

Module 2: "Capliarity"

Lecture 4: ""

The Lecture Contains:

- ☰ Concept of Interfacial Tension
- ☰ Components of Surface or Interfacial Tension (Energy)

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Concept of Interfacial Tension

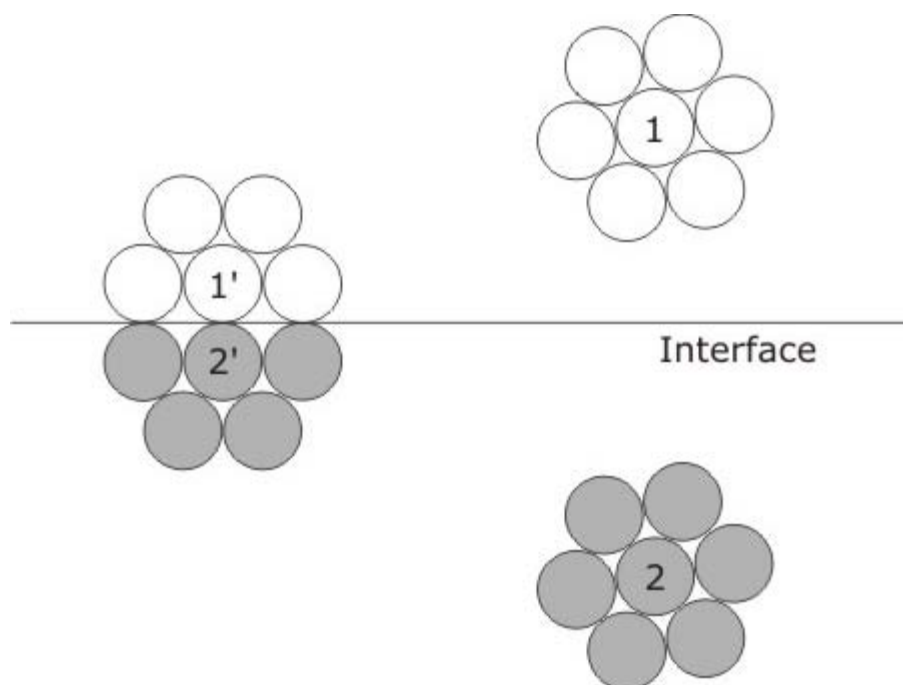


Figure 2.3 Origin of interfacial tension

First let us consider interaction energy between two molecules.

Total energy of interaction when the two molecules (1 and 2 in Fig. 2.3) are in bulk can be expressed as

$$E_b = v_{11}Z_{11} + v_{22}Z_{22} \quad (2.3)$$

where Z_{ii} is the effective coordination number and v_{ii} is the energy of interaction between a pair of i – type molecules(at equilibrium) .

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The interaction energy when they (1' and 2' in Fig. 2.3) are at the surface can be written as

$$E_s = v_{11}Z_{11s} + v_{22}Z_{22s} + v_{12}Z_{12s} + v_{21}Z_{21s} \quad (2.4)$$

where, v_{ij} is the pair-wise interaction between molecule of the type i with that of type of j . It can be shown that

$$v_{12} = v_{21} \quad (2.5)$$

$E_s - E_b$ is the energy required to form an interface/area between a pair of molecules.

If we assume that there are N 1-2 pairs of molecules at the surface then total energy of the surface can be written as

$$\gamma_{12} = N(E_s - E_b) \quad (2.6)$$

If we assume that

$$Z_{11} \cong Z_{22} \cong Z$$

$$Z_{11s} \cong Z_{22s} \cong Z/2$$

then,

$$\begin{aligned} \gamma_{12} &= N(E_s - E_b) \\ &= (NZ/2)(2v_{12} - v_{11} - v_{22}) \end{aligned}$$

$NZ/2$ is a property of the material.

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v_{11} and v_{22} are the energy of cohesion and are always a negative quantity for a condensed phase. v_{12} is the energy of adhesion. Therefore, Eq. (2.7) can be rewritten as

$$\gamma_{12} = (NZ/2)(|v_{11}| + |v_{22}| - 2|v_{12}|) \tag{2.8}$$

To use this equation we should have knowledge of the pair-wise interaction between molecules. Eq. (2.8) can be simplified further as discussed below.

