Contents

1 Introduction

Lies, damned lies, and statistics.

—Disraeli

1.1 The Subject Matter of Statistical Mechanics

The goal of statistical mechanics is to predict the macroscopic properties of bodies, especially their thermodynamic properties, on the basis of their microscopic structure.

The macroscopic properties of greatest interest to statistical mechanics are those relating to *thermodynamic equilibrium*. As a consequence, the concept of thermodynamic equilibrium occupies a central position in the field. It is for this reason that we will first review some elements of thermodynamics, which will allow us to make the study of statistical mechanics clearer once we begin it. The examination of *nonequilibrium states* in statistical mechanics is a fairly recent development (except in the case of gases) and is currently the focus of intense research. We will omit it in this course, even though we will deal with properties that are time-dependent (but always related to thermodynamic equilibrium) in the chapter on dynamics.

The microscopic structure of systems examined by statistical mechanics can be described by means of mechanical models: for example, gases can be represented as systems of particles that obey the classical equations of motion and interact by means of a phenomenologically determined potential. Other examples of mechanical models are those that represent polymers as a chain of interconnected particles, or the classical model of crystalline systems, in which particles are arranged in space according to a regular pattern, and oscillate around the minimum of the potential energy due to their mutual interaction. The models we use are, however, rather abstract and often exhibit only a faint resemblance to the basic mechanical description (more specifically, to the quantum nature of matter). How such abstract models are able to describe the behavior of actual systems is itself one of the more interesting questions of statistical mechanics, and has led to establishing the theory of universality and its foundation in the renormalization group.

The models of systems dealt with by statistical mechanics have some common characteristics. We are in any case dealing with systems with a large number of degrees of freedom: the reason lies in the corpuscular (atomic) nature of matter. Avogadro's constant, $N_A \simeq 6.022 \cdot 10^{23}\ \mathrm{mol}^{-1}$—that is, the number of molecules contained in a gram-mole (mole)—provides us with an order of magnitude of the degrees of freedom contained in a thermodynamic system. (The values of this and other fundamental physical constants are given in sec. H.) The degrees of freedom that one considers should have more or less comparable effects on the global behavior of the system.

Exercise 1.1 (On Avogadro's number) Imagine we could "mark" the water molecules contained in a small flask of 100 cc, and pour them into the sea. If we fill the flask from the sea after having waited for the flask's "marked" molecules to have distributed uniformly in the oceans, how many of the molecules can we expect to find back on average?

NOTE. The surface of the oceans equals 71% of the earth's surface, and its mean depth is 3,800 m. The molecular weight of water is equal to 18.

This state of affairs excludes the application of the methods of statistical mechanics to cases in which a restricted number of degrees of freedom "dominates" the others—for example, in celestial mechanics, although the number of degrees of freedom of the planetary system is immense, an approximation in which each planet is considered as a particle is a good start. In this case, we can state that the translational degrees of freedom (three per planet)—possibly with the addition of the rotational degrees of freedom, also a finite number—dominate all others. It follows from these considerations that one encounters quite hard problems if one naively attempts to apply statistical concepts to human sciences, such as politics. Indeed, even if a nation's political system includes a very high number of degrees of freedom, it is possible to identify some degrees of freedom that are much more important than the rest. On the other hand, statistical methods can also be applied to systems that are not strictly speaking mechanical—for example, neural networks (understood as models of the brain's components), urban thoroughfares (traffic models), and some problems of a geometric nature (for example, percolation).

The simplest statistical mechanical model is that of a large number of identical particles, free of mutual interaction, inside a container with impenetrable and perfectly elastic walls. This is the model of the **ideal gas**, which describes quite well the behavior of real gases at low densities, and more specifically allows one to derive the well-known equation of state.

The introduction of pair interactions between the particles of the ideal gas allows us to obtain the standard model for **simple fluids**. Generally speaking, this model cannot be resolved exactly and is studied by means of perturbation or numerical techniques. It allows one to describe the behavior of real gases (especially rare gases), and the liquid-vapor transition (boiling and condensation).

