

School of Physics & Astronomy

PHS4200/PHS4021 Statistical Mechanics

Lecture 4: Kinetic Theory and Boltzmann Statistics

4.1 Introduction

In this lecture we apply the methods of classical statistical mechanics to the kinetic theory of gases and to the Boltzmann statistics of distinguishable particles. Later we will examine systems that are intrinsically quantum mechanical, for which the energy levels are discrete and the Gibbs combinatorial factor (see Sec. 2.3.2) does not adequately describe the symmetry properties of a system's many particle wavefunction. For this latter scenario we need to invoke quantum statistics to describe non-classical particles. However, some of the foundational insights afforded by classical ensemble theory are applicable to quantum statistics. In a later lecture we will develop the formal theory of quantum statistical mechanics.

4.2 Kinetic Theory

Kinetic theory aims to understand the dynamics of a large number of particles (e.g., a gas of $N \sim 10^{23}$ atoms or molecules); in particular, it seeks to describe the time evolution of the distribution of particles as a function of space and time, under the action of external forces and internal collisions. The distribution function, denoted by $f(\mathbf{r}, \mathbf{p}, t)$, is defined so that the number of particles at time t , in a given volume element $d^3\mathbf{r}d^3\mathbf{p}$ in $\mathbf{r}-\mathbf{p}$ phase space (also known as μ -space) is:

$$dN = f(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{r} d^3\mathbf{p}. \quad (4.1)$$

The normalisation condition requires that:

$$\int_{\mu} dN = \int_{\mu} f(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{r} d^3\mathbf{p} = N. \quad (4.2)$$

Liouville's theorem (see Sec. 2.2) requires that the volume element $d^3\mathbf{r}d^3\mathbf{p}$ is invariant, i.e.,

$$\begin{aligned} \frac{df}{dt} &= \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \cdot \frac{d\mathbf{r}}{dt} + \frac{\partial f}{\partial \mathbf{p}} \cdot \frac{d\mathbf{p}}{dt} \\ &= \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \frac{d\mathbf{r}}{dt} + \nabla_{\mathbf{p}} f \cdot \frac{d\mathbf{p}}{dt} \\ &= 0, \end{aligned} \quad (4.3)$$

where $\nabla_{\mathbf{r}} f = (\partial f / \partial x, \partial f / \partial y, \partial f / \partial z)$ and $\nabla_{\mathbf{p}} f = (\partial f / \partial p_x, \partial f / \partial p_y, \partial f / \partial p_z)$. Using Hamilton's equations (1.1) allows us to write Eq. (4.3) as:

$$\begin{aligned} \frac{df}{dt} &= \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{r}} \cdot \frac{\partial \mathbf{r}}{\partial \mathbf{p}} \frac{\partial H}{\partial \mathbf{p}} - \frac{\partial f}{\partial \mathbf{p}} \cdot \frac{\partial \mathbf{p}}{\partial \mathbf{r}} \frac{\partial H}{\partial \mathbf{r}} \\ &= \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \nabla_{\mathbf{p}} H - \nabla_{\mathbf{p}} f \cdot \nabla_{\mathbf{r}} H \\ \Rightarrow \frac{df}{dt} &= \frac{\partial f}{\partial t} + \{f, H\} = 0. \end{aligned} \quad (4.4)$$

where $\{f, H\}$ is the Poisson bracket (see Lecture 2, Appendix A). Equation (4.4) represents the Boltzmann transport equation *without* particle collisions. For an equilibrium distribution we have $\partial f / \partial t = 0$, whence $\{f, H\} = 0$. Note that we have not yet specified the distribution function f ; however, any distribution function f that satisfies the Poisson bracket $\{f, H\} = 0$ is suitable! An important equilibrium distribution is the Maxwell-Boltzmann distribution, which we will examine in more detail in Sec. 4.2.2.

As we have already noted, Eq. (4.4) does not include collisions between particles. This situation can be remedied by adding an explicit collision term, in which case we have the full Boltzmann transport equation (which now includes collisions), i.e.,

$$\frac{\partial f}{\partial t} + \{f, H\} = \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \nabla_{\mathbf{p}} H - \nabla_{\mathbf{p}} f \cdot \nabla_{\mathbf{r}} H = \left(\frac{\partial f}{\partial t} \right)_c. \quad (4.5)$$

In general the explicit form of the collision term $(\partial f / \partial t)_c$ is difficult to calculate. However, we can proceed by making some assumptions. Namely, we assume binary elastic collisions between two structureless particles and that the velocities of the particles are uncorrelated. We will also ignore the walls of the vessel containing the particles and assume that the external forces do not affect the collisions. Even making these assumptions we are still faced with calculating the scattering cross section for a binary collision. To avoid this complexity we further assume that the effect of the collisions is to locally perturb the distribution function $f(\mathbf{r}, \mathbf{p}, t)$, from its local equilibrium value, which we denote by $f^{(0)}(\mathbf{r}, \mathbf{p}, t)$. With these assumptions we write:

$$\left(\frac{\partial f}{\partial t} \right)_c = -\frac{1}{\tau_c} (f - f^{(0)}), \quad (4.6)$$

where τ_c is the relaxation time between particle collisions. The Boltzmann transport equation (4.5) now becomes:

$$\frac{\partial f}{\partial t} + \{f, H\} = \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \nabla_{\mathbf{p}} H - \nabla_{\mathbf{p}} f \cdot \nabla_{\mathbf{r}} H = -\frac{1}{\tau_c} (f - f^{(0)}). \quad (4.7)$$

Example 4.1: Solve Eq. (4.6) for fixed position and momentum.

