

Statistical Mechanics

MP232

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CHAPTER I

Statistics applied to molecules

§ 1. The Maxwell–Boltzmann velocity distribution

In statistical mechanics one tries to use statistical methods to understand the gross properties of gases, liquids and solids. Statistical methods are almost obligatory because one is studying *macroscopic* amounts of these substances—i.e. samples containing enormous numbers of molecules. These samples are so large that having individual equations for each molecule is completely out of the question. We shall see that one can get surprisingly far, very quickly, with these statistical methods so that statistical mechanics is, from the beginning, a most rewarding and worthwhile subject.

The point of departure for our whole discussion is the study of the velocity \mathbf{v} of a gas molecule. This is studied by introducing what is called the *Maxwell–Boltzmann velocity distribution function* which we denote by

$$f(\mathbf{v}^2), \quad \text{where } \mathbf{v} = v_x\mathbf{i} + v_y\mathbf{j} + v_z\mathbf{k} \quad (1.1)$$

The precise property that defines f is the following

Definition (Maxwell–Boltzmann velocity distribution function) *The number of molecules, per unit volume, with velocities in the range \mathbf{v} to $\mathbf{v} + d\mathbf{v}$ is given by*

$$f(\mathbf{v}^2)dv_xdv_ydv_z, \quad \text{where } d\mathbf{v} = dv_x\mathbf{i} + dv_y\mathbf{j} + dv_z\mathbf{k} \quad (1.2)$$

At first sight this definition may not seem to be sufficient to specify f properly but we shall now see that it actually does allow us to derive a concrete expression for f .

A crucial matter to realise is that we are analysing a finite volume V of gas in equilibrium with its surroundings. This being so we point out that, for a gas in equilibrium there is *no preferred direction* for the velocities of the molecules, indeed, if there were such a direction molecules would accumulate in some part of V and create a higher pressure there than elsewhere. This contradicts the assumption of equilibrium since, in equilibrium, the pressure of a gas is the same everywhere.

Hence we assume, and thus require, the function f to be *isotropic* as a function of \mathbf{v} ; this means that we get the *same* dependence on velocity if we just move in one direction in velocity space. Mathematically speaking this asserts that if we fix two of v_x, v_y and v_z and vary the third that the resulting function is always the same and equal to $f(V)$ where V stands for one of v_x, v_y or v_z .

A second assumption is that the probability that a molecule have some given value for its v_x component is independent of probability that it have some given value for its v_y component and so on. Then since independent probabilities *factorise* we have

$$\begin{aligned} f(\mathbf{v}^2) &= Af(v_x)f(v_y)f(v_z) \\ \Rightarrow f(v_x^2 + v_y^2 + v_z^2) &= Af(v_x)f(v_y)f(v_z) \end{aligned} \quad (1.3)$$

where A is a possible constant which we need to make an allowance for. Actually it will turn out that we don't ever need to compute A as we can find f completely by the method presented below.

Equation 1.3 above is very important since it is enough, by itself, to determine the basic functional form of f . We proceed at once with this determination: Let $v_z = 0$ and define

$$X = v_x^2, \quad Y = v_y^2 \quad (1.4)$$

The 1.3 becomes

$$f(X + Y) = Cf(X)f(Y), \quad \text{where } C = Af(0) \quad (1.5)$$

Next if we differentiate this equation with respect to X or instead, with respect to Y , we obtain the pair of equations

$$\begin{aligned} f'(X + Y) &= Cf'(X)f(Y) \\ f'(X + Y) &= Cf(X)f'(Y) \end{aligned} \quad (1.6)$$

The LHS's are the same so we can conclude that

$$\begin{aligned} Cf'(X)f(Y) &= Cf(X)f'(Y) \\ \Rightarrow \frac{f'(X)}{f(X)} &= \frac{f'(Y)}{f(Y)} \end{aligned} \quad (1.7)$$

But $f'(X)/f(X)$ is a function of X only and $f'(Y)/f(Y)$ is a function of Y only so the only way in which these two expressions can be equal is if they are both *constant*. Thus we must have

$$\frac{f'(X)}{f(X)} = \frac{f'(Y)}{f(Y)} = -\lambda, \quad \lambda \text{ a constant} \quad (1.8)$$

But now we can easily find f for we have

$$\begin{aligned}\frac{df(X)}{dX} &= -\lambda f(X) \\ \Rightarrow f(X) &= C \exp[-\lambda X]\end{aligned}\tag{1.9}$$

and we have found f .

