

Chapter 4 The Classical Ideal Gas

4.1 Introduction

We now turn to the case of a gas of particles where the density is so low that it is possible to neglect the interactions between the particles because the interaction (potential) energy between particles is much less than the kinetic energy of each particle. In this regime, it is possible to treat the particles **independently** and to find the total energy by adding together the energies of the individual particles.

We can initially consider a single particle within a box and calculate the energy eigenstates and energy eigenvalues. Let us denote these single-particle energy eigenvalues by

$$\varepsilon_1 \leq \varepsilon_2 \leq \dots \quad (4.1)$$

Now we consider a gas of N particles. What are the energy eigenstates? **If** the particles were **distinguishable**, (as for the spins in a solid or the vibrational modes of a solid as we considered previously), we would label the states by a string such as

$$(s_1, s_2, \dots, s_N) \quad (4.2)$$

where s_i labels the state of the i 'th particle. We would calculate the partition function for one particle Z_1 and then set $Z_N = Z_1^N$.

This procedure does **not** work for **indistinguishable** particles, e.g. in a gas. This is because we **cannot** identify each particle and so the eigenstates of the multi-particle system must instead be labelled by a string such as

$$\mathbf{n}_r = (n_1, n_2, \dots, n_s, \dots) \quad (4.3)$$

where n_1 is the number of particles in (single-particle) state 1, n_2 is the number of particles in (single-particle) state 2 and so on. The number n_s is called the **occupation number** of the single-particle state s . Notice that we do not (and cannot) know which particle is in which single-particle state. The eigenstate of the *entire system* is labelled by the letter r .

The sum of the occupation numbers over all the **single-particle states** must be equal to the total number of particles, N . i.e.,

$$\sum_s n_s = N \quad (4.4)$$

and the energy of the multi-particle energy eigenstate r with occupation numbers \mathbf{n}_r is given by

$$E_r = \sum_s n_s \varepsilon_s. \quad (4.5)$$

This distinction between distinguishable and indistinguishable particles is of fundamental importance. Let us consider a simple example to make the ideas more definite. Say we have $N = 3$ particles, each of which can be in one of two (single-particle) states which we denote by $+$ and $-$. If the particles are distinguishable, there are eight 3-particle states, namely $+++$, $++-$, $+ - +$, $+ - -$, $- + +$, $- + -$, $- - +$ and $- - -$. On the other hand, if the particles are indistinguishable, all we can know is the number of particles in the $+$ state and the number in the $-$ state. If there are no restrictions on the occupation numbers of the single-particle states (see later), there are four 3-particle states, the first has $n_+ = 3$, $n_- = 0$, the second has $n_+ = 2$, $n_- = 1$, the third has $n_+ = 1$, $n_- = 2$ and the fourth has $n_+ = 0$, $n_- = 3$.

4.2 The Partition Function

4.2.1 Coping with indistinguishability

For one particle, we have

$$Z_1 = \sum_s \exp(-\beta\varepsilon_s) \quad (4.6)$$

where s is a label for a single-particle eigenstate. For the entire system, the partition function is still

$$Z_N = \sum_r \exp(-\beta E_r) \quad (4.7)$$

but we must understand r and E_r as labels and energies of the N -particle states. For N **indistinguishable** particles, where the states are distinguished by the occupation numbers \mathbf{n}_r satisfying $\sum_s n_s = N$, we find that:

$$Z_N = \sum_{\substack{n_1, n_2, \dots \\ \sum n_s = N}} \exp\left(-\beta \sum_s n_s \varepsilon_s\right) \quad (4.8)$$

The sum is over all the N -particle eigenstates which are counted by considering all the ways the occupation numbers n_1, n_2, \dots can be arranged to add up to the total number of particles N . For each valid set of occupation numbers, the energy eigenvalue of the N particles is $\sum_s n_s \varepsilon_s$. Unfortunately, it is rather difficult to evaluate this exactly, and we need to make several approximations.

The Classical Approximation

In the classical approximation, we suppose that the number of single-particle energy levels is so large compared to the number of particles N and the temperature is so high that the only important states are those for which the occupation numbers n_i are either zero or one.

