

Lecture 1

Molecular Interactions at Interfaces

The concept of **interface** refers to the boundary that separates two regions (phases) with different physical properties. Historically, when one of the phase is air / vacuum, people also refer such interface simply as **surface**. Physical and chemical phenomena associated with the interfaces exist at every length scale in our daily life, from proteins in fluid to macroscopic to circulation in atmosphere. In this lecture, we will briefly discuss about the molecular interactions at the interfaces between different materials. We will show a quantitative description of the surface tension based on molecular interactions.

1.1 The surface tension

The key property of an interface is known as the **surface tension** (or **interfacial tension** when both phases are liquid / solid), which is associated with the energy required to form the interface.¹ Here we will briefly show the origin of the surface tension and how it is related to the molecular interactions at the interface.

Consider a homogeneous bulk material (can be either liquid / solid) consists of molecule A (Figure 1.1).

The bulk cohesive energy $E_{A,\text{bulk}}$ per mole is calculated by counting the pairwise interaction energy w_{AA} between all the neighboring atoms, such that:

$$E_{A,\text{bulk}} = \frac{1}{2}w_{AA}N_AZ_b \quad (1.1)$$

where $w_{AA} < 0$ is the pairwise interaction energy between two A atoms at the equilibrium distance, N_a is the Avogadro constant, and Z_b is average number of neighboring atoms. We will discuss about the meaning of the “equilibrium distance” later. The pre-factor 1/2 is added to avoid doubling counting.

Let’s now look at the quantity w_{AA} . From the Lennard-Jones (LJ) model² of intermolecular forces, w_{AA} is negative at the equilibrium inter-molecular distance r_0 (see Figure 1.2), where r_0 is defined as the distance that $dw_{AA}/dr = 0$. As a result, we have $E_{A,\text{bulk}} < 0$, indicating that formation of bulk material is a energetically favored process. In other words, we need to pay energy to separate the bulk material and create interfaces. For the sake of

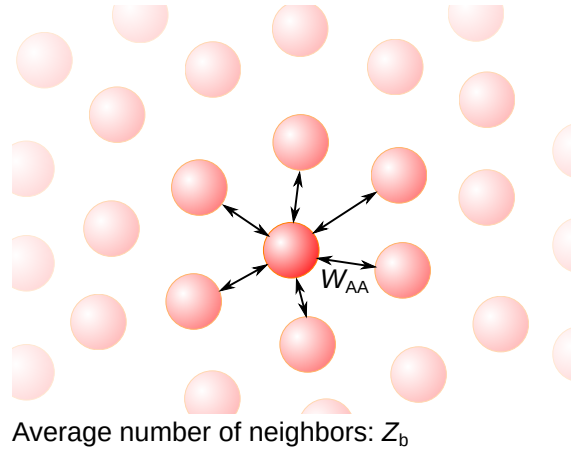


Figure 1.1: Scheme of a homogeneous bulk material. The cohesive energy $E_{A,\text{bulk}}$ is calculated from all the pairwise interaction energy.

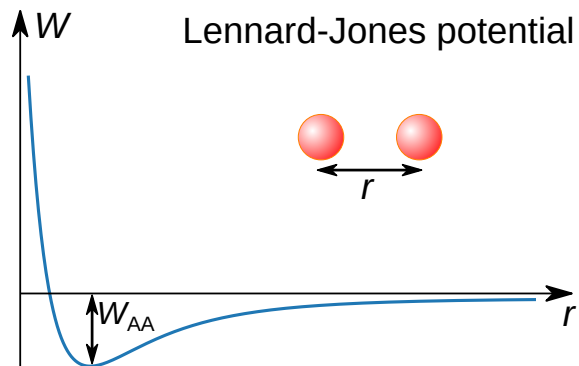


Figure 1.2: Scheme of the Lennard-Jones model of intermolecular interaction. w_{AA} is negative at the equilibrium inter-molecular distance r_0

comparison, we also define the bulk cohesive energy *per molecule*, $\tilde{E}_{A,\text{bulk}} = E_{A,\text{bulk}}/N_A$. Consider an interface between material A and vacuum (Figure 1.3), we can see that the average number of neighboring atoms on the surface becomes Z_s (smaller than Z_b), and similarly, we can define the surface cohesive energy per molecule as:

$$\tilde{E}_{A,\text{surf}} = \frac{1}{2}w_{AA}Z_s \quad (1.2)$$

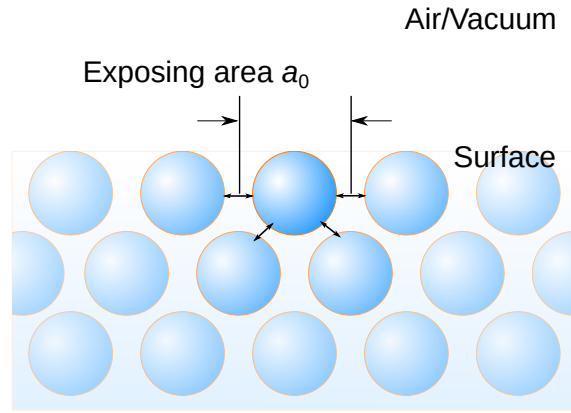


Figure 1.3: Scheme of the molecules on the surface. The coordinate number Z_s is smaller than that in the bulk material.