Returning to the velocity \mathbf{v} this means we are now allowed to write

$$f(\mathbf{v}^2) = C \exp[-\lambda \mathbf{v}^2]\tag{1.10}$$

It remains to find the actual values of the constants C and λ . We do this by showing how f is related to two separate physical properties of the gas:

- (i) The number of molecules per unit volume
- (ii) The pressure in the gas.

First if N denotes the number of molecules per unit volume inside our volume V then, since every molecule must have some velocity, however big or small, we have

$$\int d^3\mathbf{v} f(\mathbf{v}^2) = N\tag{1.11}$$

Secondly, if P is the pressure inside V and T is the temperature, then the *ideal or perfect gas law* says that

$$\begin{aligned}PV &= RT \\ \text{or } P &= NkT, \quad \text{where } k \text{ is Boltzmann's constant}\end{aligned}\tag{1.12}$$

These two conditions 1.11 and 1.12 provide us with two equations that f must satisfy and serve to determine the constants C and λ as we shall see below.

Let us find the first of these two equations—the one that is implied by 1.11—using $f(\mathbf{v}^2) = C \exp[-\lambda \mathbf{v}^2]$, 1.11 gives

$$C \int d^3\mathbf{v} \exp[-\lambda \mathbf{v}^2] = N\tag{1.13}$$

But spelling things out in more detail we know that

$$d^3\mathbf{v} = dv_x dv_y dv_z, \quad \text{and } \mathbf{v}^2 = v_x^2 + v_y^2 + v_z^2\tag{1.14}$$

so a more explicit version this integral condition is

$$\begin{aligned}C \int_{-\infty}^{\infty} dv_x dv_y dv_z \exp[-\lambda(v_x^2 + v_y^2 + v_z^2)] &= N \\ \Rightarrow C \int_{-\infty}^{\infty} dv_x dv_y dv_z \exp[-\lambda v_x^2] \exp[-\lambda v_y^2] \exp[-\lambda v_z^2] &= N \\ \Rightarrow C \int_{-\infty}^{\infty} dv_x \exp[-\lambda v_x^2] \int_{-\infty}^{\infty} dv_y \exp[-\lambda v_y^2] \int_{-\infty}^{\infty} dv_z \exp[-\lambda v_z^2] &= N\end{aligned}\tag{1.15}$$

But all three integrals appearing above are the same (they only differ in the *name* they give to their integration variable) and equal to

$$\int_{-\infty}^{\infty} dz \exp[-\lambda z^2] \quad (1.16)$$

Now this is a standard integral and one can verify from integration tables that it is given by

$$\int_{-\infty}^{\infty} dz \exp[-\lambda z^2] = \sqrt{\frac{\pi}{\lambda}} \quad (1.17)$$

Hence our condition simplifies to

$$\begin{aligned} C \left\{ \sqrt{\frac{\pi}{\lambda}} \right\}^3 &= N \\ \Rightarrow C \left(\frac{\pi}{\lambda} \right)^{3/2} &= N \end{aligned} \quad (1.18)$$

This equation we leave as it is fine as it stands and we are now ready to obtain our second condition. We do this by expressing the pressure P as a suitable integral involving f .

The pressure is obtained by examining what happens when molecules bounce off the side of volume V . Take a unit area perpendicular to the x direction. The molecules incident on this unit area in unit time lie on a cylinder of length v_x and base of unit area. The change in momentum on bouncing off the unit area for each molecule is

$$mv_x - (-mv_x) = 2mv_x \quad (1.19)$$

The number of molecules with velocity in the range \mathbf{v} to $\mathbf{v} + d\mathbf{v}$ reflected per unit time is the number of molecules in this cylinder which is

$$\begin{aligned} f(\mathbf{v}^2) dv_x dv_y dv_z \times \text{volume of the cylinder} \\ = f(\mathbf{v}^2) dv_x dv_y dv_z \times v_x \times 1 \end{aligned} \quad (1.20)$$

The resulting total momentum change, per unit time, from all these molecules is

$$2mv_x \times f(\mathbf{v}^2) dv_x dv_y dv_z v_x = 2mv_x^2 f(\mathbf{v}^2) dv_x dv_y dv_z \quad (1.21)$$

Now if we integrate over all possible values of v_x , v_y and v_z we will have the complete momentum change, per unit time, per unit area, and this is just the pressure P . In other

words we have deduced that ¹

$$P = \int_0^\infty dv_x \int_{-\infty}^\infty dv_y \int_{-\infty}^\infty dv_z 2mv_x^2 f(\mathbf{v}^2) \quad (1.22)$$

