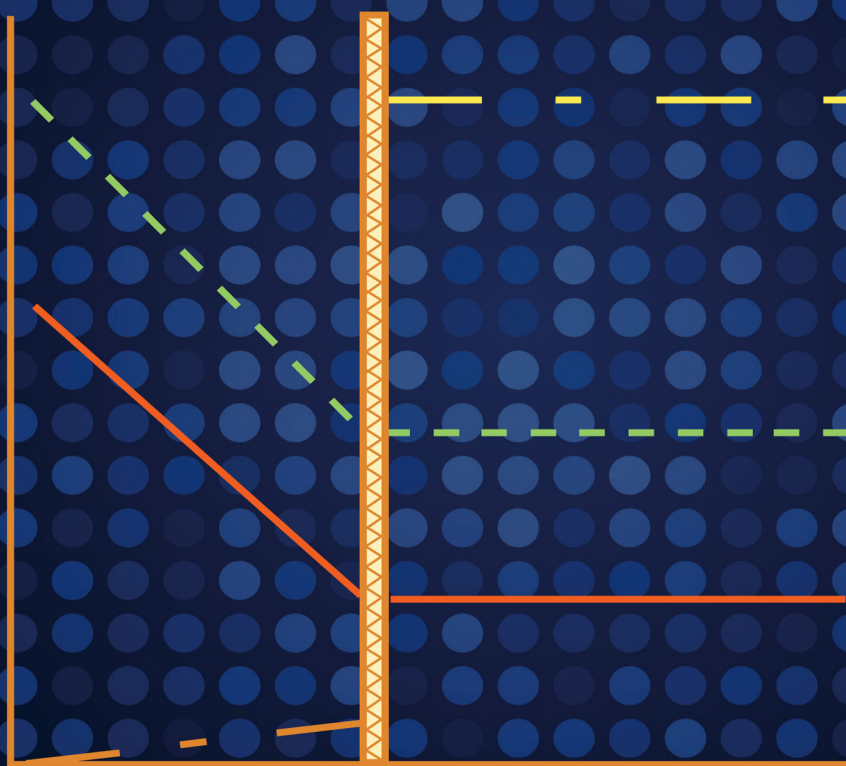


# Surface Chemistry Essentials



**K. S. Birdi**



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**K. S. Birdi**



**CRC Press**

Taylor & Francis Group

Boca Raton London New York

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# Preface

The subject related to surface chemistry is recognized as being an important area of a special branch of chemistry in everyday life. Due to the extensive literature devoted to this subject, it was realized that a book comprising only *essential* coverage would be useful. Thus, the aim of this book is to present and describe the essential details of surface chemistry. This need also arises from the fact that the area of applications in industry of this science is now extensive.

Most science students are taught physicochemical principles pertaining to gases, liquids, and solids. The matter around us is recognized to be made of these three states of matter. However, in university chemistry textbooks, only a chapter or two is devoted to the science of surface and colloid chemistry. At technical schools the case is the same; in general, it is the case worldwide. The science of surface and colloid chemistry is one of the most important in technology. The most common examples include:

- Soap bubbles
- Foam (fire fighting)
- Raindrops
- Combustion engines
- Food products
- Air pollution (fog, smog, sandstorms)
- Wastewater treatment
- Washing and cleaning
- Corrosion
- Cosmetics
- Paint and printing; adhesion; friction
- Oil and gas production, and shale oil/gas recovery (fracking process)
- Oil spills
- Plastics and polymers
- Biology and pharmaceuticals
- Milk products (milk, cheese)
- Cement
- Adhesives
- Coal (coal slurry transport)

Science students are increasingly interested in the application studies to real-world systems. Colloid and surface chemistry offers many opportunities to apply this knowledge to understanding everyday and industrial examples.

The main purpose of this book is to guide chemistry and physics students with backgrounds in the area to the level where they are able to understand many natural phenomena and industrial processes, and are able to widen their application potential to new areas of research. The text is carefully arranged such that much involved

mathematical treatment of this subject is mostly given as references. However, students should be able to do this and still maintain a good understanding of the fundamental principles involved.

Furthermore, this book contains useful data from real-world examples, which helps to explain and stimulate the reader to consider both fundamental theory and industrial applications. The latter is expanding rapidly and every decade brings new application areas in this science. Accordingly, pertinent references are provided for the more advanced students and scientists from other fields (such as biology, geology, the pharmaceutical industry, medical science, astronomy, and plastics).

Important sample questions and answers are included wherever appropriate in various sections, with detailed data and discussion. Although the text is primarily aimed at students, researchers will also find some topics of interest. A general high school background in chemistry or physics is all that is required to follow the main theme in this book.

During the past decades, it has become more obvious that students and scientists of chemistry and engineering should have some understanding of surface and colloid chemistry. The textbooks on physical chemistry do introduce this subject, but there is generally only a short chapter. Modern nanotechnology is another area where the role of surface chemistry is important. The medical diagnostic applications are another area, where both microscale and surface reactions are determined by different aspects of surface and colloid chemical principles. Drug delivery is mostly based on lipid vesicles (self-assembly structure), which are stabilized by various surface forces.

