

Chapter 2

The Ideal Gas

2.1 THE CLASSICAL IDEAL GAS

As an introduction to the methods of statistical mechanics we will investigate the properties of a simple but very important system; the *ideal gas*. The ideal gas is defined as a collection of identical particles in which the interparticle forces are negligible. It is a reasonably accurate model of a real gas at low density.

Although it will be assumed that the interparticle forces are weak enough to be neglected, one should not picture the ideal gas as a system of particles with no interactions at all. Such a system would have very peculiar physical properties. If it began in some highly exceptional state, such as one in which all of the particles were moving with exactly the same speed but in various directions, then, because of the complete absence of interparticle collisions, the velocity distribution would never change and approach a more typical one in which the particles have a wide range of speeds. In short, such a system would never come to equilibrium. When we say that the interparticle interactions are negligible we mean that we can neglect the potential energy associated with them in comparison with the kinetic energy of the gas. However, at the same time, it is necessary to assume that the particles do have frequent collisions that transfer energy from one particle to another. In this and later chapters it will be demonstrated that these two assumptions are not mutually inconsistent by showing that both of them are satisfied for many real gases over a wide range of pressure and temperature.

Any gas in which the interaction potential is negligible is called an ideal gas. However, additional simplifying assumptions will be made in order to reduce the mathematical complexity of the analysis. It will be assumed that:

1. The particles have no internal degrees of freedom, such as rotation, vibration, or electronic excitation. We will therefore treat the particles as point particles. At room temperature this is an excellent approximation for all monatomic gases, particularly the noble gases (He, Ne, etc.), but not for diatomic or other molecular gases.
2. Quantum effects are negligible. This also is an excellent approximation at ordinary temperatures and pressures. Later in this chapter, we will carry out a quantum mechanical treatment of the ideal gas and determine the range of validity of the classical analysis.

2.2 THE VELOCITY DISTRIBUTION

The focus of our study will be the velocity distribution function of an ideal gas (Fig. 2.1). It is defined by saying that, when the gas is at equilibrium, the number of particles per unit volume that have velocities within the velocity element $d^3\mathbf{v}$, centered at the velocity \mathbf{v} , is given by $f(\mathbf{v})d^3\mathbf{v}$. Due to the repeated scattering of the particles, the velocity distribution at equilibrium depends on the magnitude but not on the direction of \mathbf{v} .

In terms of the velocity distribution function it is a simple matter to calculate the pressure that would be exerted by the gas on the walls of its container. We look at a small area dA on one of the walls and

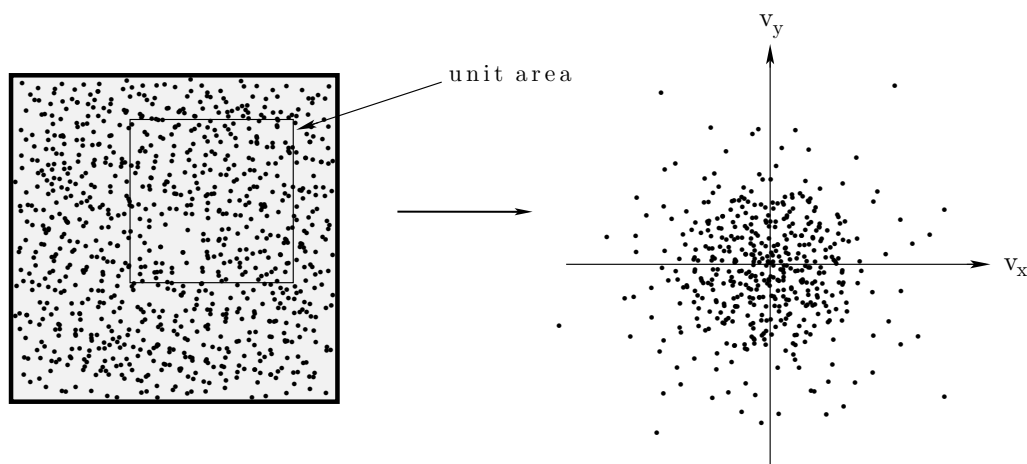


Fig. 2.1 The definition of the velocity distribution function for a two-dimensional gas. The velocity components of each particle in a unit area are plotted as a dot in the two-dimensional velocity space. When that is done, the density of dots at position (v_x, v_y) in the velocity space is defined as $f(v_x, v_y)$.

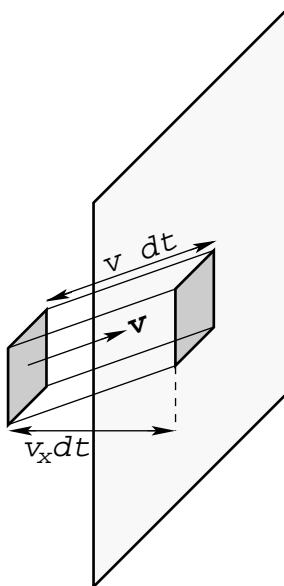


Fig. 2.2 Within the time interval dt , those particles with velocity \mathbf{v} that lie in the cylinder hit the shaded area on the wall. The density of particles with velocities within the range $d^3\mathbf{v}$ is $f(\mathbf{v}) d^3\mathbf{v}$. The volume of the cylinder is $v_x dt dA$.

assume that dA is perpendicular to the x axis with the inside of the container to the left. We consider only those particles that have velocities within some range $d^3\mathbf{v}$, centered at a velocity \mathbf{v} , and ask: “Of those particles, how many will strike the area dA within some short time interval dt ?” Unless the particles are moving toward dA (that is, unless $v_x > 0$) the answer is obviously zero. If $v_x > 0$ then the answer to the question is (see Fig. 2.2.)

$$dN = f(\mathbf{v}) d^3\mathbf{v} v_x dA dt \quad (2.1)$$

It is assumed that each particle that strikes the wall rebounds elastically. The momentum delivered to the wall by a single rebounding particle is equal to the negative of the change in the momentum of the particle. That is, it is equal to $2mv_x$. Thus the total momentum delivered to the area dA during the time interval dt by those particles within the velocity range $d^3\mathbf{v}$ is

$$2mv_x^2 f(\mathbf{v}) d^3\mathbf{v} dA dt \quad (2.2)$$

Since the force that one object exerts on another is defined as the rate at which the first object transfers momentum to the second, we can calculate the force those particles exert on dA by dividing Eq. (2.2) by dt . The pressure is obtained by dividing the force by dA . Finally, the pressure due to particles of all possible velocities is obtained by integrating over all velocities that are aimed at the wall. A velocity is aimed at the wall only if v_x is positive.

$$p = \int_{v_x > 0} 2mv_x^2 f(\mathbf{v}) d^3\mathbf{v} \quad (2.3)$$

Because the integrand is an even function of v_x it will leave the value of p unchanged if we extend the integration to all v_x and drop the factor of 2. Also, since $f(\mathbf{v})$ depends only on the magnitude of \mathbf{v} , v_x^2 can be replaced by $(v_x^2 + v_y^2 + v_z^2)/3$. This gives

$$p = \frac{1}{3} \int mv^2 f(\mathbf{v}) d^3\mathbf{v} \quad (2.4)$$

Recalling the definition of $f(\mathbf{v})$, it is easy to see that the integral is equal to twice the kinetic energy per unit volume. Since it has been assumed that the potential energy is negligible, Eq. (2.4) implies that

$$p = \frac{2}{3} \frac{E}{V}, \quad (2.5)$$

a result the reader has probably seen before.

“... the trial already made sufficiently proves the main thing, for which I here allege it; since by it, it is evident that as common air, when reduced to half its wonted extent, obtained near about twice as forcible a spring (i.e. pressure) as it had before; so this thus compressed air being further thrust into half this narrow room, obtained thereby a spring about as strong again as that it last had, and consequently four times as strong as that of the common air. ”

— Robert Boyle, *New Experiments Physico-Mechanical* (1662)

Boyle had deduced his famous law, that the pressure of a gas is inversely proportional to its volume, by capturing a quantity of air in the short closed end of a glass U tube, the other long open end of which was gradually filled with increasing amounts of mercury. The pressure was determined by the difference in the heights of the mercury columns, while the volume could be taken as proportional to the length of the entrapped air column.