Using the expression for f we get

$$\begin{aligned} P &= C \int_0^\infty dv_x (2mv_x^2) \exp[-\lambda v_x^2] \int_{-\infty}^\infty dv_y \exp[-\lambda v_y^2] \int_{-\infty}^\infty dv_z \exp[-\lambda v_z^2] \\ &= C \int_0^\infty dv_x (2mv_x^2) \exp[-\lambda v_x^2] \left(\sqrt{\frac{\pi}{\lambda}} \right)^2, \quad \text{using 1.17 twice} \end{aligned} \quad (1.23)$$

It remains to do the integral

$$\int_0^\infty dv_x (2mv_x^2) \exp[-\lambda v_x^2] \quad (1.24)$$

This integral is also standard and is given by the formula ²

$$\int_0^\infty dz z^2 \exp[-\lambda z^2] = \frac{1}{4} \frac{\sqrt{\pi}}{\lambda^{3/2}} \quad (1.27)$$

The resulting expression for the pressure P is

$$P = \frac{mC}{2} \frac{\pi^{3/2}}{\lambda^{5/2}} \quad (1.28)$$

¹ Note that the v_x integration begins at 0 whereas the v_y and v_z integrations begin at $-\infty$. This is because if we include negative values in the v_x integration we are including molecules which are heading away from the wall and we do not want this. Note too that we shouldn't really allow velocities to go to $\mp\infty$ since relativity shows that velocities cannot exceed the velocity of light c . We could correct for this but it would make little numerical difference so we leave things as we are; in any case we would also have to use relativistic masses and think about other relativistic effects if we pursued this matter properly.

² The reader who wishes can derive this formula from the earlier one 1.17: If one differentiates both sides of 1.17 with respect to λ one obtains the equation

$$-\int_{-\infty}^\infty dz z^2 \exp[-\lambda z^2] = -\frac{1}{2} \frac{\sqrt{\pi}}{\lambda^{3/2}} \quad (1.25)$$

from which we deduce that

$$\int_0^\infty dz z^2 \exp[-\lambda z^2] = \frac{1}{4} \frac{\sqrt{\pi}}{\lambda^{3/2}} \quad (1.26)$$

to which we must add our previous equation 1.18 giving the pair

$$\begin{aligned} C \left(\frac{\pi}{\lambda} \right)^{3/2} &= N \\ P &= \frac{mC}{2} \frac{\pi^{3/2}}{\lambda^{5/2}} = NkT \end{aligned} \quad (1.29)$$

These are a simple matter to solve: if we substitute for N from the first into the second we quickly find λ and then in turn we obtain C . The result is that

$$\begin{aligned} \lambda &= \frac{m}{2kT} \\ C &= N \left(\frac{m}{2\pi kT} \right)^{3/2} \end{aligned} \quad (1.30)$$

So the completed function f is given by

$$f(\mathbf{v}^2) = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] \quad (1.31)$$

and this is called the *Maxwell-Boltzmann velocity distribution function*. The reader should note that we derived its precise form with surprisingly little starting information. It is now time to see what we can learn from f .

§ 2. Equipartition of energy and average gas velocities

Now that we have a probability distribution function we can begin the calculation of various probabilistically defined averages. One of the most important of these is the average kinetic energy of a gas molecule.

First we define what we mean by the average of any physical quantity. $Q(\mathbf{v})$, say, that depends on \mathbf{v} . The average of Q , per gas molecule, is denoted by $\langle Q \rangle$ where $\langle Q \rangle$ is defined by

$$\langle Q \rangle = \frac{1}{N} \int Q(\mathbf{v}) f(\mathbf{v}^2) dv_x dv_y dv_z \quad (1.32)$$

we are interested in the case where Q is the kinetic energy E of a gas molecule so that we have

$$E = \frac{m\mathbf{v}^2}{2} \quad (1.33)$$

giving

$$\langle E \rangle = \frac{1}{N} \int \frac{m\mathbf{v}^2}{2} f(\mathbf{v}^2) dv_x dv_y dv_z \quad (1.34)$$

Using f we find that

$$\begin{aligned} \langle E \rangle &= \frac{1}{N} \int \frac{m\mathbf{v}^2}{2} N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] dv_x dv_y dv_z \\ &= \left(\frac{m}{2\pi kT} \right)^{3/2} \int \frac{m(v_x^2 + v_y^2 + v_z^2)}{2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] dv_x dv_y dv_z \end{aligned} \quad (1.35)$$

