Lecture Note #6 (Spring, 2019)

Liquid Interfaces

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

Structure of liquid/solid interface

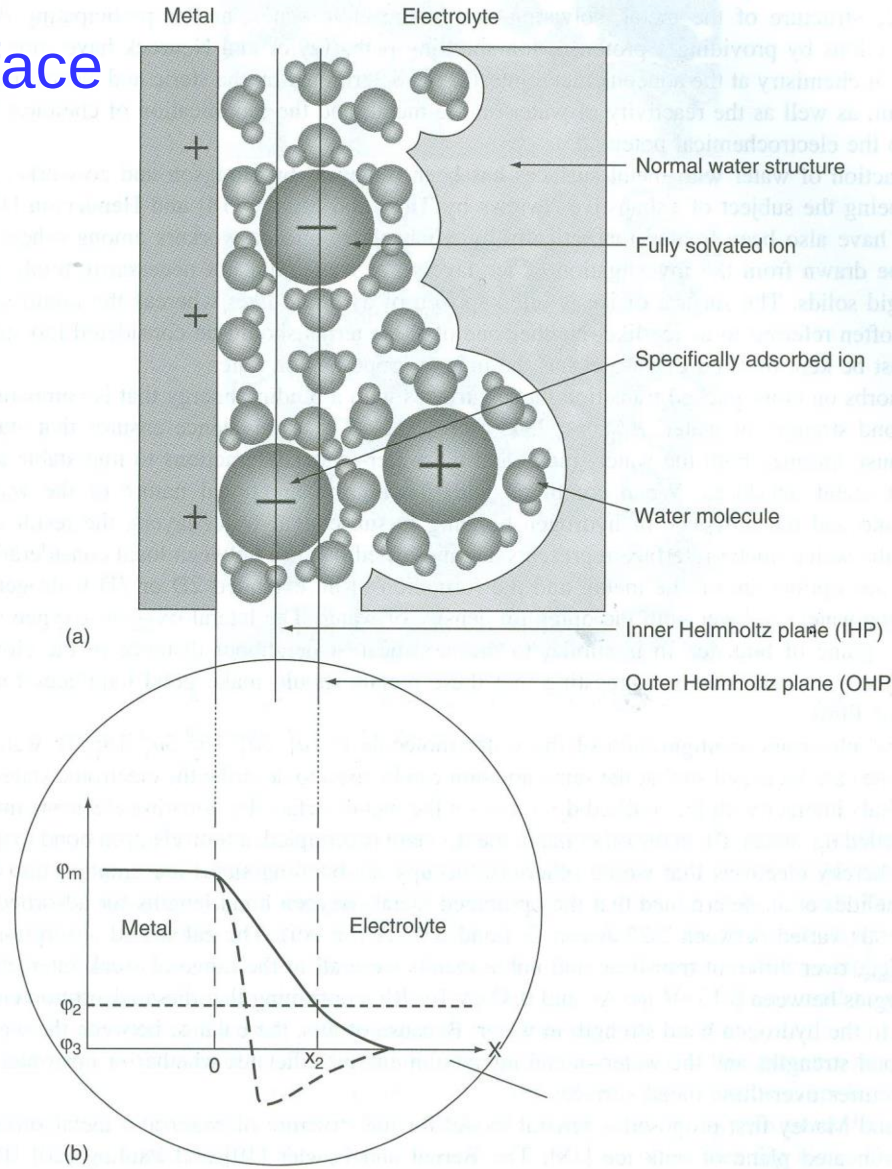

Metal
Electrolyte
Normal water structure
Fully solvated ion
Specifically adsorbed ion
Water molecule
(a)
Inner Helmholtz plane (IHP)
Outer Helmholtz plane (OHP)
φm
Metal
Electrolyte
φ2
φ3
0
x2
X
(b)

Figure 5.1 A model of the liquid/solid interface with examples of specific and non-specific adsorption. (a) The structure of the Helmholtz layers and a pure solvent is also shown. (b) The potential drop across the interface in case of non-specific (– – –) and specific (- - -) ion adsorption. ϕ_m, ϕ_s and ϕ_2 are potentials inside the metal, in the electrolyte, and at the outer Helmholtz plane x_2, respectively. A linear potential drop across the electrochemical interface is generally assumed for non-specifically adsorbing ions, while in the case of specific adsorption, a steeper potential gradient (close to the metal surface) and an "overshooting" of the potential with respect to the solution value is assumed [2]. Reproduced from D. M. Kolb, Surf. Sci. 500, 722. © 2002 with permission from Elsevier.

Structure of water/solid interface

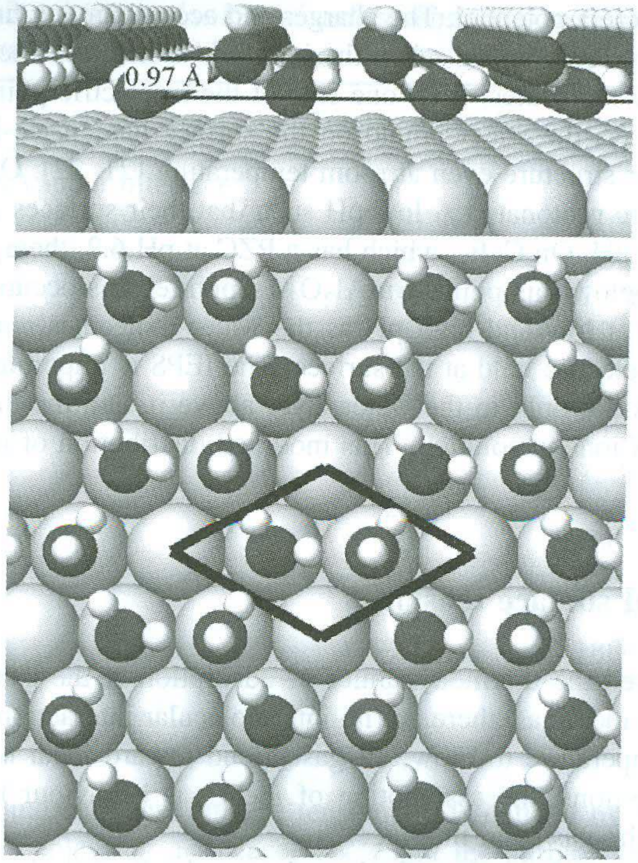
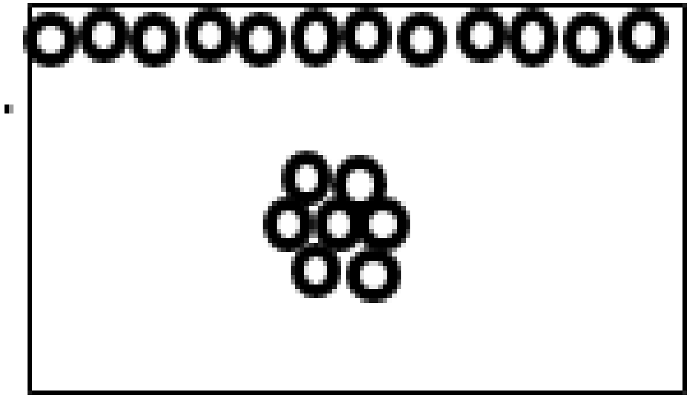


Figure 5.2 *Water bilayer structure for adsorption on closed packed metal surfaces. Reproduced from C. Clay, A. Hodgson, Curr. Opin. Solid State Mater. Sci. 9, 11. © 2005 with permission from Elsevier Science.*

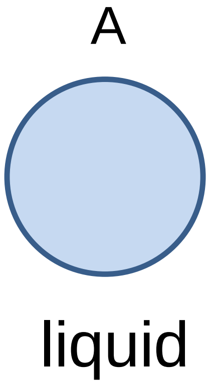
Surface energy and surface tension

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.



Definition of surface thermodynamic functions



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

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

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)

→ 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 $G^s = H^s – TS^s$,

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

- 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

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

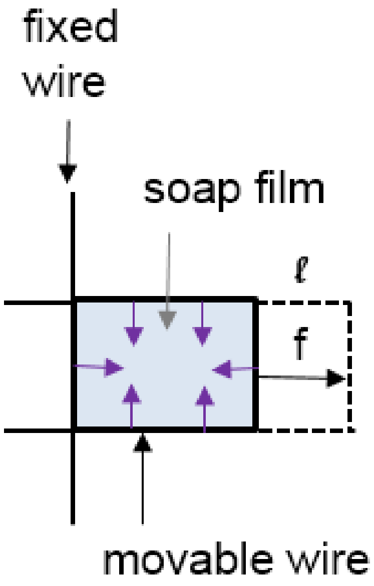
Extension of surface

- 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

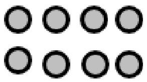
- $G_{total} = NG^0 + AG^s = NG^0 + A\gamma$; $\gamma \equiv G^s$
  work needed to create a surface
- Since, G^0 is fixed at fixed P and T conditions,
- $dG = d(A\gamma) = \gamma\, dA + A(\partial\gamma/\partial A)_{P,T}$

- 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

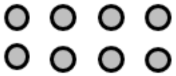
→ unstrained surface → the case for liquids

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

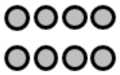
- Case II: $(\partial\gamma/\partial A)_{P,T} \neq 0$; A-dependent γ → strained surface → the case for unannealed solids.
  e.g., a cold-rolled metal sheet



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 pressure)

  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 = γ /d = (72 mN/m) /10^{-9} m = 7.2 x10^{7} Pa ~ 720 atm

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

γ in liquid: lower → lower energy required to make new surface

liquid: minimize surface area → curved structure

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

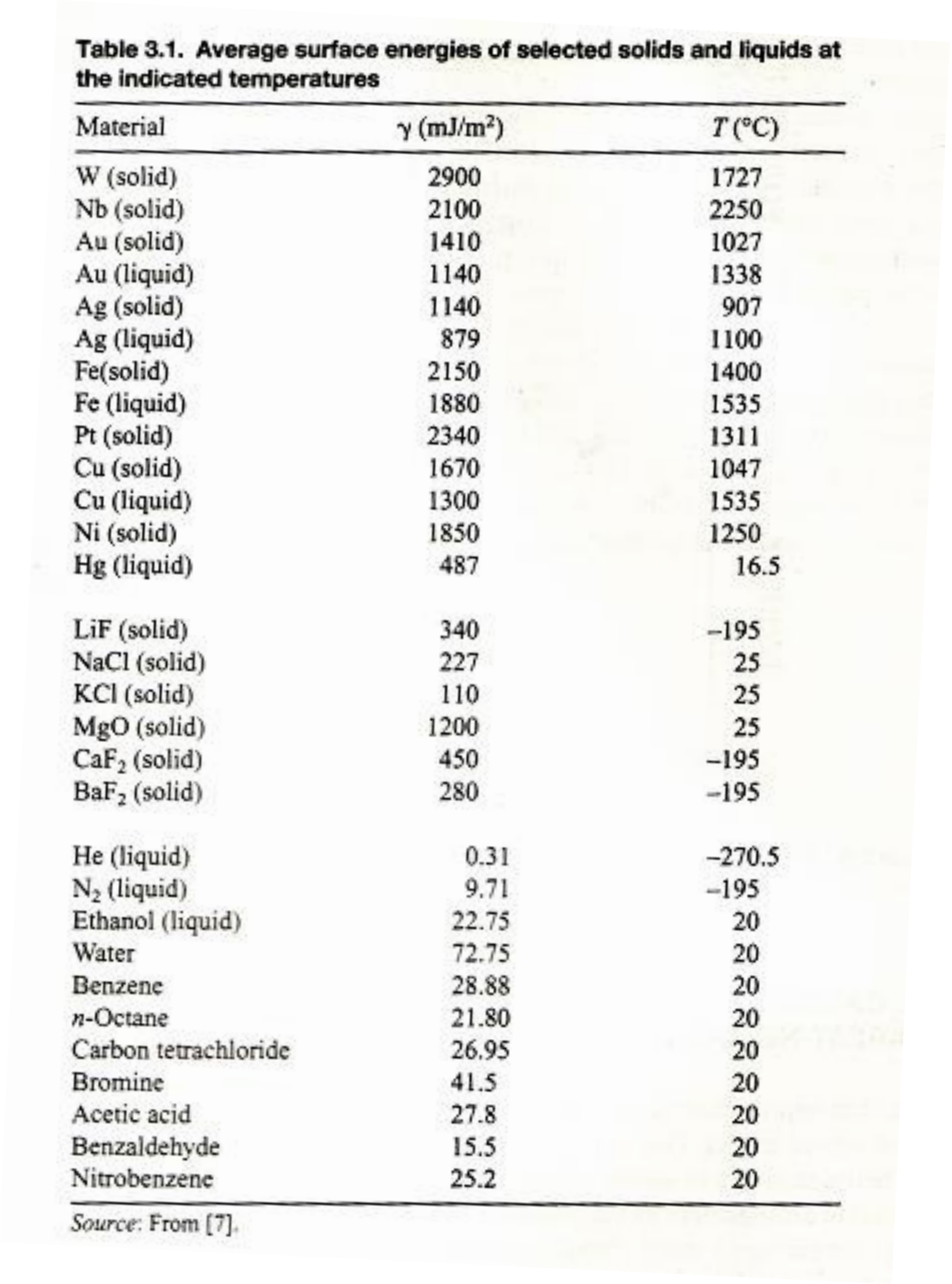


Table 3.1. Average surface energies of selected solids and liquids at the indicated temperatures

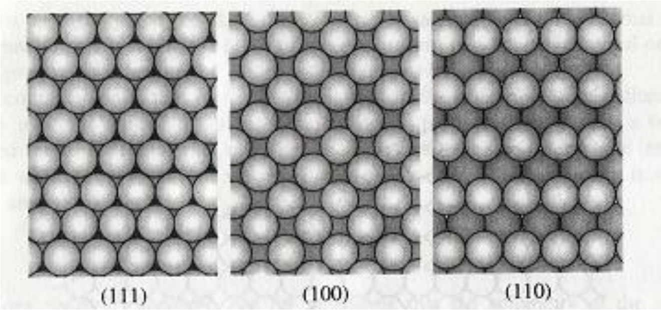
Material	γ (mJ/m^2)	T (°C)
W (solid)	2900	1727
Nb (solid)	2100	2250
Au (solid)	1410	1027
Au (liquid)	1140	1338
Ag (solid)	1140	907
Ag (liquid)	879	1100
Fe(solid)	2150	1400
Fe (liquid)	1880	1535
Pt (solid)	2340	1311
Cu (solid)	1670	1047
Cu (liquid)	1300	1535
Ni (solid)	1850	1250
Hg (liquid)	487	16.5
LiF (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

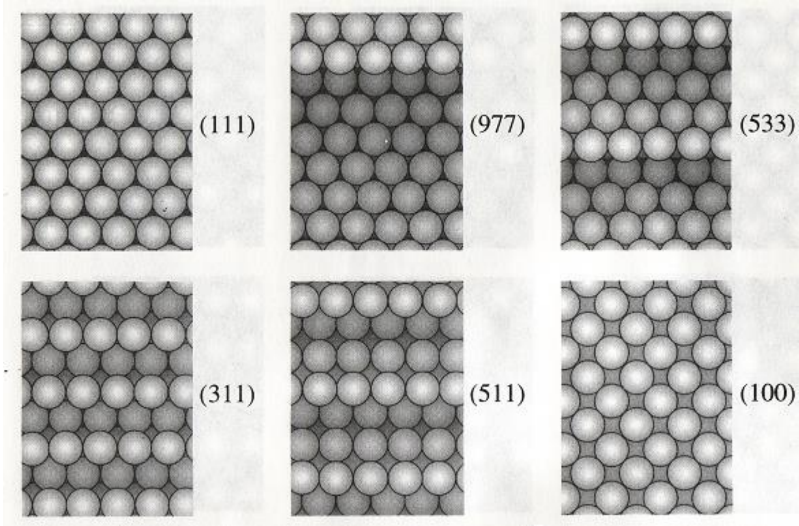
Source: From [7].

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

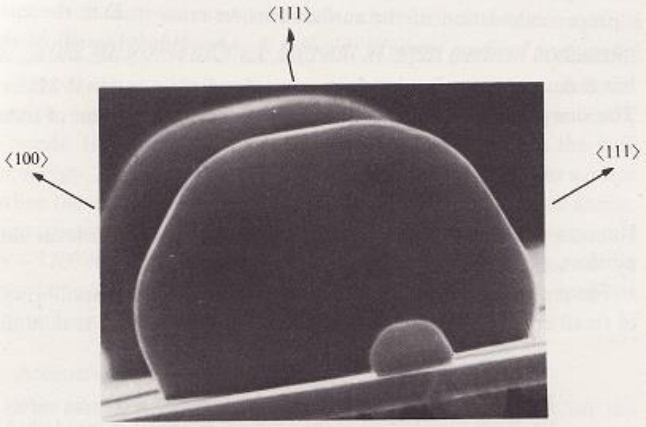
FCC (Ar, Ni, Pd, Cu, Ag, Au)




(111)
(977)
(533)
(311)
(511)
(100)

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

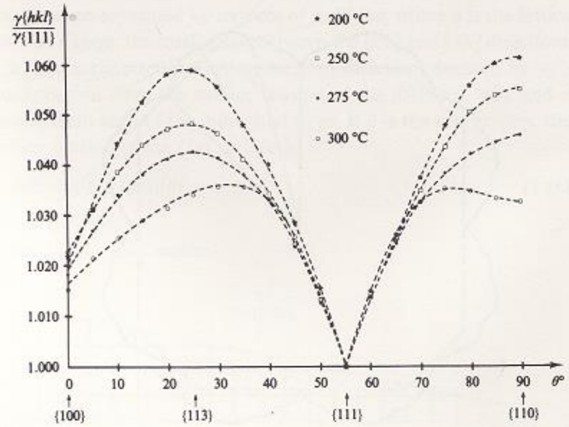
Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).



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).



Correlation between γ and $\Delta H_{\mathbf{sub}}$

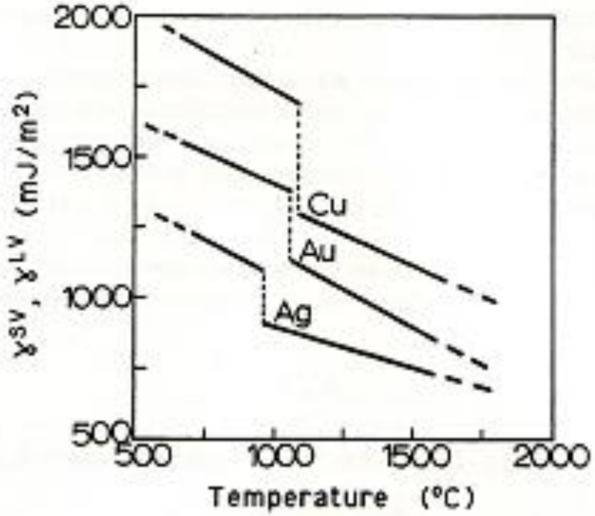
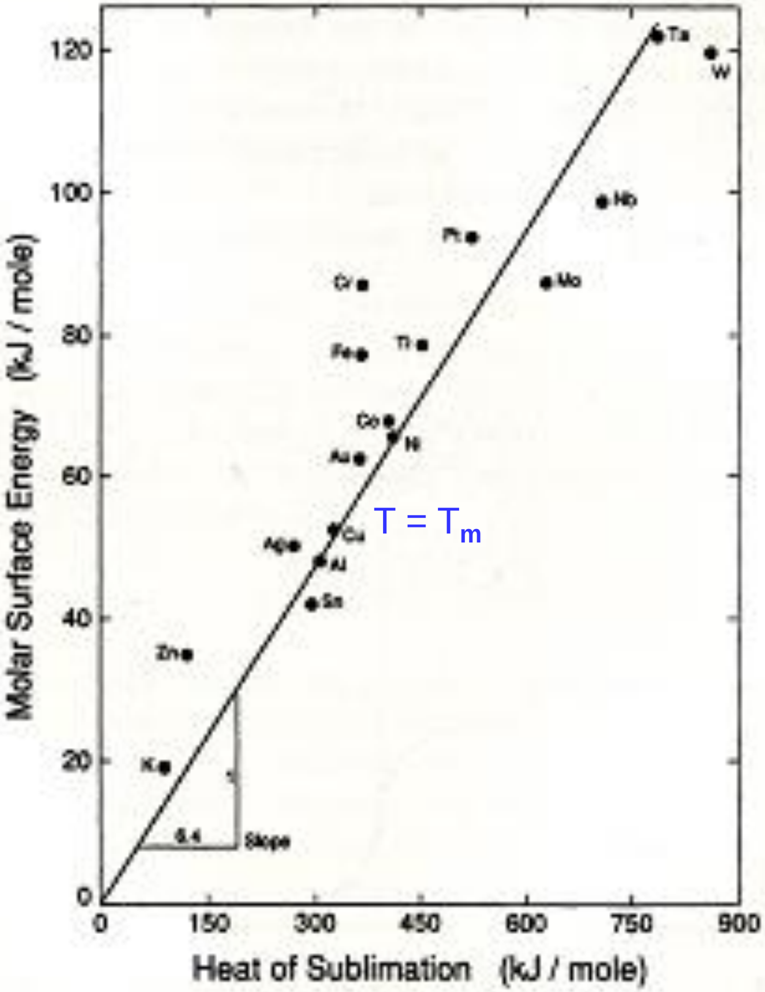


Figure 3.2. Temperature dependence of the surface energy and the solid–liquid phase transition for three f.c.c. metals. From [12].

