

Ideal gases

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1. Classical ideal gas

A classical gas is generally referred to as a gas in which its molecules move freely in space; namely, the mean separation between the molecules is \gg the size of a molecule. In this case, the forces between the molecules (when they are separated far from each other) are very weak: **the potential energy of interaction between molecules is negligible compared to the kinetic energy of the motion.**

In this case, we need not worry about the potential energy, but only about the kinetic energy of the molecules. According to QM, the kinetic energy **of a single molecule**, can take discrete values:

$$E_1, E_2, E_3, \dots E_r, \dots$$

These correspond to the quantum states of the molecule: $1, 2, \dots, r, \dots$

Consider now N molecules occupying a volume V . The gas assume a temperature T . When looking at the individual molecules, we find that n_1 are in state 1, n_2 in state 2, ... n_r are in state r .

The number n_r is called the **occupation number** of state r . The total number of molecules (at all energy levels) is N , and therefore

$$N = \sum_r n_r, \quad (1)$$

and the total energy of the gas is

$$E_{tot} = E = \sum_r n_r E_r. \quad (2)$$

Of course, studying the properties of the gas is best done using the partition function. This is easily done, as we neglect interactions, and thus we can start by considering the partition function for a single particle, which is defined by

$$Z_1 \equiv \sum_r e^{-\beta E_r}, \quad \beta \equiv \frac{1}{k_B T} \quad (3)$$

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What about the partition function of N molecules ? Here we need to be careful, since the gas molecules are **indistinguishable** from each other.

As a first (naive) attempt, we may try to simply multiply the partition function of a single molecule: e.g., if $N = 3$ molecules, we may write

$$Z_3 = \sum_r e^{-\beta E_r} \sum_q e^{-\beta E_q} \sum_s e^{-\beta E_s} = \sum_r \sum_q \sum_s e^{-\beta(E_r+E_q+E_s)} \quad ? \quad (4)$$

unfortunately, this is **WRONG**. This can be seen if we are regrouping the terms, to write

$$Z_3 = \sum_{r,(s=q=r)} e^{-3\beta E_r} + \sum_{r,(q=r)} \sum_{s,(s \neq r)} e^{-\beta(2E_r+E_s)} + \sum_r \sum_q \sum_{s,(s \neq q \neq r)} e^{-\beta(E_r+E_s+E_q)} \quad (5)$$

The first term corresponds to all 3 particles being in the same state: $r = q = s$. The middle term corresponds to 2 molecules being in the same state, but the third being in a different state; and the last corresponds for each molecule being in a different state.

The problem is, that we over-counted the states: since we cannot distinguish between the molecules, we need to be careful about how many states there really are.

- In the first term, there is no problem (the coefficient = 1).
- In the middle term, 2 of the 3 particles are in the same state: there are 3 options (AB, AC and BC), and so we must divide this term by 3.
- In the third term, there are 3! ways to put 3 particles in three different states; thus, we need to divide by 3!.

Thus, our partition function should look like

$$Z_3 = \sum_{r,(s=q=r)} e^{-3\beta E_r} + \frac{1}{3} \sum_{r,(q=r)} \sum_{s,(s \neq r)} e^{-\beta(2E_r+E_s)} + \frac{1}{3!} \sum_r \sum_q \sum_{s,(s \neq q \neq r)} e^{-\beta(E_r+E_s+E_q)} \quad (6)$$

This of course needs to be generalized to N molecules, in which

$$Z = \sum_r e^{-N\beta r} + \dots + \frac{1}{N!} \sum_{r_1}^{\text{all different states}} \dots \sum_{r_N} e^{-\beta(E_{r_1}+E_{r_2}+\dots+E_{r_N})} \quad (7)$$

In the discussion here, we are going to restrict ourselves to the **classical** regime. In this regime, **the probability of a state to be occupied by more than one molecule is very small**. This means that the **number of states is \gg number of molecules**.

Most sates will be, of course, empty; a few will contain one molecule, and negligible number contains more than one molecule.

