

Surfaces and Interfaces

University of Cambridge Part II Natural Sciences Tripos

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1 Surfaces and Interfaces

In this course we are concerned with the boundary between two phases.

Definition 1.1. A *surface* is the boundary between a condensed phase (solid or liquid) and a vapour (or vacuum) phase. An *interface* is the boundary between two condensed phases.

However, it is not uncommon to loosely call both of them “surfaces”.

This course can be loosely divided into three parts. The first part is mainly concerned about wet interfaces, the second part is mainly about dry, solid surfaces, and the final part is on adsorption.

Let’s first investigate some basic properties of the surfaces.

1.1 Surface Tension and Surface Free Energy

The creation of surfaces and interfaces often come with energy costs. This is known as the *surface free energy* (or just *surface energy*). This is easily understand if we consider a crystal structure in which there are cohesive interactions between neighbouring atoms holding materials together. A surface molecule has fewer neighbouring molecules compared with the bulk, so in order to create a surface, energy must be supplied to compensate the reduction of cohesive interactions.

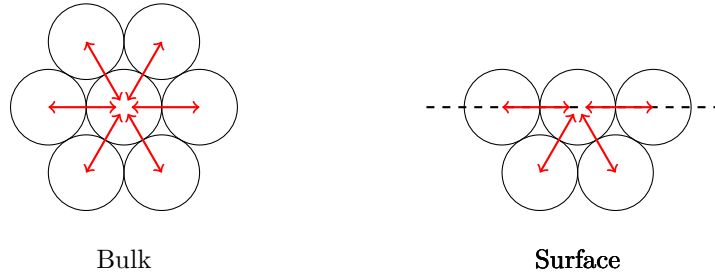


Figure 1.1: In this simple model of 2D closed pack circular atoms, a bulk atom would form 6 favourable cohesive interactions with neighbouring atoms, while a surface atom can only form 4 such interactions.

Suppose the cohesive interaction is pairwise additive, and the (negative) cohesive energy between two neighbouring particles A is ϵ_{AA} . The interaction with any particles further than the first neighbours are negligible. The bulk coordination number is $z_{A,bulk}$ and the surface coordination number is $z_{A,surf}$. Then the (positive) bulk cohesive energy per particle is

$$E_{A,bulk} = \frac{\Delta H_{vap,A}}{N_a} = -\frac{z_{A,bulk}\epsilon_{AA}}{2}, \quad (1.1)$$

and so we may calculate ϵ_{AA} experimentally by

$$\epsilon_{AA} = -\frac{2\Delta H_{vap,A}}{z_{A,bulk}\epsilon_{AA}N_A}, \quad (1.2)$$

where N_A is the Avogadro’s constant. Similarly, the cohesive energy per surface molecule is

$$E_{A,surf} = -\frac{z_{A,surf}\epsilon_{AA}}{2}. \quad (1.3)$$

We assume that the nearest neighbour spacing in the surface is approximately the same as the bulk, so the nearest neighbour interaction energy ϵ_{AA} is unchanging. Because $z_{A,surf} < z_{A,bulk}$, we clearly

reduce the cohesive energy by bringing a bulk particle onto the surface. This change in the cohesive energy per molecule is

$$\delta E = E_{A,\text{bulk}} - E_{A,\text{surf}} = -\frac{1}{2}(z_{A,\text{surf}} - z_{A,\text{bulk}})\epsilon_{AA} . \quad (1.4)$$

Therefore, if we are creating a surface (e.g. cleaving a metal into two halves), we need to do some work that is proportional to the number of surface atoms formed, and hence proportional to the area δA of the new surface.

$$\delta w = \gamma \delta A . \quad (1.5)$$

The proportionality constant is the *surface free energy*. It has both entropic and enthalpic contribution, but for solids, the entropic change is usually negligible. By (1.4), we may estimate γ by

$$\gamma = -\frac{1}{2}(z_{A,\text{surf}} - z_{A,\text{bulk}})\epsilon_{AA} N_s , \quad (1.6)$$

where N_s is the number of molecules per surface area. Note that γ is positive.

Example. Consider a fcc crystal, for which the bulk coordination number is 12 and the (111) surface atom coordination number is 9.

If we denote the close pack distance as a , then the area per surface atom is $\frac{\sqrt{3}}{2}a^2$, and so

$$N_s = \frac{2}{\sqrt{3}a^2} . \quad (1.7)$$

Hence, the surface free energy of an fcc (111) surface is

$$\gamma(111) = -\frac{3}{2}\epsilon_{AA} = -\frac{\Delta H_{\text{vap}}}{2N_A\sqrt{3}a^2} . \quad (1.8)$$

Unlike the surface energy, the *interface* energy can either be positive or negative, depending on the relative size of ϵ_{AA} , ϵ_{AB} and ϵ_{BB} , where A and B denote the two types of particles of the two interfaces. If the interface energy is positive, i.e. the formation of interface unfavourable, then the interface will shrink to a minimum possible area. If it is negative, then the interface will tend to grow and the phases will tend to dissolve in one another. Due to the entropy contribution which we have so far ignored, dissolution may occur even if the surface energy (enthalpic) is slightly positive.