Solution

For fixed \mathbf{r} and \mathbf{p} , Equation (4.6) may be treated as a simple ordinary differential equation that can be re-arranged to give:

$$\left(\frac{\partial f}{\partial t} \right)_c = -\frac{1}{\tau_c} (f - f^{(0)}) \quad \Rightarrow \quad \frac{df}{f(t) - f^{(0)}(t)} = -\frac{1}{\tau_c} dt.$$

Integrating we obtain:

$$\begin{aligned} \int_0^t \frac{df}{f(t) - f^{(0)}(t)} &= -\frac{1}{\tau_c} \int_0^t dt. \\ \Rightarrow \ln[f(t) - f^{(0)}(t)] &= -\frac{t}{\tau_c} + \text{const.} \end{aligned}$$

The constant of integration is determined from:

$$\ln[f(0) - f^{(0)}(0)] = \text{const} \quad \Rightarrow \quad \ln \left(\frac{f(t) - f^{(0)}(t)}{f(0) - f^{(0)}(0)} \right) = -\frac{t}{\tau_c},$$

or

$$f(t) = f^{(0)}(t) + [f(0) - f^{(0)}(0)] e^{-t/\tau_c}.$$

This equation shows that the collisions restore the equilibrium distribution $f^{(0)}(t)$ exponentially, with a relaxation time τ_c , i.e., as $t \rightarrow \infty$, $f(t) \rightarrow f^{(0)}(t)$.

4.2.1 The BBGKY Hierarchy

As formulated above, the Boltzmann transport equation is based on a number of *ad hoc* assumptions. One may ask is there a more comprehensive treatment of transport phenomena, which correctly describes collisions in a consistent manner, including accounting for correlations between the particles before and after the collisions. The BBGKY hierarchy¹ does just this. A full treatment of the BBGKY methodology is beyond the scope of these lectures; however, we will quote some key results of the formalism and refer the interested reader to Ref. [1] for the details. The starting point is the Hamiltonian for an ensemble of N particles

$$H(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i<j}^N V(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i=1}^N V_{ext}(\mathbf{r}_i), \quad (4.8)$$

The potential $V(\mathbf{r}_i - \mathbf{r}_j)$ describes the interparticle interactions. For a dilute gas these are dominated by binary collisions; however, in principle the formalism can account for many body interactions (i.e., 3-body, 4-body, etc). The term $V_{ext}(\mathbf{r}_i)$ describes external forces acting on the system. The BBGKY hierarchy motivates the general n -particle distribution function, defined as [1]:

$$f_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_n, t) = \frac{N!}{(N-n)!} \int_{\mu} f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N, t) \prod_{i=n+1}^N d^3\mathbf{r}_i d^3\mathbf{p}_i. \quad (4.9)$$

The distribution function f_n in Eq. (4.9) obeys a set of equations - the BBGKY hierarchy, which are specified by:

$$\frac{\partial f_n}{\partial t} = \{H_n, f_n\} + \sum_{i=1}^n \int_{\mu} \frac{\partial V(\mathbf{r}_i - \mathbf{r}_{n+1})}{\partial \mathbf{r}_i} \cdot \frac{\partial f_{n+1}}{\partial \mathbf{p}_i} d^3\mathbf{r}_{n+1} d^3\mathbf{p}_{n+1}, \quad (4.10)$$

or

$$\frac{\partial f_n}{\partial t} + \{f_n, H_n\} = \sum_{i=1}^n \int_{\mu} \frac{\partial V(\mathbf{r}_i - \mathbf{r}_{n+1})}{\partial \mathbf{r}_i} \cdot \frac{\partial f_{n+1}}{\partial \mathbf{p}_i} d^3\mathbf{r}_{n+1} d^3\mathbf{p}_{n+1}, \quad (4.11)$$

where $\{H_n, f_n\} = -\{f_n, H_n\}$ is the Poisson bracket defined in Eq. (4.4), and H_n is:

$$H_n = \sum_{i=1}^n \frac{|\mathbf{p}_i|^2}{2m} + \sum_{i<j}^n V(\mathbf{r}_i - \mathbf{r}_j) + \sum_{i=1}^n V_{ext}(\mathbf{r}_i). \quad (4.12)$$

In the absence of any interactions, Eq. (4.10) is described by the collisionless Boltzmann equation [c.f. Eq. (4.4)]. In this case, according to Liouville's theorem, the distribution function f behaves like an incompressible fluid. It is the interactions, encapsulated by the collision integral in Eq. (4.10) that accounts for how a group of n particles (in a phase space volume element $d^3\mathbf{r}d^3\mathbf{p}$) interacts with the remaining $N-n$ particles in the system. The Boltzmann transport equation (4.5) is the first equation in the BBGKY hierarchy; it describes the time evolution of the 1-particle distribution function $f_1 = f_1(\mathbf{r}, \mathbf{p}, t)$, i.e.,

$$\frac{\partial f_1}{\partial t} + \{f_1, H_1\} = \int_{\mu} \frac{\partial V(\mathbf{r}_1 - \mathbf{r}_2)}{\partial \mathbf{r}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} d^3\mathbf{r}_2 d^3\mathbf{p}_2, \quad (4.13)$$

or

$$\frac{\partial f_1}{\partial t} + \frac{\partial f_1}{\partial \mathbf{r}_1} \cdot \frac{\partial H_1}{\partial \mathbf{p}_1} - \frac{\partial f_1}{\partial \mathbf{p}_1} \cdot \frac{\partial H_1}{\partial \mathbf{r}_1} = \int_{\mu} \frac{\partial V(\mathbf{r}_1 - \mathbf{r}_2)}{\partial \mathbf{r}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} d^3\mathbf{r}_2 d^3\mathbf{p}_1 \quad (4.14)$$

