Chapter 4

Perfect Classical Gases

A perfect classical gas is an idealization of a real gas at high temperature in which (1) the interaction between the atoms is ignored and (2) the atoms are treated as classical particles. Gases were the subject of intense study and controversy during the late nineteenth and early twentieth century enveloping such well known names as Maxwell, Boltzmann and Kelvin. Statistical Mechanics developed side by side the understanding of gases. Hence a study of gases serves as an excellent introduction to statistical mechanics. To begin our study we consider firstly monatomic gases so the atoms can be taken as point particles. There is then only translational kinetic energy, $\epsilon = (p_x^2 + p_y^2 + p_z^2)/2m$. In our study we want to predict the thermodynamic properties of gases, for which we need the partition function $Z_0 = \sum s e^{-\beta \epsilon_s}$, and the distribution of the particles over their possible energies, momentum or velocities, for which we need the expected occupation of $\bar{n}_s$ of each state $s$.

4.1 The Density of States and Partition Function

From section 3.2 we know the expected number of particles in discrete state $s$ having energy $\epsilon_s$ is

$$\bar{n}_s = \frac{N}{Z_0} e^{-\beta \epsilon_s} \quad (4.1)$$

Since the particles are classical, the discrete nature of the levels can be ignored. Hence the number of particles in an interval spanning $ds$ states is

$$dN = \bar{n}_s ds$$

Also in classical mechanics we specify the state of a particle by its position in phase space $\Gamma$, e.g. it is in element $d\Gamma = d\vec{r} d\vec{p}$ lying between $\vec{r}$ and $\vec{r} + d\vec{r}$, and between $\vec{p}$ and $\vec{p} + d\vec{p}$. To proceed we need the number of states lying within
dΓ or, equivalently, the density of states per interval phase space. In section 1.5 we chose this density as one (1) state per volume $h^3$ in phase space. Hence

$$ds = \left( \frac{ds}{d\Gamma} \right) d\Gamma = g(\Gamma) d\Gamma = \frac{1}{h^3} d\Gamma$$

(4.2)

where $g(\Gamma) = \left( \frac{ds}{d\Gamma} \right) = \frac{1}{h^3}$ is the density of states in phase space. Then,

$$dN = \bar{n}_s \frac{d\Gamma}{h^3} = \bar{n}_s \frac{dV}{h^3} dy dz dp_x dp_y dp_z$$

(4.3)

To obtain the distribution of particles over the $x$ component of momentum $p_x$, for example, irrespective of their position or value of $p_x$ or $p_y$, we integrate over the volume $dV = dx dy dz$ and over $p_y$ and $p_z$ to get

$$dN = N(p_x) dp_x = \left( \frac{V}{h^3} \int dp_y \int dp_z \bar{n}_s \right) dp_x$$

(4.4)

We might also want the distribution of particles over their absolute value of momentum $|p|$, irrespective of the direction of the momentum. For this we use spherical polar coordinates and write

$$dp_x dp_y dp_z = 4\pi p^2 dp$$

Here the volume element of momentum is a spherical shell of radius $p$ and width $dp$. The number of particles having momentum $p$ is then

$$dN = \bar{n}_s \left( \frac{V}{h^3} 4\pi p^2 \right) dp$$

$$= \bar{n}_s \ g(p) dp$$

(4.5)

where $g(p) = \left( \frac{V}{h^3} 4\pi p^2 \right)$ is the density of states per interval of absolute momentum $p$. We could also obtain this more formally as

$$ds = g(\Gamma) d\Gamma = g(\Gamma) \left( \frac{d\Gamma}{dp} \right) dp = g(p) dp$$

$$g(p) = g(\Gamma) \left( \frac{d\Gamma}{dp} \right) = \frac{1}{h^3} V 4\pi p^2$$

(4.6)

If we are interested in the number of particles per energy interval we write

$$ds = g(p) dp = g(p) \left( \frac{dp}{d\epsilon} \right) d\epsilon = g(\epsilon) d\epsilon$$

Then with $\epsilon = p^2/2m$ the density of states per energy interval is

$$g(\epsilon) = g(p) \left( \frac{dp}{d\epsilon} \right) = V \frac{4\pi m}{h^3} (2m\epsilon)^{1/2}$$

(4.7)
and
\[ dN = \bar{n}_s g(\epsilon) \, d\epsilon \]
In this way we may obtain the density of states for any variable desired and in each case the number of particles takes the form
\[ dN = \text{expected occupation} \times \text{density of states} \times \text{interval} \]