Let us see what the consequence of this approximation is for the case of two particles. We first consider

$$\begin{aligned} Z_1^2 &= \left(\sum_s \exp(-\beta\varepsilon_s) \right)^2 = \sum_r \sum_s \exp[-\beta(\varepsilon_s + \varepsilon_t)] \\ &= \sum_s \exp(-2\beta\varepsilon_s) + \sum_{\substack{s \\ s \neq t}} \sum_t \exp[-\beta(\varepsilon_s + \varepsilon_t)] \end{aligned} \quad (4.9)$$

On the other hand, computing Z_2 explicitly, we find

$$Z_2 = \sum_s \exp(-2\beta\varepsilon_s) + \frac{1}{2} \sum_{\substack{s \\ s \neq t}} \sum_t \exp[-\beta(\varepsilon_s + \varepsilon_t)]. \quad (4.10)$$

The first term on the right-hand side is for the case when some $n_s = 2$ and all the other occupation numbers are zero, and the second term is for the case when there are two non-zero occupation numbers, say $n_k = 1$, $n_l = 1$. The factor of a half is needed in order to compensate for double-counting since we will have a term with $s = k$, $t = l$ and one with $s = l$ and $t = k$.

In the classical approximation, the only important states are assumed to be those in which the two particles occupy different states. Only the second set of summations are important, and we may write

$$Z_2 \approx \frac{Z_1^2}{2} \quad (4.11)$$

Similarly, for three particles,

$$Z_1^3 = \sum_s \sum_t \sum_u \exp[-\beta(\varepsilon_s + \varepsilon_t + \varepsilon_u)] \quad (4.12)$$

We now need to split the sum into the cases $s = t = u$, $s = t \neq u$, $s \neq t = u$, $s = u \neq t$ and for s , t and u all different. Retaining only the last set since they represent the cases in which the occupation numbers are at most one, we see that

$$Z_1^3 \approx \sum_{s,t,u \text{ different}} \sum \sum \exp[-\beta(\varepsilon_s + \varepsilon_t + \varepsilon_u)] \quad (4.13)$$

Compared with the expression for Z_3 on the other hand, these states are overcounted $3!$ times since there are $3!$ ways of assigning the three single-particle states with non-zero occupation to the summation indices s , t and u . We thus see that

$$Z_3 \approx \frac{Z_1^3}{3!} \quad (4.14)$$

In general, for indistinguishable particles in the classical approximation, we see that

$$Z_N \approx \frac{Z_1^N}{N!} \quad (4.15)$$

where the divisor of $N!$ arises from the indistinguishability.

4.2.2 Translational and internal partition functions

Let us now consider Z_1 , the partition function for a **single particle**, in more detail. For a **monatomic gas**, the energy is purely translational and the states are given by the energy eigenstates of a point particle inside a box. This gives rise to the single-particle translational partition function Z_1^{tr} which we shall discuss later. If the particles are more complicated (e.g. for polyatomic molecules), there are internal states of motion such as rotations and vibrations to consider as well. At this stage, we do not know enough quantum mechanics to treat these quantitatively, but in outline, there are energy ladders for the rotational and vibrational states whose rung spacings depend on the molecular parameters. For the vibrational modes, the motion is approximately simple harmonic, and so the ladder rung spacings are approximately equal. For typical molecules, the vibrational energy spacings correspond to energies in the infra-red frequency range. For the rotational modes on the other hand, the rungs are arranged so that the spacings increase linearly with the rotational quantum number. For typical molecules these spacings correspond to microwave frequencies, and so are much more closely spaced than the vibrational levels. To a reasonable approximation (ignoring for example the centrifugal force due to rotation which can affect the vibrational motion), the rotational structure simply broadens the vibrational structure as shown schematically in Figure 4.1.

In principle, once we know how to calculate all the energy levels $\varepsilon_\alpha^{\text{int}}$ associated with the internal states of motion, we can write down (and hopefully evaluate!) the internal partition function in the usual way

$$Z^{\text{int}} = \sum_{\alpha} \exp(-\beta\varepsilon_{\alpha}^{\text{int}}) \quad (4.16)$$

Note that this is a property of the molecules themselves and does not depend on quantities such as the volume of the box in which the gas is placed.

