

# Chapter 5

## Ideal Gas

Consider  $N$  identical point particles (“molecules”) contained in a box of volume  $V$ . Ignoring all interactions except with the walls, the Hamiltonian is

$$H = \frac{1}{2m} \sum_{j=1}^{3N} p_j^2 + V_{\text{walls}}, \quad (5.1)$$

where

$$V_{\text{walls}} = \begin{cases} 0, & \text{inside box,} \\ \infty, & \text{outside box.} \end{cases} \quad (5.2)$$

The potential  $V_{\text{walls}}$  keeps the molecules inside the box. Then, in the *micro-canonical* distribution,

$$\rho(H) = \frac{1}{\Omega(E)} \delta(E - H), \quad (5.3)$$

where

$$\Omega(E) = \int dq dp \delta(E - H) = V^N \int \prod_{k=1}^{3N} dp_k \delta\left(E - \frac{1}{2m} \sum_{j=1}^{3N} p_j^2\right). \quad (5.4)$$

Let us introduce the single-particle momentum distribution function

$$\mathcal{P}(p_1) = \int \rho(q_1, \dots, q_{3N}; p_1, p_2, \dots, p_{3N}) dq_1 \dots dq_{3N} dp_2 \dots dp_{3N}, \quad (5.5)$$

where  $\int \mathcal{P}(p_1) dp_1 = 1$ .  $\mathcal{P}(p_1) dp_1$  is the probability of finding  $p_1$  between the values of  $p_1$  and  $p_1 + dp_1$ . Explicitly,

$$\begin{aligned} \mathcal{P}(p_1) &= \frac{V^N}{\Omega(E)} \int \delta\left(E - \frac{p_1^2}{2m} - \frac{1}{2m} \sum_{j=2}^{3N} p_j^2\right) dp_2 \dots dp_{3N} \\ &= \frac{\int \delta\left(E - \frac{p_1^2}{2m} - \frac{1}{2m} \sum_{j=2}^{3N} p_j^2\right) dp_2 \dots dp_{3N}}{\int \delta\left(E - \frac{1}{2m} \sum_{j=1}^{3N} p_j^2\right) dp_1 \dots dp_{3N}}. \end{aligned} \quad (5.6)$$

We have here integrals over surfaces of hyperspheres. An  $n$ -sphere of radius  $r$  is defined by  $\sum_{j=1}^n x_j^2 = r^2$ . The area of a unit  $n$ -sphere is  $A_n$ , so an  $n$ -sphere of radius  $r$  has area  $S_n(r) = A_n r^{n-1}$ . Thus

$$\mathcal{P}(p_1) = \frac{\int \delta(2mE - p_1^2 - p^2) A_{3N-1} p^{3N-2} dp}{\int \delta(2mE - p^2) A_{3N} p^{3N-1} dp}, \quad (5.7)$$

where in the numerator  $p^2 = \sum_{j=2}^{3N} p_j^2$ , and in the denominator  $p^2 = \sum_{j=1}^{3N} p_j^2$ . Now, for  $r$  and  $x$  both positive,

$$\delta(r^2 - x^2) = \delta((r-x)(r+x)) = \frac{1}{2r} \delta(r-x), \quad (5.8)$$

or more generally, if  $f$  has only a simple zero at  $x = a$ , so  $f(a) = 0$  but  $f'(z) \neq 0$ , in the neighborhood of  $x = a$

$$\delta(f(x)) = \frac{1}{|f'(a)|} \delta(x-a), \quad (5.9)$$

so we conclude

$$\mathcal{P}(p_1) = \frac{A_{3N-1} (2mE - p_1^2)^{(3N-3)/2}}{A_{3N} (2mE)^{(3N-2)/2}} = \frac{A_{3N-1}}{A_{3N}} \frac{1}{\sqrt{2mE}} \left(1 - \frac{p_1^2}{2mE}\right)^{(3N-3)/2}. \quad (5.10)$$