¹ The BBGKY hierarchy is named after Bogoliubov, Born, Green, Kirkwood and Yvon. See Ref. [1], pp. 65 - 71. A discussion of the BBGKY formalism can also be found at:

<http://web.mit.edu/8.333/www/lectures/lec8.pdf>
https://en.wikipedia.org/wiki/BBGKY_hierarchy

Substituting for the 1-particle Hamiltonian H_1 , Eq. (4.14) becomes:

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} - \frac{\partial V_{ext}}{\partial \mathbf{r}_1} \cdot \frac{\partial f_1}{\partial \mathbf{p}_1} = \int_{\mu} \frac{\partial V(\mathbf{r}_1 - \mathbf{r}_2)}{\partial \mathbf{r}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} d^3 \mathbf{r}_2 d^3 \mathbf{p}_2, \quad (4.15)$$

Notice that all terms in Eq. (4.15) have the dimension of inverse time $[T]^{-1}$. Further, Eq. (4.15) includes two time scales. To see this we perform a dimensional analysis, leading to:

$$\frac{\partial V_{ext}}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} \sim \frac{1}{\tau_{ext}} \quad \text{and} \quad \frac{\partial V}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{p}_1} \sim \frac{1}{\tau_c}. \quad (4.16)$$

In our earlier analysis we identified τ_c as the relaxation time between particle collisions. We can estimate the relative magnitudes of the two time scales. For example, the speed of an atom in a gas of nitrogen atoms at room temperature (300 K) is given by the equipartition theorem:

$$\frac{1}{2} m v^2 = \frac{3}{2} k_B T \Rightarrow v = \sqrt{\frac{3 k_B T}{m}} \approx 700 \text{ m/s}. \quad (4.17)$$

If we introduce a “typical” macroscopic length scale $L \sim 10^{-2} \text{ m}$, then this sets the time scale for τ_{ext} i.e.,

$$v \approx \frac{L}{\tau_{ext}} \Rightarrow \tau_{ext} \approx \frac{L}{v} = \frac{10^{-2} \text{ m}}{700 \text{ ms}^{-1}} \approx 10^{-5} \text{ s}. \quad (4.18)$$

The collision time scale is governed by the short range interaction potential V , which is determined by the average interatomic distance $a \sim 10^{-9} \text{ m}$, whence:

$$\tau_c \approx \frac{a}{v} = \frac{10^{-9} \text{ m}}{700 \text{ ms}^{-1}} \approx 10^{-12} \text{ s}. \quad (4.19)$$

Finally, to make a connection with the Boltzmann transport equation (4.5), we state without proof (see Ref. [1]) that:

$$\left(\frac{\partial f_1}{\partial t} \right)_c = \int_{\mu} \frac{\partial V(\mathbf{r}_1 - \mathbf{r}_2)}{\partial \mathbf{r}_1} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} d^3 \mathbf{r}_2 d^3 \mathbf{p}_2. \quad (4.20)$$

Exercise 4.1: Carry out the steps leading to Eqs. (4.13) - (4.15).

Exercise 4.2: Using dimensional analysis show that Eq. (4.16) has the dimensions of inverse time $[T]^{-1}$.

Exercise 4.3: As a challenge you may like to follow Ref. [1] to derive Eq. (4.20).

Hint: A key step is to assume that the 2-particle distribution function can be factored into the product of two 1-particle distribution functions (when the particles are well separated), i.e.,

$$f_2 = f_2(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) \rightarrow f_1(\mathbf{r}_1, \mathbf{p}_1, t) f_1(\mathbf{r}_2, \mathbf{p}_2, t) \quad \text{when} \quad |\mathbf{r}_1 - \mathbf{r}_2| \gg a.$$

4.2.2 The Boltzmann \mathbf{H} -Theorem

The Boltzmann \mathbf{H} -theorem² addresses the question as to whether a system evolves to an

²The symbol \mathbf{H} (which derives from the uppercase Greek letter Eta = H) must not be confused with the Hamiltonian of the system. Unfortunately, it is standard practice to use \mathbf{H} to denote the uncertainty (or entropy) function in statistical mechanics, see e.g., <https://en.wikipedia.org/wiki/H-theorem>

equilibrium state, in which the distribution function is independent of time. For any (1-particle) distribution function f_1 that satisfies the Boltzmann transport equation (4.5), or equivalently (4.13), the **H**-theorem states that:

$$\frac{d\mathbf{H}(t)}{dt} \leq 0, \quad (4.21)$$

where the uncertainty function is defined as:

$$\mathbf{H}(t) = \int_{\mu} f_1(\mathbf{r}, \mathbf{p}, t) \ln f_1(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{r} d^3\mathbf{p}. \quad (4.22)$$

In the absence of external forces ($V_{ext} = 0$) it is reasonable to assume that the distribution function is independent of \mathbf{r} . (However, in what follows we retain \mathbf{r} explicitly in the distribution function). An important insight afforded by the **H**-theorem is that a distribution governed by the Boltzmann transport equation evolves irreversibly to an equilibrium state of maximum entropy. A proof of the **H**-theorem follows from examining the time derivative of Eq. (4.22).