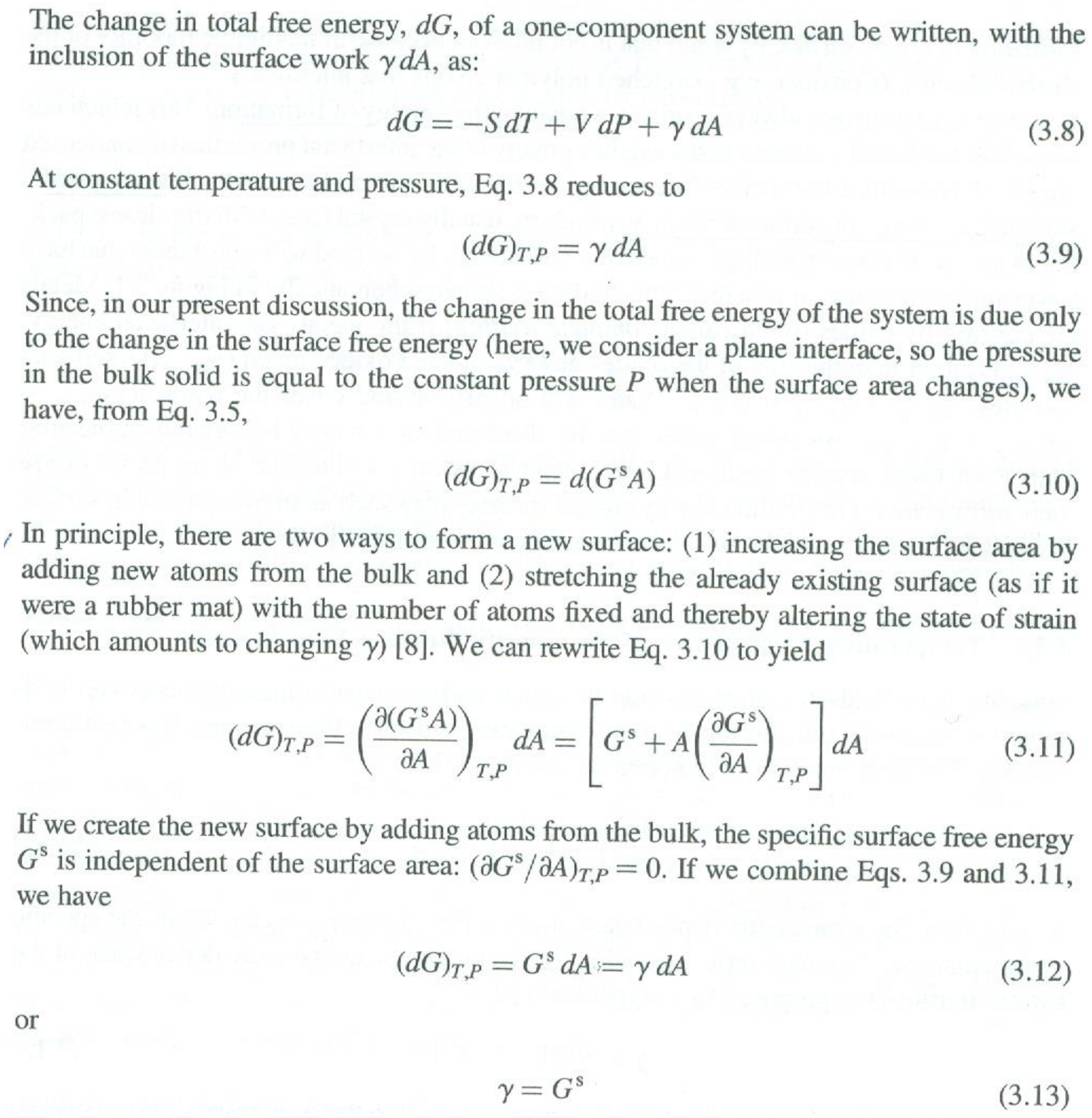
$$\gamma^{SV} \cong 1.2(\gamma^{LV})_m + 0.45(T_m - T),$$

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.

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



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

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

or

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

- 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 th 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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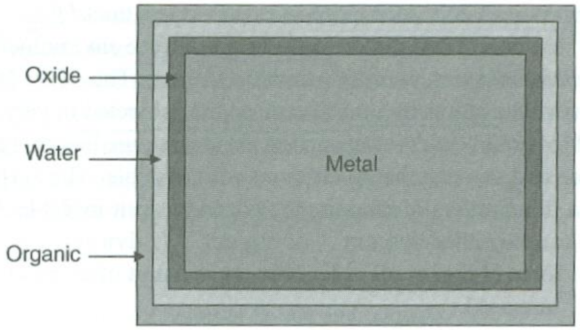


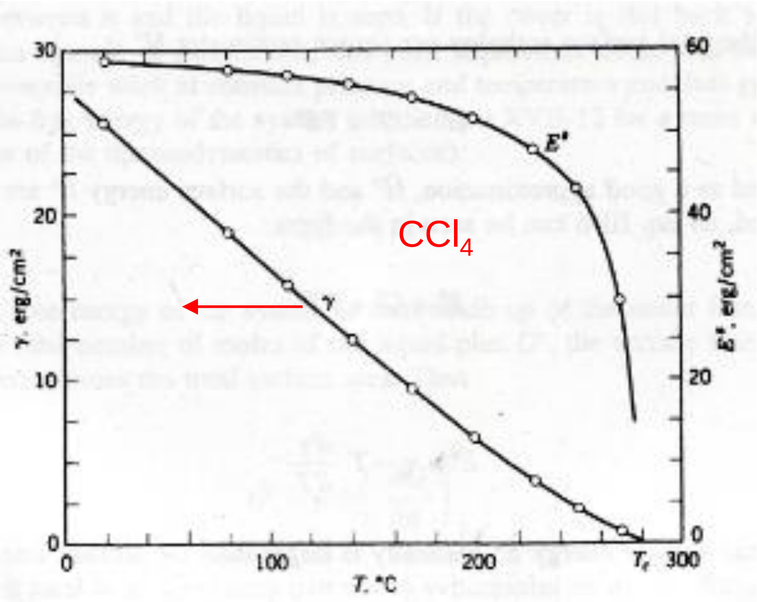
Figure 3.1. Representation of materials of lower surface energy coating materials of higher surface energy, leading to a net reduction of total surface energy ($\gamma_{\text{old surface}} > \gamma_{\text{new surface}} + \gamma_{\text{interface}}$).

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.
- $H^s = G^s + TS^s = \gamma - T(\partial\gamma/\partial T)_P$
- $H^s = U^s + PV = U^s$; 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.

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 ~ 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.



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**

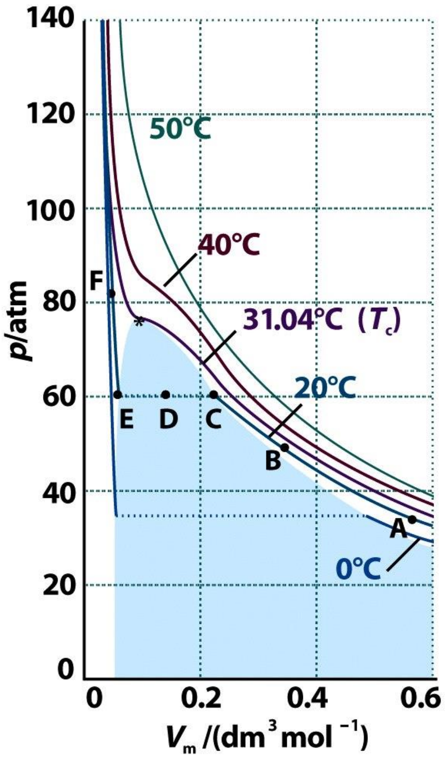


Figure 1-15
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

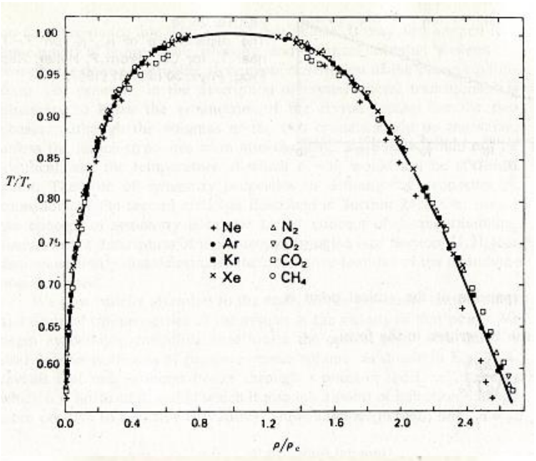


FIGURE 24.11
The liquid–gas coexistence curve for simple substances. The curve is a composite of data for Ne, Ar, Kr, Xe, N_2, O_2, CO_2, and CH_4. Note the use of the reduced variables T/T_c and ρ/ρ_c. From E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).

Surface Heat Capacity

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

Additional notes on surface tension

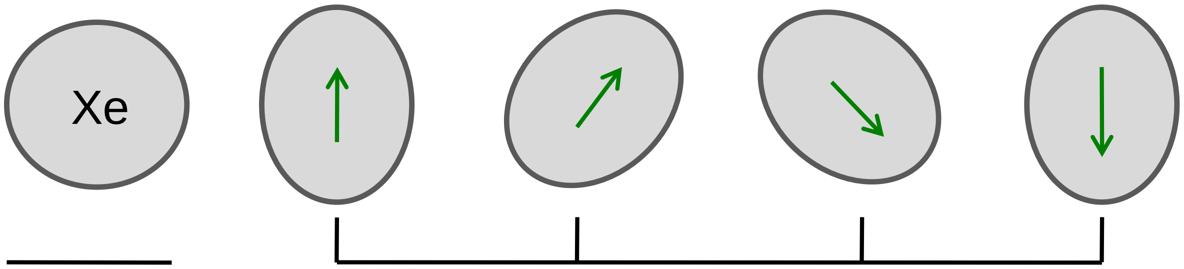
Origin of γ : attractive interatomic (solid) or intermolecular (liquid) force

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 poseses 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;

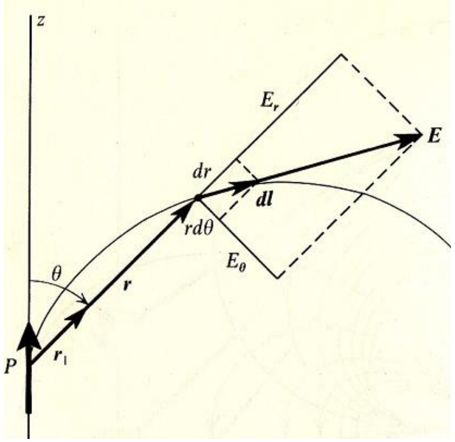
electron distribution in Xe atom



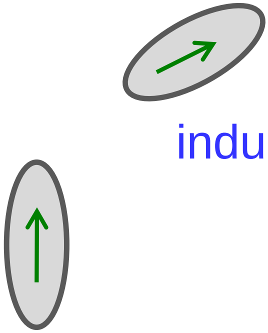
time average
with $p = 0$

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

2) Induced dipole



- Fluctuating (instantaneous) dipole produces an electric field ***E*** in space, which induces a dipole moment in another Xe atom given by
- ***p***$_{\text{ind}}$ = α***E****,* α is the electric polarizability.
- The interaction energy
  $V = - \int_{0.\,E} \boldsymbol{p}_{\text{ind}} \cdot d\boldsymbol{E} = \alpha E^2/2$
- 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, **$V(r) = - a\, \alpha^2/r^6 = - A/r^6$**, 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.



induced ***p***

fluctuating ***p***

Intermolecular interactions

1. van der Waals (Dispersion force)
   $V(r) = - A/r^6$
2. dipole-induced dipole
3. dipole-dipole
4. Hydrogen bonding

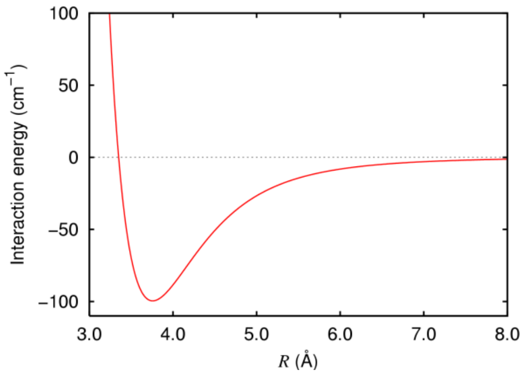
Relative magnitude

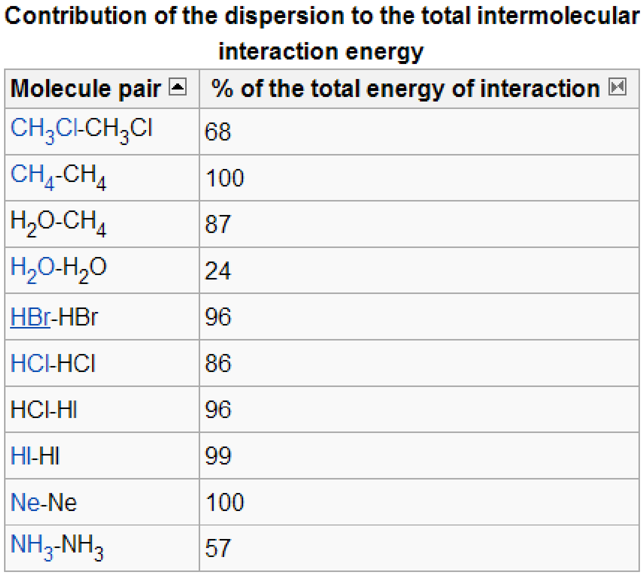
1 < 2 < 3 < 4

T_b of gases (K)

He	Ar	Xe	NH_3	H_2O	$C_{10}H_8$
4.2	87.3	165	230.7	373	491

Interaction energy of Ar-Ar





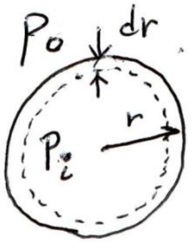
Contribution of the dispersion to the total intermolecular interaction energy

Molecule pair	% of the total energy of interaction
CH_3Cl-CH_3Cl	68
CH_4-CH_4	100
H_2O-CH_4	87
H_2O-H_2O	24
HBr-HBr	96
HCl-HCl	86
HCl-HI	96
HI-HI	99
Ne-Ne	100
NH_3-NH_3	57

Liquid Interfaces & films (curved)

Phenomena at curved surfaces

$\Delta P = P_i - P_0$

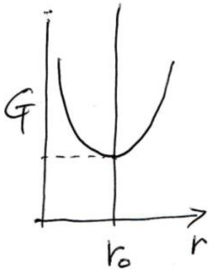


1. Pressure difference across a surface

- Liquid drop suspended in vacuum →The equilibrium shape is a sphere

→ Minimization of the surface area for a given volume.

- Can you prove it using the calculus of variation?
- The free energy change dG in contraction from r → r-dr is



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

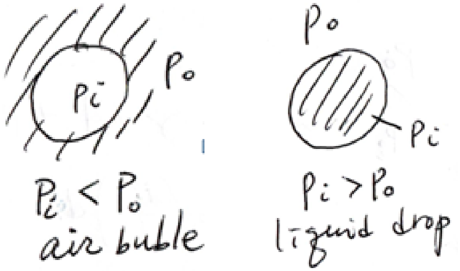
at equilibrium $dG = 0$.

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

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

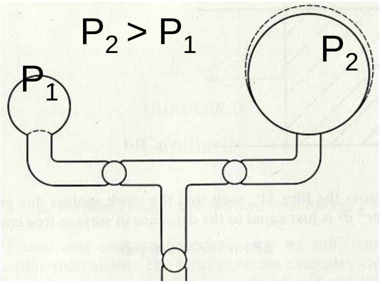
$$\Delta P = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma$$

The liquid drop is in a compressed state.



concave

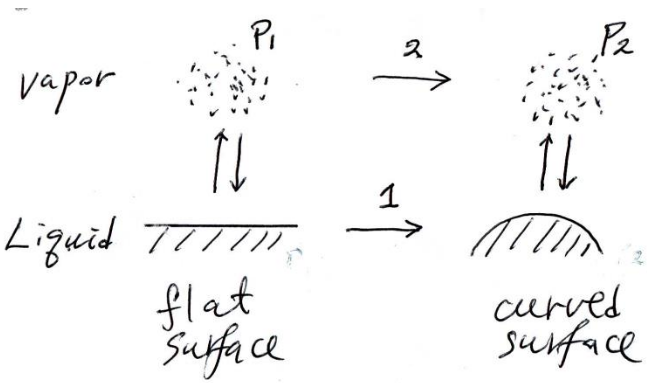
convex



The illustration of the equation of Young-Laplace

2. 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

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

Where V_m is the molar volume of the liquid, which is assumed to be constant.
The two quantities should be the same, and therefore

$$V_m \Delta P = RT\ln(P_2/P_1) \quad \text{or}$$
$$\frac{2V_m\gamma}{r} = RT\ln(P_2/P_1)$$
$$P_2/P_1 = \exp\left[\frac{2V_m\gamma}{rRT}\right]$$

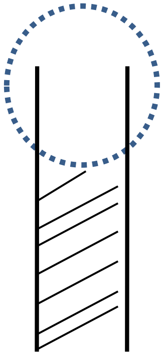
If $r = \infty$, $P_1 = P_2$
For finite r $P_2 > P_1$
For H_2O (γ = 72.8 mN/m) at 300 K
r = 1000 Å → $P_2/P_1 = 1.01$
r = 100 Å → $P_2/P_1 = 101$
r = 10 Å → $P_2/P_1 = 3.0$

Related concepts

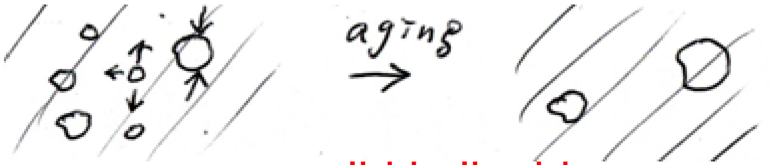
- Size-dependent solubility

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.