2.3 THE MAXWELL–BOLTZMANN DISTRIBUTION

Equation (2.5) has been obtained without using any details of the velocity distribution function other than its angle independence. Therefore, the equation gives no information about $f(\mathbf{v})$. In order to determine $f(\mathbf{v})$ one must go beyond mechanics alone and use methods derived from probability theory. The derivation of the velocity distribution is a fairly intricate argument; so it will help if we first consider a simpler problem that can be solved with exactly the same method that will be needed for that derivation. We consider three students, A , B , and C , and three rooms, numbered 1, 2, and 3. Each of the students is told to pick one of the rooms at random and go into it. We assume that the rooms are arranged symmetrically, so that there is equal probability of a given student picking each of the three rooms. A *microstate* is defined by stating which room each student has chosen. For example, “ A is in Room 2, B is in Room 3, and C is in Room 2” defines a microstate. Because each student has equal probability of entering each room, it is clear that every microstate is equally probable. We now define a *macrostate* by saying how many students are in each of the rooms. For example, “3 students are in Room 1, 0 students are in Room 2, and 0 students are in Room 3” defines a macrostate. The information needed to define a microstate is enough to allow one to calculate the corresponding macrostate but not vice versa. Thus, the microstates give more detailed information about the system. We now ask: “What is the most probable macrostate?” Since each microstate has the same probability, the probability of any macrostate is proportional to the number of microstates that correspond to it. For example, the macrostate “ $N_1 = 3$, $N_2 = 0$, and $N_3 = 0$ ” (N_n is the number of students in Room n .) has only one corresponding microstate, namely “ A is in Room 1, B is in Room 1, and C is in Room

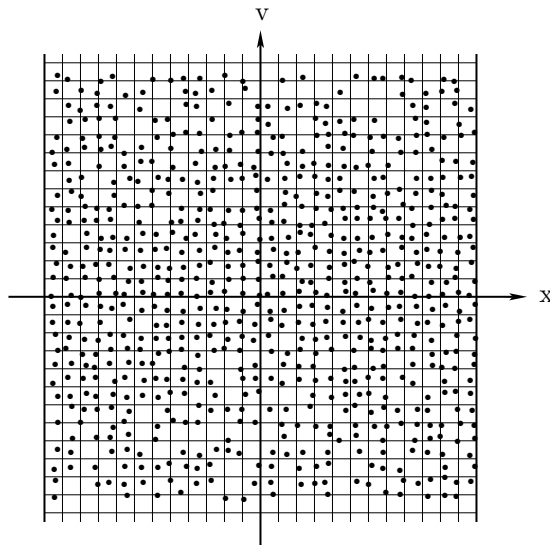


Fig. 2.3 The macrostate of the system is specified by giving the number of particles in each phase-space box. In reality, the phase-space is a six-dimensional space although it is shown here as two-dimensional.

1”. An easy calculation shows that the macrostate, “ $N_1 = 0$, $N_2 = 1$, and $N_3 = 2$ ” has 3 corresponding microstates, while the macrostate, “ $N_1 = N_2 = N_3 = 1$ ” has $3! = 6$ corresponding microstates and is thus the most probable distribution of students among rooms. The reader will soon see that, if we replace “students” by “particles” and “rooms” by “phase-space boxes” (soon to be defined), then the calculation to follow is essentially identical to the one that has just been done.

It will not greatly increase the difficulty of calculating the velocity distribution function if the problem is generalized to include an external potential field, $U(\mathbf{r})$, such as would be produced by a gravitational force. Thus, it is assumed that the energy of a particle of velocity \mathbf{v} at location \mathbf{r} is

$$E = \frac{1}{2}mv^2 + U(\mathbf{r}) \quad (2.6)$$

(It should be mentioned that it definitely would greatly increase the difficulty of the problem to include an interaction potential, that is, a potential function that depended on the distances *between* particles.) **The distribution function, which has the same meaning as before, will now depend on both \mathbf{r} and \mathbf{v} . Because of the existence of a force field, which defines a special direction at each location, it is not at all obvious that the distribution function $f(\mathbf{r}, \mathbf{v})$ will be independent of the direction of \mathbf{v} (although the results of our calculation will show that it is so).**

We are considering a system of N particles in a cubic box of volume V . The total energy of the system is E . By collisions, individual particles may change their energies, but the total energy remains fixed. The most essential assumption in our analysis is that N is an extremely large number. We conceptually decompose the volume into a very large number of little cubes, numbered 1 to K . The k th little cube is centered at \mathbf{r}_k and has a volume we call $\Delta^3 r$. We also separate the infinite space of possible velocities into an infinite number of “velocity cubes”, each of volume $\Delta^3 v$, labeled with an index $l = 1, 2, \dots$. The detailed dynamical state of the system, which we will call the *microstate* of the system, is defined by specifying the exact position and velocity of each of the N particles. That is, the microstate is specified by the $2N$ vector variables, $\mathbf{r}_1, \mathbf{v}_1, \dots, \mathbf{r}_N, \mathbf{v}_N$. If we permit a little bit of uncertainty in the definition of each particle’s position and velocity, then the microstate of the system can be specified by giving the spatial and velocity box of each particle, that is, by giving the $2N$ integer variables $k_1, l_1, \dots, k_N, l_N$. **This step has the advantage of making the set of microstates discrete. The combination of a spatial box and a velocity box is called a *phase-space box*. It can be considered as a little box in a six-dimensional phase-space with coordinates (x, y, z, v_x, v_y, v_z) . To calculate the distribution function associated with a given microstate it is quite unnecessary to know which particles are in which phase-space boxes. It is sufficient to know only how many particles are in each of the phase-space boxes.** In fact, if, for a given microstate, the *occupation number* of the phase-space box

specified by the integers k and l is called N_{kl} , then the distribution function at $(\mathbf{r}_k, \mathbf{v}_l)$ is

$$f(\mathbf{r}_k, \mathbf{v}_l) = N_{kl}/\Delta^3 r \Delta^3 v \quad (2.7)$$

We will say that the set of occupation numbers N_{kl} defines the *macrostate* of the system (see Fig. 2.3). Clearly, we are using the same definition of microstates and macrostates that we did previously in the “student and room” discussion.

We now ask the question: “How many different microstates correspond to a given macrostate?” This is just the question of how many ways there are of putting N distinguishable objects into boxes with a specified number of objects in each box. It was answered in the last chapter [see Eq. (1.24)]. The number of microstates corresponding to a given macrostate is

$$I = \frac{N!}{\prod_{(k,l)} N_{kl}!} \quad (2.8)$$

where the symbol $\prod_{(k,l)}$ means that a product is taken over all values of k and l . The product extends over all phase-space boxes. However, since $0! = 1$, and there are only a finite number of particles, only a finite number of terms in the product are not equal to unity. But a *factor* of one can be ignored. Thus the infinite product is actually a finite integer. Now that we know how many microstates correspond to any given macrostate we would like to determine which of the possible macrostates has the greatest probability of occurrence. From the principles of probability theory it is clearly impossible to do this without knowing something about the relative probabilities of the various microstates that contribute to a given macrostate. There are certain things that are known about the probability of finding the system in a given microstate.

1. A particle in the phase-space box (k, l) has an energy E_{kl} , given by

$$E_{kl} = \frac{1}{2}mv_l^2 + U(\mathbf{r}_k) \quad (2.9)$$

Therefore a macrostate defined by the occupation numbers N_{kl} has a total energy

$$E_{\text{tot}} = \sum_{(k,l)} N_{kl} E_{kl} \quad (2.10)$$

Unless E_{tot} is equal to the known system energy E , there is zero probability of finding the system in any microstate that yields that macrostate.

2. Also, unless N_{tot} , the sum of the occupation numbers for a given macrostate, is equal to the actual number of particles in the system N , there is no microstate that yields that macrostate.

Aside from these two restrictions, there is no obvious way of assigning probabilities to the vast number of possible microstates available to a large system.*

At this point we will make a completely unjustified assumption that those microstates that are not forbidden by the conditions on E_{tot} and N_{tot} are all equally probable. This is called the assumption of *equal a priori probabilities*. Much of Chapter 3 will be devoted to a careful analysis of this assumption. Here it will be used simply as a working hypothesis that will allow us to proceed in our calculation of the equilibrium distribution function $f(\mathbf{r}, \mathbf{v})$.

