

Module 3: "Thin Film Hydrodynamics"

Lecture 15: ""

The Lecture Contains:

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Energy of Adhesion

1. ΔG_{12} (Energy of adhesion in vacuum)

$$\begin{aligned}\Delta G_{12} &= \gamma_{12} - \gamma_1 - \gamma_2 \\ &= -2 \left(\sqrt{\gamma_1^{LW} \gamma_2^{LW}} + \sqrt{\gamma_1^- \gamma_2^+} + \sqrt{\gamma_1^+ \gamma_2^-} \right)\end{aligned}\quad (4.6)$$

$$< 0$$

Therefore, in vacuum ΔG_{12} is always negative.

Note: γ^-, γ^+ are all positive quantities. ΔG has units of energy per unit area.

If $1 = s, 2 = l$,

$$\begin{aligned}\gamma_l \cos \theta + \gamma_{sl} &= \gamma_s \\ \Rightarrow \Delta G_{sl} &= -\gamma_l (1 + \cos \theta)\end{aligned}$$

A lesser value of θ would mean that ΔG_{sl} is more positive. This implies that the surface would be more wettable.

2. ΔG_{132} (Energy of adhesion in the presence of an intervening fluid)

$$\begin{aligned}\Delta G_{132} &= \gamma_{12} - \gamma_{13} - \gamma_{23} \\ &= \Delta G_{132}^{LW} + \Delta G_{132}^{AB} \\ &= 2 \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}} \right) \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}} \right) \\ &\quad + 2 \left[\sqrt{\gamma_3^+} (\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}) \sqrt{\gamma_3^-} \left(\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+} \right) - \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+} \right]\end{aligned}\quad (4.7)$$

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Special cases

1. Two surfaces in polar medium

$$\Delta G_{132} = \Delta G_{132}^{LW} - 2 \left(\sqrt{\gamma_1^+ \gamma_2^-} + \sqrt{\gamma_1^- \gamma_2^+} \right)$$

If one of the surfaces were apolar, then

$$\Delta G_{132} = \Delta G_{132}^{LW}$$

If the two surfaces were monopolar with same capabilities, then also

$$\Delta G_{132} = \Delta G_{132}^{LW}$$

If $\Delta G_{132}^{LW} > 0$ there is a net **LW** repulsion. This situation occurs when $\gamma_2^{LW} > \gamma_3^{LW} > \gamma_1^{LW}$. On the other hand $\Delta G_{132}^{LW} < 0$ when $\gamma_1^{LW}, \gamma_2^{LW}$ are both either smaller than γ_3^{LW} . This situation corresponds to a net **LW** attraction.

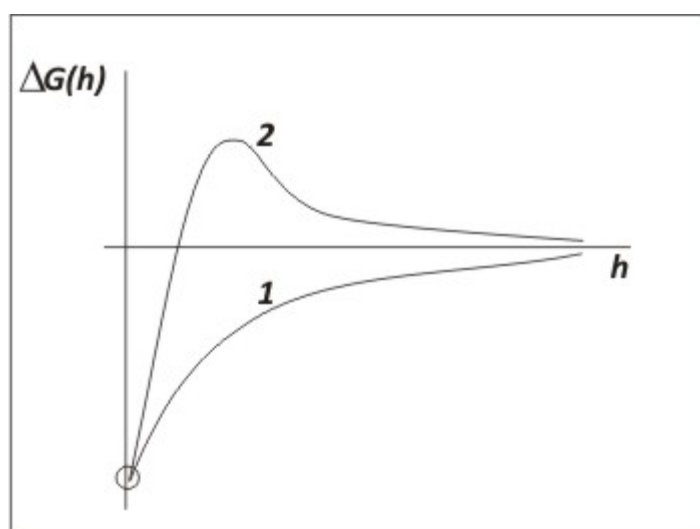


Fig. 4.2

Note: The energy of adhesion contains information only about the point shown by the circle (Fig. 4.2). It does not reveal anything about the actual shape of the energy curve. From the figure, it is clear that knowledge of this point does not give information whether the shape of the energy curve is like 1 or 2.

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2. Monopolar surfaces in water ($\gamma_s^+ \approx 0, \gamma_w^- = \gamma_w^+ = 25.5$)

$$\Delta G_{132} = \Delta G_{132}^{LW} + 2[\sqrt{\gamma_3^-}(\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - 2\sqrt{\gamma_w^-})]$$

ΔG_{132} is of order of a few dynes/cm.

Surface energies of most of the surfaces other than metals are of order of 50 dynes/cm.

There will be an *AB repulsion* between the surfaces if

$$\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} > 2\sqrt{\gamma_w^-}$$

For water, this is termed as *hydration pressure* and is given by

$$\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} > 10.1 \quad (\gamma_w^- = 25.5)$$

This condition is readily satisfied by a large number of materials in water. There is repulsion but this does not lead to molecular solution as in the case of sugar.

The concept of negative interfacial tension is closely related to hydration pressure.

$$\gamma_{lw}^{AB} + \gamma_{2w}^{AB} = \sqrt{\gamma_w^-}(2\sqrt{\gamma_w^-} - \sqrt{\gamma_1^-} - \sqrt{\gamma_2^-})$$

$$< 0, \text{ if } \Delta G_{132}^{LW} > 0$$

Thus, there is a high negative interfacial tension. This causes repulsion against the liquid.

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If $2 = w$, then

$$\Delta G_{lwl}^{AB} = -2\gamma_{lw}^{AB}$$

And since the LW component could never be positive, ΔG_{lwl}^{AB} will always be negative.