**The Partition Function**

To evaluate \( Z_o \) we again transform the discrete sum over states \( \epsilon_s \) to an integral over \( \epsilon \) as

\[
Z_o = \sum_s e^{-\beta \epsilon_s} = \int ds \ e^{-\beta \epsilon} = \int \frac{d\Gamma}{\hbar^3} e^{-\beta \epsilon}
\]

\[
= \frac{1}{\hbar^3} \int dV \int\int\int dp_x dp_y dp_z e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)}
\]

\[
= \frac{V}{\hbar^3} \int dp_x e^{-\frac{\beta}{2m}p_x^2} \int dp_y e^{-\frac{\beta}{2m}p_y^2} \int dp_z e^{-\frac{\beta}{2m}p_z^2} \quad (4.8)
\]

This is a product of three independent Laplace integrals each of value \( \left( \pi \frac{2m}{\hbar^2} \right)^{1/2} \) and

\[
Z_o = V \left( \frac{2\pi m kT}{\hbar^2} \right)^{3/2} = V/\lambda_T^3 \quad (4.9)
\]

In the last equality we have introduced the thermal wavelength of the particles

\[
\lambda_T \equiv \left( \frac{\hbar^2}{2\pi m kT} \right)^{1/2} \quad (4.10)
\]

This thermal wavelength is closely related to the de Broglie wavelength of quantum mechanics,

\[
\lambda_{deB} = \left( \frac{\hbar}{p} \right) \quad (4.11)
\]

For the momentum we write \( p = (2m\epsilon)^{1/2} \) and use the classical thermal energy \( \epsilon = \frac{3}{2}kT \) to estimate the energy of the free particle. Then

\[
\lambda_{deB} = \left( \frac{\hbar^2}{3 m kT} \right)^{1/2} = \left( \frac{2\pi}{3} \right)^{1/2} \lambda_T \quad (4.12)
\]

The \( \lambda_T, \lambda_{deB} \), provides an excellent test of whether the particles can be taken as classical particles or not. The gas is classical if \( \lambda_T \) is much less than the average inter-particle spacing, which for a gas at NTP is \( \approx 20\A \). For helium at room temperature \( \lambda_T \approx 0.5\A \).
Chapter 4.

With these preliminaries we can now explore the physics of perfect classical gases.

4.2 Distribution Functions

The Maxwell – Boltzmann Velocity Distribution

Maxwell (1847 – 1906), among his many interests in physics, was interested in the distribution of gas atoms over their possible velocities; that is, what fraction, $f(v_x)$, of the atoms have velocity $v_x$ in the range $v_x$ to $v_x + dv_x$? In 1860 Maxwell derived the result assuming the distribution over each component ($v_x, v_y,$ and $v_z$) was independent and argued that only an exponential function in the square of the velocities (a Gaussian function) had the required independent form. This derivation was not widely accepted as rigorous and we follow here Boltzmann’s method – the first rigorous derivation and hence the joint name above.

We essentially already have the result in (4.4) which gives the number of particles in momentum range $p_x$ to $p_x + dp_x$ as,

$$ N(p_x) dp_x = \frac{V}{h^3} \frac{N}{Z_o} \left( \int dp_y e^{-\beta p_y^2 / 2m} \right) \left( \int dp_z e^{-\beta p_z^2 / 2m} \right) \left( e^{-\beta p_x^2 / 2m} \right) dp_x \quad (4.13) $$

Here we see immediately that the distribution over each component is independent as Maxwell assumed and as we saw in evaluating $Z_o$. Since we seek the number in the interval $dp_x$ for any value of $p_y$ and $p_z$ we integrate over all values of $p_y$ and $p_z$. The integrations give $(2\pi m kT)^{1/2}$ for each component and substituting $Z_o = \frac{V}{h^3}(2\pi m kT)^{3/2} = V/\lambda_T^3$, we find

$$ N(p_x) dp_x = N (2\pi m kT)^{-1/2} \left( e^{-\beta p_x^2 / 2m} \right) dp_x \quad (4.14) $$