In this regime, only the last term in Equation 7 is important. Thus, the coefficients of all other terms are not so interesting; we can put all of them to be $1/N!$, and write the partition function as

$$Z = \frac{1}{N!} \left(\sum_r e^{-N\beta r} + \dots + \sum_{r_1}^{\text{all different states}} \dots \sum_{r_N} e^{-\beta(E_{r_1}+E_{r_2}+\dots+E_{r_N})} \right) \quad (8)$$

We can re-group the terms back together (but now with the correct coefficient), to get

$$Z = \frac{1}{N!} \sum_{r_1} \dots \sum_{r_N} e^{-\beta(E_{r_1}+E_{r_2}+\dots+E_{r_N})} = \frac{1}{N!} \left[\sum_r e^{-\beta E_r} \right]^N \quad (9)$$

Equation 9 is the (*approximate*) partition function for an ideal (perfect) classical gas, written in terms of the partition function of a single molecule, Z_1 .

The factor $N!$ in the denominator, arises from the fact that the molecules are **not localized**, or **indistinguishable**. This is as opposed to the paramagnet example discussed earlier, where the fact that the atoms are localized implies that we can distinguish between different atoms with the same up-spin or down-spin.

2. Calculation of the partition function

From Equation 9 we see that it is enough to find the partition function of a single molecule, Z_1 . The kinetic energy of a single molecule consists of two parts: (i) **translation** - motion of the center of of mass with respect to the walls; and (ii) **internal motion**, of rotations and vibrations of the molecules. We can thus write the energy of a molecule as

$$E_r = E_s^{tr} + E_\alpha^{int}. \quad (10)$$

We replaced the label r with s that specifies the state of the translational motion, and α - the state of internal motion.

We can thus write the partition function for a single molecule as

$$Z_1 = \sum_r e^{-\beta E_r} = \sum_s \sum_\alpha e^{-\beta(E_s^{tr}+E_\alpha^{int})} = \sum_s e^{-\beta E_s^{tr}} \sum_\alpha e^{-\beta E_\alpha^{int}} = Z_1^{tr} Z_1^{int} \quad (11)$$

Equation 11 enables us to consider the energy associated with translational and internal motion separately. This is very important, since Z_1^{tr} is the same (up to the mass m) for **any**

ideal classical gas, irrespective of its internal structure. On the other hand, Z^{int} depends on the internal properties of the gas molecules, and is therefore different for different gases. We note that being internal, Z_1^{int} is *independent of the volume* V .

2.1. Calculation of Z_1^{tr}

Let us now calculate Z_1^{tr} . In classical mechanics, the kinetic energy associated with the center of mass motion of a molecule of mass m is related to its momentum,

$$E^{tr} = \frac{1}{2m}p^2, \quad (12)$$

where p is the magnitude of the momentum. This equation holds both classically, and in QM. Thus, we get

$$Z_1^{tr} = \sum_s e^{-\beta E_s^{tr}} = \sum_s e^{-\frac{\beta p^2}{2m}} \quad (13)$$

We now need to evaluate the sum. I should stress that this is a problem that is often encountered in many branches of physics.

The key is to realize that the discrete states lie very close together, and thus they are very dense; hence we can replace the sum with an integral, by adding a function $f(p)$ which gives the number of discrete states between p and $p + dp$. This function is known as **the density of states**. We thus write

$$Z_1^{tr} = \sum_s e^{-\frac{\beta p^2}{2m}} = \int_0^\infty f(p) e^{-\frac{\beta p^2}{2m}} dp \quad (14)$$

2.1.1. Determination of the density of states, $f(p)$

Let us consider a cubical container, of length L (see Figure 1). In quantum mechanics, particles are described by **wave functions**, $\phi(\vec{r})$. We know though that the wave functions must disappear at the boundaries of the container. Thus, the particle's wave functions must be given by

$$\phi(\vec{r}) = Const \times \sin\left(\frac{n_1\pi}{L}x\right) \sin\left(\frac{n_2\pi}{L}y\right) \sin\left(\frac{n_3\pi}{L}z\right), \quad (15)$$

where n_1 , n_2 and n_3 are integral numbers (1,2,3...). It is trivial to check that for $x, y, z = \{0, L\}$, we get $\phi = 0$.

