1 Ideal Gases

1.1 Quantum Gases

This will be our first example of the statistical mechanics of a macroscopic system. \( \Phi_{nN} \) and \( E_{nN} \) can be explicitly calculated for this system, so all the thermodynamic properties can be derived. We have

\[
\mathcal{H}(N) = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2
\]  

(1)

The solution for a single particle is

\[
\psi_k(r) = V^{-1/2} e^{i\vec{k} \cdot \vec{r}}.
\]  

(2)

If we take periodic boundary conditions (the most convenient), then \( k_x = \frac{2\pi n_x}{L} \), where \( n_x \) is an integer: \( n_x = -\infty, ..., 0, 1, ... \infty \) and \( L \) is the length of a side. Also \( k_y = \frac{2\pi n_y}{L} \) and \( k_z = \frac{2\pi n_z}{L} \) in the same way. This assumes that the box is cubic, but it can be shown that this assumption is not necessary.

The single particle energy is \( \hbar^2 k^2 / 2m \), where \( m \) is the mass. Since the Hamiltonian is a simple sum of single particle operators, we can write down the product wavefunctions

\[
\Phi_{nN} = V^{-N/2} e^{i\vec{k} \cdot \vec{r}_1} e^{i\vec{k} \cdot \vec{r}_2} \ldots e^{i\vec{k} \cdot \vec{r}_N}
\]  

(3)

This would further need to be symmetrized if the particles are bosons and anti-symmetrized if they are fermions. In the latter case, there is also the spin. All of this will be discussed below, but for the moment we ignore it. Note that \( n \), the generic label we have been using for the wavefunctions, is now completely specified by giving the set of \( \vec{k} \)'s. The energy of \( \Phi_{nN} \) is

\[
E_{nN} = \sum_{i=1}^{N} \frac{\hbar^2}{2m} k_i^2 = \sum_{i=1}^{N} \epsilon_k.
\]  

(4)

A convenient device to specify the wavefunctions are the occupation numbers \( n_{\vec{k}} \). (Sorry, yet another \( n \).) Then \( \Phi_{nN} \) is specified by the set of all \( n_{\vec{k}} \), where \( n_{\vec{k}} = 0, 1, 2, \ldots \) for bosons and \( n_{\vec{k}_s} = 0, 1 \) for fermions. \( s = \pm 1 \) for spin up and spin down. We shall agree that, for fermions, the sum over \( \vec{k} \) also includes a sum over spin projections, just in order to save writing. The sum over all states is just the sum over all possible occupation numbers. We can now write down a formula for \( Q \):

\[
Q(\mu, V, T) = \sum_{\{n_{\vec{k}}\}} e^{-\beta(E - \mu N)},
\]  

(5)

where the sum runs over allowed values for the set of \( \{n_{\vec{k}}\} \),

\[
E(\{n_{\vec{k}}\}) = \sum_{\vec{k}} \epsilon_{\vec{k}} n_{\vec{k}}.
\]  

(6)
and

\[ N = \sum_{\vec{k}} n_{\vec{k}}. \]  

(7)

Thus

\[
\mathcal{Q}(\mu, V, T) = \sum_{\{n_{\vec{k}}\}} \exp[-\beta \sum_{\vec{k}} n_{\vec{k}}(\epsilon_{\vec{k}} - \mu)]
\]

\[
= \sum_{n_{\vec{k}_1}} \exp[-\beta n_{\vec{k}_1}(\epsilon_{\vec{k}_1} - \mu)] \times \sum_{n_{\vec{k}_2}} \exp[-\beta n_{\vec{k}_2}(\epsilon_{\vec{k}_2} - \mu)] \times
\]

\[
\cdots \times \sum_{n_{\vec{k}_N}} \exp[-\beta n_{\vec{k}_N}(\epsilon_{\vec{k}_N} - \mu)]
\]

\[
= \prod_{\vec{k}} \sum_{n_{\vec{k}}} \exp[-\beta n_{\vec{k}}(\epsilon_{\vec{k}} - \mu)]. \]  

(8)

