

Chapter 1

Thermodynamics and Evolution

Abstract This is an introductory, yet fundamental chapter, where all the relevant concepts that are encountered in transport phenomena are defined. After a brief introduction (Sect. 1.1) on what transport phenomena consist of, in Sect. 1.2 we describe the relation between thermodynamics and transport phenomena, by defining the condition of local equilibrium. We explain that, under very general conditions, although far from thermal and mechanical equilibrium, we can speak of thermodynamic quantities such as temperature and pressure. This idea is further explored in Sect. 1.3, where the basic concepts of continuum mechanics are briefly sketched. Then, in Sect. 1.4, we show that mass, momentum, and energy can be transported through two fundamentally different modalities, namely convection and diffusion. The former is a time reversible process due to a net movement of the fluid, and the related convective fluxes admit exact analytical expressions. On the other hand, diffusion is intrinsically irreversible, and diffusive fluxes are expressed through so called constitutive relations, that characterize the fluid at the molecular level. In the case of ideal gases, as shown in Sects. 1.5–1.7, diffusion of momentum, energy and mass can be modeled rigorously, leading to Newton’s, Fourier’s and Fick’s constitutive relations, respectively. The analogy between different transport phenomena is further explored in Sect. 1.8, showing that diffusion can be modeled through a random walk process, so that the mean square displacement of the appropriate tracer of momentum, energy or mass grows linearly with time. Finally, in Sect. 1.9, a few examples of diffusion are presented.

1.1 Introduction

Transport phenomena, as their name indicates, consist of the flows of conserved physical quantities, such as energy, momentum and matter, from one region to another within systems that are constituted of a very large number of elementary particles, like molecules or atoms. As in thermodynamics, these systems are

assumed to be continuous, although sometimes, for sake of clarity, we will refer to their molecular structures.

The main distinctive characteristics of this discipline is to unify the physical and mathematical approach of all types of transport. To clarify this point, let us consider the heat transport, when a difference of temperature between two reservoirs induces a heat flux from hot to cold regions. Now, if we consider other types of transport, we realize that they can also be interpreted in the same way, that is in terms of a cause, i.e., a *driving force*, and an effect, that is the *flux* of the transported quantity. Let us see some examples.

- A pot of water on a hot plate. The temperature difference between the two sides of the pot wall causes a heat flux from the hot side to the cold side that heats the water.
- A drop of ink in a water glass. The concentration difference between the inside and the outside of the drop induces a flux of ink from regions of high concentration to low that continues until the ink is uniformly distributed.
- A pressure difference within a pipe induces a mass flux of the fluid that is contained within the pipe from regions of high pressure to low that continues until the pressure is uniform.
- The velocity difference between two regions of a fluid induces a momentum flux from regions at high velocity to low that continues until the momentum is uniform.
- An electric potential difference induces an electric current, that is a flux of electric charge, from regions at high potential to low.

Let us consider the first example: because of the heat transported from warm to cold regions, that is from the hot plate to the water, the water temperature will increase, tending to become equal to that of the hot plate, when the heat will stop flowing. Then, the heat flux remains stationary (i.e., constant in time) only when the temperature of the hot plate and that of the water are maintained constant, for example by continuously cooling the water, i.e., an energy consuming operation. Now, since at steady state the internal energy of the pot wall is constant, this energy removal must balance the energy entering through the heat flux.

In general, an isolated physical system tends to move towards a state of stable equilibrium, where temperature, composition, pressure, momentum and electric field are uniform (i.e., constant in space). On the other hand, if the differences (or, we should say, the gradients) of these quantities, i.e., the driving forces, are non-zero, then a constant flux of energy, mass, momentum and electric charge is induced. This state of non-equilibrium can be maintained only through the introduction of an energy into the system, which is then *dissipated*¹ during the transport process. In other words, during the transport of a physical quantity some amount of

¹The term *energy dissipation* here means *heat conversion*. In fact, as the energy is conserved, it cannot be consumed.

energy is dissipated that, at steady state, must be continuously reintegrated, by introducing it into the system from the outside.

Going back to the example of the pot on the hot plate, the transport of heat does not occur with the same ease in any material, as it is easier when the pot is made of a heat conducting material. This is why we will use a pot made of aluminum (i.e., an excellent conductor) when we want to boil some water as fast as possible, while we will use a pot made of terracotta (i.e., a poor conductor) when we want to prepare a sauce, requiring small and regular heat fluxes for a long cooking time. This sort of friction, opposing heat flux, is a characteristic of our system, denoted *thermal resistance*, defined as the proportionality term between temperature gradient and heat flux. In general, in transport phenomena we assume that the driving force is proportional to the flux through a coefficient, called *resistance*, measuring the opposition of the system against transport. This resistance is the cause of the energy dissipation.

In the following, the concepts of driving force, flux and resistance will be applied to fluid mechanics, heat transport and mass transport, by deriving balance equations of three of the four physical quantities that are conserved in nature: momentum, energy and mass. The transport of the fourth quantity, namely the electric charge, will not be considered here although it can be considered as a particular case of the transport of mass and thus it can be studied following the same procedure.

1.1.1 Statics and Dynamics

If we pour hot water into a container whose walls are impermeable to the transfer of mass, momentum and heat (i.e., the container is closed, rigid and insulated), the water, that is initially subjected to internal movements, has a non-uniform temperature and is partially evaporating, eventually will stop moving, will reach a uniform temperature and will stop evaporating,² meaning that it will reach, respectively, mechanical, thermal and chemical equilibrium. In general, if we consider a complex physical system, i.e., composed of a very large number of elementary particles, and we isolate it, the system will evolve until it reaches a state, called of equilibrium, after which it will stop evolving in time. These rules are the basis of thermodynamics and constitute its two laws: the first law states that the energy of an isolated system remains constant so that, although energy can be converted from one form to another, it cannot be created nor destroyed. The second law states that, during its evolving from one state to another, an isolated system tends to assume its state of stable equilibrium.

²In other words, microscopically, the quantity of water evaporating will be balanced by that of the vapor condensing.

