1

Approach to Transport Phenomena

"A good grasp of transport phenomena is essential for understanding many processes in engineering, agriculture, meteorology, physiology, biology, analytical chemistry, materials science, pharmacy, and other areas. Transport phenomena is a well-developed and eminently useful branch of physics that pervades many areas of applied science. [...] The subject of transport phenomena includes three closely related topics: fluid dynamics, heat transfer, and mass transfer. Fluid dynamics involves the transport of *momentum*, heat transfer deals with the transport of *energy*, and mass transfer is concerned with the transport of *mass* of various chemical species." Let's approach the field of transport phenomena by trying to appreciate and elaborate this introductory quote on the importance and ubiquity of transport phenomena in science and engineering from the pioneering textbook of Bird, Stewart and Lightfoot.[1] Let's look at the topic of transport phenomena from various perspectives.

1.1 The First Three Minutes

We wake up in the morning, switch on the light, and take a shower. Our day usually begins with the flow of electric energy and water to our house. We immediately find ourselves right in the middle of transport phenomena. What a luxury.

Let's add a little drama by scaling things up. Consider (i) crude oil pipelines and (ii) high-voltage electric power transmission lines. (i) For example, the Druzhba[2] pipeline built in the early 1960s carries crude oil from the Russian heartland all the way to Germany (some 4 000 km). Some 200 000 m^3 of crude oil per day are pumped through steel tubes with a

[1] See p. 1 of Bird, Stewart & Lightfoot, *Transport Phenomena* (Wiley, 2001).
[2] Druzhba is the Russian word for friendship.

diameter of up to one meter, which implies a characteristic speed of 3 m/s. Every three days one could fill a supertanker. Pumping stations are typically required every 100 km (give or take a factor of two). (ii) Electric energy transmission in overhead power lines takes place above 100 kV. For proper load balancing and to satisfy the demand of a flourishing electricity trading market, electric energy is transported over large distances. The largest power grid, with a total power generation of 667 gigawatts, is the Synchronous Grid of Continental Europe, which serves 400 million customers in 24 countries.[3]

The length scale associated with these impressive transport challenges is of the order of the size of countries or continents. The same length scale is also involved in long-term weather forecasts or the prediction of climate changes, where large-scale transport in the atmosphere and oceans matters.

Very clearly, our life depends on transport phenomena; not just in the sense of convenience considered so far, but also in the sense of biological functions. We depend on the never-ceasing flow of blood and oxygen through our body, and drugs need to be targeted to the appropriate places in our body. On the level of cells, ions need to be transported, often against concentration gradients, which requires energy from a chemical reaction. Also muscle contraction relies on transport phenomena. These biological functions are associated with transport phenomena on a molecular length scale.

Let's add even more drama to the story. Let's not think about the first three minutes of our day or the first three minutes of this course on transport phenomena, but about the first three minutes of the Universe. Even the origin of the Universe is largely dominated by the transport of mass and energy in the presence of violent reactions between particles.[4]

The ubiquity and importance of transport phenomena should be clear from these few obvious examples. Moreover, a thorough understanding of transport phenomena is of self-evident economic and environmental importance.

Exercise 1.1 *Transport of Crude Oil and Money*

The Trans-Alaska Pipeline (see Figure 1.1) built in the 1970s carries crude oil from Prudhoe Bay to Valdez, Alaska, a distance of roughly 1300 km. Typically, 100 000 m^3 of crude oil per day are pumped through steel tubes with a diameter of more than one meter. According to the current market price of crude oil, usually given in dollars per barrel, what is the value of the crude oil passing through the Trans-Alaska Pipeline in one day?

[3] According to `en.wikipedia.org/wiki/Synchronous_grid_of_Continental_Europe`.
[4] Weinberg, *The First Three Minutes* (Basic Books, 1977).

Figure 1.1 The Trans-Alaska Pipeline starts at Pump Station 1 in Prudhoe Bay. (Figure from www.clui.org/ludb/site/alaska-pipeline-origin.)

