Relation between $\mathcal{L}$ and the Grand Potential Σ

Elegant way:

$$\Sigma = E - TS - \mu N \Rightarrow -\frac{\Sigma}{T} = S - \left(\frac{1}{T}\right)E + \left(\frac{\mu}{T}\right)N$$

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

Thus $-\frac{\Sigma}{T}$ is the Legendre transform of $S(E,V,N)$ with respect to E and N. $\left(\frac{1}{T}\right)$ is conjugate to E and $\left(\frac{-\mu}{T}\right)$ is conjugate to N.

Let's define $\beta \equiv \frac{1}{k_B T}$ and $\alpha \equiv \frac{\mu}{k_B T}$, then we can write $-\frac{\Sigma}{T}$ as a function of β, V, and α.

By behavior of Legendre transforms we then have

$$\left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial \beta}\right)_{V,\alpha} = k_B \left(\frac{\partial\left(-\frac{\Sigma}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)_{V,\alpha} = k_B(-E) = -k_B E$$

and

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

we conclude that $$\left(\frac{\partial\left(\frac{-\Sigma}{k_B T}\right)}{\partial \beta}\right)_{V,\alpha} = -E$$

and $$\left(\frac{\partial\left(\frac{-\Sigma}{k_B T}\right)}{\partial \alpha}\right)_{\beta,V} = N$$

Now consider $\ln \mathcal{Z}$ with $\mathcal{Z}$ the grand canonical partition function

$$\mathcal{Z} = \sum_i e^{-(E_i - \mu N_i)/k_B T} = \sum_i e^{-\beta E_i} e^{\alpha N_i}$$

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,\alpha} = \frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \beta}\right)_{V,\alpha} = \frac{1}{\mathcal{Z}} \sum_i e^{-\beta E_i} e^{\alpha N_i} (-E_i)$$

$$= \frac{-1}{\mathcal{Z}} \sum_i e^{-\beta(E_i - \mu N_i)/k_B T} E_i$$

$$= -\sum_i P_i E_i = -\langle E \rangle$$

P_i: probability to be in state i $\qquad$ $\langle E \rangle$: average energy in grand canonical ensemble

Similarly

$$\left(\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\mathcal{Z}}\left(\frac{\partial \mathcal{Z}}{\partial \alpha}\right)_{\beta,V} = \frac{1}{\mathcal{Z}} \sum_i e^{-\beta E_i} e^{\alpha N_i} (N_i)$$

$$= \frac{1}{\mathcal{Z}} \sum_i e^{-\beta(E_i - \mu N_i)/k_B T} N_i$$

$$= \sum_i P_i N_i = \langle N \rangle$$

average number of particles in the grand canonical ensemble

Comparing these results to our earlier results for $-\frac{\Sigma}{T}$, we identify:

$$-\frac{\Sigma}{k_B T} = \ln \mathcal{Z} \quad \text{or} \quad \boxed{\Sigma = -k_B T \ln \mathcal{Z}}$$

This is analogous to the relation between the canonical partition function and the Helmholtz free energy

$$A = -k_B T \ln Q_N$$

<u>Note:</u> From the Euler relation $E = TS - pV + \mu N$ and the Legendre transform $\Sigma = E - TS - \mu N = -pV$ we conclude

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

<u>Note:</u> taking a derivative at constant $\alpha = \frac{\mu}{k_B T} = \ln z$ is <u>NOT</u> the same as taking a derivative at constant μ.

$\uparrow$ fugacity

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

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

$$= -\sum_i P_i (E_i - \mu N_i) = -(\langle E \rangle - \mu \langle N \rangle)$$

so $$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,\mu} = -(\langle E \rangle - \mu \langle N \rangle)$$

whereas $$\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{V,z} = -\langle E \rangle$$

$\uparrow$ fixed fugacity, or fixed α

Also $\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} = \frac{1}{\mathcal{L}} \sum_i \frac{\partial}{\partial \mu} e^{-\beta(E_i - \mu N_i)}$

$$= \frac{1}{\mathcal{L}} \sum_i e^{-\beta(E_i - \mu N_i)} \beta N_i = \sum_i P_i \beta N_i = \beta \langle N \rangle$$

so $\frac{1}{\beta}\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} = \langle N \rangle$

Another way to show the relation between $\mathcal{L}$ and Σ

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

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

$$= \left(\frac{\partial (\beta \Sigma)}{\partial \beta}\right)_{V,\mu}$$

see similar result in discussion of $A = -k_B T \ln Q_N$

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

Compare these results with above

$$\left(\frac{\partial \ln \mathcal{L}}{\partial \beta}\right)_{V,\mu} = -\left(\langle E \rangle - \mu \langle N \rangle\right)$$

$$\left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} = \beta \langle N \rangle$$

and we conclude that $\ln \mathcal{L} = -\beta \Sigma$

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

Analogous to what we did for the canonical ensemble, one can show that in the thermodynamic limit, $N \to \infty$, computing in the grand canonical ensemble, with a fixed μ determining an average $\langle N \rangle$, 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 not 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.

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

$$(2) \quad \left(\frac{\partial \ln \mathcal{L}}{\partial \mu}\right)_{T,V} = \beta \langle N \rangle$$

Fluctuations of Particle Number and of Energy in the Grand Canonical Ensemble

Particle Number N what is $\langle N^2\rangle - \langle N\rangle^2$ in grand canonical ensemble?

