In indistinguishable particles

When the particles are indistinguishable, the state where particle 1 is at coordinates (q_1, p_1) and particle 2 is at coordinates (q_2, p_2) is indistinguishable from the state where particle 1 is at (q_2, p_2) and 2 is at (q_1, p_1).

In counting the number of states \( S \), we have therefore over-counted. The correct counting should be

\[
S(E, V, N) = \frac{1}{N!} \int_{E}^{E+\Delta} \frac{d\Omega}{h^{3N}} \int d^3 q_1 \cdots \int d^3 q_N
\]

where \( \Omega = 8 \pi \hbar^2 \sin \theta \).

Since there are \( N \) ways to choose which particle is at coords \((q_1, p_1)\), \((N-1)\) ways to choose which of the remaining particles are at coords \((q_2, p_2)\), etc.,

So our new result for the entropy is related to our old result by

\[
S_{\text{new}} = S_{\text{old}} - k_B \ln N! = S_{\text{old}} - k_B N \ln N + k_B N
\]

where we used Stirling's formula \( \ln N! = N \ln N - N \) for large \( N \).
The new result for the entropy of an ideal gas is thus

\[ S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left( \frac{V}{\frac{4}{3} \pi N E} \right)^{3/2} \]  

Sackur-Tetrode Eqn.

This result clearly gives an S that is now extensive and agrees with the result we got from integrating the Gibbs-Duhem relation.

We now have \( S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \) rather than the old result \( S(E, V, N) = S(\lambda E, V, \lambda N) \).

Considering the entropy of mixing, our earlier result remains unchanged if the two gases are different types.

But if the two gases are the same type, we now have

\[ S_f = S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left[ \frac{V}{N^3} \left( \frac{4}{3} \pi N E \right)^{3/2} \right] \]

\[ S_i = S(E_1 V, N_1) + S(E_2 V, N_2) \]

\[ = \frac{5}{2} k_B (N_1 + N_2) + k_B N_1 \ln \left[ \frac{V_1}{N_1^3} \left( \frac{4}{3} \pi N_1 E_1 \right)^{3/2} \right] \]

\[ + k_B N_2 \ln \left[ \frac{V_2}{N_2^3} \left( \frac{4}{3} \pi N_2 E_2 \right)^{3/2} \right] \]

Using \( E = \frac{E_1}{N_1} = \frac{E_2}{N_2} = \frac{3}{2} k_B T \) we get

\[ \Delta S = S_f - S_i = k_B N \ln \left( \frac{V}{N} \right) - k_B N_1 \ln \left( \frac{V_1}{N_1} \right) - k_B N_2 \ln \left( \frac{V_2}{N_2} \right) \]

\[ = k_B N_1 \ln \left( \frac{V N_1}{N N_1} \right) + k_B N_2 \ln \left( \frac{V N_2}{N N_2} \right) \]
But using \( V = N k_B T / p \), \( V_1 = N_1 k_B T / p \), \( V_2 = N_2 k_B T / p \)

we get \( \frac{V}{V_1} = \frac{N}{N_1} \), \( \frac{V}{V_2} = \frac{N}{N_2} \) so

\[
\Delta S = k_B N_1 \ln \left( \frac{N}{N_1} \frac{N_1}{N} \right) + k_B N_2 \ln \left( \frac{N}{N_2} \frac{N_2}{N} \right)
\]

\[
= k_B N_1 \ln (1) + k_B N_2 \ln (1) = 0
\]

desired entropy of mixing = 0 !

Note: If one has \( N_1 \) particles of one type of gas, and
\( N_2 \) particles of a different type of gas, in the same
box of volume \( V \), we have

\[
S(E, V, N_1, N_2) = S(E_1, V, N_1) + S(E_2, V, N_2)
\]

(where \( E_1 \) and \( E_2 \) must be such that the temperatures are equal)

But if both gases are the same (ie we have only
mentally divided them up into one group of \( N_1 \) and another
of \( N_2 \)) then it is NOT true that

\[
S(E, V, N) = S(E_1, V, N_1) + S(E_2, V, N_2)
\]

This will not be true because the particles are
indistinguishable. This cannot be true if
\( S \) is extensive — because \( S(E, V, N) \neq 2S \left( \frac{E}{2}, \frac{V}{2}, \frac{N}{2} \right) \),
not as the above would imply, but rather

\[
S(E, V, N) = 2 \, S \left( \frac{E}{2}, \frac{V}{2}, \frac{N}{2} \right)
\]
Consider a system of interest in contact with a thermal reservoir — i.e. system is separated from reservoir by a fixed impermeable but thermally conducting wall. Let $E$ be the energy of the system, and $E_T - E$ be the energy of the reservoir. Total energy $E_T$ is fixed. Then

$$\Omega_T(E_T) = \int \frac{d\Omega}{\Delta} \Omega(E) \Omega_R(E_T - E)$$

The plot that the system has energy $E$ is therefore

$$\phi(E) \propto \Omega(E) \Omega_R(E_T - E) = \Omega(E) e^{S_R(E_T - E)/k_B}$$

Since the reservoir is large, $E \ll E_T$, so we can expand

$$\Omega_R(E_T - E) \approx \exp \frac{1}{k_B} \left( S_R(E_T) - \frac{\partial S_R}{\partial E} (E) + \ldots \right)$$

$$= \exp \frac{1}{k_B} \left( S_R(E_T) - \frac{E}{T} \right) = \text{const} \ e^{-E/k_BT}$$