- Capillary condensation in porous materials



Oswald ripening



solid in liquid

desolution ↔ deposition process is in a dynamic equilibrium
to maintain a constant saturation solubility.

small particle → high solubility and large particle → low solubility

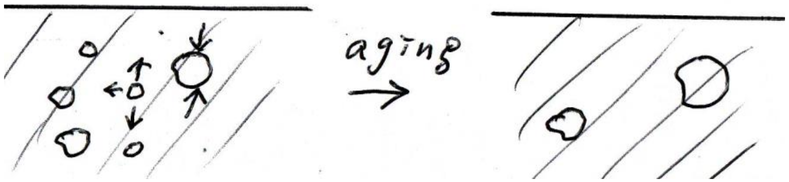
Large particles grow at the expense of the smaller particles → aging

minimize the total surface area → the way to reach a G_{min},
an equilibrium state

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

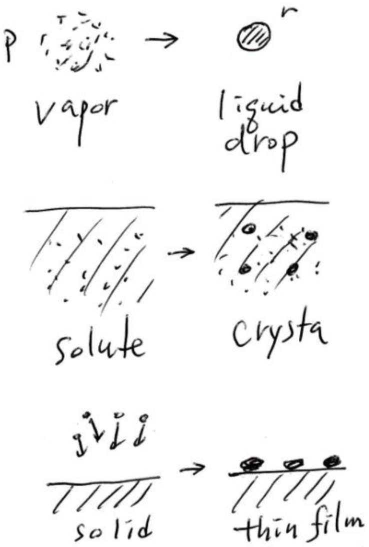
$CaCO_3$ sol → highly soluble → strong tendency of ripening (fast kinetics)

Sintering



solid in (on) solid

3. Formation of a new phase : 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 supersaturates vapor.
- Small drop has a high vapor pressure → it tends to reevaporate →
- Therefore, only droplets of a radius greater than a crital radius r_c (embryo) survive and grow.
- This process is called nucleation and the neuclei 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)

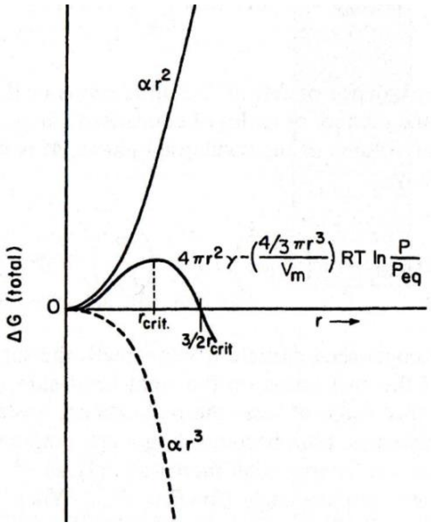
$$\Delta G = -nkT \ln P/P_0 + 4\pi r^2 \cdot \gamma$$

$$= -\frac{4}{3}\pi r^3 \frac{\rho}{M} \ln P/P_0 + 4\pi r^2 \gamma$$

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

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

M= molular weight, ρ = density
P_0 = equilibtitm vapor pressure
P/P_0 = degree of supersturation

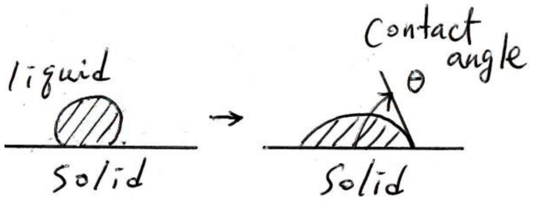


This means there is always a free energy barrier of
$\Delta G_m = 16\,\pi\,\gamma^3\, V_m /3 \{RT \ln (P/P_0)\}^2$,
which is overcome by thermal fluctuation.

* Related concepts
artificial raining: spraying dry ice particle in the damp air
seeding in crystallization: adding a ctrstal seeds in a supersaturated solution

4. Capillary rise and depression

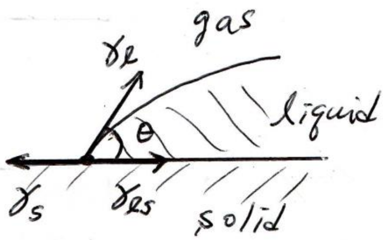
- Wetting


liquid
Solid
Contact angle
θ
Solid

$\theta = 0^o$:complete wetting
$\theta = 180^o$:complete dewetting

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

- Force balance at the interface


gas
γ_l
liquid
θ
γ_s
γ_{ls}
solid

$$\gamma_l \cos\theta + \gamma_{ls} = \gamma_s$$

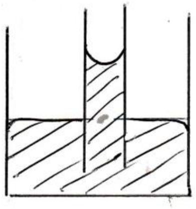
- Criteria for wetting
  When the interface area is increased by dA,

$$dG = \gamma_{ls}\, dA + \gamma_l \cos\theta\, dA - \gamma_s\, dA$$
$$= (\gamma_{ls} + \gamma_l \cos\theta - \gamma_s)\, dA = x\, dA$$

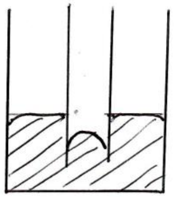
If $x < 0$ → wetting occurs, and
If $x > 0$ → dewetting occurs.

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

Capillary rise



capillary
rise



capillary
depression

- Force balance at the top of the miniscus

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 = deisity of the liquid
ρ_0 = deisity of the air

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

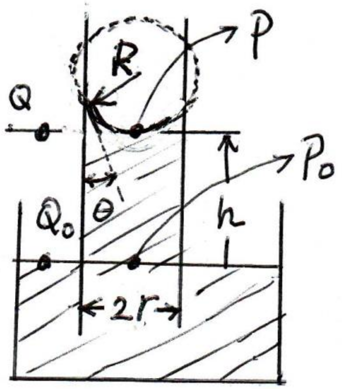
Another view

pressure difference between the points Q and Q_0 : $\Delta P = \rho_0 g h$
pressure difference between the points P and P_0 : $\Delta P = -2\gamma/R + \rho g h$

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

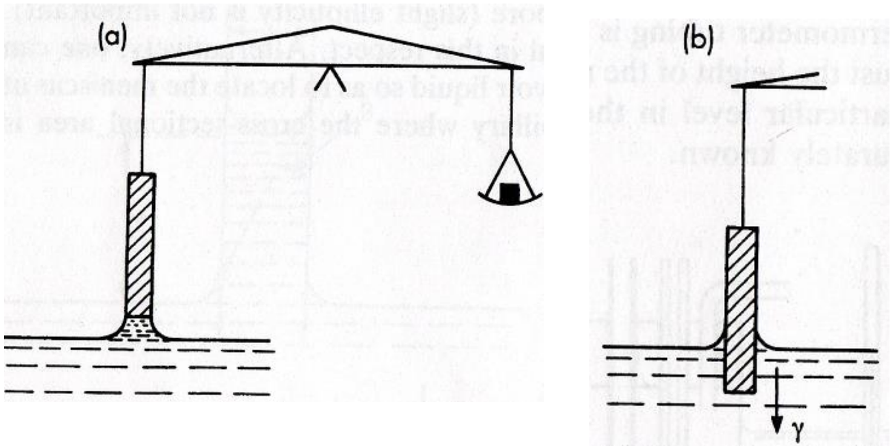
$$2\gamma/R = \Delta\rho g h \rightarrow h = 2\gamma\cos\theta / \Delta\rho g r$$

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



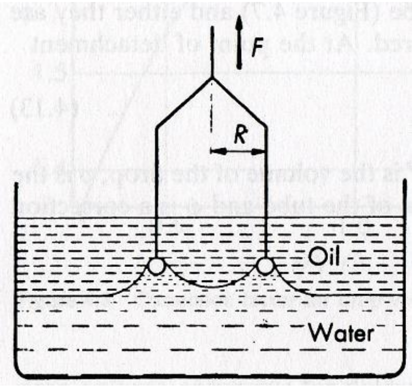
Measurements of surface tension

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

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

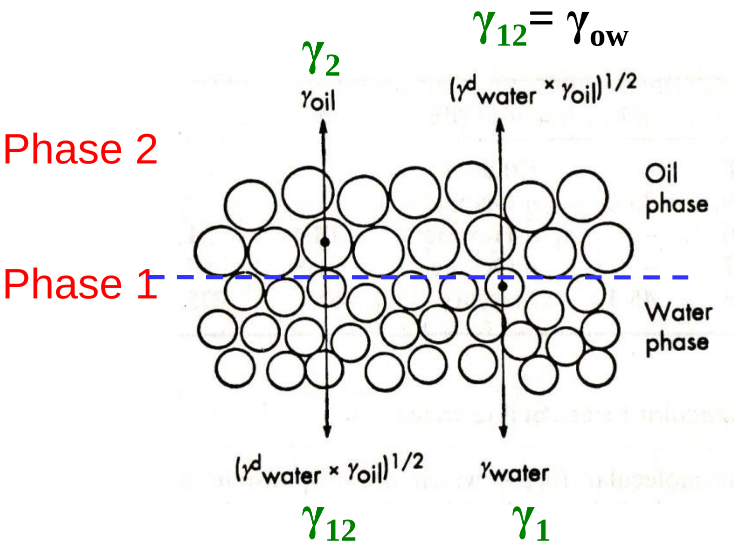
$$\gamma_i = (\gamma_1 - \gamma_{12}) + (\gamma_2 + \gamma_{21}) = \gamma_1 + \gamma_2 - 2\gamma_{12},$$

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

γ_i = **free energy per unit interfacial area**

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

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



$\gamma_{12} = \gamma_{ow}$
γ_2
γ_{oil}
$(\gamma^d_{water} \times \gamma_{oil})^{1/2}$
Phase 2
Oil phase
Phase 1
Water phase
$(\gamma^d_{water} \times \gamma_{oil})^{1/2}$
γ_{water}
γ_{12}
γ_1

Additivity of intermolecular force

$$\gamma_W = \gamma_W^d + \gamma_W^h$$

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

$$\gamma_{OW} = \gamma_O^d + (\gamma_W^d + \gamma_W^h) - 2 \times (\gamma_W^d \times \gamma_O^d)^{1/2}$$

Ex: n-hexane-water interface

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

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

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

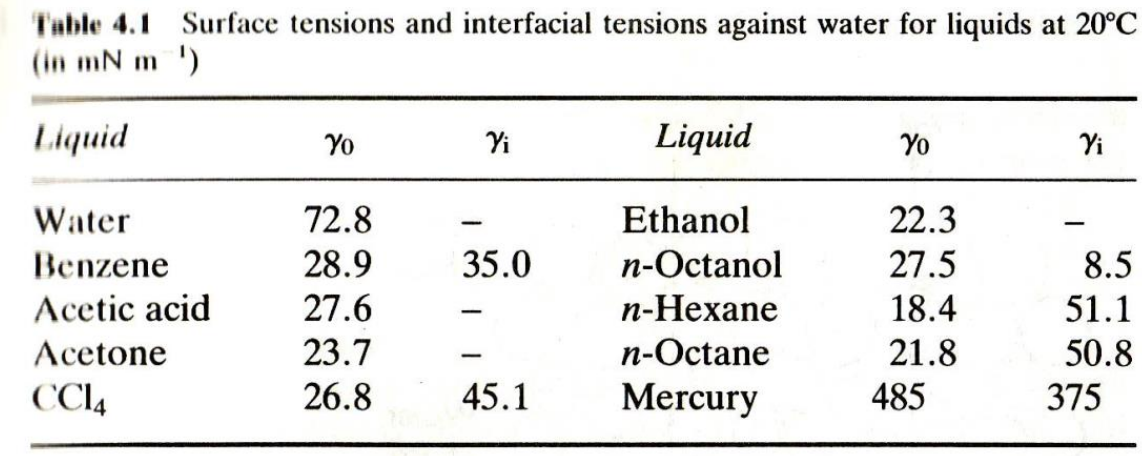


Table 4.1 Surface tensions and interfacial tensions against water for liquids at 20°C (in mN m^{-1})

Liquid	γ_0	γ_i	*Liquid*	γ_0	γ_i
Water	72.8	–	Ethanol	22.3	–
Benzene	28.9	35.0	*n*-Octanol	27.5	8.5
Acetic acid	27.6	–	*n*-Hexane	18.4	51.1
Acetone	23.7	–	*n*-Octane	21.8	50.8
CCl_4	26.8	45.1	Mercury	485	375

Surfactants, Langmuir films, Langmuir-Blodgett films, self assembly monolayers

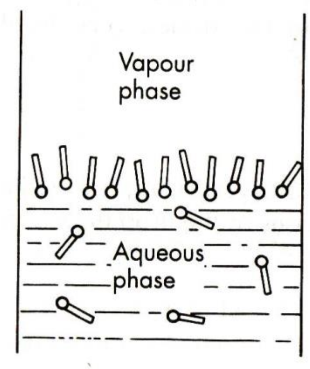
Surface tension of 2-component systems

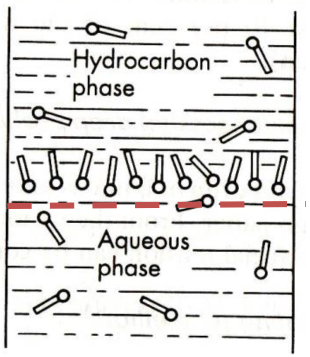
Surface activity

$$\gamma = \gamma_0 - \pi$$

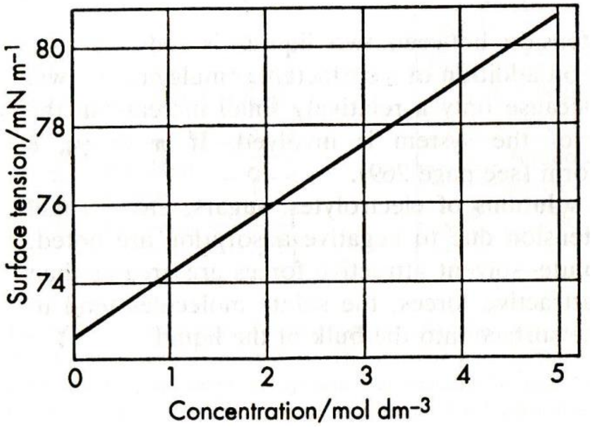
π : surface pressure(expanding pressure)
Surface active agent, surfactant

Adsorption and orientation at interfaces

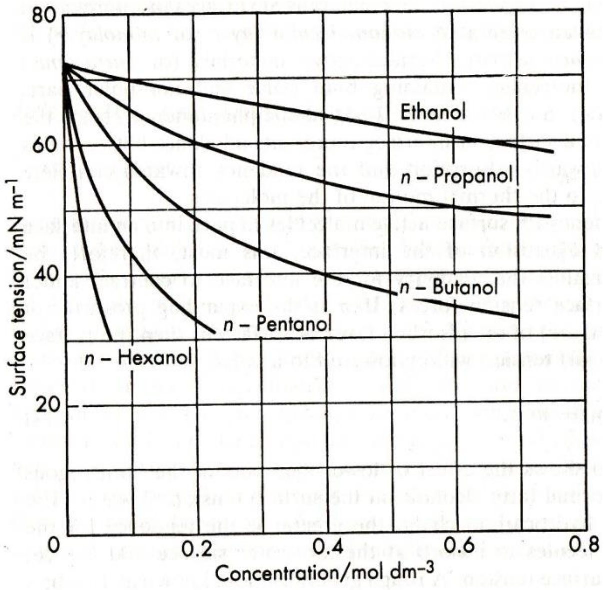

Vapour phase
Aqueous phase


Hydrocarbon phase
Aqueous phase

NaCl solution

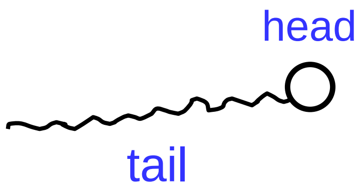


Alcohol in water



Surfactant (surface active agent)

- Molecules which drastically reduces the γ of water when added.
- Typically consists of hydrophobic hydrocarbon chain (tail) and hydrophilic group (head) such as -OH, -COOH, $-SO_3H$, $-NH_2$ etc.
- Surfactants are used in many important industrial applications.



Classification of surfactant

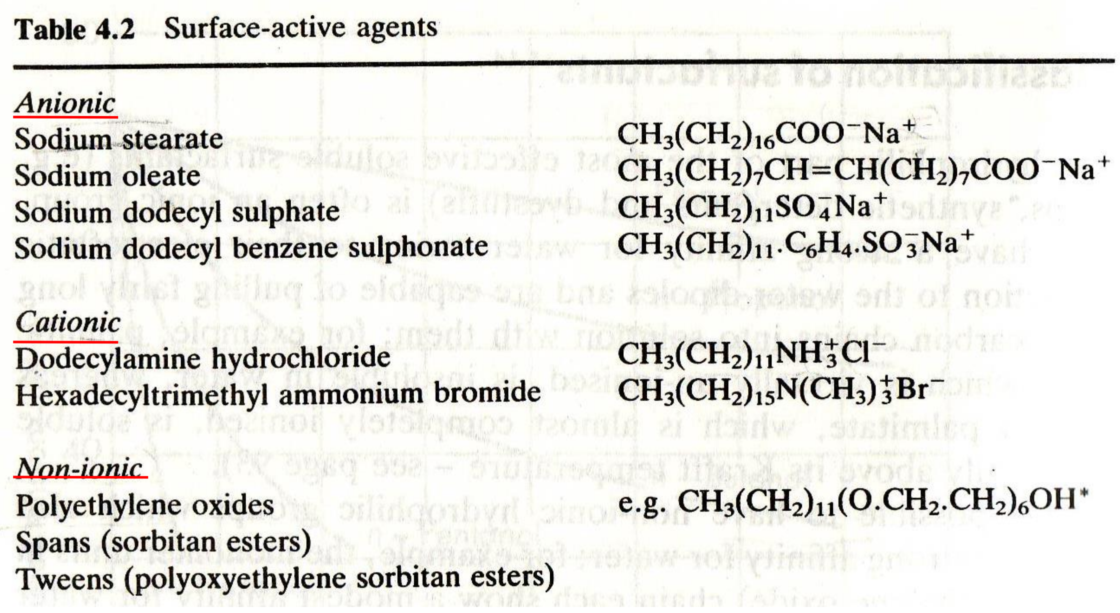


Table 4.2 Surface-active agents

Anionic	
Sodium stearate	$CH_3(CH_2)_{16}COO^-Na^+$
Sodium oleate	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO^-Na^+$
Sodium dodecyl sulphate	$CH_3(CH_2)_{11}SO_4^-Na^+$
Sodium dodecyl benzene sulphonate	$CH_3(CH_2)_{11}.C_6H_4.SO_3^-Na^+$
Cationic	
Dodecylamine hydrochloride	$CH_3(CH_2)_{11}NH_3^+Cl^-$
Hexadecyltrimethyl ammonium bromide	$CH_3(CH_2)_{15}N(CH_3)_3^+Br^-$
Non-ionic	
Polyethylene oxides	e.g. $CH_3(CH_2)_{11}(O.CH_2.CH_2)_6OH^*$
Spans (sorbitan esters)	
Tweens (polyoxyethylene sorbitan esters)	

Self-assembly of surfactant: Micelle formation

- When added in water, surfactant molecules strongly positively adsorb at the surface.
- Surfactant molecules in bulk water is thermodynamically unstable, so the bulk concentration is very small.
- The solubility of surfactants in water, especially the ones with a long alkyl chain, is very low.
- Above a certain temperature, Kraft Temperature T_K, the solubility increases rapidly because of micelle formation.
- Isolated surfactant molecules spontaneously form a stable aggregate
- (micelle) above a certain concentration, critical micelle concentration(CMC)
- Micelle formation occurs sharply at CMC like a phase transition.

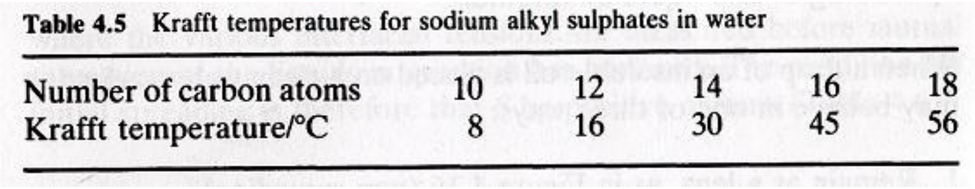
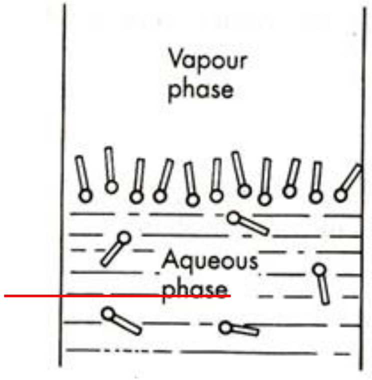
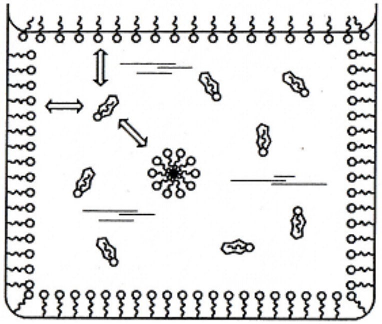


Table 4.5 Krafft temperatures for sodium alkyl sulphates in water

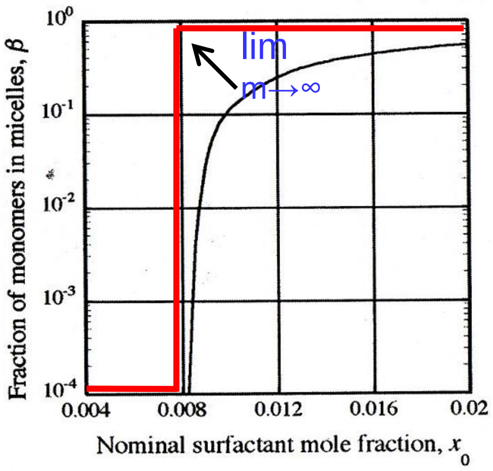
Number of carbon atoms	10	12	14	16	18
Krafft temperature/°C	8	16	30	45	56





Sharpness of CMC

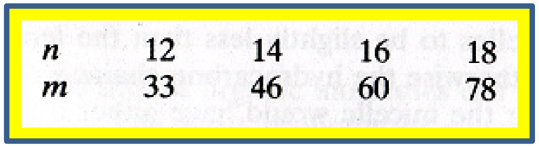
- $mS \leftrightarrow S_m$: β = fraction of monomer in micelles
  $c(1-\beta)$ $c\beta/m$
- $K = (c\beta/m) / [c(1-\beta)]^m \rightarrow \beta = \beta(c)$ at constant K
- $Kmc^{m-1} = \beta/(1-\beta)^m$
- Typically, m ~ 100 and CMC ~ 10^{-3}.
- $\beta(c)$ is plotted in the bottom Figure.
  Transition is fairly sharp → lim (m→∞) $\beta(c)$ is a step function.



