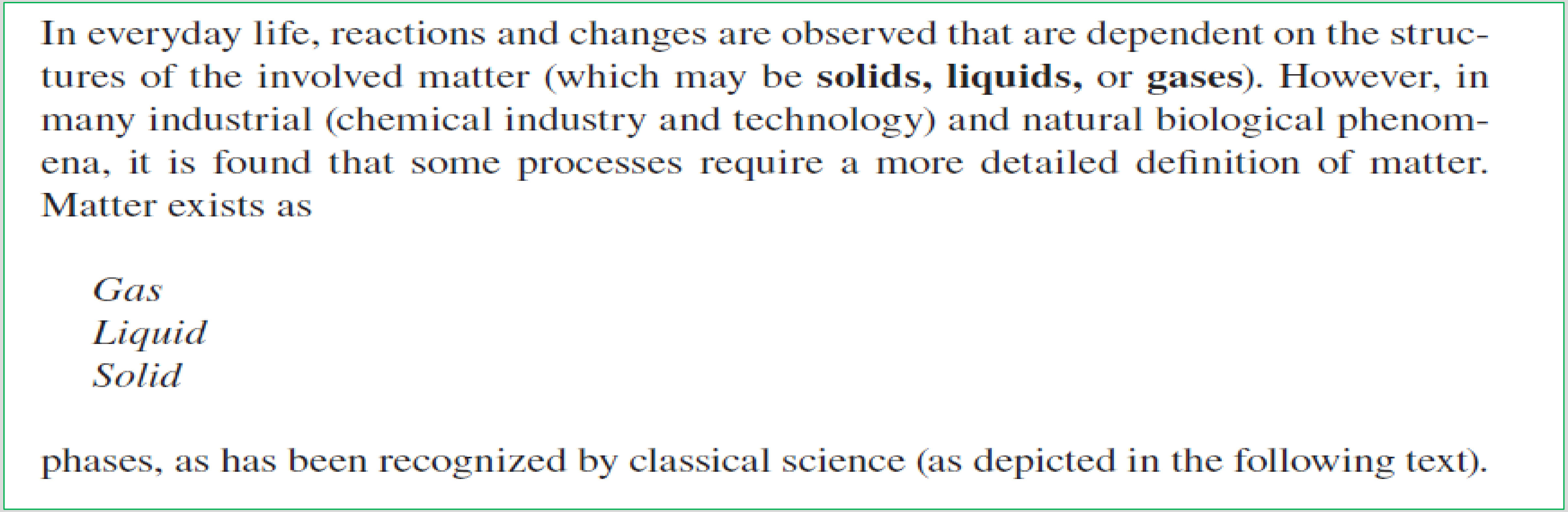
SURFACE PHENOMENON

SURFACE TENSION AND ENERGY

Introduction



In everyday life, reactions and changes are observed that are dependent on the structures of the involved matter (which may be **solids, liquids,** or **gases**). However, in many industrial (chemical industry and technology) and natural biological phenomena, it is found that some processes require a more detailed definition of matter. Matter exists as

Gas
Liquid
Solid

phases, as has been recognized by classical science (as depicted in the following text).

Solid Phase–Liquid Phase–Gas Phase

The molecules that are situated at the *interfaces* (e.g., between gas–liquid, gas–solid, liquid–solid, liquid_1–liquid_2, and solid_1–solid_2) are known to behave differently from those in the bulk phase (Adam, 1930; Aveyard and Hayden, 1973; Bakker, 1926; Bancroft, 1932; Partington, 1951; Davies and Rideal, 1963; Defay et al., 1966; Gaines, 1966; Harkins, 1952; Holmberg, 2004; Matijevic, 1969; Fendler and Fendler, 1975; Adamson and Gast, 1997; Chattoraj and Birdi, 1984; Birdi, 1989, 1997, 1999, 2002, 2009; Miller and Neogi, 2008; Somasundaran, 2006). Typical examples are

