

## 4.7: Ideal Gas Statistical Mechanics

The ordinary canonical partition function for the ideal gas was computed in [Equation \[ideal\]](#). We found

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N!} \prod_{i=1}^N \int \frac{d^d x_i d^d p_i}{(2\pi\hbar)^d} e^{-\beta \mathbf{p}_i^2 / 2m} \\ &= \frac{V^N}{N!} \left( \int_{-\infty}^{\infty} \frac{dp}{2\pi\hbar} e^{-\beta p^2 / 2m} \right)^{Nd} \\ &= \frac{1}{N!} \left( \frac{V}{\lambda_T^d} \right)^N, \end{aligned}$$

where  $\lambda_T$  is the *thermal wavelength*:

$$\lambda_T = \sqrt{2\pi\hbar^2 / m k_B T}. \quad (4.7.1)$$

The physical interpretation of  $\lambda_T$  is that it is the de Broglie wavelength for a particle of mass  $m$  which has a kinetic energy of  $k_B T$ .

In the GCE, we have

$$\begin{aligned} \Xi(T, V, \mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T, V, N) \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{V e^{\mu/k_B T}}{\lambda_T^d} \right)^N = \exp \left( \frac{V e^{\mu/k_B T}}{\lambda_T^d} \right). \end{aligned}$$

From  $\Xi = e^{-\Omega/k_B T}$ , we have the grand potential is

$$\Omega(T, V, \mu) = -V k_B T e^{\mu/k_B T} / \lambda_T^d. \quad (4.7.2)$$

Since  $\Omega = -pV$  (see §6.2), we have

$$p(T, \mu) = k_B T \lambda_T^{-d} e^{\mu/k_B T}. \quad (4.7.3)$$

The number density can also be calculated:

$$n = \frac{N}{V} = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \lambda_T^{-d} e^{\mu/k_B T}. \quad (4.7.4)$$

Combined, the last two equations recapitulate the ideal gas law,  $pV = N k_B T$ .

### Maxwell velocity distribution

The distribution function for momenta is given by

$$g(\mathbf{p}) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta(\mathbf{p}_i - \mathbf{p}) \right\rangle. \quad (4.7.5)$$

Note that  $g(\mathbf{p}) = \langle \delta(\mathbf{p}_i - \mathbf{p}) \rangle$  is the same for every particle, independent of its label  $i$ . We compute the average  $\langle A \rangle = \text{Tr} (A e^{-\beta \hat{H}}) / \text{Tr} e^{-\beta \hat{H}}$ . Setting  $i = 1$ , all the integrals other than that over  $\mathbf{p}_1$  divide out between numerator and denominator. We then have

$$\begin{aligned} g(\mathbf{p}) &= \frac{\int d^3 p_1 \delta(\mathbf{p}_1 - \mathbf{p}) e^{-\beta \mathbf{p}_1^2 / 2m}}{\int d^3 p_1 e^{-\beta \mathbf{p}_1^2 / 2m}} \\ &= (2\pi m k_B T)^{-3/2} e^{-\beta \mathbf{p}^2 / 2m}. \end{aligned}$$

Textbooks commonly refer to the *velocity distribution*  $f(\mathbf{v})$ , which is related to  $g(\mathbf{p})$  by

$$f(\mathbf{v}) d^3v = g(\mathbf{p}) d^3p . \quad (4.7.6)$$

Hence,

$$f(\mathbf{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-m\mathbf{v}^2/2k_B T} . \quad (4.7.7)$$

This is known as the *Maxwell velocity distribution*. Note that the distributions are normalized, viz.

$$\int d^3p g(\mathbf{p}) = \int d^3v f(\mathbf{v}) = 1 . \quad (4.7.8)$$

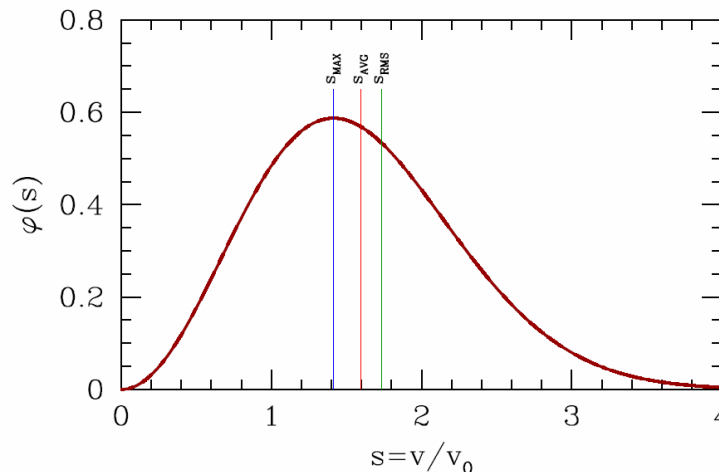


Figure 4.7.1: Maxwell distribution of speeds  $\varphi(v/v_0)$ . The most probable speed is  $v_{MAX} = \sqrt{2} v_0$ . The average speed is  $v_{AVG} = \sqrt{\frac{8}{\pi}} v_0$ . The RMS speed is  $v_{RMS} = \sqrt{3} v_0$ .