Spherical micelle

- Nearly monodispersed.
- The size is limited and it depends on the nature of the lyophobic part of the surfactant. $m\,S \leftrightarrow S_m$: S = monomer, S_m = micelle, m = aggregation number

n = # of CH_2 unit in a straight chain hydrocarbon



n	12	14	16	18
m	33	46	60	78

- Counter ion binding: counter ion /S < 1

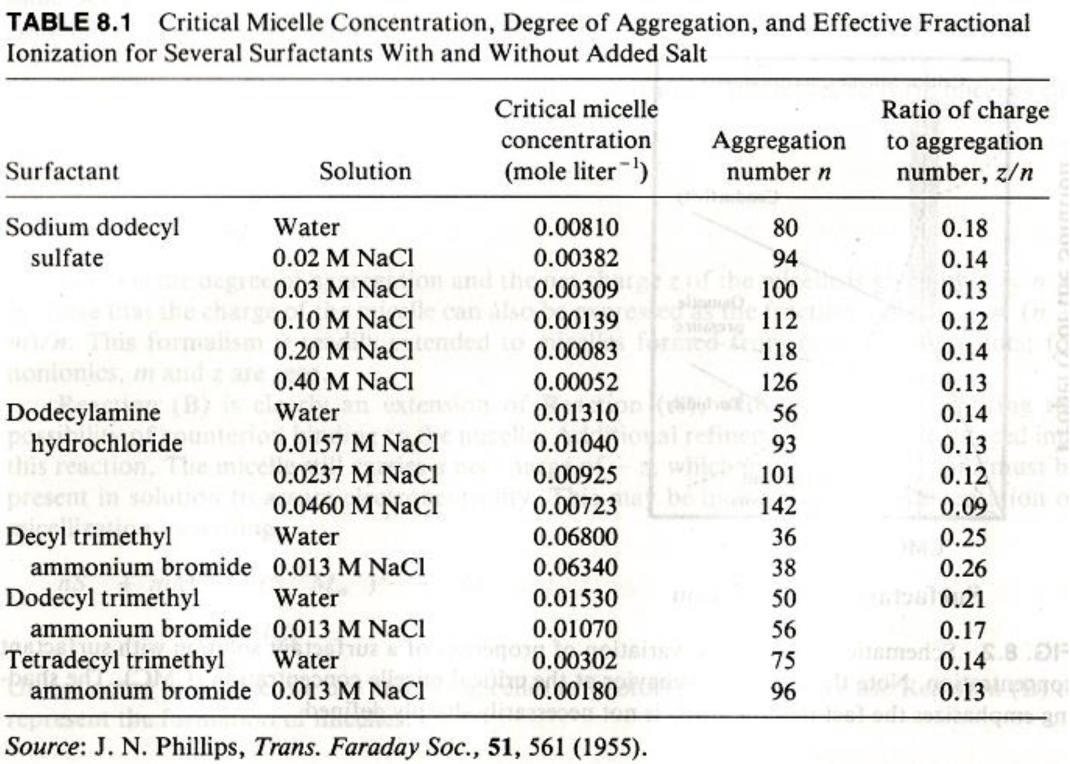
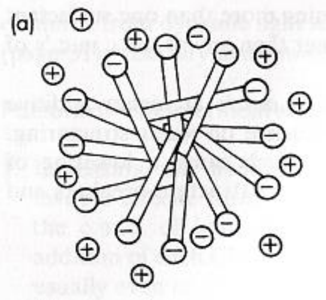


TABLE 8.1 Critical Micelle Concentration, Degree of Aggregation, and Effective Fractional Ionization for Several Surfactants With and Without Added Salt

Surfactant	Solution	Critical micelle concentration (mole liter^{-1})	Aggregation number *n*	Ratio of charge to aggregation number, *z/n*
Sodium dodecyl sulfate	Water	0.00810	80	0.18
	0.02 M NaCl	0.00382	94	0.14
	0.03 M NaCl	0.00309	100	0.13
	0.10 M NaCl	0.00139	112	0.12
	0.20 M NaCl	0.00083	118	0.14
	0.40 M NaCl	0.00052	126	0.13
Dodecylamine hydrochloride	Water	0.01310	56	0.14
	0.0157 M NaCl	0.01040	93	0.13
	0.0237 M NaCl	0.00925	101	0.12
	0.0460 M NaCl	0.00723	142	0.09
Decyl trimethyl ammonium bromide	Water	0.06800	36	0.25
	0.013 M NaCl	0.06340	38	0.26
Dodecyl trimethyl ammonium bromide	Water	0.01530	50	0.21
	0.013 M NaCl	0.01070	56	0.17
Tetradecyl trimethyl ammonium bromide	Water	0.00302	75	0.14
	0.013 M NaCl	0.00180	96	0.13

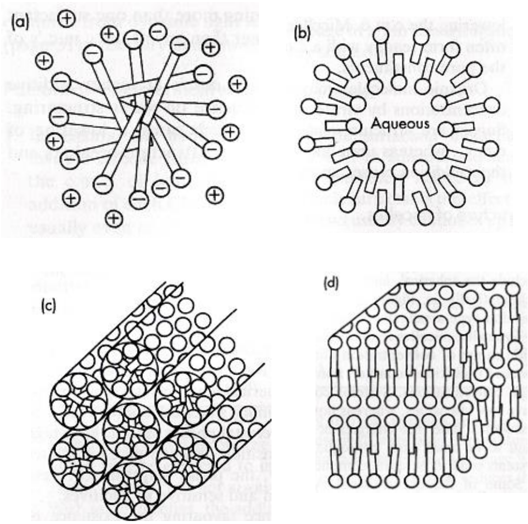
Source: J. N. Phillips, *Trans. Faraday Soc.*, **51**, 561 (1955).



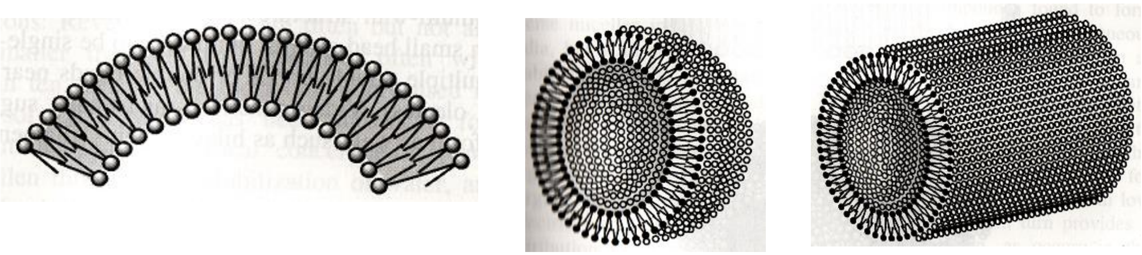
$CH_3(CH_2)_{11}\text{-O-S(-O)}_2\text{-O}^-\text{Na}^+$
Sodium dodecyl sulphate

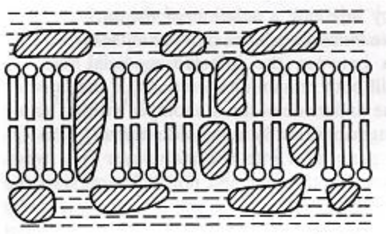
Structure of micelle

- Spherical, spherical bilayer, hexagonal, lamella
- Typically, micelles tends to be approximately spherical over a fairly wide range of concentration above CMC.
- There are often marked transition to larger, non-spherical liquid crystal structure at high concentrations.



Micelle structures; a) spherical, b) spherical vesicle bilayer, c) hexagonal, d) lamella





Biological cell membrane

Evidence for micelle formation

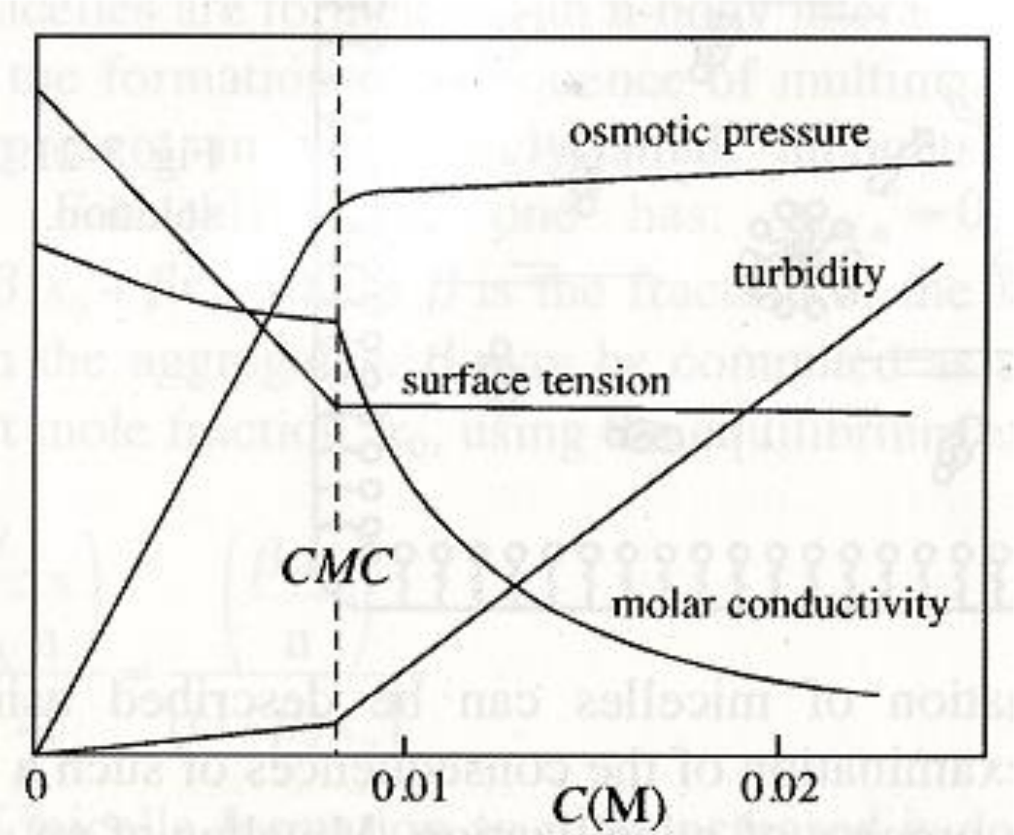


Fig. 3-20: Schematic diagram of physical property changes o aqueous solutions of sodium dodecyl sulfate at 25°C as a function of concentration.

Physical property changes at c.m.c.

1. Molar conductivity Λ of ionic surfactants

- Ions contributes to the conductivity but Λ gradually ↓ with increasing concentration because of ion-ion interactions.
- A sharp decrease in Λ above the c.m.c. due to micelle formation.
  1) The total viscous drag is reduced when micelles are formed.
  2) Counter-ions becomes kinetically a part of micelle → the net charge of a micelle z is much smaller than n, reducing the # of counter-ions avail for carrying current.
  3) The electrophoretic retardation effect of the ionic atmospheres of unattached counter-ions is greatly increases.
- the last two effects are responsible for the sharp decrease in Λ when micells are formed.

2. Osmotic pressure Π

- $\pi V = cRT$ (van't Hoff eq.)
- The # of molecules only slightly increases above c.m.c.

3. Turbidity τ

- Turbidity is due the scattering of visible light by particles.
- The scattering power increases with increasing particle size, reaching about maximum when the size is comparable to the wavelength.
- The size of an unassociated surfactant molecule is too small to appreciably scatter visible light.
- When micelle is formed, it can significantly scatter light.

4. Surface tension γ

- Surface tension sharply decreases with increasing surfactant concentration.
- However, when micelle is formed, it's concentration (number-based) increases very slowly.

Factors affecting CMC

1. Hydrophobic chain length n of straight aliphatic surfactant.

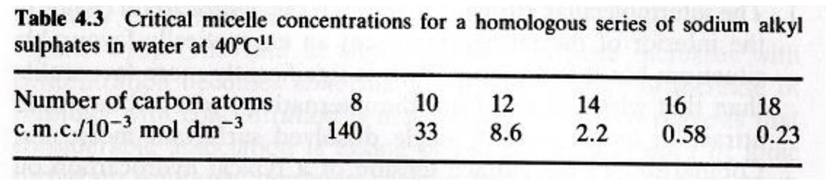


Table 4.3 Critical micelle concentrations for a homologous series of sodium alkyl sulphates in water at 40°C[11]

Number of carbon atoms	8	10	12	14	16	18
c.m.c./10^{-3} mol dm^{-3}	140	33	8.6	2.2	0.58	0.23

ionic: n→ n+1, CMC(n+1)/CMC(n) ~ 1/2

non-ionic: n→ n+1, CMC(n+1)/CMC(n)~ 1/3

log(CMC) = A – Bn : Klevens constants A and B

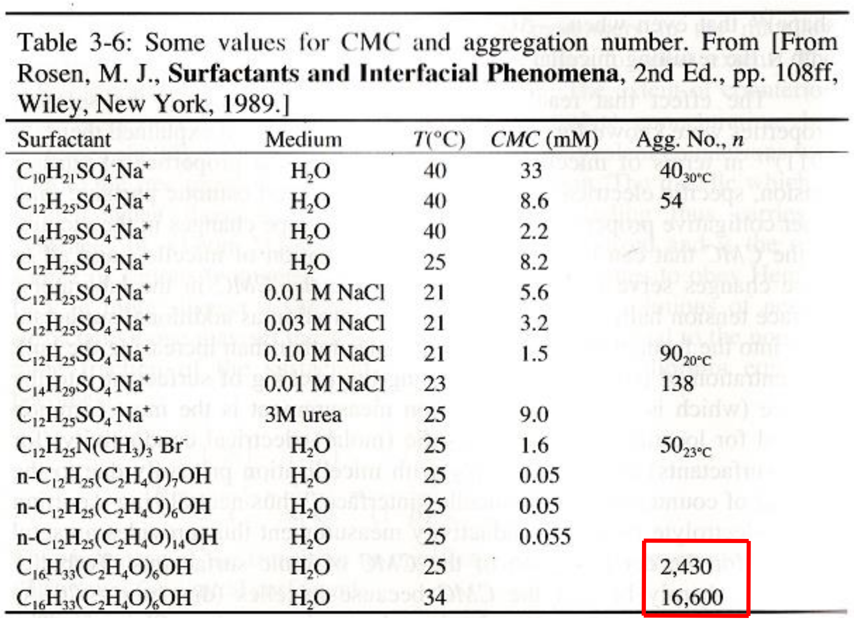
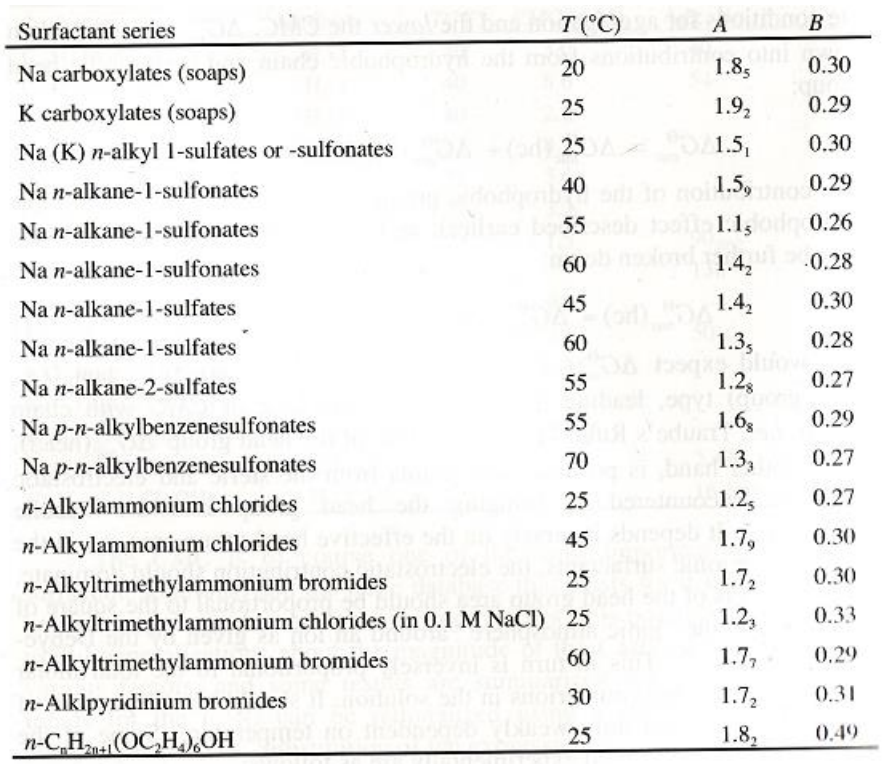


Table 3-6: Some values for CMC and aggregation number. From [From Rosen, M. J., **Surfactants and Interfacial Phenomena**, 2nd Ed., pp. 108ff, Wiley, New York, 1989.]

Surfactant	Medium	T(°C)	*CMC* (mM)	Agg. No., *n*
$C_{10}H_{21}SO_4^-Na^+$	H_2O	40	33	$40_{30°C}$
$C_{12}H_{25}SO_4^-Na^+$	H_2O	40	8.6	54
$C_{14}H_{29}SO_4^-Na^+$	H_2O	40	2.2	
$C_{12}H_{25}SO_4^-Na^+$	H_2O	25	8.2	
$C_{12}H_{25}SO_4^-Na^+$	0.01 M NaCl	21	5.6	
$C_{12}H_{25}SO_4^-Na^+$	0.03 M NaCl	21	3.2	
$C_{12}H_{25}SO_4^-Na^+$	0.10 M NaCl	21	1.5	$90_{20°C}$
$C_{14}H_{29}SO_4^-Na^+$	0.01 M NaCl	23		138
$C_{12}H_{25}SO_4^-Na^+$	3M urea	25	9.0	
$C_{12}H_{25}N(CH_3)_3^+Br^-$	H_2O	25	1.6	$50_{23°C}$
n-$C_{12}H_{25}(C_2H_4O)_7OH$	H_2O	25	0.05	
n-$C_{12}H_{25}(C_2H_4O)_6OH$	H_2O	25	0.05	
n-$C_{12}H_{25}(C_2H_4O)_{14}OH$	H_2O	25	0.055	
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	25		2,430
$C_{16}H_{33}(C_2H_4O)_6OH$	H_2O	34		16,600

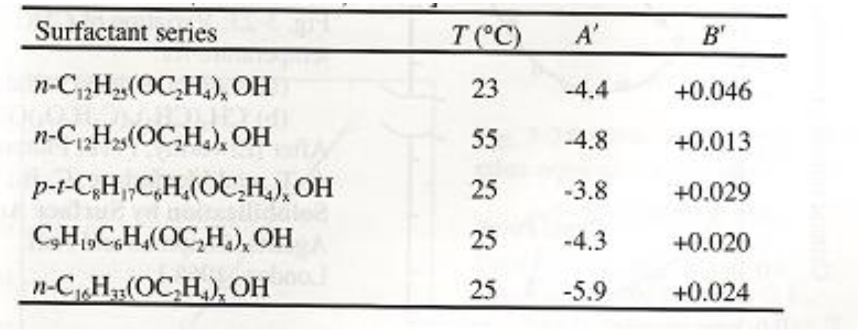
Note: n of nonionic surfactant is much larger

Ionic surfactants



Surfactant series	*T* (°C)	*A*	*B*
Na carboxylates (soaps)	20	1.8_5	0.30
K carboxylates (soaps)	25	1.9_2	0.29
Na (K) *n*-alkyl 1-sulfates or -sulfonates	25	1.5_1	0.30
Na *n*-alkane-1-sulfonates	40	1.5_9	0.29
Na *n*-alkane-1-sulfonates	55	1.1_5	0.26
Na *n*-alkane-1-sulfonates	60	1.4_2	0.28
Na *n*-alkane-1-sulfates	45	1.4_2	0.30
Na *n*-alkane-1-sulfates	60	1.3_5	0.28
Na *n*-alkane-2-sulfates	55	1.2_8	0.27
Na *p*-*n*-alkylbenzenesulfonates	55	1.6_8	0.29
Na *p*-*n*-alkylbenzenesulfonates	70	1.3_3	0.27
n-Alkylammonium chlorides	25	1.2_5	0.27
n-Alkylammonium chlorides	45	1.7_9	0.30
n-Alkyltrimethylammonium bromides	25	1.7_2	0.30
n-Alkyltrimethylammonium chlorides (in 0.1 M NaCl)	25	1.2_3	0.33
n-Alkyltrimethylammonium bromides	60	1.7_7	0.29
n-Alklpyridinium bromides	30	1.7_2	0.31
n-$C_nH_{2n+1}(OC_2H_4)_6OH$	25	1.8_2	0.49

PEO surfactants



Surfactant series	*T* (°C)	*A'*	*B'*
n-$C_{12}H_{25}(OC_2H_4)_x OH$	23	-4.4	+0.046
n-$C_{12}H_{25}(OC_2H_4)_x OH$	55	-4.8	+0.013
p-*t*-$C_8H_{17}C_6H_4(OC_2H_4)_x OH$	25	-3.8	+0.029
$C_9H_{19}C_6H_4(OC_2H_4)_x OH$	25	-4.3	+0.020
n-$C_{16}H_{33}(OC_2H_4)_x OH$	25	-5.9	+0.024

2. Type of surfactant

- Nonionic surfactants (PEO type) have lower CMC's than ionic ones for the same HC chain length and temperature: ~ an order of magnitude.
- Micelle formation of ionic surfactants is less favored because of the electrostatic repulsion between adjacent charged head groups.

