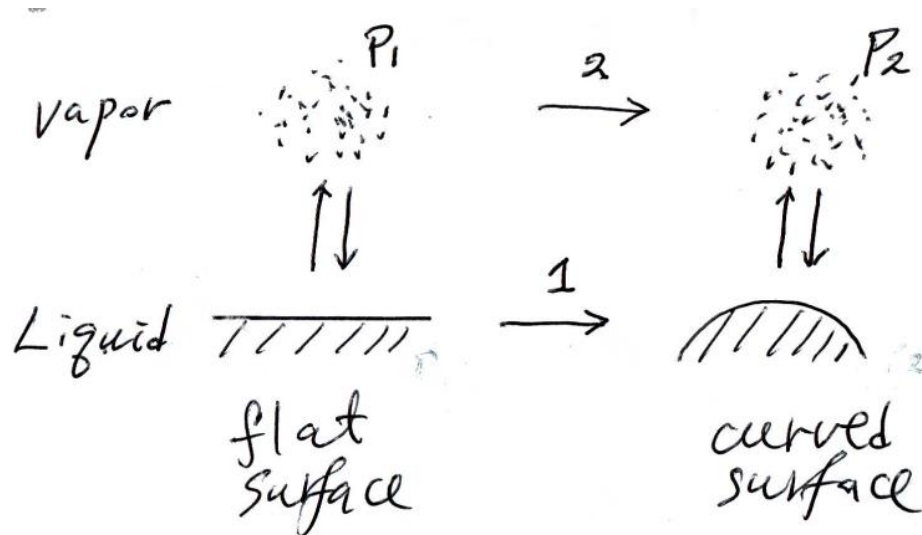
$$V_m \Delta P = RT \ln(P_2/P_1) \text{ or}$$

$$\frac{2V_m \gamma}{r} = RT \ln(P_2/P_1)$$

$$P_2/P_1 = \exp\left[\frac{2V_m \gamma}{rRT}\right]$$

Kelvin equation

P_1 : flat



If $r = \infty$, $P_1 = P_2$

For finite r $P_2 > P_1$

For H_2O ($\gamma = 72.8 \text{ mN/m}$) at 300 K , $V_m = 18 \text{ cm}^3/\text{mole}$

$$r = 1000 \text{ \AA} \rightarrow P_2/P_1 = 1.01$$

$$r = 100 \text{ \AA} \rightarrow P_2/P_1 = 1.1$$

$$r = 10 \text{ \AA} \rightarrow P_2/P_1 = 3.0$$

Smaller particle \rightarrow higher vapor pressure
 \rightarrow higher evaporation

Kelvin equation

$$RT \ln(P_r/P_o) = 2\gamma M/\rho r = 2\gamma V_m/r$$

P_o : vapor pressure, P_r : droplet vapor pressure.
 $V_m = M/\rho$, ρ : density

- Droplet: high surface free energy, higher surface to volume ratio than flat, $P_r > P_o$
 $r \rightarrow r + dr$, area $8\pi r dr \uparrow \rightarrow$ surface free energy, $8\pi r \gamma dr \uparrow$
- dn mole \uparrow from flat to droplet by r to $r + dr$
 $\rightarrow dG = dn \cdot RT \ln(P_r/P_o)$
$$dn = 4\pi r^2 dr \rho / M$$
- $8\pi r \gamma dr = dn \cdot RT \ln(P_r/P_o)$

Solubility, condensation, Oswald ripening, sintering

- Size-dependent solubility

The same concept can be equally applied to the solubility of a particle

$c_2/c_1 = \exp(2V_m \gamma / rRT)$, where c is the concentration in the solution

→ small particles at solid → greater solubility than large particles

- Capillary condensation in porous materials

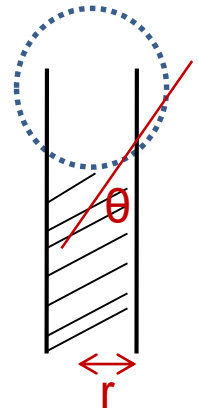
→ easy condensation in capillary at lower pressure

