What is soft matter?

<div style="text-align:right">**1**</div>

Soft matter includes a large variety of materials, typically composed of polymers, colloids, liquid crystals, surfactants, and other mesoscopic constituents. In this chapter, we shall discuss (i) what are these materials, (ii) what are the common characteristics of these materials, and (iii) what is the physics that gives such characteristics to soft matter.

1.1 Polymers

Polymers are long string-like molecules made of certain chemical units called monomers. The monomers are connected sequentially as shown in Fig. 1.1. The number of monomers in a polymer is typically several thousand, and can be as large as tens of millions. Polymers are indispensable materials in modern technology; they are used as plastics, rubbers, films, and textiles.

Polymers are also the basic molecules of life. The machinery of life is realized by proteins which are natural polymers made of amino acids. The genetic information of life is inscribed in another important class of bio-polymer, DNA.

In polymers, a variety of materials can be produced simply by changing the types of monomers and the way they are connected. Polymers are usually string-like as shown in Fig. 1.2(a), but branches can be introduced as in Fig. 1.2(b) or the strings can be cross-linked as in Fig. 1.2(c). Plastics are usually made of string-like polymers (Fig. 1.2(a)). They can be brought into a liquid state which can be easily molded into any desired shapes. On the other hand, rubbers are made of cross-linked polymers (Fig. 1.2(c)). Since the molecules are all connected, rubbers cannot flow. They change their shape under external forces, but recover their original shape when the forces are removed. The branched polymers (Fig. 1.2(b)) are intermediate, and behave like a rubbery material which can flow. The adhesives used in adhesive tapes are made of branched polymers which are intermediate between the liquid state and rubbery state.

Depending on the chemical structure of monomers, polymeric materials can be very soft, like rubbers in rubber bands, or can be very hard, like plastics in car bumpers. Materials which are hard for small strain, but become plastic for large strain have been made by mixing these monomers. New types of polymers, electro-conductive polymers, or photo-reactive polymers have been developed and are used extensively in modern technologies.
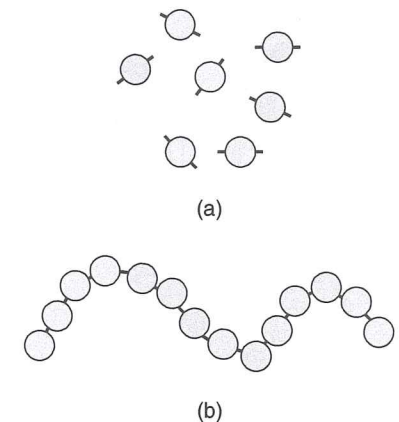

(a)

(b)

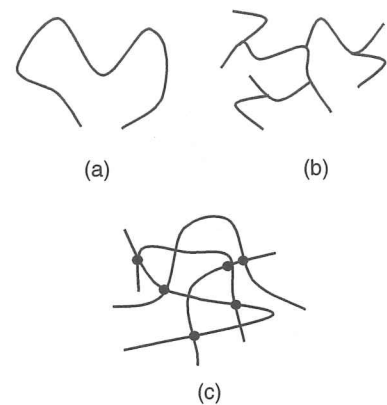**Fig. 1.1** (a) Monomer; (b) polymer.

Fig. 1.2 Various polymers made of the same monomer, but by different monomer connections. (a) Linear polymer; (b) branched polymer; (c) network polymer.

Fig. 1.3 Various phases of spherical colloids. (a) Sol; (b) gel; (c) crystal.

1.2 Colloids

Colloids are small solid particles or fluid droplets dispersed in other fluids. The diameter of colloidal particles is typically between 1 [nm] and 1 [μm] and is much larger than atomic size.

Colloids are seen in everyday life. Milk is a colloidal solution with nutritious particles (made of fat and proteins) of about 0.1 μm dispersed in water. Water colour is a colloidal solution of coloured solid particles (called pigments) dispersed in water.

Colloidal suspensions made of solid particles are fluids and can flow if the particle concentration is low, but become solid-like and cease to flow when the particle concentration becomes large. For example, water colour is a fluid when dissolved in water, but becomes solid as it dries up. The fluid state is called a sol, and the solid state is called a gel (see Fig. 1.3).

The transition from sol to gel can be induced without changing the concentration of particles. By the addition of certain chemicals to a colloidal solution, the interaction between colloidal particles can be changed, leading to a transformation from sol to gel. For example, when vinegar is added to milk, the milk becomes quite viscous and loses fluidity. This is caused by the aggregation of milk particles whose interaction becomes attractive when vinegar is added.