With the assumption of equal a priori probabilities for the allowed microstates, the probability of any allowed macrostate is proportional to I , the number of microstates corresponding to that macrostate. The *most probable macrostate* can be calculated by finding the maximum of I , considered as a function of the occupation numbers, N_{kl} , with the restrictions that $\sum N_{kl} E_{kl} = E$ and $\sum N_{kl} = N$. It turns out to be more convenient to calculate the maximum of the function

$$F = \log I = \log(N!) - \sum_{k,l} \log(N_{kl}!) \quad (2.11)$$

*To get an idea of the size of the number I in Eq. (2.8) when $N = N_A \approx 6 \times 10^{23}$, as it is for one mole of gas, we note that the dominant factor in Eq. (2.8) is the $N!$, which is of order N^N for large N . Thus $I \sim 6 \times 10^{23 \times 6 \times 10^{23}}$. That number has more than 10^{25} zeros!

(Note: All logarithms in this book are natural logarithms—The base 10 logarithm is as much of a historical curiosity as a slide rule.) Because $\log I$ is a monotonically increasing function of I , the set of occupation numbers that maximizes $\log I$ also gives the maximum of I . In Eq. (2.11) one can use *Stirling's approximation* (derived in the Mathematical Appendix), which states that $\log K! \approx K(\log K - 1)$ for $K \gg 1$. Therefore, the function that will actually be maximized is

$$F = N(\log N - 1) - \sum_{k,l} N_{kl}(\log N_{kl} - 1) \quad (2.12)$$

Applying Lagrange's method (also derived in the Mathematical Appendix) to this problem, one ignores the constraints and maximizes the function

$$G = F - \alpha \sum_{k,l} N_{kl} - \beta \sum_{k,l} N_{kl} E_{kl} \quad (2.13)$$

where α and β are two *Lagrange parameters* whose values will later be chosen so as to satisfy the constraints. Setting $\partial G / \partial N_{kl}$ equal to zero gives

$$\log N_{kl} = -\alpha - \beta E_{kl} \quad (2.14)$$

or

$$N_{kl} = C e^{-\beta E_{kl}} \quad (2.15)$$

where the constant $C = \exp(-\alpha)$. Using Eq. (2.9) to write E_{kl} in terms of \mathbf{r} and \mathbf{v} and using Eq. (2.7) to relate N_{kl} and $f(\mathbf{r}_k, \mathbf{v}_l)$, it is seen that the most probable distribution function (that is, the one with the greatest number of corresponding microstates) is of the form

$$f(\mathbf{r}, \mathbf{v}) = C \exp[-\beta(mv^2/2 + U(\mathbf{r}))] \quad (2.16)$$

This is the *Maxwell-Boltzmann distribution*. The constants C and β must be chosen to give the correct values for the total number of particles and the total energy.

2.4 THE PARTICLE DENSITY

The density of particles, irrespective of velocity, is obtained by integrating $f(\mathbf{r}, \mathbf{v})$ over all velocities.

$$\begin{aligned} n(\mathbf{r}) &= \int f(\mathbf{r}, \mathbf{v}) d^3v \\ &= C e^{-\beta U(\mathbf{r})} \int e^{-m\beta v^2/2} dv_x dv_y dv_z \\ &= C e^{-\beta U(\mathbf{r})} \left[\int_{-\infty}^{\infty} e^{-m\beta v_x^2/2} dv_x \right]^3 \\ &= C \left(\frac{2\pi}{m\beta} \right)^{3/2} e^{-\beta U(\mathbf{r})} \end{aligned} \quad (2.17)$$

The final line in Eq. (2.17) makes use of the Table of Integrals in the Mathematical Appendix. The potential function $U(\mathbf{r})$ always includes an arbitrary constant in its definition. If U is defined to be zero at some chosen location, \mathbf{r}_o , then

$$n(\mathbf{r}_o) = C \left(\frac{2\pi}{m\beta} \right)^{3/2} \quad (2.18)$$

which allows us to write Eq. (2.17) in the form

$$n(\mathbf{r}) = n(\mathbf{r}_o) e^{-\beta U(\mathbf{r})} \quad (2.19)$$

If we assume that this most probable distribution is the experimentally observed equilibrium distribution, then we see that, whenever the interaction potential energy can be neglected, the particle density at equilibrium varies with the negative exponential of the external potential.

2.5 THE EXPONENTIAL ATMOSPHERE

An important example of a system that exhibits a Maxwell–Boltzmann distribution is an ideal gas in a uniform gravitational field g . In that case $U(\mathbf{r}) = mgz$ and $n(z) = n(0) \exp[-\beta mgz]$. In the next section, we will show that the Lagrange parameter, β , is equal to $1/kT$, where k is Boltzmann’s constant and T is the absolute temperature. Thus the density, as a function of z , has the form

$$n(z) = n(0)e^{-z/h} \quad (2.20)$$

with $h = kT/mg$. The *scale height*, h , is the altitude at which $n(z) = n(0)/e$. For nitrogen at room temperature (300K) the scale height is 9 kilometers, which is reasonably descriptive of the earth’s atmosphere, although the earth’s atmosphere is by no means at equilibrium. This number clearly illustrates the fact that the variation in density due to the gravitational field would be difficult to detect in ordinary laboratory experiments where the altitudes involved are about 1 meter and therefore $n(z)/n(0) \approx 1 - 1/9000$. There are, however, two ways of bringing h down to laboratory size. One method is by increasing the mass of the particles, m . This can be easily overdone by choosing macroscopic objects as the “particles”. For $m = 1$ g the scale height is much less than the size of an atom and is again unobservable. To get a scale height of about 10 cm at room temperature, we need $m \approx 4 \times 10^{-20}$ kg. This is the mass of a particle of 2.5×10^7 atomic mass units, too large for a molecule but possible for the particles of a fine colloidal suspension. The second method is to increase g by means of a centrifuge. A modern ultracentrifuge can create an acceleration field of order 10^5 m/s². In such a field a molecule of 10 atomic mass units has a scale height of 2.5 cm.

2.6 THE IDENTIFICATION OF β

$f(\mathbf{r}, \mathbf{v}) d^3r d^3v$ is the number of particles within d^3r that have velocities in the range d^3v . If we divide this by d^3r , multiply by $mv^2/2$, and integrate over \mathbf{v} , we obtain the density of kinetic energy at position \mathbf{r} . That quantity will be written as ε_K . Thus

$$\begin{aligned} \varepsilon_K &= Ce^{-\beta U(\mathbf{r})} \int e^{-m\beta v^2/2} (mv^2/2) dv_x dv_y dv_z \\ &= \frac{3}{2} Ce^{-\beta U(\mathbf{r})} \int e^{-\beta m v_x^2/2} (m v_x^2) dv_x \int e^{-\beta m v_y^2/2} dv_y \int e^{-\beta m v_z^2/2} dv_z \\ &= \frac{3}{2} Ce^{-\beta U(\mathbf{r})} \left(\sqrt{2\pi/m\beta^3} \right) \left(\sqrt{2\pi/m\beta} \right)^2 \end{aligned} \quad (2.21)$$

The second line makes use of the fact that each of the three terms in $v^2 = v_x^2 + v_y^2 + v_z^2$ gives an equal contribution to ε_K . The third line may require another look at the Table of Integrals. Equation (2.17) now allows us to write ε_K in terms of the particle density.

$$\varepsilon_K = \frac{3}{2} n(\mathbf{r})/\beta \quad (2.22)$$

The first thing to notice is that the energy per particle, $\varepsilon_K/n(\mathbf{r})$, is independent of position. Although, at equilibrium, the density of particles varies from place to place as $e^{-\beta U}$, their distribution with respect to velocity is the same everywhere.