The wave function ϕ fulfills the three-dimensional wave equation,

$$\nabla^2\phi(\vec{r}) + k^2\phi(\vec{r}) = 0, \quad (16)$$

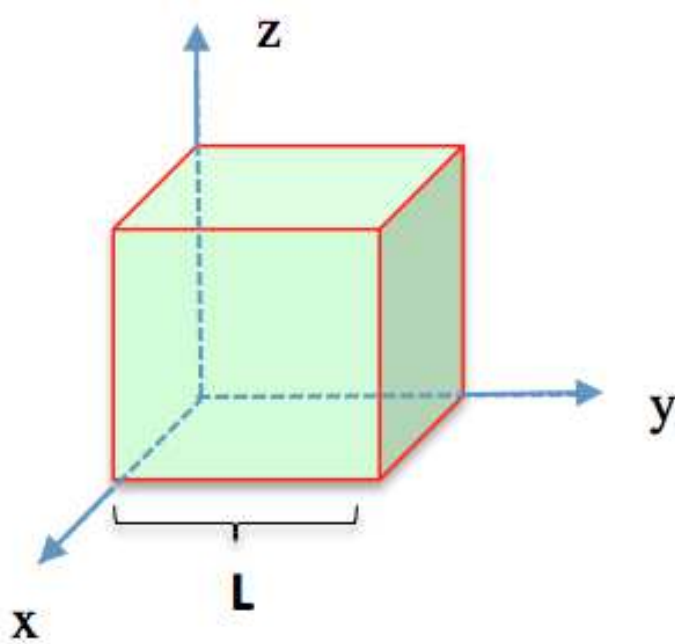


Fig. 1.— Cube enclosure

where k is the magnitude of the three-dimensional wave vector \vec{k} , describing the waves. Substituting the wave functions given in Equation 15, we get

$$k^2 = \frac{\pi^2}{L^2} (n_1^2 + n_2^2 + n_3^2) \quad (17)$$

This magnitude corresponds to wave vectors \vec{k} with components

$$\vec{k} = \left(\frac{\pi}{L}n_1, \frac{\pi}{L}n_2, \frac{\pi}{L}n_3 \right), \quad (18)$$

where again n_1 , n_2 and n_3 are integral numbers (1,2,3...).

We can now imagine for the moment how the vector \vec{k} looks like **in k space**. (see Figure 2). Since n_1 , n_2 and n_3 can get only integer values, this implies that the allowed values of \vec{k} form a cubic points with spacing between points being π/L .

The “free” volume between two points (the volume per point) in k -space is thus $(\pi/L)^3$, namely the **density** of allowed \vec{k} -vectors in k -space is $(L/\pi)^3$.

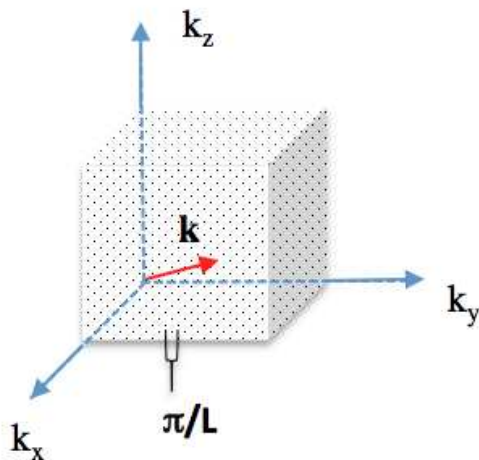


Fig. 2.— The vector \vec{k} in k -space can take only discrete values, separated by π/L .

We can calculate now the number of such normal modes of standing waves, having wave vectors whose magnitude lie in the interval k to $k + dk$. This number is equal to the number of lattice points in k -space lying between two spherical shells (centered at the origin) or radii k and $k + dk$, but only in the 1/8 of it - in which all n_1 , n_2 and n_3 are positive (see Figure 3).

This volume is $\frac{1}{8}4\pi k^2 dk$, and therefore **the number of modes of standing waves with a wave vector whose magnitude lies in the range k to $k + dk$ is**

$$f(k)dk = \frac{\frac{1}{8}4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3} = \frac{V k^2 dk}{2\pi^2}, \quad (19)$$

where $V = L^3$ is the volume of the cubic enclosed.

As a final step we recall that the momentum of a particle is related to its wave vector by

$$\vec{p} = \hbar \vec{k} = \frac{h\vec{k}}{2\pi}, \quad (20)$$

and thus

$$f(p)dp = \frac{V \times 4\pi p^2 dp}{h^3}, \quad (21)$$

where $h = 2\pi\hbar$ is Planck's constant.