- Liquid surfaces
- Surfaces of oceans (liquid–air interface)
- Solid surfaces (adhesion, glues, tapes)
- Road surface (solid–air or solid–car tire)
- Lung surface
- Washing and cleaning (surfaces, foams)
- Emulsions (cosmetics, pharmaceutical products)
- Diverse industries (oil and gas, paper, milk products)

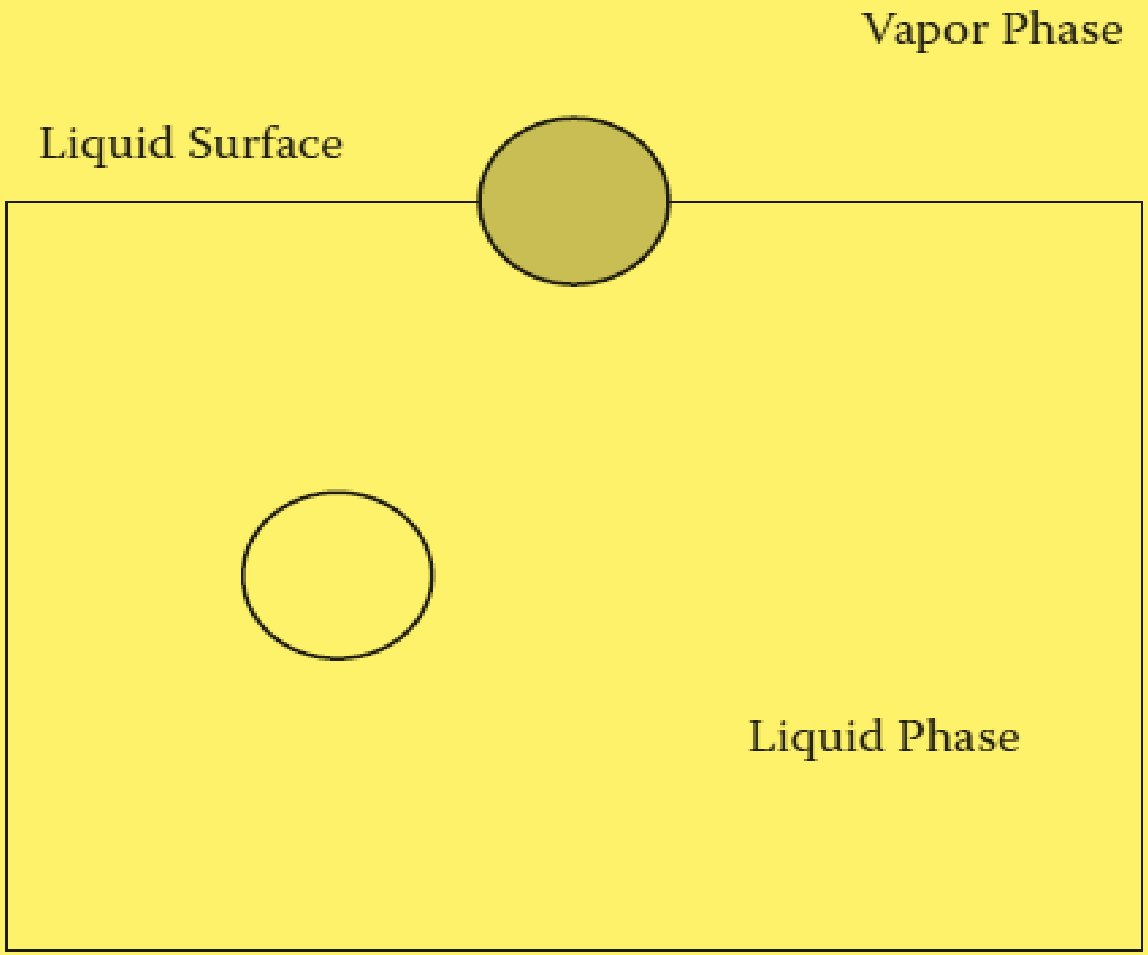
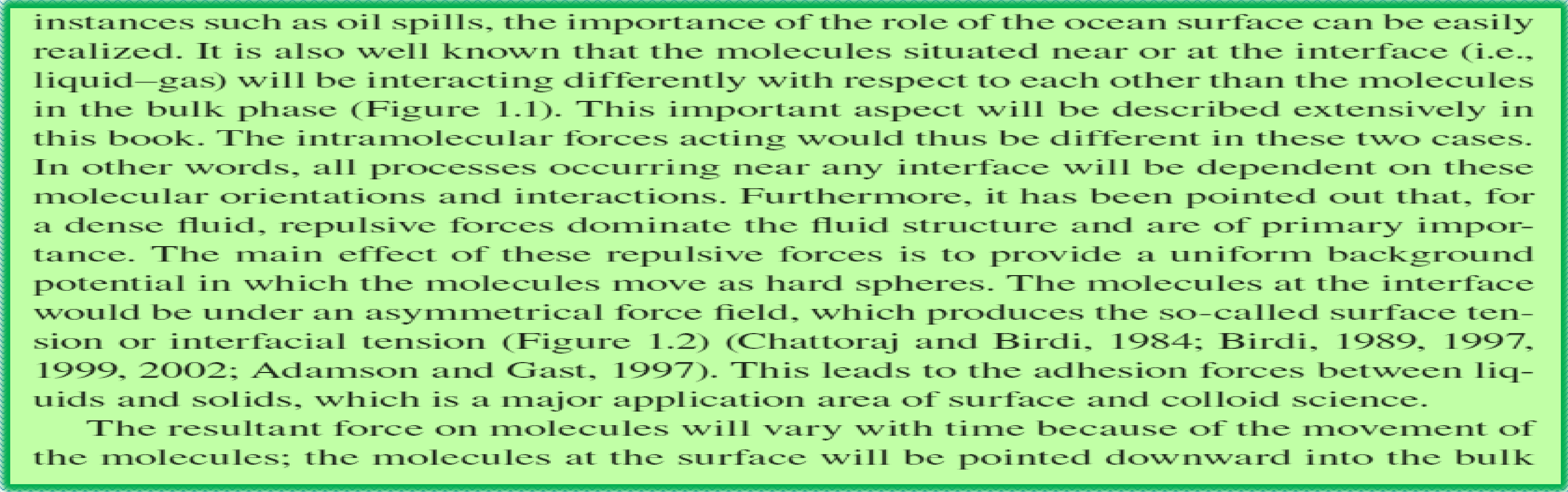
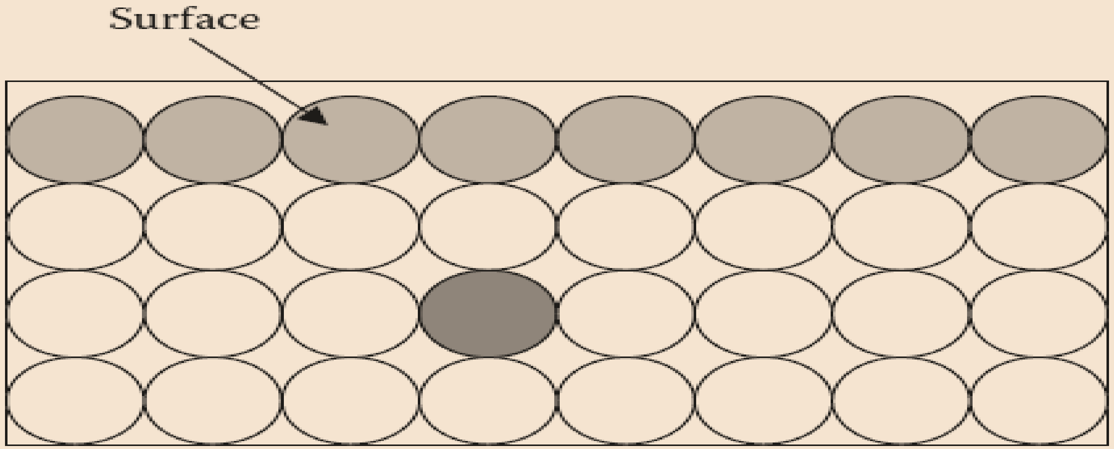