The book presents essentials and some basic considerations with respect to liquid and solid surfaces. After this introduction, the liquid–solid interface phenomenon is described. Following this, the colloid chemistry systems are discussed. The essential principles of emulsion science and technology aspects are presented. In the last chapter, more complex application examples are described. These are examples where different concepts of surface and colloid chemistry are involved in some mixed manner.

---

# 1 Introduction to Surface Chemistry Essentials

## 1.1 WHAT IS SURFACE CHEMISTRY?

Science is concerned with knowledge of the structures of matter (defined as solids, liquids, and gases) (Figure 1.1). Modern technology has shown that one needs a much more detailed picture of these structures in all kinds of processes (chemical industry and technology and natural biological phenomena). The modern application industry of science is clearly the most important area for mankind's demands (with regard to future challenges: drinking water, energy resources, food, clean air, transportation, housing, health and medicine, etc.).

---

Matter exists as:

- gas,
- liquid, and
- solid,

as has been recognized by classical science:

Solid phase → Liquid phase → Gas phase

---

Experiments show that molecules that are situated at the *interfaces* (e.g., between gas–liquid, gas–solid, liquid–solid, liquid<sub>1</sub>–liquid<sub>2</sub>, solid<sub>1</sub>–solid<sub>2</sub>) are known to behave differently (Figure 1.2) than those in the bulk phase (Bakker, 1928; Adam, 1930; Bancroft, 1932; Partington, 1951; Harkins, 1952; Davies and Rideal, 1963; Defay et al., 1966; Gaines, 1966; Matijevic, 1969; Aveyard and Hayden, 1973; Fendler and Fendler, 1975; Chatteraj and Birdi, 1984; Birdi, 1989, 1997, 2002CD, 1999, 2002, 2009, 2010a, 2010b; Adamson and Gast, 1997; Rosen, 2004; Schramm, 2005; Somasundaran, 2006; Kolasinski, 2008; Miller and Neogi, 2008; Somarajai and Li, 2010; Barnes, 2011). Typical examples are:

Liquid surfaces

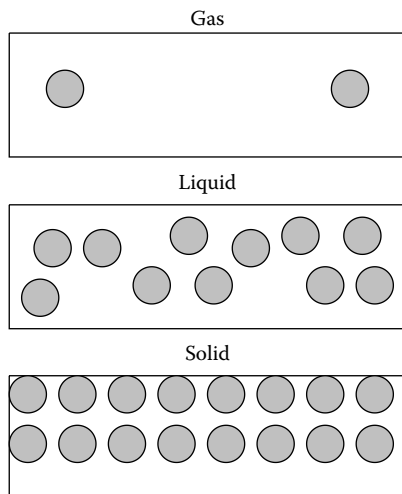
Surfaces of oceans, lakes, and rivers

Lung surface, biological cells surfaces

Solid surfaces

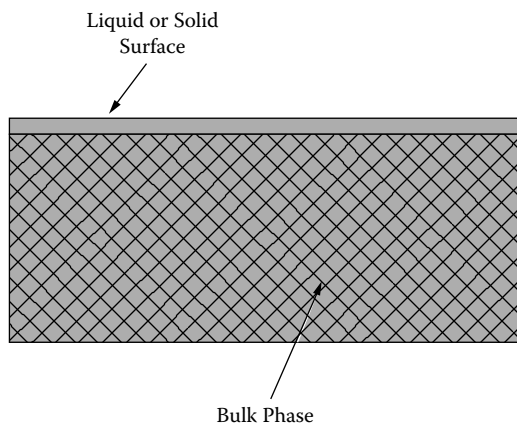
Road surfaces (car tire)

Adhesion, glues, tapes



**FIGURE 1.1** The molecular structure of a gas, liquid, and solid.

Cement industry  
Paper industry  
Construction industry (tunnels, etc.)  
Liquid–solid interfaces  
Washing and cleaning (dry cleaning)  
Wastewater treatment  
Air pollution  
Power plants



**FIGURE 1.2** Bulk phase (liquid or solid) and surface phase (molecular dimension).

Liquid–liquid interfaces (oil–water systems)

Emulsions (cosmetics, pharmaceutical products)

Diverse industries

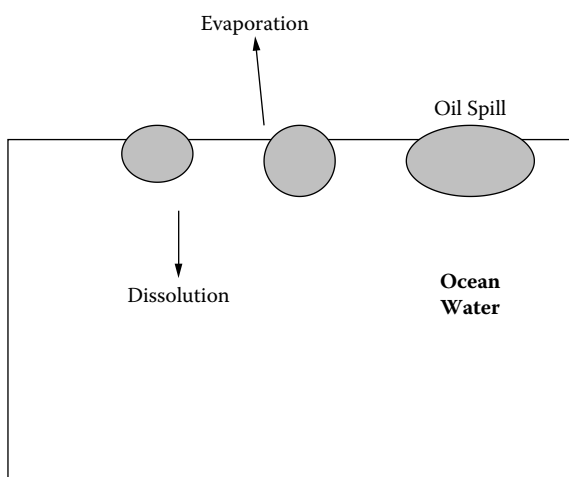
Oil and gas, and shale oil recovery (fracking technology), paper and printing, milk products

## 1.2 ESSENTIAL SURFACE CHEMISTRY CONCEPTS

The science of surface chemistry covers a very large area, and therefore some essential concepts are delineated here. More details will be covered in the rest of the book, and real practical examples will be analyzed. The classical physical chemistry will be applied throughout the book, along with suitable literature references. However, some essential principles will be delineated in appendices in each chapter.

