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1.1 The importance of interfaces

In a surprising number of important systems, the properties are not totally determined by the bulk properties of the materials of which the system is composed, as there is an appreciable contribution from a **surface** or **interface** between two materials. Although such a surface region may be extremely thin (down to a few molecular diameters) it can have a major effect on the way the system behaves.

Think for instance of the **catalytic converter**, which has been an integral part of cars produced over the last decade. As the raw exhaust gases from the engine pass over the solid metal and metallic oxide catalyst surface, a large number of reactions take place, leading to more complete oxidation of the gases and hence to a cleaner environment. The gases spend only milliseconds in contact with the surface, and yet this has a dramatic effect on the composition of the final exhaust mixture that is vented to the atmosphere. As the contact between the gases and the surface is only really with the first couple of atomic layers, the properties of the solid support, other than ensuring that the surface area is very large, are largely irrelevant. It is the surface of the catalyst that is crucial.

Another important example concerns the **inner lining of the lung**. A layer of fluid lines the alveoli, and at the surface of this fluid, in contact with the air, is a layer that is only one molecule thick composed mainly of phospholipids. This mixture of phospholipids and some proteins is known as **lung surfactant**. Lung surfactant serves to lower the amount of work required for the action of breathing, a function that is so important that if the surfactant is not fully

developed, unaided breathing is impossible. Because lung surfactant is only produced late in gestation, most infants that are born before 30 weeks gestation must be treated immediately after birth to ensure their survival. Again, it is the properties of the very outermost surface that determine the functioning of the entire system.

Again and again we encounter similar examples of the importance of surfaces. With the increasing emergence of new technologies relying on miniaturization, surface properties are growing in importance. The new and exploding field of **nanotechnology** is an obvious case where the solid surfaces of, for example, nanoparticles and mesoporous materials, are the places where the processes of interest take place. An understanding of processes occurring at surfaces is therefore relevant to many new developments.

Even though surfaces are increasingly important to modern technology, they have in fact been studied for a very long time. Reports dating from Roman times describe the calming of water by spreading oil on the surface, but arguably the beginning of the field as a scientific discipline dates from the experiments of Benjamin Franklin, reported to the Royal Society in 1774, where he describes the spreading of oil on a pond in Clapham Common, on the outskirts of London. He observed that placing as little as one teaspoon of oil on the surface calmed the ripples on a small area that quickly extended to about half an acre ($2 \times 10^3 \text{ m}^2$).

Before we can describe the complex processes that occur at surfaces, it is important to describe exactly what we mean by this term.

1.2 Surfaces and interfaces

1.2.1 Introduction

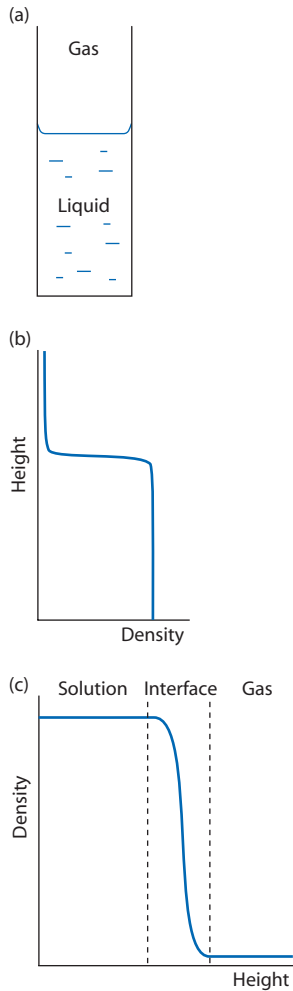
Where two homogeneous bulk phases meet there is a region of finite thickness where the properties change, often markedly, as we move from one bulk phase to the other. Such regions are known as **surfaces** or **interfaces** (although the term **interphase** would be a better description). Although we may commonly think of a surface as being of negligible thickness, in fact when we are discussing phenomena at a molecular level the thickness of the interfacial region is significant and definitely non-zero.

