Relation of Q_N to Helmholtz free energy

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

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

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

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

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

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

compare to

$$S(E,V,N) = k_B \ln \Omega(E,V,N)$$

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

$\Rightarrow$ $Q_N(T)$ is Laplace transform of $\Omega(E)$

A is Legendre tranform of E

Note: Above relates A in canonical ensemble to average energy $\begin{pmatrix}\langle E \rangle \\ \langle S \rangle\end{pmatrix}$ in canonical ensemble

But original thermodynamic definition, in which E and $S(E)$ are fixed, should better be thought of as a relation in the microcanonical ensemble. Are the two formulations equivalent? We will soon see.

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

Consider

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

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

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

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

So

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

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

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

$$= k_B T^2 \underset{\uparrow}{C_V}$$

specific heat at constant volume

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

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

Relation between Canonical A and Microcanonical A

$$A = E - TS$$

A is Legendre transform of $E(S,V,N)$ with respect to S.

Can also write

$$-\frac{A}{T} = S - \left(\frac{1}{T}\right)E \qquad \text{where } \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}$$

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

$$\Rightarrow -\frac{A}{T} = \cancel{\max_E\left[S - \frac{E}{T}\right]} \; \max_E \left[S(E,V,N) - \frac{E}{T}\right]$$

$$\text{or} \quad A = \min_E \left[E - TS(E,V,N)\right]$$

Having computed $S(E,V,N) = k_B \ln \Omega(E,V,N)$ in microcanonical ensemble, the above gives the corresponding <u>microcanonical</u> Helmholtz free energy A.

In microcanonical ensemble we can write

$$A(T,V,N) = \min_{E}\left[E - TS(E,V,N)\right] = \bar{E} - TS(\bar{E},V,N)$$

Compare now to canonical ensemble calculation of A

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

Consider $(E-TS(E))/k_BT$ expand about its ~~maximum~~ minimum at $\bar{E}$

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

$$E - TS(E) \approx \bar{E} - TS(\bar{E}) + \delta E - T\left(\frac{\partial S}{\partial E}\right)_V \delta E - \frac{1}{2}T\left(\frac{\partial^2 S}{\partial E^2}\right)_V \delta E^2$$

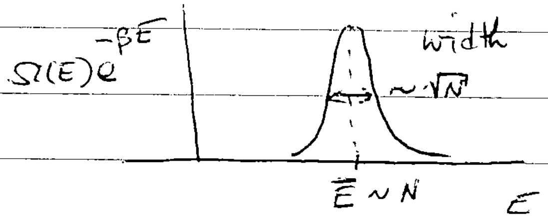
$$= \bar{E} - T\bar{S} + \delta E - T\left(\frac{1}{T}\right)\delta E - \frac{1}{2}T\frac{\partial}{\partial E}\left(\frac{1}{T}\right)_V \delta E^2$$

$\bar{S} \equiv S(\bar{E})$

$$= \bar{E} - T\bar{S} + \frac{1}{2}\frac{1}{T}\left(\frac{\partial T}{\partial E}\right)_V \delta E^2 = \bar{E} - T\bar{S} + \frac{\delta E^2}{2TC_V}$$

So

$$e^{-A/k_BT} = e^{-(\bar{E}-T\bar{S})/k_BT} \int \frac{d\delta E}{\Delta}\, \underbrace{e^{-\delta E^2/2k_BT^2C_V}}$$



integrand strongly peaked about $\delta E = 0$

$\sqrt{\langle \delta E^2\rangle} = \sqrt{k_BT^2C_V} \sim \sqrt{N}$

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

We can do the Gaussian integral : $\int dx\, e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$

$$\Rightarrow e^{-A/k_BT} = e^{-(\bar{E}-T\bar{S})/k_BT}\sqrt{2\pi k_BT^2C_V}$$

$$\Rightarrow A = \bar{E} - T\bar{S} - \frac{1}{2}k_BT\ln\left(2\pi k_BT^2C_V\right)$$

in the canonical, as compared to the microcanonical ensemble, the relative correction due to fluctuations $\sim \dfrac{\log N}{N} \to 0$ as $N\to\infty$

⇒ canonical ensemble gives same results as microcanonical ensemble in the thermodynamic limit. This is because in the limit $N\to\infty$, the most probable energy $\bar{E}$ is the same as the average energy $\langle E\rangle$; all other energies have negligible pro

Note:

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

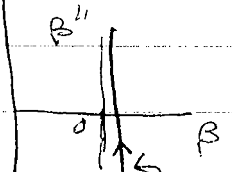
$Q_N(\beta)$ is Laplace transform of $\frac{\Omega}{\Delta}(E)$

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

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

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

where $\beta' = \mathrm{Re}(\beta) = 0^+$



contour of integration lies to right of imaginary axis

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 transf 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

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

where $\mathcal{H}^{(1)}$ is the single particle Hamiltonian that depends only on the three coordinates $\vec{q}_i$ and three momenta $\vec{p}_i$ of particle i.

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

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

factor the exponential

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

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

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

where Q_1 is the one particle partition function

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

Apply to the ideal gas.

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

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

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

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

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

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

$\ln N! = N\ln N - N$

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

$$= -k_B T\left\{ N \ln\left[\frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}\right] \overbrace{- N\ln N + N}^{\text{using Stirling's formula}} \right\}$$

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

Compute average energy

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

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

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

$\langle E \rangle = \frac{3}{2}Nk_BT$ as expected

entropy

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

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

$\nwarrow$ from derivative of log

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

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

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

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

Because in computing Q_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 Q_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 $N \to \infty$ (thermodynamic) limit, the canonical probability distribution

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

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.