With $p_x = mv_x$, we convert to velocity

$$ N(p_x) dp_x = N \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-\beta m v_x^2 / 2} dv_x = N(v_x) dv_x $$

where

$$ N(v_x) = N \left( \frac{m}{2\pi kT} \right)^{1/2} e^{-\beta m v_x^2 / 2} \quad (4.15) $$
Using $N(v_x)$ we may evaluate the average over any function, $O(v_x)$, that depends upon $v_x$ as
\[
\bar{O} = \frac{\int_{-\infty}^{\infty} dv_x \, N(v_x) \, O(v_x)}{\int_{-\infty}^{\infty} dv_x \, N(v_x)}
\]
Here, since each of the $N$ particles must have some value of $v_x$, the integration over $v_x$ catches all particles and
\[
\int_{-\infty}^{\infty} dv_x \, N(v_x) = N
\]
For these averages, it is more convenient to introduce the probability of finding a given particle with having velocity $v_x$,
\[
f(v_x) = \frac{N(v_x)}{N}.
\] (4.16)
Then
\[
\bar{O} = \int_{-\infty}^{\infty} dv_x \, f(v_x) \, O(v_x)
\]
and clearly, since the particle exists with certainty (probability = 1), we must have
\[
\int_{-\infty}^{\infty} dv_x \, f(v_x) \, O(v_x) = 1
\]
That is, the distribution is “normalized”. Then
\[
f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{\beta m}{2} v_x^2}
\] (4.17)
is Maxwell’s celebrated velocity distribution. There is clearly a similar distribution $f(v_y)$ and $f(v_z)$ over $v_y$ and $v_z$ respectively, by symmetry and with these we can calculate any velocity average. The physically interesting feature is that in equilibrium each particle velocity is not the same. Rather they are distributed randomly (about $v_x = 0$) in a Gaussian distribution. This is consistent with the central limit theorem which states that for any large enough sample of systems, the distribution of any property is always a Gaussian. Here the width of the Gaussian is proportional to $T$.

**The Absolute Velocity, Momentum and Energy Distribution**

Suppose we want the distribution over the absolute value of velocity $v$. The product
\[
f(v_x) f(v_y) f(v_z)
\]
is the probability of finding the particle having a particular value of $v_x$, $v_y$ and $v_z$. To find the probability distribution for $v$, we use spherical polar coordinates to
convert from a cube having volume $dv_x \, dv_y \, dv_z$ to spherical shell of given $v$, having volume $4\pi v^2 dv$

\[ f(v_x) f(v_y) f(v_z) \, dv_x \, dv_y \, dv_z = f(v_x) f(v_y) f(v_z) \, 4\pi v^2 \, dv \]

\[ \equiv f(v) \, dv \]

where

\[ f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{\beta m}{2} v^2} \]  

(4.18)

is the probability distribution for $f(v)$. Here

\[ \int_{0}^{\infty} f(v) \, dv = 1. \]

The integral starts at zero since only positive absolute velocities are possible.

We could easily have obtained $f(v)$ from the momentum distribution...
This gives
\[ dN = \bar{n}_s \, g(p) \, dp \]
\[ = \frac{N}{Z_o} \, e^{-\frac{\beta \, p^2}{2m}} \left( \frac{V}{\hbar^3} \, 4\pi \, p^2 \right) \, dp \]
\[ = \left[ N \, 4\pi \, \left( \frac{1}{2\pi \, kT} \right)^{3/2} \, e^{-\frac{\beta \, p^2}{2m}} \right] \, p^2 \, dp \]
\[ = N(p) \, dp \] (4.19)

The probability distribution over momentum is then
\[ f(p) = \frac{N(p)}{N} = 4\pi \left( \frac{m}{2\pi \, kT} \right)^{3/2} \, e^{-\frac{\beta \, p^2}{2m}} \] (4.20)

and substituting \( p = mv \) leads to eq. (4.18).

To get the probability distribution over energy we go back to equation (4.7),
\[ dN = \bar{n}_s \, g(\epsilon) \, d\epsilon \]
\[ = \frac{N}{Z_o} \, e^{-\beta \epsilon} \left( \frac{V}{\hbar^3} \, 4\pi \, m \, (2m\epsilon)^{1/2} \right) \, d\epsilon \]
\[ = \frac{2\pi \, N}{(\pi \, kT)^{3/2}} \, e^{-\beta \epsilon} \, \epsilon^{1/2} \, d\epsilon \]

The probability of observing a given particle with energy in the range \( \epsilon \) to \( \epsilon + d\epsilon \) is then
\[ f(\epsilon) = \frac{N(\epsilon)}{N} = \frac{2\pi}{(\pi \, kT)^{3/2}} \, e^{-\beta \epsilon} \, \epsilon^{1/2} \] (4.21)

In this way we may obtain the distribution over any coordinate. In each case it is a Gaussian (from \( \bar{n}_s \)) times a density of states factor (e.g. see Fig. 4.3).

