Next we want to show that $\mathcal{Z}$ is related to the <u>Grand Potential</u> $\Sigma(T, V, \mu) = E - TS - \mu N$

Legendre transf of E with respect to S and N

<u>First note:</u>

$$-\frac{\partial}{\partial\beta}(\ln\mathcal{Z})_{V,\mu} = \frac{-\frac{\partial\mathcal{Z}}{\partial\beta}}{\mathcal{Z}} = \frac{-\frac{\partial}{\partial\beta}\sum_i e^{-\beta(E_i-\mu N_i)}}{\sum_i e^{-\beta(E_i-\mu N_i)}}$$

$$= \frac{\sum_i (E_i-\mu N_i)\, e^{-\beta(E_i-\mu N_i)}}{\sum_i e^{-\beta(E_i-\mu N_i)}}$$

$$\boxed{-\frac{\partial}{\partial\beta}(\ln\mathcal{Z})_{V,\mu} = \langle E\rangle - \mu\langle N\rangle} \quad (1)$$

regarding $\mathcal{Z}$ as a function of T, V, μ

$$\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \frac{1}{\beta}\frac{\frac{\partial\mathcal{Z}}{\partial\mu}}{\mathcal{Z}} = \frac{1}{\beta}\frac{\frac{\partial}{\partial\mu}\sum_i e^{-\beta E_i} e^{\beta\mu N_i}}{\sum_i e^{-\beta(E_i-\mu N_i)}}$$

$$= \frac{\sum_i N_i\, e^{-\beta(E_i-\mu N_i)}}{\sum_i e^{-\beta(E_i-\mu N_i)}}$$

$$\boxed{\frac{1}{\beta}\frac{\partial}{\partial\mu}(\ln\mathcal{Z})_{T,V} = \langle N\rangle} \quad (2)$$

Next from Thermodynamics

$$\Sigma = E - TS - \mu N$$

so $E - \mu N = \Sigma + TS = \Sigma - T\left(\frac{\partial \Sigma}{\partial T}\right)_{V,\mu} = \frac{\partial(\beta\Sigma)}{\partial\beta}\Big)_{V,\mu}$

$$\Rightarrow \boxed{E - \mu N = \frac{\partial(\beta\Sigma)_{V,\mu}}{\partial\beta}}$$

(see corresponding result in discussion of $A = -k_B T \ln Q_N$)

also

$$\boxed{\left(\frac{\partial \Sigma}{\partial \mu}\right)_{T,V} = -N}$$

Comparing these last two results with (1) and (2) we conclude

$$\boxed{\Sigma = -k_B T \ln \mathcal{L}}$$

As we did in discussion of canonical ensemble, we here equated the averages $\langle E\rangle$ and $\langle N\rangle$ in the grand canonical ensemble with the thermodynamic E and N.

Note: From the Euler relation $E = TS - pV + \mu N$, and the Legendre transf $\Sigma = E - TS - \mu N$, we have

$$\Sigma = -pV \qquad \text{grand Potential} = -pV$$

$$\Rightarrow \text{pressure} \quad \boxed{p = \frac{k_B T}{V} \ln \mathcal{L}(T,V,\mu)}$$

Analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit, $N \to \infty$, computing in the <u>grand canonical</u> ensemble, with a fixed μ determining an <u>average</u> $\langle N \rangle$, gives the same result as computing in the canonical ensemble with fixed $N = \langle N \rangle$.

One can use the grand canonical ensemble even if the physical system of interest is <u>not</u> in contact with a reservoir. Just choose a T and a μ to give the desired E and N via eqns (1) and (2). Because, as $N \to \infty$, the prob for a state in the grand canonical ensemble to have some E', N' is so sharply peaked about the averages $\langle E \rangle, \langle N \rangle$, the difference from using a microcanonical ensemble at the fixed $E = \langle E \rangle$ and $N = \langle N \rangle$ is negligible.

