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1 Kinetic Theory and the Boltzmann Equation

In Section 1.2, we describe the approach to thermodynamics of elementary kinetic theory, which is based on the model of the ideal gas as an ensemble of classical point-like particles of equal mass. We also illustrate how elementary kinetic theory provides a phenomenological approach to transport phenomena, which exemplifies out-of-equilibrium stationary processes and allows us to introduce a definition of transport coefficients.

Boltzmann's approach represents a deep refinement of this elementary kinetic theory. The basic idea is that the ideal gas, as a collection of a gigantic number of mechanical particles, should be more properly described by a distribution function, rather than by the single trajectories of the particles (Section 1.3). In principle, these trajectories could be computed by the laws of mechanics, but in practice no human being can have at disposal the computational facilities to successfully accomplish this task. Boltzmann's proposal amounts to overtake this obstacle by replacing the mechanical equations of the evolution in time of all the gas particles with only one equation describing the evolution in time of their distribution function. The mathematical procedure adopted for obtaining this equation makes use of many physically plausible hypotheses, which are carefully illustrated in Section 1.4 . Among them, the hypothesis of molecular chaos (*Stosszahlansatz*) plays a crucial role: It is based on the assumption that colliding particles in a gas have no memory of their previous history, because of the gigantic number of collisions each particles goes through, before colliding again with a particle already met in the past. This assumption amounts to admit that in a gas, the states of two colliding particles are "statistically independent" of each other. This hypothesis introduces into the Boltzmann equation an effective representation of binary collisions in terms of "products of individual distribution functions," which is at the origin of the irreversible nature of this equation, despite the hypothesis that collisions between particles have to be conservative, that is, reversible and mechanical processes.

Boltzmann's equation is quite a complicated nonlinear integrodifferential equation and a general theorem, stating the existence and uniqueness of its solution, is not available. This notwithstanding, we can prove the so-called H-theorem, which allows us to conclude that the asymptotic evolution in time of the distribution function converges to the thermodynamic equilibrium, while identifying a quantity, that essentially amounts to the thermodynamic state function Entropy. In particular, in Section 1.5, we provide the proof of the H-theorem in the uniform case (i.e., in the simple situation, where the distribution function is independent of space coordinates), and we also show in Section 1.6 how this proof can be extended to the nonuniform case. In both instances, we obtain the explicit expression of the equilibrium distribution function, characterizing the thermodynamics of the ideal gas.

Boltzmann's equation allows us to work out also a fundamental theory of transport phenomena (see Section 1.7). In fact, by taking explicitly into account the quantities conserved in each binary collision process, namely, mass, momentum, and kinetic energy, we can derive the hydrodynamic equations, that account for the evolution in time of the densities of these locally conserved quantities. In the zero-order approximation, that is, when the average quantities present in the hydrodynamic equations are estimated at thermodynamic equilibrium, they describe the peculiar situation of an inviscid fluid. We conclude this chapter by showing that a perturbative approach allows us to improve the hydrodynamic equations to the first order of approximation, where they reproduce the Navier–Stokes equation and the heat equation.

1.1 Historical Perspective

The idea that thermodynamics could be related to a mechanical theory of matter dealing with a large number of particles, that is, atoms and molecules, was speculated on from the very beginning of kinetic theory in the middle of the nineteenth century. In a historical perspective, we could say that such an idea was a natural consequence of the formulation of the first principle of thermodynamics by the German natural philosopher Julius Robert von Mayer, establishing the equivalence between mechanical work and heat. This was checked in the famous experiment by the British James Prescott Joule and many contemporary physicists, among which the German Rudolf Clausius and August Karl Krönig, the British William Thomson (Lord Kelvin) and James Clerk Maxwell, and the Austrian Ludwig Eduard Boltzmann, devoted a good deal of their efforts to develop the foundations of kinetic theory.[1]