**Average Velocities**

The mean velocity of a particle, in the gas, irrespective of its direction, is
\[ \bar{v} = \frac{\int_{-\infty}^{\infty} dv \, f(v) \, v}{\int_{-\infty}^{\infty} dv \, f(v)} \] (4.22)
Chapter 4.

Figure 4.3: Classical distribution over energy states $\epsilon$.

with $f(v)$ given by (4.18), which is normalized ($\int_{0}^{\infty} dv \ f(v) = 1$). To evaluate the average we need an integral of the form

$$I_1 = \int_{0}^{\infty} e^{-\alpha v^2} \ v \ dv$$

Setting $\eta = v^2$, $d(\eta^2) = 2v \ dv = d\eta$ and we have

$$I_1 = \frac{1}{2} \int_{0}^{\infty} e^{-\alpha \eta} \ d\eta = \frac{1}{2\alpha}$$

$$I_3 = \int_{0}^{\infty} e^{-\alpha v^2} \ v^3 \ dv = -\frac{\partial}{\partial \alpha} I_1 = \frac{1}{2\alpha^2}$$

$$I_5 = \int_{0}^{\infty} e^{-\alpha v^2} \ v^5 \ dv = -\frac{\partial}{\partial \alpha} I_3 = \frac{1}{\alpha^3}$$

and so on. To check that $f(v)$ is normalized, we need Laplace’s integral

$$I_0 = \int_{0}^{\infty} e^{-\alpha v^2} \ dv = \frac{1}{2} \left( \frac{\pi}{\alpha} \right)^{1/2}$$

from which

$$I_2 = \int_{0}^{\infty} e^{-\alpha v^2} \ v^2 \ dv = -\frac{\partial}{\partial \alpha} I_0 = \frac{1}{4\alpha} \left( \frac{\pi}{\alpha} \right)^{1/2}$$

$$I_4 = \int_{0}^{\infty} e^{-\alpha v^2} \ v^4 \ dv = -\frac{\partial}{\partial \alpha} I_2 \frac{3}{8} \frac{1}{\alpha^2} \left( \frac{\pi}{\alpha} \right)^{1/2}$$
and so on. Then mean velocity is

\[
\bar{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{0}^{\infty} e^{-\frac{\beta m v^2}{2}} v^3 \, dv
\]

\[
\bar{v} = \left(\frac{8kT}{m\pi}\right)^{1/2} \tag{4.23}
\]

The mean square velocity is

\[
\bar{v}^2 = \int_{0}^{\infty} dv \, f(v) \, v^2
\]

\[
= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{0}^{\infty} dv \, e^{-\frac{\beta m v^2}{2}} v^4
\]

\[
= \frac{3}{m\beta} \tag{4.24}
\]

and

\[
\bar{v}^2 = \frac{3kT}{m}.
\]

The mean kinetic energy is then

\[
\bar{\epsilon} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT
\]

The most probable velocity is that velocity we expect to find most often. That is, at this velocity, \(f(v)\) is a maximum, i.e. \(v = v_{mp}\) at \(\frac{\partial f}{\partial v} = 0\).

Using (4.18)

\[
\frac{\partial f}{\partial v} = constant \times \left[ -e^{-\frac{\beta mv^2}{2}} v^2 \left(\frac{\beta m}{2} 2v\right) + e^{-\frac{\beta mv^2}{2}} 2v \right] = 0
\]

or

\[
v_{mp} = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \tag{4.25}
\]

We see that \(v_{mp}\) lies below \(\bar{v}\), this is because \(v_{mp}\) is close to the maximum of the Gaussian part of \(f(v)\) (See Fig. 4.2) while the density of states (proportional to \(v^2\)) extends \(v\) to higher velocities.