Fluctuations - We want to show that the grand canonical distribution is indeed sharply peaked about the average $\langle E \rangle$ and $\langle N \rangle$

Particle Number

We had $\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} (\ln \mathcal{Z})$

$$\Rightarrow \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 (\ln \mathcal{Z})}{\partial \mu^2}$$

$$= \frac{1}{\beta^2} \frac{\partial}{\partial \mu} \left(\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} \right) = \frac{1}{\beta^2} \left[\frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2} - \frac{1}{\mathcal{Z}^2} \left(\frac{\partial \mathcal{Z}}{\partial \mu} \right)^2 \right]$$

Now $\frac{1}{\beta \mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \langle N \rangle$

and $\frac{1}{\beta^2 \mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu} = \frac{1}{\beta^2} \frac{\frac{\partial^2}{\partial \mu^2} \sum_i e^{-\beta E_i} e^{\beta \mu N_i}}{\mathcal{Z}} = \langle N^2 \rangle$

So $\frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \frac{1}{\beta^2} \frac{\partial^2 \ln \mathcal{Z}}{\partial \mu^2} = \langle N^2 \rangle - \langle N \rangle^2$

$$\sigma_N^2 \equiv \langle N^2 \rangle - \langle N \rangle^2 = \frac{1}{\beta} \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} \sim N \quad \text{as } \mu, \beta \text{ \underline{intensive}}$$

So $\frac{\sigma_N}{\langle N \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0$ as $N \to \infty$

fluctuations in N vanish as $N \to \infty$

We can write σ_N^2 in terms of more familiar response functions as follows:

$$\sigma_N^2 = \frac{1}{\beta}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V}$$

write $v \equiv V/N \Rightarrow N = V/v$

$$\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} = \frac{-V}{v^2}\left(\frac{\partial v}{\partial \mu}\right)_{T,V}$$

By Gibbs-Duhem relation $\quad N d\mu = V dp - S dT$

$$d\mu = v\,dp - (S/N)\,dT$$

$\Rightarrow$ at constant T, $d\mu = v\,dp$

$$\Rightarrow \left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{v\,\partial p}\right)_{T,V} = -\frac{N^2}{V}\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_{T,V}$$

now, since both v and p are <u>intensive</u>, they are independent of $V, N \Rightarrow \left(\frac{\partial v}{\partial p}\right)_{T,V} = \left(\frac{\partial v}{\partial p}\right)_{T,N} = \left(\frac{\partial (V/N)}{\partial p}\right)_{T,N} = \frac{1}{N}\left(\frac{\partial V}{\partial p}\right)_{T,N}$

$$\text{So } \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{N}{V}\left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = -\kappa_T$$

$$\text{So } \quad \frac{\sigma_N^2}{\langle N\rangle^2} = \frac{1}{\beta N^2}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \frac{k_B T}{N^2}\frac{N^2}{V}\kappa_T$$

$$= \frac{k_B T}{V}\kappa_T$$

$$\frac{\sigma_N}{\langle N\rangle} = \sqrt{\frac{k_B T\,\kappa_T}{V}}$$

κ_T is isothermal compressibility $\sim N$ except perhaps at a phase transition

<u>Energy</u> If we write $\mathcal{L} = \sum_i e^{-\beta(E_i - \mu N_i)} = \sum_i e^{-\beta E_i} z^{N_i}$

$(z = e^{\beta\mu})$

then we have

$$-\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{z,V} = -\frac{1}{\mathcal{L}}\left(\frac{\partial \mathcal{L}}{\partial \beta}\right)_{z,V} = \frac{1}{\mathcal{L}} \sum_i E_i e^{-\beta E_i} z^{N_i} = \langle E \rangle$$

and

$$-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V} = \left(\frac{\partial^2 \ln \mathcal{L}}{\partial \beta^2}\right)_{z,V} = \frac{1}{\mathcal{L}}\left(\frac{\partial^2 \mathcal{L}}{\partial \beta^2}\right)_{z,V} - \frac{1}{\mathcal{L}^2}\left(\frac{\partial \mathcal{L}}{\partial \beta}\right)_{z,V}^2$$

where $\frac{1}{\mathcal{L}}\left(\frac{\partial^2 \mathcal{L}}{\partial \beta^2}\right)_{z,V} = \frac{1}{\mathcal{L}} \sum_i E_i^2 e^{-\beta E_i} z^{N_i} = \langle E^2 \rangle$

and $\left[\frac{1}{\mathcal{L}}\left(\frac{\partial \mathcal{L}}{\partial \beta}\right)_{z,V}\right]^2 = \left[-\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{z,V}\right]^2 = \langle E \rangle^2$

