

Surfaces and Interfaces

University of Cambridge Part II Natural Sciences Tripos

Yue Wu

*Yusuf Hamied Department of Chemistry
Lensfield Road,
Cambridge, CB2 1EW*

yw628@cam.ac.uk

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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 Thermodynamic Description of Surfaces

1.1.1 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.

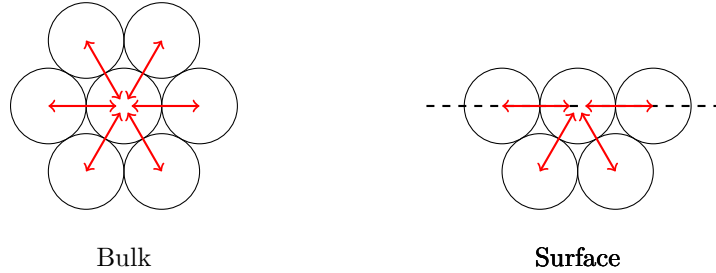


Figure 1.1: In this simple model of 2D closed pack circular atoms, a bulk atom would form 6 favourable cohesive interactions with neighbouring atoms, while a surface atom can only form 4 such interactions.

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.

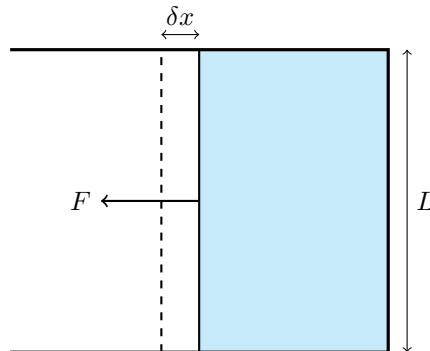


Figure 1.2: A soap film in a wire loop.

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

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