Vapor pressure:

droplet: convex(볼록) liquid surface > flat surface

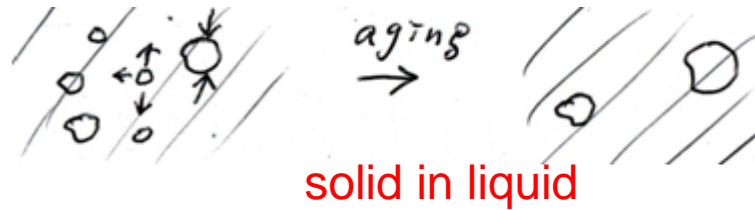
capillary: concave(오목) surface < flat surface

→ lower vapor pressure → condensation at lower pressure



For concave interface, $RT \ln(P_r/P_o) = -2V_m \gamma \cos\theta / r$

Oswald ripening



dissolution \leftrightarrow deposition process is in a dynamic equilibrium to maintain a constant saturation solubility.

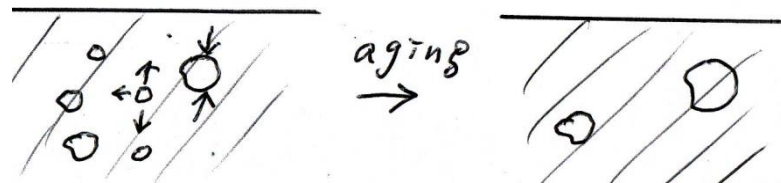
small particle \rightarrow high solubility and large particle \rightarrow low solubility

Large particles grow at the expense of the smaller particles \rightarrow aging minimize the total surface area \rightarrow the way to reach a G_{\min} , an equilibrium state

AgI sol \rightarrow highly insoluble \rightarrow little tendency of ripening (slow kinetics)

CaCO₃ sol \rightarrow highly soluble \rightarrow strong tendency of ripening (fast kinetics)

Sintering



solid in (on) solid

Nucleation and crystal growth

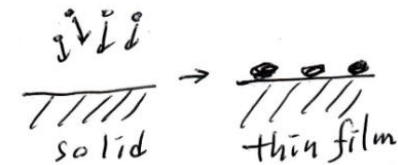
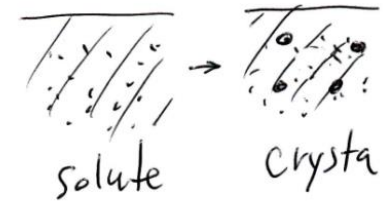
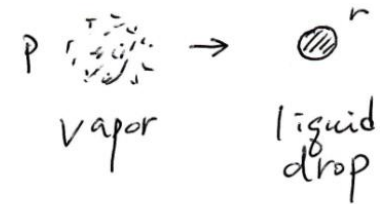
vapor → liquid drop

solute in a liquid → crystal

- In the initial stage of condensation a liquid drop of radius r is formed from a supersaturated vapor

- Small drop has a high vapor pressure → it tends to re-evaporate → Therefore, only droplets of a radius greater than a critical radius r_c (embryo) survive and grow.

- This process is called **nucleation** and the nuclei grow in time.



Consider the free energy change in nucleation of a droplet from a vapor.

nA (gas, P) → A_n (small liquid drop, r)