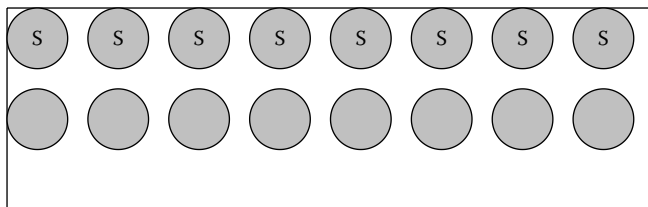
As a typical example, reactions taking place at the surface of oceans (such as solubility of oxygen,  $\text{CO}_2$ , etc.) will be expected to be different than those observed inside the seawater. Further, in some instances, such as oil spills, one can easily realize the importance of the role of surface of oceans (Figure 1.3). It has been found that part of oil evaporates, while some sinks to the bottom, and the main part remains floating on the surface of water. This process is one of the major areas of surface chemistry applications. It is also obvious that the surface of oceans plays an important role in everyday life.

It is also well known that the molecules situated near or at the interface (i.e., liquid–gas) will interact differently with respect to each other than the molecules in the bulk phase (Figure 1.4). The essential aspects of this important subject will be described extensively in this book. The intramolecular forces acting would thus be different in these two cases. In other words, all processes occurring near any interface will be dependent on these molecular orientations and interactions. Furthermore, it has been pointed out that, for a dense fluid, the repulsive forces



**FIGURE 1.3** Ocean surface and oil spill (evaporation, solution, sinking, floating states).



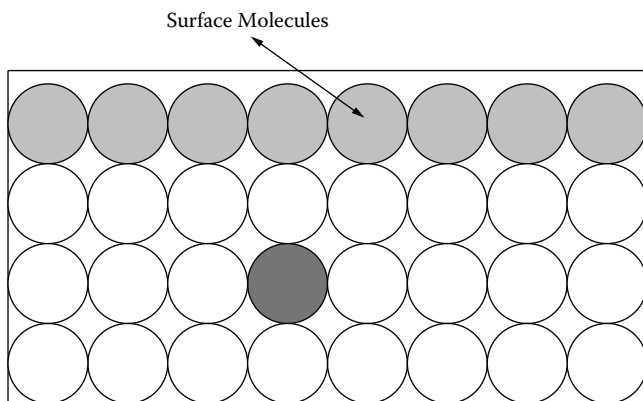


**FIGURE 1.4** Surface molecules.

dominate the fluid structure and are of primary importance. The main effect of the repulsive forces is to provide a uniform background potential in which the molecules move as hard spheres. The molecules at the interface would be under an *asymmetrical* force field, which gives rise to the so-called surface tension or interfacial tension (Figure 1.4) (Chattoraj and Birdi, 1984; Birdi, 1989, 1997, 1999, 2002; Adamson and Gast, 1997).

At a molecular level, when one moves from one phase to another, that is across an interface, this leads to adhesion forces between liquids and solids, which is a major application area of surface and colloid science (Figure 1.5).

The resultant force on molecules will vary with time because of the movement of the molecules; the molecules at the surface will be pointed downward into the bulk phase. The nearer the molecule is to the surface, the greater the magnitude of the force due to *asymmetry*. The region of asymmetry plays a very important role. Thus, when the surface area of a liquid is increased, some molecules must move from the interior of the continuous phase to the interface. Surface tension of a liquid is the force acting normal to the surface per unit length of the interface, thus tending to decrease the surface area. The molecules in the liquid phase are surrounded by neighboring molecules and these interact with one another in a symmetrical way.



**FIGURE 1.5** Intermolecular forces around a molecule in the bulk liquid (dark) and around a molecule on the surface (light) layer.

The state of solid–liquid–gas phases may be described in a simpler way as follows. These phases may be compared with a football field with people as atoms (or molecules):

- There are people sitting in their seats (solid phase).
- There are people moving in and out of their seats (liquid phase).
- There are players running around in the field (gas phase).

Note that the distance between players on the field is much larger and variable (even including collisions, exactly what also happens in the gas molecules) than those sitting in their seats, which is analogous to molecules in a gas.

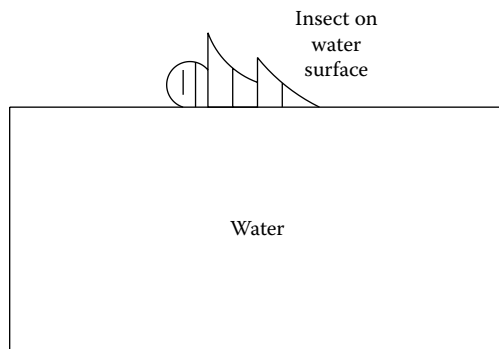
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In the gas phase, where the density is 1000 times lesser than in the liquid phase, the interactions between molecules are very weak as compared to in the dense liquid phase. Thus when one crosses the line from the liquid phase to the gas phase, there is a change in density of factor 1000. This means that while in liquid phase a molecule occupies a volume that is 1000 times smaller than when in the gas phase. The interfacial region is found to be of molecular dimension. Some experiments show it to be of one or few molecules thick.