Now the integration in 1.35 splits up into three separate integrals the first of which is

$$\left(\frac{m}{2\pi kT} \right)^{3/2} \int \frac{mv_x^2}{2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] dv_x dv_y dv_z \quad (1.36)$$

and the other two are just obtained by replacing the term $mv_x^2/2$ by $mv_y^2/2$ and $mv_z^2/2$ respectively. However it is possible to read off from this first integral the fact this it is equal to the average of just *the x-component of the kinetic energy*, i.e. we have

$$\left\langle \frac{mv_x^2}{2} \right\rangle = \left(\frac{m}{2\pi kT} \right)^{3/2} \int \frac{mv_x^2}{2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] dv_x dv_y dv_z \quad (1.37)$$

Before we evaluate this integral we make the very important observation that *all three of these integrals are equal*; in other words we have

$$\left\langle \frac{mv_x^2}{2} \right\rangle = \left\langle \frac{mv_y^2}{2} \right\rangle = \left\langle \frac{mv_z^2}{2} \right\rangle \quad (1.38)$$

This equality follows from writing down the three integrals in full and noting that one can turn any one of them into any other one by simply appropriately renaming the variables.

This property 1.38 is very important in statistical mechanics and is referred to as the *equipartition of kinetic energy* for gas molecules. The term *degree of freedom* is also used to refer to independent possible motions of a molecule; for a free gas molecule there are three independent motions corresponding to the three independent directions x , y and z . A free gas molecule is therefore said to have three degrees of freedom. Equipartition of energy is also frequently stated as the assertion each degree of freedom has the same (average) energy.

Our final task in the matter of equipartition is to actually calculate the relevant integral in 1.36. Now if we write

$$I = \left\langle \frac{mv_x^2}{2} \right\rangle = \left(\frac{m}{2\pi kT} \right)^{3/2} \int \frac{mv_x^2}{2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] dv_x dv_y dv_z \quad (1.39)$$

then

$$\langle E \rangle = 3I \quad (1.40)$$

But I is made up of the two integrals we already know: in fact I is equal to

$$\left(\frac{\lambda}{\pi}\right)^{3/2} \frac{m}{2} \int_{-\infty}^{\infty} dv_x v_x^2 \exp[-\lambda v_x^2] \int_{-\infty}^{\infty} dv_y \exp[-\lambda v_y^2] \int_{-\infty}^{\infty} dv_z \exp[-\lambda v_z^2] \quad (1.41)$$

where $\lambda = \frac{m}{2kT}$

and checking back to our previous integrals we quickly see that

$$\begin{aligned} \left(\frac{\lambda}{\pi}\right)^{3/2} \frac{m}{2} \int_{-\infty}^{\infty} dv_x v_x^2 \exp[-\lambda v_x^2] &= m \left(\frac{\lambda}{\pi}\right)^{3/2} \int_0^{\infty} dv_x v_x^2 \exp[-\lambda v_x^2] \\ &= m \left(\frac{\lambda}{\pi}\right)^{3/2} \int_0^{\infty} dz z^2 \exp[-\lambda z^2] \\ &= \frac{m}{4} \left(\frac{\lambda}{\pi}\right)^{3/2} \frac{\sqrt{\pi}}{\lambda^{3/2}}, \quad \text{using 1.27} \end{aligned} \quad (1.42)$$

and

$$\begin{aligned} \int_{-\infty}^{\infty} dv_y \exp[-\lambda v_y^2] &= \int_{-\infty}^{\infty} dv_z \exp[-\lambda v_z^2] = \int_{-\infty}^{\infty} dz \exp[-\lambda z^2] \\ &= \sqrt{\frac{\pi}{\lambda}}, \quad \text{using 1.17} \end{aligned} \quad (1.43)$$

Hence we calculate that

$$\begin{aligned} I &= \frac{m}{4} \left(\frac{\lambda}{\pi}\right)^{3/2} \frac{\sqrt{\pi}}{\lambda^{3/2}} \sqrt{\frac{\pi}{\lambda}} \sqrt{\frac{\pi}{\lambda}} \\ \Rightarrow I &= \frac{m}{4\lambda} = \frac{kT}{2}, \quad \text{since } \lambda = \frac{m}{2kT} \end{aligned} \quad (1.44)$$

But $\langle E \rangle = 3I$ so the average kinetic energy of a gas molecule of mass m at a temperature T is given by

$$\langle E \rangle = \frac{3kT}{2} \quad (1.45)$$

and we draw attention to the fact that $\langle E \rangle$ is *independent* of the mass m and only depends on the temperature T .