For bosons, this is

\[
\mathcal{Q}_B = \prod_{\vec{k}} \sum_{n_{\vec{k}}=0}^{\infty} \exp[-\beta n_{\vec{k}}(\epsilon_{\vec{k}} - \mu)]
\]

\[
= \prod_{\vec{k}} \left[ 1 - \exp[-\beta(\epsilon_{\vec{k}} - \mu)] \right]^{-1} \]  

(10)

For fermions, it is

\[
\mathcal{Q}_F = \prod_{\vec{k}} \sum_{n_{\vec{k}}=0,1} \exp[-\beta n_{\vec{k}}(\epsilon_{\vec{k}} - \mu)]
\]

\[
= \prod_{\vec{k}} \left[ 1 + \exp[-\beta(\epsilon_{\vec{k}} - \mu)] \right] \]  

(12)

Notice that it would be much more difficult to calculate \( Q \), the partition function for the canonical distribution. We would need to fix \( N \) which is a constraint on the values of the \( n_{\vec{k}} \). The unrestricted sums for \( Q \) are much easier. This is an example of what I mentioned before, that it is sometimes easier to consider variable \( N \), even though it appears to be more complicated. The equations of state for fixed \( \mu \) are

\[
\frac{PV}{kT} = \ln \mathcal{Q}_B = -\sum_{\vec{k}} \ln \left[ 1 - \exp[-\beta(\epsilon_{\vec{k}} - \mu)] \right]
\]

(14)

for bosons, and

\[
\frac{PV}{kT} = \ln \mathcal{Q}_F = \sum_{\vec{k}_s} \ln \left[ 1 + \exp[-\beta(\epsilon_{\vec{k}} - \mu)] \right]
\]

\[
= 2 \sum_{\vec{k}} \ln \left[ 1 + \exp[-\beta(\epsilon_{\vec{k}} - \mu)] \right]
\]

(15)
for fermions. I have now put in the spin factor explicitly for the fermions, which are assumed to have spin 1/2. The bosons are assumed to have spin zero, so there is no spin factor for them.

We will analyze these expressions later. Their main defect is that they involve \( \mu \), which is not easy to measure, instead of \( N \). We take care of this by finding a relationship between \( \mu \) and \( N \) as follows. The average occupation number is

\[
\overline{n}_k = \frac{1}{Q} \sum_{\{n_{\bar{k}}\}} n_{\bar{k}} \exp(\beta \mu N - \beta n_{\bar{k}} \epsilon_{\bar{k}}) = -\frac{1}{\beta} \frac{\partial \ln Q}{\partial \epsilon_{\bar{k}}}. \tag{17}
\]

Substituting the form for bosons:

\[
\overline{n}_k = -\frac{1}{\beta} \frac{\partial \ln Q_B}{\partial \epsilon_{\bar{k}}} = \frac{e^{-\beta(\epsilon_{\bar{k}} - \mu)}}{1 - e^{-\beta(\epsilon_{\bar{k}} - \mu)}} = \frac{1}{e^{\beta(\epsilon_{\bar{k}} - \mu)} - 1}. \tag{18}
\]

while for fermions

\[
\overline{n}_{\bar{k}} = -\frac{1}{\beta} \frac{\partial \ln Q_F}{\partial \epsilon_{\bar{k}}} = \frac{e^{-\beta(\epsilon_{\bar{k}} - \mu)}}{1 + e^{-\beta(\epsilon_{\bar{k}} - \mu)}} = \frac{1}{e^{\beta(\epsilon_{\bar{k}} - \mu)} + 1}. \tag{19}
\]

These expressions are known as the Bose distribution and the Fermi distribution respectively. Amazingly, they differ only in the sign of the 1 in the denominator. This sign turns out to make enormous qualitative differences in the behavior of these two kinds of systems, as we shall see. These distributions offer a short cut to the calculation of many thermodynamic properties. For example consider any operator \( \Theta \) of the form

\[
\Theta = \sum_i \theta(\vec{r}_i), \tag{20}
\]

i.e., \( \Theta \) is a sum of single-particle operators. Then

\[
< \Phi_{nN} | \Theta | \Phi_{nN} > = V^{-N} \sum_i < \exp[i \sum_i \vec{k}_i \cdot \vec{r}_i] | \theta(\vec{r}_i) | \exp[i \sum_i \vec{k}_i \cdot \vec{r}_i] > \tag{21}
\]

\[
= V^{-1} \sum_i < \exp(i \vec{k}_i \cdot \vec{r}_i) | \theta(\vec{r}_i) | \exp(i \vec{k}_i \cdot \vec{r}_i) >. \tag{22}
\]