3. Presence of electrolytes

- For ionic surfactants, addition of electrolytes(salts) lowers CMC.
- Counter ions (of added salt) near the head groups reduce the electrostatic repulsion, and therefore micelle formation is more favored.

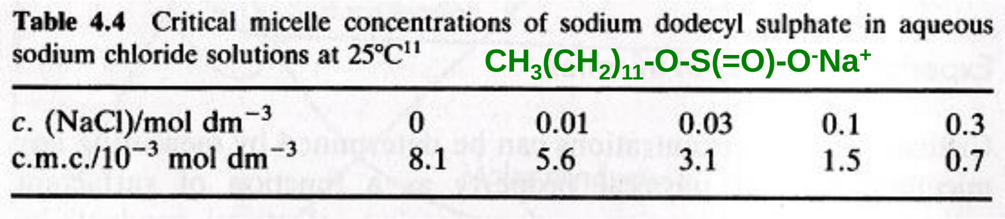


Table 4.4 Critical micelle concentrations of sodium dodecyl sulphate in aqueous sodium chloride solutions at 25°C[11]

$CH_3(CH_2)_{11}$-O-S(=O)-O^-Na^+

c. (NaCl)/mol dm^{-3}	0	0.01	0.03	0.1	0.3
c.m.c./10^{-3} mol dm^{-3}	8.1	5.6	3.1	1.5	0.7

4. Temperature

- Micelle formation is opposed by thermal agitation and CMC is expected to increases T↑. This is not always the case.
- T-dependence is, in general complex because of various competing factors.
- For ionic surfactant, the dependence is weak over a significant T-range.
- For nonionic surfactant (PEO type), CMC sharply↓ with T↑ due to the progressive dehydration of the PEO groups (Fig.3-23 b) until a point (Cloud point) is reached where very large micelles are formed, producing visible turbidity.
- The transition occurring at cloud point is sharp like a macroscopic phase transition.

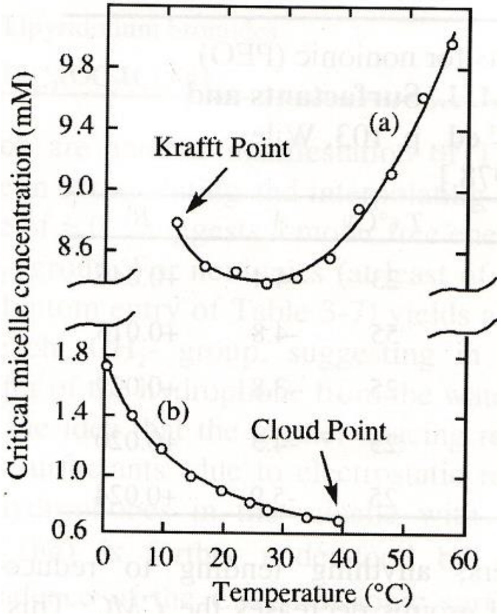


Fig. 3-23: Variation of *CMC* with temperature for:

(a) sodium dodecyl sulfate;

(b) $CH_3(CH_2)_9(C_2H_4O)_5OH$

Energetics of micellization

Interactions involved in micelle formation

Monomer

- Hydrophobic effect (breaking H-bonds among H_2O molecules (1)
- Hydration of the hydrophilic groups (2)
- Entropy of monomers wrt. Micelle (2)

Micelle

- Electrostatic repulsion between adjacent ionic head groups (1)
- Significant entropy of hydrophobic chains (1),

where (1) favors micellzation, while (2) disfavors it.

mS $\leftrightarrow$ $\mathbf{S_m}$ **;** $K = (c\beta/m) / [c(1-\beta)]^m$ **;** β = the fraction of total monomers in micelles

$\Delta G^0 = - RT \ln K$

Per mole of monomer, $\Delta G^0 = - (RT/m) \ln K$

$$= - (RT/m) \ln(c\beta/m) + RT \ln [c(1-\beta)] = RT [- \{ \ln(c\beta/m) \}/m + \ln \{c(1-\beta)\}]$$

At CMC, $\beta \sim 0$ and the 1st term ~ 0 because of a large m. Therefore,

$\Delta G^0 = RT \ln(CMC)$

$dG = VdP - SdT$, and $\Delta S^0 = - (\partial G^0/\partial T)_p$

$\Delta S^0 = - d(\Delta G^0)/dT = - RT\, d \ln(CMC)/dT - R \ln(CMC)$

$\Delta H^0 = \Delta G^0 + T\, \Delta S^0$

$= - RT^2\, d \ln(CMC)/dT$

- In general, CMC ↑ with T↑, meaning that micellization process is an exothermic process.
- As stated earlier, it is not always the case (ref. Fig.3-2 a).
- This suggests that the entropy of a micelle is not small, i.e., the inner hydrophobic part has significant freedom (motion).

TABLE 8.3 Some Thermodynamic Properties for the Micellization Process at or Near 25 °C for Various Surfactants

Surfactant	ΔG^0_{mic} (kJ mole^{-1})	ΔH^0_{mic} (kJ mole^{-1})	ΔS^0_{mic} (J K^{-1} mole^{-1})
Dodecyl pyridinium bromide	−21.0	−4.06	+56.9
Sodium dodecyl sulfate[a]	−21.9	+2.51	+81.9
N-Dodecyl-*N*,*N*-dimethyl glycine	−25.6	−5.86	+64.9
Polyoxyethylene(6) decanol	−27.3	+15.1	+142.0
N,*N*-Dimethyl dodecyl amine oxide	−25.4	+7.11	+109.0

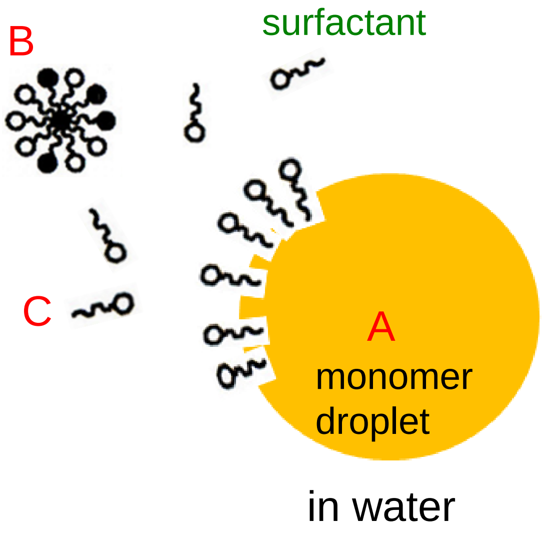
Source: Data from J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.

[a] Calculated in Example 8.4.

Solubilization

- Surfactant solutions above the CMC can solubilize otherwise insoluble organic material by incorporating it into the interior of micelles.
- Examples: the dye xylenol orange disolves only sparingly in pure water but gives a deep red solution with sodium dodecyl sulphate present above its CMC.
- Of practical importance in many applications;
  1) formulation of pharmaceutical and other water-insoluble ingredients,
  2) detergency (removal of oily soil),
  3) emulsion polymerization
  4) micellar catalysis

Emulsion polymerization: Harkins model



- Ex: polymerization of polystyrene
- Monomer distribution
  A: monomer droplet
  B: inside a micelle (solubilized)
  C: in water (dissolved, isolated)
- Polymerization occurs within micelles
  size and shape (spherical bead) regulation
- Radical polymerization
- Initiators(R·) formed in water, combining with dissolved monomers to form RM· → transferred into micelles; the probability of diffusion into a micelle is much greater than that into a monomer droplet because of much larger surface areas of micelles.

Spreading

Adhesion and cohesion

Dupré equation

- Work of adshesion $W_a = \gamma_A + \gamma_B - \gamma_{AB}$
- Work of cohesion $W_c = \gamma_A + \gamma_A - \gamma_{AA}\ (= 0) = 2\,\gamma_A$

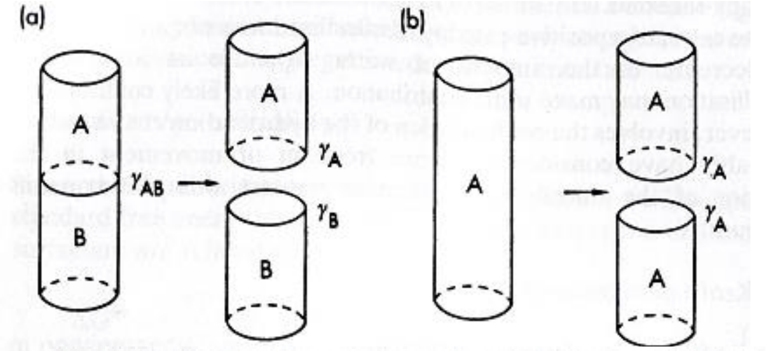
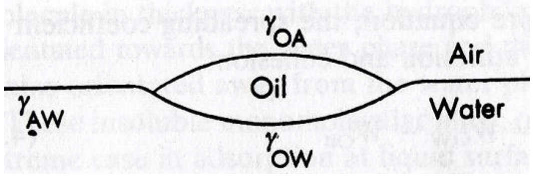


Figure 4.15 Work of adhesion (a) and of cohesion (b)

Spreading of one liquid on another

Figure 4.16 A drop of non-spreading oil on a water surface



- When a drop of an insoluble oil is placed on a clean water surface it may
  1) remain as a lens (non-spreading)
  2) spread as a thin film until it is uniformly distributed over the surface as a duplex film (a film thick enough for the two interface to be independent and posses characteristic surface tension)
  3) spread as a monolayer, leaving excess oil as lenses in equilibrium (Fig.4.17)
- If the lens in Fig, 4.16 is very thin, a contact area change of dA is accompanied by $dG = [(\gamma_O + \gamma_{OW}) - \gamma_W]\, dA = -S\, dA$

Initial spreading coefficient S

$S = \gamma_W - (\gamma_O + \gamma_{OW})$: oil on water

- If dG < 0 or S > 0: spontaneous spreading
- If dG > 0 or S < 0 :contraction of the lens
- If dG = 0 or S = 0 : equilibrium

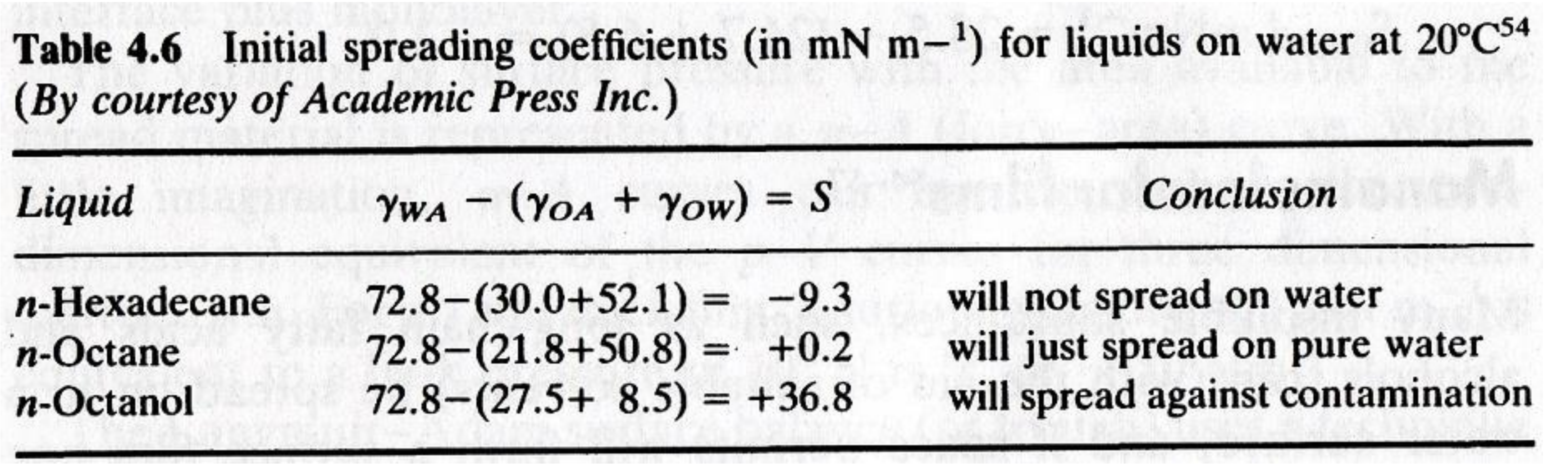


Table 4.6 Initial spreading coefficients (in mN m^{-1}) for liquids on water at 20°C[54] *(By courtesy of Academic Press Inc.)*

Liquid	$\gamma_{WA} - (\gamma_{OA} + \gamma_{OW}) = S$	*Conclusion*
n-Hexadecane	$72.8-(30.0+52.1) = -9.3$	will not spread on water
n-Octane	$72.8-(21.8+50.8) = +0.2$	will just spread on pure water
n-Octanol	$72.8-(27.5+8.5) = +36.8$	will spread against contamination

Spreading (cont'd)

- Substituting in the Dupré equation,

  $S = \gamma_W - (\gamma_O + \gamma_{OW}) = \gamma_W + \gamma_O - \gamma_{OW} - 2\gamma_O = W_{ow} - W_{oil}$

Factors influencing spreading

Impurities

- Impurities in water lowers γ_W more than it does γ_{OW}, especially if γ_{OW} is already low.

  ex: $S_{initial} = 0.2$ for n-octane on pure water

  $S_{initial} < 0$ for n-octane on contaminated water

Mutual saturation of one liquid with another

- The solubility of oil in water or vice versa at room temperature is small. However, the reduction in γ_W may be significant enough to affect spreading.
- Ex: Benzene on water

  $S_{initial} = 72.8 - (28.9 + 35.0) = 8.9 > 0$; spreading

  $S_{final} = 62.4 - (28.8 + 35.0) = -1.4 < 0$; non-spreading
- Initial spreading stops, and the film may retract slightly to form very flat lens.

- Ex: n-hexanol on water

  $S_{initial} = 72.8 - (28.9 + 35.0) = 8.9 > 0$; spreading

  $S_{final} = 28.5 - (24.7 + 6.8) = -3.0 < 0$; non-spreading

  The final state is shown in Fig. 4.17

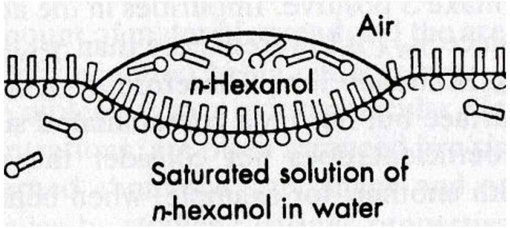


Figure 4.17 Spreading of *n*-hexanol on a water surface

Monomolecular Film

Insoluble (Langmuir) monolayer

- Surfactant molecules adsorb at the surface, resulting in the reduction of the surface tension.
  $\gamma_0 - \gamma = \pi$, where π is the spreading pressure

- The spreading pressure can be measured using a surface balance (Fig. 4.18).
- The surfactant molecules form a monolayer film.

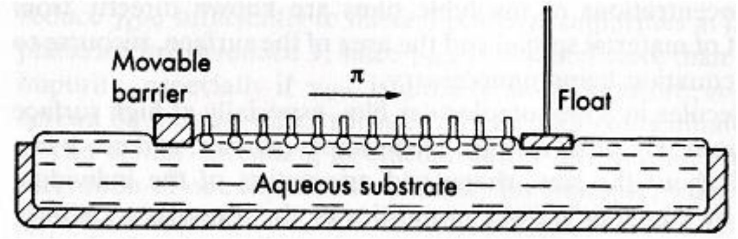


Figure 4.18 The principle of the Langmuir–Adam surface balance

Physical states of monomolecular films

- The monolayers can be roughly classified as

1. Condensed (solid) films

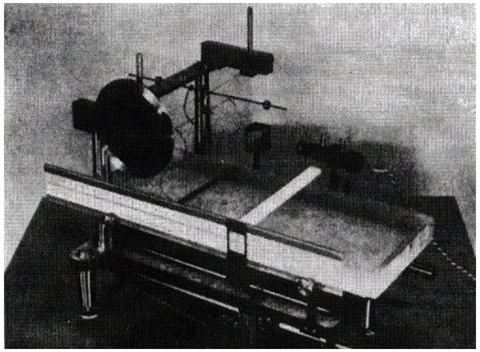
- Closely packed film with molecules steeply oriented towards the surface.

2. Liquid states

- Films are still coherent but occupy a much larger area than condensed films.
- It is like a highly compressible liquid, in this sense there is no real 3D equivalent.
- There exist a number of different expanded films, the most important being the liquid-expanded state.