Now the speed at which the kinetic energy *equals* $\langle E \rangle$ is called the *root mean square velocity* (though it is a speed rather than a velocity) and it is denoted by v_{rms} . Hence if a molecule moves with velocity \mathbf{v}_{rms} we have

$$\frac{m\mathbf{v}_{rms}^2}{2} = \frac{3kT}{2} \quad (1.46)$$

Thus

$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad (1.47)$$

and we note that v_{rms} does depend on the molecular mass m .

Example *Escape velocities and the absence of atmosphere on the Moon*

It can be very interesting to compare v_{rms} with the *escape velocity* v_e for an object from a planetary body. As an example let us do that here for the Moon.

If a body of mass m is on a planetary body of mass M and radius R then its escape velocity v_e is reached when its kinetic energy is as big as its potential energy—i.e. v_e is given by the equation

$$\begin{aligned} \frac{1}{2}mv_e^2 &= \frac{GMm}{R}, \quad (G \text{ is Newton's gravitational constant}) \\ \Rightarrow v_e &= \sqrt{\frac{2GM}{R}} \end{aligned} \quad (1.48)$$

Now suppose that the Moon has an atmosphere and that at the middle of the Lunar day the temperature has reached ³ 400^0K . Next we shall calculate and compare v_e and v_{rms} for a molecule of mass $m = 1.8 \times 10^{-25} g$. We need the following data for the various constants in the formulae

$$k = 1.38 \times 10^{-16} \text{ erg/degree}, \quad \frac{GM}{R} = 2.79 \times 10^{10}, \quad (\text{For the Moon}) \quad (1.49)$$

With this information we find that

$$\begin{aligned} v_e &= \sqrt{2 \times 2.79 \times 10^{10}} = 2.36 \times 10^5 \text{ cm/sec} \\ v_{rms} &= \sqrt{\frac{3 \times 1.38 \times 10^{-16} \times 400}{1.8 \times 10^{-25}}} = 9.59 \times 10^5 \text{ cm/sec} \end{aligned} \quad (1.50)$$

Hence

$$v_{rms} \gg v_e \quad (1.51)$$

and we expect that any atmosphere present on the Moon in the remote past to have leaked away. This is not the case for the Earth of course as the peak temperature is much less than 400^0K and the escape velocity is about $11.17 \times 10^5 \text{ cm/sec}$.

³ This is somewhat larger than the peak temperature ever reached on the Moon but remember that if there were an atmosphere a greenhouse effect would exist and raise the peak temperature by a certain amount.

§ 3. Specific heats of gases and solids

Equipartition of energy is able to explain an otherwise very puzzling experimental observation: this is that the specific heat (at constant volume) of all monatomic gases⁴ are nearly the same.

Example *The specific heat C_V of a monatomic gas*

This is how the calculation of the specific heat is done. We take a mole of a monatomic gas at temperature T . Now by equipartition the kinetic energy of each molecule is $3kT/2$, but a mole contains N_A molecules where N_A is Avogadro's number; hence the total energy of the gas is

$$\frac{3kT}{2}N_A \quad (1.52)$$

Now we raise the temperature by 1^0 thereby increasing the energy to

$$\frac{3k(T+1)}{2}N_A \quad (1.53)$$

The energy need to bring about this 1^0 rise in temperature is therefore

$$\begin{aligned} \frac{3k(T+1)}{2}N_A - \frac{3kT}{2}N_A &= \frac{3}{2}N_Ak \\ &= C_V, \quad \text{the specific heat of the gas} \end{aligned} \quad (1.54)$$

This formula for the specific heat

$$C_v = \frac{3}{2}N_Ak \quad (1.55)$$

or

$$\frac{C_v}{N_Ak} = 1.5$$

is obeyed very well by monatomic gases—cf. the table of measurements below

Gas	C_v/N_Ak
He	1.50
Ne	1.50
Ar	1.50
Kr	1.50
Xe	1.50

**The specific heats of the inert gases
measured at 1 atmosphere and $25^0 C$**

⁴ The inert gases Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr) and Xeon (Xe) are all monatomic.