FIGURE 1.1 Surface molecules (schematic).



instances such as oil spills, the importance of the role of the ocean surface can be easily realized. It is also well known that the molecules situated near or at the interface (i.e., liquid–gas) will be interacting differently with respect to each other than the molecules in the bulk phase (Figure 1.1). This important aspect 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, repulsive forces dominate the fluid structure and are of primary importance. The main effect of these 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 produces the so-called surface tension or interfacial tension (Figure 1.2) (Chattoraj and Birdi, 1984; Birdi, 1989, 1997, 1999, 2002; Adamson and Gast, 1997). This leads to the adhesion forces between liquids and solids, which is a major application area of surface and colloid science.

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



FIGu r e 1.2 Intermolecular forces around a molecule in the bulk liquid (dark) and around a molecule in the surface (light) layer (schematic).

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. The surface tension of a liquid is the force acting normal to the surface per unit length of the interface, thus tending to reduce the surface area. The molecules in the liquid phase are surrounded by neighboring molecules, and these interact with each other in a symmetrical way. 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 those in the dense liquid phase. Thus, when we pass from the liquid phase to the gas phase, there is a change in density of factor 1000. This means that, while in the liquid phase, a molecule occupies a volume that is 1000 times smaller than when it is in the gas phase.

Surface tension is the differential change of free energy with change in surface area. An increase in surface area requires that molecules from the bulk phase are brought to the surface phase. This is valid when there are two fluids or a solid and a liquid, and it is usually designated *interfacial tension*.

A molecule of a liquid attracts the molecules that surround it, and, in its turn, it is attracted by them (Figure 1.2). 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 resultant is a force directed inside the liquid. In its 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 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 the marsh treaders and water striders, exploit the surface tension to skate on the water without sinking (Figure 1.3).

Another well-known example is the floating of a metal needle (heavier than water) on the surface of water (Figure 1.4.) 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 be penetrated. One observes this *tension* when considering that a heavy iron needle (heavier than water) can be made to float on the water surface when carefully placed (Figure 1.4).

The reason a heavy object floats on water is because in order to sink, it must overcome the surface forces. This clearly shows that, at any liquid surface, there exists a tension (*surface tension*) that needs to be broken when any contact is made between the liquid surface and the material (here the steel needle). A liquid can form three types of interfaces:

1. Liquid and vapor or gas (e.g., ocean surface and air)
2. Liquid$_1$ and liquid$_2$ immiscible (water–oil, *emulsion*)
3. Liquid and solid interface (water drop resting on a solid, wetting, cleaning of surfaces, adhesion).