Example 4.2: Show that an equilibrium distribution ($\partial f_1 / \partial t = 0$) implies $d\mathbf{H} / dt = 0$.

Solution

Differentiating the **H** function in Eq. (4.22) with respect to time:

$$\begin{aligned} \frac{d\mathbf{H}(t)}{dt} &= \frac{d}{dt} \int_{\mu} f_1(\mathbf{r}, \mathbf{p}, t) \ln f_1(\mathbf{r}, \mathbf{p}, t) d^3\mathbf{r} d^3\mathbf{p} \\ &= \int_{\mu} \frac{\partial f_1(\mathbf{r}, \mathbf{p}, t)}{\partial t} [\ln f_1(\mathbf{r}, \mathbf{p}, t) + 1] d^3\mathbf{r} d^3\mathbf{p}. \end{aligned}$$

Clearly if $\partial f_1 / \partial t = 0$, then $d\mathbf{H} / dt = 0$. The inequality follows from the positivity of the integrand (e.g., see Ref. [1], Sec. 4.1).

4.3 The Maxwell-Boltzmann Distribution for an Ideal Classical Gas

An important example of a distribution function is the Maxwell-Boltzmann distribution of a classical gas. An ideal classical gas³ is comprised of “point-like” particles (i.e., atoms or molecules), which do not interact, and are assumed to have no internal structure. We can of course include internal degrees of freedom and will do so in our later discussion of thermodynamics of quantum strings in Lecture 6. The total Hamiltonian (energy) of an ideal gas comprising N particles is given by:

$$H = \sum_{i=1}^N \frac{|\mathbf{p}_i|^2}{2m} = \sum_{i=1}^N \frac{1}{2} m |\mathbf{v}_i|^2. \quad (4.23)$$

The microstate is described by coordinates $(\{\mathbf{r}_i\}, \{\mathbf{p}_i\})$, where \mathbf{r}_i and \mathbf{p}_i are the 3-space coordinates and momentum of the i -th particle, respectively. Alternatively, we can represent the state by $(\{\mathbf{r}_i\}, \{\mathbf{v}_i\})$, where \mathbf{v}_i is the velocity of the i -th particle. We want to find the probability $\mathcal{P}(\mathbf{r}, \mathbf{p}) d^3\mathbf{r} d^3\mathbf{p}$ that the particle's coordinates lie between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$, and simultaneously its momentum lies between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$. In Lecture 3 we demonstrated that the probability of finding a particle in a microstate with energy E_i is given by:

$$\mathcal{P}_i \propto e^{-\beta E_i} \quad (\beta = 1/k_B T). \quad (4.24)$$

³ For a gas of N classical particles at temperature T , the particles' average thermal de Broglie wavelength λ is considered to be much smaller than the average interparticle separation a , i.e.,

$$\frac{\lambda}{a} \approx \frac{h}{\sqrt{2mk_B T}} \left(\frac{V}{N} \right)^{-1/3} \ll 1.$$

Hence the required probability density (probability per unit volume in μ -space) is:

$$\mathcal{P}(\mathbf{r}, \mathbf{p}) \propto e^{-\beta|\mathbf{p}|^2/2m}, \quad (4.25)$$

or equivalently in terms of the velocity of the particle:

$$\mathcal{P}(\mathbf{r}, \mathbf{v}) \propto e^{-\frac{1}{2}\beta m |\mathbf{v}|^2}. \quad (4.26)$$

The average number of particles whose coordinates lie between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$, and have a velocity between \mathbf{v} and $\mathbf{v} + d\mathbf{v}$ is denoted by $f(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v}$, defined by:

$$f(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = N\mathcal{P}(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = Ce^{-\frac{1}{2}\beta m v^2}d^3\mathbf{r}d^3\mathbf{v} \quad (v = |\mathbf{v}|). \quad (4.27)$$

where N is the total number of particles in the gas and the normalisation constant C is determined from:

$$\int_{\mathbf{r}, \mathbf{v}} f(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = \int_{\mathbf{r}, \mathbf{v}} f(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = N. \quad (4.28)$$

Substituting Eq. (4.27) into Eq. (4.28) we obtain:

$$\int_{\mathbf{r}, \mathbf{v}} f(\mathbf{r}, \mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = \int_{\mathbf{r}, \mathbf{v}} Ce^{-\frac{1}{2}\beta m v^2}d^3\mathbf{r}d^3\mathbf{v} = N. \quad (4.29)$$

The integration over the coordinates yields the volume V , and hence:

$$\int_{\mathbf{r}, \mathbf{v}} Ce^{-\frac{1}{2}\beta m v^2}d^3\mathbf{r}d^3\mathbf{v} = V \int_{\mathbf{v}} Ce^{-\frac{1}{2}\beta m v^2}d^3\mathbf{v} = N, \quad (4.30)$$

or

$$C \int_{\mathbf{v}} e^{-\frac{1}{2}\beta m v^2}d^3\mathbf{v} = n \quad (n = N/V). \quad (4.31)$$