From how we defined the surface energy γ , it is clear that it should have dimension J m^{-2} . This is also be rewritten as N m^{-1} , force per unit length. This hints that the surface energy may have some alternative interpretations. Let's imagine a soap film suspended on a wire loop with one of its sides movable.

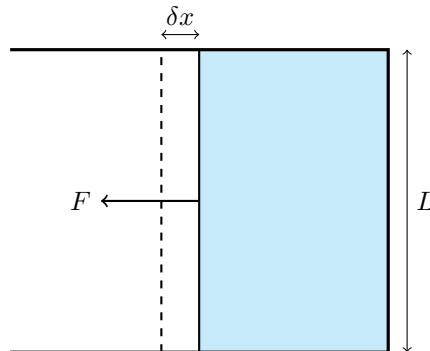


Figure 1.2: A soap film in a wire loop.

The soap film wants to contract in order to minimise its surface area, therefore exerting a force F on the movable side. If we pull this side with force F by a distance δx , remembering that the film has two surfaces (up and down), the total increase in area is $2l\delta x$, and hence the work needed to create this surface is

$$\delta w = \gamma \delta A = 2\gamma l \delta x. \quad (1.9)$$

The force exerted by the two surfaces of the film on the side of length l is therefore

$$F = \frac{\delta w}{\delta x} = 2\gamma l, \quad (1.10)$$

where each surface exerts a force

$$F = \gamma l. \quad (1.11)$$

Hence, the *surface tension*, defined as the force exerted by a surface per unit length, is exactly the surface free energy

$$\gamma = \frac{F}{l}. \quad (1.12)$$

For liquid-liquid and liquid-vapour interfaces, the equilibrium values of γ is independent of the direction, so the surface tension is uniform. This is different for solid interfaces.

The number of surface molecules is usually a very small fraction of those in the bulk. It makes an important contribution only

- (i) for a process where the bulk energy does not change;
- (ii) for very small particles (\sim nm) where the surface energy becomes comparable to the bulk energies.

1.1.1 Measurement of Surface Tension

The most common method of measuring the surface tension is to use a *Wilhelmy Plate*. Suppose the dry weight of the plate is W_0 , and when dipped into water, the measured weight becomes W . Suppose the buoyancy force is negligible and the contact angle is 0° (extra terms will be introduced into the equation without those assumptions), then the surface tension is

$$\gamma = \frac{W - W_0}{t}, \quad (1.13)$$

where t is the wetted length.

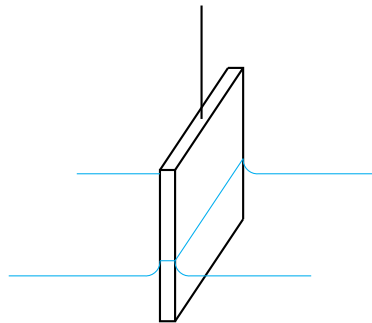


Figure 1.3: A Wilhelmy plate.

1.2 Contact Angle

One of the most common interfacial systems in everyday life is a single drop of water on a solid surface. In some cases the drop will spread and completely cover the surface, in which case we say the water completely *wet* the surface. In other cases the water will form a droplet on the surface. In this case the water does not completely wet the surface.

We characterise the wetting nature of such a solid/liquid/gas combination by the *contact angle*, θ , illustrated in the figure below. It is defined to be the angle between the surface plane and the tangent to the fluid surface at the point of contact. Take care that this angle is measured inside the liquid phase.

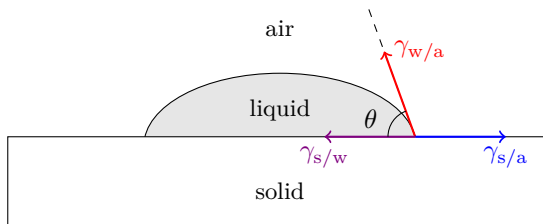


Figure 1.4: A liquid droplet on a solid surface. The phase labelled ‘air’ may be another liquid phase, in which case the corresponding interfacial tensions should be used.

The contact angle results from the three interfacial free energies at the contact point all trying to reduce their surface area. Having identified the surface energy being the same as the surface tension (force per unit length), we can see that the horizontal components of the three surface tension forces should also balance at the point of contact, otherwise the point of contact would move and the system is not in equilibrium. This gives us the *Youngs equation*

$$\gamma_{s/a} = \gamma_{s/w} + \gamma_{w/a} \cos \theta. \quad (1.14)$$

The contact angle is a measure of ‘wettability’. If the water does not like the surface (high $\gamma_{s/w}$), then the drop can avoid contacts with the surface by increasing the contact angle. In the upper limit of $\theta = 180^\circ$, we say the surface is completely dry. On the other hand, if $\gamma_{s/a} \geq \gamma_{s/w} + \gamma_{w/a}$, the formation of a liquid layer in between the solid/air surface is clearly energetically favourable, so the contact angle would be 0° . In this case we say the surface is completely wet, or it spreads on the surface. For $0^\circ < \theta < 90^\circ$, the surface is incompletely wet and for $90^\circ < \theta < 180^\circ$, the surface is incompletely dry. A common hydrophobic material in everyday life is Teflon (PTFE) which has a contact angle with water of 120° .