Obviously, we have $\tilde{E}_{A,\text{surf}}$ less negative than $\tilde{E}_{A,\text{bulk}}$ due to $Z_s < Z_b$. We define the **surface tension** γ as the energy required to create the interface per unit area. Consider that each molecule A occupies a surface area of a_0 . The surface tension between A and vacuum / air, γ_A , can be written using our previous knowledge:

$$\begin{aligned} \gamma_A &= \frac{\tilde{E}_{A,\text{surf}} - \tilde{E}_{A,\text{bulk}}}{a_0} \\ &= \frac{1}{2a_0}w_{AA}(Z_s - Z_b) \end{aligned} \quad (1.3)$$

which is **always** larger than 0. Note that this conclusion is only valid when discussing the interface with vacuum / air, as we will see the later the definition of interfacial tension γ_{AB} is different.

The unit of surface tension is [Energy]/[Area], usually expressed in $\text{J}\cdot\text{m}^{-2}$ or $\text{mJ}\cdot\text{m}^{-2}$. Alternatively the surface tension is also written in unit of [Force]/[Length], e.g. $\text{N}\cdot\text{m}^{-1}$, which characterizes the force acting per length acting along the interfacial boundary line (the origin of the term “tension”). The surface tension of different materials can vary quite a lot, here are the values of surface tension for several typical liquids:³

- $\gamma_{\text{Ag}}(1200\text{ }^\circ\text{C}) = 878\text{ mJ}\cdot\text{m}^{-2}$
- $\gamma_{\text{Hg}}(25\text{ }^\circ\text{C}) = 489\text{ mJ}\cdot\text{m}^{-2}$

- $\gamma_{\text{Water}} (25\text{ }^\circ\text{C}) = 72.8\text{ mJ}\cdot\text{m}^{-2}$
- $\gamma_{\text{Octane}} (25\text{ }^\circ\text{C}) = 20\text{ mJ}\cdot\text{m}^{-2}$

Such difference in the value of γ has great impact on some physical properties of the liquids. Here are several questions that you can think of:

1. Is it easier for a solid object to float on water ($\gamma = 72.8\text{ mJ}\cdot\text{m}^{-2}$) or ethanol ($\gamma = 22\text{ mJ}\cdot\text{m}^{-2}$)?
2. Is it easier to create bubbles from pure water or water with 1 mM surfactant ($\gamma \approx 30\text{ mJ}\cdot\text{m}^{-2}$)?

1.2 The interfacial tension

Similar to the case of a surface in vacuum / air, there is also an interfacial tension between two different materials. For a interface formed between two phases consist of molecules A and B, respectively (Figure 1.4), the interfacial tension γ_{AB} is defined as the energy per area required to create such interface. We can calculate γ_{AB} in the following way:

- Separate the interface to get the surfaces of materials A and B, respectively. This process requires ΔW_{AB} (work of adhesion) per unit area.
- The two newly created surfaces of A and B have surface energies of γ_A and γ_B , respectively.

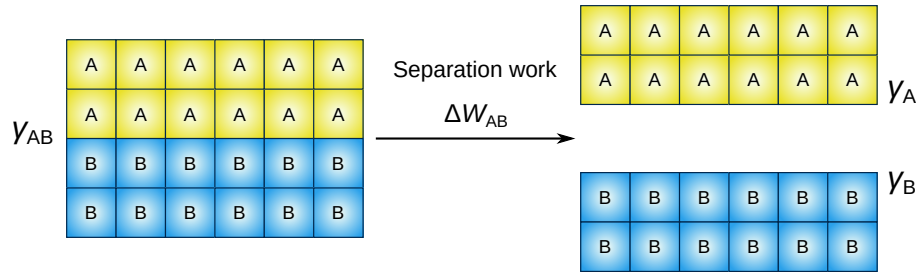


Figure 1.4: The interfacial tension between A and B phases. A work of adhesion ΔW_{AB} is required to separate the interface and create new surfaces of A and B with vacuum / air.

