Dependence on the number of particles

Quantities like E, F, φ and H are extensive = have the property of additivity. From this one may conclude how they depend on the number of particles.

An extensive thermodynamic function — a homogeneous function of 1-st order wrt extensive macroscopic parameters.

For example, we wrote $E = E(S, V)$

Introducing the number of particles N,

$$E = N\, f\left(\frac{S}{N}, \frac{V}{N}\right)$$

Similarly,

$$F = N\, f\left(\frac{V}{N}, T\right)$$

$$\varphi = N\, f(P, T)$$

$$H = N\, f\left(\frac{S}{N}, P\right)$$

Consider N as a variable

$$dE = T\,dS - P\,dV + \mu\, dN$$

where $\boxed{\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \text{ — chemical potential}}$

Similarly,

$$dF = -S\,dT - P\,dV + \mu\,dN$$
$$d\varphi = -S\,dT + V\,dP + \mu\,dN$$
$$dH = T\,dS + V\,dP + \mu\,dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \left(\frac{\partial \varphi}{\partial N}\right)_{T,P} = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

$\rightarrow$ Chemical potential may be obtained from any of these thermodynamic functions

Then from the form $\varphi = N f(P,T)$ and $\mu = \left(\frac{\partial \varphi}{\partial N}\right)_{P,T}$ it follows that

$$\boxed{\varphi = \mu N}$$

It implies also that when considered as a function of P and T, the chemical potential is independent of N.

From the formula above,

$$-S\,dT + V\,dP + \mu\,dN \equiv d\varphi = d\mu\,N + \mu\,dN$$

$$\rightarrow \quad d\mu\,N = -S\,dT + V\,dP$$

$$d\mu = -s\,dT + v\,dP$$

s and v - entropy and volume per molecule

S and V - entropy and volume p

Consider a volume in space which may exchange particles with the environment.

In that case,

$$dF = -S\,dT + \mu\,dN$$

Let us define some thermodynamic potential which uses variable μ in place of N

$$d(F - \mu N) = -S\,dT - N\,d\mu$$

– that will do, $F - \mu N$

However, $\mu N = \varphi$. Then $F - \mu N = F - \varphi = -PV$

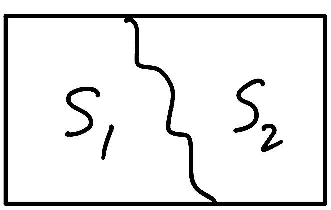
$$\boxed{\Omega = -PV}$$

The differential

$$d\Omega = -S\,dT - N\,d\mu$$

$$\Omega = \Omega(T, \mu)$$

Let's assume a body is in equilibrium



This body may be inhomogeneous, e.g., due to an external field

Maximise the total entropy

$$\frac{\partial S}{} = \frac{\partial S_1}{} + \frac{\partial S}{} \frac{\partial N_2}{} = \frac{\partial S_1}{} - \frac{\partial S_2}{} = 0$$

$$\frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S}{\partial N_2}\frac{\partial N_2}{\partial N_1} = \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} = 0$$

Use that $dE = TdS + \mu dN \rightarrow dS = \frac{dE}{T} - \frac{\mu}{T} dN$

Thus, $\frac{\mu_1}{T_1} = \frac{\mu_2}{T_2}$

In equilibrium $T_1 = T_2$

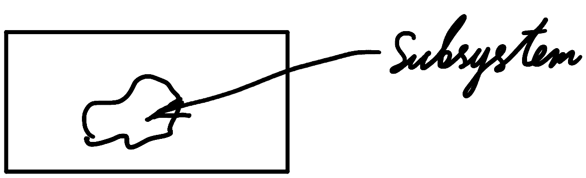
Thus, $\mu = \text{const}$ in the system

Gibbs distribution for a variable number of particles

Subsystem = system in a closed volume

N - number of particles within this volume

w_{nN} - prob-ty to have N particles and be in the n-th state



$$w_{nN} \propto e^{S_{env}(E_0 - E_{nN},\, N_0 - N)}$$

Expand in both E_{nN} and N to 1st order

We'll use that $TdS = dE + PdV - \mu dN$

$$\rightarrow dS = \frac{dE}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\rightarrow dS = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$$

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

Thus, $S_{env}(E_0 - E_{nN}, N_0 - N) \approx S_{env}(E_0, N_0) - \frac{E_{nN}}{T} + \frac{\mu N}{T}$

From here,

$$\boxed{w_{nN} \propto e^{\frac{\mu N - E_{nN}}{T}}}$$

We will use $S = -\langle \ln w_{nN} \rangle =$

$$= \frac{E}{T} - \frac{\mu \bar{N}}{T} + \ln \tilde{Z} = S$$

$$\rightarrow -\ln \tilde{Z} = \frac{1}{T}(E - \mu\bar{N} - TS) = \frac{\Omega}{T}$$

$$\boxed{w_{nN} = e^{\frac{\Omega - E_{nN}}{T}}}$$