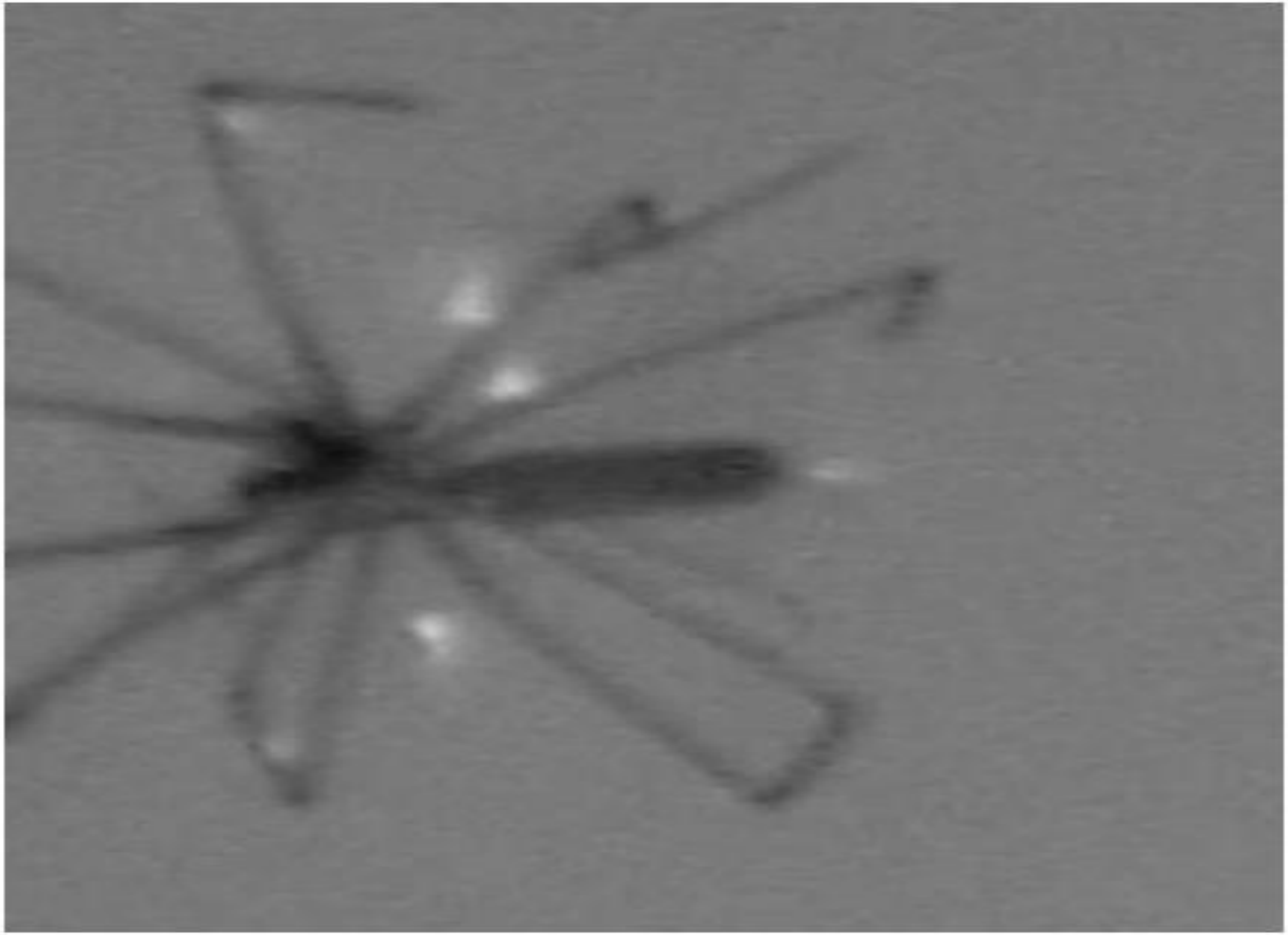


FIGURE 1.3 Insect strides on the surface of water.