1.2 Complex Systems

In spite of their striking importance, the transport phenomena discussed in the preceding section are of a rather basic type, at least, as they have been presented. In modern applications, we usually deal with far more complex systems. A few examples should suffice to illustrate this point and to indicate some important implications for this course.

What happens with crude oil after it has been transported? It enters a chemical plant where it is processed and refined into more useful products. In such an oil refinery, we encounter transport in a huge number of pipes carrying various streams of different fluids between chemical processing units, such as distillation towers and cracking units, where separation processes and chemical reactions are taking place during the flow. Among the components separated in an oil refinery are the feedstocks for the syntheses of various kinds of polymers, or plastics. Finally, very complex flow situations of highly viscoelastic fluids occur in polymer processing operations, such as injection molding or film blowing. There is a really long way to go for crude oil.

In meteorology, atmospheric flow phenomena on a wide range of length scales are affected by a number of other systems and phenomena, such as ocean circulations. Nontrivial boundary conditions play an important role and phase transitions (evaporation, condensation, melting) are ubiquitous phenomena, the occurrence of which may be of particular interest.

We have already seen that transport processes in biological systems occur on very different length scales ranging from the meter scale of our body to the 1–100 μm scale of cells. These transport phenomena are coupled to many further biophysical and biochemical processes over a large range of length scales.

The briefly sketched complexity of many transport phenomena of interest has some immediate implications. Once we have understood the basic structure of balance equations and the constitutive assumptions for the fluxes occurring in these equations, we are faced with a number of serious challenges. How do we obtain all the material properties, such as transport coefficients, occurring in these equations? How do we actually solve rather large sets of coupled equations? How do we formulate physically meaningful boundary conditions, and how do we get the additional material information possibly contained in them? In this course we build up increasing knowledge about these questions and consider increasingly complex applications.

The experimental measurement of material properties related to transport is a challenging topic. In Chapter 7, we describe the most basic ideas for measuring transport coefficients, such as viscosity, thermal conductivity, and diffusivity. Microbead rheology provides another alternative to investigate momentum transport, as discussed in Chapter 25. By developing the theory of dynamic light scattering in Chapter 26, we obtain an alternative tool for measuring transport coefficients. Thorough foundations for discussing boundary conditions and expressing the physics happening at boundaries and interfaces are laid in Chapters 13–15.

Statistical mechanics offers an alternative theoretical path to obtain material properties, which allows the development of basic ideas for the kinetic theories of gases (Chapter 21) and polymeric liquids (Chapter 22). Further applications of methods for bridging scales include porous media (Chapter 23) as well as molecular motors and ion pumps (Chapter 24).

Once we have the equations, the boundary conditions, and all the required material information, we need to solve the equations. We typically deal with nonlinear and often coupled partial differential equations. Finite element and finite difference methods are important tools to solve such equations, and can be implemented using several commercial software packages. In some cases, the lattice Boltzmann method offers an interesting alternative (inspired by the kinetic theory of gases, but going far beyond it). To solve some illustrative problems with very simple simulation programs, we introduce Brownian dynamics at an early stage (Chapter 3).

1.3 Classical Field Theories

Transport implies the flow of certain quantities in space, and it takes time. For example, mass can move from point to point in space. To describe this transport of mass, it is convenient to assign a mass density to every point in space so that we end up with mass density fields that change in space and time. Similarly, momentum and energy density fields arise naturally, and velocity and temperature fields may be convenient alternatives. In modeling transport phenomena, we are interested in the time-evolution equations for such hydrodynamic fields, that is, we actually deal with classical field theories. The most well-known field equations of transport theory are the Navier–Stokes–Fourier equations of hydrodynamics (to be developed in Chapters 5 and 6 and briefly summarized in Section 7.1), which provide the basic and quite universal description of the flow of mass, momentum, and energy. As a consequence of convection, these field equations are *nonlinear* in the hydrodynamic fields and hence exhibit a very rich behavior of solutions, including turbulence. Complex fluids, often referred to as soft matter, require even more complicated field theories, typically with additional fields describing the local structure of the complex fluid (Chapter 12).

