Now $N + N_R = N_T$ is fixed, $E + E_R = E_T$ is fixed

V, V_R are fixed

Similar to what we had for the canonical ensemble, the density of states for the total system of reservoir + system of interest is

$$g_T(E_T, V, V_R, N_T) = \int dE \sum_N g(E, V, N)\, g_R(E_T - E, V_R, N_T - N)$$

or for the number of states $\Omega = g\Delta$ (Δ is small energy interval as before)

$$\Omega_T(E_T, V, V_R, N_T) = \int \frac{dE}{\Delta} \sum_N \Omega(E, V, N)\, \Omega_R(E_T - E, V_R, N_T - N)$$

$$= \int \frac{dE}{\Delta} \sum_N \Omega(E, V, N)\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

probability density for system to have E and N is proportional to the number of states (of the total system) that have the system with E and N

$$P(E, N) \propto \frac{\Omega(E, V, N)}{\Delta}\, e^{S_R(E_T - E, V_R, N_T - N)/k_B}$$

expand

$$S_R(E_T - E, V_R, N_T - N) \simeq S_R(E_T, V_R, N_T) + \frac{\partial S_R}{\partial E_R}(-E_R)$$

$$+ \left(\frac{\partial S_R}{\partial N_R}\right)(-N)$$

$$= S_R - \frac{E}{T} + \frac{\mu N}{T}$$

$$P(E, N) \propto \frac{\Omega(E, V, N)}{\Delta}\, e^{-(E - \mu N)/k_B T}$$

Normalize

$$P(E, N) = \frac{\frac{\Omega}{\Delta}(E, V, N)\, e^{-(E - \mu N)/k_B T}}{\sum_N \int \frac{dE}{\Delta} \Omega(E, V, N)\, e^{-E/k_B T}\, e^{\mu N/k_B T}}$$

probability density for system to have E and N

$$\mathbb{P}(E,N) = \frac{\frac{\Omega(E,V,N)}{\Delta}\, e^{-(E-\mu N)/k_BT}}{\sum_N \int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-(E-\mu N)/k_BT}}$$

$P(E,N)$ is normalized, ie $\sum_N \int dE\, P(E,N) = 1$

the denominator in the above expression for $P(E,N)$ defines the grand canonical partition function

$$\boxed{\begin{aligned} \mathcal{L}(T,V,\mu) &\equiv \sum_N \left[\int \frac{dE}{\Delta}\, \Omega(E,V,N)\, e^{-E/k_BT} \right] e^{\mu N/k_BT} \\ &= \sum_N Q_N(T,V)\, z^N \end{aligned}}$$

where we define the fugacity $z \equiv e^{\mu/k_BT}$

If we can label the microscopic states of the system by the index i, such that state i has total energy E_i and contains N_i particles, then we can write

$$Q_N(T,V) = \sum_{\substack{i \text{ such} \\ \text{that } N_i = N}} e^{-E_i/k_BT}$$

and so

$$\mathcal{L} = \sum_N \left[\sum_{\substack{i \text{ such that} \\ N_i = N}} e^{-E_i/k_BT} \right] e^{\mu N/k_BT}$$

$$\mathcal{L} = \sum_i e^{-(E_i - \mu N_i)/k_BT}$$

where now sum on i is over all states with no restriction on N_i

Return now to probability density

$$\mathcal{P}(E,N) = \frac{\frac{\Omega}{\Delta} e^{-(E-\mu N)/k_BT}}{\mathcal{L}}$$

Since Ω just counts the number of $\underbrace{\text{states}}_{\text{of the system}}$ with energy E and number of particles N, and all these states are equally likely, the probability to be in any particular state i is just

$$\boxed{P_i = \frac{e^{-(E_i-\mu N_i)/k_BT}}{\mathcal{L}}}$$

This is the obvious generalization of what we had earlier for the canonical ensemble

Note: these expressions for $\mathcal{L}$, P_i, $\mathcal{P}(E,N)$ etc, make NO reference to the reservoir!

Relation between $\mathcal{Z}$ 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 $\beta = \frac{1}{k_B T}$ 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

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

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

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

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

probability to be in state i — 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 $\quad \Sigma = E - TS - \mu N = -pV$
we conclude

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

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

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

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

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

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

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

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

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

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

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

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