The solidification of colloids usually occurs by random aggregation of particles as shown in Fig. 1.3(b). If the particles are carefully made to have the same size and shape, they can form a regular structure, very much like the usual atomic crystal as shown in Fig. 1.3(c). Such colloidal crystals show strong diffraction of light in the same way as X-ray diffraction in atomic crystals. Since the lattice constants of colloidal crystals are of the order of 0.5 [μm], the diffraction is seen as an iridescent colour scattered by these crystals.

There are a variety of colloidal particles, of various shapes (spherical, rod-like, or plate-like particles), and of various surface properties which are used in daily life as well as in industrial applications.

1.3 Surfactants

Oil and water are a typical example of antagonistic pairs. Usual materials are classified into either hydrophilic (water-loving) or oleophilic (oil-loving). Materials which dissolve in oil usually do not dissolve in water, i.e., oleophilic materials are usually hydrophobic (water hating), and vice versa. Surfactants are a special class of so-called amphiphilic materials which can dissolve in both water and oil. Surfactant molecules are made of two parts, one part is hydrophilic, and the other part is hydrophobic (i.e., oleophilic) (see Fig. 1.4(a)). Surfactant molecules can dissolve in water by forming the structure shown in Fig. 1.4(b), where the hydrophilic part is exposed to water encapsulating the hydrophobic part. Such a molecular assembly is called a micelle. On the other hand, surfactant
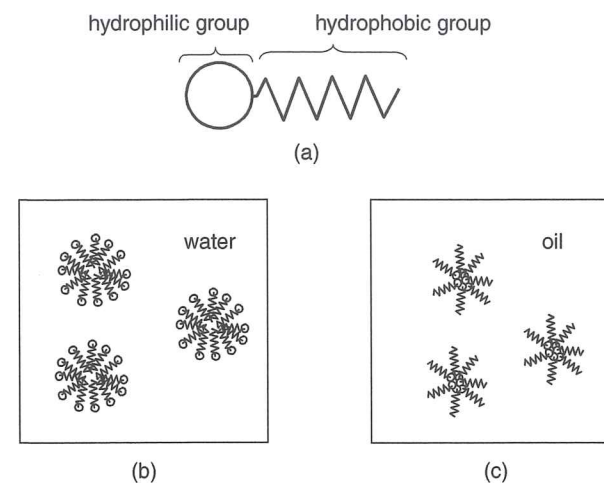

Fig. 1.4 (a) Surfactant molecule; (b) micelles formed in water, (c) inverse micelles formed in oil.

molecules can dissolve in oil by exposing the hydrophobic group to oil concealing the hydrophilic group in an inverted micelle (Fig. 1.4(c)).

Depending on the surfactants, micelles can take various shapes including spheres, cylinders, or lamellae (see Fig. 1.5). Spherical micelles typically consist of several tens of molecules, but cylindrical and lamellar micelles can be much larger than this, as large as millions or billions of molecules. Although the size and shape of the micelles are primarily determined by the structure of the surfactant molecules, they can vary depending on the environment, solvent type, temperature, and surfactant concentration, etc.

Surfactants are used in soaps and detergents in our daily life. Due to their amphiphilic molecular nature, surfactant molecules prefer to sit at the interface between oil and water. Therefore, if a surfactant is added to the mixture of oil and water, surfactant molecules tend to assemble at the oil–water interface. To accommodate these amphiphilic molecules, the interfacial area must increase. Accordingly, the oil becomes encapsulated in small droplets coated by surfactant, and is dispersed in water. This is the basic mechanism for the function of detergents (see Fig. 1.6). The term surfactant comes from this function; it is an abbreviation of 'surface activating agents'.

Surfactants are important in dispersion technology. This is the technology of using surfactants to make seemingly homogeneous materials from components that do not form stable mixtures in usual conditions, for
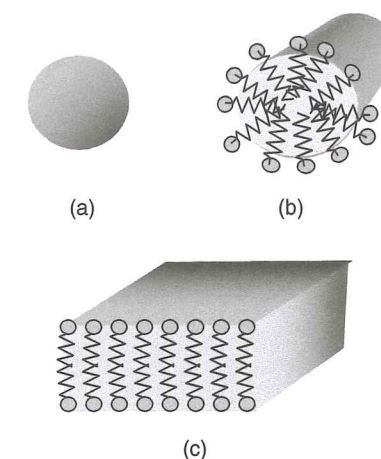

Fig. 1.5 Various structures of micelles formed by surfactants. (a) A spherical micelle; (b) a cylindrical micelle; (c) a lamellar bilayer.
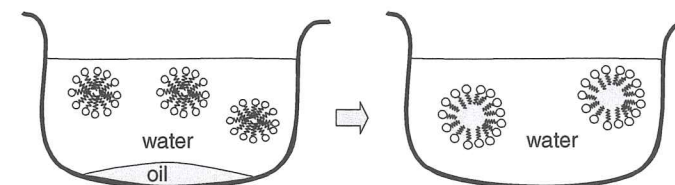

Fig. 1.6 Dispersion of oil droplets in water by the action of surfactants.

example oil and water, or inorganic particulates and water. The standard way is to break the material into fine grains (particles or droplets) in other materials with the aid of surfactants. The surfactants coat the surface of the dispersed materials and prevent their aggregation. This technology is important in many applications (for example, cosmetics and food) as well as in creating new functional materials.