All field theories are idealizations and must be expected to lead to difficulties when variations from point to point are taken too literally. Below a certain length scale, the atomic nature of matter must affect the validity of field theories. For a gas under normal conditions, the mean free path of the gas atoms or molecules between collisions is of the order of 0.1 μm so that nonlocality effects must be taken into account below this length scale. If we consider volume elements of the size of a few nanometers, even for liquids instead of gases, the number of atoms or molecules contained in such a volume becomes so small that fluctuation effects need to be taken into account. Modified hydrodynamic theories work down to amazingly small length scales, but eventually field theories for continua need to be given up and atoms or molecules and their interactions need to be considered explicitly. As even atoms consist of much smaller particles,[5] these interactions are not the fundamental ones, but typically van der Waals forces. The even more surprising success of the hydrodynamic approach in extracting information on the properties and dynamics of quark–gluon plasmas created in relativistic heavy-ion collisions calls for explanation.[6]

[5] The famous Rutherford experiment (published in 1911) revealed that an atom possesses a very small positively charged nucleus with a diameter of the order of 10^{-14} m and, a century later, the Large Hadron Collider in Geneva (officially inaugurated in 2008) allows us to probe the structure of matter down to some 10^{-20} m.

[6] Baier *et al.*, *Phys. Rev.* C **73** (2006) 064903.

The above discussion of continuum field theories and length scales has two important practical implications for our treatment of transport phenomena. (i) There are further challenges for investigating transport phenomena, namely those posed by *nonlocality and fluctuation effects*. To understand these effects, we need to stretch the theory to its limits. (ii) All our equations for transport phenomena result from coarse graining and hence must account for the *emergence of irreversibility and dissipation*. This observation has important consequences for the structure of "good" equations for modeling transport phenomena. Nonequilibrium thermodynamics,[7] ideally supported by statistical mechanics, provides the proper setting for formulating equations for coarse grained systems.

- Large-scale transport has a direct impact on our everyday life, e.g. transport in pipelines, electric power grids . . .
- Transport is at the heart of many engineering tasks: chemical reactor design, materials processing, aerodynamical optimization (airplanes, vehicles) . . .
- Transport is at the heart of many problems in the natural sciences: atmospheric sciences (climatology, meteorology), life sciences (blood circulation, muscle contraction, ecosystems), cosmology (expansion of the Universe, galaxy formation and evolution) . . .
- Transport often occurs in complex coupled systems involving a wide range of length scales and a variety of dynamic material properties and boundary conditions.
- As transport takes place in space and time, we deal with partial differential equations for the evolution of coupled fields; the laws of nonequilibrium thermodynamics set the structure of the field equations and necessitate fluctuation effects.

[7] de Groot & Mazur, *Non-Equilibrium Thermodynamics* (Dover, 1984); Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, 2005).

2
The Diffusion Equation

One of the most famous equations in the field of transport phenomena is the diffusion equation. Its wide-ranging importance is underlined by the fact that, depending on the context, it is known by various names. In a probabilistic interpretation, it is usually referred to as a Fokker–Planck equation, which is a special type of Kolmogorov's forward equation for memoryless stochastic processes.[1] In the context of Brownian motion, the name Smoluchowski equation is most appropriate. The variety of names nicely indicates that this equation is not only useful for describing the transport phenomenon of mass diffusion; we will actually encounter it many times, in particular, also in the description of momentum and heat transport and in polymer kinetic theory. In the present chapter, we introduce it to describe the flow of probability. In doing so, we present the basic theme of transport phenomena, including some important concepts, tools, and results.