3. 2D Gaseous films

- Molecules are separate and move about the surface independently.
- Surface pressure is exerted on the 2D barrier by a series of collisions



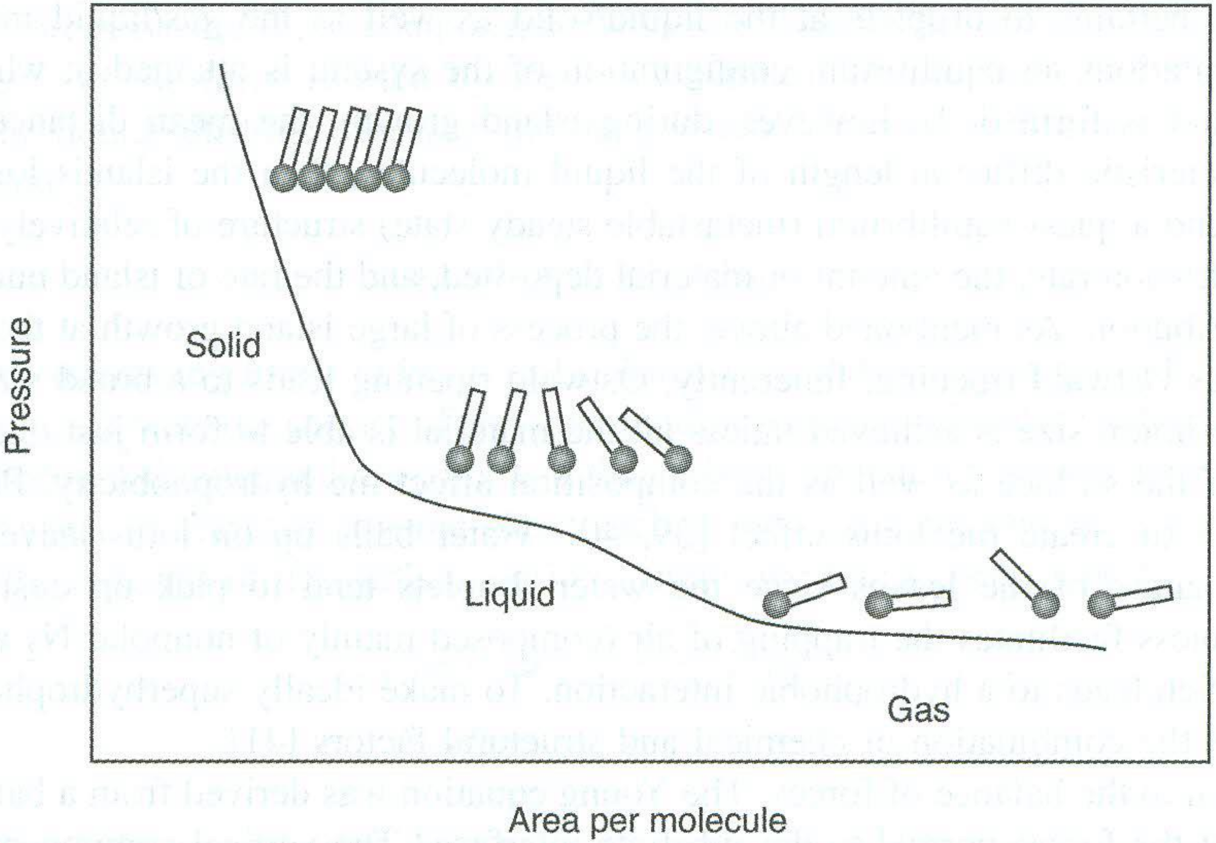

Solid
Liquid
Gas
Pressure
Area per molecule

Figure 5.5 *Phase diagram of surface pressure versus area per molecule (amphiphile) in a Langmuir film. The (hydrophobic) tails should only be considered rigid in the solid-like phase in which tail–tail interactions lock them into an ordered structure.*

Gaseous films

- Molecules in a gaseous film behaves like a 2D gas.
- Equation of state:

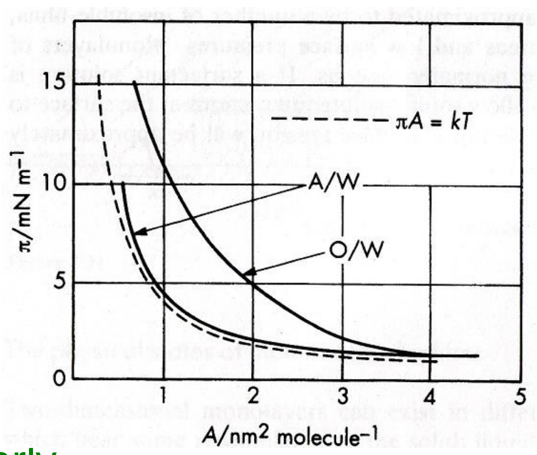
$\Gamma_2 = - c_2 / RT\ (d\gamma / dc_2)$, where Γ_2 is in mole/unit surface area.
$\pi = \gamma_0 - \gamma = bc_2$ at low concentration, and $d\gamma / dc_2 = - b = - \pi / c_2$.
$\Gamma_2 = - c_2 / RT\ (- \pi / c_2) = \pi / RT$,
$\Gamma_2 = n_2 \text{ (mole)}/\mathcal{A} = N_2 \text{ (molecules)}/\mathcal{A} N_A = \pi / RT = \pi / RT$
$\mathcal{A} N_A / N_2 = RT/ \pi \rightarrow \mathcal{A} / N_2 = kT / \pi$

Let **A** be the average surface area taken by a molecule, $A = \mathcal{A} / N_2$

$\boxed{\pi A = kT}$

- It is just a 2D ideal gas law.
- As for 3D van der Waals equation,
- $(\pi - \pi_0)(A - A_0) = kT$ is more appropriate for real gases.

- Ex: For CTAB (cetyl trimethyl ammonium bromide) $C_{16}H_{33}N(CH_3)_3^+Br^-$ at water- air interface, $\pi A = kT$ approximately holds, for



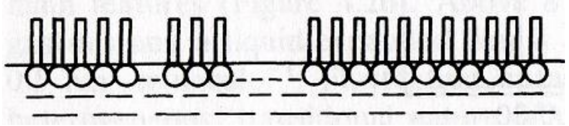
π – A curves for CTAB at Water-air and water-oil Interfaces at 20 °C

- The electrostatic repulsion between the ionic head group is nearly compensated by the attractive force between the alkyl chains.

- At water-oil interface, π is much larger for a given A because the repulsion $F = q^2/ 4\pi\varepsilon r$ is much stronger due to a smaller dielectric constant $\varepsilon_r (= \varepsilon/\varepsilon_0)$ of the oil.

Condensed films

Fig. 4.23

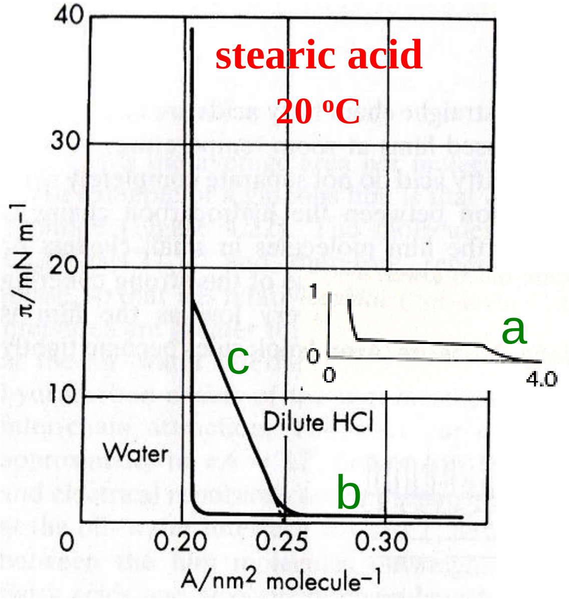


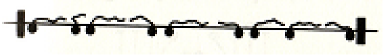
- Higher straight chain fatty acids such as stearic acid $CH_3(CH_2)_{16}COOH$ and palmitic acid$CH_3(CH_2)_{14}COOH$ are examples of condensed films.
- The cohesion (attractive interaction) is strong for these molecules, thus forming clusters and islands (Fig. 4.23) .
- Because of this strong cohering tendency the surface pressure remains very low as the film is compressed and then rises rapidly when the molecules become tightly packed together.

Ex: $\pi - A$ curves for stearic acid spread on HCl solution at 20 °C (bottom Fig)

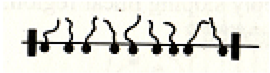
- At very low pressure molecular orientation is random and tilted (a)
- In the horizontal region the molecules are lifted up (b). The compressibility is large (easily compressible) and the pressure rise is very small.
- Initial pressure rise at **0.25 nm²** → initial packing of end groups.
- $\pi - A$ curve becomes very steep at **0.205 nm²** → more efficient packing by staggering and interlocking of the end groups.

- Limiting surface are = 0.20-0.22 nm² for straight chain fatty acid irrespective of the chain length.
- This value is close to the cross-section of crystalline SA measured by X-ray diffraction.
- Further compression beyond this limit will eventually lead to collapse or buckling of the film.

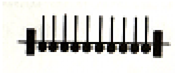




a) expanded

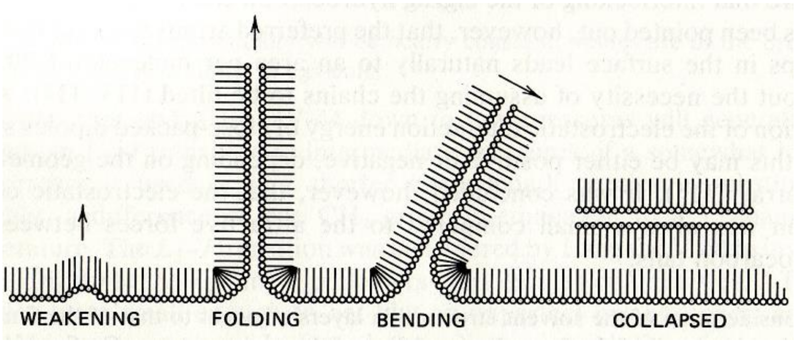


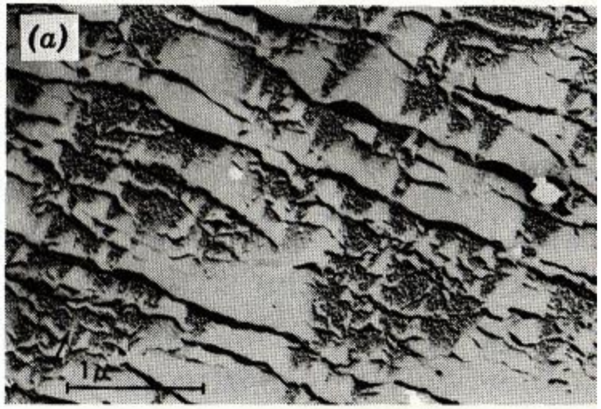
b) partially compressed

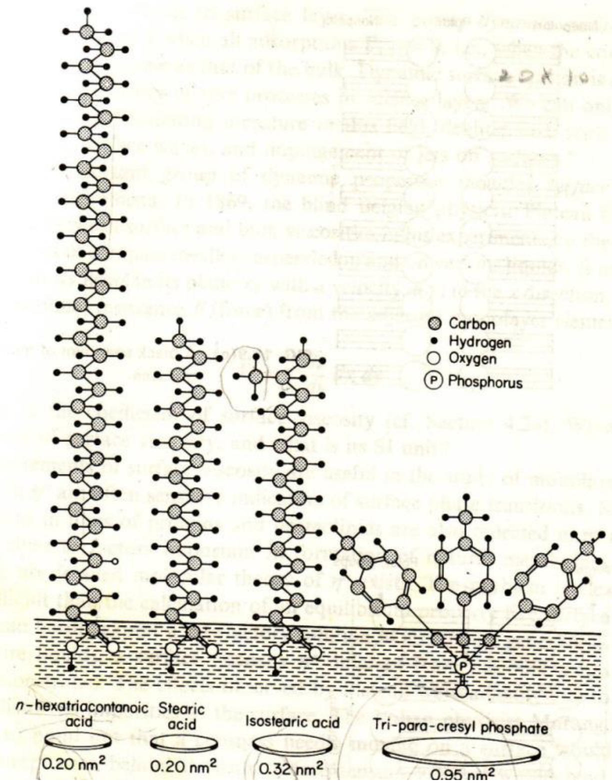


c) compressed

Various forms of film deformation beyond the elastic limit.


WEAKENING
FOLDING
BENDING
COLLAPSED



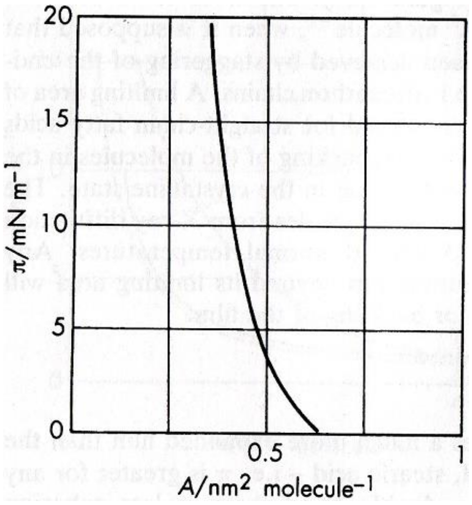

Carbon
Hydrogen
Oxygen
P Phosphorus
n-hexatriacontanoic acid
Stearic acid
Isostearic acid
Tri-para-cresyl phosphate
0.20 nm²
0.20 nm²
0.32 nm²
0.95 nm²

Cross-sectional areas of various surfactant molecules measures from the $\pi - A$ curves

Expanded films

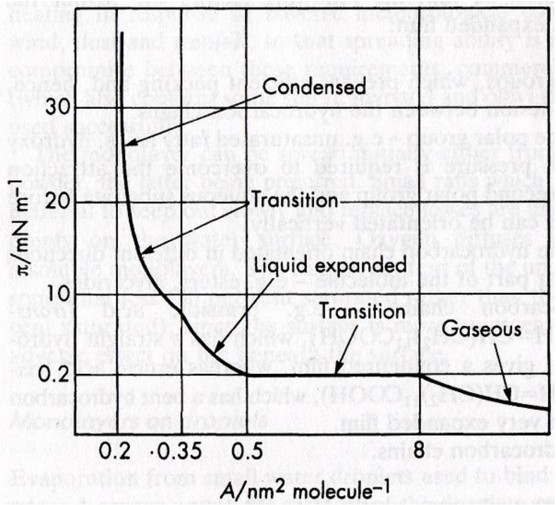
Oleicacid
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

- Oleicacid gives a much more expanded film than the corresponding saturated acid, stearic acid.
- Because of the double bond there is less cohesion between the hydrocarbon chains than the stearic acid and a greater affinity for the aqueous surface.
- So π is larger for a given A .



$\pi - A$ curve for oleicacid on water at **20 °C**

- The **$\pi - A$** curve for myristicacid,$CH_3(CH_2)_{12}COOH$, spread on 0.1 M HCl at **14 °C** (bottom Fig.) shows its overall resemblance to the p-V curve of a 3D real gas.
- But the liquid expanded state has no 3D equivalent.



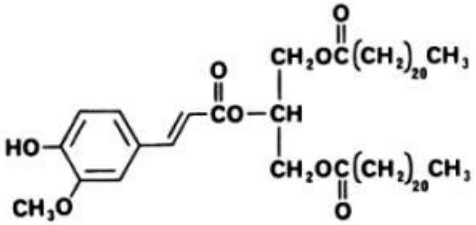
Factors influencing the physical state of monomolecular films

- Lateral cohesion between the end groups(attraction)
- Cohesion depends on the geometry and orientation of the HC chain
- Affinity for the aqueous phase (attraction)
- A longer HC chain has a higher tendency for cohesion
- The transition temperature is lowered by ~ 5- 8 ^{o}C by adding one more CH_2 group.

The following factors will favor the formation of an expanded films;

1. Bulky head groups (ex: $-SO_4$, $- PO_4$) prevent efficient packing and, hence, maximum cohesion between the HC chains.
2. More than one polar head groups- e.g. unsaturated fatty acids, hydroxy acids.
3. More than one HC chain oriented in different directionsn for the polar part of the molecule- e.g. esters, glycerides
4. Bent HC chains gives very expanded films.
5. Branched HC chains.
6. The nature of the substrates.

- PH is very important for ionizable monolayers.
- The repulsion between ionized COO^- groups favors the formation of gaseous or liquid-expanded films at low T.
- Dissolved electrolytes have a profound effect on the state of the film; Ex: Ca2+ ions form insoluble calcium soaps with fatty acid films (unless the pH is very low), thus making the film more condensed.



triiglyceride

Film deposition

Langmuir-Blodgett film

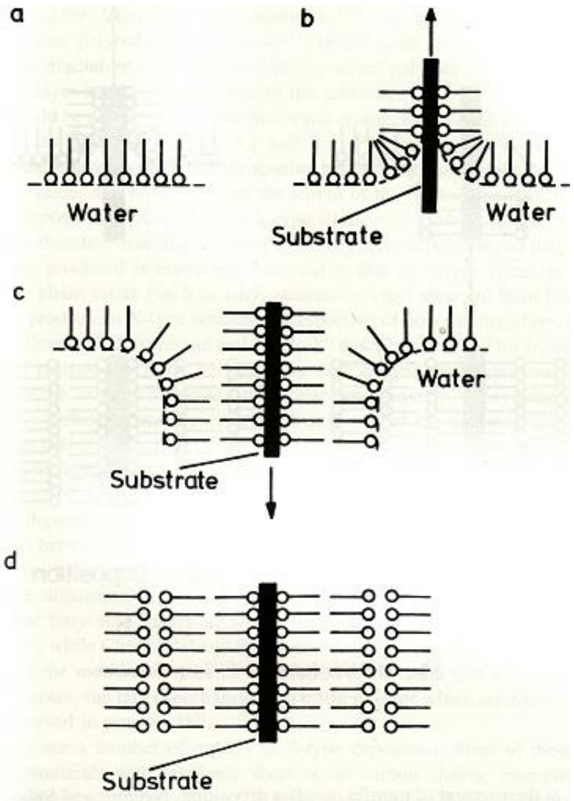

a
b
Water
Substrate
Water
c
Water
Substrate
d
Substrate

Figure 3.1. Y-type Langmuir–Blodgett film deposition.

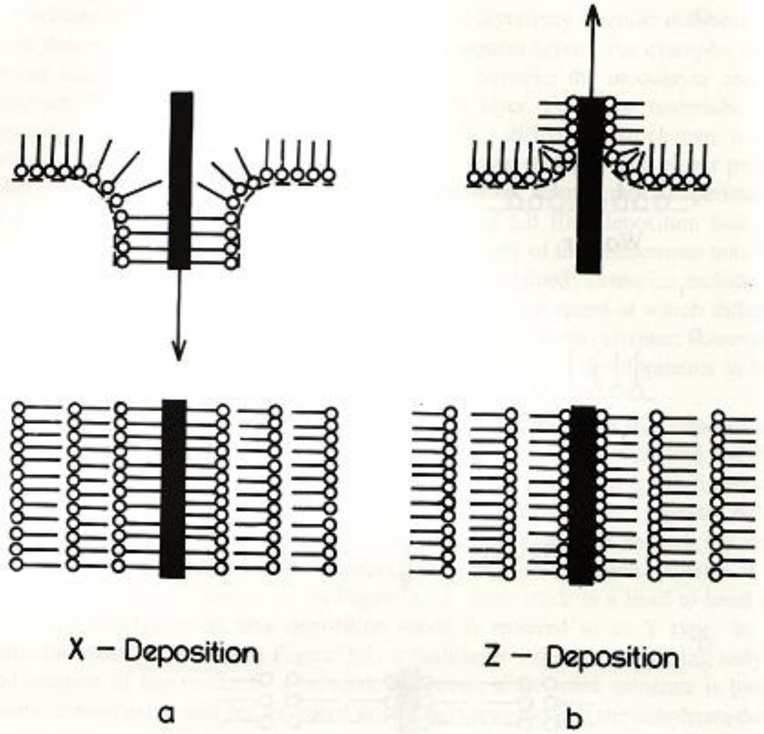

X – Deposition
Z – Deposition
a
b

Figure 3.2. (a) X-type deposition; (b) Z-type deposition.

Controlling parameters: pH, surface pressure etc.

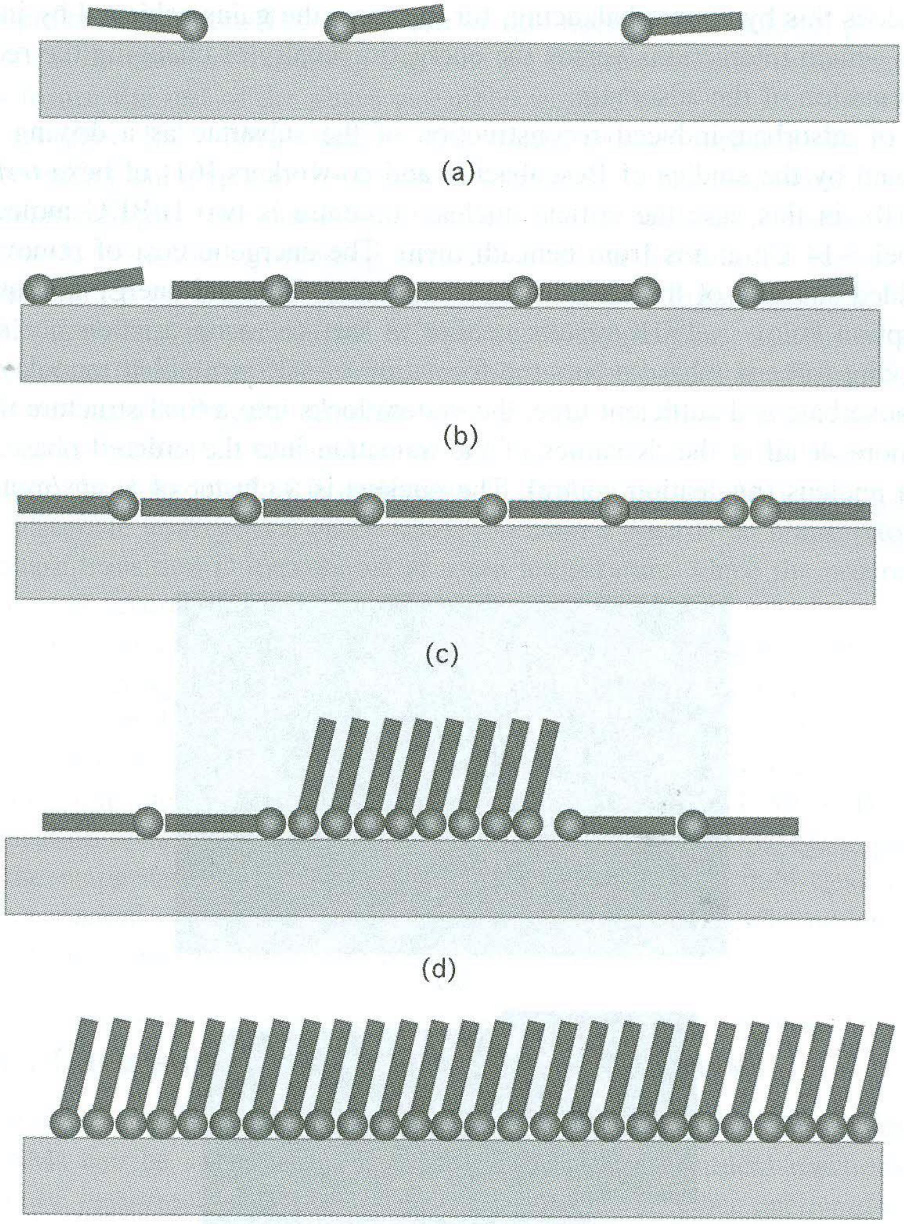


Figure 5.11 *Mechanism of self assembly: (a) disordered, mobile lattice gas; (b) lattice gas plus ordered islands; (c) saturated surface-aligned phase; (d) nucleation of solid-phase islands; (e) saturated solid phase. Self-assembly progresses in stages, as long as a sufficient supply of adsorbates is available, until the thermodynamically most favoured final state is reached. Not depicted in the figure is a reconstruction of the surface, which often accompanies the process.*

Thermodynamics of liquid Interfaces

Thermodynamics of surface (or interface)

- The surface tension γ of a pure solvent changes when a solute is added.
- $\Delta\gamma$ ($= \gamma - \gamma_0$) depends on the concentration c of the solute.
- Thermodynamics can tell the functional relation $\Delta\gamma(c)$.
- The thermodynamic equations for a bulk need to be modified when applied for a surface.

