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

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

where

$$V_{\text{walls}} = \begin{cases} 0, \text{inside box}, \\ \infty, \text{outside box}. \end{cases} \tag{5.2}$$

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

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

where

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

Let us introduce the single-particle momentum distribution function

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

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,

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

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

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

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,

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

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 $x = a$

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

so we conclude

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

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

$$\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}. \tag{5.11}$$

Then, the n-fold integral

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

can also be evaluated in hyperspherical coordinates as

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

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

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

The gamma function is the generalization of the factorial function:

$$\Gamma(x+1) = x\Gamma(x) = x!. \tag{5.15}$$

n	A_n
0	0
1	2
2	2π
3	4π
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	πr^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:

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

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:

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

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

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

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

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

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

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

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

or

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

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,

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

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

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

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

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

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

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

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 Δp_x is transfered to the wall in a time Δt is

$$P = \frac{F}{A} = \langle\frac{\Delta p_x}{\Delta t}\rangle\frac{1}{A}. \tag{5.26}$$

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

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

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

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

or

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

But the ensemble average is

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

The integral here can be expressed as a gamma function,

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

Alternatively, we could consider the Gaussian integral:

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

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

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

or, the average kinetic energy per degree of freedom is

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

as it must be! That is,

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

But we know from the ideal gas law that

$$PV = NkT, \tag{5.36}$$

so we conclude that

$$E = \frac{3}{2}NkT, \tag{5.37}$$

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

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

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

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

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

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

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

$$\mathcal{P} \sim e^{-1.7\times 10^{11}} \tag{5.41}$$

—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:

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

Thus the single particle distribution function is

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

where the partition function is

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

Thus we have

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

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

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

which is the Maxwell-Boltzmann distribution (5.38).