1.2.1 Rough Surfaces

The Youngs equation holds for flat surfaces. When the surface is rough, an approximate equation for the contact angle actually observed is given by

$$\cos \theta_{\text{obs}} = r \cos \theta_{\text{flat}}, \quad (1.15)$$

where r is the roughness ratio given by the ratio between the actual and projected solid surface area of a surface. It is unity for a flat surface and greater than one for any surface not completely flat. This equation is based on the assumption that the liquid penetrates into the valleys of the rough surface. Note that the direction of the change in apparent contact angle depends on value of the contact angle relative to 90° . If the contact angle for the flat surface is bigger than 90° , then the roughness will make the apparent contact angle even bigger, giving rise to *superhydrophobic materials*. However, if the contact angle of the flat surface is less than 90° , then roughness will decrease the apparent contact angle, leading to *superhydrophilicity*.

We can understand superhydrophobicity (superhydrophilicity) by considering the movement of the water front over a rough surface. As the water moves a short distance across the surface, the actual area of the new, unfavourable contacts is much more than the flat surface. Hence the surface appears to have a much bigger contact angle. This is the origin of the superhydrophobic nature of the lotus leaf.

1.3 Calculation of Free Energies of Interfaces

We usually have tabulated values of surface free energies (i.e. between some phase with the air), but we rarely have the interfacial free energies between any two phases of interests. It would be nice if there is some way to calculate the interfacial free energy from the surface free energies of the two individual phases.

The basic idea would be decomposing the surface free energy into different contributions, and one then estimates these different contributions by a series of measurements using liquids with known behaviours. The overall interfacial free energy between two materials can then be calculated using some combination rules.

1.3.1 Owens–Wendt Method

The Owens–Wendt method decomposes the surface free energy into two contributions: a dispersion term and a polar term

$$\gamma = \gamma^d + \gamma^p. \quad (1.16)$$

Some values for common solids and liquids are shown below.

Material	$\gamma^d / \text{mJ m}^{-2}$	$\gamma^p / \text{mJ m}^{-2}$	$\gamma / \text{mJ m}^{-2}$
Liquids			
hexadecane	27.8	0.0	27.8
α -bromonaphthalene	44.4	0.0	44.4
diiodomethane	50.8	0.0	50.8
ethane diol	29.0	19.0	48.0
formamide	39.0	19.0	58.0
water	21.8	51.0	72.8
mineral oil	25.0	0.0	25.0
olive oil	31.4	1.6	33.0
sunflower oil	33.6	0.0	33.6
Solids			
quartz	52.0	44.0	96.0
glass	42.0	34.0	76.0
PET	35.0	4.0	39.0
PVC	43.0	4.0	47.0
skin	40.0	8.0	48.0
PE	30.0	1.3	31.3
PP	27.0	0.1	27.1
PTFE	17.0	0.6	17.6
stainless steel	33.8	6.2	40.0

For two materials in contact, the interfacial free energy is given by

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} - 2\sqrt{\gamma_1^p \gamma_2^p}. \quad (1.17)$$

For the particular case of a liquid drop on a solid in air, the contact angle is

$$\cos \theta = -1 + \frac{2}{\gamma_l} \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \right). \quad (1.18)$$

For example, if one would like to measure the surface free energy of a solid, one can first measure the contact angle of a non-polar liquid (e.g. hexadecane), from which we can calculate γ_s^d . Then we would measure the contact angle of any liquid with non-zero dispersive surface energy, from which we can obtain γ_s^p .

1.3.2 Good-van Oss-Chaudhury Theory

It breaks the surface free energy into a dispersive and a term for acidity (γ^+) and basicity (γ^-), also known as electron acceptor and donating term

$$\gamma = \gamma^d + 2\sqrt{\gamma^+ \gamma^-}. \quad (1.19)$$

The combination rule for the interfacial free energy is

$$\gamma_{12} = \left(\sqrt{\gamma_1^d} - \sqrt{\gamma_2^d} \right)^2 + 2 \left(\sqrt{\gamma_1^+} - \sqrt{\gamma_2^+} \right) \left(\sqrt{\gamma_1^-} - \sqrt{\gamma_2^-} \right), \quad (1.20)$$

and the contact angle in air is

$$\cos \theta = -1 + \frac{2}{\gamma_l} \left(\sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^+ \gamma_l^-} + \sqrt{\gamma_s^- \gamma_l^+} \right). \quad (1.21)$$

2 Surface Measurement Techniques I

As we shall see later, it is often very difficult to study surfaces experimentally. This is because the surface material is usually only a tiny fraction of the bulk, and the surface is sometimes inaccessible when sandwiched between two phases. Hence, we need techniques that are *surface specific*, which only information from the surface will be detected, and the bulk material will show no signal. In many cases the technique will only be *surface sensitive* with a large contribution from the surface but there are still some bulk contribution.