So $\phi(E) \propto \Omega(E) e^{-E/k_BT} = e^{S(E)/k_B - E/k_BT} = e^{-A/k_BT}$

$$\Rightarrow \phi(E) = \frac{\Omega(E) e^{-E/k_BT}}{\Delta Q_N(T,V)}$$

where

$$Q_N(T,V) = \int \frac{d\Omega}{\Delta} \Omega(E) e^{-E/k_BT}$$

is the canonical partition function

normalization $\int dE \phi(E) = 1$

If energy levels are discrete $Q_N(T,V) = \sum E_i \Omega(E_i) e^{-E_i/k_BT}$
Using the density of states

\[ g(E) = \frac{1}{N!} \int \frac{dg_i \int dp_i}{\hbar^{3N}} \delta(H(g_i, p_i) - E) \]

\[ \Omega(E) = g(E) \Delta \]

Then \[ Q_N(T, V) = \int dE \, g(E) e^{-E/k_BT} \]

Probability \[ p(E) = \frac{g(E)e^{-E/k_BT}}{Q_N(T, V)} \]

Combining the above

\[ Q_N(T, V) = \frac{1}{N!} \int \frac{dg_i \int dp_i}{\hbar^{3N}} e^{-H(g_i, p_i)/k_BT} \]

The density of states \( g(E) \) has built into it all the information about a system as far as its thermodynamic behavior is concerned.

If one knows \( g(E) \), then one can compute the entropy \[ S(E) = k_B \ln \Omega(E) = k_B \ln \int g(E) \delta [H(g_i, p_i)] \]

or one can compute the canonical partition function \[ Q_N(T, V) = \int dE \, g(E) e^{-E/k_BT} \].
In the canonical ensemble, the energy of the system of interest is not fixed, but follows a probability distribution set by a fixed temperature. The temperature determines the average energy. The canonical ensemble does not depend on any details of the reservoir, except its being large!

In thermodynamics we saw that when one wishes to use $T$ as the variable instead of $S$, the potential to use is the Helmholtz free energy $A(T,V,N)$. We will now see that there is a direct relation between $A$ and the canonical partition function $Q_N$.

In the canonical ensemble, the average energy is:

$$\langle E \rangle = \int dE \; E \; P(E)$$

average value of probability density to have energy $E$

$$P(E) = \frac{g(E) e^{-E/k_BT}}{Q_N(T,V)}$$

define $\beta = 1/k_BT$ then

$$\langle E \rangle = \frac{\int dE \; E \; g(E) e^{-\beta E}}{\int dE \; g(E) e^{-\beta E}} = -\frac{\partial}{\partial \beta} \left[ \int dE \; g(E) e^{-\beta E} \right]$$

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial \beta} \ln \left[ \int dE \; g(E) e^{-\beta E} \right] = -\frac{\partial}{\partial \beta} \ln Q_N(T,V)$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N(T,V)$$
Relation between $Q_N$ and Helmholtz free energy $A$

$$A = E - TS \Rightarrow E = A + TS = A - T \left( \frac{\partial A}{\partial T} \right)_{V,N}$$

$$E = A - T \left( \frac{\partial A}{\partial T} \right)_{V,N} = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{A}{T} \right) \right]_{V,N}$$

$$= \left[ \frac{\partial (A/T)}{\partial (VT)} \right]_{V,N} = \left[ \frac{\partial (\beta A)}{\partial \beta} \right]_{V,N}$$

$$\Rightarrow E = -\frac{\partial}{\partial \beta} (-\beta A)$$

Compare with $\langle E \rangle = -\frac{\partial}{\partial \beta} (\ln Q_N)$

$$\Rightarrow A(T,V,N) = -k_B T \ln Q_N(T,V)$$

Another way to write the above is:

$$-\frac{A}{T} = k_B \ln Q_N$$

Note: $-\frac{A}{T}$ is the Legendre transform of $S$ with respect to $E$

Given $S(E,V,N)$, $\left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}$

$\Rightarrow$ Legendre transform of $S$ with respect to $E$ is:

$$S - \frac{E}{T} = \frac{1}{T} (TS - E) = -\frac{A}{T}$$
Now compare

\[- \frac{A}{T} = k_B \ln Q_N \quad \text{\(Q_N\) is canonical partition function}\]

\[S = k_B \ln \Omega \quad \Omega \text{ is microcanonical partition function}\]

the thermodynamic potential is the log of the partition function

\[- \frac{A}{T} = S - \frac{E}{T} \quad -\frac{A}{T} \text{ is Legendre transform of } S\]

\[Q_N = \int \frac{dE}{h} \Omega(E) e^{-\beta E} \quad Q_N \text{ is Laplace transform of } \Omega\]

This holds more generally: If one takes the Laplace transform of a partition function, the corresponding thermodynamic potential of the new partition function is just the Legendre transform of the original thermodynamic potential.

There is still one point to check out more carefully

\[E = -\frac{\partial}{\partial \beta} (-\beta A) \quad \text{is a result within the microcanonical ensemble}\]

\[\text{if we started with } S(E,V,N) \text{ with } E \text{ fixed at Legendre transform to get } A\]

\[\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N \quad \text{is a result within the canonical ensemble, with }\]

\[E \text{ fluctuations - only the average } \langle E \rangle \text{ is fixed by the temperature } T.\]
Alternatively:

\[-\frac{A}{T}\] computed from the Legendre transform of \(S\)

in the microcanonical Helmholtz free energy

\[\frac{A}{T} = k_B \ln Q_N\] computed from the canonical partition function \(Q\) is the canonical Helmholtz free energy

How do we know the two are really the same?

In other words, how do we know that the thermodynamic properties computed within the microcanonical ensemble will agree with the thermodynamic properties computed within the canonical ensemble?

How do we know that the two ensembles give equivalent results?

The results will be equivalent if the fluctuations of \(E\) about its average \(<E>\) can be ignored.

We will see that this in fact the case in the "thermodynamic limit" of \(N \to \infty\).