The remaining integral involves the product of three real Gaussian integrals⁴, which are readily evaluated to give:

$$\begin{aligned} C \int_{\mathbf{v}} e^{-\frac{1}{2}\beta m v^2}d^3\mathbf{v} &= C \left(\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\beta m v_x^2} dv_x \right) \left(\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\beta m v_y^2} dv_y \right) \left(\int_{-\infty}^{+\infty} e^{-\frac{1}{2}\beta m v_z^2} dv_z \right) = n \\ \Rightarrow \quad C \left(\frac{2\pi}{\beta m} \right)^{3/2} &= n \quad \text{or} \quad C = n \left(\frac{\beta m}{2\pi} \right)^{3/2} \quad (n = N/V). \end{aligned} \quad (4.32)$$

The Maxwell-Boltzmann velocity distribution function may now be written as:

$$f(\mathbf{v})d^3\mathbf{r}d^3\mathbf{v} = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/k_B T} d^3\mathbf{r}d^3\mathbf{v}, \quad (4.33)$$

where the coordinate variable \mathbf{r} is omitted from f as it does not explicitly appear in the distribution function. We are also interested in the distribution of speeds, regardless of the direction in which the particles are moving. Examples 4.3 - 4.5 illustrate how one obtains the Maxwellian distribution of speeds for an ideal classical gas, and calculates properties of the distribution.

⁴ The standard Gaussian integral is expressed as:

$$\int_{-\infty}^{+\infty} e^{-\frac{1}{2}ax^2} dx = \sqrt{\frac{2\pi}{a}}.$$

Example 4.3: Determine the Maxwell distribution of speeds for an ideal classical gas.

Solution

The average number of particles per unit volume with speed $v = |\mathbf{v}|$, which lie in the range between v and $v + dv$, is defined as:

$$n(v)dv = \int_{v < |\mathbf{v}| < v+dv} f(\mathbf{v})d^3\mathbf{v}.$$

Since the integral is defined over a spherical shell of inner radius v and thickness dv , we can write:

$$n(v)dv = \int_{v < |\mathbf{v}| < v+dv} f(\mathbf{v})d^3\mathbf{v} \approx f(v) \int_{v < |\mathbf{v}| < v+dv} 4\pi v^2 dv \approx 4\pi f(v)v^2 dv.$$

If we take dv as a differential element then the above approximations become exact. Substituting for $f(v)$ from Eq. (4.33), we obtain the Maxwell distribution⁵ of speeds:

$$n(v)dv = 4\pi n \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} dv.$$

Figure 4.1 shows the Maxwell distribution for a gas of particles for three temperatures.

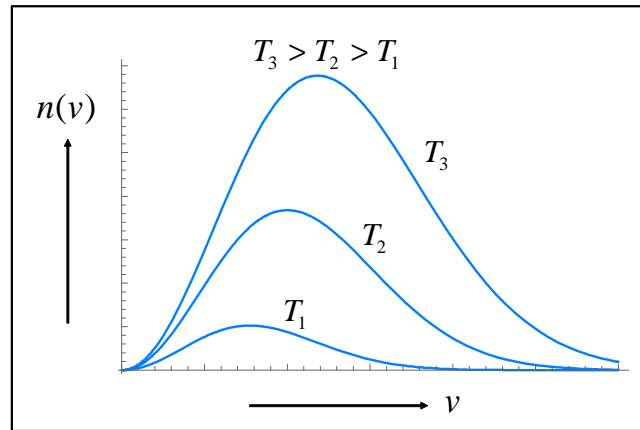


Figure 4.1: The Maxwellian distribution of particle speeds for three temperatures ($T_3 > T_2 > T_1$) in an ideal classical gas. Note that the peak of each distribution represents the most probable speed.

Example 4.4: Determine the average speed of the particles in the Maxwell distribution.

Solution

The average speed of the particles is given by:

⁵ This distribution was first derived by James Clerk Maxwell in 1860. See Maxwell, J. C., “*Illustrations of the dynamical theory of gases. Part I. On the motions and collisions of perfectly elastic spheres*”, Philosophical Magazine, 4th series, 19: 19-32 (1860). This paper can be accessed at:

https://books.google.com.au/books?id=YU7AQAAMAAJ&pg=PA19&redir_esc=y#v=onepage&q&f=false

$$\langle v \rangle = \frac{1}{n} \int_0^{\infty} v n(v) dv.$$

Note that we have introduced the “normalisation” $n^{-1} = V/N$, since $n(v)$ is defined as the number of particles per unit volume; hence the overall “normalisation” is $1/N$, as one would expect! Substituting for $n(v)$ from Example 4.3, we obtain:

$$\langle v \rangle = \frac{1}{n} \int_0^{\infty} v n(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2k_B T} dv.$$

Using the standard integral

$$\int_0^{\infty} \xi^n e^{-\alpha \xi^2} d\xi = \frac{1}{2} \Gamma\left(\frac{n+1}{2}\right) \alpha^{-(n+1)/2} \Rightarrow \int_0^{\infty} \xi^3 e^{-\alpha \xi^2} d\xi = \frac{1}{2} \Gamma(2) \alpha^{-2} = \frac{1}{2} \alpha^{-2},$$

we obtain:

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^3 e^{-mv^2/2k_B T} dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{1}{2} \left(\frac{m}{2k_B T} \right)^{-2} = \sqrt{\frac{8k_B T}{\pi m}}.$$

Example 4.5: Calculate the root mean square speed of the particles in the Maxwell distribution.

