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Introduction

The topic of this book is forces acting between interfaces. There is no clear, unique definition of an interfacial force. One possible definition is as follows: Interfacial forces are those forces that originate at the interface. For example, electrostatic double-layer forces are caused by surface charges at the interface. Such a definition would, however, not include van der Waals forces. For van der Waals interaction, the surface atoms do not have a distinct role compared to the bulk atoms. Still, van der Waals forces substantially contribute to the interaction between small particles. One could define surface forces as all interactions that increase proportionally to the interfacial area. Then, for certain geometries gravitation should also be included. Gravitation is, however, not described here. On the other hand, hydrodynamic interactions would be excluded because they depend also on the specific shape of interacting interfaces and not only on the interfacial area.

We take a pragmatic approach and discuss all forces that are relevant in systems that have a small characteristic length scale and whose structure and dynamics are dominated by interfaces rather than gravitation and inertia. In this sense, this book is about the structure and dynamics of systems with a small characteristic length scale. At this point, we need to specify two terms: "interface" and "characteristic length scale."

An interface is the area that separates two phases. If we consider the solid, liquid, and gas phases, we immediately get three combinations of interfaces: the solid–liquid, the solid–gas, and the liquid–gas interfaces. The term surface is often used synonymously, although interface is preferred for the boundary between two condensed phases and in cases where the two phases are named explicitly. For example, we talk about a solid–gas interface but a solid surface. Interfaces can also separate two immiscible liquids such as water and oil. These are called liquid–liquid interfaces. Interfaces may even separate two different phases within one component. In a liquid crystal, for example, an ordered phase may coexist with an isotropic phase. Solid–solid interfaces separate two solid phases. They are important for the mechanical behavior of solid materials. Gas–gas interfaces do not exist because gases mix.

Often, interfaces and colloids are discussed together. Colloid is a synonym for a colloidal system. Colloidal systems are disperse systems in which one phase has dimensions in the order of 1 nm to 1 μm (Figure 1.1). The word "colloid" comes
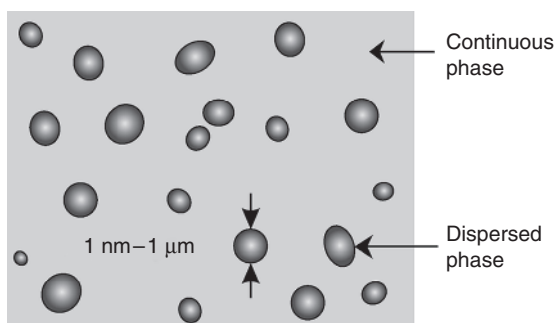
Figure 1.1 Schematic of a dispersion.

Continuous phase

Dispersed phase

1 nm–1 μm

from the Greek word for glue and was used the first time in 1861 by Graham.[1] He applied it to materials that seemed to dissolve but were not able to penetrate a membrane, such as albumin, starch, and dextrin. A colloidal dispersion is a two-phase system that is uniform on the macroscopic but not on the microscopic scale. It consists of grains or droplets of one phase in a matrix of the other phase.

Different kinds of dispersions can be formed. Most of them have important applications and have special names (Table 1.1). While there are only 3 types of interfaces, we can distinguish 10 types of disperse systems because we have to discriminate between the continuous, dispersing (external) phase and the dispersed (inner) phase. In some cases, this distinction is obvious. Nobody will, for instance, mix up fog with a foam although in both cases a liquid and a gas are involved. In other cases, the distinction between continuous and inner phases cannot be made because both phases might form connected networks. Some emulsions, for instance, tend to form a bicontinuous phase, in which both phases form an interwoven network.

Table 1.1 Types of dispersions.

Continuous phase	Dispersed phase	Term	Examples
Gas	Liquid	Aerosol	Clouds, fog, smog, hairspray
	Solid	Aerosol	Smoke, dust, pollen
Liquid	Gas	Foam	Lather, whipped cream, foam on beer
	Liquid	Emulsion	Milk, skin creams
	Solid	Sol	Ink, muddy water, dispersion paint
Solid	Gas	Porous solids[a]	Partially sintered or pressed powders
		Foam	Styrofoam, soufflés
	Liquid	Solid emulsion	Butter
	Solid	Solid suspension	Concrete

a) Porous solids have a bicontinuous structure while in a solid foam the gas phase is clearly dispersed.