Here the sum runs only over occupied states \( \vec{k}_i \). Hence

\[
< \Phi_{nN} | \Theta | \Phi_{nN} > = \sum_{\bar{k}} n_{\bar{k}} \theta_{\bar{k}}, \tag{23}
\]

where the sum is over all \( \bar{k} \) and

\[
\theta_{\bar{k}} \equiv V^{-1} < \exp(i \vec{k} \cdot \vec{r}) | \theta(\vec{r}) | \exp(i \vec{k} \cdot \vec{r}) >. \tag{24}
\]

So now

\[
\bar{\theta} = \frac{1}{Q} \sum_{\{n_{\bar{k}}\}} e^{\beta(E - \mu N)} < \Phi_{nN} | \theta(\vec{r}) | \Phi_{nN} > \tag{25}
\]

\[
= \frac{1}{Q} \sum_{\bar{k}} \theta_{\bar{k}} \sum_{\{n_{\bar{k}}\}} e^{\beta(E - \mu N)} n_{\bar{k}} \tag{26}
\]

\[
= \sum_{\bar{k}} \overline{n}_{\bar{k}} \theta_{\bar{k}}. \tag{27}
\]
This formula holds good for bosons or fermions if the appropriate form for \( n_\vec{k} \) is put in. For fermions one must sum over spin as well as \( \vec{k} \). Our goal, to get the total number of particles, is now easy. For bosons:

\[
\overline{N} = \sum_{\vec{k}} \overline{n}_{\vec{k}} = \sum_{\vec{k}} \frac{1}{e^{\beta(\vec{k}) - \mu} - 1}
\]

(28)

while for fermions:

\[
\overline{N} = \sum_{\vec{k}_s} \overline{n}_{\vec{k}_s} = \sum_{\vec{k}_s} \frac{1}{e^{\beta(\vec{k}_s) - \mu} + 1}.
\]

(29)

We will analyze these expressions below. First we would like to see how they reduce to the classical case. This should occur when coherence effect due to the overlap of the wavefunctions becomes negligible. This means high temperature or low density. The precise condition is

\[
kT > \frac{\hbar^2 n^{2/3}}{2m}.
\]

(30)

In order to evaluate these expressions, we use the fact that

\[
\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z),
\]

(31)

so that the \( \vec{k} \) vectors sit at the sites of a simple cubic lattice. Each cell of the lattice has a volume \( \Omega = (2\pi/L)^3 = (2\pi)^3/V \), where \( V \) is the volume of the gas. To approximate the sum by an integral, therefore, we write the Riemann approximation for the integral,

\[
\int d^3k \ f(\vec{k}) = \frac{(2\pi)^3}{V} \sum_{\vec{k}} f(\vec{k}),
\]

(32)

which is a good approximation whenever \( f \) is slowly varying on the scale of \( 2\pi/L \). This will almost always be true.

1.2 Classical Ideal Gas

Now we would like to get the classical limit of the above equations. To do so we will give a slightly more careful treatment of the wavefunctions. These are

\[
\Phi_N(\{\vec{r}_i\}) = V^{-N/2}(N!)^{-1/2} \sum_{\mathcal{P}} \delta_{\mathcal{P}} \exp\left[i \sum_i \vec{k}_i \cdot (\mathcal{P}\vec{r}_i)\right].
\]

(33)

This is similar to what we had above, only we have put in the symmetry properties explicitly. \( \mathcal{P} \) represents all the permutations of the \( \vec{r}_i \), and \( \delta_{\mathcal{P}} = 1 \) if the particles are bosons, and \( \delta_{\mathcal{P}} = \pm 1 \), depending on whether \( \mathcal{P} \) is even or odd, for fermions. (For fermions, consider only one spin direction for now.) For two particles

\[
\Phi_2(\vec{k}, \vec{k}') = \frac{1}{\sqrt{2V}} \left(e^{i\vec{k}\cdot\vec{r}_1 + i\vec{k}'\cdot\vec{r}_2} \pm e^{i\vec{k}\cdot\vec{r}_2 + i\vec{k}'\cdot\vec{r}_1}\right),
\]

(34)
but for many particles the wavefunction is too long to write down.