The translational and internal motions of the particles are essentially independent and so

$$\varepsilon_s \equiv \varepsilon_{t\alpha} = \varepsilon_t^{\text{tr}} + \varepsilon_{\alpha}^{\text{int}}. \quad (4.17)$$

where s labels the translational energy levels and α labels the internal energy levels. The total partition function is simply the product

$$Z_1 = \sum_s \exp(-\beta\varepsilon_s) = \left(\sum_t \exp(-\beta\varepsilon_t^{\text{tr}}) \right) \left(\sum_{\alpha} \exp(-\beta\varepsilon_{\alpha}^{\text{int}}) \right) = Z_1^{\text{tr}}(\beta, V) Z^{\text{int}}(\beta) \quad (4.18)$$

In the following, we shall mainly be concerned about the translational partition function, but it is appropriate to make a few qualitative remarks about the effects that the internal partition function produces. At very low temperatures, when the thermal energy is much less than the separation between the rungs of the rotational ladder, the internal degrees of freedom are “frozen out” and the heat capacity of the gas is similar to that of a monatomic gas. At higher temperatures, the rotational motion begins to participate in the internal

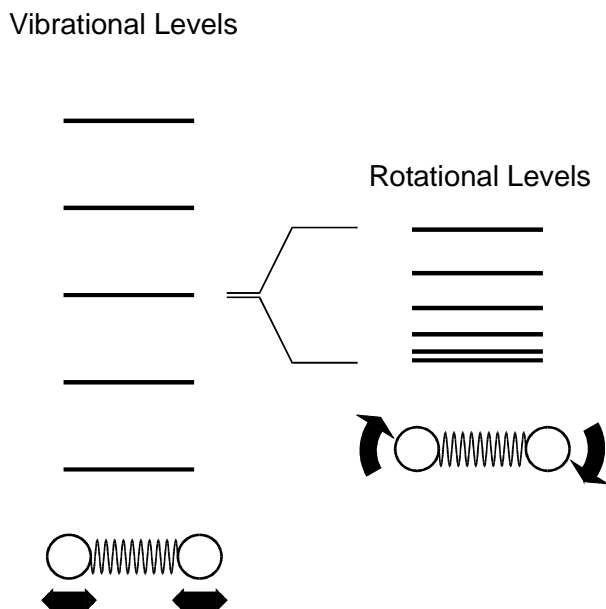


Figure 4.1 Schematic representation of energy level structure of a diatomic molecule due to vibrational and rotation motions.

energy, increasing the heat capacity by $\frac{1}{2}k$ per “rotational degree of freedom” per molecule. This is the usual situation at room temperature. At yet higher temperatures, the vibrational degrees of freedom increase the heat capacity further. Once the temperature is high enough to fully excite all the rotational and vibrational modes, the heat capacity tends to a constant (cf. the law of Dulong and Petit).

4.2.3 Calculating the translational partition function

In order to find the translational partition function, it is necessary to know the states of a single point particle in a three-dimensional box. Consider a particle of mass m in a cubical box of length L defined by $0 \leq x, y, z \leq L$. The energy eigenstates are

$$u(x, y, z) = \mathcal{N} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad (4.19)$$

where \mathcal{N} is a normalization constant. The energy eigenvalues are

$$\varepsilon_{\mathbf{n}} = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (4.20)$$

where $n_x, n_y, n_z \in \{1, 2, \dots\}$. For convenience, we wish to replace the discrete energies by a continuum of levels and define a density of states such that $f(E) dE$ gives the number of modes with energy between E and $E + dE$.

The number of states with energy less than E' is given by the number of points with positive integer coordinates in the positive octant of a sphere of radius $\sqrt{2mL^2 E' / (\pi \hbar)^2}$. As in the previous chapter, this may be estimated by finding the volume of the portion of the sphere and dividing this by the volume of the cell representing each state. We can find $f(E)$ by equating its integral between 0 and E' (which gives the number of states in this energy range) and the estimated number of states:

$$\int_0^{E'} f(E) dE = \frac{1}{8} \frac{4}{3} \pi \left(\sqrt{\frac{2mL^2 E'}{\pi^2 \hbar^2}} \right)^3 \quad (4.21)$$

Differentiating and simplifying yields

$$f(E) = \left(\frac{2m}{\hbar^2} \right)^{3/2} \frac{V E^{1/2}}{4\pi^2} \quad (4.22)$$

where $V = L^3$ is the volume of the box. Note that this is the density of states for a **single particle**.