This formula does *not work* for diatomic gases. The reason that this formula is restricted to monatomic gases is that for molecules with more than 1 atom there are additional degrees of freedom associated with inter-atomic oscillations and rotation of the molecules and these degrees of freedom must also have average energy $kT/2$; there are also considerable modifications due to quantum mechanics which tells us that these non-kinetic energies are *quantised*.

Actually we can also illustrate how additional degrees of freedom affect calculations of specific heat by looking at the specific heats of *solids*. We turn to this now.

Example *The specific heat of solids*

A solid has *six* degrees of freedom rather than three. This is because have three potential energy degrees of freedom as well as their three kinetic ones. Since equipartition says that each degree of freedom has energy $kT/2$ —then the average energy $\langle E \rangle$ of a solid molecule is given by

$$\langle E \rangle = 6 \cdot \frac{kT}{2} = 3kT \quad (1.56)$$

so the specific heat C_V for solids is twice that for gases giving us

$$C_V = 3N_A k \quad (1.57)$$

and this formula is obeyed well by solids.

§ 4. The most probable velocity of a gas molecule

In addition to the *average* speed v_{rms} of a gas molecule one can introduce the most probable speed which we write as \tilde{v} . We shall now see that \tilde{v} is close, but not identical, to the average speed v_{rms} .

Let us start with the Maxwell–Boltzmann distribution function f . Then the molecules with speed (remember we are disregarding direction of velocities now) in the range v to $v + dv$, lie in a shell in velocity space of radius v and thickness dv . hence the number of molecules, per unit volume, with speed in this range is

$$\begin{aligned} f(v) \times \{\text{the volume of this shell}\} \\ = f(v)4\pi v^2 dv \end{aligned} \quad (1.58)$$

We now *define* the most probable velocity \tilde{v} as the velocity that *maximises* this number. In other words simple calculus tells us that it is the speed for which we have

$$\begin{aligned} \frac{d}{dv}(4\pi v^2 f(v)) &= 0 \\ \Rightarrow 8\pi v f(v) + 4\pi v^2 f'(v) &= 0 \\ \Rightarrow 2f(v) + v f'(v) &= 0 \end{aligned} \quad (1.59)$$

Now we substitute in

$$f(v) = N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] \quad (1.60)$$

obtaining

$$2N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] + v \left(-\frac{mv}{kT} \right) N \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m\mathbf{v}^2}{2kT} \right] = 0 \quad (1.61)$$

which simplifies to

$$\begin{aligned} 2 - \frac{mv^2}{kT} &= 0 \\ \Rightarrow v &= \sqrt{\frac{2kT}{m}} \end{aligned} \quad (1.62)$$

So we see that the most probable velocity \tilde{v} is given by

$$\tilde{v} = \sqrt{\frac{2kT}{m}} \quad (1.63)$$

but that the average velocity v_{rms} is given by

$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad (1.64)$$

We note that $v_{rms} \neq \tilde{v}$ but, numerically, they are of the same *order of magnitude*. It may be useful to notice that they have a simple temperature-independent ratio, namely

$$\frac{\tilde{v}}{v_{rms}} = \sqrt{\frac{2}{3}} = 0.816 \quad (1.65)$$

Thus v_{rms} is about 19% bigger than \tilde{v} .

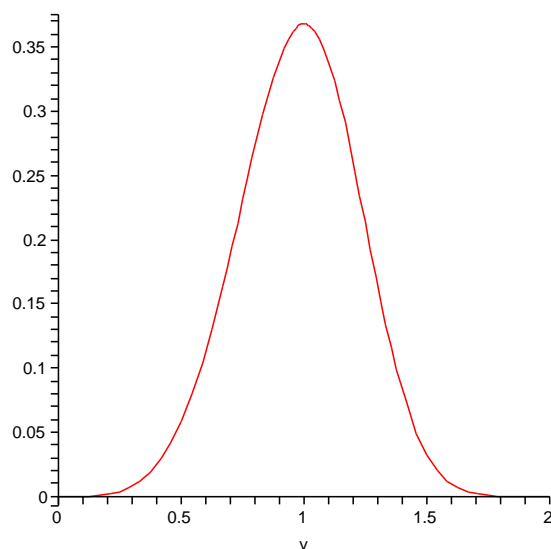
From the above calculation one sees that the key function in determining most probable velocity \tilde{v} is the combination

$$\mathbf{v}^2 f(\mathbf{v}^2)$$

rather than

$$f(\mathbf{v}^2)$$

itself. It is useful, therefore, to know the shape of the graph of $v^2 f(v^2)$ and so we display it below



The graph of $v^2 f(v^2)$.