For the classical case we can calculate the canonical partition function just as easily as the grand canonical one, so that is what we do. For a gas of \( N \) particles:

\[
Q = \sum_{\{\vec{k}\}} \langle \Phi_N(\{\vec{k}\}) | e^{-\beta \mathcal{H}_c} | \Phi_N(\{\vec{k}\}) \rangle. \tag{35}
\]

The set \( \{\vec{k}\} \) of all choices of \( \vec{k} \) gives the set of all wavefunctions. However, permuting the \( \vec{k} \)'s does not produce a new state, because the particles are indistinguishable. Thus to sum over all states we must integrate over the momenta and divide by \( N! \).

Writing this out explicitly:

\[
Q = (N!)^{-2} \frac{V^N}{(2\pi)^{3N}} \int d^3k_1 d^3k_2 \ldots d^3k_N \exp\left[-\frac{\beta \hbar^2}{2m} \sum_i k_i^2\right] \times \sum_p \sum_{p'} \delta_p \delta_{p'} \int \exp[-i \sum_i \vec{k}_i \cdot (\mathcal{P} \vec{r}_i) + i \sum_i \vec{k}_i \cdot (\mathcal{P}' \vec{r}_i)] d^3r_1 d^3r_2 \ldots d^3r_N \tag{36}
\]

All the \( \mathcal{P}' \) give the same contribution. Hence

\[
Q = (N!)^{-1} (2\pi)^{-3N} \int d^3k_1 d^3k_2 \ldots d^3k_N \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\left[-\frac{\beta \hbar^2}{2m} \sum_i k_i^2\right] \tag{37}
\]

\[
\sum_p \delta_p \exp\left[i \sum_i \vec{k}_i \cdot (\mathcal{P} \vec{r}_i) - i \sum_i \vec{r}_i \cdot \vec{r}_i\right]. \tag{38}
\]

Multiply and divide this result by

\[
\prod_i \int \exp\left[-\frac{\beta \hbar^2 k_i^2}{2m}\right] d^3k_i \tag{39}
\]

to get

\[
Q = (N!)^{-1} (2\pi)^{-3N} \int d^3k_1 d^3k_2 \ldots d^3k_N \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\left[-\frac{\beta \hbar^2}{2m} \sum_i k_i^2\right] \tag{40}
\]

\[
\sum_p \delta_p f(\vec{r}_1 - \mathcal{P} \vec{r}_1) \times f(\vec{r}_2 - \mathcal{P} \vec{r}_2) \times \cdots \times f(\vec{r}_N - \mathcal{P} \vec{r}_N), \tag{41}
\]

where

\[
f(\vec{r}) = \frac{\int \exp\left[-\frac{\beta \hbar^2 k^2}{2m}\right] e^{i\vec{k} \cdot \vec{r}} d^3k}{\int \exp\left[-\frac{\beta \hbar^2 k^2}{2m}\right] d^3k} = \frac{\int \exp\left[-\frac{\beta \hbar^2}{2m} \left(k + i\vec{r}/\beta \hbar^2\right)^2\right] d^3k}{\int \exp\left[-\frac{\beta \hbar^2 k^2}{2m}\right] d^3k} \tag{42}
\]

\[
e^{-m \vec{r}^2/2\beta \hbar^2} = e^{-\pi \nu^2/\lambda^2}, \tag{43}
\]

where

\[
\lambda \equiv \frac{(2\pi \hbar^2)}{(mkT)^{1/2}}, \tag{44}
\]

\[
5
\]
which is called the thermal de Broglie wavelength. We may now extract the classical limit. Consider the function

\[ f(\vec{r}_i - \mathcal{P}\vec{r}_i) = \exp\left[-\pi(\vec{r}_i - \mathcal{P}\vec{r}_i)^2/\lambda^2\right]. \]  