Solution

The root mean square speed $v_{rms} = \sqrt{\langle v^2 \rangle}$ is determined by calculating:

$$\begin{aligned} \langle v^2 \rangle &= \frac{1}{n} \int_0^{\infty} v^2 n(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^4 e^{-mv^2/2k_B T} dv \\ &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{1}{2} \Gamma\left(\frac{5}{2}\right) \left(\frac{m}{2k_B T} \right)^{-5/2}, \end{aligned}$$

where we have used the standard integral. Noting that $\Gamma(5/2) = \frac{3}{4}\Gamma(1/2) = \frac{3}{4}\sqrt{\pi}$, we obtain:

$$\langle v^2 \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{1}{2} \Gamma\left(\frac{5}{2}\right) \left(\frac{m}{2k_B T} \right)^{-5/2} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{3\sqrt{\pi}}{8} \left(\frac{m}{2k_B T} \right)^{-5/2} = \frac{3k_B T}{m}.$$

Hence the root mean square speed is:

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}.$$

Note that we could have anticipated this result from the equipartition theorem (see Sec. 2.3.1), since $\frac{1}{2}mv^2 = 3k_B T/2$. It is also evident that $v_{rms} > \langle v \rangle > v_p$, where v_p is the most probable speed (see Exercise 4.4).

Exercise 4.4: Show that the most probable speed v_p of a particle in the Maxwell distribution (i.e., where $n(v)$ is a maximum) is given by:

$$v_p = \sqrt{\frac{2k_B T}{m}}.$$

Exercise 4.5: Show that the average kinetic energy of the particles in the Maxwell distribution is:

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}k_B T.$$

4.4 Langevin's Theory of Paramagnetism

Classical statistical mechanics can be applied to understand the behaviour of paramagnetic ions. Consider a system of N atoms, each with an intrinsic magnetic moment of magnitude μ . The Hamiltonian in the presence of an external magnetic induction field \mathbf{B} is:

$$H(\mathbf{q}, \mathbf{p}, B) = H(\mathbf{q}, \mathbf{p}) - \mu B \sum_{i=1}^N \cos \alpha_i \quad (B = |\mathbf{B}|), \quad (4.34)$$

where $H(\mathbf{q}, \mathbf{p})$ is the Hamiltonian of the system in the absence of an external field, and α_i is the angle between the magnetic moment of the i -th atom and the \mathbf{B} -field. The negative sign in Eq. (4.34) ensures that the lowest energy corresponds to the moments aligned with the direction of the external magnetic field (which we take to point in the z -direction). To find the induced magnetic moment (magnetisation) we need only consider the potential energy of the dipoles, which depends on the orientations of the dipoles with respect to the direction of the external \mathbf{B} -field, i.e.,

$$U = -\mu B \sum_{i=1}^N \cos \alpha_i. \quad (4.35)$$

The canonical partition function of the system is:

$$Z(\beta, B, N) = \sum_{\{\alpha_i\}} \exp \left(\beta \mu B \sum_{i=1}^N \cos \alpha_i \right), \quad (4.36)$$

where the summation is over all orientations of all dipoles. The total energy of the system is simply a sum of the individual dipole energies, hence we have:

$$\begin{aligned} Z(\beta, B, N) &= \sum_{\{\alpha_i\}} \exp \left(\beta \mu B \sum_{i=1}^N \cos \alpha_i \right) \\ &= \sum_{\alpha_1, \alpha_2, \dots, \alpha_N} e^{\beta \mu B (\cos \alpha_1 + \cos \alpha_2 + \dots + \cos \alpha_N)} \\ &= \sum_{\alpha_1, \alpha_2, \dots, \alpha_N} \prod_{i=1}^N e^{\beta \mu B \cos \alpha_i} \\ &= \prod_{i=1}^N \left(\sum_{\alpha_i} e^{\beta \mu B \cos \alpha_i} \right). \end{aligned} \quad (4.37)$$

Since we are assuming that there is no interaction between the dipoles, Eq. (4.37) shows that the canonical partition function may be written as:

$$Z(\beta, B, N) = [Z(\beta, B, 1)]^N, \quad (4.38)$$

where

$$Z(\beta, B, 1) = \sum_{\alpha} e^{\beta \mu B \cos \alpha}. \quad (4.39)$$

The average induced magnetisation \mathbf{M} of the system will be in the direction of the \mathbf{B} -field, with its magnitude given by:

$$M = |\mathbf{M}| = \left\langle \sum_{i=1}^N \mu \cos \alpha_i \right\rangle_{\{\alpha_i\}}. \quad (4.40)$$

where the average is over all dipole orientations. To determine this average we note that:

$$\frac{\partial \ln Z(\beta, B, N)}{\partial B} = \frac{\partial}{\partial B} \ln [Z(\beta, B, 1)]^N = N \frac{\partial}{\partial B} \ln \left(\sum_{\alpha} e^{\beta \mu B \cos \alpha} \right). \quad (4.41)$$

Hence we have:

$$N \frac{\partial}{\partial B} \ln \left(\sum_{\alpha} e^{\beta \mu B \cos \alpha} \right) = \frac{N \sum_{\alpha} (\beta \mu \cos \alpha) e^{\beta \mu B \cos \alpha}}{\sum_{\alpha} e^{\beta \mu B \cos \alpha}} = N \beta \langle \mu \cos \alpha \rangle. \quad (4.42)$$