### 4.3 Doppler Broadening

As an application of the Maxwell – Boltzmann velocity distribution, we examine the broadening of atomic spectral lines observed from atoms in a gas.
For example, if an electron in an atom is excited to a higher energy state $\epsilon_s$, a photon of energy $h\nu_o = \epsilon_s - \epsilon_1$ is emitted when the electron returns to its original state $\epsilon_1$. (The electron could be excited in this specific way by a laser), the atom then emits radiation at characteristic wavelength $\lambda_o = c/\nu_o$, where $c$ is the velocity of light. An observer fixed with respect to the atom sees a sharp spectral line at this wavelength $\lambda_o$. However, due to the distribution of velocities of atoms in a gas, a distribution of spectral wavelengths is observed from atoms in a gas.

To find this distribution, consider an atom traveling to the right away from the observer with a velocity $v_x$ (See Fig. 4.4). During one period, $\tau_0$, the atom travels a distance $d = v_x \tau_0$. The wavefront at the end of the period takes an additional time $\delta t = d/c = v_x \tau_0/c$ to reach the observer than did the previous wavefront one period earlier. The apparent or observed period, $\tau$, between points of equal phase reaching the observer is then

$$\tau = \tau_0 + \delta t = \tau_0 \left(1 + \frac{v_x}{c}\right)$$

and the apparent wavelength, $\lambda = c\tau$, is

$$\lambda = \lambda_o \left(1 + \frac{v_x}{c}\right)$$

This is referred to as the Doppler wavelength shift. For example, for stars receding rapidly from earth ($v_x$ large) the apparent wavelength of starlight is substantially shifted toward the red end of the spectrum (the red shift).

Consider now a gas of atoms having a Maxwellian distribution of velocities. This velocity distribution will lead via (4.17) and (4.26) to a distribution of observed wavelengths. This distribution, $f(\lambda) \, d\lambda$, giving the probability of observing a given ‘photon’ with wavelength in the range $\lambda$ to $\lambda + d\lambda$, is obtained from $f(v_x) \, dv_x$ as

$$f(\lambda) \, d\lambda = f(v_x) \left(\frac{d\lambda}{dv_x}\right) \, dv_x = f(v_x) \, dv_x$$

then from (4.26)

$$f(\lambda) = f(v_x) \left(\frac{d\lambda}{dv_x}\right)^{-1} = f(v_x) \frac{c}{\lambda_o}$$

which is

$$f(\lambda) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \frac{c}{\lambda_o} e^{-\frac{m\beta}{2} c^2 \left(\frac{\lambda - \lambda_o}{\lambda_o}\right)^2}$$

(4.27)
This is a Gaussian distribution of wavelengths centered at the characteristic wavelength $\lambda_o$. It gives the fraction, $f(\lambda)$, of intensity observed at wavelength $\lambda$ and is correctly normalized to

$$\int_{-\infty}^{\infty} f(\lambda) \, d\lambda = 1$$

In spectroscopic studies of atoms the aim is usually to measure $\lambda_o$ as accurately as possible. Without the velocity brodening a single (line) wavelength $\lambda_o$ would be observed and the atomic energy levels can be obtained precisely. Doppler broadening simply introduces error. The full width at one half the maximum (FWHM) of the Doppler distribution $W_D = 2 \lambda_o c (\frac{2kT}{m} \log 2)^{\frac{1}{2}}$ can be reduced by reducing the temperature of the gas. The Doppler width is particularly a problem if we wish to measure the lifetime, $\tau_s$, the excited state $s$.

This lifetime introduces a "natural width" $W_s \sim 2 \tau_s^{-1}$ to the spectral line. The shape of this natural width is usually Lorentian. The total FWHM of the observed line due to the natural and Doppler broadening (if both assumed Gaussian) is $(W_s^2 + W_D^2)^{\frac{1}{2}}$. Clearly $\tau_s$ can not even be estimated unless $W_D << W_s$.

### 4.4 Thermodynamic Properties

Once the free energy

$$F = -kT \log Z$$

of a body is known, all other thermodynamic properties can be obtained by differentiating this free energy. For a perfect gas of monatomic, classical atoms

$$Z = \frac{Z_o^N}{N!} = \left(\frac{eZ_o}{N}\right)^N$$

(4.28)

where $Z_0 = V/\lambda^3_0 = Z_{\text{trans}}$ is the translational partition function of a single atom in the gas. The free energy is then

$$F = -N \left[kT \log \left(\frac{eZ_o}{N}\right)\right]$$

(4.29)

which is clearly an extensive thermodynamic function as required. The pressure exerted by the gas is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = NkT \frac{\partial}{\partial V} \left(\log \frac{eZ_o}{N}\right)_T = \frac{NkT}{V}$$

which gives the familiar perfect gas equation of state

$$pV = NkT$$

(4.30)
Chapter 4.