Negative interfacial tension implies that there will be a spontaneous increase in the area in order to minimize the energy. In case of gels, this leads to swelling.

$$\Delta G_{132}$$

$$= 2 \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}} \right) \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}} \right) \\ + 2 \left[\sqrt{\gamma_3^+} (\sqrt{\gamma_1^-} + \sqrt{\gamma_2^-} - \sqrt{\gamma_3^-}) + \sqrt{\gamma_3^-} (\sqrt{\gamma_1^+} + \sqrt{\gamma_2^+} - \sqrt{\gamma_3^+}) - \sqrt{\gamma_1^+ \gamma_2^-} - \sqrt{\gamma_1^- \gamma_2^+} \right]$$

3. Apolar or weakly polar surfaces in water

$$\Delta G_{132} = \Delta G_{132}^{LW} - 4\sqrt{\gamma_3^- \gamma_3^+}$$

If $3 = w$

$$\Delta G_{132} = \Delta G_{132}^{LW} - 102 < 0$$

This is strongly negative because AB interactions are much larger compared to LW interactions. This strong interaction is termed as *hydrophobic attraction (force)* and this could be a long range force.

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Hydrophilic Repulsion

Repulsion between two solute particles means leads to greater solubility of the solute. On the other hand, attraction between two solute particles would lead to phase separation and result in lesser solubility.

Solubility of Solute (1) in water

$$\Delta G_{lwl} S_c = kT \ln S$$

Here S_c is the contactable surface area between the molecules,

k is the Boltzmann constant,

S is the solubility (mol/l), and

T is the temperature

$$\therefore S = \exp \frac{\Delta G S_c}{kT}$$

A higher ΔG or S_c means higher solubility. And if $\Delta G < 0$ then the solute has a low solubility.

$$\Delta G_{lwl} = -2\gamma_{lw}$$

Thus, for solutes which are highly soluble in water, the interfacial tension is negative.

At 20°C, $kT = 4.05 \times 10^{-21} \text{ J} = 4.05 \times 10^{-14} \text{ ergs}$

$$S_c \propto (\text{MW})^{2/3} \quad (4.9)$$

Table 4.3. Solubility of some compounds having high molecular weights.

	MW	ΔG_{lw1}	S_c	S (%)
Dextran	10000	+1.13	0.4	> 50
Polyethylene oxide	6000	+2.78	0.212	> 50

Adsorption on a surface

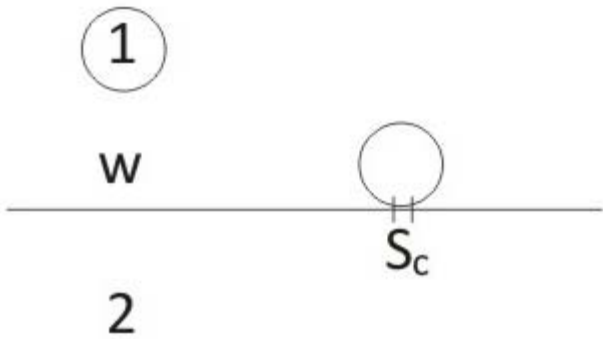
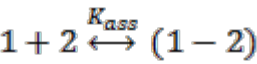


Fig. 4.3: Adsorption on a surface in presence of water

Adsorption is a pseudo-chemical reaction in equilibrium.



$$\Delta G_{lw2} S_c = -kT \ln K_{ass} \tag{4.10}$$

If $\Delta G_{lw2} < -10kT$ then $K_{ass} \sim 2 \times 10^4 \text{ l/mol}$.

Such an adsorption finds use in many applications like chromatography separation schemes. In such separation schemes, a solute is first adsorbed and then desorbed. Several modes of liquid chromatographic separations are possible. Some of them have been discussed below.

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1. Ion-exchange

In this scheme the electrostatic interaction between solute and matrix is employed.

$$\Delta G = \Delta G^{LW} + \Delta G^{AB} + \Delta G^{EL}$$

where, ΔG^{EL} is modulated..

2. Reversed Phase Liquid Chromatography (RPLC)

In this method, a hydrophobic solute is passed through a hydrophobic matrix where it is absorbed. In the next stage, it is desorbed by passing a solvent through the packed bed. The solvent is chosen such that the solute is "solvent-philic"

3. Hydrophobic Interaction Liquid Chromatography (HILC)

Many solutes, like most of the proteins, are hydrophilic and need to be made hydrophobic. This is done by treating them with appropriate compounds. For example, we can add $(\text{NH}_4)_2\text{SO}_4$ [1 M solution] or Ca^{2+} ions. Ca^{2+} ions are much more hydrophobic and if they bind themselves with the solute, the solute itself becomes hydrophobic. These ions decrease the value of γ^- making the solute more monopolar.

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Table 4.4. Interfacial tension

	γ_{lf}	Remarks
Sucrose/water	-29.5	Spontaneously soluble
Dextran/water	-8.9	Spontaneously soluble
Sucrose/formamide	-8	Spontaneously soluble
Dextran/formamide	-12.5	Doesn't solublize. Instead swells like a gel
PMMA/water	+15	Insoluble

4. Water and apolar liquid

$$\gamma_{12} = \gamma_{12}^{LW} + 2 \left[\sqrt{\gamma_1^+ \gamma_1^-} + \sqrt{\gamma_2^- \gamma_2^+} - \sqrt{\gamma_1^- \gamma_2^+} - \sqrt{\gamma_1^+ \gamma_2^-} \right]$$

1 = apolar liquid

2 = water

γ_{12} would be in a narrow range (51-54 dyne/cm) which means that the two liquids would be immiscible and a clear interface would be observed.

Table 4.5: Interfacial tension

	γ_{12}	Remarks
Water/formamide	-8.1	Soluble
Water/glycerol	-8.7	Soluble
Water/DMSO	-10.7	Soluble
Water/EG	-14.9	Soluble
Water/hexadecane	>51	immiscible