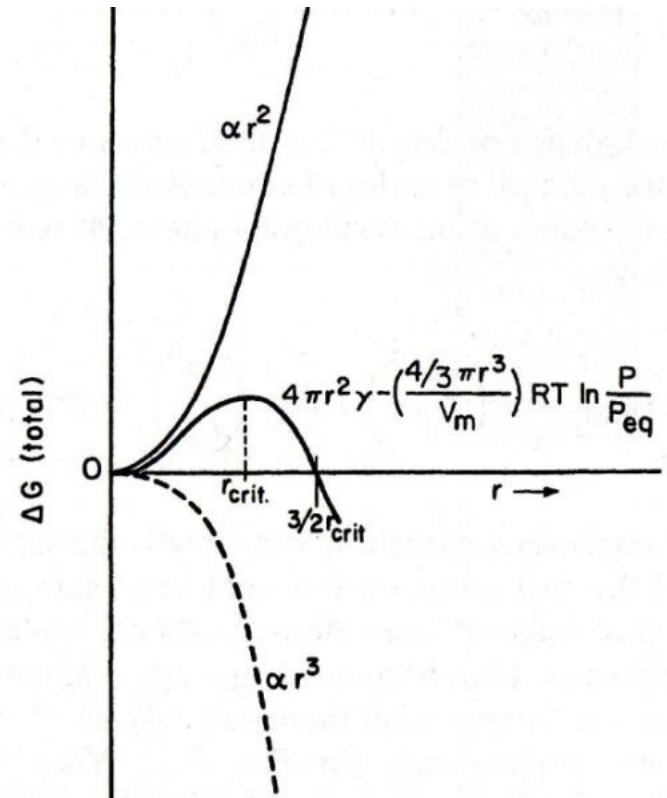
$$\Delta G = -nRT \ln(P/P_0) + 4\pi r^2 \gamma$$

$$= -(4/3)\pi r^3 (\rho/M) RT \ln(P/P_0) + 4\pi r^2 \gamma$$

M = molecular weight, ρ = density
 P_0 = equilibrium vapor pressure
 P/P_0 = degree of supersaturation

$$d(\Delta G)/dr = 0 \text{ at } r = r_c$$

$$r_c = 2\gamma V_m / RT \ln(P/P_0)$$



This means there is always a free energy barrier of

$$\Delta G_m = 16 \pi \gamma^3 V_m / 3 [RT \ln (P/P_0)]^2$$

which is overcome by thermal fluctuation.

* Related concepts

artificial raining: spraying dry ice particle in the damp air

seeding in crystallization: adding a crystal seeds in a supersaturated solution

- $P > P_o \rightarrow$ liquid \uparrow
 $P < P_o \rightarrow$ vaporize

$$dn = 4\pi r^2 dr \rho / M \rightarrow n = (4/3)\pi r^3 \rho / M, \quad \text{molar volume } V_m = M/\rho$$

$$dG = VdP - SdT$$

at const T (isothermal), $dG = VdP$

$\rightarrow \Delta G = -nRT \ln(P/P_o) +$ consider surface free energy

+ γ : impede growth (성장 방해)

$r_c \sim 0.6 \sim 1$ nm (50 ~ 100 atoms or molecules)

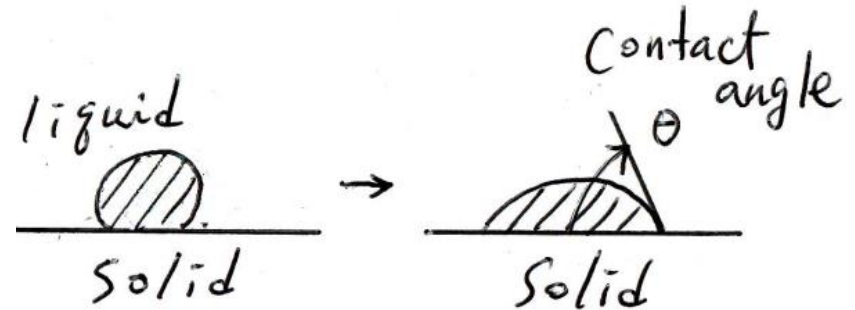
- (i) Small particle ($r < r_c$) \rightarrow 2nd term dominant, $r^2 \uparrow \rightarrow \Delta G \uparrow$
- (ii) $r > r_c \rightarrow$ 1st term dominant, r^3 faster than $r^2 \rightarrow$ spontaneous

Capillary rise and depression

- Wetting

$\theta = 0^\circ$: complete wetting

$\theta = 180^\circ$: complete dewetting



- Wetting occurs to minimize the total free energy which includes the surface and **interfacial** free energies

