

Indistinguishable Particles

When the particles are indistinguishable, the state where particle 1 is at coordinates (q_1, p_1) and where 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 computing the number of states Ω we have therefore over counted. The correct counting should be

$$\Omega(E, V, N) = \frac{1}{N!} \int \frac{dq_i \int dp_i}{h^{3N}} \\ E \leq H(q_i, p_i) \leq E + \Delta$$

$N!$ 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 ~~def~~ result for the entropy is related to our ~~old~~ 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

$$S(E, V, N) = \frac{5}{2} k_B N + k_B N \ln \left[\frac{V}{h^3 N} \left(\frac{4}{3} \pi m \frac{E}{N} \right)^{3/2} \right] \quad \text{Sackur-Tetrode Equ.}$$

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

$$\left[\begin{array}{l} \text{We now have } \lambda S(E, V, N) = S(\lambda E, \lambda V, \lambda N) \text{ rather} \\ \text{than the old result } \lambda S(E, V, N) = S(\lambda E, V, \lambda N) \end{array} \right]$$

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

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

$$S_i = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$$

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

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

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

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

$$= k_B N_1 \ln \left(\frac{V N_1}{V_1 N} \right) + k_B N_2 \ln \left(\frac{V N_2}{N V_2} \right)$$

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

$$\begin{aligned}\Delta S &= k_B N_1 \ln\left(\frac{N}{N_1} \frac{N_1}{N}\right) + k_B N_2 \ln\left(\frac{N}{N_2} \frac{N_2}{N}\right) \\ &= k_B N_1 \ln(1) + k_B N_2 \ln(1) = 0\end{aligned}$$

entropy of mixing = 0 as desired!

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

$$S(E, V, N_1, N_2) = S_1(E_1, V, N_1) + S_2(E_2, V, N_2)$$

(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 $S(E, V, N) \neq 2S\left(\frac{E}{2}, V, \frac{N}{2}\right)$,

~~but~~ as the above would imply, but rather

$$S(E, V, N) = 2S\left(\frac{E}{2}, \frac{V}{2}, \frac{N}{2}\right)!$$

Canonical Ensemble

Consider a system of interest in contact with a thermal reservoir - i.e. system is separated from reservoir by a fixed impenetrable 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

$$\Omega_T(E_T) = \int \frac{dE}{\Delta} \underbrace{\Omega(E)}_{\text{system}} \underbrace{\Omega_R(E_T - E)}_{\text{reservoir}}$$

The prob that the system has energy E is therefore

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

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

$$\begin{aligned} \Omega_R(E_T - E) &\approx \exp \frac{1}{k_B} \left\{ S_R(E_T) - \frac{\partial S_R}{\partial E_R}(E) + \dots \right\} \\ &= \exp \frac{1}{k_B} \left\{ S_R(E_T) - \frac{E}{T} \right\} = \text{const} e^{-E/k_B T} \end{aligned}$$

$$\text{So } P(E) \propto \Omega(E) e^{-E/k_B T} = e^{S(E)/k_B - E/k_B T} = e^{-A/k_B T}$$

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

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

where

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

is the canonical partition function

if energy levels are discrete $Q_N(T, V) = \sum_{E_i} \Omega(E_i) e^{-E_i/k_B T}$

Using the density of states

$$g(E) = \frac{1}{N!} \int \frac{dq_i}{h^{3N}} \int dp_i \delta(H(q_i, p_i) - E)$$

↳ Gibbs correction due to indistinguishable particles

$$\Omega(E) = g(E)\Delta$$

then $Q_N(T, V) = \int dE g(E) e^{-E/k_B T}$

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

Combining the above

$$Q_N(T, V) = \frac{1}{N!} \int \frac{dq_i}{h^{3N}} \int dp_i e^{-H(q_i, p_i)/k_B T}$$

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 $S(E) = k_B \ln \Omega(E) = k_B \ln [g(E)\Delta]$

Or one can compute the canonical partition function

$$Q_N(T, V) = \int dE g(E) e^{-E/k_B T}$$

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 \uparrow \uparrow probability density to have energy E

$$P(E) = \frac{g(E) e^{-E/k_B T}}{Q_N(T, V)}, \quad Q_N = \int dE g(E) e^{-E/k_B T}$$

define $\beta \equiv 1/k_B T$ then

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

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

$$\boxed{\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N(T, V)}$$

Relation between Q_N and Helmholtz free energy A

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

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

$$= \left(\frac{\partial (A/T)}{\partial (1/T)} \right)_{V, N} = \left(\frac{\partial (\beta A)}{\partial \beta} \right)_{V, N}$$

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

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

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

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

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

Q_N is canonical partition function

$$S = k_B \ln \Omega$$

Ω is microcanonical partition function

the thermodynamic potential is the log of the partition function

$$-\frac{A}{T} = S - \frac{E}{T}$$

$-\frac{A}{T}$ is Legendre transform of S

$$Q_N = \int \frac{dE}{\Delta} \Omega(E) e^{-\beta E}$$

Q_N is Laplace transform of Ω

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 thermo potential.

There is still one point to check out more carefully

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

is a result within the microcanonical ensemble

i.e. we started with $S(E, V, N)$ with E fixed and Legendre transformed to get A

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N$$

is a result within the canonical ensemble, with

E fluctuating - only the average E is fixed by the temperature T .

Alternatively :

$-\frac{A}{T}$ computed from the Legendre transform of S is the microcanonical Helmholtz free energy

$-\frac{A}{T} \equiv k_B \ln Q_N$ computed from the canonical partition function Q_N 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~~ 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 $\langle E \rangle$ can be ignored.

We will see that this is in fact the case in the "thermodynamic limit" of $N \rightarrow \infty$.