1 Thomas Graham, 1805–1869. British chemist, professor in Glasgow and London.

The characteristic length scale of a system can often be given intuitively. For example, for a spherical particle one would use the radius, and for a thin film the thickness. For more complex systems, intuition, however, leads to ambiguous results. We suggest using the ratio of the total volume V divided by the total interfacial area A of a system as the characteristic length scale: $\lambda_c = V/A$. For a sphere of radius r_s, the characteristic length scale is $\lambda_c = r_s/3$. For a thin film, it is equal to the thickness. For a dispersion of spherical particles with a volume fraction ϕ, the total volume of the system is $V = N4\pi r_s^3/(3\phi)$, where N is the number of particles. With a total surface area of $A = N4\pi r_s^2$, we get a characteristic length scale of $\lambda_c = r_s/(3\phi)$.

■ Example 1.1

If aluminum is electrochemically oxidized under appropriate circumstances, porous layers of many microns thickness with regular pores of diameters between 15 and 400 nm can be made [1, 2]. After etching away the aluminum support, free membranes are obtained (Figure 1.2). What is the characteristic length scale of a porous alumina membrane? The volume of a piece of membrane of facial area A_0 and thickness h_0 is $V = h_0 A_0$. With a radius of the cylindrical pores of r_c and a distance between neighboring pores of d, we get a total surface area $A = N2\pi r_c h_0$. Here, N is the number of pores. We neglect the top and bottom surfaces and the sides. For a two-dimensional hexagonal packing of the pores we get $N = A_0/(d^2 \sin 60°)$. This leads to

$$\lambda_c = \frac{\sin\ 60°}{2\pi}\ \frac{d^2}{r_c}. \tag{1.1}$$

With typical values $d = 200$ nm and $r_c = 50$ nm, we get $\lambda_c = 110$ nm. Increasing the radius of the pores at constant interporous spacing decreases the characteristic length scale.
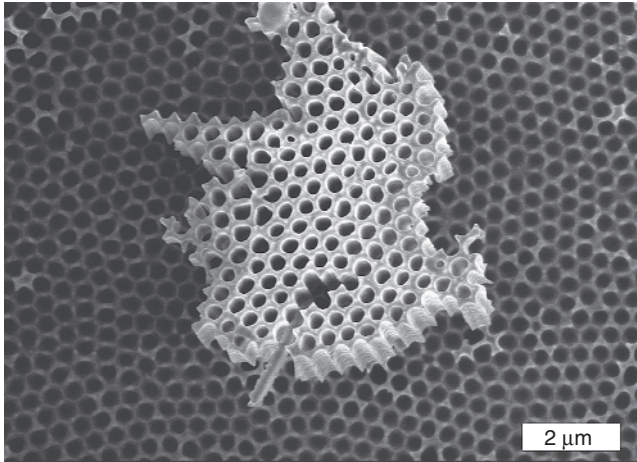
Figure 1.2 Scanning electron microscopic image of a piece of a porous aluminum oxide membrane lying on top of a continuous membrane. (Courtesy of H. Duran.)

Surface forces determine the structure and dynamics of soft systems with small characteristic length scales. This certainly includes nanosystems with $\lambda_c \leq 100$ nm. Depending on the specific situation, it can also include systems with larger length scales. A typical system is a liquid with dispersed particles. If the particles attract each other, they will aggregate. Often, aggregation is not desired and the surfaces are naturally or artificially designed to give rise to repulsive forces. If the particles repel each other, they do not aggregate and the dispersion is stable. The same arguments hold for emulsions, for example, an oil-in-water emulsion. If the oil drops repel each other, they remain dispersed and the emulsion is stable. Otherwise, they coagulate, form larger and larger drops, and eventually form a continuous oil phase.

Our knowledge of surface forces is mainly about relatively stable systems. Typically, these systems are at or close to equilibrium. We would like to point out that surface forces also determine the dynamics of systems far away from equilibrium. This topic is, however, still in its infancy. Owing to the increased number of parameters and the fact that systems far away from equilibrium depend on their specific history, they are more complex and difficult to understand.