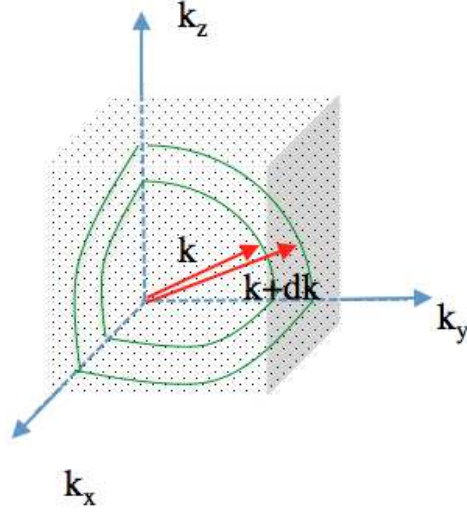


Fig. 3.— Counting the number of \vec{k} vectors in the positive (1/8) shell between $k..k + dk$ in k -space.

We can now return to Equation 14, and write

$$Z_1^{tr} = \int_0^\infty f(p) e^{-\frac{\beta p^2}{2m}} dp = \int_0^\infty \frac{V 4\pi p^2}{h^3} e^{-\frac{\beta p^2}{2m}} dp \quad (22)$$

We thus have an integral of the form

$$I_n(a) = \int_0^\infty x^n e^{-ax^2} dx \quad a > 0 \quad (23)$$

($x \rightarrow p$, $n = 2$, $a = \beta/2m$). This is a standard integral, whose solution can be found in mathematical handbooks. Specifically,

$$I_2(a) = \frac{1}{4a} \left(\frac{\pi}{a}\right)^{1/2}. \quad (24)$$

We can now finally solve for the partition function,

$$Z_1^{tr} = \frac{4\pi V}{h^3} \int_0^\infty p^2 e^{-\frac{\beta p^2}{2m}} dp = \frac{4\pi V}{h^3} \times \left[\frac{2m}{4\beta} \left(\frac{2m\pi}{\beta}\right)^{1/2} \right] = V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} = V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \quad (25)$$

Substituting this result back into the partition function of N particles (Equation 9), we get

$$Z = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} (Z_1^{int})^N \quad (26)$$

3. Helmholtz free energy

After finding an expression for the partition function, we can now work out Helmholtz free energy, $F = E - TS = -k_B T \ln Z$,

$$\begin{aligned} F = -k_B T \ln Z &= -k_B T (-\ln N! + N \ln Z_1^{tr} + N \ln Z_1^{int}) \\ &= -N k_B T \left(\ln \left(\frac{e}{N} \right) + \ln Z_1^{tr} + \ln Z_1^{int} \right) \\ &= -N k_B T \left(\ln \left[\frac{eV}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + \ln Z_1^{int} \right) \end{aligned} \quad (27)$$

where in the second line we have used Stirling's formula, $\ln N! = N \ln N - N = N \ln(N/e)$, or

$$N! = \left(\frac{N}{e} \right)^N \quad (28)$$

All thermodynamic properties of the classical gas follow from Equation 27. We note that F is automatically **extensive**: N/V cancels, and thus $F \propto N$.

We see that the Helmholtz free energy can be divided into two contributions:

$$F = F^{tr} + F^{int}, \quad (29)$$

where F^{tr} is **the same** for all ideal gases, while $F^{int} = -N k_B T \ln Z_1^{int}$ depends on the internal property of the specific gas.

Example. (I) Let us use the Helmholtz free energy to calculate the pressure. Recall that

$$F = E - TS; \quad dF = -pdV - SdT, \quad (30)$$

from which

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = - \left(\frac{\partial F^{tr}}{\partial V} \right)_T - \left(\frac{\partial F^{int}}{\partial V} \right)_T \quad (31)$$

but F^{int} depends only on the internal properties of the molecule, and not on the volume; thus the last term in Equation 31 vanishes, and we are left with

$$p = - \frac{\partial}{\partial V} \left(-N k_B T \ln \left[\frac{eV}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \right)_{T=const} \quad (32)$$

We can write the \ln term as

$$\ln \left[\frac{eV}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] = \ln V + \ln \left[\frac{e}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \quad (33)$$

and thus

$$p = -\frac{\partial}{\partial V}(-Nk_B T \ln V) = \frac{Nk_B T}{V}, \quad (34)$$

from which the Equation of state

$$pV = Nk_B T \quad (35)$$

immediately follows.