Equation (4.42) enables the average induced magnetisation (4.40) to be determined from:

$$M = \left\langle \sum_{i=1}^N \mu \cos \alpha_i \right\rangle_{\{\alpha_i\}} = N \langle \mu \cos \alpha \rangle = \frac{N}{\beta} \frac{\partial \ln Z(\beta, B, 1)}{\partial B} = \frac{1}{\beta} \frac{\partial \ln Z(\beta, B, N)}{\partial B}. \quad (4.43)$$

To proceed we evaluate the “1-particle” partition function $Z(\beta, B, 1)$, allowing the angle α to vary continuously as is demanded of a classical system! Further we must also integrate over all solid angles defined by $\Omega = (\alpha, \varphi)$, where $\varphi \in [0, 2\pi]$ is the azimuthal angle. Hence we have:

$$Z(\beta, B, 1) = \int_{\varphi=0}^{2\pi} \int_{\alpha=0}^{\pi} e^{\beta \mu B \cos \alpha} d\Omega = \int_{\varphi=0}^{2\pi} \int_{\alpha=0}^{\pi} e^{\beta \mu B \cos \alpha} \sin \alpha d\alpha d\varphi = 2\pi \int_{\alpha=0}^{\pi} e^{\beta \mu B \cos \alpha} \sin \alpha d\alpha. \quad (4.44)$$

Equation (4.44) is evaluated by letting $\xi = \cos \alpha$, whence we have:

$$Z(\beta, B, 1) = -2\pi \int_{-1}^1 e^{\beta \mu B \xi} d\xi = 2\pi \int_{-1}^1 e^{\beta \mu B \xi} d\xi = \frac{2\pi}{\beta \mu B} (e^{\beta \mu B} - e^{-\beta \mu B}) = \frac{4\pi}{\beta \mu B} \sinh(\beta \mu B). \quad (4.45)$$

The induced magnetisation is calculated from Eq. (4.43), i.e.,

$$\begin{aligned} M &= \frac{N}{\beta} \frac{\partial \ln Z(\beta, B, 1)}{\partial B} = \frac{N}{\beta} \frac{\partial}{\partial B} \ln \left(\frac{4\pi}{\beta \mu B} \sinh(\beta \mu B) \right) \\ &= \frac{N}{\beta} \left[\beta \mu \frac{\cosh(\beta \mu B)}{\sinh(\beta \mu B)} - \frac{1}{B} \right] \\ &= N \mu L(\theta), \end{aligned} \quad (4.46)$$

where $\theta = \mu B / k_B T$ and $L(\theta)$ is the Langevin function⁶ defined as:

$$L(\theta) = \coth \theta - \frac{1}{\theta} \quad (\theta = \mu B / k_B T). \quad (4.47)$$

The average magnetic moment per dipole is:

$$\langle \mu \rangle = \frac{M}{N} = \mu L(\theta). \quad (4.48)$$

Exercise 4.6: Carry out the steps leading to Eq. (4.46)

4.4.1 Curie's Law

The Langevin theory provides an explanation of Curie's law, which applies to paramagnetic

⁶The Langevin function provides a classical description of paramagnetism. In Lecture 5 we will treat this problem from a quantum mechanical perspective, which leads to the Brillouin function. The Langevin function is considered to be the classical limit of the Brillouin function, see e.g.,

https://en.wikipedia.org/wiki/Brillouin_and_Langevin_functions

materials. Starting with the definition of the magnetic susceptibility per dipole:

$$\begin{aligned}
 \chi &= \chi(T) = \frac{1}{N} \frac{\partial M}{\partial B} \\
 &= \frac{1}{N} \frac{\partial}{\partial B} (N\mu L(\theta)) \quad \left(\theta = \frac{\mu B}{k_B T} \right) \\
 &= \mu \frac{\partial L(\theta)}{\partial \theta} \frac{\partial \theta}{\partial B} \\
 &= -\frac{\mu^2}{k_B T} \left(\frac{\cosh^2 \theta - \sinh^2 \theta}{\sinh^2 \theta} \right) + \frac{1}{\theta^2} \frac{\mu^2}{k_B T} \\
 &= \frac{\mu^2}{k_B T} \left(\frac{1}{\theta^2} - \operatorname{cosech}^2 \theta \right).
 \end{aligned} \tag{4.49}$$

For high temperatures (or very weak magnetic fields) $\theta \ll 1$, and the Langevin function can be written as a (truncated) series expansion, i.e.,

$$L(\theta) = \coth \theta - \frac{1}{\theta} = \frac{1}{3}\theta - \frac{1}{45}\theta^3 + O(\theta^5) \approx \frac{1}{3}\theta. \tag{4.50}$$

In this limiting case, the magnetisation of the system is given by:

$$M = N\mu L(\theta) \approx \frac{1}{3}N\mu\theta = \frac{N\mu^2}{3k_B T}B, \tag{4.51}$$

so that the susceptibility is:

$$\chi(T) = \lim_{B \rightarrow 0} \left(\frac{\partial M}{\partial B} \right) = \frac{N\mu^2}{3k_B T} = \frac{C}{T}. \tag{4.52}$$

Equation (4.52) is Curie's law, with the Curie constant given by $C = N\mu^2/3k_B$.

