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

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

(5.1)

where

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

(5.2)

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

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

(5.3)

where

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

(5.4)

Let us introduce the single-particle momentum distribution function

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

(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,

$$\mathcal{P}(p_1) = \frac{V^N}{\Omega(E)} \int \delta \left( E - \frac{p_1^2}{2m} - \frac{1}{2m} \sum_{j=2}^{3N} p_j^2 \right) dp_2 \ldots dp_{3N}$$

$$= \frac{\int \delta \left( E - \frac{p_1^2}{2m} - \frac{1}{2m} \sum_{j=2}^{3N} p_j^2 \right) dp_2 \ldots dp_{3N}}{\int \delta \left( E - \frac{1}{2m} \sum_{j=1}^{3N} p_j^2 \right) dp_1 \ldots dp_{3N}}.$$  

(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

\[
P(p_1) = \frac{\int \delta(2mE - p_1^2 - p^2) A_{3N-1} p^{3N-2} dp}{\int \delta(2mE - p^2) A_{3N} p^{3N-1} dp},
\]

(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,

\[
\delta(r^2 - x^2) = \delta((r - x)(r + x)) = \frac{1}{2r} \delta(r - x),
\]

(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 \( x = a \)

\[
\delta(f(x)) = \frac{1}{|f'(a)|} \delta(x - a),
\]

(5.9)

so we conclude

\[
P(p_1) = \frac{A_{3N-1}(2mE - p_1^2)^{(3N-3)/2}}{A_{3N}(2mE)^{(3N-2)/2}} = \frac{A_{3N-1}}{A_{3N} \sqrt{2mE}} \left( 1 - \frac{p_1^2}{2mE} \right)^{(3N-3)/2}.
\]

(5.10)

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

\[
\int_{-\infty}^{\infty} dx e^{-x^2} = \sqrt{\pi}.
\]

(5.11)

Then, the \( n \)-fold integral

\[
\int \exp\left( - \sum_{j=1}^{n} x_j^2 \right) dx_1 \ldots dx_n = \left( \int_{-\infty}^{\infty} dx e^{-x^2} \right)^n = \pi^{n/2}
\]

(5.12)

can also be evaluated in hyperspherical coordinates as

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

(5.13)

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

\[
\Gamma(x) = \int_0^{\infty} \frac{dt}{t} t^{x-1} e^{-t}, \quad \text{Re} \, x > 0.
\]

(5.14)

The gamma function is the generalization of the factorial function:

\[
\Gamma(x + 1) = x \Gamma(x) = x!.
\]

(5.15)
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:

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

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

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

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

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

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

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
\[ \frac{p^2}{2m} \ll 2\sqrt{3N} \left( \frac{E'}{3N} \right). \quad (5.21) \]

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

Next, we need to obtain a more tractable approximation for the ratio of gamma functions. Write
\[
\ln \frac{\Gamma \left( \frac{3N}{2} \right)}{\Gamma \left( \frac{3N}{2} - \frac{1}{2} \right)} = \ln \Gamma \left( \frac{3N}{2} \right) - \ln \Gamma \left( \frac{3N}{2} - \frac{1}{2} \right) \\
\approx \frac{1}{2} \frac{d}{d(3N/2)} \ln \Gamma \left( \frac{3N}{2} \right) \approx \frac{1}{2} \left[ \ln \Gamma \left( \frac{3N}{2} \right) - \ln \Gamma \left( \frac{3N}{2} - 1 \right) \right] \\
= \frac{1}{2} \left\{ \ln \left[ \left( \frac{3N}{2} - 1 \right) \Gamma \left( \frac{3N}{2} - 1 \right) \right] - \ln \Gamma \left( \frac{3N}{2} - 1 \right) \right\} \\
\approx \frac{1}{2} \ln \frac{3N}{2}. \quad (5.23) \]

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

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
\[ P = \frac{F}{A} = \langle \Delta p_x, \frac{1}{\Delta t} \rangle A. \quad (5.26) \]

For particles of momentum \(p_1\) each collision with the wall transfers momentum \(\Delta p_x = 2p_1\), so
\[
\frac{\Delta p_x}{\Delta t} = 2p_1 \times \frac{\text{number of collisions}}{\text{sec}} = 2p_1 \times \frac{\text{number of molecules}}{\text{volume}} \times \frac{\text{volume}}{\text{sec}} \\
= 2p_1 \frac{N}{V} A v_1 = \frac{2p_1^2 N}{m L}. \quad (5.27) \]
where the velocity of the particle in the $x$ direction is $v_1 = p_1 / m$. Therefore, the pressure is

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

or

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

But the ensemble average is

$$\langle \frac{p_1^2}{m} \rangle = \frac{1}{\sqrt{2\pi m (2E/3N)}} \int_{-\infty}^{\infty} \frac{p_1^2}{m} e^{-p_1^2/[2m(2E/3N)]} dp_1$$

$$= \frac{2}{\sqrt{\pi}} \left( \frac{2E}{3N} \right) \int_{-\infty}^{\infty} x^2 e^{-x^2} dx. \quad (5.30)$$

The integral here can be expressed as a gamma function,

$$\int_{-\infty}^{\infty} x^2 e^{-x^2} dx = 2 \int_{0}^{\infty} t e^{-t^2} \frac{dt}{\sqrt{t}} = \Gamma(3/2) = \frac{\sqrt{\pi}}{2}. \quad (5.31)$$

Alternatively, we could consider the Gaussian integral:

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

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

$$PV = N kT, \quad (5.36)$$

so we conclude that

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

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

Room temperature corresponds to \( kT = 1/40 \text{ eV} \), so for \( N = 10^{22} \)
\[
\sqrt{3N} kT \sim 4 \times 10^9 \text{ eV} = 4 \text{ GeV}.
\] (5.40)

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

\[
P \sim e^{-1.7 \times 10^{11}}.
\] (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:

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

Thus the single particle distribution function is

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

where the partition function is

\[
Z = V^N \int dp_1 \ldots dp_{3N} e^{-\beta \sum_{j=1}^{3N} p_j^2/2m} = V^n \left( \int dp e^{-\beta p^2/2m} \right)^{3N/2} = V^N \left( \frac{2\pi m}{\beta} \right)^{3N/2}.
\] (5.44)

Thus we have

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

or, with \( \beta = 1/kT \),

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

which is the Maxwell-Boltzmann distribution (5.38).