1.4   Liquid crystals

Condensed states of matter are usually classified into two states: the crystalline state where the molecules are ordered, and the liquid state where the molecules are disordered. For certain materials, molecules form a semi-ordered state between crystal and liquid. Such materials are called liquid crystals.

Consider, for example, a material made of rod-like molecules. In the crystalline state, the molecules are regularly placed on lattice sites and are completely aligned as in Fig. 1.7(a). In this state, there is complete order in position and orientation. In the liquid state, the position and orientation of molecules are both random (Fig. 1.7(d)). In the liquid crystalline state, molecules are intermediately ordered between these two states.

A class of liquid crystals, nematics, is illustrated in Fig. 1.7(b). Here the molecules retain the orientational order, while there is no positional order. The nematic liquid crystal is a fluid which has anisotropy: it flows when the container is tilted, but it is anisotropic and shows birefringence. Another class of liquid crystals, smectics, is illustrated in Fig. 1.7(c). Here, in addition to the orientational order, there is a partial positional order: the molecules are regularly placed along a certain direction (the z-axis in Fig. 1.7(c)), but their positions are random in the x–y plane.
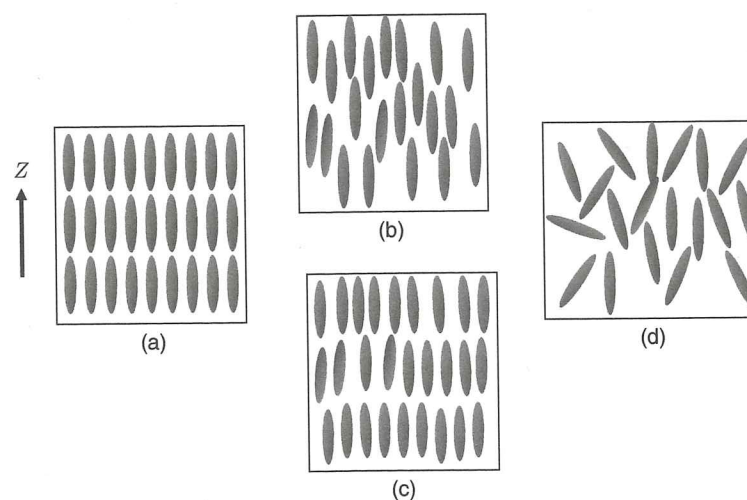

Fig. 1.7 Various phases of materials made of rod-like molecules. (a) Crystal; (b) nematic liquid crystal; (c) smectic liquid crystal; (d) isotropic liquid.

Nematic liquid crystals are extensively used in display devices since their optical properties are easily controlled by an electric field. The changes in the optical properties of liquid crystals are also used as sensors. Strong fibres (used in bullet-proof jackets) are made from liquid crystalline polymers since polymer chains are strongly oriented in liquid crystals.

1.5   What is common in soft matter?

As we have seen, soft matter includes a large class of materials.[1] A natural question is then what is common in these materials, and why are they discussed in the framework of 'soft matter'.

What is common in the above materials is that they all consist of structural units that are much larger than atoms. Polymer molecules typically consist of millions of atoms. Colloidal particles of diameter 0.1 [μm] involve billions of atoms. Molecules constituting surfactants and liquid crystals are not very large (including only tens or hundreds of atoms), but they form ordered structures and move together in a large unit: surfactant molecules form micelles which move as a collective entity, and liquid crystalline molecules move together when they rotate.

The fact that soft matter consists of large molecules or assemblies of molecules which move collectively gives two characteristics to soft matter:

(a) Large and nonlinear response. Soft matter shows a large response to weak forces. Polymer molecules consisting of tens of thousands of atoms are easily deformed, and this gives the softness of rubbers and gels. Colloidal particles form a very soft solid, which is used in cosmetics and paints. The optical properties of liquid crystals are easily changed by an electric field as we have seen. Such large responses cannot be described by linear relations between the force and the response. For example, rubbers can be elongated by several hundred percent of their initial length and their mechanical responses cannot be described by a linear relation between the stress and strain. The nonlinear response is quite important in soft matter.