4.4.2 Van Leeuwen's Theorem

Classical statistical mechanics can be used to prove van Leeuwen's theorem; namely, the phenomenon of diamagnetism does not exist in classical physics. We begin with the Hamiltonian of a system of N charged particles in the absence of an external magnetic field, which is written as:

$$H = H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N). \tag{4.53}$$

The same system in the presence of an external field $\mathbf{B} = \nabla \times \mathbf{A}$, where \mathbf{A} is the vector (gauge) potential, has a Hamiltonian of the form (in Gaussian units⁷):

⁷ In the Gaussian system of units, also known as cgs units (see e.g., J. D. Jackson, *Classical Electrodynamics*, 2nd edition, 1975, pp. 811-821), the magnitude of the force between two charges q_1 and q_2 separated by a distance r in vacuum is defined by:

$$F = k_1 \frac{q_1 q_2}{r^2},$$

where the constant of proportionality $k_1 = 1$. Similarly the force per unit length between two infinitely long wires, carrying currents I_1 and I_2 , separated by a distance r in vacuum is:

$$\frac{dF}{dl} = 2k_2 \frac{I_1 I_2}{r},$$

where $k_1/k_2 = c^2$.

$$H = H(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1 - e\mathbf{A}_1/c, \mathbf{p}_2 - e\mathbf{A}_2/c, \dots, \mathbf{p}_N - e\mathbf{A}_N/c), \quad (4.54)$$

where each particle has charge e and \mathbf{A}_i is the vector potential at position \mathbf{r}_i . Note that in the presence of a magnetic field, the usual kinematical momentum $\mathbf{p}_i = m\dot{\mathbf{r}}_i$ ($i = 1, 2, \dots, N$) is replaced by the canonical momentum $\mathbf{p}_i \rightarrow \boldsymbol{\pi}_i = \mathbf{p}_i - e\mathbf{A}_i/c$. The partition function for a system of N charged particles in the presence of an external magnetic field is:

$$Z(\beta, B, N) = \frac{1}{N! h^{3N}} \int_{\Gamma} \dots \int \exp(-\beta H(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1 - e\mathbf{A}_1/c, \dots, \mathbf{p}_N - e\mathbf{A}_N/c)) \prod_{i=1}^N d^3\mathbf{r}_i d^3\mathbf{p}_i. \quad (4.55)$$

We now make the following transformation:

$$\boldsymbol{\pi}_i = \mathbf{p}_i - \left(\frac{e}{c}\right)\mathbf{A}_i \Rightarrow d^3\mathbf{p}_i = d^3\boldsymbol{\pi}_i. \quad (4.56)$$

The partition function (4.55) is independent of the vector potential, and is given by:

$$Z(\beta, B, N) = \frac{1}{N! h^{3N}} \int_{\Gamma} \dots \int \exp(-\beta H(\mathbf{r}_1, \dots, \mathbf{r}_N; \boldsymbol{\pi}_1, \dots, \boldsymbol{\pi}_N)) \prod_{i=1}^N d^3\mathbf{r}_i d^3\boldsymbol{\pi}_i. \quad (4.57)$$

The induced magnetisation along the \mathbf{B} -direction is [see Eq. (4.43)]:

$$\mathbf{M} = |\mathbf{M}| = \left\langle -\frac{\partial H}{\partial B} \right\rangle = k_B T \frac{\partial \ln Z(\beta, B, N)}{\partial B}. \quad (4.58)$$

The partition function (4.57) is independent of \mathbf{A} , and since $\mathbf{B} = \nabla \times \mathbf{A}$, the partition function must also be independent of \mathbf{B} , whence the magnetisation is zero, i.e.,

$$\mathbf{M} = k_B T \frac{\partial \ln Z(\beta, B, N)}{\partial B} = 0. \quad (4.59)$$

The classical averaging procedure leads to van Leeuwen's theorem - there can be no diamagnetism in classical statistical mechanics. The reason for this becomes apparent when we examine the integrals in Eq. (4.55) over momentum space. The magnetisation can be written as:

$$\mathbf{M} = N\langle \boldsymbol{\mu} \rangle = N \frac{\int_{\mathbf{r}} \int_{\mathbf{p}} \boldsymbol{\mu} e^{-\beta H(\{\mathbf{r}\}, \{\mathbf{p}\})} \prod_{i=1}^N d^3\mathbf{r}_i d^3\mathbf{p}_i}{\int_{\mathbf{r}} \int_{\mathbf{p}} e^{-\beta H(\{\mathbf{r}\}, \{\mathbf{p}\})} \prod_{i=1}^N d^3\mathbf{r}_i d^3\mathbf{p}_i}. \quad (4.60)$$

The integrals over momenta range from $-\infty$ to $+\infty$, and therefore adding a vector potential can only shift the origin in \mathbf{p} -space; however, it will not effect the limits of integration. Since the vector potential always enters the Hamiltonian as an addition to the kinematical momentum (i.e., $\boldsymbol{\pi}_i = \mathbf{p}_i - e\mathbf{A}_i/c$), it can be transformed away!

References

- [1] Huang, K., *Statistical Mechanics* (2nd Edition, John Wiley and Sons, 1987). Chapters 3 and 4.
- [2] Kardar, M., *Statistical Physics of Particles* (Cambridge University Press, 2007). Chapter 3. A pdf of this textbook is available at:
[http://home.basu.ac.ir/~psu/Books/%5BMeheran_Kardar%5D_Statistical_Physics_of_Particles\(BookFi.org\).pdf](http://home.basu.ac.ir/~psu/Books/%5BMeheran_Kardar%5D_Statistical_Physics_of_Particles(BookFi.org).pdf)