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*Surface tension* is the differential change of free energy with change of surface area. An increase in surface area requires that molecules from the bulk phase are brought to the surface phase. The same is valid when there are two fluids or a solid–liquid; it is usually designated *interfacial tension*. A molecule of a liquid attracts the molecules that surround it and in turn it is attracted by them (Figure 1.5). For the molecules that are inside a liquid, the resultant of all these forces is neutral and all of them are in equilibrium by reacting with each other. When these molecules are on the surface, they are attracted by the molecules below and by the lateral ones, but not toward the outside. The result is a force directed inside the liquid. In turn, the cohesion among the molecules supplies a force tangential to the surface. So, a fluid surface behaves like an elastic membrane that wraps and compresses the liquid below the surface molecules. The surface tension expresses the force with which the surface molecules attract each other. It is common observation that due to the surface tension it takes some effort for some bugs to climb out of the water in lakes. On the contrary, other insects, such as marsh treaders and water striders, exploit the surface tension to skate on the water without sinking (Figure 1.6).

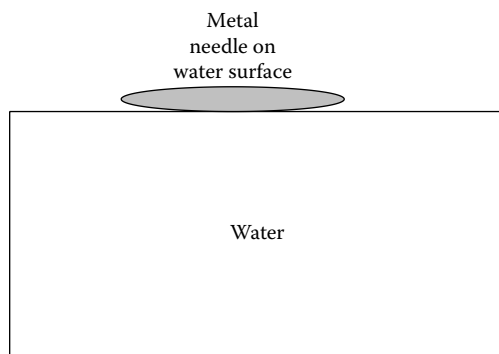
Insects that move about on the surfaces of lakes are actually also collecting food from the surface of the water. Another well-known example is the floating of a metal needle (or any object heavier than water) on the surface of water (Figure 1.6). The surface of a liquid under tension maintains a sort of skin-like structure. In other words, energy is required to carry any object from the air through the surface of a liquid. The surface of a liquid can thus be regarded as the plane of potential energy. It may be assumed that the surface of a liquid behaves as a membrane (at a molecular scale) that stretches across and needs to be broken in order to penetrate. One



**FIGURE 1.6** An insect (many different kinds of insects, including mosquitoes) strides on the surface of water.

observes this tension when considering that a heavy iron needle (heavier than water) can be made to float on a water surface when carefully placed (Figure 1.7).

The reason a heavy object can float on water is due to the fact that in order for it to sink it must overcome the surface forces. Of course, if one merely drops the metal object it will overcome the surface tension force and sink. This clearly shows that at any liquid surface a tension exists (surface tension) that needs to be broken when any contact is made between the liquid surface and the material (here, the metal needle). There are ample examples on the surfaces of rivers and lakes, where stuff is seen floating about. Based on the same principles, it has been found that the smooth hull of a ship exerts less resistance to sail than a rough bottom, thus saving energy.



**FIGURE 1.7** An iron needle (or any similar metal object) floats on the surface of water (only if carefully placed, otherwise it should sink due to gravity forces). The best procedure is to place the metal object on a piece of paper, and then place the paper on the surface of the water. As the paper sinks, the metal object remains floating.

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**Definition of liquid interfaces:**

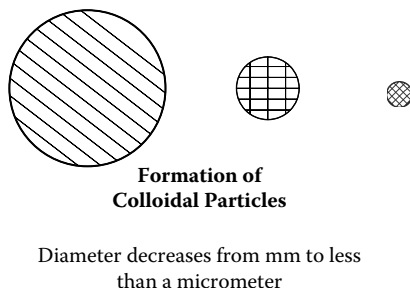
1. Liquid and vapor or gas (for example, ocean surface and air)
2. Liquid<sub>1</sub> and liquid<sub>2</sub> immiscible (water–oil, emulsion)
3. Liquid and solid interface (water drop resting on a solid, wetting, cleaning of surfaces, adhesion)

**Definition of solid surfaces or interfaces:**

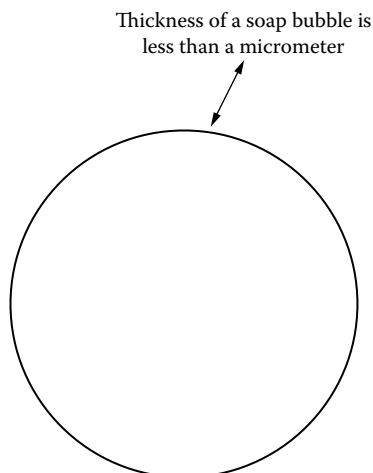
1. Solid<sub>1</sub>–solid<sub>2</sub> (cement, adhesives)
- 

An analogous case would be when the solid is crushed and the surface area increases per unit gram (Figure 1.8). For example, finely divided talcum powder has a surface area of 10 m<sup>2</sup> per gram. Active charcoal exhibits surface areas corresponding to over 1000 m<sup>2</sup> per gram. This is an appreciable quantity and its consequence will be shown later. Qualitatively, it should be noted that work has to be put into the system when the surface area increases (both for liquids or solids or any other interface). Cement is mainly based on the energy used to make the particles as small as possible, such that the cost is dependent on this process.