$dU = dq + dw = TdS - P\,dV$ for single-component bulk

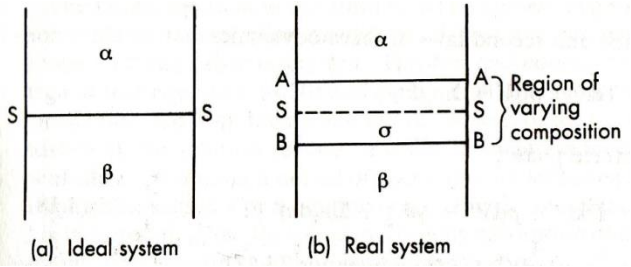
$dU = dq + dw = TdS - P\,dV + \Sigma\, \mu_i dn_i$ for multi-component bulk

$U = TS - PV + \Sigma\, \mu_i n_i$ integration at constant T,P, and μ_i

$$\boxed{dU = SdT - VdP + \Sigma\, n_i d\mu_i = 0}$$

Gibbs dividing surface (interface)

- The interface of a real system is blurred.
- The system is considered consisting of
  α phase + βphase + σ plane (ideal abrupt interface)
- The choice of the locus of the σ plane is arbitrarily.



$dU^\sigma = dq + dw = TdS^\sigma - P\,dV^\sigma + \gamma\, dA + \Sigma\, \mu dn_i^\sigma$; surface, multi-component

$U^\sigma = q + w = TS^\sigma - P\,V^\sigma + \gamma\, A + \Sigma\, \mu n_i^\sigma$

$$\boxed{dU^\sigma = S^\sigma\, dT - V^\sigma\, dP + A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0}$$ Gibs-Duhem equation (extended to include the surface)

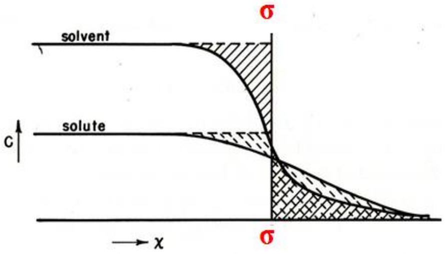
Gibbs adsorption equation

- In general, the concentration profile of solute is different from that of solvent.
- $dU^\sigma = S^\sigma dT - V^\sigma dP + A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$
- $A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$ at constant T and P
- $n_i^{total} = n_i^\alpha + n_i^\beta + n_i^\sigma$, where n is the number of molecules (solvent or solute).→ Material conservation

  $\Gamma_i \equiv n_i^\sigma/A$: surface excess
- $A\, d\gamma + \Sigma\, n_i^\sigma d\mu_i = 0$ and $d\gamma = -\Sigma\, (n_i^\sigma/A) d\mu_i = -\Sigma\, \Gamma_i\, d\mu_i$
- For a binary system, solvent (phase1) + solute (phase 2),

  $d\gamma = -(\Gamma_1\, d\mu_1 + \Gamma_2\, d\mu_2)$
- The position of the σ plane is conveniently taken so that $\Gamma_1 = 0$ for the solvent.
- Then, $d\gamma = -\Gamma_2\, d\mu_2$
- $\mu_2 = \mu_2{}^0 + RT \ln a_2$ For a dilute solution, $a_2 \sim c_2$
- $d\mu_2 = -RT\, (dc_2/c_2)$

  $\boxed{\Gamma_2 = -c_2 / RT\, (d\gamma / dc_2)}$: Gibbs adsorption equation
- $\Gamma_2 > 0$ (+ adsorption): accumulation of solute at the surface (interface).
  Namely, the solute likes to be at the surface (interface).
- $\Gamma_2 < 0$ (- adsorption): depletion of solute at the surface (interface).
  The solute tends to avoid the surface (interface).
- If $\Gamma_2 > 0$, i.e., $d\gamma / dc_2 < 0$, γ decreases with increasing solute concentration.
- Surfactant molecules which causes a large $\Delta\gamma < 0$ strongly positively adsorbs at surface (interface)



concentration profile along the x direction (⊥σ)

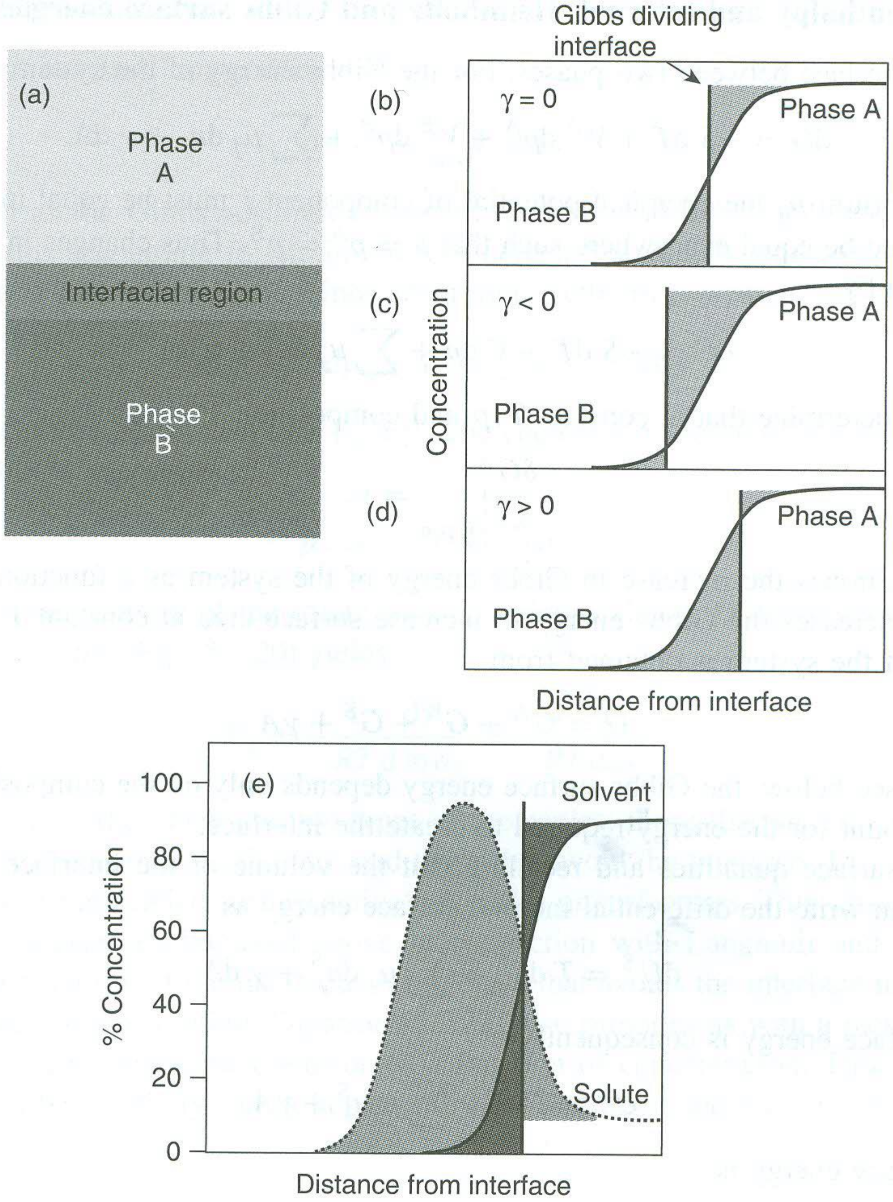

Gibbs dividing interface
(a)
Phase A
Interfacial region
Phase B
(b)
γ = 0
Phase A
Phase B
(c)
γ < 0
Phase A
Phase B
Concentration
(d)
γ > 0
Phase A
Phase B
Distance from interface
100
(e)
Solvent
80
60
40
20
0
% Concentration
Solute
Distance from interface

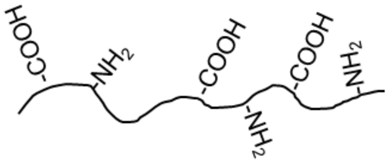
Figure 5.13 *The definition of the Gibbs model of an interface. (a) The system is composed of two homogeneous phases separated by an interfacial region. (b)–(d) In the interfacial region, the composition varies. The Gibbs surface is drawn at an arbitrary plane in the interfacial region, conventionally such that the surface excess of one component vanishes as shown in (b). (e) In a solution, the composition of a solute near the interface is generally not the same as in the bulk and the Gibbs surface is drawn such that the surface excess of the solvent vanishes.*

Electrified and charged Interfaces

Origin of the charge at colloidal surfaces

1. Ionization

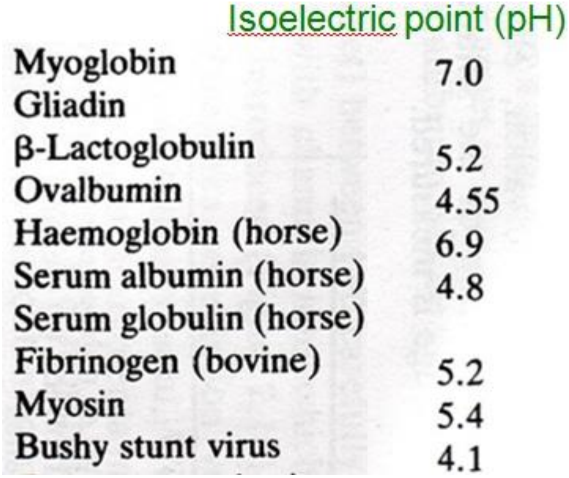
- Proteins acquire their charge by ionization of –COOH and NH_2 group.
- The degree of ionization, hence the charge, is pH-dependent.
- Isoelectric point (pH) : the pH at which the net charge is zero
- Experimentally measured electrophoretic mobility can provide information on the sign and magnitude of the surface charge



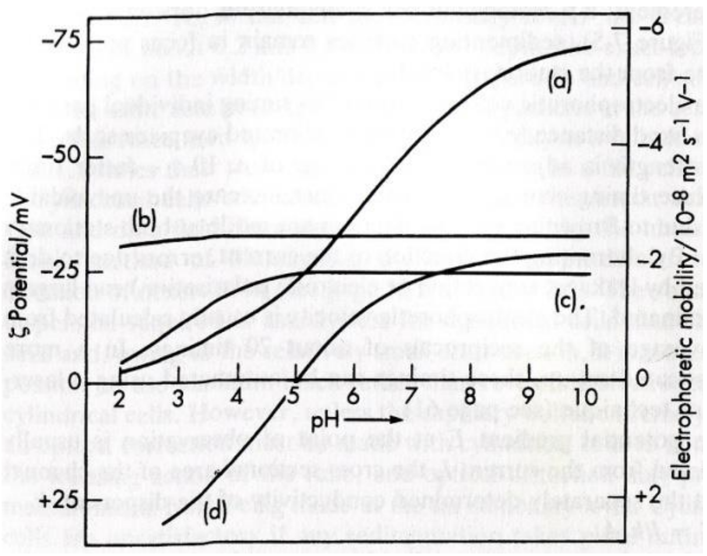
proteins

$-COOH \rightarrow -COO^{-} + H^{+}$

$-NH_2 + H^{+} \rightarrow -NH_3^{+}$

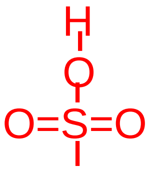


	Isoelectric point (pH)
Myoglobin	7.0
Gliadin	
β-Lactoglobulin	5.2
Ovalbumin	4.55
Haemoglobin (horse)	6.9
Serum albumin (horse)	4.8
Serum globulin (horse)	
Fibrinogen (bovine)	5.2
Myosin	5.4
Bushy stunt virus	4.1



a) HC oil droplet, b) Sulfonated PS
c) Arabic acid (carboxylated polymer),
d) Serum albumin adsorbed on to oil droplets

2. Ion adsorption



$$\begin{array}{c} H \\ | \\ O \\ | \\ O{=}S{=}O \\ | \end{array}$$

Sulfonic acid

- Unequal adsorption of (+) and (-) ions at colloid surfaces form the bulk solution.
- Ions may be electrolytes, the ubiquitous H^+ and OH^- present in the solution.
  *(+) ions are usually small and so more hydrated than (-) ions.
  * (-) ions are less hydrated and easily polarized.
- Larger hydrated (+) ions have a smaller adsorption tendency: weaker electrostatic interaction with the surface.
- Surfaces in contact with aqueous media are more often (-)ly charged than (+)ly charged.

- Hydrocarbon oil droplets and even air bubbles in aqueous media are (-)ly charged, which can be explained in terms of Gibbs adsorption at the interface:
  * The smaller (+) ions usually have a more negative adsorption at the interface than (-) ions.
  * (-) ions dislike to be at the interface than (+) ions do.
  * $\gamma\uparrow$ by addition of NaCl in water has the same origin.

ex: μ (oil droplet) = $-6\times10^{-8}\ m^2/V.s$ vs. μ (Cl^- ion) = $-7.8\times10^{-8}\ m^2/V.s$

Electrophoresis: $F = F_{elec} - F_{fric} = 0$ at equilibrium → $qE = fv_d = 6\pi\eta a v_d$

mobility $\mu \equiv v_d/E = q/6\pi\eta a$

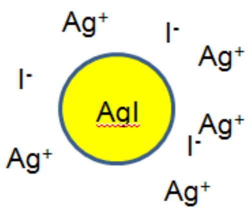
* Similar μ values mean that the oil droplet has a very large surface charge.

3. Ion dissolution

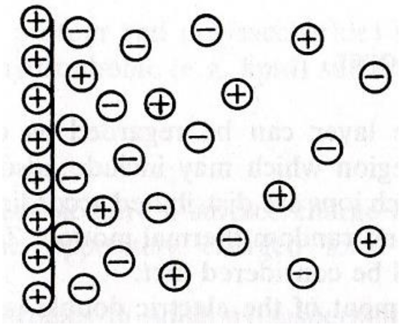
- Ionic substances can acquire a surface charge by unequal dissolution of (+) and (-) ions.
  Ex: $AgI(s) \leftrightarrow Ag^+(aq) + I^-(aq)$: $K_{sp} = [Ag^+][I^-] \sim 10^{-16}$ at RT.
  * Zero point of charge is achieved at $pAg = 5.5 \rightarrow [Ag^+] = 3.16 \times 10^{-6}$ M
  * The smaller Ag^+ ion is less strongly bound than I^- ion in AgI(s) and so it is mobile.
- The smaller ion has a stronger tendency of solvation (hydration) than a larger ion.
  $Ag^+(s) \rightarrow Ag^+(aq)$; ΔG_{Ag} and $I^-(s) \rightarrow I^-(aq)$; $\Delta G_I > \Delta G_{Ag}$ (more negative).

- Additionally added Ag^+ or I^- ions can modify the surface charge by via adsorption.
  * Thus, Ag^+ or I^- is called the potential-determining ion.

- H+ and OH- ions are the potential-determining ions for hydrous metal oxide sols.
  * $-M\text{-}OH + H^+ \rightarrow -M\text{-}OH_2^+$
  * $-M\text{-}OH + OH^- \rightarrow -M\text{-}O^- + H_2O$

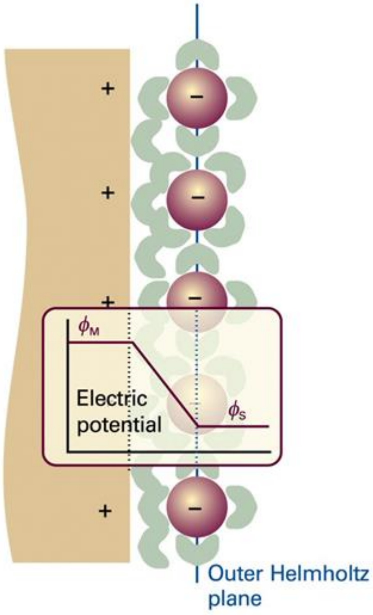


Diffuse (electrical) double layer



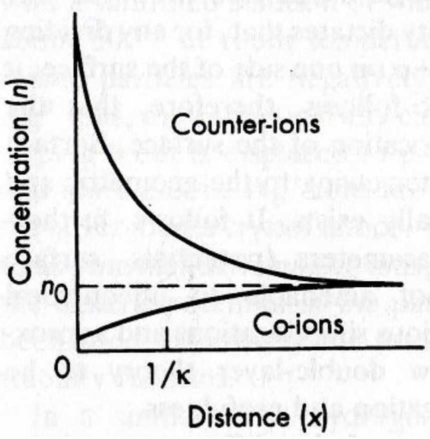
- Electrolytes present in the solution.
- Electrical neutrality.
- Coions and counter ions
- Coions are repelled and counter-ions are attracted by the surface charges.
- How are these ions distributed near the charged surface ?

Helmholtz model



- Simplest model but it does not accurately represent the actual double layer.
- **Inner** Helmholtz plane: charged surface
- **Outer** Helmholtz plane: fixed distance from the surface equal to the **radius of a solvated counter-ion**.
- Inner region: only solvent molecules present.
- Outside OHP: random distribution of both ions.
- Electrical potential variation as show in the right figure.

Gouy-Chapman model



Assumptions

1. Uniformly charged flat surface of infinite extent.
2. Ions in the diffuse layer are point charges.
3. Symmetrical ions of z^+z^- type.

Boltzmann distribution law.