Equation (2.5), which relates the energy density to the pressure, and the ideal gas equation of state, give the relation $\varepsilon_K = \frac{3}{2} p = \frac{3}{2} n(\mathbf{r}) kT$. A comparison of this relation with Eq. (2.22) allows us to identify the Lagrange parameter, β , with $1/kT$.

$$\beta = 1/kT \quad (2.23)$$

2.7 THE MAXWELL DISTRIBUTION

If no external force field exists, then $U = 0$ and the Maxwell–Boltzmann distribution becomes the simpler Maxwell distribution, which depends on velocity alone.

$$f(\mathbf{v}) = Ce^{-\frac{1}{2}mv^2/kT} \quad (2.24)$$

Using Eq. (2.17) with $U = 0$ and n equal to a constant, we can eliminate C and write the Maxwell distribution in terms of n and T .

$$f(\mathbf{v}) = \left(\frac{m}{2\pi kT} \right)^{3/2} n e^{-mv^2/2kT} \quad (2.25)$$

Because $v^2 = v_x^2 + v_y^2 + v_z^2$, the distribution function factors into three uncorrelated probability functions involving the three velocity components.

$$f(\mathbf{v}) = nP(v_x)P(v_y)P(v_z) \quad (2.26)$$

where $P(v_x) dv_x$ is the probability of finding a given particle with its x component of velocity in the range dv_x . Clearly, $P(v_x)$ is given explicitly as

$$P(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} \quad (2.27)$$

Although it may seem slightly surprising, Eq. (2.26) shows that the fact that a particular particle has a large x component of velocity in no way affects the probability of its having large y or z components.

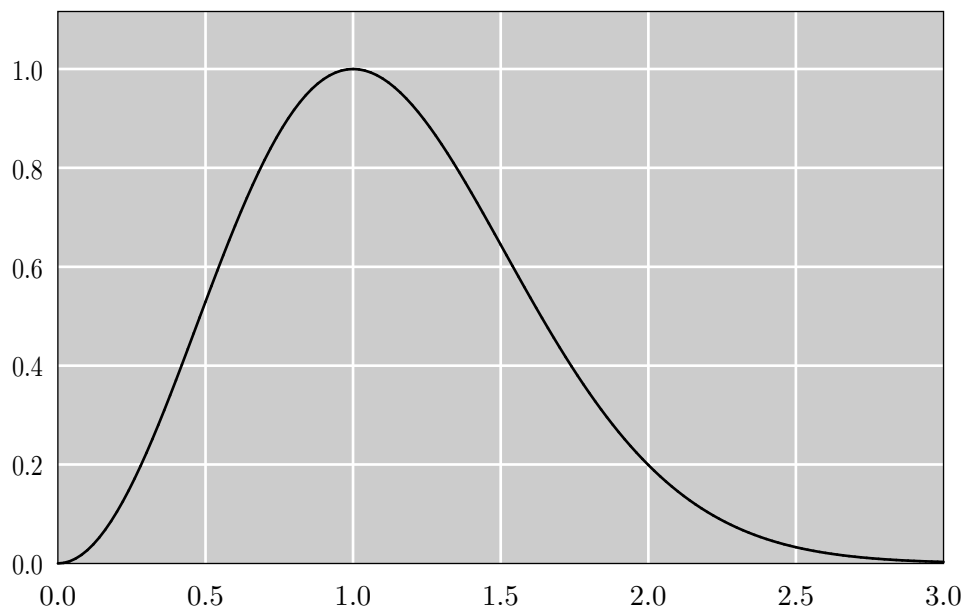


Fig. 2.4 The Maxwell speed distribution. The ratio of $P(v)$ to $P(v_o)$ is plotted as a function of v/v_o , where $v_o = \sqrt{2kT/m}$ is the *most probable speed*.

2.8 THE SPEED DISTRIBUTION

We define $F(v) dv$ as the density of particles with speeds within the range v to $v + dv$ (see Fig. 2.4). $F(v) dv$ is equal to $f(\mathbf{v})$ times $4\pi v^2 dv$, where the second factor is just the volume of the region in velocity space corresponding to the given speed range. Therefore,

$$F(v) = 4\pi v^2 n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \quad (2.28)$$

The average speed of the particles of a gas at temperature T is given by

$$\bar{v} = \frac{1}{n} \int_0^{\infty} F(v) v dv \quad (2.29)$$

The integration is straightforward and gives

$$\bar{v} = \left(\frac{8kT}{\pi m}\right)^{1/2} \quad (2.30)$$

In order to get an idea of the typical velocities involved in thermal motion, we evaluate \bar{v} for helium and radon at $T = 300$ K.

$$(\text{He}) \bar{v} = 1.26 \times 10^3 \text{ m/s}; \quad (\text{Rn}) \bar{v} = 2.72 \times 10^2 \text{ m/s} \quad (2.31)$$

The *root-mean-square* velocity is defined as $v_{\text{rms}} = (\overline{v^2})^{1/2}$. It can easily be calculated by making use of the fact that the average kinetic energy per particle is $\frac{3}{2}kT$. That is

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT \quad (2.32)$$

which gives

$$v_{\text{rms}} = (3kT/m)^{1/2} \quad (2.33)$$

2.9 THE VERY DILUTE GAS

In an ideal gas, there is a length ℓ , called the *mean free path*, that is defined as the average distance that a gas particle travels between collisions with the other gas particles. In Exercise 2.17 it is shown that, for particles of diameter D , the mean free path is given by the formula $\ell = 1/(\sqrt{2}\pi D^2 n)$, where n is the gas density. For argon, a typical noble gas, at standard temperature and pressure (STP), the mean free path is about 10^{-5} m. This is much larger than the typical distance between a particle and its nearest neighbor, which, for the same system, is about 10^{-9} m.

In the problems and exercises, there are a number of calculations involving the flow of particles from an ideal gas through a small hole in the container wall. These calculations involve a geometrical length a , namely, the size of the hole. Although the mean free path is much larger than the nearest neighbor distance, it is usually much smaller than the geometrical distance a . This means that a particle that is destined to pass through the hole will usually collide many times with other particles on its way out. When this is so (that is, when $a \gg \ell$), the calculation of flow through the hole is very complicated and will not be attempted in this book. Here we will restrict ourselves to making calculations in the opposite limit, in which $a \ll \ell$. Because ℓ is proportional to $1/n$, this case occurs only in a very dilute ideal gas. Thus, when it is stated that an ideal gas is *very dilute*, what is meant is that the mean free path is much larger than any geometrical lengths that appear in the problem.

“The modern atomists have therefore adopted a method which is, I believe, new in the department of mathematical physics, though it has long been in use in the section of Statistics. When the working members of Section F get hold of a report of the Census, or any other document containing the numerical data of Economic and Social Science, they begin by distributing the whole population into groups, according to age, income-tax, education, religious belief, or criminal convictions. The number of individuals is far too great to allow of their tracing the history of each separately, so that, in order to reduce their labour within human limits, they concentrate their attention on a small number of artificial groups. The varying number of individuals in each group, and not the varying state of each individual, is the primary datum from which they work.”

— J. C. Maxwell (in *Nature*, 1873)

2.10 IDEAL QUANTUM SYSTEMS

The method that was used to derive the Maxwell–Boltzmann distribution for a classical system can be applied, with only minor modifications, to calculate the equilibrium properties of a quantum-mechanical system of noninteracting particles in an external potential. First, we will have to review the quantum mechanics of systems of many identical particles. The reader who is already familiar with this material or who is willing to accept the results of the analysis “on faith” can jump to Section 2.13.

A single particle in a potential field $U(\mathbf{r})$ is described by the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (2.34)$$

Therefore, its Hamiltonian operator is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \quad (2.35)$$

A system of two identical particles in a potential field $U(\mathbf{r})$ has a Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla_1^2 + U(\mathbf{r}_1)\right)\psi(\mathbf{r}_1, \mathbf{r}_2) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 + U(\mathbf{r}_2)\right)\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2) \quad (2.36)$$

where $\nabla_1^2 = \partial^2/\partial x_1^2 + \partial^2/\partial y_1^2 + \partial^2/\partial z_1^2$ with a corresponding equation for ∇_2^2 . The Hamiltonian operator for that system is thus

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 + U(\mathbf{r}_1) - \frac{\hbar^2}{2m}\nabla_2^2 + U(\mathbf{r}_2) \quad (2.37)$$

The generalization is obvious; a system of N identical particles in an external potential $U(\mathbf{r})$ is described by the Hamiltonian operator

$$H_N = \sum_{j=1}^N \left(-\frac{\hbar^2}{2m}\nabla_j^2 + U(\mathbf{r}_j)\right) \quad (2.38)$$

To calculate the N -particle energy eigenstates of this system it is only necessary to solve the following single-particle Schrödinger equation.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)u_n(\mathbf{r}) = E_n u_n(\mathbf{r}) \quad (2.39)$$

The problem of actually solving this equation for particular potential functions will not be discussed here. It will simply be assumed that it has been done and that the complete set of single-particle eigenfunctions $u_n(\mathbf{r})$ and eigenvalues E_n is known.