Suppose medium 2 is an inert gas. In that case the term v_{22} and v_{12} can be neglected because there will be very few molecules of 2 at the surface to have any significant effect.

$$\begin{aligned} \gamma_{12} &= (NZ/2)(|v_{11}|) \\ &= \gamma_1 \text{ (surface tension of material 1)} \end{aligned} \tag{2.9}$$

Similarly if 2 is the condensed phase

$$\begin{aligned} \gamma_{12} &= (NZ/2)(|v_{22}|) \\ &= \gamma_2 \text{ (surface tension of material 2)} \end{aligned} \tag{2.10}$$

Now Eq. (2.8) can be rewritten as

$$\gamma_{12} = \gamma_1 + \gamma_2 - (NZ/2)(2|v_{12}|) \tag{2.11}$$

where, $(NZ/2)(2|v_{12}|)$ is the energy of adhesion, and γ_1 and γ_2 are the energies of cohesion of the two materials.

From Eq. (2.11) it is clear that higher the interaction energy between the two materials, the lower will be the interfacial tension.

From Eq.(2.1), energy of adhesion is,

$$\begin{aligned}\Delta G_{12} &= (\gamma_{12} - \gamma_1 - \gamma_2) \\ &= -(NZ/2)(2|v_{12}|) \\ &< 0 \text{ (always)}\end{aligned}\quad (2.12)$$

This shows that adhesion of two surfaces in an inert gas or vacuum is always energetically (thermodynamically) favorable.

Therefore, knowledge of intermolecular interactions can help us to calculate ΔG_{12}

. If in between there is another condensed phase 3 then,

$$\Delta G_{123} = (\gamma_{12} - \gamma_{13} - \gamma_{23}) \quad (2.13)$$

Note that unlike in the case of two phases, here ΔG_{123} can be either positive or negative.

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Components of Surface or Interfacial Tension (Energy)

The surface tension (energy) term can be resolved into as many components as are types of intermolecular interactions,

$$\gamma_{ij} = \gamma_{ij}^{LW} + \gamma_{ij}^{AB} + \dots$$

The superscript **LW** denotes "Lipshutz–van der Waals" interaction. This term is always present irrespective of whether there is any chemical interaction or not.

The superscript AB denotes the "Acid-Base" interaction. This has to be taken into account when conjugate polar interactions are present between two molecules.

(A) LW interaction

In orbitals in molecules, there are random fluctuations in the electron cloud which may create a weak dipole. This dipole induces an opposite dipole in the neighboring electron cloud. This opposite polarity results in a force of attraction between them. This is the origin of **LW** interaction. This force is always attractive.

$$v_{ij}^{lw} = \sqrt{v_{ii}^{lw} v_{jj}^{lw}} \quad (2.14)$$

Substituting this value in Eq. (2.11), we get

$$\gamma_{12}^{lw} = \gamma_1^{lw} + \gamma_2^{lw} - (Nz/2) \left[2\sqrt{v_{11}^{lw} v_{22}^{lw}} \right]$$

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

$$\gamma_{12}^{lw} = (\gamma_1^{lw} - \gamma_2^{lw})^2 > 0$$

Note that γ has units of force per unit length or energy per unit area.

A hydrophilic molecule in water will exhibit negative interfacial tension. If interfacial tension is positive then the surface would decrease its area in order to reduce the total surface energy. On the other hand, if interfacial tension is negative then the surface would increase its area in order to reduce the total surface energy.

(B) A-B interactions

First let us introduce some notations:

γ_i^- = electron donor parameter or proton acceptor parameter (It is basically a measure of the propensity of the substance to donate an electron)

γ_i^+ = electron acceptor parameter or proton donor parameter.

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^-} \sqrt{\gamma_i^+}$$
$$\gamma_{ij}^{AB} = 2 \left[\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_j^+ \gamma_i^-} - \sqrt{\gamma_i^- \gamma_j^+} - \sqrt{\gamma_i^+ \gamma_j^-} \right]$$

Here we see that γ_{ij}^{AB} can be negative.

For two materials, calculation of the interfacial tension between them requires the knowledge of six parameters $\gamma_i^{LW}, \gamma_j^{LW}, \gamma_i^-, \gamma_i^+, \gamma_j^-$ and γ_j^+ that is three for each material.

For a material,

$$\gamma_i = \gamma_i^{LW} + 2\sqrt{\gamma_i^+ \gamma_i^-} \tag{2.17}$$

Surface tension may be affected by various factors.If the temperature increases, the interfacial tension also increases. Surface tension is also very sensitive to impurities. Presence of impurities generally decreases the surface tension.

The surface tensions of some frequently encountered liquids are listed in Table 2.

Table 2.1

Substance (L)	Surface tension, $\gamma_L - v$ (dynes/cm or mJ/m ²)	Interfacial tension, $\gamma_L - water$ (dynes/cm or mJ/m ²)	$-\frac{d\gamma}{dT}$
Water (pure)	72.8	-	0.16
Octane	21.8	51	0.095
Dodecane	25.44	52.9	0.088
Hexadecane	27.46	53.77	0.085
Benzene	28.88	35	0.13