- Force balance at the interface

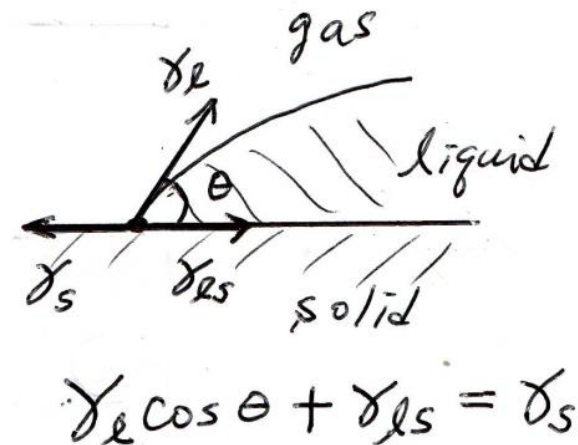
- Criteria for wetting

When the interface area is increased by dA ,

$$\begin{aligned} dG &= \gamma_{ls} dA + \gamma_l \cos \theta dA - \gamma_s dA \\ &= (\gamma_{ls} + \gamma_l \cos \theta - \gamma_s) dA = x dA \end{aligned}$$

If $x < 0 \rightarrow$ wetting occurs, and

If $x > 0 \rightarrow$ dewetting occurs.



There is a certain contact angle for which $x = 0$: equilibrium contact angle

Capillary rise

- Force balance at the top of the meniscus

Total wetting force = gravitational force of the water column

$$2\pi r \gamma \cos \theta = (\rho - \rho_0) (\pi r^2 h) g = \Delta\rho (\pi r^2 h) g$$

ρ = density of the liquid

ρ_0 = density of the air

$$h = 2 \gamma \cos \theta / \Delta\rho g r$$

Another view

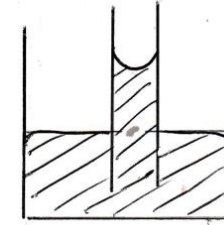
pressure difference between the points Q and Q₀ : $\Delta P = \rho_0 g h$

pressure difference btwn the points P and P₀ : $\Delta P = - 2 \gamma / R + \rho g h$

The two ΔP 's should be the same. $r = R \cos \theta$

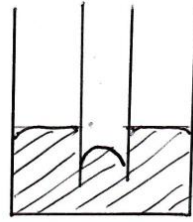
$$2 \gamma / R = \Delta\rho g h \rightarrow h = 2 \gamma \cos \theta / \Delta\rho g r$$

More accurately, $h' = h + r/3$



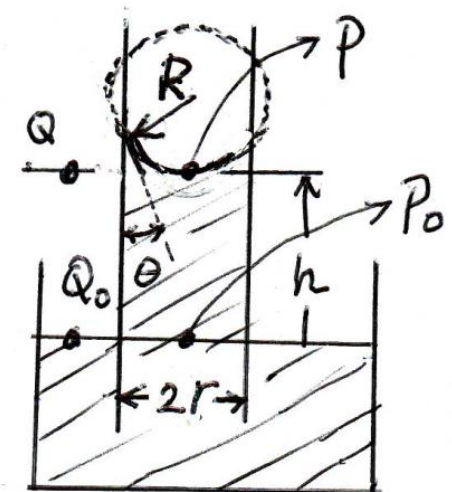
capillary
rise

$$\gamma_c > \gamma_l$$



capillary
depression

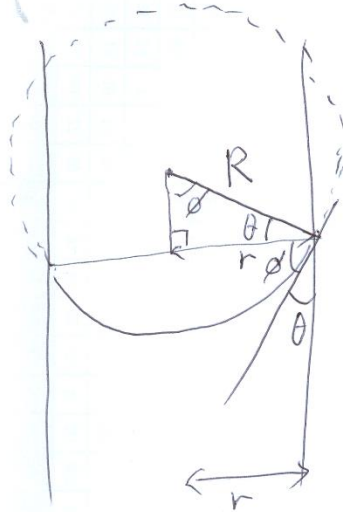
$$\gamma_c < \gamma_l$$



$$\Delta p = \frac{2\gamma}{r}$$

$r \downarrow \rightarrow \Delta p \uparrow$ (large P_i (internal pressure))