A complete set of eigenfunctions for the N -particle problem can now be constructed simply by taking arbitrary products of the single-particle eigenfunctions. For example, for $N = 3$, the function

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = u_1(\mathbf{r}_1)u_1(\mathbf{r}_2)u_4(\mathbf{r}_3) \quad (2.40)$$

satisfies the Schrödinger equation

$$\sum_1^3 \left(-\frac{\hbar^2}{2m}\nabla_j^2 + U(\mathbf{r}_j)\right)\psi = E\psi \quad (2.41)$$

with the eigenvalue $E = 2E_1 + E_4$.

2.11 WAVE FUNCTION SYMMETRIES—BOSONS

Even though the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, given above, is a solution of the Schrödinger equation for a three-particle system, it is *not* an acceptable wave function for a real system of three identical particles. The wave function of any system of identical particles must satisfy a symmetry condition when the coordinates of any two particles are interchanged. The detailed form of the symmetry condition depends on the type of particle. There are two possibilities. Bose–Einstein particles are particles with integer values for their total angular momentum (measured in units of \hbar). Fermi–Dirac particles have half-integer ($\frac{1}{2}$, $\frac{3}{2}$, etc.) values for their total angular momentum. A system of Bose–Einstein particles (also called *bosons*) must have a wave function whose value is unchanged whenever the coordinates of any pair of particles are interchanged. That is, for a three-boson system,

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3) = \psi(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2), \text{ etc.} \quad (2.42)$$

The unsymmetric wave function of Eq. (2.40) may be converted to a properly symmetrized Bose–Einstein wave function by taking an equally weighted average over all permutations of the particle coordinates, \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 .

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = C \sum_{\text{perm}} u_1(\mathbf{r}_{\alpha_1})u_1(\mathbf{r}_{\alpha_2})u_4(\mathbf{r}_{\alpha_3}) \quad (2.43)$$

where $(\alpha_1, \alpha_2, \alpha_3)$ is a permutation of $(1, 2, 3)$, C is a normalization constant, and the sum is over all $3!$ permutations. The reader can easily verify that this wave function is properly symmetric and that it is

still an eigenfunction of the Schrödinger equation with the same eigenvalue as before. This symmetrization procedure can be generalized as follows.

For a system of N bosons, we choose any finite sequence of nonnegative integers, N_1, N_2, \dots, N_K that satisfy the condition $N_1 + \dots + N_K = N$. We call them *occupation numbers*. Some of the N_j s may be zero. We then construct the function

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = C \sum_{\text{perm}} \underbrace{u_1(\mathbf{r}_{\alpha_1}) \cdots u_1}_{N_1 \text{ factors}} \underbrace{u_2 \cdots u_2}_{N_2 \text{ factors}} \cdots \underbrace{u_K \cdots u_K}_{N_K \text{ factors}}(\mathbf{r}_{\alpha_N}) \quad (2.44)$$

where, in this case, $(\alpha_1, \dots, \alpha_N)$ is a permutation of $(1, \dots, N)$ and the sum is over all $N!$ permutations. It is obvious that the function ψ is symmetric in its arguments. It is also an eigenfunction of H_N with an energy eigenvalue equal to

$$E = N_1 E_1 + \dots + N_K E_K \quad (2.45)$$

For an N -particle Bose–Einstein system, there is one such energy eigenfunction for each distinct set of occupation numbers satisfying the constraint

$$N_1 + \dots + N_K = N \quad (2.46)$$

2.12 FERMIONS

For a system of Fermi–Dirac particles, the wave function must be completely antisymmetric, rather than symmetric. That is, it must satisfy the condition (we give an example with $N = 3$)

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = -\psi(\mathbf{r}_2, \mathbf{r}_1, \mathbf{r}_3) = -\psi(\mathbf{r}_1, \mathbf{r}_3, \mathbf{r}_2) \quad (2.47)$$

In this case the N -particle wave functions are constructed somewhat differently. Since all fundamental fermions are spin- $\frac{1}{2}$ particles, we will only consider that case.* We have to introduce variables to describe the spin degrees of freedom of the particle. The state of a spin- $\frac{1}{2}$ particle can be defined by a combination of a position vector \mathbf{r} that says where the particle is and a spin variable σ , whose only possible values are $+1$ or -1 . The value of σ gives the z component of the spin angular momentum, divided by $\hbar/2$. We will use a single symbol, x_j , for the combination of the spatial variable and the spin variable of the j th particle.

$$x_j = (\mathbf{r}_j, \sigma_j) \quad (2.48)$$

As before, we first solve the single-particle Schrödinger equation for the sequence of single-particle eigenfunctions and eigenvalues

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + U(x)\right)u_n(x) = E_n u_n(x) \quad (2.49)$$

We now choose any sequence of N single-particle eigenfunctions, u_{K_1}, \dots, u_{K_N} , and construct the N -particle wave function

$$\psi(x_1, \dots, x_N) = C \sum_{\text{perm}} (-1)^P u_{K_1}(x_{\alpha_1}) \cdots u_{K_N}(x_{\alpha_N}) \quad (2.50)$$

where, as for the boson case, the sum is taken over all $N!$ permutations of the variables x_1, \dots, x_N and where $(-1)^P$ is $+1$ for an even permutation and -1 for an odd permutation. A more compact way of writing Eq. (2.50) is to use the definition of a determinant and write ψ as (again we take $N = 3$)

$$\psi(x_1, x_2, x_3) = C \begin{vmatrix} u_{K_1}(x_1) & u_{K_1}(x_2) & u_{K_1}(x_3) \\ u_{K_2}(x_1) & u_{K_2}(x_2) & u_{K_2}(x_3) \\ u_{K_3}(x_1) & u_{K_3}(x_2) & u_{K_3}(x_3) \end{vmatrix} \quad (2.51)$$

Permuting the variables x_1 and x_2 in this equation merely results in a permutation of the first two columns of the determinant, which has the effect of changing its sign. Therefore, ψ has the necessary antisymmetry

* Nuclei of spin $3/2$, $5/2$, etc. may also be treated as single Fermi–Dirac particles by a trivial modification of the formalism given here.

properties. If, in Eq. (2.51), any two of the indices K_1, K_2 , and K_3 are equal, then two rows of the determinant will be identical and therefore the determinant will vanish, yielding the unacceptable wave function $\psi = 0$. Thus, in choosing the functions u_{K_1}, \dots, u_{K_N} , one must choose N *different* eigenfunctions. It is not difficult to verify that the function $\psi(x_1, \dots, x_N)$ defined by Eq. (2.50) is a solution of the N -particle Schrödinger equation

$$\sum_{i=1}^N \left(-\frac{\hbar^2}{2m} \nabla_i^2 + U(x_i) \right) \psi = E\psi \quad (2.52)$$

with

$$E = \sum_{i=1}^N E_{K_i} \quad (2.53)$$

For Fermi–Dirac systems, one can also describe the N -particle eigenfunctions by a set of occupation numbers, N_1, N_2, \dots as follows. We define

$$N_K = \begin{cases} 1, & \text{if } K \in \{K_1, \dots, K_N\} \\ 0, & \text{otherwise} \end{cases} \quad (2.54)$$

With this definition Eqs. (2.45) and (2.46) are still valid. However, whereas for boson systems there was one N -particle energy eigenstate for every distinct set of nonnegative integers summing to N , for fermions those integers are restricted to the values 0 and 1. This restriction is the *Pauli exclusion principle*.