The mechanistic approach to thermodynamics was pushed to its extreme consequences in the work by Boltzmann in the last decades of the nineteenth century. His celebrated transport equation represents a breakthrough in modern science, and still today we cannot avoid expressing our astonishment about the originality and deep physical intuition of the Austrian physicist. Despite being inspired by a specific model, namely, the ideal gas, the main novelty of Boltzmann equation was that it represents the evolution of a distribution function, rather than the trajectories of individual particles in the gas. Boltzmann realized quite soon that the only way to describe the behavior of a large number of particles (a mole of a gas contains an Avogadro number of particles, $N_A \simeq 6.022 \times 10^{23}$) was to rely on a statistical approach, where the laws of probability had to be merged into the description of physical laws. We want to point out that the success of Boltzmann equation is not limited to establishing the foundations of equilibrium statistical mechanics. In fact, it also provides a description of the evolution toward equilibrium by the derivation of hydrodynamic equations associated with the conservation of mechanical quantities, that is, number, momentum, and energy of particles. These equations provide a mathematical basis for the theory of transport phenomena and a physical definition of transport coefficients in

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[1] The reader should consider that all of these scientists were assuming the validity of the atomic hypothesis, despite no direct experimental evidence of the existence of atoms and molecules available at that time.

terms of basic quantities of kinetic theory, such as the mean free path, the average speed of particles, the heat capacity, and so on.

This notwithstanding, a good deal of contemporary scientists strongly criticized his equation as cumbersome or even paradoxical. In order to be properly interpreted, the reason for such a tough opposition to Boltzmann theory has to be framed into the cultural and philosophical debate of the time, when materialism was tightly conjugated to determinism and both of these philosophical categories had come to a deep crisis, in a rapidly changing world. Such cultural trends strongly influenced also the scientific community, where many distinguished physicists and chemists openly stated that they did not believe in the atomistic hypothesis, because it was considered a premise to a materialistic view of nature. In that boiling cultural environment, where different views and options were fighting daily inside the society, the debate among scientists such as Boltzmann, Ostwald, Loschmidt, Zermelo, and Poincaré[2] was certainly based on scientific arguments, but the aggressiveness of the contenders, emerging in some overheated disputes, frequently overtook the standards of a purely academic confrontation.

On a technical ground, it should be said that the main difficulties in understanding Boltzmann equation are not met in its mathematical derivation. They rather stem from finding a logical plausibility to the hypotheses that originate it. What appeared odd to his opposers was how one could obtain a time irreversible equation (consistent with the second law of thermodynamics) starting from time reversible dynamical rules at atomic level. Even the reader, which approaches for the first time this topic, might be puzzled by this seemingly contradictory scenario.

In order to dissipate doubts and cast the problem in the proper perspective, it is worth pointing out that the time irreversibility of Boltzmann equation has not a mechanical origin, but it is a consequence of what Boltzmann called the *Stosszahlansatz*. In modern words, we could translate it in “hypothesis of molecular chaos.” It contains far from trivial concepts and one cannot fail to be astonished by the deep intuition of Boltzmann, who did not possess the refined mathematical tools that nowadays (after more than a century of mathematical progresses in ergodic theory) allow us to provide his *Stosszahlansatz* the support of a rigorous mathematical theory. We can safely state that if the main Boltzmann legacy to physical sciences was his equation and its applications, a not less relevant legacy to the development of mathematical sciences was the hint for building up a rigorous basis for his ergodic hypothesis.

We want to conclude by pointing out the truly paradoxical aspect of Boltzmann’s life as a scientist. Many of his contemporaries considered him as the last priest of mechanicism, although, in a modern perspective, it can be easily realized that his work is the starting point of the end of mechanicism, intended as a purely deterministic approach to natural phenomena. In fact, his distribution function can be interpreted as a probability and his *Stosszahlansatz* is formulated on the basis of probabilistic assumptions. Unknowingly, he was paving the pathway that led to quantum mechanics. In fact, at the end of the nineteenth century his younger colleague and opposer, the German Max Planck, in order to provide

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[2] Wilhelm Ostwald and Ernst Zermelo were German, Johann Josef Loschmidt was Austrian, and Henri Poincaré was French.

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a theoretical explanation of the black-body spectrum, adapted Boltzmann statistical theory of the ideal gas to a gas of radiation at thermodynamic equilibrium: The main conceptual consequences were the existence of energy *quanta* and the identification of the scale of inaccuracy of a dynamical state in configuration space, given by the Planck's constant.