In total, the interfacial tension between A and B is:

$$\gamma_{AB} = \gamma_A + \gamma_B - \Delta W_{AB} \quad (1.4)$$

A very crude assumption is that the coordinate numbers Z_s and Z_b , as well as the average area a_0 are the same for both A and B phases. Under such consideration we can express γ_{AB} as:

$$\gamma_{AB} = \frac{1}{a_0}(Z_b - Z_s) \left[w_{AB} - \frac{1}{2}(w_{AA} + w_{BB}) \right] \quad (1.5)$$

where w_{AA} , w_{BB} and w_{AB} are the intermolecular energies between A-A, B-B and A-B, respectively. Now we see that γ_{AB} depends on the relative magnitudes between 3 interaction energies. As we will see later, this explains the different wetting behaviors of surfaces.

However, in real materials, the assumption of same Z_b and Z_s may not apply. According to the Lennard-Jones model we discuss in Figure 1.2, the intermolecular potential between two molecules A and B, $\Phi(r)$, as a function of the intermolecular distance r , consists of an attraction term ($\propto -1/r^6$) and a repulsive term ($\propto 1/r^{12}$). An example of the LJ potential is shown in Figure 1.5.

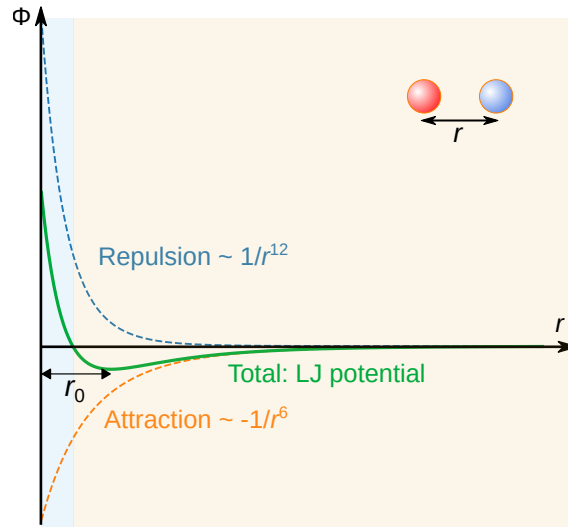


Figure 1.5: Lennard-Jones potential $\Phi(r)$ between two molecules as a function of r (green solid line), constructed by a repulsive term (blue dashed line) and an attraction term (red dashed line).

Since the repulsive part is prominent only for distances close to the inner core of the atoms, we can consider the $1/r^6$ attractive potential energy alone, i.e. $\Phi(r) = -\beta/r^6$, where $\beta (>0)$ is the coefficient associated with the van der Waals (vdW) interaction. At equilibrium distance r_0 , $\Phi(r_0)$ becomes the w_{AB} that we define previously in Equation 1.5.

Consider two semi-infinite objects 1 (consists of molecule A) and 2 (consists of molecule B) with separation d as shown in Figure 1.6, the total vdW potential energy between the two objects Φ_{12} , is calculated as the summation of pairwise interaction potential energy, such that:

$$\begin{aligned}
 \Phi_{12}(d) &= \sum_{N_1} \sum_{N_2} -\frac{dN_1 dN_2}{2} \frac{\beta}{r^6} \\
 &= \sum_{dV_1} \sum_{dV_2} -\frac{(\rho_1 dV_1)(\rho_2 dV_2)}{2} \frac{\beta}{r^6} \\
 &= -\frac{\beta \rho_1 \rho_2}{2} \iint_{1,2} \frac{dV_1 dV_2}{r^6}
 \end{aligned} \tag{1.6}$$

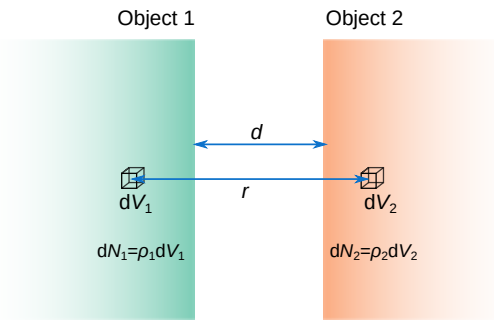


Figure 1.6: Scheme for the summation of pairwise interaction potential between two macroscopic objects 1 and 2.

where ρ_1, ρ_2 are the number densities of molecules in objects 1 and 2, respectively, dV_1 and dV_2 are infinitely small volumes in 1 and 2, respectively, and r is the distance between dV_1 and dV_2 . The integral is done with $r = d$ to $r = \infty$.