Now we must calculate  $A_n$ . A standard trick is to use the Gaussian integral

$$\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}. \quad (5.11)$$

Then, the  $n$ -fold integral

$$\int \exp\left(-\sum_{j=1}^n x_j^2\right) dx_1 \dots dx_n = \left(\int_{-\infty}^{\infty} dx e^{-x^2}\right)^n = \pi^{n/2} \quad (5.12)$$

can also be evaluated in hyperspherical coordinates as

$$\int_0^{\infty} e^{-r^2} A_n r^{n-1} dr = \frac{A_n}{2} \int_0^{\infty} e^{-t} t^{(n-2)/2} dt = \frac{A_n}{2} \Gamma\left(\frac{n}{2}\right), \quad (5.13)$$

where we have changed variables  $r^2 = t$ , so  $2r dr = dt$ , and recognized the Euler definition of the gamma function,

$$\Gamma(x) = \int_0^{\infty} \frac{dt}{t} t^x e^{-t}, \quad \text{Re } x > 0. \quad (5.14)$$

The gamma function is the generalization of the factorial function:

$$\Gamma(x+1) = x\Gamma(x) = x!. \quad (5.15)$$

$n$	$A_n$
0	0
1	2
2	$2\pi$
3	$4\pi$
4	$2\pi^2$
5	$8\pi^2/3$

Table 5.1: The areas of unit spheres in 0 through 5 dimensions.

$n$	$S_n(r)$
0	1
1	$2r$
2	$\pi r^2$
3	$4\pi r^3/3$
4	$\pi^2 r^4/2$
5	$8\pi^2 r^5/15$

Table 5.2: The volumes of spheres of radius  $r$  in 0 through 5 dimensions.

Thus we obtain the following formula for the area of a unit sphere in  $n$  dimensions:

$$A_n = \frac{2\pi^{n/2}}{\Gamma(n/2)}. \quad (5.16)$$

Using the fact that  $\Gamma(1/2) = \sqrt{\pi}$ , which is the same statement as Eq. (5.11), we obtain the values seen in Table 5.1. The volume of an  $n$ -sphere is obtained by integration:

$$\begin{aligned} V_n(r) &= \int_0^r S_n(r') dr' = \int_0^r A_n r'^{n-1} dr' \\ &= A_n \frac{1}{n} r^n = \frac{2\pi^{n/2}}{n\Gamma(n/2)} r^n = \frac{\pi^{n/2} r^n}{\Gamma(\frac{n}{2} + 1)}. \end{aligned} \quad (5.17)$$

Values of  $V_n$  for low  $n$  are shown in Table 5.2.

Now we return to Eq. (5.10). This now becomes

$$\mathcal{P}(p_1) = \frac{\Gamma(3N/2)}{\Gamma((3N-1)/2)} \frac{1}{\sqrt{2\pi mE}} \left(1 - \frac{p_1^2}{2mE}\right)^{\frac{3}{2}(N-1)}. \quad (5.18)$$

Up to this point we have made no approximation. We will now make an approximation based on the assertion that  $N$  is very large. Then

$$(1-x)^n = e^{n \ln(1-x)} = e^{-nx - nx^2/2 - nx^3/3 - \dots} \approx e^{-nx}, \quad (5.19)$$

where the higher terms in the expansion of the logarithm are negligible provided  $nx^2/2 \ll 1$ . If this is true here, then

$$\frac{p_1^2}{2mE} \ll \sqrt{\frac{4}{3N}}, \quad (5.20)$$

or

$$\frac{p_1^2}{2m} \ll 2\sqrt{3N} \left( \frac{E}{3N} \right). \quad (5.21)$$

The left-hand side of this equation is the kinetic energy of the first molecule due to motion in the  $x$  direction, while the last factor on the right,  $E/3N$ , is the energy per degree of freedom. These two quantities should be comparable, so if  $N$  is large this inequality should be well satisfied. Thus, to an excellent approximation,

$$\mathcal{P}(p_1) = \frac{\Gamma\left(\frac{3}{2}N\right)}{\Gamma\left(\frac{3}{2}N - \frac{1}{2}\right)} \frac{1}{\sqrt{2\pi m E}} e^{-\frac{3N}{2} \frac{p_1^2}{2mE}}. \quad (5.22)$$