Example. (II) Energy of an ideal gas: Recall that

$$E = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{V,N} \quad (36)$$

While we could find E directly using Equation 36, we will use the Helmholtz free energy, which is easier.

$$F = -k_B T \ln Z \quad \Rightarrow \quad \ln Z = -\beta F, \quad (37)$$

or

$$\begin{aligned} E &= \left(\frac{\partial \beta F}{\partial \beta}\right)_{V,N} = \beta \left(\frac{\partial F}{\partial \beta}\right)_{V,N} + F \\ &= \beta \left(\frac{\partial F^{tr}}{\partial \beta}\right)_{V,N} + F^{tr} + \beta \left(\frac{\partial F^{int}}{\partial \beta}\right)_{V,N} + F^{int}. \end{aligned} \quad (38)$$

Using

$$F^{tr} = -\frac{N}{\beta} \ln \left[\frac{eV}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] = -\frac{N}{\beta} \left(\ln \left[\frac{eV}{N} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right] - \frac{3}{2} \ln \beta \right) \quad (39)$$

We can write

$$\frac{\partial F^{tr}}{\partial \beta} = \frac{N}{\beta^2} \ln \left[\frac{eV}{N} \left(\frac{2\pi m}{h^2} \right)^{3/2} \right] + \frac{3N}{2} \left(-\frac{1}{\beta^2} \ln \beta + \frac{1}{\beta} \cdot \frac{1}{\beta} \right) = \frac{3N}{2\beta^2} + \frac{N}{\beta^2} \ln \left[\frac{eV}{N} \left(\frac{2\pi m}{\beta h^2} \right)^{3/2} \right] \quad (40)$$

By comparing to Equation 39, we note that the last term is simply $-F^{tr}/\beta$, and we can thus write

$$E^{tr} = \beta \left(\frac{\partial F^{tr}}{\partial \beta}\right)_{V,N} + F^{tr} = \frac{3N}{2\beta} - F^{tr} + F^{tr} = \frac{3}{2} N k_B T \quad (41)$$

4. Entropy in classical gas

Using Equation 30, $dF = -pdV - SdT$, we can express the entropy in terms of Helmholtz free energy,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \quad (42)$$

We saw in Equation 29 that $F = F^{tr} + F^{int}$, and thus

$$S = - \left(\frac{\partial F^{tr}}{\partial T} \right)_{V,N} - \left(\frac{\partial F^{int}}{\partial T} \right)_{V,N} = S^{tr} + S^{int} \quad (43)$$

Thus, the entropy has contributions due to both the translational motion and the internal energy of the molecules.

Furthermore, using Equation 27 (or Equation 39),

$$F^{tr} = -Nk_B T \ln \left[\frac{eV}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right]$$

we can write

$$\begin{aligned} S^{tr} = - \left(\frac{\partial F^{tr}}{\partial T} \right)_{V,N} &= Nk_B \frac{\partial}{\partial T} \left[T \left(\ln \frac{eV}{N} + \frac{3}{2} \ln \frac{2\pi mk_B}{h^2} + \frac{3}{2} \ln T \right) \right] \\ &= Nk_B \left(\ln \frac{V}{N} + 1 + \frac{3}{2} \ln \frac{2\pi mk_B}{h^2} + \frac{3}{2} \ln T \right) + Nk_B T \cdot \frac{3}{2} \frac{1}{T} \\ &= Nk_B \left(\ln \frac{V}{N} + \frac{3}{2} \ln \frac{2\pi mk_B}{h^2} + \frac{3}{2} \ln T + \frac{5}{2} \right) \end{aligned} \quad (44)$$

Recall that we have previously shown that $S = N(c_V \ln T + k_B \ln(V/N) + Const)$; Now we got the full equation, with the value of the constant known.

When looking at Equation 44, we see that at $T \rightarrow 0$, $\ln T \rightarrow -\infty$ and thus $S^{tr} \rightarrow -\infty$, which is in contradiction, of course, with the 3rd law. Thus this equation cannot be correct in this limit.