The preceding models are of a classical (that is, not quantum) nature and can be applied only when the temperatures are not too low. The quantum effects that follow from the inability to distinguish particles from one another are very important, and can be dealt with at the introductory level if one omits interactions between particles. In this fashion, we obtain models for **quantum gases**, further distinguished as **fermions** or **bosons**, depending on the nature of the particles.

The model of **noninteracting fermions** describes the behavior of conduction electrons in metals fairly well, once one redefines the dependence of their energy on their momentum in a suitable way. The thermodynamic properties are governed by the Pauli exclusion principle.

The model of **noninteracting bosons** has two important applications: radiating energy in a cavity (also known as **black body**) can be conceived as a set of particles (**photons**) that are bosonic in nature; moreover, helium (whose most common isotope, He, is bosonic in nature) exhibits, at low temperatures, a remarkable series of properties that can be interpreted on the basis of the noninteracting boson model. Actually, the transition of ^{4}He to a superfluid state, also referred to as the λ **transition**, is connected to the **Einstein condensation**, which occurs in a gas of noninteracting bosons at high densities. Obviously, interactions between helium atoms are not negligible, but their effects can be studied by means of analytic methods such as perturbation theory.

In many of the statistical models we will describe, however, the system's fundamental elements will not be "particles," and the fundamental degrees of freedom will not be mechanical (position and velocity or impulse). If we want to understand the origin of ferromagnetism, for example, we focus on the degrees of freedom that are most relevant for the phenomenon, such as the orientation of the magnetic moments of the electrons, called their **spin**. The spin, being of a quantum nature, can assume only a finite number of values. The simplest case is when there are only two values—in this fashion, we obtain a simple model of ferromagnetism, known as the **Ising model**, which is by far the most studied model in statistical mechanics. The ferromagnetic solid is therefore represented as a regular lattice in space, where for each point of the lattice there is a spin variable that can assume the values $+1$ and -1. This model allows one to describe the paramagnet-ferromagnet transition, as well as other similar transitions.

1.2 Statistical Postulates

The behavior of a mechanical system is determined not only by its structure, represented by the equations of motion, but also by its initial conditions. Therefore the laws of mechanics are not enough by themselves to define the behavior of a mechanical system that contains a large number of degrees of freedom if nothing is said about the relevant initial conditions. It is therefore necessary to complete the description of the system with some additional postulates—the statistical postulates in the strict sense of the word—that concern these initial conditions.

The path to arrive at the formulation of statistical postulates is fairly twisted. In the following section, we discuss the relatively simple case of an ideal gas. We conjecture the distribution of the positions and velocities of particles in an ideal gas at equilibrium, following Maxwell's reasoning in a famous article [Maxw60], and we see how the equation of state of the ideal gas follows from this conjecture and the laws of mechanics. What this argument does not prove is that this distribution is conserved—in other words, if the equilibrium distribution of positions and velocities of the particles holds at a certain instant in time, it also holds at each following instant, as the system evolves according to its equations of motion. It is also necessary to show that if the initial distribution is different from the equilibrium one, the actual distribution approaches the equilibrium one as a consequence of the system's evolution—that is, that the system "naturally" approaches equilibrium. Boltzmann's great contribution was to state clearly the problems mentioned above and to make a bold attempt at their solution.

1.3 An Example: The Ideal Gas

1.3.1 *Definition of the System*

In the model of an ideal gas, one considers N point-like bodies (or particles), with mass equal to m, identical to one another, free of mutual interaction, inside a container of volume V whose walls are perfectly reflecting. The mechanical state of the system is identified by the position vector $\boldsymbol{r}_i$ and the velocity vector $\boldsymbol{v}_i$ (both three-dimensional vectors) of each particle i. These vectors evolve according to the laws of mechanics.