The single-particle partition function is

$$Z_1^{\text{tr}} = \sum_{\mathbf{n}} \exp(-\beta \varepsilon_{\mathbf{n}}) \approx \int_0^{\infty} f(E) \exp(-\beta E) \, dE \quad (4.23)$$

$$= \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{V}{4\pi^2} \int_0^{\infty} E^{1/2} \exp(-\beta E) \, dE \quad (4.24)$$

Changing variables to $u = E^{1/2}$,

$$Z_1^{\text{tr}} = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{V}{2\pi^2} \int_0^{\infty} u^2 e^{-\beta u^2} \, du \quad (4.25)$$

$$= \left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \quad (4.26)$$

where we have used $\int_0^{\infty} x^2 \exp(-\beta x^2) \, dx = \frac{1}{4} \sqrt{\pi/\beta^3}$.

4.2.4 Total Partition Function

Including the internal degrees of freedom and considering N particles, the total partition for the gas is given by

$$Z(T, V, N) = \frac{[Z_1^{\text{tr}}(T, V) Z^{\text{int}}(T)]^N}{N!} \quad (4.27)$$

$$= \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N [Z^{\text{int}}(T)]^N \quad (4.28)$$

From the partition function, we can compute the free energy of the gas:

$$F = -kT \log Z \quad (4.29)$$

$$= -kT \log \left\{ \frac{1}{N!} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N [Z^{\text{int}}(T)]^N \right\} \quad (4.30)$$

$$= -NkT \log \left\{ \frac{eV}{N} \left(\frac{2\pi mkT}{h^2}\right)^{3/2} Z^{\text{int}}(T) \right\} \quad (4.31)$$

where in the last line, we have used the approximation $\log N! = N \log N - N = N \log(N/e)$.

Note that F is an **extensive** function, i.e., if we replace N by λN and V by λV , the result is that F becomes λF . We need the divisor $N!$ in the partition function for this to happen.

4.3 Validity Criterion for Classical Regime

As discussed above, a gas in the classical regime is one in which the occupation numbers of most of the single-particle states are zero, a few have occupation number one, and there are essentially no states with more than one particle. This will be the case if the mean number of particles in each single-particle state is very small, i.e.,

$$\bar{n}_s \ll 1 \text{ for every translational state } s. \quad (4.32)$$

Since the particles are independent,

$$\begin{aligned}\bar{n}_s &= Np_s \\ &= N \frac{\exp[-\beta\varepsilon_s^{\text{tr}}]}{Z_1^{\text{tr}}} = \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \exp[-\beta\varepsilon_s^{\text{tr}}]\end{aligned}\quad (4.33)$$

A sufficient condition for all the \bar{n}_s to be much less than one is for

$$\frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \ll 1 \quad (4.34)$$

How can we interpret this inequality? For particles at temperature T , we shall see later that $E^{\text{tr}} = \frac{3}{2}kT$, so the mean square momentum is

$$\overline{p^2} = 3mkT. \quad (4.35)$$

The de Broglie wavelength associated with this root mean square momentum is

$$\lambda_{\text{dB}} = \frac{h}{(\overline{p^2})^{1/2}} = \frac{h}{\sqrt{3mkT}}, \quad (4.36)$$

which is called the **thermal de Broglie wavelength**. The validity criterion can then be written as

$$\left(\frac{3}{2\pi} \right)^{3/2} \lambda_{\text{dB}}^3 \left(\frac{N}{V} \right) \ll 1. \quad (4.37)$$

Ignoring the numerical factor and writing $V/N = l^3$ where l is the mean inter-molecular distance, the condition for the classical regime may be written as

$$\frac{l}{\lambda_{\text{dB}}} \gg 1. \quad (4.38)$$

For helium at 273 K and at atmospheric pressure, we find $l = 3.3$ nm and $\lambda_{\text{dB}} = 76$ pm, so that $l \gg \lambda_{\text{dB}}$. However, at approximately 3 K, $l \approx \lambda_{\text{dB}}$ and we expect quantum effects to become important. On the other hand, if we consider the conduction electrons in a metal, the low mass of $m = 9 \times 10^{-31}$ kg leads to rather large thermal de Broglie wavelengths. As a result, quantum effects are important below $\approx 10^5$ K.

4.4 The Equation of State

From the fundamental relation

$$dE = TdS - PdV + \mu dN \quad (4.39)$$

and the definition of the free energy $F = E - TS$, we see that

$$dF = -SdT - PdV + \mu dN \quad (4.40)$$

Thus

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{NkT}{V} \quad (4.41)$$

where we have used (4.31) for the free energy.

