

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

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

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

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

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

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

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

Using the density of states

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

↑ 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

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

Boltzmann factor $e^{-H/k_B T}$

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

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

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~~

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

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

ie 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 .

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 ~~micro~~ 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 $N \rightarrow \infty$.

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

Consider

$$\begin{aligned}\frac{\partial \langle E \rangle}{\partial \beta} &= \frac{\partial}{\partial \beta} \left[\frac{\int \frac{dE}{\Delta} E \Omega(E) e^{-\beta E}}{Q_N} \right] \\ &= \frac{\int \frac{dE}{\Delta} E \Omega(E) e^{-\beta E} (-E)}{Q_N} - \frac{\int \frac{dE}{\Delta} E \Omega(E) e^{-\beta E}}{Q_N^2} \frac{\partial Q_N}{\partial \beta} \\ &= -\langle E^2 \rangle - \langle E \rangle \frac{\partial \ln Q_N}{\partial \beta}\end{aligned}$$

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

So the fluctuation in the energy E is:

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

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

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

↑ specific heat at constant volume

Note: $\langle E \rangle \sim N$, $C_V \sim N$

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

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:

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

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

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

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

Canonical A

- ① compute $A(T) = -k_B T \ln Q_N(T)$

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

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

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

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

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

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

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

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

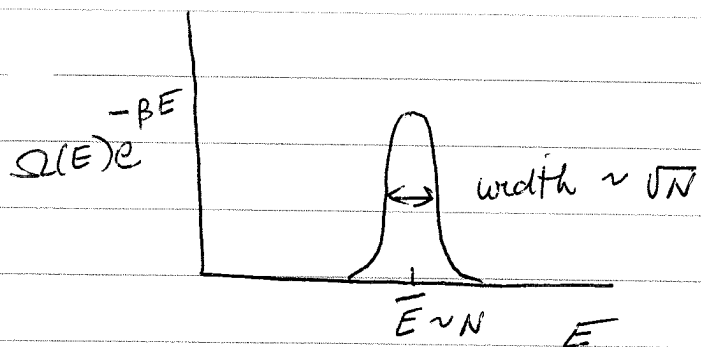
$$= A_{\text{micro}} + \frac{\delta E^2}{2 T C_V} \quad \text{where used}$$

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

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

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

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



We can do the Gaussian integration to explicitly evaluate Q_N

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

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

take logs

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

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

↑
canonical
Helmholtz
free energy

↑
microcanonical
Helmholtz
free energy

↑
correction due to
fluctuations in energy

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

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

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

⇒ the canonical ensemble gives the same results as the microcanonical ensemble, provided one takes the thermodynamic limit $N \rightarrow \infty$.

this is because as $N \rightarrow \infty$, 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.

Average energy $\langle E \rangle$ vs. the most probable energy $\bar{E}$ in the canonical ensemble.

In our earlier discussion of fluctuations in the canonical ensemble we expanded

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V}$$

now we continue the expansion to $O(\delta E^3)$

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V} + \frac{1}{3!} T \frac{\partial^3 S}{\partial E^3} \bigg|_{E=\bar{E}} \delta E^3$$

Note $\frac{\partial^3 S}{\partial E^3} \sim \frac{1}{N^2}$ since $S \sim N$ and $E \sim N$ are both extensive

so we can write

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V} - \frac{\gamma}{N^2} \delta E^3$$

where γ is some constant that does not increase with N (it can depend on T)

Now compute $\langle \delta E \rangle = \langle E \rangle - \bar{E}$

$$\langle \delta E \rangle = \frac{\int \frac{d\delta E}{\Delta} e^{-(E - TS(E))/k_B T} \delta E}{\int \frac{d\delta E}{\Delta} e^{-(E - TS(E))/k_B T}}$$

$$\approx \frac{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V} + \frac{\gamma \delta E^3}{N^2 k_B T}} \delta E}{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V} + \frac{\gamma}{N^2} \frac{\delta E^3}{k_B T}}$$

$$\approx \frac{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma \delta E^3}{N^2 k_B T}\right) \delta E}{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma \delta E^3}{N^2 k_B T}\right)}$$

where we expanded $e^{\frac{\gamma \delta E^3}{N^2 k_B T}} \approx 1 + \frac{\gamma \delta E^3}{N^2 k_B T}$
for $N \rightarrow \infty$