1.3.2 *Maxwell's Postulates*

The assumption is that the vectors are distributed "randomly," and more specifically that:

1. The velocity and position vectors pertaining to different particles are independent of one another. This hypothesis certainly does not apply, among other examples, to particles that are very close to each other, because the position of two particles that are very close is undoubtedly influenced by the forces that act between them. One can, however, expect that if the gas is very diluted, deviations from this hypothesis will have negligible consequences. If one accepts the hypothesis of independent particles, we can describe the state of the system by giving, for each value of $\boldsymbol{r} = (x, y, z)$ and $\boldsymbol{v} = (v_x, v_y, v_z)$, the number $\mathrm{d}N$ of particles whose position is located within a box, with sides $\mathrm{d}\boldsymbol{r} = (\mathrm{d}x, \mathrm{d}y, \mathrm{d}z)$ placed around $\boldsymbol{r}$, and that are simultaneously driven by a velocity whose vector lies in a box of sides $\mathrm{d}\boldsymbol{v} = (\mathrm{d}v_x, \mathrm{d}v_y, \mathrm{d}v_z)$ around the vector $\boldsymbol{v}$: we then have $\mathrm{d}N = f(\boldsymbol{r}, \boldsymbol{v})\, \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{v}$. This defines the single-particle probability distribution $f(\boldsymbol{r}, \boldsymbol{v})$.
2. Position is independent of velocity (in the sense given by probability theory), and therefore the probability distribution $f(\boldsymbol{r}, \boldsymbol{v})$ factorizes: $f(\boldsymbol{r}, \boldsymbol{v}) = f^{(r)}(\boldsymbol{r}) f^{(v)}(\boldsymbol{v})$.
3. Density is uniform in the space occupied by the gas, and therefore $f^{(r)}(\boldsymbol{r}) = N/V = \rho = \text{const.}$ if $\boldsymbol{r}$ is inside the container, and equal to zero otherwise.
4. The velocity components are mutually independent, and we have therefore $f^{(v)}(\boldsymbol{v}) = f^{(x)}(v_x) f^{(y)}(v_y) f^{(z)}(v_z)$.
5. The distribution $f^{(v)}(\boldsymbol{v})$ is isotropic in velocity space, so that $f^{(v)}(\boldsymbol{v})$ depends in actual fact only on the magnitude $v = |\boldsymbol{v}|$ of $\boldsymbol{v}$.

The basic properties of probability distributions are summarized in sec. A.

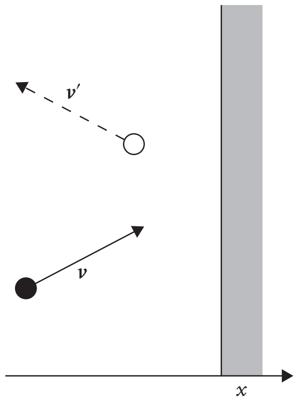

FIGURE 1.1. Derivation of the relation between average speed and pressure. The particle driven by velocity $\boldsymbol{v}$ is about to hit the wall. After the impact, it will have velocity $\boldsymbol{v}'$, in which the x component (normal to the wall) has changed sign.

Exercise 1.2 Prove that the only distribution that satisfies postulates 4 and 5 is a Gaussian:

$$f^{(v)}(\boldsymbol{v}) \propto \exp\left(-\lambda v^2\right),$$

where λ is a positive constant. Show that

$$\langle v^2 \rangle = \frac{3}{2\lambda},$$

and that therefore the average kinetic energy is given by

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3m}{4\lambda}.$$

1.3.3 *Equation of State*

We now prove that Maxwell's postulates allow us to derive the equation of state for ideal gases and provide a microscopic interpretation of absolute temperature in terms of kinetic energy.

Let us consider a particle of velocity $\boldsymbol{v} = (v_x, v_y, v_z)$ that, coming from the left, hits a wall parallel to the plane (yz) (see figure 1.1). After the impact, it is driven by velocity $\boldsymbol{v}' = (-v_x, v_y, v_z)$. The change $\Delta \boldsymbol{p}$ in its momentum $\boldsymbol{p}$ is given by $\Delta \boldsymbol{p} = \boldsymbol{p}' - \boldsymbol{p} = m(\boldsymbol{v}' - \boldsymbol{v}) = m(-2v_x, 0, 0)$. The number of impacts of this type that occur in a time interval Δt on a certain region of the wall of area S is equal to the number of particles driven by velocity $\boldsymbol{v}$ that are contained in a box of base equal to S and of height equal to $v_x\,\Delta t$. The volume of this box is equal to $S\,v_x\,\Delta t$, and the number of these particles is equal to $\rho f^{(v)}(\boldsymbol{v})\,v_x\,S\,\Delta t$.