2.13 MICROSTATES AND MACROSTATES

Having reviewed these aspects of many-particle wave functions, we are ready to apply the procedure used on the classical ideal gas to ideal quantum systems. The basic idea is to define a microstate and a macrostate and then to calculate the number of microstates corresponding to each macrostate. Assuming that the microstates have equal probabilities, one then calculates the most probable macrostate and identifies it with the macrostate of the system at equilibrium.

We have seen that, for a system of identical particles, the wave function is uniquely defined by specifying the set of quantum state occupation numbers, N_1, N_2, N_3, \dots , where N_k gives the number of particles in the k th single-particle quantum state, which has energy E_k . If the particles are Bose–Einstein particles, then each N_k can be any nonnegative integer, but if the particles are Fermi–Dirac particles, then each N_k can only be either 0 or 1.

The identification of the microstates of the system seems fairly straightforward. The microstate of a system is the detailed dynamical state of the system. But one cannot specify more about a quantum-mechanical system than its wave function. Therefore we will identify the microstate of the system with the wave function of the system. If the system is known to have N particles and the system energy is known to be E , then any set of occupation numbers satisfying the conditions

$$\sum_k N_k = N \quad (2.55)$$

and

$$\sum_k N_k E_k = E \quad (2.56)$$

will define a possible microstate.

The definition of a macrostate is not quite so simple. Looking at the definition of a macrostate that was used in the classical analysis would strongly suggest that the macrostate also should be defined as the set of occupation numbers, N_k , since that gives the number of particles in each single-particle state. Such an identification of the system macrostates leads to very undesirable results. There is then exactly one microstate for each macrostate. Making an assumption of equal a priori probabilities for the microstates would trivially imply that the macrostates were also equally probable, eliminating any possibility of calculating a “most probable” macrostate.

Although defining the macrostate of the system as the set of occupation numbers has a great formal similarity to what was done before, it does not really stand up to close scrutiny. The macrostate is meant to

be the realistically observable state of the system. However, for a macroscopic system, the spacing between adjacent discrete single-particle energy levels is so small that the detection of individual levels is many orders of magnitude beyond realistic measurement. For example, for particles of one atomic mass in a container of one cubic meter, the level spacing depends upon the energy and, at the energy value of $E = kT$ with $T = 300\text{ K}$, the spacing between adjacent levels is $3.7 \times 10^{-51}\text{ J}$ (see Problem 2.21). To get some idea of what this energy spacing means, we might note that, for a particle of typical thermal velocity ($\sim 10^3\text{ m/s}$), it would correspond to a change in velocity of $\Delta v = 2.2 \times 10^{-27}\text{ m/s}$. Such a change would be far beyond any practical experimental detection.

What we will do to define a meaningful macrostate of the system is to group the almost continuous energy spectrum into a large number of narrow energy ranges that we will call *energy bins*. In the case mentioned, if we choose 10^{12} bins within the range $0 < E < kT$, then each one would contain about 10^{19} discrete levels and have an energy range of about 10^{-33} J . The levels in the k th energy bin have an average energy of ε_k , which will be assigned to all the levels in that bin. The k th bin contains a large number K_k of discrete energy states. We now describe a macrostate of the system by specifying the number of particles, call it ν_k , within the states of the k th energy bin for all k .

2.14 QUANTUM DISTRIBUTION FUNCTIONS

We first want to calculate $I(K_k, \nu_k)$, the number of ways of distributing the ν_k indistinguishable particles within the K_k energy states of the k th bin. For the case of bosons, in which any number of particles can be put into a single state, that calculation is equivalent to determining how many ways there are of choosing K_k occupation numbers N_i satisfying the restriction, $\sum N_i = \nu_k$. This is left as a problem for the reader. The result is

$$I(K_k, \nu_k) = \frac{(K_k + \nu_k - 1)!}{(K_k - 1)! \nu_k!} \quad (\text{bosons}) \quad (2.57)$$

For fermions, where the N_i can only be 0 or 1, we can interpret the K_k quantum states as K_k coins, of which the filled ones are heads and the empty ones tails. The problem is then equivalent to the problem of determining the number of ways of arranging K_k coins to get ν_k heads. That was solved in the last chapter. The answer is just the binomial coefficient

$$I(K_k, \nu_k) = \frac{K_k!}{(K_k - \nu_k)! \nu_k!} \quad (\text{fermions}) \quad (2.58)$$

The total number of microstates corresponding to a given macrostate is obtained by multiplying the $I(K_k, \nu_k)$ for all k . That is,

$$I = \prod_k I(K_k, \nu_k) \quad (2.59)$$

As before, the most probable macrostate will be determined by maximizing $\log I - \alpha N - \beta E$, where α and β are Lagrange parameters that have been introduced to take into account the restriction to fixed total particle number and fixed energy. The fermion case will be done explicitly, and the boson case left as an exercise. The function that must be maximized is

$$\begin{aligned} F &= \log \left(\prod_k \frac{K_k!}{(K_k - \nu_k)! \nu_k!} \right) - \alpha \sum_k \nu_k - \beta \sum_k \nu_k \varepsilon_k \\ &= \sum_k \left[K_k (\log K_k - 1) - (K_k - \nu_k) (\log (K_k - \nu_k) - 1) \right. \\ &\quad \left. - \nu_k (\log \nu_k - 1) - \alpha \nu_k - \beta \varepsilon_k \nu_k \right] \end{aligned} \quad (2.60)$$

The use of Stirling's approximation is valid when applied to the bin occupation numbers ν_k . Note, however, that it would be quite invalid if used for the individual state occupation numbers N_i . Setting $\partial F / \partial \nu_k = 0$, we get the following equation for the bin occupation numbers of the most probable macrostate.

$$\log[(K_k - \nu_k) / \nu_k] = \alpha + \beta \varepsilon_k \quad (2.61)$$

which gives

$$\nu_k = \frac{K_k}{e^{\alpha + \beta \varepsilon_k} + 1} \quad (2.62)$$

Since the energy differences of the states in the k th bin are negligible, Eq. (2.62) clearly implies that the average occupation of any individual state in that bin is $\nu_k/K_k = 1/(e^{\alpha + \beta \varepsilon_k} + 1)$. Thus, at equilibrium, the average occupation number of the n th single-particle state, of energy ε_n , is given by the well-known Fermi–Dirac distribution function

$$\bar{N}_n = f_{\text{FD}}(\varepsilon_n) = \frac{1}{e^{\alpha + \beta \varepsilon_n} + 1} \quad (2.63)$$

For bosons, the equivalent result is

$$\bar{N}_n = f_{\text{BE}}(\varepsilon_n) = \frac{1}{e^{\alpha + \beta \varepsilon_n} - 1} \quad (2.64)$$

The Lagrange parameter, β , has the same relationship to the absolute temperature as it had in the classical distribution. That is, $\beta = 1/kT$. The Lagrange parameter α , called the *affinity*, is essentially a normalization constant that must be adjusted so that the sum of \bar{N}_n over all quantum states is equal to the number of particles in the system.

2.15 THE QUANTUM MECHANICAL IDEAL GAS

In order to understand the relationship between the quantum-mechanical distribution functions that we have just derived and the Maxwell distribution for a classical ideal gas, we will consider a quantum mechanical ideal gas, that is, a system of noninteracting bosons or fermions with no external potential. If the external potential $U(\mathbf{r})$ is taken to be zero, then the single-particle Schrödinger equation is

$$-\frac{\hbar^2}{2m} \nabla^2 u(\mathbf{r}) = E u(\mathbf{r}) \quad (2.65)$$

If this equation is solved within a cube of volume L^3 , using periodic boundary conditions,

$$u(x, y, z) = u(x + L, y, z) = u(x, y + L, z) = u(x, y, z + L) \quad (2.66)$$

then the single-particle eigenstates are plane waves

$$u(\mathbf{r}) = L^{-3/2} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \quad (2.67)$$

of momentum

$$(p_x, p_y, p_z) = \frac{h}{L} (K_x, K_y, K_z) \quad (2.68)$$

where $h = 2\pi\hbar$ and K_x , K_y , and K_z are integers. If the momentum eigenvalues are plotted in a three-dimensional momentum space, they form a cubic lattice in which the distance between neighboring points (the lattice constant) is h/L (see Fig. 2.5). The corresponding energy eigenvalues are $E_p = p^2/2m$. The average occupation of one of the momentum eigenstates is