\rightarrow liquid \uparrow (liquid rise) \rightarrow = hydrostatic pressure
to decrease total free energy



$$R \cos \theta = r$$

$$R = \frac{r}{\cos \theta}$$

$$\Delta \rho g h = \frac{2\gamma}{R} = \frac{2\gamma}{r} \cos \theta$$

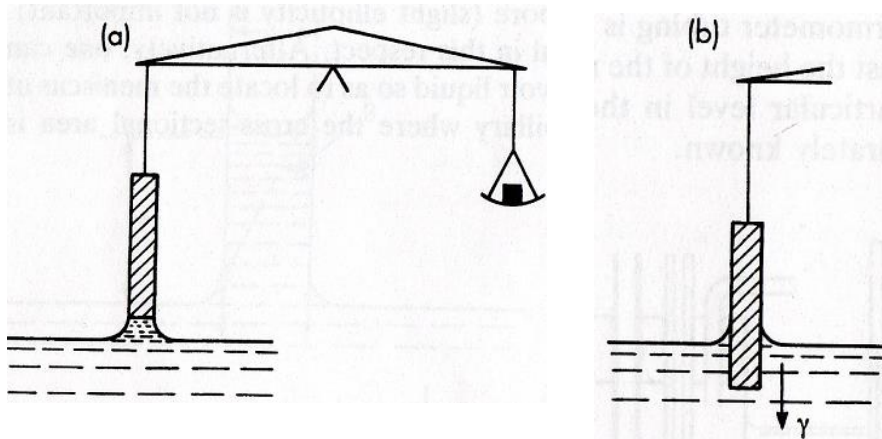
$\Delta \rho$: density difference between
liquid and gas pressure

$$\text{if } \theta = 0 \rightarrow \gamma = \frac{1}{2} r h \Delta \rho g$$

$$\gamma \uparrow \text{ or } r \downarrow \Rightarrow h \uparrow$$

Measurements of surface tension

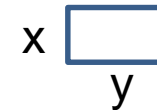
Measurement of interfacial tension by the ring method



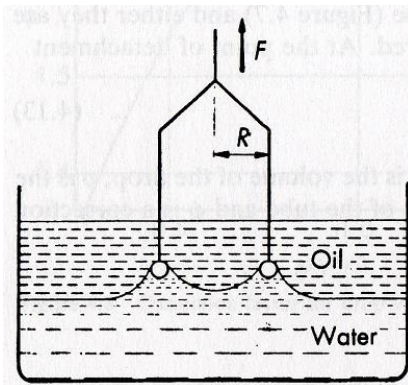
Wilhelmy plate methods: (a) detachment; (b) static

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

Assume $\theta = 0$



Perimeter, $2(x + y)$



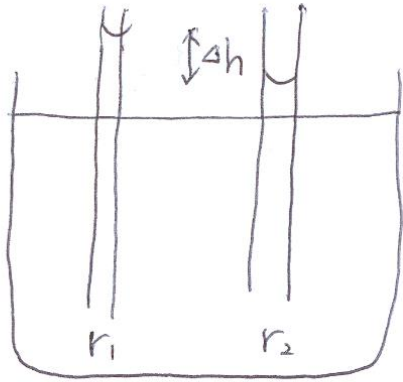
$$\gamma = \frac{\beta F}{4\pi R}$$

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

Correction factor β



Ring perimeter,
 $2\pi R + 2\pi R$

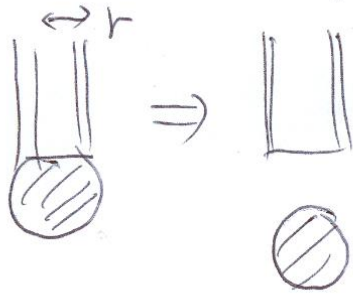


$$\gamma = \frac{1}{2} r_1 h_1 \Delta \rho g = \frac{1}{2} r_2 h_2 \Delta \rho g$$