1.2 Kinetic Theory

1.2.1 The Ideal Gas

The basic model for understanding the mechanical foundations of thermodynamics is the ideal gas. It is a collection of N identical particles of mass m that can be represented geometrically as tiny homogeneous spheres of radius r. One basic assumption of the ideal gas model is that we are dealing with a diluted system; that is, the average distance δ between particles is much larger than their radius,

$$\delta = \left(\frac{1}{n}\right)^{\frac{1}{3}} \gg r, \tag{1.1}$$

where $n = N/V$ is the density of particles in the volume V occupied by the gas.[3] In the absence of external forces, particles move with constant velocity[4] until they collide pairwise, keeping their total momentum and energy constant (elastic collisions[5]). It can be easily realized that in such a diluted system, multiple collisions are such rare events that they can be neglected for practical purposes.

Now we want to answer the following question: What is the rate of these collisions and the average distance run by a particle between subsequent collisions? We can estimate these quantities by considering that a particle moving with velocity $\mathbf{v}$ in a time interval Δt can collide with the particles that are contained in a cylinder of basis $\sigma = 4\pi r^2$ (called cross section) and height $|\mathbf{v}|\Delta t$; see Fig. 1.1. For the sake of simplicity, we can assume that all the particles inside the cylinder are at rest with respect to the moving particle, so that we can estimate the number of collisions as

$$\mathcal{N}_{coll} = n\sigma|\mathbf{v}|\Delta t. \tag{1.2}$$

Accordingly, the number of collisions per unit time is given by the expression

$$\frac{\mathcal{N}_{coll}}{\Delta t} = n\sigma|\mathbf{v}| \tag{1.3}$$

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[3] For a real gas of hydrogen molecules at room temperature (300 K) and atmospheric pressure (1 atm), $\delta \sim 10^{-6}$ m and $r \sim 10^{-10}$ m.

[4] One could argue that at least gravity should be taken into account, but its effects are generally negligible in standard conditions. An example where gravity has relevant, measurable effects will be studied in Section 2.2: It is the Brownian motion of colloidal particles (see Fig. 2.2).

[5] This hypothesis amounts to assuming that the particles of the gas are rigid spheres, so that they do not suffer any deformation in the collision process. In fact, in a real gas the energy transferred to the internal degrees of freedom of the molecules can be practically neglected in standard conditions.

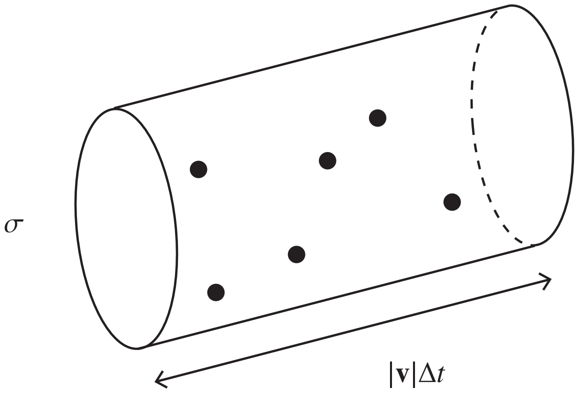

Fig. 1.1 Illustration of the concept of cross section. The black dots in the cylinder spanned by the cross section σ represent the centers of molecules hit in the time interval Δt by a molecule moving at speed v.

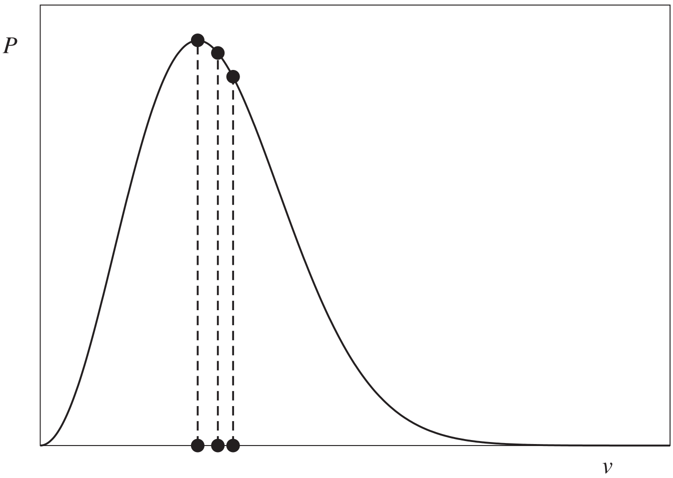

Fig. 1.2 The Maxwell distribution, Eq. (1.5). We indicate, from left to right, the most likely velocity $v_{\max}$, the average velocity $\langle v\rangle$, and the square root of the average square velocity, $\langle v^2\rangle^{1/2}$, whose expressions are given in Eq. (1.6).