So, thermodynamics tells us that the evolution of an isolated system progresses towards its stable equilibrium state, always conserving its total energy. However, if we wish to know how such evolution takes place, thermodynamics offers no help. In fact, despite its misleading name, thermodynamics is the science that studies complex systems at equilibrium, so it is of little help in studying *transformations*, that are all processes taking place in non-equilibrium conditions. For example, in the previous instance with hot water, thermodynamics predicts that the water will reach a final equilibrium temperature and it even indicates what this temperature will be, but it cannot say anything about how long this process will take, nor how it will happen.

At this point, it would be tempting to conclude that thermodynamics is useless: after all, when we look around, all surrounding systems are far from being at equilibrium. Our body, for example, is constantly out of thermal equilibrium when it is alive, because its 37 °C temperature rarely coincides with the ambient temperature, and equilibrium is reached only after its death. Our conclusion, however, would be wrong because thermodynamics indicates also the limits and the constraints of any process. For example, our body succeeds in maintaining its state of thermal non-equilibrium at the expense of a given energy input contained within the air and the food that we inject. Thermodynamics predicts the minimum input of energy that we must inject in order to produce the minimum work that is necessary to remain alive. However, if we want to determine in which way and how fast this energy input will be dissipated, thermodynamics is of no help: to do that, we must know how energy (and mass and momentum, as well) moves from one region to another. This is the subject of *transport phenomena*.

1.2 Local Equilibrium

In this section, we want to determine when a system can be regarded to be, locally, at thermodynamic equilibrium, so that all thermodynamic variables (temperature, pressure, entropy, internal energy, chemical potential, fugacity, etc.) can be still defined and we can apply, locally, all the thermodynamic relations. This is the so-called condition of *local equilibrium*.

The importance of the condition of local equilibrium is obvious: while some ideal processes (including reversible processes) can be described as if they were composed of a series of equilibrium states and therefore can be successfully modeled using thermodynamics, real systems typically evolve through states that are far from equilibrium (even when their initial and final states are at equilibrium) so that thermodynamics cannot, strictly speaking, be applied. Yet, when we study, for example, a heat exchanger, in which heat passes from a hot to a cold source and a fluid flows from high pressure to low, we encounter terms such as temperature and pressure distribution, i.e., we use terms, such as temperature and pressure, which were introduced in thermodynamics to characterize equilibrium systems. This would seem to indicate that even in conditions of apparent non-equilibrium, in

which the temperature and pressure are not uniform, these variables can be sometimes defined *locally* and in this section we intend to study when this is possible.

We know that in a system composed of a finite number N of particles and maintained at thermodynamic equilibrium, any thermodynamic intensive variables A fluctuates around its equilibrium value, \bar{A} , which is constant in time and uniform in space, so that the relative value of these fluctuations, $\delta A/\bar{A}$, is proportional to $1/\sqrt{N}$. Thus, we can say that a system is in a condition of equilibrium when these local fluctuations are greater than the variations due to spatial or temporal inhomogeneity of \bar{A} . More precisely, a system is in a condition of local equilibrium when the following two conditions are met:

- (a) You can divide the system into elementary volumes (which constitute what are generally referred to as “material points”) that are large enough to contain a large number N of particles, so that the fluctuations δA of each physical quantity A are small, i.e., $\delta A/\bar{A} \ll 1$.
- (b) The variation of A due to the macroscopic gradient $\nabla \bar{A}$ is smaller than the fluctuations δA . Similar considerations apply to the temporal variations of \bar{A} .

Therefore, denoting by λ the linear dimension of these elementary volumes, the condition of local equilibrium requires that:

$$\frac{\lambda |\nabla \bar{A}|}{\bar{A}} \leq \frac{\delta A}{\bar{A}} \ll 1. \quad (1.2.1)$$

For example, in a gaseous system, assuming we want to define any quantity within a 0.1 % accuracy (i.e., $\delta A/\bar{A} = 10^{-3}$) and since $\delta A/\bar{A} \propto 1/\sqrt{N}$, where N is the number of particles contained in the elementary volumes, the volume will contain $N \approx 10^6$ elementary particles, occupying a volume $\lambda^3 \approx N/n \approx 10^{-14} \text{ cm}^3$, corresponding to a linear dimension $\lambda \approx 0.1 \text{ } \mu\text{m}$. Note that the number density n of an (ideal) gas is:

$$n = \frac{\rho N_A}{M_w} = \frac{10^{-3} \text{ g/cm}^3 \cdot 6 \times 10^{23} \text{ part./moli}}{10 \text{ g/moli}} \approx 10^{20} \frac{\text{part}}{\text{cm}^3}. \quad (1.2.2)$$

Hence we see, for example, that the maximum gradient of temperature that we can impose while satisfying the condition of local equilibrium is $\nabla \bar{T} \approx 10^{-3} \bar{T}/\lambda$, and therefore for ordinary temperatures the condition of local equilibrium requires: $\nabla \bar{T} < 10^4 \text{ K/cm}$, which is clearly satisfied in all reasonable cases. For liquid or solid systems, the condition of local equilibrium is applicable even more easily.

At this point, we need to think about how to change the fundamental thermodynamic concepts of pressure, temperature and density when they are applied to non-homogeneous and non-stationary systems, in particular in the case of fluids in motion. We realize now that the last two variables do not require any fundamental “revision”: as they are related to the energy and mass of the system, they are in fact

inherently scalar quantities and, therefore, can be defined as the temperature $T(\mathbf{r}, t)$ and the density $\rho(\mathbf{r}, t)$ of the system at a point \mathbf{r} and at a certain time t . In contrast, when applied to a continuous system, the concept of pressure, being related to the momentum of the system, must be reconsidered in the context of continuum mechanics.

1.3 Introduction to Continuum Mechanics

In a macroscopically continuous system, the particles that compose it microscopically are subjected to external forces, such as gravity or electric fields, as well as to forces due to intermolecular interactions. Depending on the magnitude of such forces, the system is defined as solid, liquid or gaseous. If we imagine to divide the system into two parts through a separation surface, each part will exert a force on the other, equal to the sum of the intermolecular forces that the particles located on one side exert on those located on the other side of the surface. At the macroscopic level, this force per unit area is called stress, σ , and can be decomposed into its two components, normal and tangential with respect to the separation surface (see Fig. 1.1). The normal component is called pressure, p , while the tangential is the shear stress τ .