The total momentum $\Delta \boldsymbol{P}$ transmitted from the wall to the gas, during the time interval Δt, is therefore

$$\Delta \boldsymbol{P} = \int_0^{+\infty} \mathrm{d}v_x \int_{-\infty}^{+\infty} \mathrm{d}v_y \int_{-\infty}^{+\infty} \mathrm{d}v_z\, f^{(v)}(\boldsymbol{v})\,\rho\,S\,\Delta t\,(-2m)\,v_x^2\,\boldsymbol{i}, \tag{1.1}$$

where $\boldsymbol{i} = (1, 0, 0)$ is the versor of the x axis. In this expression, the integral over v_x runs only on the region $v_x > 0$ because only those particles that are moving toward the right contribute to pressure on the wall.

The total force that the wall exercises on the gas is given by $\boldsymbol{F} = -\Delta \boldsymbol{P}/\Delta t$, and therefore the pressure p is given by

$$p = \frac{|\boldsymbol{F}|}{S} = 2m\rho \cdot \frac{1}{2} \langle v_x^2 \rangle = \frac{\rho m}{2\lambda}. \tag{1.2}$$

In this equation, the factor 1/2 comes from the integration over v_x, which runs only on the region $v_x > 0$. It is well known that the equation of state for perfect gases takes the form

$$pV = nRT, \tag{1.3}$$

where $n = N/N_{\mathrm{A}}$ is the number of moles, T is the absolute temperature, and $R \simeq 8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is the gas constant. By introducing the **Boltzmann constant** k_{B},

$$k_{\mathrm{B}} = \frac{R}{N_{\mathrm{A}}} \simeq 1.381 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}, \tag{1.4}$$

and the particle density

$$\rho = \frac{N}{V}, \tag{1.5}$$

eq. (1.3) can be written

$$p = \rho\, k_{\mathrm{B}} T. \tag{1.6}$$

If we compare this expression with eq. (1.2), we obtain the constant λ:

$$\lambda = \frac{m}{2k_{\mathrm{B}}T}. \tag{1.7}$$

The distribution of the component v_x of the velocity, taking into account the normalization condition, is then given by

$$f^{(v_x)}(v) = \left(\frac{m}{2\pi\, k_{\mathrm{B}} T}\right)^{1/2} \exp\left(-\frac{mv^2}{2k_{\mathrm{B}}T}\right). \tag{1.8}$$

Analogous laws hold for the distributions of v_y and v_z. Then the distribution of the speed $v = |\boldsymbol{v}|$ is given by the following expression, known as the **Maxwell distribution**:

$$\phi(v) = \int \mathrm{d}\boldsymbol{v}\, \delta\,(v - |\boldsymbol{v}|)\, f^{(\boldsymbol{v})}(\boldsymbol{v}) = \left(\frac{m}{2\pi\, k_{\mathrm{B}} T}\right)^{3/2} 4\pi v^2 \exp\left(-\frac{mv^2}{2\, k_{\mathrm{B}} T}\right), \tag{1.9}$$

where $\delta(x)$ is the **Dirac delta** "function" (cf. sec. A.8), defined by

$$\int \mathrm{d}x\, f(x)\, \delta(x - x_0) = f(x_0), \tag{1.10}$$

where $f(x)$ is an arbitrary smooth function.

Exercise 1.3 (On Maxwell's distribution)

1. Evaluate the root mean square speed $v_{\mathrm{RMS}} = \sqrt{\langle v^2 \rangle}$ of a gas obeying Maxwell's distribution $\phi(\boldsymbol{v})$ in d dimensions. Give the corresponding numerical value for air in three dimensions at room temperature ($T = 300$ K). Air is made by 2/3 of nitrogen (molecular weight 28) and 1/3 of oxygen (molecular weight 32).

2. Evaluate the value v of the speed in a Maxwell distribution at temperature T for a gas of molecules of mass m in d dimensions that corresponds to the maximal probability density. Compare it with the root mean square speed.