The mean energy of the gas may be found from

$$\begin{aligned}\bar{E} &= F + TS = F - T \frac{\partial F}{\partial T} \\ &= \frac{3}{2}NkT + NkT^2 \frac{d}{dT} [\log Z_{\text{int}}(T)]\end{aligned}\quad (4.42)$$

The first term on the right-hand side is the translational kinetic energy while the second term is the energy due to the internal motion (rotation and vibration). The fact that the right hand side depends only on the temperature and is independent of the volume is Joule's law.

4.5 The Entropy

From the fundamental relation we see that

$$\begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_{V,N} \\ &= Nk \left\{ \frac{3}{2} \log T + \log V - \log N + \frac{5}{2} + \frac{3}{2} \log \left(\frac{2\pi mk}{h^2} \right) \right\} + N \frac{\partial}{\partial T} \{ kT \log Z^{\text{int}}(T) \} \end{aligned} \quad (4.43)$$

The translational part of the entropy is the same as the result we derived earlier using classical thermodynamics for a monatomic gas, except that we now have an explicit formula for the constant, namely $\frac{5}{2} + \frac{3}{2} \log \left(\frac{2\pi mk}{h^2} \right)$.

4.6 The Maxwell Speed Distribution

Let us consider the distribution of speeds of the particles in a gas. This only involves the translational part of the motion. Since the speed is related simply to the translational energy, we first consider the probability that the translational energy of a **single particle** lies within the range E to $E + dE$.

This probability is the product of two factors. The first factor is the related to the density of states for a single particle calculated in (4.22) since $f(E) dE$ gives the number of available states in this energy range. The second factor is the probability that a such a state is occupied by a particle which is simply given by the Boltzmann distribution $\exp(-\beta E) / Z_1^{\text{tr}}$. Thus

$$\begin{aligned} p(E) dE &= \text{Pr}(\text{A particle has energy between } E \text{ and } E + dE) = \frac{f(E) e^{-\beta E}}{Z_1^{\text{tr}}} dE \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{E}{k^3 T^3} \right)^{1/2} \exp \left(-\frac{E}{kT} \right) dE \end{aligned} \quad (4.44)$$

If we normalize E using the relationship $\varepsilon = E / (kT)$, this simplifies to

$$p(\varepsilon) d\varepsilon = \frac{2}{\sqrt{\pi}} \varepsilon^{1/2} \exp(-\varepsilon) d\varepsilon \quad (4.45)$$

We can now change the variables to find the probability density for the speed v . Recall that if E and v are related monotonically, the probability densities are related by

$$p(v) = p(E) \left| \frac{dE}{dv} \right|. \quad (4.46)$$

Notice that we are (mis)using the same symbol p to denote the probability density of different variables. Here $E = \frac{1}{2}mv^2$ which is monotonic over the range $v \geq 0$, $E \geq 0$, and so

$$\begin{aligned} p(v) &= \frac{2}{\sqrt{\pi}} \left(\frac{mv^2}{2k^3 T^3} \right)^{1/2} \exp \left(-\frac{mv^2}{2kT} \right) |mv| \\ &= \frac{4}{\sqrt{\pi}} v^2 \left(\frac{m}{2kT} \right)^{3/2} \exp \left(-\frac{mv^2}{2kT} \right) \end{aligned} \quad (4.47)$$

This is the Maxwell speed distribution for a gas. The **most probable** speed is found by finding v_{max} such that $p'(v_{\text{max}}) = 0$. This yields

$$v_{\text{max}} = \left(\frac{2kT}{m} \right)^{1/2} \quad (4.48)$$

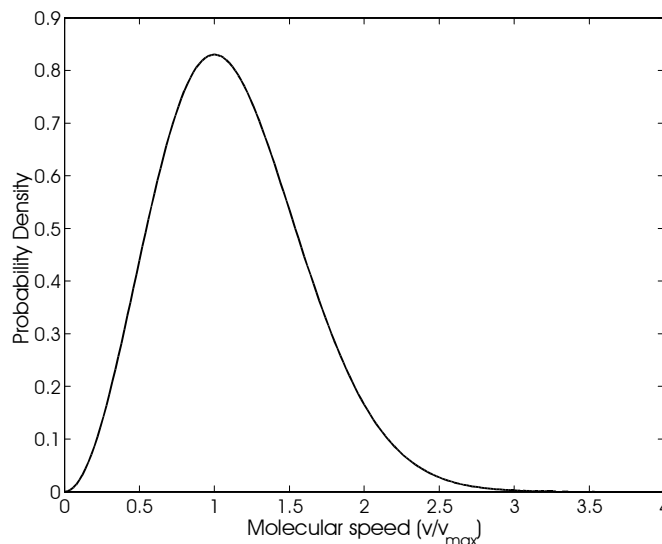


Figure 4.2 Maxwell speed distribution for molecules in an ideal gas

If we normalize v using the relationship $u = v/v_{\max}$, the probability density of u is

$$p(u) = \frac{4}{\sqrt{\pi}} u^2 \exp(-u^2) \quad (4.49)$$

This is shown in Figure 4.2.