In solid bodies, the intermolecular forces are so strong that elementary particles have their own fixed position (think of the atoms in a crystal lattice), so that, macroscopically, solids tend to maintain their shape. In contrast, fluids deform freely, and when they are sheared they change their shape, as layers of fluid slide relative to one another. During this sliding, microscopic friction forces develop within the fluid, that translate macroscopically into a shear stress. When the fluid is

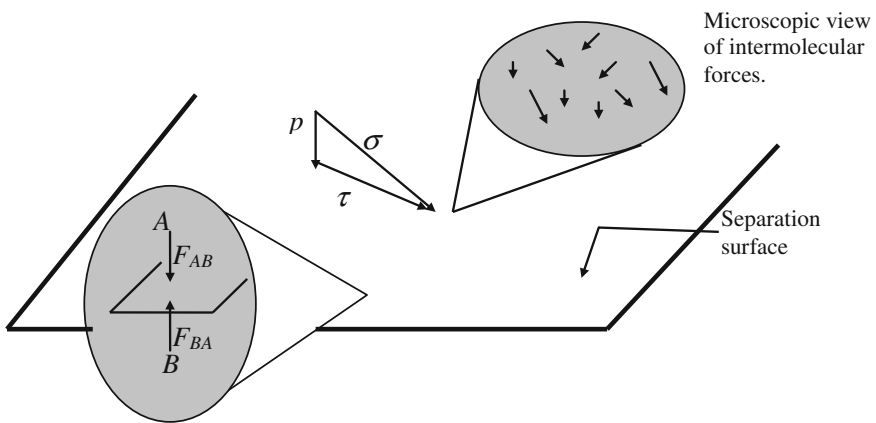


Fig. 1.1 Normal and tangential components of a surface force with respect to the separation surface

at rest, however, these dissipative forces are obviously absent, and therefore, as we shall see, only normal stresses, i.e., pressure, are present.

As is well known from thermodynamics, the state of a pure substance at equilibrium, such as a fluid at rest, is completely determined as long as two independent variables are fixed.³ Therefore, for a given temperature T and pressure p , the fluid density ρ is fixed.⁴ If the density changes are very small compared to variations in T and p , the fluid can be approximated as incompressible, while when such changes are significant, the fluid is compressible (just think of the ideal gas, where ρ is proportional p/T). Typically, liquids are assumed to be incompressible and gases are compressible, even if, obviously, there are cases in which large temperature excursions cause relevant density changes in liquids as well while, conversely, in other processes the changes of pressure and temperature are so small that the gas density can be considered constant.

1.3.1 Pressure

As we have seen in the previous section, the pressure is the force per unit area applied in a direction perpendicular to the surface of an object. More precisely, it is the limit of the force/area ratio when the area tends to zero, with $[p] = \text{M L}^{-1}\text{T}^{-2}$. The SI unit of pressure is the Newton per square meter, which is called the *Pascal* (Pa), i.e., $1 \text{ Pa} = 1 \text{ N m}^{-2}$. As 1 Pa corresponds to the pressure exerted by a 1 g weight on a $10 \text{ cm} \times 10 \text{ cm}$ area, it is very small, thus pressures are often expressed in kilopascals.

Now, we can imagine to draw a surface about any point of a fluid at rest, separating the fluid into two parts. Each of these two parts will exert an equal and opposite force on the other, because if it were not so, the net force resulting from the action of the fluid on the surface will cause the movement of the fluid.⁵ Indeed, a simple force balance on the two faces of the element of volume of infinitesimal thickness of Fig. 1.2 shows that $p_{up} = p_{down}$, that is the pressure of the fluid located on one side of the separation surface is equal to the pressure of the fluid on the other side. As for the tangential stresses, although the force balance of Fig. 1.2 shows that $\tau_{up} = \tau_{down}$, these tangential forces would cause a relative sliding of the fluid layers, so that we may conclude that the shear stresses in a fluid at rest are null.

At this point, the fundamental question that we ask is whether the pressure exerted at a point depends on the orientation of the surface, that is whether the ratios,

³This is a consequence of Gibbs' phase rule.

⁴The density is the inverse of the specific volume and is defined as a mass per unit volume, $[\rho] = \text{M L}^{-3}$. Within the SI system, it is measured in Kg m^{-3} .

⁵Microscopically, the stress exerted by the fluid located on one side of the separating surface on the fluid located on the other side is equal to the sum of all the forces F_{AB} describing the interaction between all pairs of molecules A and B located on opposite sides of the separating surface (see Fig. 1.1). Clearly, as $F_{AB} = -F_{BA}$, we may conclude that $\sigma_{up} = \sigma_{down}$.

Fig. 1.2 Pressure and shear forces exerted by a fluid on both sides of a virtual surface

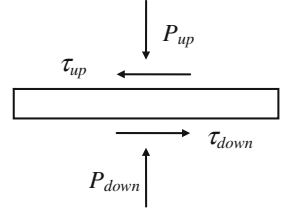
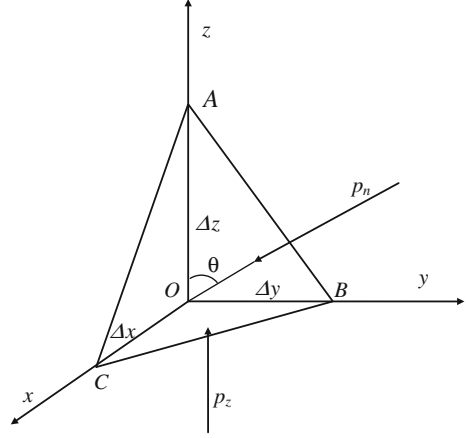