and the average time between collisions reads

$$\tau \equiv \frac{\Delta t}{\mathcal{N}_{coll}} = \frac{1}{n\sigma|\mathbf{v}|}. \tag{1.4}$$

A quantitative estimate of τ can be obtained by attributing to $|\mathbf{v}|$ the value $\langle v\rangle$ of the equilibrium average of the modulus of the velocity of particles, v, in the ideal gas, according to Maxwell distribution (see Fig. 1.2),

$$P(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2T}\right), \tag{1.5}$$

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where T is the temperature of the ideal gas at equilibrium. Using such distribution, we obtain the expressions

$$v_{\max} = \sqrt{\frac{2T}{m}}, \qquad \langle v\rangle = \sqrt{\frac{8T}{\pi m}} = \frac{2}{\sqrt{\pi}} v_{\max}, \qquad \text{and} \qquad \langle v^2\rangle^{1/2} = \sqrt{\frac{3T}{m}} = \sqrt{\frac{3}{2}} v_{\max}, \tag{1.6}$$

for the most likely velocity, the average velocity, and the square root of the average square velocity, respectively.

We can now rewrite (1.4) as

$$\tau = \frac{1}{n\sigma\langle v\rangle} \tag{1.7}$$

and determine the average distance run by a particle between two collisions, that is, its mean free path, by the expression

$$\lambda = \langle v\rangle\tau = \frac{1}{n\sigma}. \tag{1.8}$$

This formula corresponds to the case of a single moving particle colliding with target particles that are supposed to be immobile. But this is not the case, because in reality the target particles also move and a better estimate of τ and λ can be obtained using the formula

$$\tau = \frac{1}{n\sigma\langle v_r\rangle}, \tag{1.9}$$

where v_r is the modulus of the relative velocity v_r, which follows the distribution

$$P_r(v_r) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{2T}\right)^{3/2} v_r^2 \exp\left(-\frac{m v_r^2}{4T}\right). \tag{1.10}$$

This formula is a consequence of the general observation that the sum (or the difference) of two Gaussian variables is a Gaussian variable whose variance is the sum of their variances. In this case, $\mathbf{v}_r = \mathbf{v}_1 - \mathbf{v}_2$, with $\mathbf{v}_{1,2}$ satisfying the Maxwell distribution (1.5) and the doubling of the variance explains why the exponent $(mv^2/2T)$ in Eq. (1.5) now becomes $(mv_r^2/4T)$. Then, the prefactor changes accordingly, in order to keep $P_r(v_r)$ normalized.

With Eq. (1.10) at hand, we can evaluate

$$\langle v_r\rangle = \sqrt{\frac{16T}{\pi m}} = \sqrt{2}\langle v\rangle \tag{1.11}$$

and obtain

$$\tau = \frac{1}{\sqrt{2} n\sigma\langle v\rangle}, \tag{1.12}$$

from which we can evaluate the mean free path,

$$\lambda = \langle v\rangle\tau = \frac{1}{\sqrt{2} n\sigma}. \tag{1.13}$$

It is worth noting that the ratio between λ and τ gives $\langle v\rangle$, not $\langle v_r\rangle$, because one particle travels an average distance λ in time τ.

We can finally use the formula (1.13) to evaluate the mean free path for a gas at room temperature and pressure. In this case, λ is typically $O(10^{-7}\text{m})$, which is three orders

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of magnitude larger than the typical size r of a particle, $O(10^{-10}\text{m})$, and one order of magnitude smaller than the distance between particles, $\delta = (1/n)^{1/3} = O(10^{-6}\text{m})$.

1.2.2 Transport Phenomena

Transport processes concern a wide range of phenomena in hydrodynamics, thermodynamics, physical chemistry, electric conduction, magnetohydrodynamics, and so on. They typically occur in physical systems (gases, liquids, or solids) made of many particles in the presence of inhomogeneities. Such a situation can result from nonequilibrium conditions (e.g., the presence of a macroscopic gradient of density, velocity, or temperature), or simply from fluctuations around an equilibrium state.