The **mean speed** is given by

$$\bar{v} = \int_0^{\infty} v p(v) dv \quad (4.50)$$

$$= v_{\max} \int_0^{\infty} u p(u) du = \frac{2}{\sqrt{\pi}} v_{\max} \quad (4.51)$$

and the **root mean square** speed is $v_{\text{rms}} = (\overline{v^2})^{1/2}$, where

$$\overline{v^2} = v_{\max}^2 \int_0^{\infty} u^2 p(u) du = \frac{3}{2} v_{\max}^2 \quad (4.52)$$

and so

$$v_{\text{rms}} = \sqrt{\frac{3}{2}} v_{\max} \quad (4.53)$$

The Gamma Function

Note that the last few integrals were carried out with the help of the **gamma function**

$$\Gamma(x) \equiv \int_0^{\infty} t^{x-1} \exp(-t) dt \quad (4.54)$$

It is easy to show (check!) using integration by parts that

$$\Gamma(x+1) = x\Gamma(x). \quad (4.55)$$

Since $\Gamma(1) = 1$, we see that $\Gamma(n) = (n-1)!$ if n is an integer. Substituting $t = u^2$ in the definition of the Γ function, we see that

$$\Gamma(x) = 2 \int_0^{\infty} u^{2x-1} \exp(-u^2) du \quad (4.56)$$

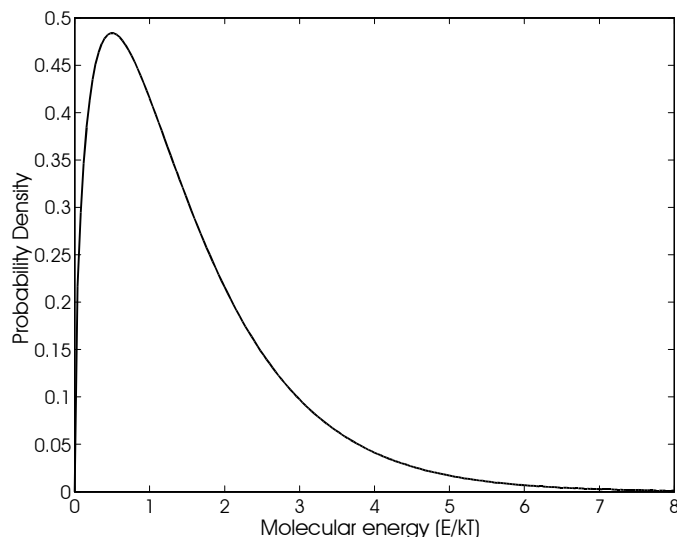


Figure 4.3 Maxwell energy distribution for the energy of a single particle in a gas

Thus the Γ function is also useful for evaluating **Gaussian integrals** of the form

$$\int_0^{\infty} u^n \exp(-u^2) du = \frac{1}{2} \Gamma\left(\frac{n+1}{2}\right) \quad (4.57)$$

For n odd, the right hand side reduces to a factorial and may be evaluated readily. On the other hand, if n is even, the argument of the Γ function is a half-integer. These may be evaluated as follows: Setting $n = 0$, we see that

$$\int_0^{\infty} \exp(-u^2) du = \frac{1}{2} \Gamma\left(\frac{1}{2}\right) \quad (4.58)$$

From the properties of Gaussians, recall that the integral on the left hand side is $\frac{1}{2}\sqrt{\pi}$, and so

$$\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \quad (4.59)$$

Using the recursion relation (4.55), we see that if m is an integer,

$$\Gamma\left(m + \frac{1}{2}\right) = \frac{(2m-1)!!}{2^m} \sqrt{\pi} \quad (4.60)$$

where we define

$$(2m-1)!! \equiv (2m-1) \times (2m-3) \times \dots \times 3 \times 1. \quad (4.61)$$

4.7 Energy probability density for 1 particle and for N particles

As calculated above, the probability density for the energy of a **single particle** is given by

$$p(E) = \frac{2}{\sqrt{\pi}} \left(\frac{E}{k^3 T^3}\right)^{1/2} \exp\left(-\frac{E}{kT}\right) \quad (4.62)$$

This is illustrated in Figure 4.3.