Fig. 1.3 Forces on a fluid element at rest



$$p_x = \lim_{\Delta S \rightarrow 0} \frac{\Delta F_x}{\Delta S_x}; \quad p_y = \lim_{\Delta S \rightarrow 0} \frac{\Delta F_y}{\Delta S_y}; \quad p_z = \lim_{\Delta S \rightarrow 0} \frac{\Delta F_z}{\Delta S_z},$$

are equal to each other. After all, although in thermodynamics we take for granted that the pressure is a scalar,⁶ so that $p_z = p_y = p_x$, this is by no means obvious. To answer this question, consider the tetrahedron of Fig. 1.3, built around the Cartesian axes xyz , and write the forces exerted on its faces by the surrounding fluid along, for example, the z direction. Since those are pressure forces (in fact, with no fluid movement, the forces are perpendicular to the surfaces), the force balance will include the force $F_z = p_z S_{OBC}$ exerted on the OBC face, the z component of the force $F_n = p_n S_{ABC}$ exerted on the ABC face, and the gravity force, i.e.,

$$p_z S_{OBC} - p_n S_{ABC} \cos \theta - \rho g V_{OABC} = 0,$$

where ρ is the fluid density, g the acceleration of gravity, $V_{OABC} = \Delta x \Delta y \Delta z / 6$ is the volume of the tetrahedron, θ is the angle indicated in figure, while p_z and p_n are the

⁶This is due to the fact that the pressure, p , is thermodynamically conjugated with the volume, V : as V is a scalar, so is p .

mean pressures exerted by the fluid on the corresponding faces. Now, considering that $S_{OBC} = \Delta x \Delta y / 2$, $S_{OBC} = \Delta x \Delta y / (2 \cos \theta)$, dividing by $\Delta x \Delta y / 2$ we obtain:

$$p_z = p_n + \rho g \Delta z / 3.$$

At this point, squeezing the tetrahedron towards the origin, keeping the angle θ constant, obviously Δz tends to zero, while the mean pressures will be replaced by the local pressures at the origin, indicating that $p_z = p_n$. Similar consideration can be drawn along the other directions, so that we may conclude that

$$p_x = p_y = p_z = p, \quad (1.3.1)$$

indicating that the pressure at a point in a static fluid is independent of the orientation of the surface.

1.3.2 Shear Stresses

In the previous sections we have repeatedly stated that the shear stress is related to the internal friction of the fluid. The easiest way to see it is to note that, given two adjacent layers of fluid that are moving with different speeds, due to the mutual attraction the slower molecules will tend to accelerate, retarding those that move more rapidly, which is tending, at the end, to cancel any difference in speed. In the case of a gas, the same result is obtained as an effect of molecular diffusion: faster molecules diffuse in regions populated by slower particles and, through the consequent collisions, transmit momentum to the slower molecules. Obviously, if no force were applied from the outside, the velocity difference between the two layers could not be maintained and the fluid would end up moving with a uniform velocity. At the macroscopic level, these molecular interactions can be seen (see Fig. 1.4) as a net flux of momentum, J_Q , directed along the direction normal to the fluid motion. The momentum flux, being the momentum that crosses the unit area per unit time, is a force per unit area, i.e., it has the same units as a stress.

This same mechanism, by which two adjacent fluid threads tend to move at the same speed, can be described through the shear stresses τ , which are “friction” forces along the direction of motion of the fluid. Now, considering that the shear stress has the same units as the momentum flux, the forces acting on the faces of a

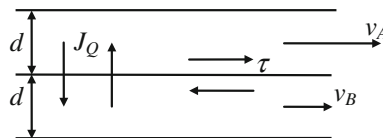
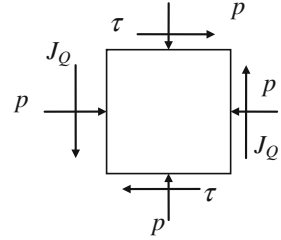


Fig. 1.4 Momentum fluxes and shear stresses

Fig. 1.5 Forces acting on the faces of a fluid element



fluid element are indicated in Fig. 1.5, where we have taken into account that: (1) as already noted, in a force balance at a microscopic level the volumetric forces, such as gravity, are negligible compared to the surface forces, and therefore can be omitted; (2) the pressure is independent of the direction of the surface on which it acts; (3) the two shear stresses acting on the horizontal surfaces must be equal to each other, as shown by a simple balance of forces; the same goes for the two momentum fluxes J_Q acting on the vertical surfaces. Hence, imposing that the moment of the forces indicated in Fig. 1.5 be equal to zero yields:

$$\tau = J_Q, \quad (1.3.2)$$

indicating that, as a consequence of the angular momentum balance, shear stress and momentum flux have equal magnitude, though they are perpendicular to each other.

1.4 Convection and Diffusion

Physical quantities such as mass, momentum, and energy can be transported in two fundamentally different ways. The first mode, called convection, is related to the overall, macroscopic motion of the medium in which these quantities are defined. Thus, for example, the convective transport of energy (heat) consists of the net motion of a warmer fluid towards a colder region: through their coherent motion, the fluid molecules carry a thermal energy, related to the fluid temperature. The same can be said of the convective transport of mass and momentum, where the fluid molecules carry a mass or a momentum.

The second mode of transport is diffusion, in which mass, momentum and energy move from one point to another without any net displacement of matter; as we will see in Sects. 1.5 and 1.6, diffusion is related to the incoherent motion of the fundamental constituents of the medium. In the case of energy transport, this mechanism refers to the process in which heat moves from the warmer to the colder regions of a body without the particles making up the body having any overall, coherent motion (think of a metal spoon that heats up when immersed in a hot

liquid). In the case of momentum transport, diffusion is the process by which faster fluid threads can accelerate adjacent slower ones; therefore, J_Q in Eq. (1.3.2) is of a diffusive type.

In the following, we describe transport phenomena in terms of fluxes of mass, momentum, and energy, defined as the amount of, respectively, mass, momentum, and energy that cross a surface of unit area per unit time.