(46)

If \( \mathcal{P} = \) identity permutation, then

\[ f(\vec{r}_i - \mathcal{P}\vec{r}_i) = f(0) = 1 \]  

(47)

for all \( \vec{r}_i \). If \( \mathcal{P} \neq \) the identity permutation, then \( \vec{r}_i \neq \mathcal{P}\vec{r}_i \) for some \( \vec{r}_i \). \( f(\vec{r}_i - \mathcal{P}\vec{r}_i) \) will then be small if the separation of \( \vec{r}_i \) and \( \mathcal{P}\vec{r}_i \) is large compared with \( \lambda \). This will be the case if the interparticle spacing \( (V/N)^{1/3} \) is much greater than \( \lambda \), or \( (V/N)^{2/3} >> 2\pi\hbar^2/mkT \). Hence for low densities or high temperatures, we have

\[ Q = (N!)^{-1}(2\pi)^{-3N} \int d^3k_1 \ldots d^3k_N \int d^3r_1 \ldots d^3r_N \exp\left[-\frac{\beta\hbar^2}{2m} \sum_i k_i^2\right] \]  

(48)

\[ = (N!)^{-1} \frac{1}{h^{3N}} \int d^3p_1 \ldots d^3p_N \int d^3r_1 \ldots d^3r_N \exp\left[-\beta H(\vec{p}, \vec{r})\right] \]  

(49)

Here we have used the relation \( \vec{p} = h\vec{k} \).

This is exactly the classical partition function for an ideal gas. We did not talk about purely classical statistical mechanics, but, simply stated, the prescription for calculating the partition function is this: integrate \( \exp(-\beta H) \) over classical phase space \( p \) and \( r \) for all the particles, with \( H \) being the classical Hamiltonian. For an ideal gas \( H = \sum_i p_i^2/2m \). The peculiar and very \textit{ad hoc} thing is the factor in front. In classical mechanics phase space needs to be divided into cells such that \( dp_i dr_i = \hbar \) (the quantum constant!) for counting purposes. Furthermore, even in classical mechanics particles must be regarded as indistinguishable to get the counting of states correctly, meaning that we need to multiply \( Q \) by the factor \( (N!)^{-1} \) - the Gibbs paradox. It is impossible to obtain this factor consistently with classical reasoning. You can see why we used quantum, rather than classical, physics to derive statistical mechanics.

The good thing about the formula is that it allows us to calculate the first quantum correction to the classical partition function. The expression

\[ \sum_{\mathcal{P}} \delta_{\mathcal{P}} f(\vec{r}_1 - \mathcal{P}\vec{r}_1) \times f(\vec{r}_2 - \mathcal{P}\vec{r}_2) \times \cdots \times f(\vec{r}_N - \mathcal{P}\vec{r}_N) \]  

(50)

is equal to unity in the classical approximation when only \( \mathcal{P} = \) identity counts. The next term is when \( \mathcal{P} \) contains only one interchange. For example when particles 1 and 2 are interchanged:

\[ \mathcal{P}(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_i, \ldots \vec{r}_j, \ldots \vec{r}_N) = (\vec{r}_1, \vec{r}_2, \ldots \vec{r}_j, \ldots \vec{r}_i \ldots \vec{r}_N) \]  

(51)

and we must sum all all such pairwise interchanges. Now let \( f_{ij} = f(\vec{r}_i - \vec{r}_j) \). Then

\[ \sum_{\mathcal{P}} \delta_{\mathcal{P}} f(\vec{r}_1 - \mathcal{P}\vec{r}_1) \times f(\vec{r}_2 - \mathcal{P}\vec{r}_2) \times \cdots \times f(\vec{r}_N - \mathcal{P}\vec{r}_N) = 1 \pm \sum_{i<j} f_{ij}^2 \]  

(52)
Here the upper (lower) sign is for bosons (fermions).