The surface chemistry of small particles is an important part of everyday life (such as, dust, talcum powder, sand, raindrops, and emissions). Let us define what is meant by *colloid chemistry* and its relation to surface chemistry. This was already defined a century ago by Thomas Graham. A particle having dimensions in the range of 10<sup>−9</sup> m (10 Å) to 10<sup>−6</sup> m (1 μm) was considered to be colloidal. The nature and relevance of colloids is one of the main current research topics (Birdi, 2002, 2010a). Colloids are an important class of materials, intermediate between bulk and molecularly dispersed systems. The colloid particles may be spherical, but in some cases one dimension can be much larger than the other two (as in a needlelike shape). The size of particles also determines whether they can be seen by the naked eye. Colloids are not visible to the naked eye or under an ordinary optical microscope.



**FIGURE 1.8** Formation of fine (colloidal) particles (such as talcum powder, active charcoal, or cement). (The size is less than a micrometer.)



**FIGURE 1.9** Soap bubble of thickness (micrometer or less).

The scattering of light can be suitably used to see such colloidal particles (such as dust particles). The size of colloidal particles then may range from  $10^{-4}$  to  $10^{-7}$  cm. The units used are as follows:

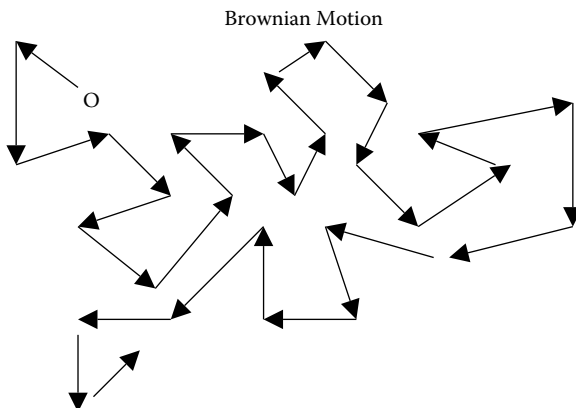
$$1\ \mu\text{m} = 10^{-6}\ \text{m}$$

$$1\ \text{nm} = 10^{-9}\ \text{m}$$

$$1\ \text{\AA} (\text{Angstrom}) = 10^{-8}\ \text{cm} = 0.1\ \text{nm} = 10^{-10}\ \text{m}$$

Nanodimension can be imagined by considering the following simple examples: Hair: 1/1000th diameter is about nanosize. The thickness of soap bubbles varies from micro- to nanometer colored rings (in Figure 1.9). Actually, a soap bubble is the closest thing that can be seen by the naked eye that is of molecular dimension.

In surface chemistry there is a great need for suitable range of dimensions as needed for a variety of systems. As seen here, the range of dimensions is manifold. Accordingly, a unit Angstrom ( $\text{\AA} = 10^{-8}\ \text{cm}$ ) was used for systems of molecular dimension (famous Swedish scientist). However, the most common unit is the nanometer ( $10^{-9}\ \text{m}$ ), which is mainly used for molecular scale features. In recent years, nanosize (nanometer range) particles are of much interest in different applied science systems (*nano* from Greek and means “dwarf”). Nanotechnology is actually strongly getting a boost from the last decade of innovation, as reported in the surface and colloid literature (Rao, 2011). In fact, light scattering is generally used to study the size and size distribution of such systems. Since colloidal systems consist of two or more phases and components, the interfacial area to volume ratio becomes very significant. Colloidal particles have a high surface area to volume ratio compared with bulk materials. A significant proportion of the colloidal molecules lie within, or close to, the interfacial region. Hence, the interfacial region has significant control over the



**FIGURE 1.10** Brownian motion. Dust particles in the air are sometimes observed moving in jumps. This is due to molecular collisions between the gas molecules and the dust particles.

properties of colloids. To understand why colloidal dispersions can either be stable or unstable we need to consider the following:

1. The effect of the large surface area to volume ratio (for example, 1000 m<sup>2</sup> surface area per gram of solid [active charcoal])
2. The forces operating between the colloidal particles
3. Surface charges are very important characteristics of such systems.