3. Evaluate the probability distribution function for the kinetic energy of a gas following Maxwell's distribution, i.e., the probability density that the kinetic energy of a randomly chosen particle has the value κ:

$$f(\kappa) = \int \mathrm{d}\boldsymbol{v}\, \delta\left(\kappa - \frac{1}{2} m v^2\right) \phi(\boldsymbol{v}).$$

Exercise 1.4 (Gas in a gravity field) Let us consider a gas of particles of mass m, at equilibrium with a uniform temperature T in a gravity field, described by the acceleration $\boldsymbol{g}$ pointing vertically downward. The gas particles obey the Maxwell distribution. Let S_1 and S_2 be two horizontal surfaces, at heights z_1 and $z_2 > z_1$, respectively. We denote by ρ_i, $i \in \{1, 2\}$ the numerical density close to S_i.

By considering the condition that, in a time interval of duration Δt, as many particles originating from S_1 cross S_2 as vice versa, derive a relation between ρ_i and z_i ($i \in \{1, 2\}$). Neglect the effects of collisions between S_1 and S_2.

Exercise 1.5 (Knudsen gas) Let us consider a gas distributed in two containers placed side by side, both at a very small density, at pressures and temperatures (p_1, T_1) and (p_2, T_2). The two containers are connected by a very small opening, such that the thermal equilibrium of the two systems is not perturbed. There is molecular equilibrium when the flux of particles through the opening from container 1 to container 2 is equal to the flux of particles from container 2 to container 1.

1. Show that in this situation there is a simple relation between (p_1, T_1) and (p_2, T_2).

2. Evaluate the small change in (p_i, T_i), $i = 1, 2$, that obtains in a short time interval Δt.

Exercise 1.6 (Drag in a gas) Let us consider an ideal gas made of particles of mass m, with numerical density $\rho = N/V$, at temperature T. Using Maxwell's distribution, evaluate the drag applied by the gas on a small disk of radius R moving at velocity $\boldsymbol{v}$, where $\boldsymbol{v}$ is parallel to the axis of the disk. We assume that R is much smaller than the interatomic distance $\rho^{-1/3}$ and that v is much smaller than the characteristic speed of the particles.

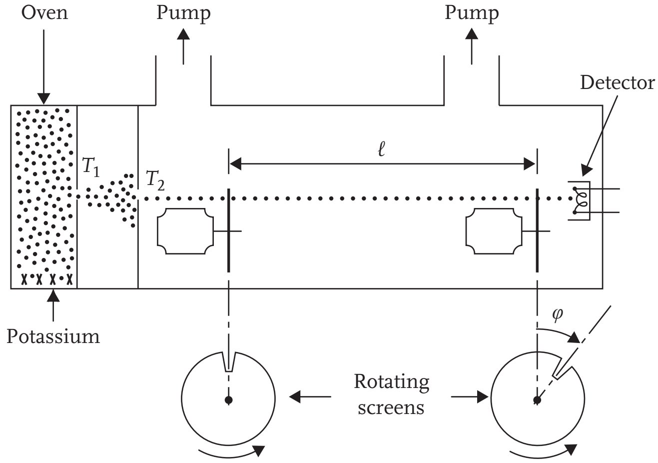

FIGURE 1.2. The Marcus and McFee experiment. Based on [Marc59].

1.3.4 The Marcus and MacFee experiment

The Maxwell distribution can be measured directly by means of experiments on the molecular beams. We will follow the work by Marcus and McFee [Marc59]. A diagram of the experiment is given in figure 1.2. Potassium atoms are heated to a fairly high temperature (a few hundred degrees Celsius) in an oven. The oven is equipped with a small opening that allows the beam to escape. A screen with a small hole is placed a bit further away, in order to have a well-aligned beam. In the region traversed by the beam, a vacuum is maintained by a pump. Two rotating screens, set at a distance ℓ from each other, act as velocity selectors. Each is endowed with a narrow gap, and they rotate together with angular velocity ω. The two gaps are out of phase by an angle φ. Therefore, only particles driven by a velocity $v = \ell\omega/\varphi$ will be able to pass through both gaps, hit the detector, and be counted. If we denote the total beam intensity by j_0, and the solid angle by which the detector is seen from the opening by $\mathrm{d}\Omega$, the number of particles driven by a velocity between v and $v + \mathrm{d}v$ that hit the detector in a given unit of time is given by

$$j\,\mathrm{d}v\,\mathrm{d}\Omega = \frac{1}{\mathcal{Z}}\,j_0 v\,\phi(v)\,\mathrm{d}v\,\mathrm{d}\Omega = \frac{j_0\,m^2}{2\pi\,(2k_\mathrm{B}T)^2}\,v^3\,\exp\left(-\frac{mv^2}{2k_\mathrm{B}T}\right)\,\mathrm{d}v\,\mathrm{d}\Omega, \tag{1.11}$$

where the normalization constant $\mathcal{Z}$ is chosen so that the total particle flux equals j_0.