$$\bar{N}_p = \frac{1}{e^{\alpha + p^2/2mkT} \pm 1} \quad (2.69)$$

where the + sign is taken for fermions and the – sign for bosons. This must be compared with the Maxwell distribution, which, in momentum variables, is

$$f(\mathbf{p}) = C e^{-p^2/2mkT} \quad (2.70)$$

2.16 THE CLASSICAL LIMIT

If $e^\alpha \gg 1$, then the second term in the denominator of Eq. (2.69) will be negligible, giving

$$\bar{N}_p \approx e^{-\alpha} e^{-p^2/2mkT} \quad (2.71)$$

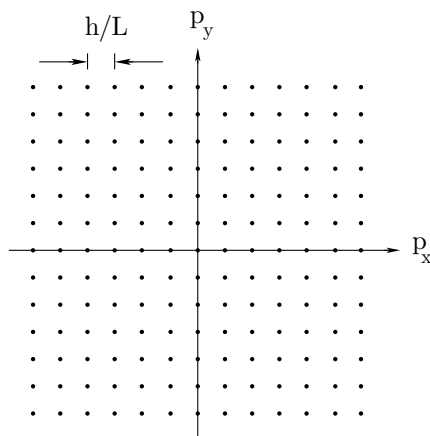


Fig. 2.5 The possible values of the momentum of a particle in a periodic box form a lattice in momentum space. The picture shown would be appropriate for a particle in two dimensions. Along each axis, the spacing between allowed values is h/L . For a three-dimensional system the density of momentum eigenvalues is $(L/h)^3$.

and the quantum-mechanical distributions will reduce to the Maxwell distribution. One way of interpreting the criterion $e^\alpha \gg 1$ is to note that it implies that the average occupation of every momentum state is much less than one.

In order to express the condition $e^\alpha \gg 1$ in terms of the macroscopic parameters of the system, let us assume that it is valid and evaluate the normalization sum for the quantum-mechanical distribution.

$$\sum_{\mathbf{p}} \bar{N}_{\mathbf{p}} = \sum_{\mathbf{p}} e^{-\alpha - p^2/2mkT} = N \quad (2.72)$$

where N is the number of particles in the system and the sum is taken over all allowed momentum eigenvalues. Using the fact that the density of momentum eigenvalues in momentum space is $(L/h)^3 = V/h^3$, where V is the volume of the system, the sum over the discrete values of \mathbf{p} may be converted to an integral over a continuous vector variable

$$\frac{V e^{-\alpha}}{h^3} \int e^{-p^2/2mkT} d^3\mathbf{p} = N \quad (2.73)$$

The integral can be evaluated in terms of the standard Gaussian integral, given in the Table of Integrals.

$$\int e^{-p^2/2mkT} d^3\mathbf{p} = \left(\int_{-\infty}^{\infty} e^{-p_x^2/2mkT} dp_x \right)^3 = (2\pi mkT)^{3/2} \quad (2.74)$$

If we define a *thermal de Broglie wavelength* λ by

$$\lambda \equiv \frac{h}{\sqrt{2\pi mkT}} \quad (2.75)$$

then the normalization condition gives

$$e^{-\alpha} = (N/V)\lambda^3 \quad (2.76)$$

Therefore, $e^{-\alpha}$ is equal to the average number of particles in a volume λ^3 . If that number is much less than one, then the classical approximation is justified. λ is the de Broglie wavelength of a particle with energy πkT , which is about twice the average energy of the particles in a gas at temperature T .

It is important to make clear what aspect of quantum mechanics is responsible for making the quantum distributions differ from the classical momentum distribution. It is not the discreteness of the quantum states, which is completely undetectable for a macroscopic system. Rather, it is the symmetry requirements on the many-particle wave functions. One way to see how the symmetry requirements affect the momentum distribution is to consider the mapping between classically described N -particle momentum states and quantum-mechanical ones. In order to simplify the analysis, we will artificially discretize the classical states

so that the single-particle momentum states are mapped one-to-one. A classical N -particle momentum state is defined by giving the momentum values of the N distinguishable particles, $(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$. If all N momentum values are different, then there are $N!$ classical states that map into a single Bose–Einstein or Fermi–Dirac N -particle quantum state. If we could ignore the probability of multiple occupancy of a single momentum state, then, averaging some quantity, such as the momentum distribution, over all classical N -particle states with total energy E , would be equivalent to averaging over $N!$ copies of the N -particle quantum states with the same energy and would therefore yield the same result. To see the effects of the quantum symmetry requirements, let us consider the mapping of a classical state in which $\mathbf{p}_1 = \mathbf{p}_2$. Then there are only $\frac{1}{2}N!$ classical states that are mapped into a single Bose–Einstein quantum state. Thus an average over the classical states would deemphasize this double-occupancy state by a factor of two in comparison with an average over Bose–Einstein N -particle states. That is, the Bose–Einstein symmetry requirement increases the probability of double occupancy in comparison with the classical system. In contrast, for a Fermi–Dirac system, there is no N -particle quantum state corresponding to the $\frac{1}{2}N!$ classical states. The Fermi–Dirac symmetry requirement prohibits double occupancy entirely. From this point of view, it is clear why the criterion for the validity of the classical approximation is that the average occupation of any single-particle quantum state be much less than one.

2.17 A CRITICAL EVALUATION

What are the deficiencies of the general calculational method used in this chapter? The major weaknesses of the technique are the following:

1. There is an obvious lack of logical precision and general principles in choosing our definitions of microstates and macrostates. It is not at all clear that our results do not depend on these somewhat arbitrary choices.
2. No justification, other than convenience, has been given for the assumption of equal a priori probabilities of all allowed microstates. Since that assumption is at the base of all the calculations, the whole logical structure is built upon sand.
3. There is no obvious way of applying the method to systems with interactions that cannot be neglected. For such systems, the energy cannot be written as a sum involving independent occupation numbers of any kind, nor is there any way of defining microstates and macrostates in terms of such occupation numbers.
4. In general, there is no logical “room” for adding extra assumptions, such as equal a priori probability. The time evolution of an actual system is determined by the laws of mechanics (or quantum mechanics). If the results of using any extra assumptions always agree with those of mechanics, then they are a logical consequence of the laws of mechanics, and it should be possible to show that fact. If they do not agree with the laws of mechanics, then the extra assumptions are wrong.

Although the method introduced in this chapter is very useful for calculating the properties of a wide variety of physical systems, it cannot really serve as a general logical foundation for statistical mechanics. In the next chapter we will sketch the outlines of such a general logical foundation, and, throughout the book, we will periodically return to the question of foundations to fill in more of the details.

PROBLEMS

2.1 (a) Make some reasonable estimate for the size of a cube containing 1000 grains of sand. (b) Using the above estimate, calculate the dimensions of a cube containing 10^{24} grains of sand.

2.2 For a relativistic particle, the relationships between velocity, momentum, and energy are $\mathbf{p} = m\mathbf{v}/\sqrt{1-(v/c)^2}$ and $E = mc^2/\sqrt{1-(v/c)^2}$. For an ideal gas of relativistic particles, determine whether the pressure is a function of the energy density, E/V , independent of the details of the velocity distribution? (Note that the relativistic energy defined here includes the rest energy, mc^2 .)

2.3 For an extremely relativistic gas, $v \approx c$ for most of the particles. Show that, for such a system, the pressure is related to the energy density by $p = \frac{1}{3}E/V$.

2.4 If, from an ideal gas at temperature T , we choose two particles at random, then the velocities of the

two particles are statistically independent. What are the probability distributions for their center-of-mass and relative velocities? Are those two random variables statistically correlated?

2.5 A container of volume V contains a very dilute ideal gas at density n and temperature T . The container is surrounded by vacuum and has a small hole of area A . At what rate do particles pass through the hole?

2.6 For the system described in Problem 2.5, calculate the rate at which the gas loses energy and calculate the temperature of the remaining gas as a function of time. Assume that the rate of leakage is small enough that the remaining gas is always uniform and at equilibrium.

2.7 For a classical ideal gas at temperature T , calculate the average value of $\sqrt{|\mathbf{p}|}$, where \mathbf{p} is the momentum of a gas particle.