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

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

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

Now $\frac{1}{\beta\mathcal{Z}}\frac{\partial\mathcal{Z}}{\partial\mu} = \frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \langle N\rangle$ so second term above is $\langle N\rangle^2$

and

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

$$= \frac{1}{\beta^2\mathcal{Z}}\sum_i e^{-\beta(E_i-\mu N_i)}(\beta N_i)^2$$

$$= \sum_i \rho_i N_i^2 = \langle N^2\rangle$$ the first term above

So

$$\sigma_N^2 \equiv \langle N^2\rangle - \langle N\rangle^2 = \frac{1}{\beta}\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V}$$ $\sim N$ since $\langle N\rangle$ is extensive while β and μ are intensive

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

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

We can write σ_N^2 in terms of a more familiar response function κ_T as follows:

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

write $v = \frac{V}{N} \Rightarrow N = \frac{V}{v}$

volume per particle is intensive

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

$$= V\left(\frac{\partial(1/v)}{\partial\mu}\right)_{T,V} = -\frac{V}{v^2}\left(\frac{\partial v}{\partial\mu}\right)_{T,V}$$

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

so, $d\mu = v\,dp - \left(\frac{S}{N}\right)dT$

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

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

Now since both v and p are intensive, they must be independent of N and V

$$\Rightarrow \left(\frac{\partial v}{\partial p}\right)_{T,V} = \left(\frac{\partial v}{\partial p}\right)_{T,N} = \left(\frac{\partial(V/N)}{\partial p}\right)_{T,N} = \frac{1}{N}\left(\frac{\partial V}{\partial p}\right)_{T,N}$$

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

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

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

κ_T is the isothermal compressibility

Fluctuation of the energy

Recall that in the canonical ensemble we had

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

$$= k_B T^2 C_V$$

specific heat at constant volume

We now want to see how the fluctuation of N in the grand canonical ensemble will effect the fluctuation of E.

We have $\mathcal{L} = \sum_i e^{-\beta(E_i - \mu N_i)} = \sum_i e^{-\beta E_i} z^{N_i}$

fugacity $z = e^{\beta\mu}$

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

$$= \sum_i \mathcal{P}_i E_i = \langle E\rangle$$

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

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

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

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

In above it was crucial that derivates were taken at constant $z = e^{\beta\mu}$

Note $\sigma_E^2 = -\left(\frac{\partial \langle E \rangle}{\partial \beta}\right)_{z,V}$ E is extensive so $\sim N$
β is intensive
so $\sigma_E^2 \sim N$

then $\frac{\sigma_E}{\langle E \rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0$ as $N \to \infty$

We now want to write σ_E in terms of more familiar response functions. To do so we want to take our derivative $\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{z,V}$ at constant z and rewrite in terms of derivatives at constant N.

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

where the above follows from regarding E as a function of T, N, V and then N as a function of z, V, T, and then applying the chain rule to differentiate

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

Now $\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = C_V$ specific heat at constant volume

so this first term in $(*)$ is same as in the canonical ensemble. The second term gives the additional fluctuations in E that arise because N is fluctuating

For the second term one can show

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

proof left to the reader

Then

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

where the last step comes from our earlier calculation of σ_N

So finally

$$\sigma_E^2 = k_B T^2\left\{ C_V + \left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\frac{1}{T}\left(\frac{\partial\langle E\rangle}{\partial N}\right)_{T,V}\beta\,\sigma_N^2\right\}$$

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

as in canonical ensemble

additional fluctuations in E due to fluctuations in N

Note, $C_V \sim N$ extensive

$\dfrac{\partial\langle E\rangle}{\partial N} \sim \dfrac{\text{extensive}}{\text{extensive}} \sim$ intensive

$\sigma_N^2 \sim N$ extensive

So $\sigma_E^2 \sim N$ is extensive and

$$\frac{\sigma_E}{\langle E\rangle} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \quad \text{as we saw before}$$

Proof

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{\partial}{\partial T}\left[\frac{1}{\mathcal{L}}\sum_i e^{-\beta E_i} z^{N_i} N_i\right]_{z,V}$$

$$= \frac{1}{\mathcal{L}}\sum_i e^{-\beta E_i} z^{N_i} N_i \left(\frac{E_i}{k_B T^2}\right)$$

$$- \frac{1}{\mathcal{L}^2}\left(\sum_i e^{-\beta E_i} z^{N_i} N_i\right)\left(\sum_i e^{-\beta E_i} z^{N_i}\left(\frac{E_i}{k_B T^2}\right)\right)$$

$$= \frac{1}{k_B T^2}\left(\langle NE\rangle - \langle N\rangle\langle E\rangle\right)$$

while

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

$$= \frac{1}{T}\frac{1}{\mathcal{L}}\sum_i e^{-\beta E_i} e^{\beta \mu N_i} \beta N_i E_i$$

$$- \frac{1}{T}\frac{1}{\mathcal{L}^2}\left(\sum_i e^{-\beta E_i} e^{\beta \mu N_i} E_i\right)\left(\sum_i e^{-\beta E_i} e^{\beta\mu N_i} \beta N_i\right)$$

$$= \frac{1}{k_B T^2}\left(\langle NE\rangle - \langle E\rangle\langle N\rangle\right)$$

So $\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial \langle E\rangle}{\partial \mu}\right)_{T,V}$