$$\Delta h = h_1 - h_2$$

$$\gamma = \frac{\Delta \rho g r_1 r_2 \Delta h}{2(r_1 - r_2)}$$

Drop-volume, drop-weight method



$$\gamma = \frac{\phi \cdot m \cdot g}{2\pi r}$$

$$= \frac{\phi V \rho g}{2\pi r}$$

ϕ : correction factor
 ρ : density of liquid
 m : mass of the drop
 V : volume

force of drop weight, $g \cdot m \cdot t_{\max}$ t_{\max} : lifetime of drop

$$m g t_{\max} = \gamma \cdot 2\pi r$$

Interfacial tension

- Force /unit surface area for a pure liquid = γ
- Force /unit interface area at a liquid-liquid interface/unit length = γ_i
- The total unbalanced force acting on the molecules at the interface

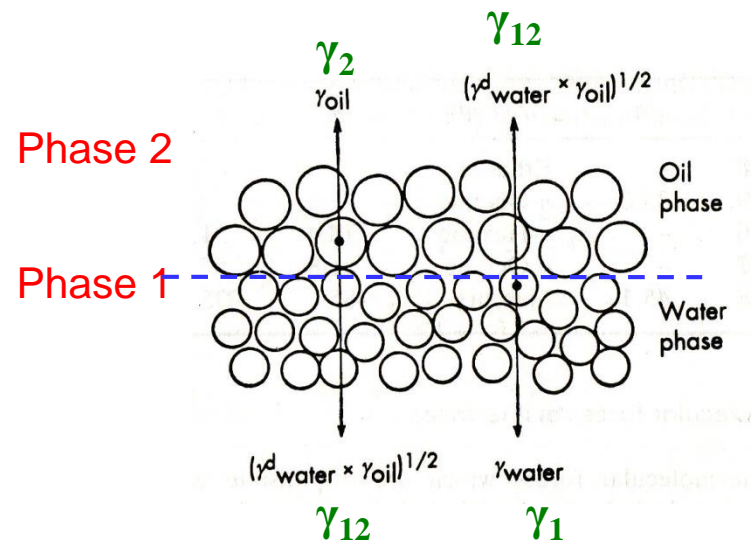
$$\gamma_i = (\gamma_1 - \gamma_{12}) + (\gamma_2 - \gamma_{21}) = \gamma_1 + \gamma_2 - 2\gamma_{12}$$

where $\gamma_{12} = \gamma_{21}$ (action-reaction)

γ_i = free energy per unit interfacial area

If 1 and 2 are the same materials, $\gamma_i = 0$

- Consider the case where 2 surfaces are brought from infinity to contact



Additivity of intermolecular force

$$\gamma_w = \gamma_w^d + \gamma_w^h$$

Dispersion force (van der Waals) + hydrogen bonding

$$\gamma_{\text{Hg}} = \gamma_{\text{Hg}}^d + \gamma_{\text{Hg}}^m$$

Dispersion force (van der Waals) + metal bonding

$$\gamma_{\text{ow}} = \gamma_o^d + (\gamma_w^d + \gamma_w^h) - 2 \times (\gamma_w^d \times \gamma_o^d)^{1/2}$$

Ex: n-hexane-water interface

Hydrocarbon:

$$51.1 = 18.4 + 72.8 - 2 \times (\gamma_w^d \times 18.4)^{1/2}$$

Dispersion force only

$$\gamma_w^d = 21.8 \text{ mNm}^{-1}$$

$$\gamma_w^h = 72.8 - 21.8 = 51.0 \text{ mNm}^{-1}$$

H₂O, Hg → high γ
hydrogen bonding,
Metal bonding

Table 4.1 Surface tensions and interfacial tensions against water for liquids at 20°C (in mN m⁻¹)

<i>Liquid</i>	γ_o	γ_i	<i>Liquid</i>	γ_o	γ_i
Water	72.8	–	Ethanol	22.3	–
Benzene	28.9	35.0	<i>n</i> -Octanol	27.5	8.5
Acetic acid	27.6	–	<i>n</i> -Hexane	18.4	51.1
Acetone	23.7	–	<i>n</i> -Octane	21.8	50.8
CCl ₄	26.8	45.1	Mercury	485	375

cf. colloidal particle

- The dispersed particles with a size of $1\text{nm}(10^{-9}\text{m}) \sim 10\mu\text{m}$ may be solid particles, liquid drops, macromolecules (polymers, proteins) etc
- A colloidal system can be made by combination of various phases
- **Areas of colloidal systems**