The kinetic theory of transport phenomena provides a unified phenomenological description of these apparently unlike situations. It is based on the assumption that even in nonequilibrium conditions, gradients are small enough to guarantee that local equilibrium conditions still hold. In particular, the kinetic approach describes the natural tendency of the particles to transmit their properties from one region to another of the fluid by colliding with the other particles and eventually establishing global or local equilibrium conditions.

The main success of the kinetic theory is the identification of the basic mechanism underlying all the above-mentioned processes: the transport of a microscopic quantity (e.g., the mass, momentum, or energy of a particle) over a distance equal to the mean free path λ of the particles, that is, the average free displacement of a particle between two subsequent collisions (see Eq. (1.13)). By this definition, we are implicitly assuming that the system is a fluid, where each particle is supposed to interact with the others only through mutual collisions.

Here we assume that we are dealing with a homogeneous isotropic system, where λ, the mean free path, is the same at any point and in any direction in space. Without prejudice of generality, we consider a system where a uniform gradient of the quantity $A(\mathbf{x})$ is established along the z-axis, and $A(x, y, z) = A(x', y', z) = A(z)$ for any x, x', y, and y'. In particular, we assume that $A(z)$ is a microscopic quantity, which slowly varies at constant rate along the coordinate z of an arbitrary Cartesian reference frame. We consider also a unit surface S_1 located at height z and perpendicular to the z-axis; see Fig. 1.3(a). Any particle crossing the surface S_1 last collided at an average distance $\pm\lambda$ along the z-axis, depending on the direction it is moving. The net transport of the quantity $A(z)$ through S_1 amounts to the number of crossings of S_1 from each side in the unit time. Consistently with the assumption of local equilibrium we attribute the same average velocity $\langle v \rangle$ to all particles crossing S_1. Isotropy and homogeneity of the system imply also that one-third of the particles move on average along the z-axis, half of them upward and half downward. Accordingly, S_1 is crossed along z in the unit time interval by $\frac{1}{6} n\langle v \rangle$ particles in each direction.

The net flux of $A(z)$ through S_1 is given by

$$\Phi(A) = \frac{1}{6}\langle v \rangle \left[n(z-\lambda)A(z-\lambda) - n(z+\lambda)A(z+\lambda) \right]. \tag{1.14}$$

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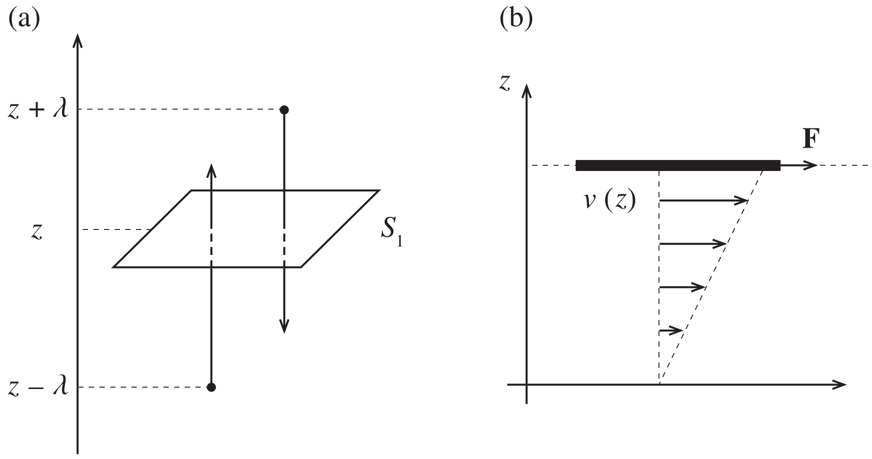

Fig. 1.3 (a) The surface S_1, normal to the $\hat{z}$ axis, is crossed by particles from both sides. Assuming particles move along the $\hat{z}$ axis, their most recent collision occurred at height $z-\lambda$ $(z+\lambda)$ if their speed is positive (negative). (b) A gradient of velocity along the z-axis in a liquid, produced by a plate at the liquid surface that is constrained to move at a finite speed by the application of a force F.