For a **single particle**, the **most probable** translational energy is

$$E_{\max} = \frac{1}{2} kT \quad (4.63)$$

and the **mean** translational energy is

$$\int_0^{\infty} E p(E) dE = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \left(\frac{E}{kT}\right)^{3/2} \exp\left(-\frac{E}{kT}\right) dE = \frac{3}{2} kT \quad (4.64)$$

which agrees with (4.42). The **variance** of the energy is

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{3}{2} (kT)^2 \quad (4.65)$$

so that $\Delta E = \sqrt{3/2} kT$. Note that the mode and mean are quite different due to the asymmetric shape of the energy probability density curve.

We now wish to calculate the energy probability density for the gas of N particles. We can do this using a trick involving the partition function. Recall that if $f(E) dE$ is the number of energy eigenstates with energy between E and $E + dE$, the partition function and the probability density for the energy are given by

$$Z(\beta) = \int_0^{\infty} f(E) \exp(-\beta E) dE \quad (4.66)$$

$$p(E) = \frac{f(E) \exp(-\beta E)}{Z(\beta)} \quad (4.67)$$

These results hold both for a single particle and for the entire gas, with the appropriate substitutions. For a single particle, we found that

$$f_1(E) \propto E^{1/2} V \text{ and } Z_1^{\text{tr}} \propto \beta^{-3/2} V \quad (4.68)$$

so that

$$p_1(E) \propto \beta^{3/2} E^{1/2} \exp(-\beta E) \quad (4.69)$$

The normalization constant is easily found to be $2/\sqrt{\pi} = 1/\Gamma(\frac{1}{2})$.

For N particles, we know that,

$$Z_N^{\text{tr}} = \frac{(Z_1^{\text{tr}})^N}{N!} \propto \beta^{-3N/2} V^N \quad (4.70)$$

but we do not yet know $f_N(E)$ or $p_N(E)$. If we assume that $f_N(E)$ can be written as a power law in E and V , i.e., if

$$f_N(E) \propto E^p V^q \quad (4.71)$$

for some p and q , we can use (4.66) to help us find p and q , since

$$\beta^{-3N/2} V^N \propto \int_0^{\infty} E^p V^q \exp(-\beta E) dE \quad (4.72)$$

$$= \frac{1}{\beta^{p+1}} \int_0^{\infty} u^p V^q \exp(-u) du \quad (4.73)$$

where we have substituted $u = \beta E$. Comparing the powers of β and V shows that

$$p = \frac{3N}{2} - 1 \text{ and } q = N \quad (4.74)$$

Now that we know $f_N(E)$, we can determine $p_N(E)$, the desired probability density of the energy of the gas, using (4.67):

$$p_N(E) \propto \frac{E^{3N/2-1} V^N \exp(-\beta E)}{\beta^{-3N/2} V^N} = \beta^{3N/2} E^{3N/2-1} \exp(-\beta E) \quad (4.75)$$

Evaluating the normalization constant gives

$$p_N(E) = \frac{\beta^{3N/2} E^{3N/2-1} \exp(-\beta E)}{\Gamma(3N/2)} \quad (4.76)$$

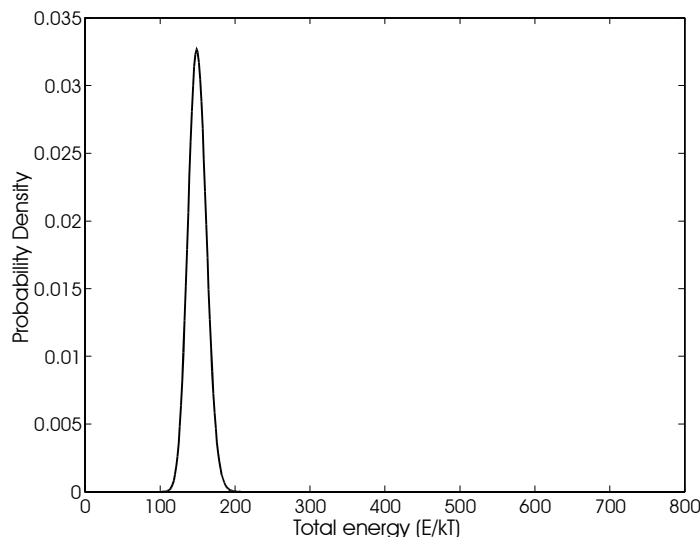


Figure 4.4 Total energy probability density for a gas of $N = 100$ particles.