If we are only interested in averaging functions of  $v = |\mathbf{v}|$  which are isotropic, then we can define the *Maxwell speed distribution*,  $\tilde{f}(v)$ , as

$$\tilde{f}(v) = 4\pi v^2 f(\mathbf{v}) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T} . \quad (4.7.9)$$

Note that  $\tilde{f}(v)$  is normalized according to

$$\int_0^\infty dv \tilde{f}(v) = 1 . \quad (4.7.10)$$

It is convenient to represent  $v$  in units of  $v_0 = \sqrt{k_B T/m}$ , in which case

$$\tilde{f}(v) = \frac{1}{v_0} \varphi(v/v_0) \quad , \quad \varphi(s) = \sqrt{\frac{2}{\pi}} s^2 e^{-s^2/2} . \quad (4.7.11)$$

The distribution  $\varphi(s)$  is shown in Figure 4.7.1. Computing averages, we have

$$C_k \equiv \langle s^k \rangle = \int_0^\infty ds s^k \varphi(s) = 2^{k/2} \cdot \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2} + \frac{k}{2}\right) . \quad (4.7.12)$$

Thus,  $C_0 = 1$ ,  $C_1 = \sqrt{\frac{8}{\pi}}$ ,  $C_2 = 3$ , The speed averages are

$$\langle v^k \rangle = C_k \left( \frac{k_B T}{m} \right)^{k/2} . \quad (4.7.13)$$

Note that the average *velocity* is  $\langle \mathbf{v} \rangle = 0$ , but the average *speed* is  $\langle v \rangle = \sqrt{8k_B T/\pi m}$ . The speed distribution is plotted in Figure 4.7.1.

## Equipartition

The Hamiltonian for ballistic (massive nonrelativistic) particles is quadratic in the individual components of each momentum  $\mathbf{p}_i$ . There are other cases in which a classical degree of freedom appears quadratically in  $\hat{H}$  as well. For example, an individual normal mode  $\xi$  of a system of coupled oscillators has the Lagrangian

$$L = \frac{1}{2} \dot{\xi}^2 - \frac{1}{2} \omega_0^2 \xi^2, \quad (4.7.14)$$

where the dimensions of  $\xi$  are  $[\xi] = M^{1/2}L$  by convention. The Hamiltonian for this normal mode is then

$$\hat{H} = \frac{p^2}{2} + \frac{1}{2} \omega_0^2 \xi^2, \quad (4.7.15)$$

from which we see that both the kinetic as well as potential energy terms enter quadratically into the Hamiltonian. The classical rotational kinetic energy is also quadratic in the angular momentum components.

Let us compute the contribution of a single quadratic degree of freedom in  $\hat{H}$  to the partition function. We'll call this degree of freedom  $\zeta$  – it may be a position or momentum or angular momentum – and we'll write its contribution to  $\hat{H}$  as

$$\hat{H}_\zeta = \frac{1}{2} K \zeta^2, \quad (4.7.16)$$

where  $K$  is some constant. Integrating over  $\zeta$  yields the following factor in the partition function:

$$\int_{-\infty}^{\infty} d\zeta e^{-\beta K \zeta^2 / 2} = \left( \frac{2\pi}{K\beta} \right)^{1/2}. \quad (4.7.17)$$

The contribution to the Helmholtz free energy is then

$$\Delta F_\zeta = \frac{1}{2} k_B T \ln \left( \frac{K}{2\pi k_B T} \right), \quad (4.7.18)$$

and therefore the contribution to the internal energy  $E$  is

$$\Delta E_\zeta = \frac{\partial}{\partial \beta} (\beta \Delta F_\zeta) = \frac{1}{2\beta} = \frac{1}{2} k_B T. \quad (4.7.19)$$

We have thus derived what is commonly called the *equipartition theorem* of classical statistical mechanics:

We now see why the internal energy of a classical ideal gas with  $f$  degrees of freedom per molecule is  $E = \frac{1}{2} f N k_B T$ , and  $C_V = \frac{1}{2} N k_B$ . This result also has applications in the theory of solids. The atoms in a solid possess kinetic energy due to their motion, and potential energy due to the spring-like interatomic potentials which tend to keep the atoms in their preferred crystalline positions. Thus, for a three-dimensional crystal, there are six quadratic degrees of freedom (three positions and three momenta) per atom, and the classical energy should be  $E = 3 N k_B T$ , and the heat capacity  $C_V = 3 N k_B$ . As we shall see, quantum mechanics modifies this result considerably at temperatures below the highest normal mode (phonon) frequency, but the high temperature limit is given by the classical value  $C_V = 3\nu R$  (where  $\nu = N/N_A$  is the number of moles) derived here, known as the *Dulong-Petit limit*.

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