Since n and A vary weakly on the scale λ, one can use a first-order Taylor expansion and rewrite Eq. (1.14) as

$$\Phi(A) = -\frac{1}{3}\langle v\rangle\lambda\frac{\partial(nA)}{\partial z}. \tag{1.15}$$

This calculation can be performed more carefully by introducing explicitly the Maxwell distribution function of particle velocities at equilibrium. Nonetheless, one recovers the same result.

It is worth noting that the density n can be assumed to be constant in some circumstances. If so, since λ is inversely proportional to n the flux $\Phi(A)$ and the resulting kinetic coefficient are independent of the density n. Let's start with the simplest case, the transport of mass, where such assumption is basically wrong because the current is induced by a density gradient along the z-axis. In this case, $A(z)$ is a constant and

$$\Phi(n) = -\frac{1}{3}\langle v\rangle\lambda\frac{\partial n}{\partial z} = -D\frac{\partial n}{\partial z}, \tag{1.16}$$

where the quantity $D = \frac{1}{3}\langle v\rangle\lambda$ defines the diffusion coefficient of particles inside the fluid. This expression is equal to the definition of D through Eq. (2.19), $D = \lambda\langle v\rangle/d$, because in the calculation here above $d = 3$. In a real physical situation, D depends both on the diffusing substance and the medium of diffusion. At room temperature, a gas in air typically has $D \simeq 0.3$ cm^{2}s^{-1}; the diffusion coefficient of a liquid in water is typically of the order $D \simeq 10^{-5}$ cm^{2}s^{-1}; a gas in a solid has a much smaller diffusivity of the order $D \simeq 10^{-9}$ cm^{2}s^{-1}.

Other cases of physical interest correspond to the situations where a gradient of velocity or temperature is present and the density n is assumed to be constant, so $\Phi(A) = -\frac{1}{3}n\langle v\rangle\lambda\frac{\partial A}{\partial z}$. If there is a gradient of velocity, we assume that the fluid flows with constant macroscopic

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velocity $v(z)$ parallel to the (x, y)-plane. In such a situation, there is a net transport of kinetic momentum $mv(z)$ (m is the mass of a particle), yielding a shear stress $\Phi(mv(z))$ between the fluid layers laying on the (x, y) plane (see Fig. 1.3(b)):

$$\Phi(mv(z)) = -\frac{1}{3}nm\langle v\rangle\lambda\frac{\partial v(z)}{\partial z} = -\eta\frac{\partial v(z)}{\partial z}, \tag{1.17}$$

where the quantity $\eta = \frac{1}{3}nm\langle v\rangle\lambda = \frac{m\langle v\rangle}{3\sqrt{2}\sigma}$ defines the viscosity of the fluid. As anticipated, the viscosity of an ideal fluid turns out to be independent of the density n, therefore of the pressure. This counterintuitive conclusion was first derived by Maxwell, and its experimental verification sensibly contributed to establish in the scientific community a strong consensus on the atomistic approach of kinetic theory. It is worth stressing that such a conclusion does not hold when dealing with very dense fluids. At room temperature, diluted gases typically have η of order 10 μPa·s, while in water and blood, η is of the order of few millipascal-second and honey at room temperature has $\eta \approx 1$ Pa·s (called Poiseuille, Pl).

It remains to consider the case when $A(z)$ is the average kinetic energy of particles $\bar{\epsilon}(z)$. At equilibrium, the energy equipartition condition yields the relation $n\bar{\epsilon}(z) = \rho C_V T(z)$, where $\rho = mn$ is the mass density of particles, C_V is the specific heat at constant volume, and $T(z)$ is the temperature at height z. The net flux of kinetic energy $\Phi(\bar{\epsilon})$ can be read as the heat transported through the fluid along the z-axis,

$$\Phi(\bar{\epsilon}) = -\frac{1}{3}n\langle v\rangle\lambda\frac{\partial\bar{\epsilon}}{\partial z} = -\frac{1}{3}\rho C_V\langle v\rangle\lambda\frac{\partial T(z)}{\partial z} = -\kappa\frac{\partial T(z)}{\partial z}, \tag{1.18}$$

where the quantity $\kappa = \frac{1}{3}\rho C_V\langle v\rangle\lambda = \frac{mC_V\langle v\rangle}{3\sqrt{2}\sigma}$ defines the heat conductivity. Also κ is found to be independent of n. The variability of κ in real systems is less pronounced than for other kinetic coefficients: In fact, a very good conductor such as silver has $\kappa \simeq 400\ \mathrm{Wm^{-1}K^{-1}}$, while for cork, an effective heating insulator, it drops down to 4×10^{-2} in the same units.