We can find the most probable energy, the mean energy and the standard deviation of the energy for the gas. This gives

$$E_{\max} = \left(\frac{3}{2}N - 1 \right) kT \quad (4.77)$$

$$\langle E \rangle = \frac{3}{2}NkT \quad (4.78)$$

$$\Delta E = \sqrt{\frac{3N}{2}}kT \quad (4.79)$$

Thus

$$\frac{\Delta E}{E} = \sqrt{\frac{2}{3N}} \quad (4.80)$$

which becomes very small as $N \rightarrow \infty$. Figure shows the probability density for $N = 100$. It is apparent that for large N , the most probable energy is very close to the mean energy and the energy is very well defined. Since we have assumed that the particles are independent, it is not surprising that the mean energy and energy variance are simply N times the values for a single particle.

4.8 Maxwell Velocity Distribution

We are sometimes interested in the distribution of a single **component** of the particle velocity rather than in the speed which is the **magnitude** of the velocity. Since there is no preferred direction within a gas, we can calculate the velocity distribution from the speed distribution and the assumption of isotropy.

Consider a spherical polar coordinate system and an elementary area on the surface of a sphere of radius v bounded by polar angles $[\theta, \theta + d\theta]$ and azimuthal angles $[\phi, \phi + d\phi]$. The area of this element is

$$A = (v d\theta) (v \sin \theta d\phi) = v^2 \sin \theta d\theta d\phi \quad (4.81)$$

Given that particles travel isotropically, the probability that a particle starting from the origin will pass through this elementary area is

$$p(\theta, \phi) d\theta d\phi = \frac{v^2 \sin \theta d\theta d\phi}{4\pi v^2} = \frac{1}{4\pi} \sin \theta d\theta d\phi. \quad (4.82)$$

From the Maxwell speed distribution, the probability that a particle has speed lying between v and $v + dv$ is given by (4.49), namely

$$p(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{v}{v_{\max}} \right)^2 \exp \left[- \left(\frac{v}{v_{\max}} \right)^2 \right] \left(\frac{dv}{v_{\max}} \right) \quad (4.83)$$

where v_{\max} is given by (4.48). Since the speed and direction are independent, we expect that the probability that a particle has speed lying between v and $v + dv$, polar angle lying between θ and $\theta + d\theta$ and azimuthal angle lying between ϕ and $\phi + d\phi$ is

$$p(v, \theta, \phi) dv d\theta d\phi = \frac{1}{\pi^{3/2}} \left(\frac{v}{v_{\max}} \right)^2 \exp \left[- \left(\frac{v}{v_{\max}} \right)^2 \right] \left(\frac{1}{v_{\max}} \right) \sin \theta dv d\theta d\phi. \quad (4.84)$$

We now wish to convert from spherical polar to Cartesian coordinates. The probability densities are related by

$$p(v_x, v_y, v_z) dv_x dv_y dv_z = p(v, \theta, \phi) dv d\theta d\phi \quad (4.85)$$

where the Jacobian of the transformation is

$$dv_x dv_y dv_z = v^2 \sin \theta dv d\theta d\phi \quad (4.86)$$

Thus we find

$$p(v_x, v_y, v_z) = \frac{1}{\pi^{3/2} v_{\max}^3} \exp \left[- \left(\frac{v_x^2 + v_y^2 + v_z^2}{v_{\max}^2} \right) \right] \quad (4.87)$$

We expect this joint probability density to factorize

$$p(v_x, v_y, v_z) = p(v_x) p(v_y) p(v_z) \quad (4.88)$$

and so the one-dimensional distribution of each velocity component is

$$p(v_x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left[- \frac{1}{2} \frac{v_x^2}{\sigma^2} \right] \quad (4.89)$$

where $\sigma^2 = \frac{1}{2} v_{\max}^2 = (kT/m)$. This is simply a Gaussian with zero mean and variance σ^2 .