2.1 A Partial Differential Equation

By a first glance at the Fokker–Planck or diffusion equation in one space dimension,

$$\frac{\partial p(t,x)}{\partial t} = -\frac{\partial}{\partial x}\Big[A(t,x)p(t,x)\Big] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\Big[D(t,x)\,p(t,x)\Big], \qquad (2.1)$$

one recognizes a second-order partial differential equation for the evolution of some function $p(t,x)$ of two real arguments involving coefficient functions $A(t,x)$ and $D(t,x)$. Here we simply assume $D(t,x) \geq 0$, but later will show that this follows from the second law of thermodynamics (see Exercise 2.4). In many cases, the given coefficient functions A and D are independent of their first argument, t. The goal of this chapter is to bring the reader

[1] See, for example, Chapter 3 of Gardiner, *Handbook of Stochastic Methods* (Springer, 1990).

from this superficial perspective to a deep understanding of the physical meaning and implications of the diffusion equation (2.1). The reader shall recognize the physical meaning of the coefficient functions A and D, and will develop a feeling for the significance of the occurrence of first- and second-order derivatives on the right-hand side of the evolution equation (2.1). It is important to develop a sound physical understanding of such second-order partial differential equations because they are at the heart of transport phenomena.

2.2 Probability Flux, Drift, and Diffusion

To assign intuitive names to the unknown function p and the given coefficient functions A and D in the diffusion equation (2.1), we consider diffusion from the perspective of Brownian motion, that is, the motion of a large particle in a surrounding fluid consisting of much smaller particles. The historical prototype of that kind of system is pollen in water, for which in 1828 the botanist Robert Brown (1773–1858) published his observation of a very irregular and unpredictable motion of particles in the absence of external forces (other researchers had observed this "Brownian motion" more than a century before Brown, but he was the first to establish Brownian motion as an important phenomenon and to investigate it in more detail[2]). The origin of this motion was much later discovered to lie in the enormously frequent collisions between the Brownian particle and the many surrounding fluid particles which are in incessant thermal motion.

A Brownian particle moves on a stochastic trajectory that is continuous but so irregular that its velocity cannot be defined (see Figure 2.1). The mass density is concentrated in the time-dependent position of the Brownian particle, and the mass flux is an even more singular object. On the other hand, the probability density for the location of the Brownian particle is a smooth function and there occurs a smooth flux of probability that leads to a smearing and broadening of the distribution. In this chapter, we focus on the evolution of the probability density, or on the flow of probability.

Marian Smoluchowski was the first to introduce a diffusion equation of the form (2.1) to describe Brownian motion in 1906. In this context, one interprets $p(t, x)$ as the probability density for finding the Brownian particle around the position x at time t. If we are interested in the probability of finding the Brownian particle between fixed positions x_1 and x_2 (where we

[2] An interesting survey of the history of Brownian motion can be found in §§2–4 of the monograph *Dynamical Theories of Brownian Motion* by Edward Nelson (Princeton, 1967). The early history of the stochastic description of Brownian motion has been reviewed by Subrahmanyan Chandrasekhar in *Rev. Mod. Phys.* **15** (1943) 1.

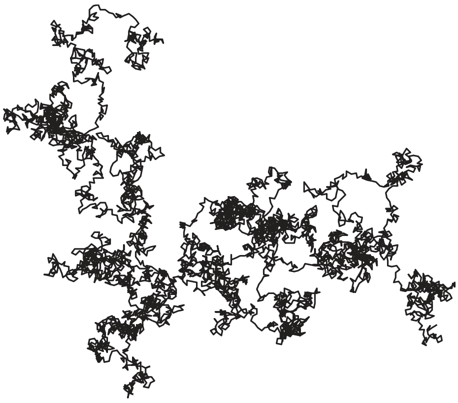

Figure 2.1 Trajectory of a Brownian particle.

assume $x_1 < x_2$), we have the evolution equation

$$\frac{d}{dt}\int_{x_1}^{x_2} p(t,x)dx = -\int_{x_1}^{x_2} \frac{\partial}{\partial x} J(t,x)dx = J(t,x_1) - J(t,x_2), \tag{2.2}$$

with the quantity $J(t,x)$ read off from the diffusion equation (2.1),

$$J(t,x) = A(t,x)p(t,x) - \frac{1}{2}\frac{\partial}{\partial x}\Big[D(t,x)\,p(t,x)\Big]. \tag{2.3}$$