The scales in the above graph are in arbitrary units—we are just displaying the shape—but the maximum, as we have just calculated, occurs at $v = \tilde{v}$.

If we choose the gas to be Helium at $300^0 K$ then, using the fact that $k = 1.38 \times 10^{-16}$ *erg/degree* and, for Helium, $m = 6.64 \times 10^{-24} g$, we readily calculate that

$$\begin{aligned}\tilde{v} &= \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2 \times 1.38 \times 10^{-16} \times 300}{6.64 \times 10^{-24}}} \\ &= 1.1166 \times 10^5 \text{ cm/sec} \\ &\equiv 4,020 \text{ kph} \\ &\equiv 2,512 \text{ mph}\end{aligned}$$

To end this section let us quote some v_{rms} values: we know that

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

and that the molecular masses of Helium, Nitrogen and Oxygen are given by

$$\begin{aligned}m_{He} &= 6.64 \times 10^{-24} g \\ m_{N_2} &= (28/4) \cdot m_{He} \\ m_{O_2} &= (32/4) \cdot m_{He}\end{aligned}$$

and so, with $T = 300^0 K$, we compute the v_{rms} values shown in the table below

Gas	v_{rms} at $T = 300^0 K$
He	4,923 <i>kph</i>
N	1,860 <i>kph</i>
O	1,740 <i>kph</i>

Some values of v_{rms} for gases at $300^0 K$

We see that a typical gas molecule at room temperature is a very fast moving object.

§ 5. The mean free path of a gas molecule

The picture that we now have of a typical gas is quite dramatic. It consists of large numbers of molecules which, at room temperature, are moving around with speeds of thousands of kilometres per hour. This being the case molecular collisions are continually occurring and we would now like to calculate the average distance a molecule can be expected to travel before undergoing a collision. This distance is called the *mean free path* and is denoted by λ .

To find λ we reason as follows: Let a molecule be represented by a sphere of diameter d . Then, in time dt , the probability of one collision is the probability of finding a molecule within a cylinder of radius d and length $v_{rms}dt$ —this is because a molecule traces out a cylinder of this radius and length in dt seconds. Hence the average number of collisions as the molecule traces out this cylinder is

$$\begin{aligned} N \times \text{volume of this cylinder} \\ = N \times (\pi d^2) \times (v_{rms}dt) \end{aligned} \quad (1.66)$$

These collisions take place during a total time dt so the number of collisions per sec is just

$$\frac{N \times (\pi d^2) \times (v_{rms}dt)}{dt} = N\pi d^2 v_{rms} \quad (1.67)$$

But, if λ is the mean free path, we can write

$$\begin{aligned} \lambda &= \frac{\text{distance travelled in unit time}}{\text{number of collisions in unit time}} \\ &= \frac{v_{rms} \times 1}{N\pi d^2 v_{rms}} \\ &= \frac{1}{N\pi d^2} \end{aligned} \quad (1.68)$$

So we have our formula λ which is

$$\lambda = \frac{1}{N\pi d^2} \quad (1.69)$$

One should note that λ is independent of both the temperature T and the density ρ .

Example *A simple molecular look at electrical resistance*

We can use ideas from statistical mechanics, including the notion of mean free path. to give a rough model for the electrical resistance of a typical conductor.

Inside a conductor, through which a current is passing, there is a current density \mathbf{J} and an electric field \mathbf{E} and, moreover, these two vectors are proportional so that we have

$$\mathbf{J} = \sigma \mathbf{E} \quad (1.70)$$

But \mathbf{J} is also related to the charge q and drift velocity \mathbf{v}_d via the equation

$$\mathbf{J} = N \mathbf{v}_d q \quad (1.71)$$

where N is the number of electrons per unit volume. The equation of motion for a drifting electron is

$$\begin{aligned} \frac{d}{dt}(mv_d) &= q|\mathbf{E}|, \quad \text{where } v_d = |\mathbf{v}_d| \\ \Rightarrow mv_d &= q|\mathbf{E}|t + C, \quad C \text{ a constant} \end{aligned} \quad (1.72)$$