If \( f_{ij} \) is very small (as we are assuming), then

\[
1 \pm \sum_{i<j} f_{ij}^2 \approx \prod_{i<j} (1 \pm f_{ij}^2) = e^{-\beta \sum_{i<j} \tilde{V}_{ij}},
\]  

(53)

where

\[
\tilde{V}_{ij} = -kT \ln(1 \pm f_{ij}^2) = -kT \ln \{1 \pm \exp[-2\pi(\vec{r}_i - \vec{r}_j)^2/\lambda^2]\}. \tag{54}
\]

\( Q \) then becomes

\[
Q = (N!)^{-1} \pi^{-3N} \int d^3k_1 d^3k_2 \ldots d^3k_N \int d^3r_1 d^3r_2 \ldots d^3r_N \exp\left[\frac{-\beta \hbar^2}{2m} \sum_{i=1}^N k_i^2 - \beta \sum_{i<j} \tilde{V}_{ij}\right]. \tag{55}
\]

It can now be seen why we rewrote the correction in the way we did. The effect of the symmetry of the wavefunction is exactly like an effective potential which pairs of particles feel. It is attractive for bosons and repulsive for fermions, in accord with the idea that the Pauli principle acts to keep fermions apart, and there should be a corresponding attraction for bosons.

Having understood the basis for the partition function of an ideal gas, let us move on to the consequences. At high temperatures and low densities, we have

\[
Q = \frac{1}{N! \hbar^{3N}} \int d^3p_1 d^3p_2 \ldots d^3p_N \int d^3r_1 d^3r_2 \ldots d^3r_N \times \tag{56}
\]

\[
\exp\left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m}\right] \sum_{i,n} \exp\left[-\beta \epsilon_{i,n}\right]. \tag{57}
\]

Here \( \vec{p}_i \) and \( \vec{r}_i \) are the three-dimensional center of mass momenta and coordinates of the molecules. If, in addition, particle \( i \) has internal degrees of freedom with energy levels \( \epsilon_{i,n} \), then these must be included as well. We have assumed that the particles are identical, so the levels are the same for each: \( \epsilon_{i,n} = \epsilon_n \). Also, the density is assumed to be sufficiently low that interactions between particles are not important.

In this case, the total energy is the sum of the individual energies. Now let

\[
Q_{int} = \sum_n \exp[-\beta \epsilon_n]. \tag{58}
\]

Then

\[
Q = V^N (N! \hbar^{3N})^{-1} \pi^{3N/2} \left(\frac{2m}{\beta}\right)^{3N/2} (Q_{int})^N. \tag{59}
\]

Now we use Stirling’s approximation:

\[
\ln(N!) = \sum_{n=1}^N \ln n \approx \int_0^N \ln x \,dx = N \log N - N = N \ln(N/e) \tag{60}
\]

to write the free energy as

\[
A = -kT \ln Q = -NkT \ln \left[\frac{eV}{N} \left(\frac{mkT}{2\pi \hbar^2}\right)^{3/2} Q_{int}(T)\right]. \tag{61}
\]
Note that $Q_{\text{int}}$ is independent of volume. A useful form for $A(V,T)$ is

$$A = -NkT \ln(eV/N) + Nf(T),$$  \hspace{1cm} (62)

where

$$f(T) = -kT \ln \left[ \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} Q_{\text{int}}(T) \right].$$  \hspace{1cm} (63)

The equation of state is given by

$$P = -\left( \frac{\partial A}{\partial V} \right)_T = NkT/V.$$  \hspace{1cm} (64)

### 1.2.1 Internal degrees of freedom

At long last, we have derived the simplest prediction of statistical mechanics, the ideal gas equation of state. Another basic characteristic of ideal gases is that the internal energy depends only on the temperature. This comes from

$$U = A + TS = A - T \left( \frac{\partial A}{\partial T} \right)_V$$  \hspace{1cm} (65)

$$= -NkT \ln \frac{eV}{N} + Nf(T) - T(-Nk \ln \frac{eV}{N}) - NTf'(T)$$  \hspace{1cm} (66)

$$= Nf(T) - NTf'(T).$$  \hspace{1cm} (67)

This is a function of temperature alone. The specific heat may also be obtained in terms of $f(T)$:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$  \hspace{1cm} (68)

$$= Nf'(T) - Nf'(T) - NT''(T)$$  \hspace{1cm} (69)

$$= -NTf''(T).$$  \hspace{1cm} (70)

$f(T)$ affects $C_V$, but not the equation of state.