Next, we need to obtain a more tractable approximation for the ratio of gamma functions. Write

$$\begin{aligned} \ln \frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N}{2} - \frac{1}{2}\right)} &= \ln \Gamma\left(\frac{3N}{2}\right) - \ln \Gamma\left(\frac{3N}{2} - \frac{1}{2}\right) \\ &\approx \frac{1}{2} \frac{d}{d(3N/2)} \ln \Gamma\left(\frac{3N}{2}\right) \approx \frac{1}{2} \left[ \ln \Gamma\left(\frac{3N}{2}\right) - \ln \Gamma\left(\frac{3N}{2} - 1\right) \right] \\ &= \frac{1}{2} \left\{ \ln \left[ \left(\frac{3N}{2} - 1\right) \Gamma\left(\frac{3N}{2} - 1\right) \right] - \ln \Gamma\left(\frac{3N}{2} - 1\right) \right\} \\ &\approx \frac{1}{2} \ln \frac{3N}{2}. \end{aligned} \quad (5.23)$$

This result can also be easily obtained through use of the Stirling approximation. In fact, keeping the next correction we obtain

$$\frac{\Gamma\left(\frac{3N}{2}\right)}{\Gamma\left(\frac{3N}{2} - \frac{1}{2}\right)} \approx \left(\frac{3N}{2}\right)^{1/2} - \frac{1}{4} \left(\frac{3}{2N}\right)^{1/2} + O(N^{-3/2}). \quad (5.24)$$

Thus, starting from the microcanonical ensemble, we have derived the famous Maxwell-Boltzmann distribution of momenta (or velocities):

$$\mathcal{P}(p_1) = \frac{1}{\sqrt{2\pi m(2E/3N)}} e^{-p_1^2/[2m(2E/3N)]}. \quad (5.25)$$

From this we can calculate the pressure, by considering collisions of particles moving in the  $+x$  direction with a perpendicular wall of area  $A$ , in a box of length  $L$  in the  $x$  direction, where the volume of the box is therefore  $V = AL$ . The pressure for one collision, where a momentum  $\Delta p_x$  is transferred to the wall in a time  $\Delta t$  is

$$P = \frac{F}{A} = \left\langle \frac{\Delta p_x}{\Delta t} \right\rangle \frac{1}{A}. \quad (5.26)$$

For particles of momentum  $p_1$  each collision with the wall transfers momentum  $\Delta p_x = 2p_1$ , so

$$\begin{aligned} \frac{\Delta p_x}{\Delta t} &= 2p_1 \times \frac{\text{number of collisions}}{\text{sec}} = 2p_1 \times \frac{\text{number of molecules}}{\text{volume}} \times \frac{\text{volume}}{\text{sec}} \\ &= 2p_1 \frac{N}{V} A v_1 = \frac{2p_1^2 N}{m L}, \end{aligned} \quad (5.27)$$

where the velocity of the particle in the  $x$  direction is  $v_1 = p_1/m$ . Therefore, the pressure is

$$P = \frac{N}{V} \int_{p_1 > 0} dp_1 \frac{2p_1^2}{m} \mathcal{P}(p_1) = \frac{N}{V} \langle \frac{p_1^2}{m} \rangle, \quad (5.28)$$

or

$$PV = N \langle \frac{p_1^2}{m} \rangle. \quad (5.29)$$

But the ensemble average is

$$\begin{aligned} \langle \frac{p_1^2}{m} \rangle &= \frac{1}{\sqrt{2\pi m(2E/3N)}} \int_{-\infty}^{\infty} \frac{p_1^2}{m} e^{-p_1^2/[2m(2E/3N)]} dp_1 \\ &= \frac{2}{\sqrt{\pi}} \left( \frac{2E}{3N} \right) \int_{-\infty}^{\infty} x^2 e^{-x^2} dx. \end{aligned} \quad (5.30)$$