By varying φ or ω, one can measure the particle flow at various velocities v. We can introduce the variable $\eta = v\sqrt{m/k_\mathrm{B}T}$, thus obtaining a law that is independent of both m and T:

$$\frac{j\,\mathrm{d}v}{j_0\,\mathrm{d}\Omega} = \frac{\eta^3}{2}\,\exp\left(-\frac{\eta^2}{2}\right)\,\mathrm{d}\eta. \tag{1.12}$$

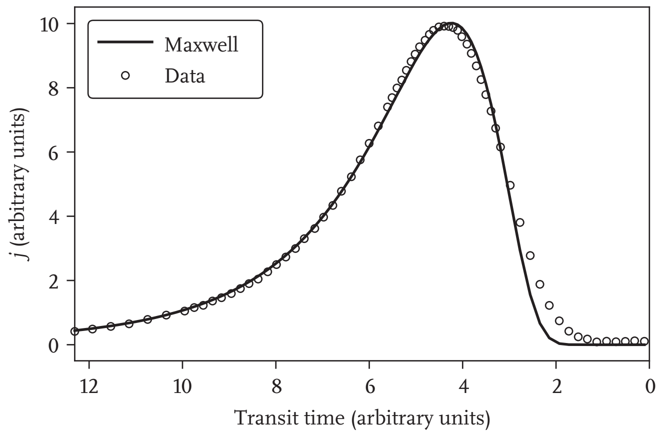

FIGURE 1.3. Particle flux as a function of the transit time between the two disks in the Marcus and McFee experiment at 157°C. The line is a straightforward fit to the Maxwell distribution. The discrepancy at high velocity (small transit time) is due to the fact that the disks do not instantaneously interrupt the particle flow. Based on [Marc59].

This law is well suited to experimental proof, which is shown in figure 1.3. In order to arrive at a quantitative agreement with the results of the experiment, it is necessary to take into account the fact that the disks do not instantaneously interrupt the particle flow and that therefore there are uncertainties in the velocity selection.

1.4 Conclusions

We have therefore been able to show that, if one formulates some statistical hypotheses about the distribution of the velocities of the particles, the equation of state of ideal gases is compatible with the ideal gas model. In the argument we have laid out, there is, however, no proof that the statistical hypotheses concerning the distribution of position and velocity of particles are compatible with the laws of mechanics. In order to prove this compatibility, we need to establish some hypotheses about initial conditions. We will therefore be satisfied if we manage to prove that for "almost all" initial conditions that satisfy certain criteria, the statistical properties of the relevant distributions are "almost always" valid. These considerations will be incomplete, however, since it is not clear how hypotheses that are valid for almost all initial conditions can be relevant to explain the result of a specific experiment, carried out with specific initial conditions.

The statistical postulates are ultimately founded in thermodynamics. S.-K. Ma stressed in [Ma85] that they can be summarized by the relation (discovered by Boltzmann) between thermodynamic entropy and a mechanical quantity: the volume of the accessible phase space. In order to clarify the nature of the entropy and what we mean by volume of accessible phase space, it is necessary to briefly discuss the principles of thermodynamics, which is done in the next chapter.

Recommended Reading

The kinetic theory of gases is treated in greater detail in a large number of works. A brief but careful introduction can be found in K. Huang, *Statistical Mechanics*, New York: Wiley, 1987. A classic reference work is R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford, UK: Oxford University Press, 1938 (reprinted New York: Dover, 1979). The (often surprising) history of the kinetic theory has been retraced by S. G. Brush, *The Kind of Motion We Call Heat*, Amsterdam: North-Holland, 1976.

Author Index

Subject Index

Page numbers in italics refer to tables and figures.