probability density for system to have E and N

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

$P(E,N)$ 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

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

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

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

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

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

Alternatively - for classical indistinguishable particles

Consider system + reservoir to be a a fixed T in a canonical ensemble

Canonical partition function for system + reservoir, with volume $V_T = V + V_R$ and number particles $N_T = N + N_R$, is

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \int_{V_T} dq_i \int dp_i \, e^{-\beta \mathcal{H}_T}$$

$\mathcal{H}_T$ is total Hamiltonian

Imagine dividing the combined system into the "system of interest" with N particles in V, and the reservoir with N_R particles in V_R.

The system of interest is weakly interacting with the reservoir, so

$$\mathcal{H}_T = \underbrace{\mathcal{H}}_{\text{system of interest}} + \underbrace{\mathcal{H}_R}_{\text{Reservoir}}$$

and $$\int_{V_T} dq_i = \int_{V+V_R} dq_i = \int_V dq_i + \int_{V_R} dq_i$$

$$Q_{N_T}(T, V_T) = \frac{1}{h^{3N_T} N_T!} \prod_{i=1}^{3N_T} \underbrace{\left(\int_V dq_i + \int_{V_R} dq_i \right)}_{} \int dp_i \, e^{-\beta \mathcal{H}} e^{-\beta \mathcal{H}_R}$$

expand out this product of factors - each term will correspond to a certain number N particles in V, and the remainder $N_R = N_T - N$ in V_R

Because the particles are indistinguishable, it does not matter which N of the N_T are in V and which N_R are in V_R. Each such term contributes the same amount. We can therefore consider just one such term, and multiply it by the number of ways to put N in V, with the remainder in V_R. The number of such ways is $\dfrac{N_T!}{N!\,N_R!}$

$$Q_{N_T}(T,V_T) = \frac{1}{h^{3N_T}N_T!}\sum_{N=0}^{N_T}\frac{N_T!}{N!\,N_R!}\left(\prod_{i=1}^{3N}\int_V dq_i\int dp_i\, e^{-\beta H}\right)\left(\prod_{j=1}^{3N_R}\int_{V_R} dq_j\int dp_j\, e^{-\beta H_R}\right)$$

$$= \sum_{N=0}^{N_T}\left(\frac{1}{h^{3N}N!}\prod_{i=1}^{3N}\int_V dq_i\int dp_i\, e^{-\beta H}\right)\left(\frac{1}{h^{3N_R}N_R!}\prod_{j=1}^{3N_R}\int_{V_R} dq_j\int dp_j\, e^{-\beta H_R}\right)$$

$$Q_{N_T}(T,V_T) = \sum_{N=0}^{N_T} Q_N(T,V)\,Q^R_{N_R}(T,V_R)$$

probability that there are N particles in V is therefore proportional to the weight this term has in the above sum

$$P(N) \propto Q_N(T,V)\,Q^R_{N_R}(T,V_R) = Q_N(T,V)\,e^{-A_R(T,V_R,N_R)/k_BT}$$

expand

$$A_R(T,V_R,N_R) = A_R(T,V_R,N_T-N)$$

$$\simeq A_R(T,V_R,N_T) - \left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} N$$

$$= \underset{\substack{\uparrow\\ \text{indep of } N}}{\text{const}} - \mu N$$

$$\left(\frac{\partial A_R}{\partial N}\right)_{T,V_R} = \mu_R = \mu$$

So

$$P(N) \propto Q_N(T,V)\, e^{\mu N/k_B T}$$

$$P(N) = \frac{Q_N(T,V)\, e^{\mu N/k_B T}}{\sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}}$$

where we set $N_T \to \infty$ in upper limit of sum

Define $z = e^{\mu/k_B T}$

grand canonical partition function

$$\mathcal{L}(z,T,V) \equiv \sum_{N=0}^{\infty} Q_N(T,V)\, e^{\mu N/k_B T}$$

Substitute for Q_N to get

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

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

as before.

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

Elegant way:

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

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

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

$\left(\frac{1}{T}\right)$ is the conjugate variable to E

$\left(-\frac{\mu}{T}\right)$ is the conjugate variable to N

Let us define $\beta \equiv \left(\frac{1}{k_B T}\right)$, $\alpha \equiv \left(\frac{\mu}{k_B T}\right)$

Then we can write $-\frac{\Sigma}{T}$ as a function of (β, V, α), with

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

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

where above follows since $\frac{1}{T}$ and $\frac{-\mu}{T}$ are conjugate to E and N

we conclude that

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

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

Now consider $\ln \mathcal{L}$. We have

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

$$= \sum_i e^{-\beta E_i} e^{\alpha N_i}$$

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

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

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

prob to be in state i

average energy in grand canonical ensemble

Similarly,

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

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

← average number of particles in grand canonical ensemble

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

$$-\frac{\Sigma}{k_B T} = \ln \mathcal{Z}$$

or

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

this is analogous to

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

for the canonical ensemble.

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

$$\Sigma = -pV$$

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

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

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

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

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

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

fixed fugacity

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

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

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

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

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

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

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

$\left\{\begin{array}{l}\text{see similar result} \\ \text{in discussion of} \\ A = -k_B T \ln Q\end{array}\right.$

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

Compare these to results on previous page:

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

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

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

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

~~Thust~~ 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.