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] \qquad n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right]$$

$$\rho = ze(n_+ - n_-) = zen_0\left(\exp\left[\frac{-ze\psi}{kT}\right] - \exp\left[\frac{+ze\psi}{kT}\right]\right) = -2zen_0 \sinh\frac{ze\psi}{kT}$$

$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} \qquad \frac{d^2\psi}{dx^2} = \frac{2zen_0}{\epsilon}\sinh\frac{ze\psi}{kT}$$

Poisson-Boltzmann equation

Boundary conditions: $\psi(0) = \psi_0$ at the flat surface and $d\psi/dx = 0$ at $x = \infty$.

$$\psi = \frac{2kT}{ze}\ln\left(\frac{1+\gamma\exp[-\kappa x]}{1-\gamma\exp[-\kappa x]}\right) \qquad \gamma = \frac{\exp[ze\psi_0/2kT]-1}{\exp[ze\psi_0/2kT]+1}$$

$$\kappa = \left(\frac{2e^2n_0z^2}{\epsilon kT}\right)^{½} = \left(\frac{2e^2N_Acz^2}{\epsilon kT}\right)^{½} = \left(\frac{2F^2cz^2}{\epsilon RT}\right)^{½}$$

1/ κ = Debye screening = avg. EDL
(shielding) length thickness

Debye-Hückel approximation

If $ze\psi_0/2kT \ll 1$ $(kT/e = 25.6 \text{ mV at } 25°\text{C})$

$$n_+ = n_0 \exp\left[\frac{-ze\psi}{kT}\right] = n_0(1 - ze\psi/kT)$$

$$n_- = n_0 \exp\left[\frac{+ze\psi}{kT}\right] = n_0(1 + ze\psi/kT)$$

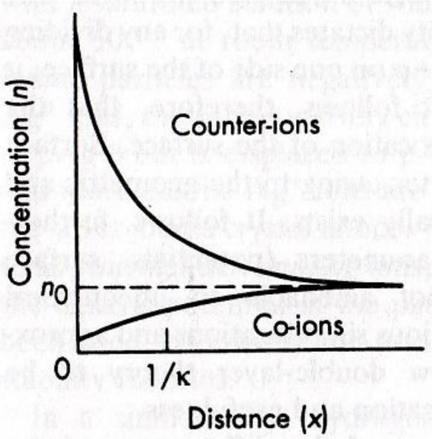
$$\rho = ze(n_+ - n_-) = -2zen_0 \frac{ze\psi}{kT}$$

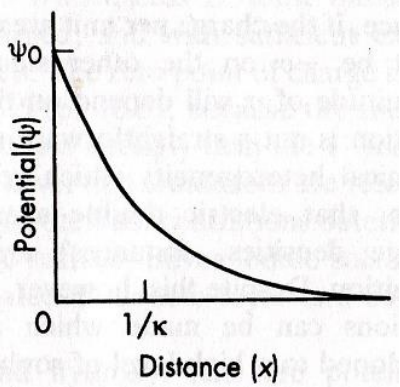
$$\frac{d^2\psi}{dx^2} = -\frac{\rho}{\epsilon} = (2n_0 z^2 e^2/\varepsilon kT)\psi = \kappa^2 \psi$$

$$\frac{d^2\psi}{dx^2} - \kappa^2 \psi = 0 \rightarrow \psi = \psi_0 \exp[-\kappa x]$$

- $\psi = \psi_0 \exp(\kappa x)$ was discarded because of $d\psi/dx = 0$ at $x = \infty$.

$$\sigma_0 = -\int_0^\infty \rho dx \rightarrow \sigma_0 = \epsilon\kappa\psi_0$$





Surface charge vs. surface potential

$$\sigma_0 = \epsilon\kappa\psi_0$$

- Meaning of $1/\kappa$: thick of diffuse double layer.
- ψ_0 determined by σ_0 and κ or
  σ_0 determined by ψ_0 and κ

For a symmetrical electrolyte at 25 °C

$$\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{\frac{1}{2}} \text{m}^{-1}$$

$\kappa \sim 1$ nm for $c = 0.1$ M and
$\kappa \sim 10$ nm for $c = 10^{-3}$ M
of 1:1 electrolyte

Two cases

1) ψ_0 fixed and σ_0 adjusted:

- When the surface charge is due to adsorption of potential-determining ion. ex: AgI sol.
  → ψ_0 is determined by the concentration of Ag^+ (and I^-) ions in solution.
- Addition of inert electrolyte increases κ and results in more adsorption of ion to keep ψ_0 approximately constant.

2) σ_0 fixed and ψ_0 adjusted:

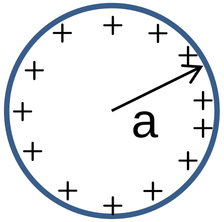
- The charge density at an ionogenic surface remains constant upon adding an inert electrolyte and ψ_0 decreases.
  ex: protein solution

Gouy-Chapman model for spherical interface

$$\nabla^2 \psi = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{r^2\mathrm{d}\psi}{\mathrm{d}r}\right) = \frac{2zen_0}{\epsilon}\sinh\frac{ze\psi}{kT} \qquad (7.11)$$

within Debye-Hückel approximation

$$\nabla^2\psi = \kappa^2\psi$$



Boundary conditions

$$\psi = 0,\ \mathrm{d}\psi/\mathrm{d}r = 0 \text{ at } r = \infty;$$

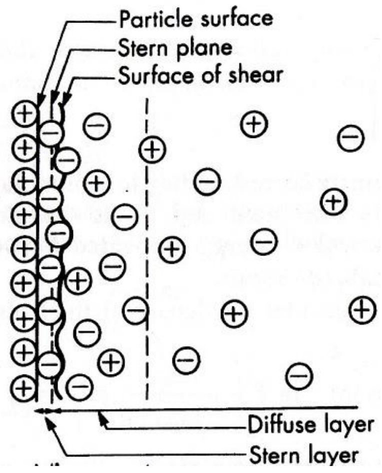
$$\psi = \psi_0 \frac{a}{r} \exp[-\kappa(r - a)]$$

- Debye-Hückel approximation (zeψ << ~ 25 meV) is often not a good one for colloid and surface phenomena. Unapproximated, numerical solution to eq.(7.11) can be computed.

Stern model

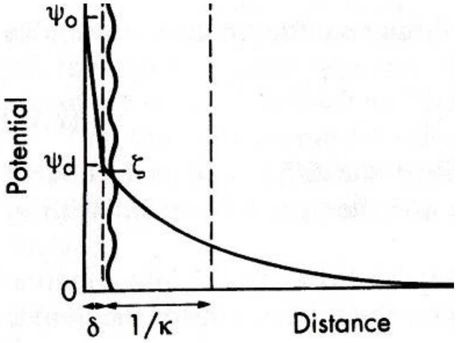
Modification of the Gouy-Chapman model by considering

1. Finite size of ion: ions cannot approach the surface (Stern plane) within the radius of hydrated ion.
2. Specific ion adsorption in the Stern layer is included.
3. EDL is divided into two parts: inner part + diffuse DL, the boundary of which is the Stern plane.
4. Surface of sheer is located outside of the Stern plane because of the hydrated ions
5. The potential at the sheer plane is called electrokinetic or zeta (ζ) potential, which can be measured experimentally.

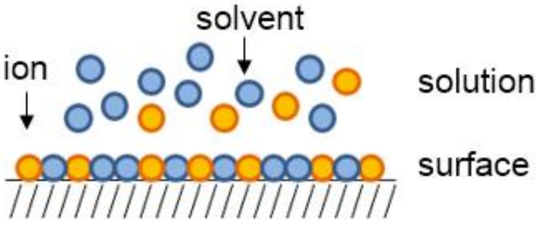


Inner part of EDL(Stern layer)

- Thickness of δ ~ 5 Å
- Specifically adsorbed ions may be present.
- Oriented solvent molecules in the Stern layer has a smaller ε'(~5 -10) < ε(= 78.5 for H_2O) due to mutual depolarization.



Specific ion adsorption



- Counter-ion adsorption in Stern plane
- I(bulk) + S(surf) ↔ I(surf) + S(bulk); solvent =1, ion = 2

  $K' = a_2^s a_1^b / a_1^s a_2^b$

- Assuming a 2D ideal solution for the adsorbed layer
- $a_i \sim c_i = n x_i$; n = total moles/unit surface area, x_i = mole fraction
- $a_2^s / a_1^s = x_2^s / x_1^s = x_2^s / (1- x_2^s)$
- $K' a_2^b / a_1^b = a_1^s / a_2^s = x_2^s / (1-x_2^s)$
- Solving for x_2^s, **$x_2^s = K' (a_2^b / a_1^b) / \{(1+ K'(a_2^b / a_1^b)\} = 1/ \{1+ (a_1^b / K' a_2^b)\}$**
- Since **$x_2^s + x_1^s = 1$**, **$x_2^s = \theta$** (coverage).
- Letting **$K' / a_1^b = K$** (a new constant), **$\theta = K a_2^b / (1+ K a_2^b)$.**
- This is one form of the Langmuir adsorption isotherm.

  cf: for gas adsorption **$\theta = Kp / (1+Kp)$**

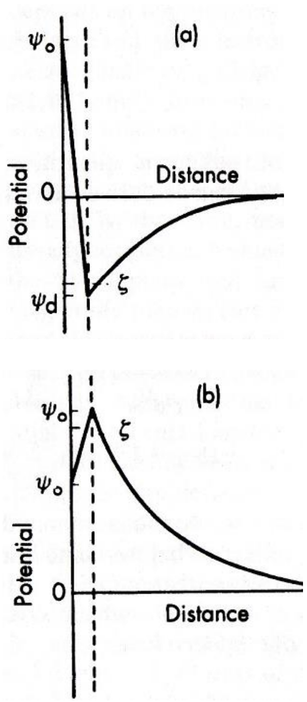
- $\Delta G^0 = - RT \ln K$
- $\Delta G^0 = \Delta H^0 - T\Delta S^0 \sim \Delta H^0 = \Delta E^0$ (no PV term involved)

  $= N_A (ze\, \psi_d + \Phi) \rightarrow K = \exp\{- N_A (ze\, \psi_d + \Phi)/RT\}$

  (Φ = van der Waals term)

- The electrical interaction is the dominant term at RT.
- Let σ_1 is the surface charge density due to specifically adsorbed ions.
- $x_2^s = \sigma_1 / \sigma_m = 1/ \{1+ (a_1^b / K a_2^b)\} \sim 1/ \{1+ (c_1^b / K c_2^b)\}$
- $c_1^b / c_2^b = (1/V_m) / (n_0/N_A)$, where V_m is the molar volume of solvent.

- **$\sigma_1 = \sigma_m / [1+ (N_A / V_m n_0) \exp\{(ze\psi_d + \Phi)/kT\}]$**



a) Reversal of charge due to the adsorption of surface-active or polyvalent counter-ions.

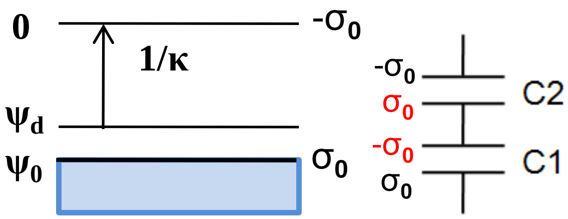
b) Adsorption of surface-active co-ions.

Capacitance of EDL

- Usually counter-ion adsorption is dominant.
- Adsorption of polyvalent ions can result is charge reversal.

I. If there is no specifically adsorbed ions

$$C_1 = \frac{\sigma_0}{\psi_0 - \psi_d} \quad \text{and} \quad C_2 = \frac{\sigma_0}{\psi_d} \quad \rightarrow \quad \psi_d = \frac{C_1 \psi_0}{C_1 + C_2}$$



II. If specifically adsorbed ions are present

$\sigma_0 + \sigma_1 + \sigma_2 = 0$; electrical neutrality

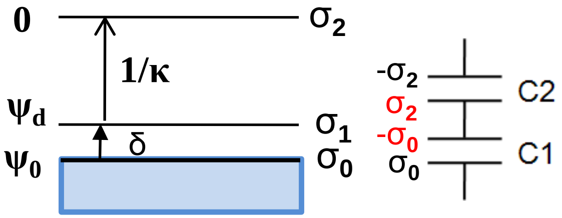
$$\sigma_0 = \frac{\epsilon'}{\delta}(\psi_0 - \psi_d), \quad \sigma_1 = \frac{\sigma_m}{1 + \frac{N_A}{n_0 v_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]}$$

$$\sigma_0 + \sigma_1 + \sigma_2 =$$

$$\frac{\epsilon'}{\delta}(\psi_0 - \psi_d) + \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]} - (8n_0 \epsilon kT)^{1/2} \sinh\frac{ze\psi_d}{2kT} = 0$$

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2},$$

$$C_2 = \frac{\sigma_2}{\psi_d} = \epsilon\kappa = 2.28\left(\frac{cz^2}{\text{mol dm}^{-3}}\right)^{1/2} \text{F m}^{-2} \text{ for aqueous electrolyte at } 25°\text{C} \qquad (1)$$



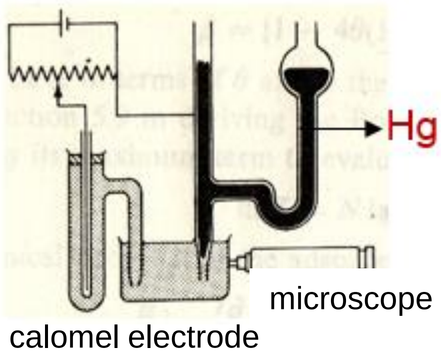
- For Hg- aqueous electrolyte interfaces C can be measured from electrocapillary measurements and
- for AgI- aqueous electrolyte interfaces from potentiometric measurements.
- C_2 can be calculated from the eq.(1) above.
- Then, from $C_1 = \epsilon'/\delta$ (Stern layer capacitance) can be obtained.
- For the AgI- aqueous electrolyte interface C1! 0.1- 0.2 Fm^{-2}.
- Taking δ = 5 Å, one gets **ε'** = 5-10 (<< ε = 78.5 for H_2O at RT) → ordering of H_2O in the Stern layer.

Electrocapilarity

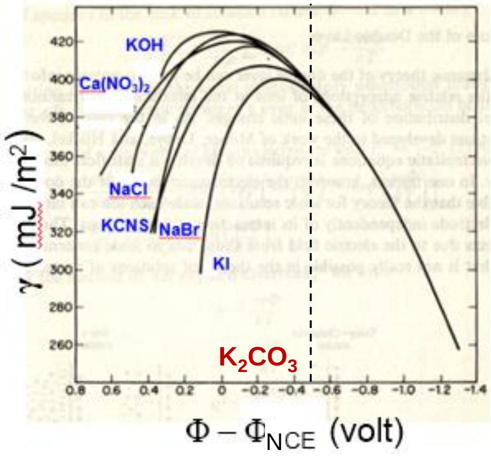
Lippmann apparatus

- Ideally non-polarizable normal calomel electrode (reference)
- Hg electrode in contact with nonreactive salt solution (ideally polarizable electrode).
- When a potential Φ is to the Hg electrode, charge accumulates at its surface.
- Simultaneously, the γ of Hg changes to cause a shift of the meniscus, which is observed with a microscope.
- $dG = \gamma\, dA + \Phi\, dQ$ at fixed T,P, and μ.
- Similarly to the Gibbs-Duhem equation,
  $A\, d\gamma + Q\, d\Phi = 0 \rightarrow (\partial\gamma / \partial\Phi)_{T,P,\mu} = - Q/A = \sigma$
- The capacitance of the EDL is
  $C = (\partial Q / \partial\Phi)/A = -(\partial^2\gamma / \partial\Phi^2)$; constant → parabolic γ - Φ curve.

- γ is maximum when the surface is not charged.
- For an inert electrolyte such as K_2CO_3, γ_{max} occurs at $\Phi - \Phi_{NCE} = - 0.48$ V.
- For other electrolytes the maximum shifts due to specific ion adsorption.
  Ex: - ion adsorption (OH^-, Cl^-, Br^-, CNS^- etc.) as shown in the Figure.

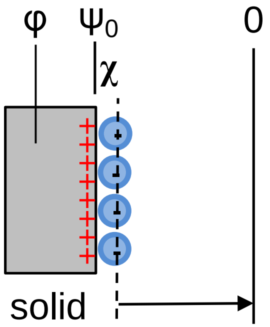


Lippmann apparatus



electrocapillary curve

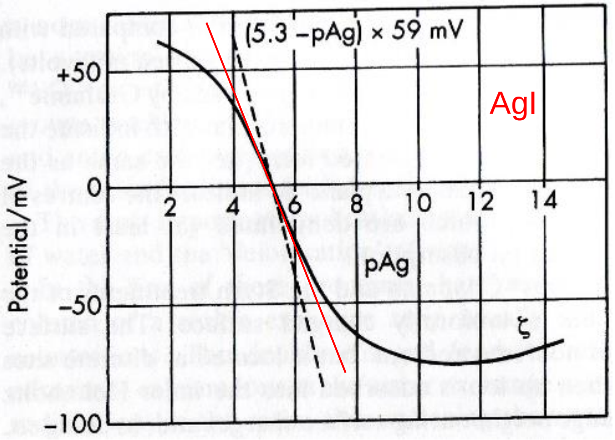
Surface potentials



- The measurable electric potential difference φ between the solid interior and the bulk solution varies according to the Nernst equation; $E = E^o - RT \ln Q/ \nu F$
  Ex: For a AgI-aqueous electrolyte interface
  $d\varphi /d(pAg) = - 2.303\, RT/F$ (= - 59 mV at 25 C)
- $\varphi = \psi + \chi$, where χ is due to adsorbed ions and orientation dipolar solvent.

- Experimentally, $\left(\frac{d\zeta}{d(pAg)}\right)_{\zeta \to 0}$ = - 40 mV at RT was found.
- $$\left(\frac{d\zeta}{d(pAg)}\right)_{\zeta \to 0} = \left(\frac{d\psi_0}{d(pAg)}\right)\left(\frac{d\psi_d}{d\psi_0}\right)_{\zeta \to 0} = -59\frac{C_1}{C_1+C_2}\,\mathrm{mV}$$ **(1)**

- The measures C_1 and C_2 values are qualitatively consisten with the above eq.(1)
- The Stern layer model and the assumptions made are qualitatively correct.



Electrokinetic Phenomena

Relative motion between charged surface and diffuse double layer

1. Electrophoresis: $\mathscr{E}$ → charge particle movement.
2. Electro-osmosis: $\mathscr{E}$ → DL layer movement against fixed surface charge.
3. Streaming potential: DL layer movement → $\mathscr{E}$ generation.
4. Sedimentation potential: charge particle movement → $\mathscr{E}$ generation.

- All arising from the relative movement of particle with respect to the liquid.
- $\mathscr{E}$ field → relative motion: Electrophoresis, electro-osmosis
- relative motion → $\mathscr{E}$ field: Streaming potential,
  sedimentation potential

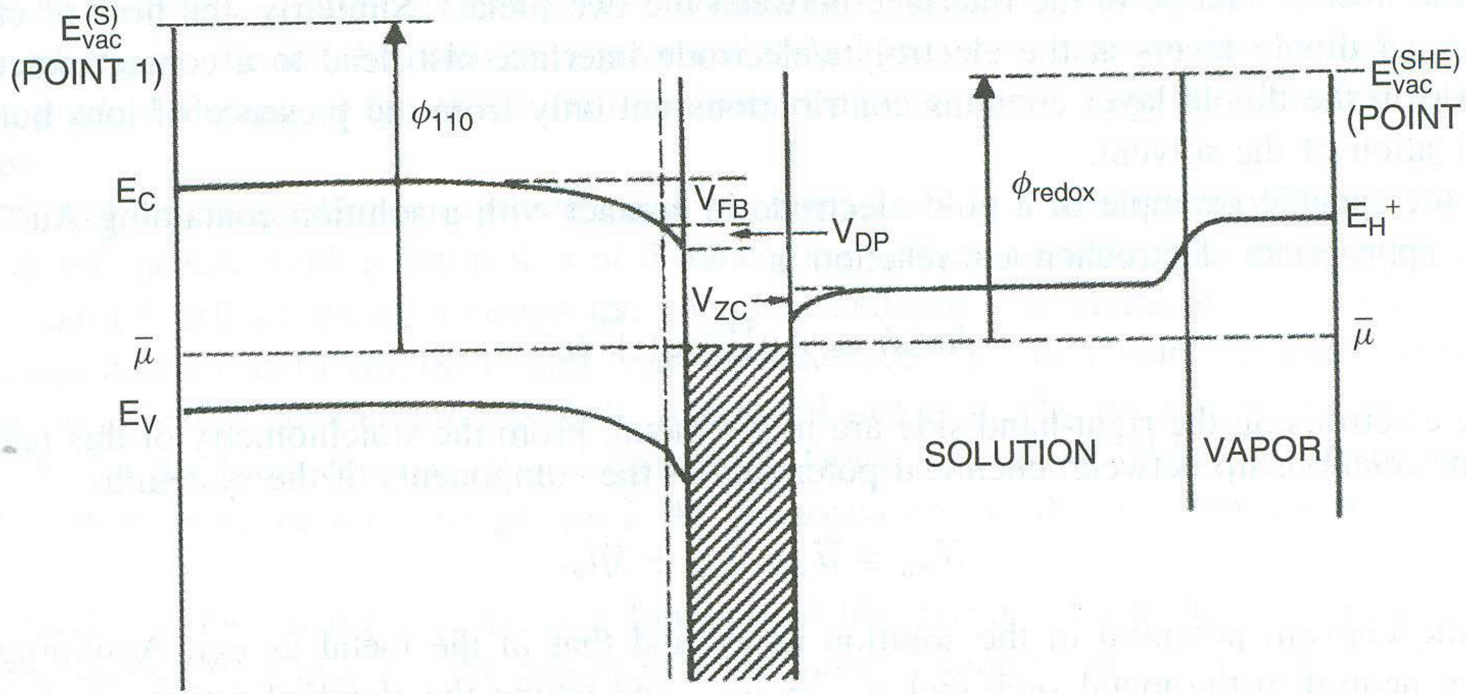

$E_{vac}^{(S)}$
(POINT 1)
ϕ_{110}
E_C
V_{FB}
V_{DP}
V_{ZC}
$\bar{\mu}$
E_V
ϕ_{redox}
$E_{vac}^{(SHE)}$
(POINT 2)
E_{H^+}
$\bar{\mu}$
SOLUTION
VAPOR

Figure 5.14 *An energy level diagram depicting the levels associated with the connection of a semiconductor electrode to a standard hydrogen electrode. Reproduced from H. Reiss, A. Heller, J. Phys. Chem., 89, 4207. ©1985 with permission from the American Chemical Society.*