The origin of this lies in our assumption of **classical gas**: recall that in the derivation of the partition function (equation 8, we have assumed that the probability of a state to have more than a single particle is $\ll 1$; equivalently, we assumed that there is a very low probability of an occupation number $n_r > 1$.

Let us look at the validity of this condition: The probability of a gas to be in a state of translational energy E_s^{tr} is

$$P_s = \frac{e^{-\beta E_s^{tr}}}{Z_1^{tr}}. \quad (45)$$

Therefore, the average number of particles in this state is

$$\langle n_s \rangle = NP_s = N \frac{e^{-\beta E_s^{tr}}}{Z_1^{tr}}. \quad (46)$$

The condition for being in the classical regime is $n_s \ll 1$, or

$$N e^{-\beta E_s^{tr}} \frac{1}{V} \left(\frac{2\pi mk_B T}{h^2} \right)^{-3/2} \ll 1 \quad (47)$$

Thus, in order to satisfy the condition in Equation 47, we require either (i) $N/V \ll 1$ - very low density, or (ii) high temperatures.

Note that the inequality in Equation 47 also holds in the limit $h \rightarrow 0$; This is the classical limit used by Maxwell and Boltzmann, hence the statistics we derived is known as **Maxwell-Boltzmann statistics**.

4.1. Validity of the classical gas assumption

Recall that in QM, a particle with momentum p acts like a wave, with an associated **de Broglie wavelength**,

$$\lambda_{dB} = \frac{h}{p} = \frac{h}{\sqrt{2mE^{tr}}}. \quad (48)$$

Using Equation 41, we can write

$$\lambda_{dB} = \frac{h}{\sqrt{2m(3/2)k_B T}} = \frac{h}{\sqrt{3mk_B T}} = \frac{1}{\sqrt{3}} \left(\frac{h^2}{mk_B T} \right)^{1/2} \quad (49)$$

With Equation 49, we can write

$$\frac{N}{V} \left(\frac{h^2}{2\pi mk_B T} \right)^{3/2} = \frac{N}{V} \left(\frac{1}{2\pi} \right)^{3/2} \left(\sqrt{3}\lambda_{dB} \right)^3 \ll 1 \quad (50)$$

(note that if the condition in Equation 50 is fulfilled, then obviously the condition in Equation 47 is).

The density N/V is related to the mean distance between the particles, $\langle l \rangle$,

$$\langle l \rangle = \left(\frac{V}{N} \right)^{1/3} \quad (51)$$

and therefore the condition in Equation 50 (hence equation 47) reads

$$\left(\frac{\lambda_{dB}}{\langle l \rangle} \right)^3 \ll 1, \quad (52)$$

namely, in classical gas **the de Broglie wavelength must be small compared to the mean separation between the molecules**.

Example (I). Look at Helium at 273°K. The molar mass is 4 g mole⁻¹, and the density is 0.166 g cm⁻³. Thus,

$$\left(\frac{\lambda_{dB}}{\langle l \rangle} \right)^3 \sim 10^{-5} \ll 1, \quad (53)$$

Generally, equation 52 gives the condition when quantum effects become important - $\langle l \rangle \approx \lambda_{dB}$.

Example (II). Look at conducting electrons in metal. Being freely mobile, in many respects these behave like gas. In copper, for example at 273°K the molar mass is 63.54 g mole⁻¹, and the density is 8.96 g cm⁻³. Thus,

$$\left(\frac{\lambda_{dB}}{\langle l \rangle}\right)^3 \simeq 2.3 \times 10^4 \gg 1, \quad (54)$$

and we cannot neglect quantum mechanical effects - this cannot be considered a classical gas, as some occupation numbers will be greater than 1.

5. Maxwell's velocity distribution - I

Once the partition function is known, we can use it to study the energy, momentum and velocity distribution among the gas molecules.