2.8 The law of partial pressures states that the pressure exerted by a mixture of ideal gases is equal to the sum of the pressures that would be exerted by each of the gases separately at the same temperature. Derive the law of partial pressures.

2.9 For the system described in Problem 2.5, assume that the wall is infinitely thin, so that a particle that enters the hole always exits the container without colliding with the side of the hole. Assume that, of the particles that leave during some time interval Δt , a fraction $\phi(v) dv$ have speed within the range dv . Calculate the speed distribution $\phi(v)$ and explain why it does not agree with Eq. (2.28).

2.10 The purpose of this problem is to estimate the average distance that a particle in a gas travels between collisions. That distance is called the *mean free path*. Take as a model of the gas a set of hard spheres of radius a . To simplify the calculation, assume that the spheres are frozen in their random locations. Assume that the average volume per particle is much larger than the hard sphere volume [$V/N \gg (4\pi/3)a^3$]. Consider a hard sphere moving through this set of fixed scatterers. (a) Calculate the probability ΔP that it will be scattered within a short distance Δx . (b) Using that result, calculate the probability $P(x)$ that it will travel a distance x , without being scattered. (c) Calculate the average distance that the particle will move before being scattered. Compare your result with the exact formula given in Exercise 2.17. (d) Estimate the mean free path for neon at a temperature of 300 K and a pressure of 1 atmosphere, taking $a = 1.3 \text{ \AA}$.

2.11 Given 30 students to distribute in 3 rooms, calculate the number of microstates that correspond to the macrostate “10 students are in each room.”

2.12 A circular cylinder, with a radius of 10 cm, contains a nitrogen gas at a pressure of one atmosphere and a temperature of 300 K. If the cylinder is rotated about its axis, the centrifugal force increases the density at the periphery relative to that at the center. At what angular velocity would the ratio of the two densities be equal to 2?

2.13 The Maxwell distribution does not guarantee that the total energy is exactly E , but only that that is its average value. For one mole of ideal gas at 300 K, calculate the fractional uncertainty in the energy, $\Delta E/E$. (Hint: Assume that the velocities of the particles are N statistically independent random variables.)



Fig. 2.6

2.14 At $t = 0$, a one-dimensional classical ideal gas is contained in the region $0 < x < L$ (Fig. 2.6). The gas has an initial temperature T_0 and a density n_0 . The gas particles have mass m . The wall at $x = 0$ reflects all particles that hit it. The wall at $x = L$ allows any particle that hits it to pass through with a probability ϵ , that is much less than one and is independent of the particle's energy. Otherwise the particle is reflected with no change in its energy. (a) Calculate the rate at which the system loses particles and energy at $t = 0$. (b) Assuming that the particles remaining always have a Maxwell distribution, but with slowly varying density and temperature, derive and solve a differential equation for $T(t)$.

2.15 Generalize the derivation leading to the Maxwell–Boltzmann distribution to the case of an ideal gas

containing two types of particles, A and B . Assume that there are N_A A particles and N_B B particles with masses m_A and m_B , respectively. Since they may interact differently with external force fields, they may, in general, experience different potentials, $U_A(\mathbf{r})$ and $U_B(\mathbf{r})$. The result should be that $f_i(\mathbf{r}, \mathbf{v}) = n_i(\mathbf{r}_{io})(m_i/2\pi kT)^{3/2} \exp[-(m_i v^2/2 + U_i(\mathbf{r}))/kT]$, where $i = A$ or B and $U_i(\mathbf{r}_{io}) = 0$.

2.16 Use the results of Problem 2.15 to show that, in a mixed ideal gas, the average kinetic energy per particle of the A particles is the same as that of the B particles. This is a restricted form of what is called the *equipartition theorem*. The general form will be derived later.

2.17 A system is composed of a large number N of elementary subsystems (one might picture the subsystems as atoms in a crystal lattice). Each subsystem can exist in one of three quantum states, with energies 0, 1, or 2 electron volts. Determine the number of microstates of the total system such that N_1 subsystems have energy $\varepsilon_1 = 0$ eV, N_2 subsystems have energy $\varepsilon_2 = 1$ eV, and N_3 subsystems have energy $\varepsilon_3 = 2$ eV. Assuming that each possible microstate has equal probability, determine the most probable values of N_1 , N_2 , and N_3 , given that the total energy is $E = 0.5N$ eV.

2.18 Consider an ideal gas, composed of atoms that have K discrete possible internal energy states, of energy, ε_k ($k = 1, \dots, K$). Using an analysis similar to that which led to the Maxwell–Boltzmann distribution, derive the distribution function $f(k, \mathbf{v})$, where $f(k, \mathbf{v}) d^3\mathbf{v}$ is the number of particles per unit volume in internal energy state k with velocity in $d^3\mathbf{v}$.

2.19 Using Lagrange’s method, find the minimum of the function $x^2 + 2y^2$, subject to the constraint $x^3 + y^3 = 1$.

2.20 In 1876, J. Loschmidt argued that the Maxwell–Boltzmann distribution must be wrong. He said that, at equilibrium in a uniform gravitational field, an ideal gas should be warmer at the bottom than at the top because of the facts that every particle that moves from the bottom to the top slows down in the field and every particle that moves from the top to the bottom speeds up. Thus, in order to have the exchange of particles between bottom and top not change the distribution, it is necessary that the average speed of the particles at the bottom be larger than the average speed of the particles at the top. Explain why Loschmidt was wrong. Take the special case of a purely one-dimensional gas (in the z direction) of completely noninteracting particles in a constant gravitational field.

2.21 A globular cluster is a large collection of stars that is gravitationally held together in a more or less spherically symmetric distribution. Treat such a cluster as a gas of noninteracting, equal-mass stars in a gravitational potential $U(r)$. The gravitational potential must be determined *self-consistently*, using the Poisson equation, which can be written as $dU/dR = GM(R)/R^2$, where $M(R) = 4\pi m \int_0^R n(r)r^2 dr$ is the mass of all the stars within a radius R . Choosing $U(0) = 0$ and using Eq. (2.19) for $n(r)$, show that no equilibrium solution exists for a single globular cluster in empty space. This shows that globular clusters are never truly at equilibrium. They very gradually “boil off” stars, causing the cluster to steadily, but very slowly, diminish in size. [Hint: For an isolated globular cluster, $n(r) \rightarrow 0$ as $r \rightarrow \infty$.]

2.22 At very high temperatures a hydrogen gas becomes completely ionized and may be viewed as a mixed ideal gas of protons and electrons. One can assume that relativistic effects become important when the rms velocity of the electrons is larger than $.1c$. At what temperature would that occur?

2.23 Consider a quantum-mechanical system of four particles in a one-dimensional harmonic oscillator potential. The one-particle energy eigenvalues are $(n + \frac{1}{2})\hbar\omega$ and are nondegenerate. For Bose–Einstein particles and Fermi–Dirac particles, determine the number of four-particle quantum states with an energy of $8\hbar\omega$. Assume that the Fermi–Dirac particles have zero spin, although that can be shown to be impossible.

2.24 Derive Eq. (2.57) for the number of ways of distributing ν bosons within K states. Hint: The diagrams in Fig. 2.7 show three ways of distributing five particles among three states. How many such diagrams are there?

Fig. 2.7



2.25 Consider a spinless particle of mass m , in a cubic periodic box of side L . (a) Calculate $N(E)$, the number of energy eigenfunctions with energies less than or equal to E . (b) $dN(E)/dE$ gives the number of eigenstates per unit energy interval. Its inverse is the average spacing between energy eigenvalues. Show that, for m equal to one atomic mass unit, $L = 1$ m, and $E/k = 300$ K, the estimate given in Section 2.13 for the energy spacing is correct.

2.26 Consider a system of spinless one-dimensional particles in a harmonic oscillator potential of angular frequency ω . The energy spectrum is then $\varepsilon_n = (n + \frac{1}{2})\hbar\omega$. Using Eqs. (2.63) and (2.64), evaluate the number of particles in the system as a function of the *affinity* α and the temperature T for the case $\alpha \gg 1$ for both fermions and bosons. (Hint: the infinite sum may be easily evaluated.)