We can work out the integral in Equation 1.6 in two steps: (i) get the potential energy between a single molecule A with the bulk object 2 $\Phi_{A \rightarrow 2}$, and (ii) integrate $\Phi_{A \rightarrow 2}$ inside the object 1. For $\Phi_{A \rightarrow 2}$, the integral of dV_2 can be efficiently carried out using the ring integral (Figure 1.7):

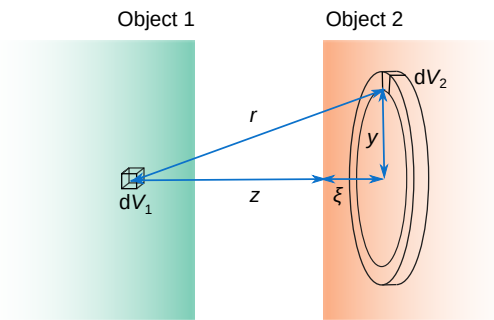


Figure 1.7: Ring integral of the interaction between a molecule A and the macroscopic object 2.

$$\begin{aligned} \Phi_{A \rightarrow 2} &= - \int_0^{2\pi} d\theta \int_0^\infty d\xi \int_0^\infty dy \frac{\beta \rho_2 y}{(\sqrt{(z + \xi)^2 + y^2})^6} \\ &= - \frac{\pi \beta \rho_2}{6z^3} \end{aligned} \quad (1.7)$$

where z is the distance from A to the interface of object 2, ξ, y and θ are the local coordinates inside object B. We can see from Equation 1.7, that the power law of the vdW interaction changes from $1/r^6$ to $1/z^3$, a consequence of the existence of all pairwise interactions. The rest of our task is to further integrate $\Phi_{A \rightarrow 2}$ inside object 1. Consider the area of the object

1 is S , we have

$$\begin{aligned}\Phi_{12}(d) &= \int_d^\infty \Phi_{A \rightarrow 2} S \rho_1 dz \\ &= S \int_d^\infty -\frac{\pi\beta\rho_1\rho_2}{6z^3} dz \\ &= -\frac{\pi\beta\rho_1\rho_2}{12d^2} S\end{aligned}\tag{1.8}$$

Consider the fact that $\Phi_{12}(d \rightarrow \infty) = 0$, we can relate ΔW_{AB} with Φ_{12} by $\Delta W_{AB}(d) = [\Phi_{12}(d \rightarrow \infty) - \Phi_{12}(d)]/S = -\Phi_{12}(d)/S$, which is finally written as:

$$\begin{aligned}\Delta W_{AB} &= \frac{\pi\beta\rho_1\rho_2}{12d^2} \\ &= \frac{A_{12}}{12\pi d^2}\end{aligned}\tag{1.9}$$

where the constant $A_{12} = \pi^2\beta\rho_1\rho_2$ is called the Hamaker constant⁴ between objects 1 and 2. The Hamaker constants for different materials can be found in the literature (for example Reference [5]), making it the one of the standard parameters in surface science. We see again that the power law of the interaction energy between two bulk objects further changes to $1/d^2$, i.e. the range vdW interaction between two macroscopic objects is much longer than intermolecular interactions.

With this knowledge we can finally calculate γ_A , γ_B and γ_{AB} . We can easily find that $\gamma_A = \Delta W_{AA}/2$ due to its definition, therefore we get: $\gamma_A = \frac{A_{AA}}{24\pi d_{AA}^2}$ and similar for γ_B . For γ_{AB} we have:

$$\gamma_{AB} = \gamma_A + \gamma_B - \Delta W_{AB} = \frac{A_{AA}}{24\pi d_{AA}^2} + \frac{A_{BB}}{24\pi d_{BB}^2} - \frac{A_{AB}}{12\pi d_{AB}^2}\tag{1.10}$$

Usually we assume that $d_{AA} \approx d_{BB} \approx d_{AB}$ (see Reference [6], Chapter 13.13), and $A_{AB} \approx \sqrt{A_{AA}A_{BB}}$, as a consequence we can estimate γ_{AB} using:

$$\gamma_{AB} \approx (\sqrt{\gamma_A} - \sqrt{\gamma_B})^2\tag{1.11}$$

which indicates γ_{AB} is usually positive. There are several indications from Equation 1.11:

- The interfacial tension between the same material γ_{AA} is always 0.
- The high energy surface dominates the interfacial tension, i.e. $\gamma_{AB} \approx \gamma_A$ when $\gamma_A \gg \gamma_B$, and *vice versa*.

So far we have seen how the surface and interfacial tensions come from molecular interactions with an intuitive theory. We will discuss more about the origin of the parameter β and Hamaker constant A of the vdW interactions as well as the modern understanding of the interfacial interactions in Lectures 9 and 10.

References

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