The internal energy of the gas is

\[ U = \frac{\partial}{\partial \beta} (\beta F)_V = -N \frac{\partial}{\partial \beta} \left( \log \frac{Z_o N}{N} \right)_V = N \frac{3}{2} kT \]

This gives the familiar principle of equipartition result; each degree of freedom (three translational here) of a classical particle has average energy \( \frac{1}{2} kT \). The energy per mole (1 mole contains \( N_o \) atoms and \( kN_o = R \)) is \( U = \frac{3}{2} RT \). The molar specific heats are:

(a) At constant volume

\[ c_v \equiv \left( \frac{dQ}{dT} \right)_V = \left( \frac{dU}{dT} \right)_V = \frac{3}{2} R \]  

(b) At constant pressure

\[ c_p \equiv \left( \frac{dQ}{dT} \right)_p = \left( \frac{dU}{dT} \right)_p + p \left( \frac{dV}{dT} \right)_p = \frac{3}{2} R + R = \frac{5}{2} R \]  

This gives a specific heat ratio for a monatomic gas,

\[ \frac{c_p}{c_v} = \frac{5}{3} \]

The chemical potential is from (4.28)

\[ \mu \equiv \left( \frac{\partial F}{\partial N} \right)_{T,V} = -kT \log \left( \frac{Z_o N}{N} \right) \]  

or

\[ e^{\beta \mu} = \frac{N}{Z_o} \]

With this expression we may write \( \bar{n}_s \), the expected number of atoms in single atom state \( s \), in the compact form

\[ \bar{n}_s = \frac{N}{Z_o} e^{-\beta \epsilon_s} = e^{-\beta (\epsilon_s - \mu)} \]  

This will be most suggestive when we seek more general probability distributions and when we compare classical and quantum systems.

The entropy of the gas is most interesting and holds a special place in the development of statistical mechanics. This is, from (4.28),

\[ S_{trans} = -\left( \frac{\partial F}{\partial T} \right)_V = kN \left[ \log \left( \frac{V}{N} \right) + \frac{3}{2} \log \left( \frac{2\pi m kT}{\hbar^2} \right) + \frac{5}{2} \right] \]  

This is denoted the translational entropy since it arises from the translational energy states in \( Z_{trans} \). This is the famous Sachur–Tetrode equation named
after the two physicists who independently (in 1910 and 1911) verified its correctness experimentally.

The Sachur–Tetrode equation is important for two reasons. Firstly, note that $S$ is a correctly extensive quantity as it should be. If we had not divided $Z_o$ by $N!$ in (4.28), to correct the Boltzmann counting (see section 3.2), the first term of (4.35) would be $kN \log (V)$ which increases faster than $N$. This result verified the need to divide by $N!$ originally proposed to avoid Gibb’s paradox. Secondly, $S$ depends explicitly upon $h$ and is the only thermodynamic property except $F$ and $\mu$ that does. Thus the validity of (4.35) verified the choice, $h^3$, of volume occupied by a single state in phase space selected in section 1.5. This raised a problem of rigor for Boltzmann’s method of most probable distribution applied to classical gases. We noted in section 3.1 that the expected occupation of a single state, $\bar{n}_s$, was $\bar{n}_s \approx e^{\beta\mu} \sim 1/30,000$ for a gas at STP with this cell size.

Boltzmann’s mathematical method on the other hand requires $n_s$ large so we may use Stirling’s approximation and differential calculus. We shall see these problems are neatly side stepped in Gibbs re-interpretation of Boltzmann’s mathematical model.

### 4.5 Diatomic Molecules

Many gases are made up of diatomic molecules, for example $H_2$, $O_2$ and $N_2$. The gas molecule then has internal structure and energy other than translational energy. To correctly describe a diatomic gas we must include these internal energy states of the molecule when evaluating the partition function.