(b) Slow and non-equilibrium response. The collectivity of soft matter slows down their dynamics. The response time of simple liquids is of the order of 10^{-9} [s], while it can be billions or more times longer (1 [s] to 10^4 [s]) in solutions of polymers and colloids. Consequently, the properties of the non-equilibrium state, or the dynamics in the non-equilibrium state, are quite important in soft matter.

These characteristics are the results of the fact that the fundamental structural units of soft matter are very large. The reason can be understood by the following examples.

Consider a tube containing a solution in which the density of solute is slightly larger than that of solvent. If the tube is rotated as shown in

[1] The materials discussed here do not cover the whole class of soft matter. Other materials, such as granular materials and glassy materials, are often included in soft matter, but will not be discussed in this book.

(a)

(b)

Fig. 1.8 When a tube containing a solution is rotated, the heavier component (assumed to be the solute) is pushed outward by the centrifugal force, and the concentration becomes non-uniform. In a solution of monomers, the concentration changes little as in (a). On the other hand, if these monomers are connected to form large polymers, a large concentration gradient is created as in (b).

[2] m can be expressed as $m = \Delta\rho v$, where $\Delta\rho$ is the difference in the density of solute and solvent, and v is the volume of the solute molecule. Equation (1.1) is derived from the fact that the centrifugal force acting on the particle at x is $m\omega^2 x$.
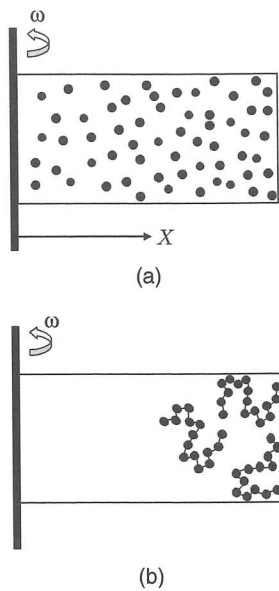
Fig. 1.8, the solute will be pushed outward by the centrifugal force. This effect is expressed by the potential energy for the solute molecule

$$U(x) = -\frac{1}{2}m\omega^2 x^2 \tag{1.1}$$

where m is the effective mass of the solute molecule,[2] ω is the angular velocity, and x is the distance from the rotation centre. At equilibrium, the probability of finding the particle at x is given by the Boltzmann distribution

$$P(x) \propto \exp\left(-\frac{U(x)}{k_B T}\right) \propto \exp\left(\frac{m\omega^2 x^2}{2k_B T}\right) \tag{1.2}$$

For small solute molecules, the factor $m\omega^2 x^2/k_B T$ is small, and hence the solution remains essentially homogeneous in the container. Now suppose that the monomers are transformed to polymers consisting of N monomers. Since the mass of the polymer is Nm, the probability changes as

$$P'(x) \propto \exp\left(\frac{Nm\omega^2 x^2}{2k_B T}\right) \tag{1.3}$$

For large N, the factor $Nm\omega^2 x^2/k_B T$ becomes non-negligible, and the polymer moves to the outer end of the tube. Indeed, polymer molecules are often separated from polymer solutions by centrifugal forces. This method is not practical for monomer solutions since the angular velocity needed to separate monomers is very large.

The same considerations apply in controlling the molecular orientation in liquid crystals. The orientation of the molecules constituting liquid crystals can be controlled by an electric or magnetic field. In the isotropic phase, the field needed to change the molecular orientation is very large, but in the liquid crystalline phase, the required field becomes small since the molecules in the liquid crystalline phase rotate collectively.

In the following chapters, we shall first discuss the equilibrium properties of several typical soft matter systems, polymers, colloids, surfactants, and liquid crystals. Next, we shall discuss non-equilibrium phenomena such as relaxation, diffusion, permeation, flow, and deformation. The last chapter is devoted to ionic soft matter. Through these discussions, we would like to demonstrate that the principles of physics are working in these seemingly complex systems.

1.6   Summary of this chapter

Soft matter includes a large class of materials (polymers, colloids, surfactants, and liquid crystals, etc.). A common feature of these materials is they all consist of large structural units. This gives two characteristics to soft matter:

(1) large and nonlinear responses;

(2) slow and non-equilibrium responses.

Further reading

(1) *Fragile Objects: Soft Matter, Hard Science and the Thrill of Discovery*, Pierre Gilles de Gennes, Jacques Badoz, translated by Axel Reisinger, Copernicus (1996).

(2) *Introduction to Soft Matter: Synthetic and Biological Self-Assembling Materials*, Ian W. Hamley, Wiley (2007).

(3) *Soft Condensed Matter*, Richard A. L. Jones, Oxford University Press (2002).