For a Gaussian distribution, only the even moments are non-vanishing

$$\langle \delta E \rangle \approx \frac{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V}} \left(\frac{\gamma}{N^2 k_B T}\right) \delta E^4}{\int d\delta E e^{-\frac{\delta E^2}{2k_B T^2 C_V}}}$$

$$= \left(\frac{\gamma}{N^2 k_B T}\right) \cdot (k_B T^2 C_V)^2 \cdot \frac{3}{2}$$

where we used
$$\frac{\int_{-\infty}^{\infty} dx e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} x^4}{\int_{-\infty}^{\infty} dx e^{-\frac{1}{2} \frac{x^2}{\sigma^2}}} = 3\sigma^4$$

But the main point is $C_V \sim N$

so
$$\langle \delta E \rangle \sim \frac{1}{N^2} \cdot N^2 \sim O(1)$$

The relative difference between average and most probable energy therefore scales as

$$\frac{\langle E \rangle - \bar{E}}{\langle E \rangle} = \frac{\langle \delta E \rangle}{\langle E \rangle} \sim \frac{1}{N} \rightarrow 0 \text{ as } N \rightarrow \infty$$

①

Stirling's Formula

In lecture we used the saddle point approx to discuss the relation between the Helmholtz free energy in the canonical vs. the micro canonical ensemble. The saddle pt approx is also how one derives Stirling's approx for $n!$.

Consider the integral

$$I = \int_0^{\infty} dx x^n e^{-x}$$

integrate by parts

$$I = -x^n e^{-x} \Big|_0^{\infty} + \int_0^{\infty} n x^{n-1} e^{-x} dx$$

boundary term vanishes at its limits so

$$I = \int_0^{\infty} dx n x^{n-1} e^{-x}$$

integrate by parts again

$$I = \int_0^{\infty} dx n(n-1) x^{n-2} e^{-x}$$

and so on to get

$$I = \int_0^{\infty} dx n(n-1)(n-2) \dots (1) e^{-x} = n!$$

(2)

Now evaluate I in saddle pt approx.

Define $U(x) = -x + n \ln x$

$$I = \int_0^{\infty} dx e^{U(x)}$$

expand $U(x)$ about its maximum

$$\begin{aligned} U(\bar{x}) &= -n + n \ln n \\ U'(x) &= -1 + \frac{n}{x} \Rightarrow \bar{x} = n \text{ is the maximum} \\ U''(x) &= -\frac{n}{x^2} \Rightarrow U''(\bar{x}) = -\frac{1}{n} \\ U'''(x) &= \frac{2n}{x^3} \Rightarrow U'''(\bar{x}) = \frac{2}{n^2} \\ U^{(4)}(x) &= -\frac{6n}{x^4} \Rightarrow U^{(4)}(\bar{x}) = -\frac{6}{n^3} \end{aligned}$$

For $\delta x = x - \bar{x}$,

$$U(x) \approx -n + n \ln n - \frac{\delta x^2}{2n} + \frac{1}{6} \frac{2}{n^2} \delta x^3 - \frac{1}{24} \frac{6}{n^3} \delta x^4 + \dots$$

$$= -n + n \ln n - \frac{\delta x^2}{2n} + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \dots$$

$$I = \int_0^{\infty} dx e^{-n + n \ln n} e^{-\delta x^2/2n} \underbrace{e^{\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}}}_{\text{expand for small } \delta x}$$

$$\approx \int_{-\infty}^{\infty} d\delta x e^{-n + n \ln n} e^{-\delta x^2/2n} \left[1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + o(\delta x^6) \right]$$

$$= e^{-n + n \ln n} \int_{-\infty}^{\infty} d\delta x e^{-\delta x^2/2n} \left[1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \dots \right]$$

$$= e^{-n + n \ln n} \sqrt{2\pi n} \left[1 + \frac{\langle \delta x^3 \rangle}{3n^2} - \frac{\langle \delta x^4 \rangle}{4n^3} + \dots \right]$$

(3)

Now $\langle \delta x^3 \rangle = 0$, $\langle \delta x^4 \rangle \sim n^2$, So

$$I = n! = e^{-n+n \ln n} \sqrt{2\pi n} \left[1 + O\left(\frac{1}{n}\right) \right]$$

$$\begin{aligned} \ln n! &= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + \ln(1 + O(\frac{1}{n})) \\ &= \underbrace{n \ln n - n}_{\text{these are the leading terms}} + \underbrace{\frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi}_{\text{these are next order corrections}} + O(\frac{1}{n}) \end{aligned}$$