**Rotation**

As a simple model of a diatomic molecule, Boltzmann proposed a rigid dumbbell; the two atoms are assumed to be point masses connected by a rigid massless link of length $l$ (see Fig. 4.6). The dumbbell can then rotate about the two axes (z and y axes) perpendicular to the link. Since the atoms are assumed point particles, the angular momentum of rotation about the axis of the link (x axis) is zero and can be ignored. More importantly, because the link is assumed
rigid, the two atoms cannot vibrate along the line of the link. This assumption of
rigidity, needed by Boltzmann to correctly explain the specific heat of diatomic
gases, was criticized by many at the time, since matter cannot be exactly rigid.
We know that interatomic bonds can be stretched and broken. The model was
however, generally accepted as the best available at the time since it predicted
the observed gas behaviour (for the wrong reasons as we shall see). The internal
energy of the molecule is then

$$
\epsilon_{\text{rot}} = \frac{1}{2} I \omega_1^2 + \frac{1}{2} I \omega_2^2
$$

(4.36)

where $I$ is the moment of inertia. We now use this model to calculate the
diatomic gas specific heat.

The energy states of the gas molecules are

$$
\epsilon_s = \epsilon_{\text{trans}} + \epsilon_{\text{rot}}
$$

Since the energies are simply additive the single molecule partition function, $Z_o$,
breaks up into a product of a translational and rotational partition function

$$
Z_o = \sum_s e^{-\beta \epsilon_s} = Z_{\text{trans}} \times Z_{\text{rot}}
$$

(4.37)

where $Z_{\text{trans}}$ is (4.9) and

$$
Z_{\text{rot}} = \sum_{\text{rot states}} e^{-\beta \epsilon_{\text{rot}}}
$$

(4.38)

We consider first rotation in 1D around an axis, say the $z$ axis in Fig. 4.6. In this
1D rotation, the angle $\phi$ plays the role of length and the angular momentum,
$L_\phi = I \omega$, the role of momentum. An element of 1D rotational phase space is
d$\Gamma = d\phi \, dL_\phi$. The rotational energy is $\epsilon_s = \frac{1}{2I} L_\phi^2 = \frac{1}{2} I \omega^2$ so that the rotational
Statistical Mechanics.

The partition function is

\[ Z_{\text{rot}} = \int ds \ e^{-\beta \epsilon_s} = \int d\Gamma \left( \frac{ds}{d\Gamma} \right) e^{-\beta \epsilon_s} \]

\[ = \frac{1}{\hbar} \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dL_\phi \ e^{-\frac{\beta}{2I} L_\phi^2} = 2\pi \left( \frac{2\pi IkT}{\hbar^2} \right)^{1/2} \]

\[ = \left( \frac{2\pi IkT}{\hbar^2} \right)^{1/2}. \]  

(4.39)

In 2D, for rotation of the dumbbell molecule about 2 axes (the y and z axes), the molecule rotates on a spherical surface with total solid angle \( \Omega = 4\pi \). An element of phase space is \( d\Omega \ dL_\phi \ dL_\phi \) and

\[ Z_{\text{rot}} = \sum_{\text{rot states}} e^{-\beta \epsilon_{\text{rot}}} = \frac{1}{\hbar^2} \int d\Omega \int d(I\omega_1) \int d(I\omega_2) e^{-\beta \epsilon_{\text{rot}}} \]

\[ = 4\pi \left( \frac{IkT}{\hbar^2} \right). \]  

(4.40)

The partition function of the gas is

\[ Z = \frac{Z_0^N}{N!} = \frac{Z_{\text{trans}}^N \times Z_{\text{rot}}^N}{N!} \]  

(4.41)

\( Z \) from \( Z \) we may again evaluate any gas property. The internal energy is

\[ U = -\frac{\partial}{\partial \beta} (\log Z) = -N \frac{\partial}{\partial \beta} (\log Z_{\text{trans}}) - N \frac{\partial}{\partial \beta} (\log Z_{\text{rot}}) \]  

(4.42)

with a rotational contribution

\[ U_{\text{rot}} = -N \frac{\partial}{\partial \beta} (\log Z_{\text{rot}}) = N kT \]

The specific heat per mole due to exciting the rotations is then

\[ c_v (\text{rot}) = R \]  

(4.43)

and the total for the gas is

\[ c_v (\text{total}) = c_v (\text{trans}) + c_v (\text{rot}) = \frac{5}{2} R \]  

(4.44)

In this model the rotation adds two additional degrees of freedom per molecule, each of energy \( \frac{1}{2} kT \). This makes a total of five degrees of freedom for the molecule. The ratio of \( c_p \) to \( c_v \) is

\[ \frac{c_p}{c_v} = \left( 1 + \frac{2}{5} \right) = 1.40 \]  

(4.45)
which agreed with the observed value and lead to acceptance of the rigid molecule picture proposed by Boltzmann.