Now let us evaluate $f(T)$ in various cases. A monatomic gas will generally have a ground state energy $\epsilon_0$ for each atom and the first excited state $\epsilon_1$, will be well separated from $\epsilon_0$:

$$\epsilon_1 - \epsilon_0 \sim 1eV.$$  \hspace{1cm} (71)

This corresponds to a temperature of about $10^4K$. Assume $T << 10^4K$. Now choose energies such that $\epsilon_0 = 0$. Then $Q_{\text{int}} \approx 1$, and we have

$$f(T) = -kT \ln \left[ \left( \frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right].$$  \hspace{1cm} (72)
which we may rewrite as

$$f(T) = -\frac{3kT}{2} \left[ \ln T + \ln \left( \frac{mk}{2\pi \hbar^2} \right) \right]$$

(73)

which gives:

$$f'(T) = -\frac{3k}{2} \left[ 1 + \ln T + \ln \left( mk/2\pi \hbar^2 \right) \right],$$

(74)

and

$$f''(T) = -\frac{3k}{2T},$$

(75)

which yields

$$C_V = -NTf''(T) = \frac{3}{2} Nk$$

(76)

The dimensionless specific heat per particle is $c_v = C_V/Nk = 3/2$.

Let us now consider temperatures high enough that excited state of the particles have some reasonable chance of being occupied.

For diatomic gases, two cases are possible: homonuclear (same atoms) and heteronuclear (different atoms). Let us do the simpler heteronuclear case first. The molecule can be thought of as a springy dumbbell. The energy levels are

$$\epsilon_{\ell n} = \hbar \omega(n + 1/2) + \hbar^2 \ell(\ell + 1)/2I,$$

(77)

where $\omega$ is the natural frequency of the spring ($\hbar \omega/k \sim 10^3 K$ or $10^4 K$), and $I$ is the moment of inertia ($\hbar^2/2Ik \sim 10K$ or $10^2 K$). $n$ and $\ell$ are nonnegative integers. Then

$$Q_{\text{int}} = \sum_{n=0, \ell=0}^{\infty} \exp[-\beta \epsilon_{\ell n}] = Q_{\text{rot}} Q_{\text{vib}},$$

(78)

where

$$Q_{\text{rot}} = \left( \sum_{\ell=0}^{\infty} \exp[-\beta \hbar^2 \ell(\ell + 1)/2I] \right)^N \equiv q_{\text{rot}}^N,$$

(79)

and

$$Q_{\text{vib}} = \left( \sum_{n=0}^{\infty} \exp[-\beta \hbar \omega(n + 1/2)] \right)^N \equiv q_{\text{vib}}^N.$$

(80)

The $2\ell + 1$ factor takes care of the degeneracy of an angular momentum state $\ell$.

The free energy may be written as

$$A = -kT \log(Q_{\text{mon}} Q_{\text{rot}} Q_{\text{vib}}) = A_{\text{mon}} + A_{\text{rot}} + A_{\text{vib}}.$$

(81)

Here $A_{\text{mon}}$ is the free energy of a monatomic gas, calculated above, and

$$A_{\text{rot}} = -kT \log Q_{\text{rot}} = -NkT \log q_{\text{rot}}$$

(82)

$$A_{\text{vib}} = -kT \log Q_{\text{vib}} = -NkT \log q_{\text{vib}}.$$
Let us first consider the rotational part:

\[ q_{\text{rot}} = \sum_{\ell=0}^{\infty} \exp[-\beta \hbar^2 \ell (\ell + 1)/2I], \]  

(84)

This cannot be summed analytically, but we can easily do some limiting cases. The most important is high temperature or small \( \beta \), since \((\beta \hbar^2/2I) \ll 1\) for almost all gases - because they liquefy before the temperature is low enough to probe the rotational levels, i.e., the boiling temperature \( T_b \) satisfies \( kT_b > \hbar^2/2I \). Hydrogen and its isotopes are the exception. For \((\beta \hbar^2/2I) \gg 1\), we may approximate the sum by an integral

\[ q_{\text{rot}} = \int_{0}^{\infty} (2x+1)e^{-\beta \hbar^2 (x^2+x)/2I} \, dx, \]  

