Canonical Ensemble

Consider a system of interest in contact with a thermal reservoir – ie 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

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

total number of states available at energy E_T

Since all states are assumed to be equally likely in the microcanonical ensemble for the total system, then the probability for the system of interest to have energy E is given by

$$p(E) \propto \underbrace{\Omega(E)\Omega_R(E_T - E)}_{\text{total number of states available when system of interest has energy } E} = \Omega(E)\, e^{S_R(E_T - E)/k_B}$$

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

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

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

So $p(E) \propto \Omega(E)\, e^{-E/k_B T} = e^{S(E)/k_B - E/k_B T}$

$$\Rightarrow \quad \boxed{p(E) = \frac{\Omega(E)\, e^{-E/k_B T}}{\Delta\, Q_N(T,V)}} \qquad \text{normalization} \quad \int dE\, p(E) = 1$$

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* $\quad Q_N(T,V) = \sum_{E_i} \Omega(E_i)\, e^{-E_i/k_B T}$

Using the density of states

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

{ Gibbs correction due to indistinguishable particles

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

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

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

Combining the above

$$Q_N(T,V) = \frac{1}{N!}\int \frac{dq_i \int dp_i}{h^{3N}} \, \underbrace{e^{-\mathcal{H}(q_i,p_i)/k_BT}}_{\text{Boltzman factor } e^{-\mathcal{H}/k_BT}}$$

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

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 <u>not</u> fixed, but follows a probability distribution set by a fixed temperature. The temperature determines the <u>average</u> energy. The canonical ensemble does <u>not</u> depend on any details of the reservoir, except its being <u>large</u>!

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 <u>average energy</u> is:

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

average value ↗ ↖ probability density to have energy E

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

define $\beta \equiv 1/k_BT$ then

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

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

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

Now compare

$-\frac{A}{T} = k_B \ln Q_N$ $\quad$ Q_N is <u>canonical partition function</u>

$S = k_B \ln \Omega$ $\quad$ Ω is <u>microcanonical partition function</u>

the thermodynamic potential is the log of the partition function

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

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

$E = -\frac{\partial}{\partial \beta}(-\beta A)$ $\quad$ is a result within the <u>microcanonical ensemble</u>
ie we started with $S(E,V,N)$ with E <u>fixed</u> and Legendre transformed to get $A(T,V,N)$

$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q_N$ $\quad$ is a result within the <u>canonical ensemble</u> with E <u>fluctuating</u> - only the <u>average</u> E is fixed by the temperature T.

Relation between Q_N and Helmholtz free energy A

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

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

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

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

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

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

or: $A = E - TS$

$\Rightarrow -\frac{A}{T} = S - \left(\frac{1}{T}\right)E$

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

$\Rightarrow \frac{\partial(-A/T)}{\partial(1/T)} = -E$

$\Rightarrow \frac{\partial(A/T)}{\partial(1/T)} = E$

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~~

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

We expect these must be the same since fluctuations about $\langle E \rangle$ should vanish in thermo limit of very large systems

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 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 in fact the case in the "thermodynamice limit" of $N \to \infty$.

Energy fluctuations

– In canonical ensemble, E is not fixed, but has a prob distr. How wide is the distr in E?

Consider

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

$$= \frac{\int \frac{dE}{\Delta} E\,\Omega(E)e^{-\beta E}(-E)}{Q_N} - \frac{\int \frac{dE}{\Delta} E\,\Omega(E)e^{-\beta E}}{Q_N^2}\frac{\partial Q_N}{\partial \beta}$$

$$= -\langle E^2\rangle - \langle E\rangle \frac{\partial}{\partial \beta}\ln Q_N$$

$$= -\langle E^2\rangle + \langle E\rangle^2 \qquad \text{since } \langle E\rangle = -\frac{\partial}{\partial \beta}\ln Q_N$$

So the fluctuation in the energy E is:

$$\langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial \langle E\rangle}{\partial \beta} = \frac{\partial^2}{\partial \beta^2}\left(\ln Q_N\right) = -\frac{\partial^2}{\partial \beta^2}(\beta A)$$

Note: $\langle (E-\langle E\rangle)^2\rangle = \langle E^2 - 2E\langle E\rangle + \langle E\rangle^2\rangle$

$$= \langle E^2\rangle - 2\langle E\rangle\langle E\rangle + \langle E\rangle^2 = \langle E^2\rangle - \langle E\rangle^2$$

So fluctuation in energy is

$$\langle (E-\langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2 = -\frac{\partial \langle E\rangle}{\partial \beta} = -k_B\frac{\partial \langle E\rangle}{\partial (1/T)} = k_B T^2 \frac{\partial \langle E\rangle}{\partial T}$$

$$= k_B T^2 C_V$$

specific heat at constant volume

Note: $\langle E\rangle \sim N$, $C_V \sim N$ both are extensive

$$\Rightarrow \frac{\sqrt{\langle E^2\rangle - \langle E\rangle^2}}{\langle E\rangle} = \frac{\sqrt{k_B T^2 C_V}}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \to 0 \text{ as } N\to\infty$$

Relation between canonical and microcanonical A

We now investigate the effect that the energy fluctuations have on the canonical Helmholtz free energy A, as compared to the microcanonical Helmholtz free energy

microcanonical A:

① compute $S(E) = k_B \ln \Omega(E)$ from the microcanonical partition function $\Omega(E)$

② take Legendre transform of S with respect to E to get $-\frac{A}{T} = S - \frac{E}{T}$ this gives the microcanonical A

We will write the Legendre transform as follows:

$$-\frac{A(T)}{T} = \max_E \left[S(E) - \frac{E}{T} \right]$$

or $$A(T) = \min_E \left[E - TS(E) \right]$$

let $\bar{E}$ be this minimizing value of E

$$A_{micro} = \bar{E} - TS(\bar{E})$$

Canonical A

① compute $A(T) = -k_B T \ln Q_N(T)$

Consider now the computation of $Q_N = e^{-A/k_B T}$

$$Q_N = e^{-A/k_BT} = \int \frac{dE}{\Delta}\, \Omega(E)\, e^{-E/k_BT} \qquad \text{use } S = k_B \ln \Omega$$

$$= \int \frac{dE}{\Delta}\, e^{S(E)/k_B}\, e^{-E/k_BT}$$

$$= \int \frac{dE}{\Delta}\, e^{-(E - TS(E))/k_BT}$$

Consider the exponent $E - TS(E)$ and expand to 2^{nd} order about its minimum at $\bar{E}$. $\quad E = \bar{E} + \delta E$

$$E - TS(E) = \underbrace{\bar{E} - TS(\bar{E})}_{0^{th}\text{ order}} + \underbrace{\delta E - T\left(\frac{\partial S}{\partial E}\right)_{V,N} \delta E}_{1^{st}\text{ order}} \underbrace{- \frac{1}{2} T \left(\frac{\partial^2 S}{\partial E^2}\right)_{V,N} \delta E^2}_{2^{nd}\text{ order}}$$

$$= \underset{\parallel}{A_{micro}} + \underbrace{\delta E - T\left(\frac{1}{T}\right)\delta E}_{\text{cancel}} - \frac{1}{2} T \left(\frac{\partial (1/T)}{\partial E}\right)_{V,N} \delta E^2$$

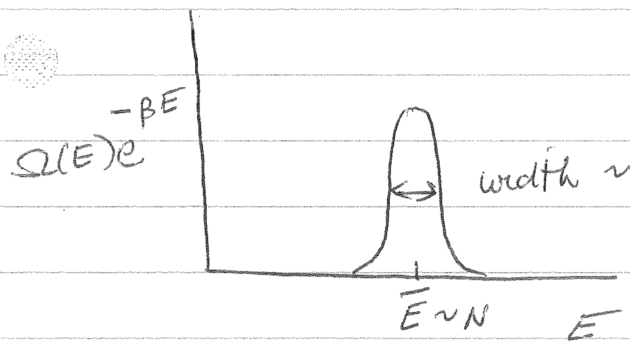
$$= A_{micro} + \frac{1}{2}\frac{1}{T}\left(\frac{\partial T}{\partial E}\right)_{V,N} \delta E^2$$

$$= A_{micro} + \frac{\delta E^2}{2TC_V} \qquad \text{where used} \quad \left(\frac{\partial T}{\partial E}\right)_{V,N} = \frac{1}{\left(\frac{\partial E}{\partial T}\right)_{V,N}} = \frac{1}{C_V}$$

$$Q_N = e^{-A/k_BT} = \int \frac{d\,\delta E}{\Delta}\, e^{-A_{micro}/k_BT}\, e^{-\delta E^2/2k_BT^2C_V}$$

we have a Gaussian integral – integrand is sharply peaked at $\delta E = 0$ with width $\sqrt{\langle \delta E^2 \rangle} = \underset{\sim \sqrt{N}}{\sqrt{k_B T^2 C_V}}$

so $\dfrac{\sqrt{\langle \delta E^2 \rangle}}{\bar{E}} \sim \dfrac{\sqrt{N}}{N} = \dfrac{1}{\sqrt{N}}$ small fluctuations



We can do the Gaussian integration to explicitly evaluate Q_N

use $\int dx\, e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$

$$Q_N = e^{-A/k_BT} = e^{-A_{micro}/k_BT} \frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta}$$

take logs

$$A = A_{micro} - k_BT \ln\left(\frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta}\right)$$

$$A = A_{micro} - \frac{1}{2}k_BT \ln\left(\frac{2\pi k_B T^2 C_V}{\Delta^2}\right)$$

canonical Helmholtz free energy — microcanonical Helmholtz free energy — correction due to fluctuations in energy

Note: $A \sim A_{micro} \sim N$, $C_V \sim N$

so the correction term between A and A_{micro} has relative size

$$\frac{A - A_{micro}}{A} \simeq \frac{\ln N}{N} \rightarrow 0 \quad \text{as } N \rightarrow \infty$$

$\Rightarrow$ the canonical ensemble gives the same results as the microcanonical ensemble, provided one takes the <u>thermodynamic limit</u> $N \to \infty$.

This is because as $N \to \infty$, the most probable energy $\bar{E}$ is the same as the average energy $\langle E \rangle$, and all other energies have negligible probability to occur.