We note also that the entropy of the gas has increased, from the monatomic case, due to the additional number of rotational states available to the molecules. This is from (4.40) and (4.41),

\[
S = \frac{\partial}{\partial T} (-kT \log Z)
\]

\[
= S_{\text{trans}} + kN \log Z_{\text{rot}} + Nk
\]

\[
= S_{\text{trans}} + kN \log \left( \frac{8\pi^2 \epsilon I kT}{h^2} \right)
\]

\[
= S_{\text{trans}} + S_{\text{rot}}
\]

This is from (4.46)

Since the partition functions are a product, the entropies must be additive.

We note here that for polyatomic molecules in which the atoms are not co-linear, rotation around three axes takes place. This adds an additional rotational degree of freedom. The molecule then has \( f = 6 \) degrees of freedom (3 translational and 3 rotational) so that

\[
c_v = f \frac{1}{2} R = 3 R
\]

\[
\frac{c_p}{c_v} = \left( 1 + \frac{2}{f} \right) = 1.33 \quad \text{(polyatomic gases)} \quad (4.47)
\]

### Vibration

We now remove the assumption that the dumbbell is rigid and allow the atoms of the diatomic molecule to vibrate along the line joining them. Instead we represent the interatomic bond by a spring having restoring force \(-\gamma u\), where \(u\) is the displacement of the interatom separation from its equilibrium value. This assumes the force is linear which leads to harmonic vibration about the equilibrium separation. In this model, the energy of the diatomic molecule is

\[
\epsilon = \frac{1}{2} M \vec{r}^2 + \frac{1}{2} \mu \dot{u}^2 + \frac{1}{2} \gamma u^2 + \epsilon_{\text{rot}}
\]

where \(M = m_1 + m_2\) is the total mass and \(\mu = \frac{m_1 m_2}{m_1 + m_2}\) is the reduced mass of the molecule.
Since $\epsilon_{\text{trans}}$, $\epsilon_{\text{vib}}$ and $\epsilon_{\text{rot}}$ are again simply additive, the molecular partition function is again a product

$$Z_o = Z_{\text{trans}} \times Z_{\text{vib}} \times Z_{\text{rot}}$$ (4.49)

where $Z_{\text{trans}}$ and $Z_{\text{rot}}$ are given by (4.9) and (4.40) as before and

$$Z_{\text{vib}} = \sum_{\text{vib states}} e^{-\beta \epsilon_{\text{vib}}}$$

$$\epsilon_{\text{vib}} = \frac{1}{2} \mu \dot{u}^2 + \frac{1}{2} \gamma u^2$$

Since $u$ is one dimensional, the phase space element is just $d\Gamma = du \ d(\mu \dot{u})$ with one cell (state) occupying an area $h$. The

$$Z_{\text{vib}} = \int \int \frac{du \ d(\dot{u})}{h} e^{-\beta \epsilon_{\text{vib}}}$$

$$= \frac{1}{h} \left[ \mu \int_{-\infty}^{\infty} d\dot{u} \ e^{-\beta \frac{1}{2} \mu \dot{u}^2} \right] \left[ \int_{-\infty}^{\infty} du \ e^{-\beta \frac{1}{2} \gamma u^2} \right]$$

$$= \frac{1}{h} \left( \frac{2\pi \mu}{\beta} \right)^{\frac{1}{2}} \left( \frac{2\pi}{\beta \gamma} \right)^{\frac{1}{2}}$$

or

$$Z_{\text{vib}} = \frac{2\pi kT}{h} \left( \frac{\mu}{\gamma} \right)^{\frac{1}{2}}$$ (4.50)

The vibrational energy of the gas is

$$U_{\text{vib}} = -\frac{\partial}{\partial \beta} (N \log Z_{\text{vib}}) = kT$$ (4.51)

giving a total of

$$U = U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} = \frac{3}{2} kT + kT + kT = \frac{7}{2} kT$$

The molar specific heat at constant volume is

$$c_v = \frac{7}{2} R$$ (4.52)
and
\[
\frac{c_p}{c_v} = \left(1 + \frac{2}{7}\right) = 1.29
\]  \hfill (4.53)

The problem with classical kinetic theory begin here because this value of $c_v$ is above the observed value of $\approx \frac{5}{2} R$ and $\frac{c_p}{c_v} = 1.29$ is below the observed ratio of 1.40. This result is independent of the magnitude of the restoring force constant $\gamma$, provided it is finite.