(85)

because the integrand changes little on replacing \( x \) with \( x+1 \). Let \( u = \beta \hbar^2 (x^2+x)/2I \). Then

\[ q_{\text{rot}} = (2I/\beta \hbar^2) \int_{0}^{\infty} e^{-u} \, du = 2I/\beta \hbar^2, \]  

(86)

and

\[ A_{\text{rot}} = -NkT \log(2\pi kT/\hbar^2). \]  

(87)

The associated entropy and specific heat are

\[ S_{\text{rot}} = -\langle \partial A_{\text{rot}}/\partial T \rangle_V = Nk \log(2I kT/\hbar^2) + Nk \]  

(88)

and

\[ C_{\text{rot}} = T \langle \partial S_{\text{rot}}/\partial T \rangle_V = Nk. \]  

(89)

At low temperatures we need consider only the \( l=1 \) term:

\[ q_{\text{rot}} = 1 + 3e^{-\beta \hbar^2/I} \]  

(90)

and

\[ A_{\text{rot}} \approx -NkT \log(1 + 3e^{\beta \hbar^2/I}) \approx -3NkT e^{-\hbar^2/IkT} \]  

(91)

\[ S_{\text{rot}} = -\langle \partial A_{\text{rot}}/\partial T \rangle_V = 3Nk(1 + \frac{\hbar^2}{Ik}) e^{-\hbar^2/IkT} \]  

(92)

The specific heat is

\[ C_{\text{rot}} = T \langle \partial S_{\text{rot}}/\partial T \rangle_V = \frac{3N \hbar^2}{IT^2} e^{-\hbar^2/IkT} \]  

(93)

The only homonuclear cases of experimental interest are \( H_2 \) and \( D_2 \). Let us concentrate on \( H_2 \). The nuclei are protons, which must satisfy the restriction that their wavefunction is antisymmetric under interchange of nuclear coordinates. \( \ell = \text{even} \) is symmetric and \( \ell = \text{odd} \) is antisymmetric for the spatial part. But there is the nuclear spin wavefunction as well. Here \( S = 1 \) is symmetric and three-fold degenerate, and \( S = 0 \) is antisymmetric and nondegenerate. Hence \((\ell = \text{even}, S = 0), (\ell = \text{odd}, \)
$S = 1$) are the possible states. The first is called parahydrogen, the second is called orthohydrogen. We now obtain

$$q_{\text{rot}} = 3 \sum_{\ell = \text{odd}} (2\ell + 1)e^{-\beta \hbar^2 \ell (\ell + 1)/2I} + \sum_{\ell = \text{even}} (2\ell + 1)e^{-\beta \hbar^2 \ell (\ell + 1)/2I}. \quad (94)$$

I won’t analyze this expression further, except to pose the following exercise: show that the ratio of ortho-to para-hydrogen goes from zero to three as $T$ goes from 0 to $\infty$. This result holds in equilibrium. In practice, it is very difficult to change nuclear spins by collisions, that is, to achieve ortho-para equilibrium. If the ortho-para ratio is fixed by the initial conditions, the free energy is then just the sum of free energies for two distinct species.

The vibrational part is very easy and does not depend on the identity (or lack thereof) of the nuclei:

$$q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n+1/2)} = e^{-\beta \hbar \omega/2}(1 - e^{-\beta \hbar \omega})^{-1}, \quad (95)$$

which gives

$$A_{\text{vib}} = NkT \ln(1 - e^{-\beta \hbar \omega}) + N\hbar \omega/2 \quad (96)$$

and

$$S_{\text{vib}} = -(\partial A_{\text{vib}}/\partial T)|_\nu = - Nk \ln(1 - e^{-\beta \hbar \omega}) + (N\hbar \omega/kT)(e^{\beta \hbar \omega} - 1)^{-1} \quad (97)$$

and finally the measurable quantity

$$C_{\text{vib}} = N\left(\frac{\hbar^2 \omega^2}{kT^2}\right)e^{\hbar \omega/kT}(e^{\hbar \omega/kT} - 1)^{-2}. \quad (98)$$