In Equation 45 we calculated the probability of the gas molecules to be in (translational) energy state E_s^{tr} . Using the same idea, the probability of a particle to have momentum in the range $p..p + dp$ is given by

$$\begin{aligned} P(p)dp &= \frac{e^{-\frac{p^2}{2mk_B T}}}{Z_1} f(p)dp = e^{-\frac{p^2}{2mk_B T}} \left[V \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right]^{-1} \frac{V 4\pi p^2}{h^3} dp \\ &= \frac{4\pi p^2}{(2\pi mk_B T)^{3/2}} e^{-\frac{p^2}{2mk_B T}} dp \end{aligned} \quad (55)$$

This is a **probability distribution**, and must be normalized. Let us check that this is indeed the case:

$$\int_0^\infty P(p)dp = 1, \quad (56)$$

or

$$\int_0^\infty P(p)dp = \frac{4\pi}{(2\pi mk_B T)^{3/2}} \int_0^\infty p^2 e^{-\frac{p^2}{2mk_B T}} dp. \quad (57)$$

The integral is a standard one, which we have already seen (see Equation 24), $I_2(a) = \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4a} \left(\frac{\pi}{a}\right)^{1/2}$. We thus find

$$\int_0^\infty P(p)dp = \frac{4\pi}{(2\pi mk_B T)^{3/2}} \left[\frac{1}{4/(2mk_B T)} \left(\frac{\pi}{1/(2mk_B T)} \right)^{1/2} \right] = 1; \quad (58)$$

The probability distribution is indeed normalized, as expected.

5.1. speed distribution

Instead of momentum, we may be interested in finding the probability that the gas molecules have a certain velocity, \vec{v} . Since $p = mv$, $dp = mdv$. Thus,

$$P(v)dv = 4\pi v^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}} dv \quad (59)$$

The **most probable speed** is given by setting $dP(v)/dv = 0$ (namely, finding the maximum of the distribution), and is

$$v_{\max} = \sqrt{\frac{2k_B T}{m}} \quad (60)$$

We can further find some characteristic speeds of the gas, such as the **mean speed**

$$\langle v \rangle = \int_0^\infty v P(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv = \frac{2}{\sqrt{\pi}} v_{\max} \quad (61)$$

and the root-mean-square (RMS) speed, $v_{rms} = \sqrt{\langle v^2 \rangle}$,

$$\langle v^2 \rangle = \int_0^\infty v^2 P(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^4 e^{-\frac{mv^2}{2k_B T}} dv \quad (62)$$

or $v_{rms} = \sqrt{\frac{3}{2}} v_{\max} = \sqrt{\frac{3k_B T}{m}}$.

The Maxwell's velocity distribution is plotted in Figure 4. This is an a-symmetric distribution, with a tail at high speeds. If we had a mixed gas with different species, the species will have the same mean energy, but each will have its own speed distribution.

6. Maxwell's velocity distribution - II

So far, we have discussed the distribution of the **magnitude** of velocities; namely, we didn't consider any particular *direction*. Let us look now at a given direction in space, say \vec{x} . Thus, we now ask: what is the probability that a particle will have velocity with x -component in the range $v_x..v_x + dv_x$?

While we could repeat a similar derivation to that used earlier, a quicker approach is to use the **speed distribution** which we have already calculated in Equation 59. We note that since $d^3\vec{v} = 4\pi v^2 dv$, we can write this equation as

$$P(\vec{v})d^3\vec{v} = d^3\vec{v} \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_B T}}. \quad (63)$$

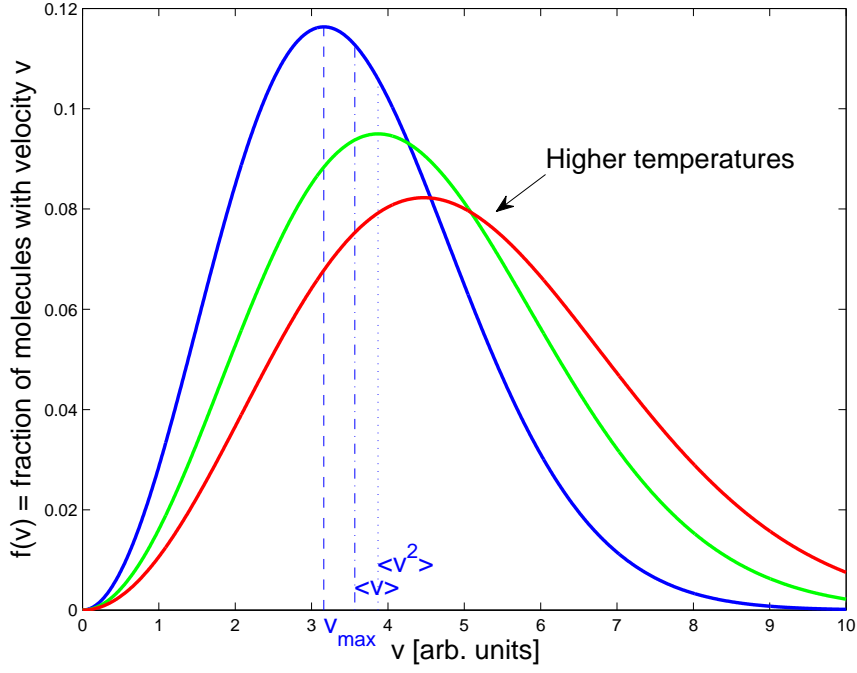


Fig. 4.— Maxwell’s speed distribution.