1.4.1 Convective Fluxes

As previously noted, during convection all fluid particles move with the same, ensemble velocity v . Therefore, within a fluid moving with a uniform velocity v , consider a cylinder of section S and length $v\Delta t$ (see Fig. 1.6); in a time interval Δt , the fluid mass $M_c = \rho V$, with $V = Sv\Delta t$ the volume of the cylinder, will cross the section S . Therefore, based on the definition of mass flux as the mass M_c divided by S and by Δt , we obtain:

$$J_{M_c} = \frac{M_c}{S\Delta t} = \rho v. \quad (1.4.1)$$

In the same way, the convective flux of momentum, J_{Q_c} , equals the ratio of the momentum Q_c contained in this cylinder and the product of S by Δt , where Q_c is the product of the momentum per unit volume, $Q_c/V = \rho v$, by the volume, $V = Sv\Delta t$, i.e.,

$$J_{Q_c} = \frac{Q_c}{S\Delta t} = \rho v^2. \quad (1.4.2)$$

Finally, the convective flux of internal energy J_{U_c} , equals the ratio of the internal energy U_c contained in this cylinder and the product of S by Δt , where U_c is the product of the internal energy per unit volume, $U_c/V = \rho c_v(T - T_0)$, by the volume, $V = Sv\Delta t$, i.e.,

$$J_{U_c} = \frac{E_c}{S\Delta t} = \rho c_v v(T - T_0). \quad (1.4.3)$$

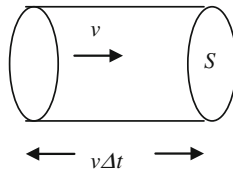


Fig. 1.6 Fluid moving with a uniform velocity

Here c_v is the specific heat per unit mass, while $T - T_0$ is the temperature change relative to an arbitrary temperature reference, T_0 .

In general, the convective flux of any quantity A is $J_A = av$, where $a = A/V$ is the density of A .

1.4.2 Diffusive Fluxes and Constitutive Relations

In the previous Section we studied the interaction between adjacent fluid threads and saw that: (1) the flux of momentum in a direction perpendicular to the motion, which is diffusive in nature (as there is no convection in that direction) is equal to the shear stress in the longitudinal direction; (2) shear stress and shear rate are linked to each other. In fact, the relationship between shear stress and shear rate, called constitutive relation of the shear stress, is one of the fundamental dynamic properties of a fluid.

Typically, as the velocity gradient increases, the shear stress also increases, i.e., the curve $\tau = \tau(dv/dz)$ is monotonically increasing. The study of the relationship between shear stress and shear rate is the main subject of rheology.

The simplest rheological behavior of fluids is that of the so-called Newtonian fluids, in which the shear stress is proportional to the velocity gradient. All gases, most of pure liquids and solutions with low molecular weight (e.g., oils and dilute solutions of polymers) behave as Newtonian fluids and therefore follow *Newton's constitutive relation*:

$$\tau = -\mu \frac{dv}{dz}. \quad (1.4.4)$$

where μ is the fluid *viscosity*, sometimes also called *dynamic viscosity*, which then expresses the internal friction, or the internal resistance of the fluid to flow. Dimensionally, the viscosity has units $[\mu] = \text{M L}^{-1}\text{T}^{-1}$ and in the SI system it is expressed in $\text{N m}^{-2} \text{ s}$, i.e., $\text{kg s}^{-1} \text{ m}^{-1}$, commonly called *Poiseuille*.⁷ In CGS units, instead, the *Poise* (P) is used, which is defined as $1 P = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}$ or, more conveniently, in *centipoise* ($1 \text{ cP} = 0.01 P$). The viscosity of water at room temperature is about $1 \text{ cP} = 10^{-3} \text{ kg/ms}$. In summary: $1 \text{ Poiseuille} = 10 P = 1000 \text{ cP}$.

The constitutive equation of the shear stress can be rewritten as:

$$J_{Qd} = -v \frac{d(\rho v)}{dz}, \quad (1.4.5)$$

establishing that the diffusive momentum flux, J_{Qd} , is proportional to the gradient of the momentum density $q = \rho v$, through a proportionality coefficient $v = \mu/\rho$.

⁷Both poiseuille and poise are named after Jean Léonard Marie Poiseuille (1797–1869), a French physicist and physiologist.

The quantity ν is called *kinematic viscosity* has units L^2T^{-1} and is expressed in m^2/s in the SI system.

This equation is similar to *Fourier's constitutive relation*⁸ for the diffusive transport of heat (commonly called *conduction*),

$$J_{Ud} = -k \frac{dT}{dz}, \quad (1.4.6)$$

where J_{Ud} is the diffusive heat flux, i.e., a flux of internal energy, while k is the coefficient of thermal conductivity. Denoting by c_v the specific heat per unit mass, whereas $u = c_v (T - T_0)$ is the specific internal energy (per unit mass) and ρu is the energy density (i.e., the internal energy per unit volume), Fourier's law states that the diffusive flux of internal energy is proportional to the energy density gradient via the coefficient of thermal diffusivity $\alpha = k/\rho c_v$, that is,

$$J_{Ud} = -\alpha \frac{d(\rho u)}{dz}. \quad (1.4.7)$$

Thermal diffusivity α has the same units, L^2T^{-1} , as kinematic viscosity ν and therefore in the SI system it is expressed in m^2/s .

The Eqs. (1.4.5) and (1.4.7) are similar to *Fick's constitutive relations*,⁹ describing the specific (i.e., per unit mole or mass) diffusive transport of a species A in a mixture,

$$J_{Ad} = -D \frac{dc_A}{dz}, \quad (1.4.8)$$

where the diffusive flux of A is proportional to the gradient of concentration (that is the molar density, or the number of moles per unit volume) through a diffusion coefficient, D , having again units of L^2T^{-1} .

Therefore, kinematic viscosity, ν , thermal diffusivity, α , and molar diffusivity, D , all have the same L^2T^{-1} units. For sake of convenience, these quantities are expressed in the CGS system, defining the *Stokes* ($1 S = 1 \text{ cm}^2/s$) and the *centistokes* ($1 \text{ cS} = 0.01 S$), where $1 \text{ m}^2/s = 10^4 S = 10^6 \text{ cS}$. Physically, ν is a measure of the “rate” of momentum diffusion, i.e., how rapidly it can propagate in the absence of convection, exclusively due to molecular interactions. In the same way, α e D indicate the “rate” at which heat or mass can diffuse in the absence of any coherent motion due to convection.