We shall *assume* that we can take the constant C to be zero so that

$$v_d = \frac{q|\mathbf{E}|t}{m} \quad (1.73)$$

and since $\mathbf{J} = \sigma \mathbf{E}$ we obtain a formula for the conductivity σ which is

$$\sigma = \frac{Nq^2t}{m} \quad (1.74)$$

There remains the task of finding a value for t : we choose t to be the *mean free time*, i.e. the mean time between collisions. This means that

$$\frac{\lambda}{t} = v_{rms} \quad (1.75)$$

and so

$$\sigma = \frac{Nq^2}{m} \frac{\lambda}{v_{rms}} \quad (1.76)$$

However we know that

$$\lambda = \frac{1}{N\pi d^2}, \quad v_{rms} = \sqrt{\frac{3kT}{m}} \quad (1.77)$$

so

$$\sigma = \frac{q^2}{m} \frac{1}{\pi d^2} \sqrt{\frac{m}{3kT}} \quad (1.78)$$

which is a simple, rough and ready, expression for the electrical conductivity involving only molecular quantities.

§ 6. The onset of quantum corrections to $f(\mathbf{v}^2)$.

We would like to be able to understand when our arguments will have to take account of quantum effects—so far we have ignored any quantum mechanical considerations. We need a criterion for the onset of quantum effects and we shall take this to be the following: *quantum effects cannot be ignored when the quantum mechanical wavelength⁵ λ_q is of the same order of magnitude as the average separation s of the gas molecules.*

Now the quantum mechanical wavelength λ_q is related to the momentum, which we shall take to be given by $m\tilde{v}$, of a gas molecule by the usual Planck relation

$$\lambda_q = \frac{\hbar}{m\tilde{v}} \quad (1.79)$$

And, since

$$\tilde{v} = \sqrt{\frac{2kT}{m}} \quad (1.80)$$

we obtain

$$\begin{aligned} \lambda_q &= \frac{\hbar}{m} \sqrt{\frac{m}{2kT}} \\ \Rightarrow \lambda_q &= \frac{\hbar}{\sqrt{2mkT}} \end{aligned} \quad (1.81)$$

Next let the average separation of the gas molecules be s then for quantum effects to be negligible we require

$$s \gg \lambda_q \quad (1.82)$$

But s can be calculated by considering there to be a total of N_T molecules inside a volume V so that they completely fill it giving

$$\begin{aligned} V &= N_T s^3 \\ \Rightarrow s &= \left(\frac{N_T}{V} \right)^{-1/3} \\ \Rightarrow s &= N^{-1/3} \end{aligned} \quad (1.83)$$

But, for a perfect gas,

$$\begin{aligned} P &= NkT \\ \Rightarrow N &= \frac{P}{kT} \end{aligned} \quad (1.84)$$

⁵ Usually the quantum mechanical wavelength is denoted by λ , but we have already used λ for the mean free path, so we use λ_q for the quantum mechanical wavelength

Hence our condition for validity of the classical approximation (i.e. for ignoring quantum effects) is

$$\frac{\lambda_q}{s} \ll 1 \quad (1.85)$$

and using $\lambda_q = \hbar/\sqrt{2mkT}$ and $s = N^{-1/3}$ we get

$$\frac{\hbar N^{1/3}}{\sqrt{2mkT}} \ll 1 \quad (1.86)$$

but $N = P/kT$ so this makes the condition become

$$\frac{\hbar}{\sqrt{2mkT}} \left(\frac{P}{kT} \right)^{1/3} \ll 1 \quad (1.87)$$

which is the same as

$$\frac{\hbar}{2mk} \ll \frac{\sqrt{T}}{P^{1/3}} (kT)^{1/3} = \left(\frac{k}{P} \right)^{1/3} T^{5/6} \quad (1.88)$$

Hence, by taking the 6/5th root of this relation, we can state our condition for validity of the classical approximation to be a lower bound on the temperature, namely

$$T \gg \left\{ \frac{\hbar}{\sqrt{2mk}} \left(\frac{P}{k} \right)^{1/3} \right\}^{6/5} \quad (1.89)$$

and this, though slightly ugly, is the condition we were after.

Contents

CHAPTER I

Statistics applied to molecules	1
§ 1 <i>The Maxwell–Boltzmann velocity distribution</i>	1
§ 2 <i>Equipartition of energy and average gas velocities</i>	6
§ 3 <i>Specific heats of gases and solids</i>	10
§ 4 <i>The most probable velocity of a gas molecule</i>	11
§ 5 <i>The mean free path of a gas molecule</i>	14
§ 6 <i>The onset of quantum corrections to $f(\mathbf{v}^2)$.</i>	16