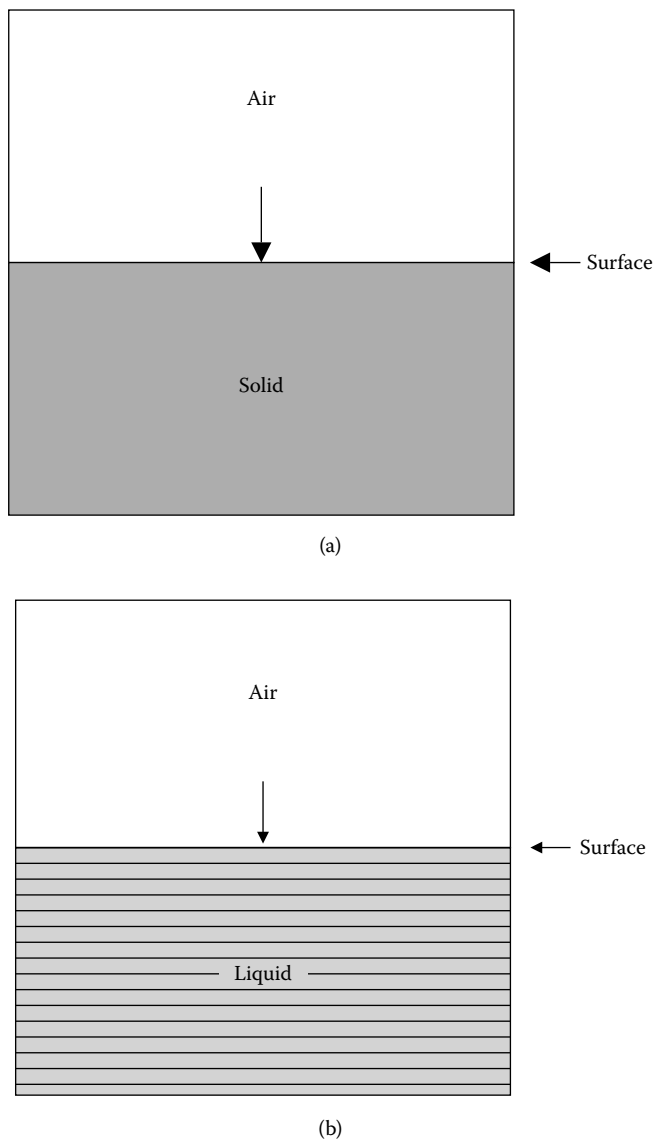
There are some very special characteristics that must be considered about colloidal particle behavior: size and shape, surface area, and surface charge density. The *Brownian motion* of the particles is a much-studied field (Figure 1.10). The *fractal* nature of surface roughness has recently been shown to be of importance (Birdi, 1993). Recent applications have been reported where *nanocolloids* have been employed. It is thus found that some terms are needed to be defined at this stage. The definitions generally employed are as follows. *Surface* is a term used when one considers the dividing phase between:

- Gas–liquid
- Gas–solid

Interface (Figure 1.11) is the term used when one considers the dividing phase:

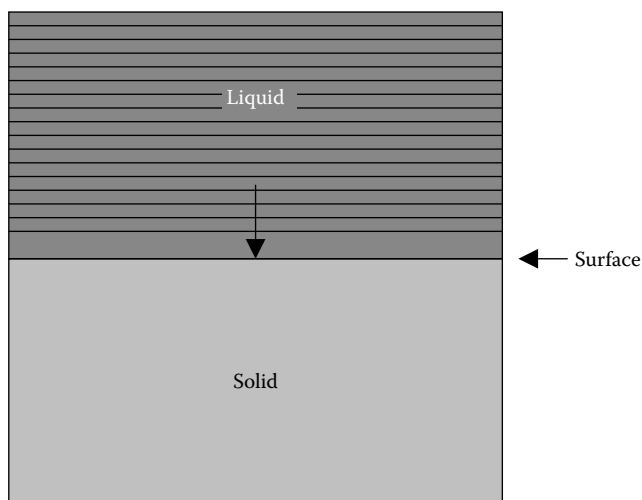
- Solid–liquid (colloids)
- Liquid<sub>1</sub>–liquid<sub>2</sub> (oil–water, emulsion)
- Solid<sub>1</sub>–solid<sub>2</sub> (adhesion, glue, cement)

It is obvious that surface tension may arise due to a degree of unsaturation of the bonds that occurs when a molecule resides at the surface and not in bulk. The term *surface tension* is used for solid–vapor or liquid–vapor interfaces. The term *interfacial tension* is more generally used for the interface between two liquids (oil–water), two solids, or a liquid and solid. It is, of course, obvious that in a one-component

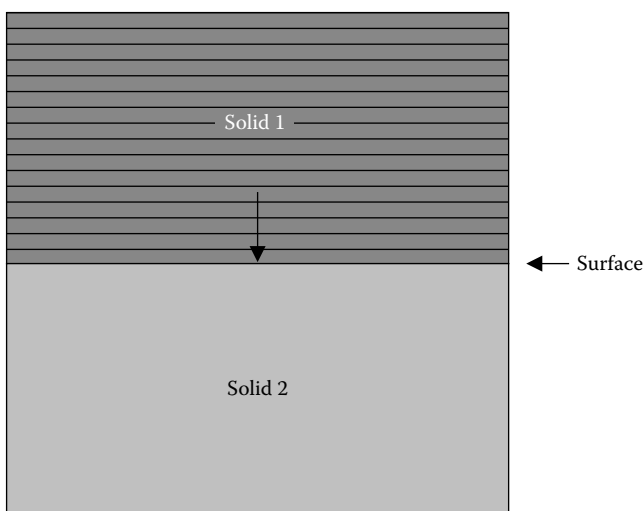


**FIGURE 1.11** Different interfaces: (a) solid–gas (air), (b) liquid–gas (air), (c) solid–liquid, (d) solid 1–solid 2. (*Continued*)

system the fluid is uniform from the bulk phase to the surface. However, the *orientation* of the surface molecules will be different from those molecules in the bulk phase in all systems. For instance, in the case of water, the orientation of molecules inside the bulk phase will be different from those at the interface. The hydrogen bonding will orient the oxygen atom toward the interface. The question one may ask, then, is how sharply does the density change from that of being fluid to that of gas



