

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 $N \rightarrow \infty$.

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

Consider

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

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

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

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

So the fluctuation in the energy E is:

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

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

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

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} . $E = \bar{E} + \delta E$

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

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

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

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

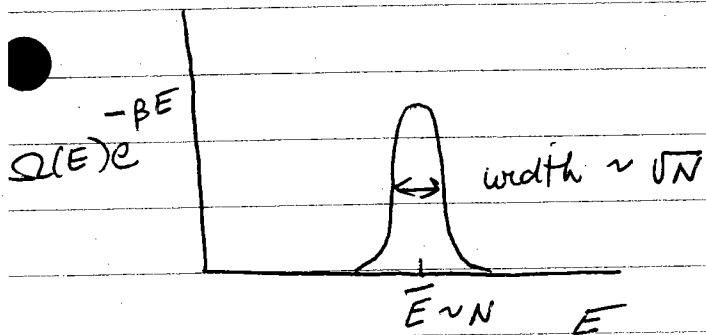
where used

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

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

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

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



We can do the gaussian integration to explicitly evaluate Q_N

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

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

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

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

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.

Note:

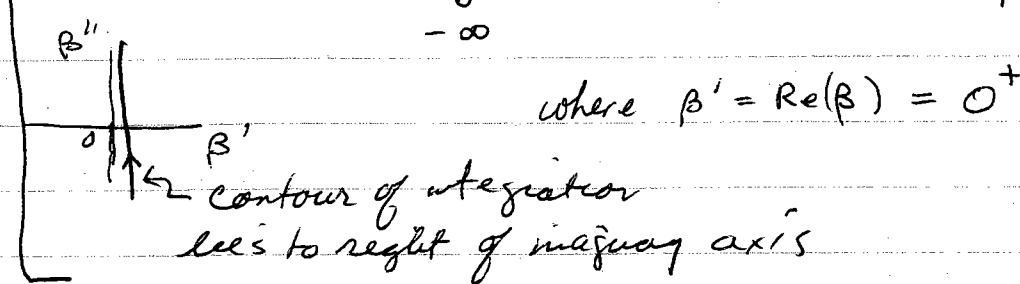
$$Q_N(\beta) = \int \frac{dE}{\Delta} \Omega(E) e^{-\beta E}$$

$Q_N(\beta)$ is Laplace transform of $\frac{\Omega(E)}{\Delta}$

$\Rightarrow \frac{\Omega}{\Delta}$ is inverse Laplace transform of Q_N

$$\frac{\Omega(E)}{\Delta} = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q_N(\beta) d\beta \quad (\beta' > 0)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\beta' + i\beta'') E} Q_N(\beta' + i\beta'') d\beta''$$



entropy $S = k_B \ln \Omega$

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

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

Helmholtz free energy
is Legendre transform of S with
respect to E

Thermodynamic potentials which are Legendre transforms
of each other, have ensemble partition functions
that are Laplace transforms of each other.

Factorization of canonical partition function - the ideal gas

Consider a system of N noninteracting particles

$$\rightarrow \mathcal{H}[\vec{q}_i, \vec{p}_i] = \sum_{i=1}^N \mathcal{H}^{(i)}(\vec{q}_i, \vec{p}_i)$$

where $\mathcal{H}^{(i)}$ is the single particle Hamiltonian that depends only on the three coordinates \vec{q}_i and three momenta \vec{p}_i of particle i .

$$Q_N = \frac{1}{N! h^{3N}} \left(\prod_{i=1}^N \int d\vec{q}_i d\vec{p}_i \right) e^{-\beta \mathcal{H}}$$

$$= \frac{1}{N!} \left(\prod_{i=1}^N \int \frac{d\vec{q}_i d\vec{p}_i}{h^3} \right) e^{-\beta \sum_j \mathcal{H}^{(j)}(\vec{q}_j, \vec{p}_j)}$$

factor the exponential

$$= \frac{1}{N!} \prod_{i=1}^N \left(\int \frac{d\vec{q}_i d\vec{p}_i}{h^3} e^{-\beta \mathcal{H}^{(i)}(\vec{q}_i, \vec{p}_i)} \right)$$

↑
factor for particle i is
identical to factor for particle j

$$\rightarrow \boxed{Q_N = \frac{1}{N!} (Q_1)^N} \quad \text{for noninteracting particles}$$

where Q_1 is the one particle partition function

$$Q_1 = \int \frac{d\vec{q} d\vec{p}}{h^3} e^{-\beta H^{(1)}(\vec{q}, \vec{p})}$$

Apply to the ideal gas.

$$H^{(1)}(\vec{q}, \vec{p}) = \frac{p^2}{2m}$$

$$Q_1 = \int \frac{d\vec{q}}{h^3} \int d\vec{p} e^{-\beta \frac{p^2}{2m}}$$

$$\int d\vec{q} = V \quad \text{volume of system}$$

$$\int d\vec{p} e^{-\beta \frac{p^2}{2m}} = \left(\frac{2\pi m}{\beta} \right)^{3/2} \quad \text{3D Gaussian integral}$$

$$Q_1 = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

$$\Rightarrow Q_N = \frac{1}{N!} \left(\frac{V}{h^3} \right)^N (2\pi m k_B T)^{3N/2}$$

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

$\ln N! = N \ln N - N$
using Stirling's formula

$$= -k_B T \left\{ N \ln \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] - N \ln N + N \right\}$$

$$A(T, V, N) = -k_B T N - k_B T N \ln \left[\frac{V}{h^{3N}} (2\pi m k_B T)^{3/2} \right]$$

Compute average energy

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

$$= -\frac{\partial}{\partial \beta} \left(N + N \ln \left[\frac{V}{h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{3/2} \right] \right)$$

$$= -N \frac{\partial}{\partial \beta} (\ln \beta^{-3/2}) = \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta}$$

$$\langle E \rangle = \frac{3}{2} N k_B T \quad \text{as expected}$$

entropy

$$S = -\left(\frac{\partial A}{\partial T} \right)_{V,N} = k_B N + k_B N \ln \left[\frac{V}{h^{3N}} (2\pi m k_B T)^{3/2} \right]$$

$$+ k_B T N \frac{3}{2} \left(\frac{1}{T} \right)$$

~ from derivative of log

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

substitute in $k_B T = \frac{2}{3} \frac{E}{N}$ to get

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

We have recovered the Sackur-Tetrode equation which we earlier derived from the microcanonical ensemble! Canonical and microcanonical approaches are equivalent.

Because in computing Ω_N we sum over all states with any energy, as compared to computing Ω where we restrict the sum to states in a particular energy shell E , it is usually easier to compute Ω_N , rather than Ω .

We introduced the canonical distribution as a means of describing a physical system in contact with a heat bath.

The canonical distrib gives the same result as the microcanonical because in the $N \rightarrow \infty$ (thermodynamic) limit, the canonical probability distribution

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

approaches a delta-function at the most probable energy = average energy, as set by the temperature T .

We could alternatively introduced the canonical ensemble just as a mathematical trick for computing $\Omega(E)$, removing the constraint of constant energy E by means of a Lagrange multiplier.