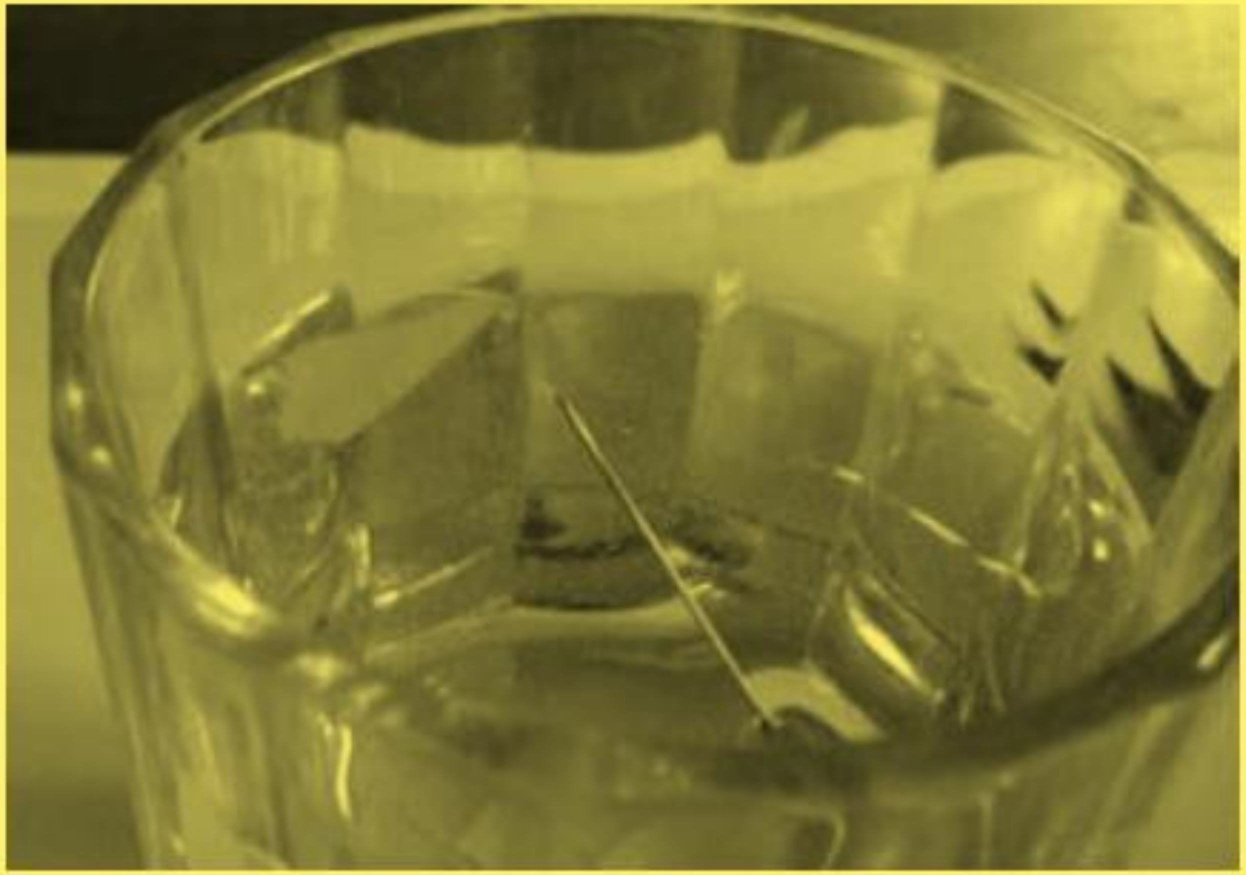


FIGURE 1.4 An iron needle floats on the surface of water (*only if carefully placed*; otherwise, it should sink due to gravity forces).

The surface chemistry of *small particles* is an important part of everyday life (such as dust, talcum powder, sand, raindrops, emissions, etc.). The designation *colloid* is used for particles that are of small dimension and that cannot pass through a membrane with a pore size ca. 10^{-6} m (= micrometer [μm]) (Thomas Graham described this about a century ago).

The nature and relevance of colloids is one of the main current research topics (Birdi, 2002). They are an important class of materials, intermediate between bulk and molecularly dispersed systems. Colloid particles may be spherical but, in some cases, one dimension can be much larger than the other two (as in a needle-like 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. The scattering of light can be suitably used to see such colloidal particles (such as dust particles, etc.). Their size then may range from 10^{-4} to 10^{-7} cm. The units used are as follows:

1 μm = 10^{-6} m
1 nm = 10^{-9} m
1 Å (Angstrom) = 10^{-8} cm = 0.1 nm = 10^{-10} m