(c)



(d)

**FIGURE 1.11** (Continued) Different interfaces: (a) solid–gas (air), (b) liquid–gas (air), (c) solid–liquid, (d) solid 1–solid 2.

(a change by a factor of 1000). Is this transition region a monolayer deep or many layers deep? Many studies have been reported where this subject has been investigated. *Gibbs adsorption theory* (Defay et al., 1966; Chattoraj and Birdi, 1984; Birdi, 1989, 1999, 2002, 2009, 2010a) considers the surface of liquids to be monolayer. The surface tension of water decreases appreciably with the addition of very small quantities of *soaps and detergents*. Gibbs adsorption theory relates the change in



surface tension to the change in soap concentration. The experiments that analyze the spread monolayers are also based on one molecular layer. The latter data conclusively indeed verifies the Gibbs assumption (as described later). Detergents and other (soaps, etc.) similar kinds of molecules are found to exhibit self-assembly characteristics. The subject related to *self-assembly monolayer* (SAM) structures will be treated extensively (Birdi, 1999). However, no procedure that can provide information by a direct measurement exists. This subject will be described later herein. The composition of the surface of a solution with two components or more would require additional comments.

*Colloids* (the Greek word for “glue-like”) are a wide variety of systems consisting of finely divided particles or macromolecules (such as, glue, gelatin, proteins) which are found in everyday life. Typical colloidal suspensions that are found in everyday life are provided in Table 1.1. Further, colloidal systems are widespread in their occurrence and have biological and technological significance. There are three types of colloidal systems (Adamson and Gast, 1997; Lyklema, 2000; Birdi, 2002, 2009; Dukhin and Goetz, 2002):

1. In simple colloids, clear distinction can be made between the disperse phase and the disperse medium, for example, simple emulsions of oil-in-water (O/W) or water-in-oil (W/O).
2. Multiple colloids involve the coexistence of three phases of which two are finely divided, for example, multiple emulsions (mayonnaise, milk) of water-in-oil-in-water (W/O/W) or oil-in-water-in-oil (O/W/O).
3. Network colloids have two phases forming an interpenetrating network, for example, polymer matrix.

The colloidal (in the form as solids or liquid drops) stability is determined by the free energy (surface free energy or the interfacial free energy) of the system. The

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**TABLE 1.1**  
**Typical Colloidal Systems**

| Dispersed      | Continuous | System Name                                                                                        |
|----------------|------------|----------------------------------------------------------------------------------------------------|
| Liquid         | Gas        | Aerosol fog, spray                                                                                 |
| Gas            | Liquid     | Foam, thin films, froth, fire extinguisher foam                                                    |
| Liquid         | Liquid     | Emulsion (milk), mayonnaise, butter                                                                |
| Solid          | Liquid     | Sols, AgI, photography films, suspension wastewater, cement, oil recovery (shale oil), coal slurry |
| Corpuscles     | Serum      | Biocolloids (blood, blood coagulants)                                                              |
| Hydroxyapatite | Collagen   | Bone, teeth                                                                                        |
| Liquid         | Solid      | Solid emulsion (toothpaste)                                                                        |
| Solid          | Gas        | Solid aerosol (dust)                                                                               |
| Gas            | Solid      | Solid foam (polystyrene), insulating foam                                                          |
| Solid          | Solid      | Solid suspension/solids in plastics                                                                |

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main parameter of interest is the large surface area exposed between the dispersed phase and the continuous phase. Since the colloid particles move about constantly, their dispersion energy is determined by the Brownian motion. The energy imparted by collisions with the surrounding molecules at temperature  $T = 300\text{ K}$  is  $3/2 k_B T = 3/2 \cdot 1.38 \cdot 10^{-23} \cdot 300 = 0.6 \cdot 10^{-20}\text{ J}$  (where  $k_B$  is the Boltzmann constant). This energy and the intermolecular forces would thus determine the colloidal stability.

In the case of colloid systems (particles or droplets), the kinetic energy transferred on collision will be thus  $k_B T = 10^{-20}\text{ J}$ . However, at a given moment there is a high probability that a particle may have a larger or smaller energy. Further, the probability of total energy several times  $k_B T$  (over 10 times  $k_B T$ ) becomes very small. The instability will be observed if the ratio of the barrier height to  $k_B T$  is around 1 to 2 units.