The properties of the interfacial region are particularly important when one of the phases is dispersed as many very small particles in the other phase, because of the dramatic increase in surface area. The two phases are usually referred to as the **disperse phase** and the **continuous phase**. Examples include colloids, emulsions, aerosols, and some natural and synthetic polymers. Often the particles are below the resolution limit of the optical microscope ($<0.5 \mu\text{m}$) but above the molecular size range. Table 1.1 illustrates how the surface area increases if we take a disperse phase of total volume 1 cm^3 and subdivide it into smaller and smaller cubic particles.

Thus, for example, 1 cm^3 of disperse phase divided into cubic particles with sides of $0.1 \mu\text{m}$ (within the size range of most colloids) has an interfacial area of 60 m^2 .

Table 1.1. Effect of subdivision into cubic particles on the surface area of a disperse phase with a total volume of 1 cm³.

Number of particles	Particle volume/m ³	Length of cube edge/m	Total surface area/m ²
1	10 ⁻⁶	10 ⁻²	0.0006
10 ³	10 ⁻⁹	10 ⁻³	0.006
10 ⁶	10 ⁻¹²	10 ⁻⁴	0.06
10 ⁹	10 ⁻¹⁵	10 ⁻⁵	0.6
10 ¹²	10 ⁻¹⁸	10 ⁻⁶	6
10 ¹⁵	10 ⁻²¹	10 ⁻⁷	60

**Figure 1.1.** Density profile across the gas–liquid interface. The graph in (b) corresponds to the sample (a) and in (c) it has been rearranged into a more customary orientation. Dashed lines in (c) indicate the interfacial region.

1.2.2 Types of interface

Because there are three types of bulk phase, it is possible to classify interfaces based on the nature of the bulk phases that lie on either side of the interface. Thus there are five types of interface:

$$\left. \begin{array}{l} \text{gas–liquid} \quad \text{G–L} \\ \text{liquid 1–liquid 2} \quad \text{L}_1\text{–L}_2 \end{array} \right\} \text{fluid interfaces}$$

$$\left. \begin{array}{l} \text{gas–solid} \quad \text{G–S} \\ \text{liquid–solid} \quad \text{L–S} \\ \text{solid 1–solid 2} \quad \text{S}_1\text{–S}_2 \end{array} \right\} \text{non-fluid or solid interfaces}$$

Of course all gases mix with one another so there are no gas–gas interfaces. Usually with this notation the less dense phase will be shown first: G–L rather than L–G, for example.

When three bulk phases meet in a line, this line is known as a *triple interface*.

1.2.3 Defining the interfacial region

Taking an intensive property, such as density, and scanning its value from, say, a liquid phase through the interface to a gas phase would give a plot such as that in Figure 1.1.

In this case the density shows a smooth transition from the high density of the liquid to the much lower density of the gas. The bulk phases can be separated from the interface by two surfaces parallel to one another and positioned so that the bulk phases are homogeneous and uniform (uniform density in this case) while the inhomogeneity and non-uniformity are contained entirely within the interfacial region lying between the two surfaces. The dashed lines in Figure 1.1(c) illustrate this point.

We will see later that for some properties the transition from one bulk phase to another does not follow a smooth monotonic transition such as that in Figure 1.1. For example, the concentrations of some solutes (particularly marked with the surfactants, see Section 4.6) at the vapour–solution interface

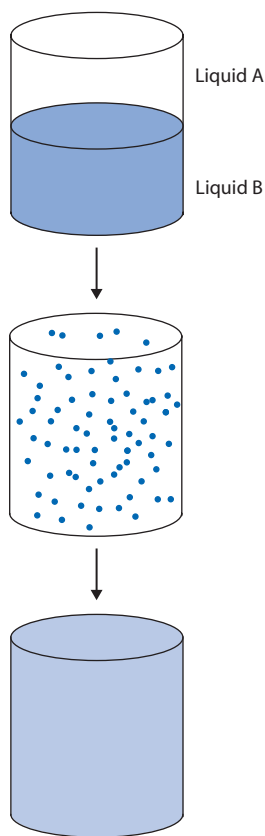


Figure 1.3. The spontaneous increase in surface area that would occur between two liquids if the surface tension were negative. This does not occur for immiscible liquids!