⁸Jean Baptiste Joseph Fourier (1768–1830) was a French mathematician and physicist.

⁹Adolf Eugen Fick (1829–1901) was a German physician and physiologist.

1.5 Viscosity

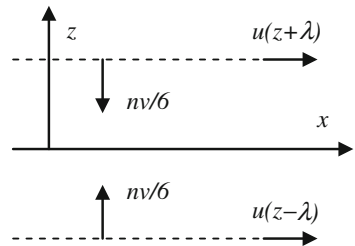
Consider a gas of uniform density, ρ , and temperature, T , that moves macroscopically along the x direction with an average velocity, $u = u(z)$, depending on the transverse coordinate, z . As the gas molecules are subjected to thermal fluctuations, in addition to the this macroscopic (i.e., average) movement there is a chaotic motion as well, characterized by an average velocity v , with $v \approx \sqrt{3kT/m} \ll u$, where m is the mass of a single molecule. Now, of the n molecules per unit volume composing the gas, about one-third will have a velocity directed along the z -axis and half of these, or $n/6$ molecules, will have an average velocity v in the $+z$ direction and $n/6$ molecules in the $-z$ direction. Therefore, on average, there will be $nv/6$ molecules per unit time passing through a unit area of the $z = \text{constant}$ plane from the bottom to the top (that is, $nv/6$ is the upwards average molecular flux), and the same number of molecules will flow downward (see Fig. 1.7). On average, these molecules have had their last collision with another molecule at a distance from the z plane equal to the mean free path λ . Therefore, since the mean longitudinal velocity, u , is a function of z , each molecule that cross the z plane moving downwards will be carrying a momentum (i.e., its x -component) equal to $mu(z + \lambda)$, while those moving upward will be carrying a momentum $u(z - \lambda)$. This suggests that the net transport of the x -momentum along the $+z$ -direction, i.e., the diffusive momentum flux (because there is no convective transport along the z -direction) is given by:

$$J_{Qd} = \tau = \left(\frac{1}{6}nv\right)[mu(z - \lambda)] - \left(\frac{1}{6}nv\right)[mu(z + \lambda)], \quad (1.5.1)$$

where we have considered that momentum flux is equal to the shear stress. Expanding $u(z)$ in Taylor series, and neglecting higher-order terms, we obtain:

$$u(z + \lambda) = u(z) + \lambda \frac{du}{dz} + \dots \quad \text{and} \quad u(z - \lambda) = u(z) - \lambda \frac{du}{dz} + \dots$$

Fig. 1.7 Flow field at a molecular scale



so that,

$$J_{Qd} = \tau = -\mu \frac{du}{dz}. \quad (1.5.2)$$

where μ is the viscosity,

$$\mu = \frac{1}{3}nm\lambda v = \frac{1}{3}\rho\lambda v, \quad (1.5.3)$$

with $\rho = mn$ denoting the fluid density. This result, obtained by Maxwell in 1860, allows us to make some interesting predictions. In fact, the mean free path can be easily estimated by considering that the number of molecules, moving with a mean velocity v , hitting a given “target” molecule during the time interval Δt is equal to the number of molecules contained in a cylinder having as a base the cross section $\sigma_0 = \pi d^2$ (where d is the molecular diameter) and $v\Delta t$ as its height (trivially, during the time interval Δt , the target molecule will be hit solely by the molecules contained within that cylinder). This implies that the number of collisions per unit time is πnvd^2 and the mean time interval between two successive collisions is

$$\tau = \frac{1}{\pi nvd^2}.$$

Therefore, we see that the mean free path is:

$$\lambda = v\tau = \frac{1}{\pi nd^2} \left(= \frac{1}{n\sigma_0} \right). \quad (1.5.4)$$

Finally, considering that $v \approx \sqrt{kT/m}$, we may conclude that the viscosity of a gas is ¹⁰

$$\mu \approx \frac{\sqrt{mkT}}{d^2} \left(\approx \frac{1}{\sigma_0} \sqrt{mkT} \right). \quad (1.5.5)$$

The most interesting feature of this result is that μ does not depend on n , and therefore is independent of the pressure. In fact, as we increase pressure, and therefore density, the number of intermolecular collisions will increase, as there will be more molecules carrying momentum along the transversal direction, but, as the mean free path decreases, the contribution of each of these collisions will decrease in the same proportion. It should be noted, however, that this analysis applies only to low density fluids, where $d \ll \lambda$, while as λ decreases it loses its validity. In particular, in liquids, where $d \approx \lambda$, it must be radically modified.

¹⁰A more rigorous analysis shows that $\lambda = (\sqrt{2}n\sigma_0)^{-1}$ and $v = [(8kT)/(\pi m)]^{1/2}$.

The other conclusion we can draw from this analysis is that in gases $\mu \propto \sqrt{T}$, i.e., viscosity increases with temperature. In fact, considering that collisions between molecules are partially inelastic, we find that the cross section tends to decrease with temperature, obtaining at the end $\mu \propto T^{0.7}$. This behavior is very different from that of liquids, where viscosity decreases as temperature increases, due to a decrease of the strength of the intermolecular interaction.

1.6 Thermal Conductivity

Here, we want to model the transport of heat induced by a temperature gradient. Consider that each molecule carries an internal energy $\varepsilon = mc (T - T_0)$, where c is the specific heat per unit mass, m is the mass of a molecule and T_0 is a reference temperature. Proceeding as in the previous section (see Fig. 1.8), we find that the net transport of internal energy (i.e., the heat flux) along the $+z$ -direction is given by Eq. (1.5.1), with $\varepsilon = mc (T - T_0)$ replacing mu ,

$$J_{Ud} = \left(\frac{1}{6}nv\right)[\varepsilon(z - \lambda)] - \left(\frac{1}{6}nv\right)[\varepsilon(z + \lambda)]. \quad (1.6.1)$$

Expanding $\varepsilon(z) = mc [T(z) - T_0]$ in Taylor series, and neglecting higher-order terms, we obtain:

$$T(z + \lambda) = T(z) + \lambda \frac{dT}{dz} + \dots \quad T(z - \lambda) = T(z) - \lambda \frac{dT}{dz} + \dots$$