We can thus interpret $J(t,x_1)$ as the influx and $J(t,x_2)$ as the outflux of probability, as illustrated in Figure 2.2. More generally, $J(t,x)$ is the probability flux at position x and time t. If the right-hand side of an evolution equation for the density of some quantity is written in the derivative form, the quantity behind the derivative is the corresponding flux. Proper sign conventions need to be chosen; we here use a positive sign for a flux in the direction of increasing x. It is natural to assume that the probability density and flux vanish at infinity. According to (2.2), the total probability $\int p(t,x)dx = 1$ is then conserved in time.

To learn more about the coefficient functions A and D, we define averages of suitable functions $f(x)$ performed with the probability density $p(t,x)$,

$$\langle f \rangle_t = \int_{-\infty}^{\infty} f(x)p(t,x)dx. \tag{2.4}$$

Assuming that the function $f(x)$ is sufficiently smooth (for example, that it possesses piecewise continuous second-order derivatives), we obtain the following evolution equation for averages from the diffusion equation (2.1) after some integrations by parts and neglecting the probability density and

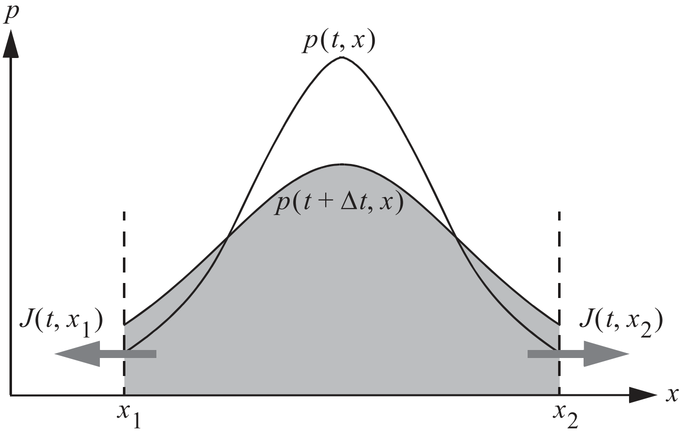

Figure 2.2 In the time interval from t to $t + \Delta t$, probability flows out of the interval $[x_1, x_2]$ (note that the flux $J(t, x_1)$ is negative).

flux at infinity,

$$\frac{d\langle f\rangle_t}{dt} = \left\langle A\frac{df}{dx}\right\rangle_t + \frac{1}{2}\left\langle D\frac{d^2 f}{dx^2}\right\rangle_t . \tag{2.5}$$

Of particular interest are the moments $\langle x^n\rangle_t$, where n is a positive integer. If we use $f(x) = x$ in (2.5), we find the following evolution equation for the first moment or average position,

$$\frac{d\langle x\rangle_t}{dt} = \langle A\rangle_t . \tag{2.6}$$

On average, the coefficient function A describes the velocity of the Brownian particle, say due to the presence of a gravitational or some other external field. This is a systematic, deterministic effect known as drift. The intuitive concept of velocity is given by the rate of change of the position resulting from the motion of a particle. Equation (2.6) expresses this idea on average. Equation (2.3) suggests a different concept of velocity in terms of the probability flux: velocity = (non-diffusive) probability flux/probability density. This alternative concept leads to a velocity field without referring to individual particle trajectories. If we consider $f(x) = x^2$ in (2.5), we further obtain

$$\frac{d\langle x^2\rangle_t}{dt} = 2\langle Ax\rangle_t + \langle D\rangle_t . \tag{2.7}$$

Equation (2.7) is the key to interpreting D. Even in the absence of systematic drift effects (that is, for $A = 0$), the second moment $\langle x^2\rangle_t$ increases with the rate $\langle D\rangle_t$. We hence arrive at the interpretation of D as the diffusion