One can conclude that the transport coefficients, that is, the diffusion constant D, the viscosity η, and the heat conductivity κ, are closely related to each other and depend on a few basic properties of the particles, such as their mass m, their average velocity $\langle v\rangle$, and their mean free path λ. For example, by comparing the definitions of κ and η, one finds the remarkable relation

$$\frac{\kappa}{\eta} = \alpha C_V, \tag{1.19}$$

with $\alpha = 1$. In real systems, the constant α takes different values, which depend on the presence of internal degrees of freedom (e.g., $\alpha = \frac{5}{2}$ for realistic models of monoatomic gases).

The conceptual relevance of the relation (1.19) is that it concerns quantities that originate from quite different conditions of matter. In fact, on the left-hand side, we have the ratio of two transport coefficients associated with macroscopic nonequilibrium conditions, while on the right-hand side, we have a typically equilibrium quantity, the specific heat at constant volume. After what has been discussed in this section, this observation is far from mysterious: By assuming that even in the presence of a macroscopic gradient of physical quantities equilibrium conditions set in locally, the kinetic theory provides a unified theoretical approach for transport and equilibrium observables.

1.3 Distribution Function in Molecular Space

A real gas is a collection of a large number N of molecules (typically 10^{19} particles/cm^3) interacting by short-range forces. In order to simplify the problem, we assume that all molecules are identical (in particular, they have the same mass m), that the laws of their mutual interactions are ruled by suitable short-range conservative forces, and, moreover, that quantum and relativistic effects can be neglected. One further simplification amounts to assume that each molecule can be represented as a point particle (i.e., we ignore its internal degrees of freedom), obeying the laws of Newtonian dynamics in the three-dimensional space

$$\dot{\mathbf{r}}_i(t) = \mathbf{v}_i(t) \tag{1.20a}$$

$$m\dot{\mathbf{v}}_i(t) = \mathbf{F}_i(t), \tag{1.20b}$$

with $i = 1, \cdots, N$ (we have used the shorthand notation $\dot{a}$ for the derivative of a with respect to time). This is a system of $6N$ first-order differential equations, where $\mathbf{r}_i$ and $\mathbf{v}_i$ are the position and the velocity vectors of the i-th particle; $\mathbf{F}_i$ is the total conservative force acting of the i-th particle, which results from some conservative pairwise interaction potential between particles, gravity, inertial forces, and those exerted by the walls of the container, which confine the portion of space available to the gas. In practice, we are assuming that the total conservative force $\mathbf{F}_i$ acting on each particle contains a complete information about the physical properties of the system.

In principle, the time evolution of the gas could be determined by solving the $6N$ equations of motion (1.20) for any given set of initial conditions $\mathbf{r}_i(0)$ and $\mathbf{v}_i(0)$. In practice, it is evident that solving this problem for a macroscopic gas is far beyond any realistic possibility.[6]

But do we really need to know the dynamical state of all the molecules in the gas at any given time in order to obtain physical inferences about its thermodynamic properties? In order to extract relevant physical information, that is, those accessible to experimental observations, we are rather interested in measuring some observables, which involve only macroscopic average properties of the gas. For instance, what we operatively define as a measure of the pressure of a gas is a space and time average of the instantaneous force that each single molecule exerts on the walls of the container. It is important to observe that in a microscopic perspective, such a quantity may greatly vary both in space and time; nonetheless for the sake of physical significance, we have to assume that all instantaneous microscopic processes combine, yielding well-defined average macroscopic quantities (irrespectively of equilibrium or nonequilibrium macroscopic states of the gas). Upon these remarks, we are naturally led to consider a less detailed description of the dynamical state of a gas than the one contained in Eq. (1.20).

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[6] Nowadays, the computational discipline named *molecular dynamics* tackles explicitly the problem of integrating very large sets of dynamical equations relying upon the power of modern computers. Anyway, even if large, the number of dynamical equations which can be integrated by this method remains many orders of magnitude smaller than N_A.