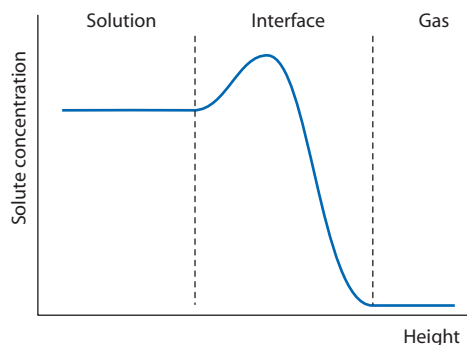


Figure 1.2. Concentration profile for a solute at the gas–solution interface.

may reach values very much higher than those in either bulk phase and exhibit a profile such as that in Figure 1.2.

The solute in Figure 1.2 is said to be *adsorbed* at the interface. This term will be defined and discussed in more detail in Chapter 3.

1.3 Stable interfaces

For any system at equilibrium, the free energy is at a minimum. If the system contains an interface, it is reasonable to expect that the interface would contribute to the free energy, and that this contribution would be a function of the area, A . We might expect that this contribution would take the form:

$$G = \gamma A + \text{other terms.} \quad (1.1)$$

In this equation, the coefficient γ is known as the **surface tension** or **interfacial tension**. If the system is stable it follows that γ must be positive, for if it were negative, an increase in area would lead to a lowering of the free energy, and therefore the surface area would spontaneously expand. This would ultimately lead to the dissolving of one substance in the other. Figure 1.3 illustrates how this process might occur for two liquids. In fact, the opposite occurs for immiscible liquids, suggesting that for a stable interface γ must be positive and that at equilibrium the interfacial area will tend to a minimum in order to minimize the free energy. This process provides the driving force for many of the phenomena that will be discussed in following chapters.

Equation (1.1) also indicates that processes that lower the value of the interfacial tension would also be thermodynamically favoured. This is, then, a second force capable of driving interfacial processes. The phenomenon of **adsorption** is an important example.

1.4 Key concepts

Although the topic of interfacial science is vast, we have attempted to introduce the crucial areas in the subsequent chapters. In this section we give a broad overview of the field.

1.4.1 Surface tension

Probably the most important concept of all, particularly when dealing with interfaces in which both phases are fluids, is that of surface tension. The existence of surface tension, and the effects which arise as a consequence, play a major role in the behaviour of systems containing interfaces. Because surface tension represents extra energy which is proportional to the area, systems attempt to minimize their surface area, resulting in the familiar fact that drops of liquid in air and bubbles are spherical. Many effects are more subtle, however, and are only evident if the interface is curved.

1.4.2 Wetting

The shapes of liquid droplets and the wetting of solid surfaces are determined principally by the forces acting at the relevant interfaces. These forces determine, for example, whether a liquid drop will spread over a solid surface or roll up into a ball, whether liquid will rise up the narrow gaps between the fibres of a wick, whether water will penetrate through the weave of an umbrella cloth, and contribute to the rise of sap in the stems of plants.

We are all familiar with the non-stick properties of TeflonTM, which benefits from the tendency of liquids not to wet the surface, and fabrics designed to be non-wetting have the potential to be self-cleaning and never need washing!

1.4.3 Adsorption

A major consideration of interfaces is that the two phases normally have quite different properties, and frequently materials that are soluble in one or both phases will find it energetically favourable to concentrate (or deplete) at the interface. The main example is the class of materials called surfactants, which are molecules that are designed to have a part that prefers one phase and another part that prefers the other. Such materials adsorb at the interface, and this is crucial to a number of processes, such as detergency, in which oils can be dispersed in water when naturally they are very insoluble.