Aerosols	Foodstuffs
Agrochemicals	Ink
Cement	Paint
Cosmetics	Paper
Dyestuffs	Pharmaceuticals
Emulsions	Plastics
Fabrics	Rubber
Foams	Soil

- **Applications**

Adhesion

Chromatography

Detergency

Electrophoretic deposition

Emulsion polymerisation

Food processing

Grinding

Heterogeneous catalysis

Ion exchange

Lubrication

Oil-well drilling

Ore flotation

Precipitation

Road surfacing

Sewage disposal

Soil conditioning

Sugar refining

Water clarification

Water evaporation control

Water repellency

Wetting

- **Factors to contribute the overall of a colloidal system**

Particle size

Particle shape and flexibility

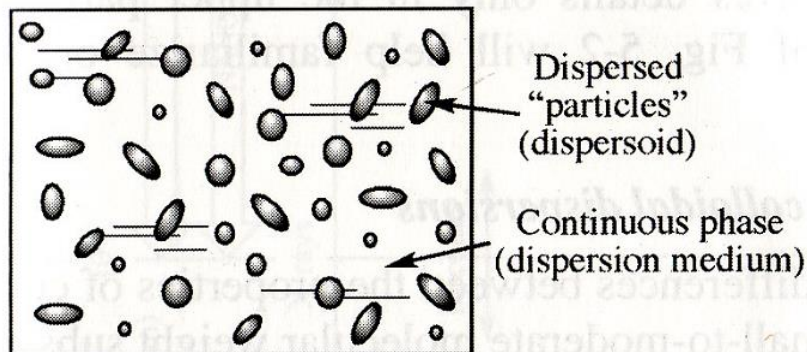
Surface (including electrical) properties

Particle-particle interactions

Particle-solvent interactions

Classification of colloidal systems

- Dispersions



		<u>dispersoid</u>		
		s	l	g
dispersion medium	s	o	o	o
	l	o	o	o
	g	o	o	x

Table 1.1 Types of colloidal dispersion

<i>Dispersed phase</i>	<i>Dispersion medium</i>	<i>Name</i>	<i>Examples</i>
Liquid	Gas	Liquid aerosol	Fog, liquid sprays
Solid	Gas	Solid aerosol	Smoke, dust
Gas	Liquid	Foam	Foam on soap solutions, fire-extinguisher foam
Liquid	Liquid	Emulsion	Milk, mayonnaise
Solid	Liquid	Sol, colloidal suspension; paste (high solid concentration)	Au sol, AgI sol; toothpaste
Gas	Solid	Solid foam	Expanded polystyrene
Liquid	Solid	Solid emulsion	Opal, pearl
Solid	Solid	Solid suspension	Pigmented plastics

- e.g. oil-in-water (O/W) emulsion & water-in-oil (W/O) emulsion

- ‘*sol*’ is used to distinguish colloidal suspensions from macroscopic suspensions. When the dispersion medium is aqueous: ‘*hydrosol*’. If the dispersed phase is polymeric in nature: ‘*latex*’
c.f. *gel*: solid appearance which all of the solvent becomes mechanically trapped and immobilized within this network

Importance of interface

- A characteristic feature of colloidal dispersions is the large area to volume ratio for the particles involved
- Characteristic surface properties such as adsorption and electric double layer at the interface play an important part in determining the physical properties of the system as a whole
- Even a small amount of additives can significantly modify the interfaces, hence influencing the overall bulk properties
- Surface science is closely linked to colloid science; indeed colloid science is a part of surface science

Lyophilic and lyophobic systems

- lyophilic (liquid-loving) and lyophobic (liquid-hating): in aqueous, *hydrophilic and hydrophobic*