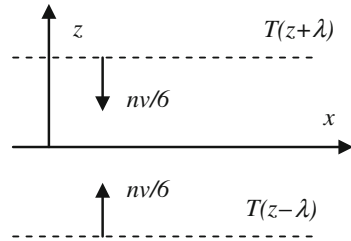
so that,

$$J_{Ud} = -k \frac{dT}{dz}, \quad (1.6.2)$$

where k is the thermal conductivity,

$$k = \frac{1}{3} \rho c \lambda v, \quad (1.6.3)$$

Fig. 1.8 Temperature field at a molecular scale



with $\rho = mn$. Finally, substituting for the mean free path, λ , from Eq. (1.5.4), together with the mean fluctuating velocity, $v \approx \sqrt{kT/m}$, we obtain:

$$k \approx \frac{c}{d^2} \sqrt{mkT} \left(\approx \frac{c}{\sigma_0} \sqrt{mkT} \right). \quad (1.6.4)$$

Thus, in gases, thermal conductivity, like viscosity, does not depend on pressure; variations of k with temperature, instead, depend on how the specific heat depends on temperature. Comparing (1.6.3) with (1.5.3) we see that:

$$\alpha = \frac{k}{\rho c} = \frac{\mu}{\rho} = v = \frac{1}{3} \lambda v \quad \Rightarrow \quad Pr = \frac{v}{\alpha} = 1, \quad (1.6.5)$$

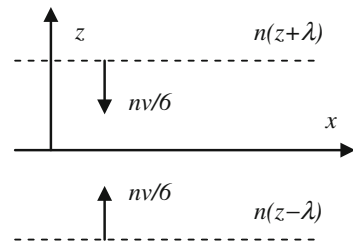
where Pr indicates the *Prandtl* number. Therefore, we see that in ideal gases thermal diffusivity is equal to momentum diffusivity (that is, kinematic viscosity). In reality, we find experimentally that for real gases the Prandtl number is approximately 0.7; considering the drastic approximation in the above analysis, this discrepancy is extraordinarily small. Finally, note that in liquids the two diffusivities can be very different from each other, as it can happen that $Pr \gg 1$ (think of glycerin or motor oils) or $Pr \ll 1$, as in quicksilver (see Appendix 1).

1.7 Molecular Diffusivity

Here, we want to model the molecular transport of a chemical species A within a binary mixture, induced by a concentration gradient (see Fig. 1.9). In this case, consider that each molecule of species A carries a mass m from regions with concentration $c_A(z + \lambda)$ to regions with concentration $c_A(z - \lambda)$, where $c_A = mn$. Again, proceeding as in the previous two sections, we obtain the following expression for the mass flux of species A :

$$J_{Ad} = \left(\frac{1}{6} mv \right) [n(z - \lambda)] - \left(\frac{1}{6} mv \right) [n(z + \lambda)]. \quad (1.7.1)$$

Fig. 1.9 Concentration field at a molecular scale



Expanding $n(z)$ in Taylor series, and neglecting higher-order terms, we obtain:

$$n(z + \lambda) = n(z) + \lambda \frac{dn}{dz} + \dots; \quad n(z - \lambda) = n(z) - \lambda \frac{dn}{dz} + \dots,$$

so that,

$$J_{Ad} = -D \frac{dc_A}{dz}, \quad (1.7.2)$$

where D is the coefficient of molecular diffusion (or diffusivity),

$$D = \frac{1}{3} \lambda v. \quad (1.7.3)$$

Finally, substituting the expressions for the mean fluctuating velocity, v , and the mean free path, λ , we obtain:

$$D \approx \frac{1}{nd^2} \sqrt{\frac{kT}{m}} \left(\approx \frac{1}{n\sigma_0} \sqrt{\frac{kT}{m}} \right). \quad (1.7.4)$$

Thus, we conclude that $D \propto 1/P$ and $D \propto \sqrt{T}$.

Comparing (1.7.3) with (1.6.5), we see that in ideal gases all three diffusivities are equal to each other, i.e.,

$$D = \alpha = v \quad \Rightarrow \quad Sc = \frac{v}{D} = 1, \quad (1.7.5)$$

where Sc indicates the *Schmidt* number. Experimentally, for real gases we find that the Schmidt number is approximately 0.7, that is very close to the Prandtl number. In liquids (and solids, where applicable), however, the results are very different. In fact, while in gases D , α e v are close to one another, with magnitudes of, approximately, $10^{-1} \text{ cm}^2/\text{s}$, in liquids D is of $O(10^{-5} \text{ cm}^2/\text{s})$, while α and v are of $O(10^{-2} \text{ cm}^2/\text{s})$ in many cases, so that Sc turns out to be of $O(10^3)$. A qualitative explanation of this fact can be found in Sect. 14.4.

1.8 Molecular Diffusion as an Example of Random Walk

Molecular diffusion can also be modeled as the random movement of the gas molecules, assuming that their mutual collisions are statistically independent from one another. The displacement vector \mathbf{R} of each molecule after N collisions is the sum of N elementary displacements \mathbf{r}_i , each describing the distance traveled by the molecule between two successive collisions,

$$\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i. \quad (1.8.1)$$

Obviously, since each elementary displacement is random, that is $\langle \mathbf{r}_i \rangle = \mathbf{0}$, then we have $\langle \mathbf{R} \rangle = \mathbf{0}$. This result agrees with the fact that all diffusive processes do not involve any net displacement of matter. Now assuming, for sake of simplicity, that each elementary displacement has the same length, with $|\mathbf{r}_i| = \ell$, we obtain:

$$\langle R^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle = \sum_{i=1}^N \langle r_i^2 \rangle + \sum_{i=1}^N \sum_{j \neq i=1}^N \langle \mathbf{r}_i \cdot \mathbf{r}_j \rangle = N\ell^2. \quad (1.8.2)$$

This result can be justified by considering the case $N = 2$: the product $\langle \mathbf{r}_1 \cdot \mathbf{r}_2 \rangle$ equals $\ell^2 \langle \cos \theta \rangle$, where θ is the angle between the two vectors. As this angle is random, the product is zero.