The integral here can be expressed as a gamma function,

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 2 \int_0^{\infty} t e^{-t} \frac{1}{2} \frac{dt}{\sqrt{t}} = \Gamma(3/2) = \frac{\sqrt{\pi}}{2}. \quad (5.31)$$

Alternatively, we could consider the Gaussian integral:

$$\int_{-\infty}^{\infty} dx x^2 e^{-\lambda x^2} = -\frac{d}{d\lambda} \int_{-\infty}^{\infty} dx e^{-\lambda x^2} = -\frac{d}{d\lambda} \sqrt{\frac{\pi}{\lambda}} = \frac{1}{2} \sqrt{\frac{\pi}{\lambda^3}}, \quad (5.32)$$

which, when evaluated at  $\lambda = 1$  gives the same result. Thus we conclude

$$\langle \frac{p_1^2}{m} \rangle = \frac{2E}{3N}, \quad (5.33)$$

or, the average kinetic energy per degree of freedom is

$$\langle \frac{p_1^2}{2m} \rangle = \frac{E}{3N}, \quad (5.34)$$

*as it must be!* That is,

$$PV = N \left( \frac{2E}{3N} \right). \quad (5.35)$$

But we know from the ideal gas law that

$$PV = NkT, \quad (5.36)$$

so we conclude that

$$E = \frac{3}{2} NkT, \quad (5.37)$$

which is just the equipartition theorem for  $3N$  degrees of freedom. Using this connection, the single-momentum distribution function reads

$$\mathcal{P}(p_1) = \frac{1}{\sqrt{2\pi mkT}} e^{-p_1^2/2mkT}. \quad (5.38)$$

According to Eq. (5.21), this is valid if

$$\frac{p_1^2}{2m} \ll \sqrt{3N} \left( \frac{2E}{3N} \right) = \sqrt{3N} kT. \quad (5.39)$$

Room temperature corresponds to  $kT = 1/40$  eV, so for  $N = 10^{22}$

$$\sqrt{3N} kT \sim 4 \times 10^9 \text{ eV} = 4 \text{ GeV}. \quad (5.40)$$

What is the probability of finding a particle in the gas with such a huge energy?

$$\mathcal{P} \sim e^{-1.7 \times 10^{11}} \quad (5.41)$$

—it will *never* happen.

Finally, we close this chapter by deriving the Maxwell-Boltzmann distribution from the canonical distribution. This is immediate, because of the exponential form for the density:

$$\rho(H) = \frac{1}{Z} e^{-\beta H}. \quad (5.42)$$

Thus the single particle distribution function is

$$\mathcal{P}(p_1) = \frac{V^N}{Z} \int dp_2 \dots dp_{3N} e^{-\beta \sum_{j=1}^N p_j^2/2m}, \quad (5.43)$$

where the partition function is

$$\begin{aligned} Z &= V^N \int dp_1 \dots dp_{3N} e^{-\beta \sum_{j=1}^N p_j^2/2m} = V^n \left( \int dp e^{-\beta p^2/2m} \right)^{3N} \\ &= V^N \left( \frac{2\pi m}{\beta} \right)^{3N/2}. \end{aligned} \quad (5.44)$$

Thus we have

$$\mathcal{P}(p_1) = \frac{e^{-\beta p_1^2/2m} (2\pi m/\beta)^{(3N-1)/2}}{(2\pi m/\beta)^{3N/2}} = \left( \frac{\beta}{2\pi m} \right)^{1/2} e^{-\beta p_1^2/2m}, \quad (5.45)$$

or, with  $\beta = 1/kT$ ,

$$\mathcal{P}(p_1) = \frac{1}{\sqrt{2\pi m kT}} e^{-p_1^2/2mkT}, \quad (5.46)$$

which is the Maxwell-Boltzmann distribution (5.38).