So

$$-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V} = \langle E \rangle^2 - \langle E \rangle^2 \equiv \sigma_E^2$$

Now $-\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V} = k_B T^2 \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V}$

And

$$\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V} = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} + \left(\frac{\partial \langle E \rangle}{\partial N}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{z,V}$$

follows from regarding E as function of T, N, V and N as func of (z, V, T)

$E(T, N, V) = E(T, N(z, V, T), V)$

One can show by explicit computation that

$$\left(\frac{\partial \langle N\rangle}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial \langle E\rangle}{\partial \mu}\right)_{T,V} = \frac{1}{k_B T^2}\left[\langle EN\rangle - \langle E\rangle\langle N\rangle\right]$$

and $\left(\frac{\partial \langle E\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \langle E\rangle}{\partial N}\right)_{T,V}\left(\frac{\partial \langle N\rangle}{\partial \mu}\right)_{T,V} = \left(\frac{\partial \langle E\rangle}{\partial N}\right)_{T,V} \beta\, \sigma_N^2$

So:

$$\sigma_E^2 = k_B T^2 \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{z,V} = k_B T^2 \left(\frac{\partial \langle E\rangle}{\partial T}\right)_{N,V} + \frac{k_B T^2}{T}\left(\frac{\partial \langle E\rangle}{\partial N}\right)_{T,V}^2 \beta \sigma_N^2$$

$$\sigma_E^2 = k_B T^2 C_V + \left(\frac{\partial \langle E\rangle}{\partial N}\right)_{T,V}^2 \sigma_N^2$$

this is fluctuation in E in <u>canonical ensemble</u>

this is additional fluctuation in E due to fluctuations in N

Grand Canonical partition function for non-interacting systems

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Q_N(T,V)$$

for non-interacting particles we saw

$$Q_N(T,V) = \frac{1}{N!}\left[Q_1(T,V)\right]^N$$ indistinguishable particles (as in ideal gas)

$$= \left[Q_1(T,V)\right]^N$$ distinguishable particles (as in paramagnetic spins)

$\Rightarrow$ Indistinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(zQ_1)^N}{N!} = e^{zQ_1}$$

Distinguishable

$$\mathcal{Z} = \sum_{N=0}^{\infty} (zQ_1)^N = \frac{1}{1 - zQ_1}$$ ← must have $zQ_1 < 1$ for series to converge

Ideal gas

For a single gas of particles

$$Q_1 = \int \frac{d^3p \int d^3r}{h^3} \, e^{-\beta p^2/2m} = (2\pi m k_B T)^{3/2} \frac{V}{h^3}$$

$$= V f(T)$$

will have this form even for a more complicated gas in which the particles may have internal degrees of freedom.

$$\mathcal{Z} = e^{zQ_1} = e^{zVf(T)} \qquad \ln \mathcal{Z} = zVf(T)$$

grand potential $\Sigma = -k_B T \ln \mathcal{Z} = -k_B T z V f(T) = -pV$

$$p = k_B T z f(T) \qquad z = e^{\beta\mu}$$

$$N = -\frac{\partial \Sigma}{\partial \mu} = -\frac{\partial \Sigma}{\partial z}\frac{\partial z}{\partial \mu} = k_B T V f(T) \beta e^{\beta\mu}$$

$$= z V f(T)$$

Combine the above

$$\left.\begin{aligned} \frac{p}{k_B T} &= z f(T) \\ \frac{N}{V} &= z f(T) \end{aligned}\right\} \Rightarrow pV = N k_B T$$

$$E = -\left(\frac{\partial}{\partial\beta} \ln \mathcal{Z}\right)_{z,V} = k_B T^2 \left(\frac{\partial}{\partial T} \ln \mathcal{Z}\right)_{z,V}$$

$$= k_B T^2 z V \frac{df}{dT} = k_B T^2 N \frac{(df/dT)}{f} = k_B T^2 N \left(\frac{\partial \ln f}{\partial T}\right)$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = 2 k_B T N \frac{\partial \ln f}{\partial T} + k_B T^2 N \frac{\partial^2 \ln f}{\partial T^2}$$