The idea that two species ( $\text{solid}_1\text{--solid}_2$ ) should interact with one another, so that their mutual potential energy can be represented by some function of the distance between them, has been described in the literature. Furthermore, colloidal particles frequently adsorb (and even absorb) ions from their dispersing medium (such as in groundwater treatment and purification). Sorption that is much stronger than what would be expected from dispersion forces is called *chemisorption*, a process that is of both chemical and physical interest. For example, in a recent report it was mentioned that finely divided iron particles could lead to enhanced photosynthesis in oceans (resulting in the binding of large amounts of  $\text{CO}_2$  from air). This could lead to control of the global warming effect. In fact, specific processes are being investigated that will lead to effective carbon capture (i.e.,  $\text{CO}_2$  capture) from such industries as coal (Krungeleviclut et al., 2012).

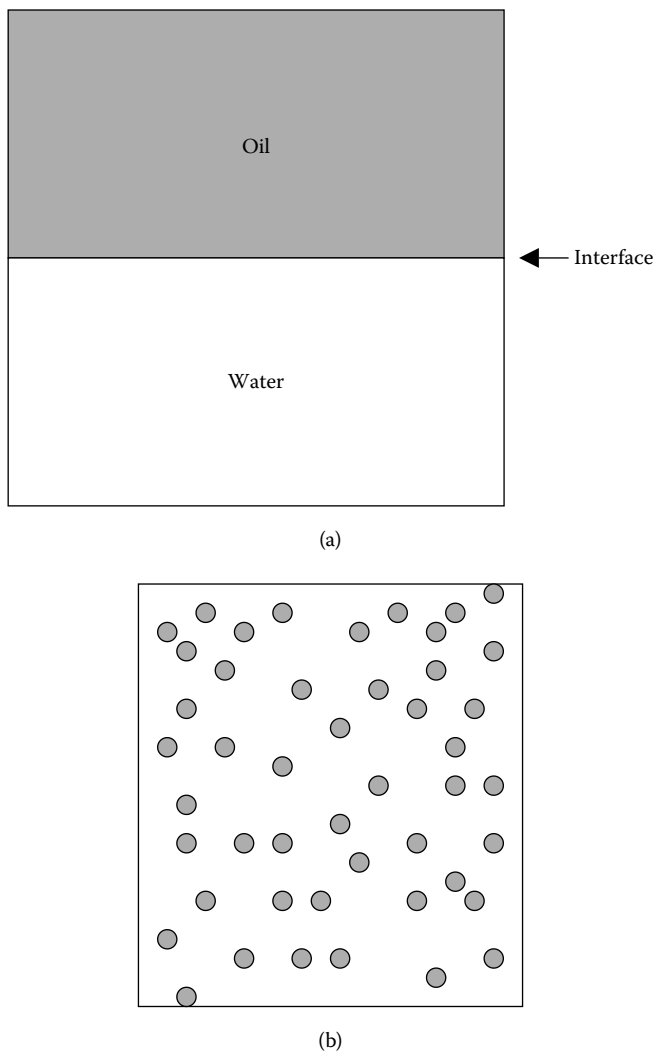
As one knows from experience, oil and water do not mix (Figure 1.12), which suggests that these systems are dependent on the oil–water interface. The liquid<sub>1</sub>–liquid<sub>2</sub> (oil–water) interface is found in many systems, most important is the world of *emulsions*.

The trick in using emulsions is based on the fact that one can apply both water and oil (the latter is insoluble in water) simultaneously. Further, one can then include other molecules that may be soluble in either phase (water or oil). This obviously leads to the common observation where we find thousands of applications of emulsions. It is very important to mention here that nature actually uses this trick in most of the major biological fluids. The most striking example is milk. The emulsion chemistry of milk is one of the most complex, and has still not been well investigated. Paint consists of polymer molecules dispersed in the water phase. After application, water evaporates leaving behind a glossy layer of paint.

In fact, the state of mixing oil and water is an important example of interfacial behavior at liquid<sub>1</sub>–liquid<sub>2</sub>. Emulsions of oil–water systems are useful in many aspects of daily life: milk, foods, paint, oil recovery, pharmaceutical, and cosmetics.

When olive oil is mixed with water, upon shaking, one will get the following:

- About 1 mm diameter oil drops are formed.
- After a few minutes the oil drops merge together and two layers (oil and water) are again formed.



**FIGURE 1.12** (a) Oil–water phases, (b) emulsion (oil drops mixed with water).

However, if suitable substances are added, which changes the surface forces, the olive oil drops that are formed can be very small (micrometer range). The latter leads to a stable emulsion.

The emulsion stability is basically stable depending on the size of the oil drops, in addition to other factors, dispersed in the water phase.

Low stability = large oil drops

Long stability = small drops

Very long stability = microsize drops

In addition, these considerations are important with regard to the different systems as follows: paints, cements, adhesives, photographic products, water purification, sewage disposal, emulsions, chromatography, oil recovery, paper and print industry, microelectronics, soap and detergents, catalysts, and biology (cell, virus). In some oil–surfactant–water–diverse components, liquid crystal (LC) phases (lyotropic LC) are observed. These lyotropic LC are indeed the basic building blocks in many applications of emulsions in technology. LC structures can be compared with a layer cake where each layer is molecular thick. It is thus seen that surface science pertains to investigations that take place at two different phases.

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