Adsorption is not restricted to liquid–liquid interfaces. Gases adsorb on to solids, a fact which is exploited in the routine measurement of surface areas of powders, and is an essential part of the catalysis of many gas phase reactions such as those that occur in the catalytic converters of nearly all cars. Such catalysis is also essential in many aspects of chemical industry.

Adsorption also leads to methods of fabrication of thin films, as thin as a single molecular layer. Methods exist which begin with a single layer at the air–water interface (the Langmuir–Blodgett technique) to build up multilayer films one layer at a time, and other methods use the ability of molecules to adsorb and self-assemble at the interface of a solution and a solid surface (known as self-assembled monolayers). Monolayers on an air–water interface can also be used to retard the evaporation of water, which is a major concern with open water storage dams in dry climates.

1.4.4 Emulsions

Emulsions, defined loosely as small droplets of one immiscible liquid in another, are very common, although frequently we might not recognize their presence. Common household products in which emulsions are frequently present are foods, paints, and cosmetics. To take paints as an example, these days most paints are water based. The water acts as a dispersion medium for an emulsion of polymer particles. After application, the water evaporates and the polymer particles coalesce to form a protective film.

Because emulsions are inherently unstable, preferring to minimize the surface area of the interface by individual droplets merging together, there is an enormous amount of science in the stabilization of emulsions in order to improve the effectiveness and marketability of products. This field is closely related to adsorption and surfactants, as the stabilization of emulsions relies on the use of surfactants in nearly all cases.

1.4.5 Colloids

Closely related to emulsions, colloids are very small solid particles in a liquid medium. They are also very common in industry and household products, and even particulates in air pollution represent a colloidal dispersion. Like emulsions, the major issue with colloids is their tendency to aggregate and achieving stability is usually the goal in formulation of products. This requires a detailed understanding of the charged nature of the solid–liquid interface, and the effects of added salts and other conditions.

1.4.6 Membranes

No biological organisms as we know them would exist without the existence of cell membranes, which separate two liquid phases which would otherwise mix. The other function of membranes is to allow the controlled movement of molecules into and out of cells, which is a remarkably complex task achieved by equally remarkable materials. These are primarily molecules known as lipids and special proteins called membrane proteins.

Knowledge gained from the study of biological membranes is increasingly being used to design better drug delivery systems.

FURTHER READING

The literature of interfacial science

There is an extensive literature dealing with surface chemistry and its various manifestations. This ranges from reports from Roman times of calming waves by the spreading of oil; through Benjamin Franklin's experiments (1774) with monolayers on a pond in London; the development of the first film balance by Agnes Pockels (1891) in the kitchen of her parents' home; the development of a theory to describe the

adsorption of gases on solids by Brunauer, Emmett and Teller (1938); the formulation of a theory for the stability of lyophobic colloids by Deryaguin and Landau (1941) and Verwey and Overbeek (1948); cloud seeding experiments by Langmuir and Schaefer (1946) and by Vonnegut (1946); and the experiments of Mansfield and Vines (1955 to 1962) on the retardation of water evaporation from large storages, to the many research and review papers currently being published in international journals of high repute.

A large number of books have been published on various aspects of interfacial science. Many of these will be found in the **Further reading** sections near the end of each chapter of this book. Also listed under this heading are relevant review articles, mostly from one of the review journals or series devoted to our topic.

Original research is generally published in specialist journals, while there is also a small number of papers in more general journals. The titles of these journals can be seen in the references at the end of each chapter.

Chapter references

In each chapter the references are shown by author and year of publication. For example, Peng, *et al.* (2001). A book reference may also include a chapter or page number. At the end of the chapter the references to books and major review articles are listed alphabetically under **Further reading**.