Note, for harmonic degrees of freedom (ie $\vec{p}$, or harmonic internal degrees of freedom, such as internal vibrations of molecule) $f \propto T^n$ for some power n (for single particle, $n = 3/2$)

$$\Rightarrow \quad \frac{\partial \ln f}{\partial T} = \frac{\partial}{\partial T}(n \ln T) = \frac{n}{T}$$

$$\frac{\partial^2 \ln f}{\partial T^2} = \frac{-n}{T^2}$$

ideal gas law

and so

$$E = n k_B T N = n p V \Rightarrow \frac{E}{V} = n p$$

$$C_V = 2 n k_B N - k_B T^2 N \left(\frac{-n}{T^2}\right) = n k_B N$$

Helmholtz free energy

$$A = \Sigma + \mu N = -k_B T z V f(T) + k_B T (\ln z) z V f$$

$$= z V k_B T f(T) \left[\ln z - 1 \right]$$

$$= N k_B T \left[\ln z - 1 \right]$$

$$A(T,V,N) = N k_B T \left[\ln \left(\frac{N}{V f(T)} \right) - 1 \right]$$

above agrees with direct result from canonical ensemble:

$$Q_N = \frac{V^N f^N}{N!} \Rightarrow A = -k_B T \ln Q_N = -k_B T \ln \left(\frac{V^N f^N}{N!} \right)$$

$$= -k_B T N \ln V f + k_B T (N \ln N - N)$$

$$= -N k_B T + N k_B T \ln (N/Vf)$$

entropy

$$S = -\left(\frac{\partial A}{\partial T} \right)_{V,N} = N k_B \left[\ln \left(\frac{N}{V f(T)} \right) - 1 \right]$$

$$- N k_B T \frac{d(\ln f)}{dT}$$

For distinguishable particles

- corresponds to situation where particles are <u>localized</u> - so we can distinguish them by their spatial location.

Now expect $Q_1 = \phi(T)$ is not proportional to V as the particles are localized.

$$\mathcal{L} = \frac{1}{1 - zQ_1} = \frac{1}{1 - z\phi(T)}$$

(if $Q_1 \propto V$, then series would not converge!)

$$\Sigma = -k_B T \ln \mathcal{L}$$

$$N = -\frac{\partial z}{\partial \mu}\frac{\partial \Sigma}{\partial z} = -\beta e^{\beta\mu}(-k_B T)\frac{1}{\mathcal{L}}\frac{\partial \mathcal{L}}{\partial z}$$

$$= z\,(1 - z\phi)\frac{(+\phi)}{(1 - z\phi)^2} = \frac{z\phi}{1 - z\phi}$$

$$N = \frac{z\phi}{1 - z\phi} \Rightarrow (1 - z\phi)N = z\phi$$

$$N = z\phi(1 + N)$$

$$z\phi = \frac{N}{1+N} \simeq 1 - \frac{1}{N} \quad \text{for } N \gg 1$$

$$E = -\left(\frac{\partial}{\partial\beta}\ln\mathcal{L}\right)_{z,V} = k_B T^2\left(\frac{\partial}{\partial T}\ln\mathcal{L}\right)_{z,V}$$

$$= k_B T^2 (1 - z\phi)\frac{+z\, d\phi/dT}{(1 - z\phi)^2}$$

$$E = \frac{k_B T^2\, z(d\phi/dT)}{1 - z\phi} \cong k_B T^2 N \frac{(d\phi/dT)}{\phi} = k_B T^2 N\left(\frac{d\ln\phi}{dT}\right)$$

$$A = \Sigma + \mu N = -k_B T \ln\left(\frac{1}{1-z\phi}\right) + k_B T (\ln z) N$$

$$= k_B T \left[\ln(1 - z\phi) + N \ln z \right]$$

use $1 - z\phi \simeq 1/N$ and $z \simeq 1/\phi$
to get

$$A = -k_B T N \ln \phi(T) + O(\ln N)$$