At this point, it can be proved¹¹ that ℓ is proportional to the mean free path λ that was used in the previous sections through the following relation:

$$\ell = \sqrt{2}\lambda = \sqrt{2}v\tau, \quad (1.8.3)$$

where τ is the mean time interval between two successive collisions and v is the mean velocity along any direction. Finally, considering that

$$N = (\Delta t)/\tau,$$

we obtain:

$$\langle R^2 \rangle = 6D(\Delta t), \quad (1.8.4)$$

where we have defined the diffusivity coefficient as in Eq. (1.7.3), i.e.,

$$D = \frac{1}{3}\lambda v. \quad (1.8.5)$$

Note that by decomposing the molecular motion along the three Cartesian directions x , y and z , and defining $R^2 = X^2 + Y^2 + Z^2$, we obtain:

$$\langle X^2 \rangle = \langle Y^2 \rangle = \langle Z^2 \rangle = 2D(\Delta t). \quad (1.8.6)$$

So, the diffusion process can be described in two different ways. On one hand, we assume that the system is non-homogeneous and consider the molecular flux resulting from the applied concentration gradient: the ratio between these quantities,

¹¹F. Reif, "Statistical Thermal Physics", McGraw Hill, p. 486.

which are sometimes referred to as *thermodynamic flux* and *thermodynamic force*, defines the coefficient of gradient diffusion. On the other hand, consider a homogeneous system and follow the random motion of a single molecule, due to its thermal fluctuations: (one half of) the time growth of its mean square displacement defines the coefficient of self-diffusion. The fact that the coefficients of gradient diffusion and of self-diffusion are equal to each other is by no means obvious and constitutes perhaps the simplest example of application of the fluctuation-dissipation theorem, proved by H.B. Callen and T.A. Welton in 1951.

1.9 Examples of Diffusive Processes

Suppose we have a uniform solid slab at room temperature, and imagine that at time $t = 0$ the wall temperature changes abruptly. At this point, the temperature inside the slab begins to change, with larger delay with respect to $t = 0$ as we move farther away from the walls. Indeed, at a distance l from the wall, the abrupt change in wall temperature will be felt only after a time of order $t = l^2/\alpha$, where α denotes thermal diffusivity. Thus, if the body under examination has a linear dimension L , it will take a time of order L^2/α for the body to reach roughly the new equilibrium state, with the temperature everywhere equal to the given wall temperature (see Fig. 1.10).

In the same way, if in a glass containing, for example, water at rest we introduce a small drop of ink, we see that after an interval of time t the size of the droplet will be of order $l = \sqrt{(Dt)}$; then, assuming that the glass has a linear dimension L , after a time of order L^2/D a steady state will be reached, where the ink concentration is uniform and the water in the glass has a uniform color.

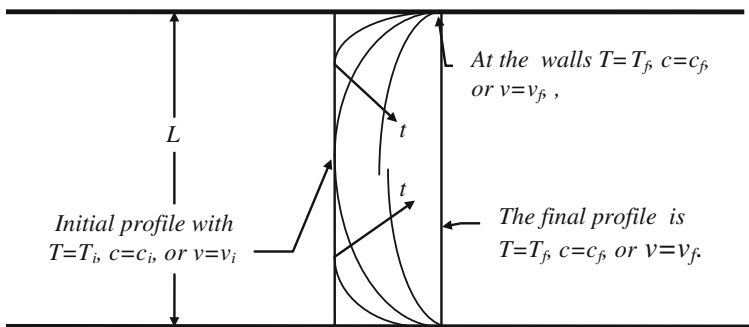


Fig. 1.10 Profiles of temperature T , concentration c and velocity v as a function of time in a system (a solid or a fluid) located between two plates at a distance L , when T , c and v change abruptly at the walls. The characteristic time to reach steady state equals the ratio between L^2 and the diffusivity of energy (i.e., α), mass (i.e., D), or momentum (i.e., ν)

Now, as we understand the diffusion of energy as almost the same as the diffusion of mass, we can move on to the study of the diffusion of momentum, showing that this process obeys the same rules. Suppose we have a fluid between two plates, initially at rest (see Fig. 1.10), and assume that at time $t = 0$ the two plates are set in motion.¹² Again the fluid velocity, and therefore its momentum, within the system will begin to change, but not immediately. Indeed, the abrupt change in wall velocity will be felt at a distance l from the wall after a time $t = l^2/\nu$, where ν is the kinematic viscosity. Thus, if the distance between the plates is equal to L , it will take a time of order L^2/ν for the system to reach, roughly, its steady state, with a uniform velocity profile.

Note that, although the units of α , D and ν are identical to one another, their numerical values are very different. For example, typical values for water are: $\alpha \approx 10^{-3} \text{ cm}^2/\text{s}$, $D \approx 10^{-5} \text{ cm}^2/\text{s}$ and $\nu \approx 10^{-2} \text{ cm}^2/\text{s}$. Therefore, the rate for mass diffusion is much slower than that for both thermal and momentum diffusion.

1.10 Problems

- 1.1 On Thanksgiving in the U.S., turkeys are sold in supermarkets with the following table attached, indicating the cooking time as a function of turkey mass. Based on what we saw in Sect. 1.8, we expect that the cooking time should be proportional to the square of the typical size of the turkey, so that:

$$(\text{cooking time}) \times (\text{mass of turkey})^{-2/3} = C = \text{constant}$$

- Compare this prediction with the experimental data of the table.
- Determine the thermal diffusivity of the meat (obviously, its mean value) and compare it with that of water.

Mass (kg)	Cooking time per unit mass (min/kg)
2.5–4.5	45–55
4.5–7.5	40–45
8.0–11.5	35–40

¹²Another set of examples is when one of the two walls is set in motion, or changes its temperature or composition, while the other is fixed. In this case, the steady state corresponds to a linear velocity, temperature or concentration profile, and, again, in each case the time required to reach these final conditions is of the order of L^2/α , L^2/D and L^2/ν , respectively.

Transport Phenomena in Multiphase Flows

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2015, XV, 459 p. 156 illus., Hardcover

ISBN: 978-3-319-15792-4