Equation 59 is obtained by integrating over all directions of the velocity vector \vec{v} , while keeping its magnitude within the range $v..v + dv$.

Since the magnitude of the velocity is

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

and since $d^3\vec{v} = dv_x dv_y dv_z$, we can split Equation 63 into 3 identical equations in the three directions (x, y, z). The x -component will read

$$P(v_x)d^3v_x = dv_x \left(\frac{m}{2\pi k_B T} \right)^{1/2} e^{-\frac{mv_x^2}{2k_B T}}. \quad (64)$$

This distribution is plotted in Figure 5. From symmetry it is clear that

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x P(v_x) dv_x = 0 \quad (65)$$

Furthermore,

$$\langle |v_x| \rangle = 2 \int_0^{\infty} v_x P(v_x) dv_x = \left(\frac{2k_B T}{\pi m} \right)^{1/2}, \quad (66)$$

and

$$\langle v_x^2 \rangle = 2 \int_0^\infty v_x^2 P(v_x) dv_x = \frac{k_B T}{m} \quad (67)$$

from which we find that $(v_x)_{rms} = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{k_B T}{m}}$. Obviously, the same result holds for v_y and v_z ; Thus

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle$$

in accordance to the discussion following Equation 62.

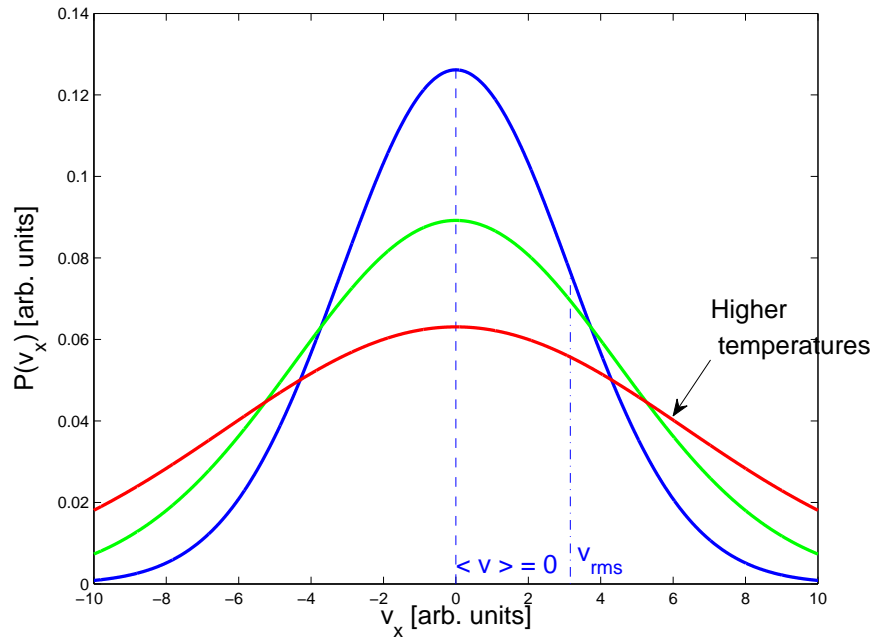


Fig. 5.— Maxwell's velocity distribution.

The velocity of gas molecules can be measured in several methods. Among them

- Mechanical velocity selector
- Doppler broadening of spectral lines:

$$\omega(v_x) = \omega_0 \left(1 \pm \frac{v_x}{c} \right)$$

Thus, Gaussian distribution of the x -component of velocity leads to Gaussian shape of the spectral lines:

$$I(\omega) \propto \exp\left(-\frac{mc^2(\omega_0 - \omega)^2}{2k_B T \omega_0^2}\right)$$