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Last time:

$$\lim_{\mathcal{N}\to\infty} \frac{\langle n_{rs}\rangle}{\mathcal{N}} \approx \frac{n^*_{rs}}{\mathcal{N}} =$$

distribution that maximizes $P_{r,s}$

$$= \frac{e^{-\alpha N_r - \beta \epsilon_s}}{\sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}} = P_{r,s}$$

Now α and β can be obtained if we know $\langle N\rangle$ and $\langle \bar{\epsilon}\rangle$ for our system:

$$\bar{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta \epsilon_s}}{\sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}} = -\frac{\partial}{\partial \alpha}\underbrace{\left\{\ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}\right\}}_{q\text{-potential}}$$

$$= -\frac{\partial q}{\partial \alpha}$$

$$\bar{E} = \frac{\sum_{r,s} \epsilon_s e^{-\alpha N_r - \beta \epsilon_s}}{\sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}} = -\frac{\partial}{\partial \beta}\left\{\ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}\right\}$$

$$= -\frac{\partial q}{\partial \beta}$$

$$q = \ln \sum_{r,s} e^{-\alpha N_r - \beta \epsilon_s}$$

q-potential.

Grand partition function:

$$q = \ln\left\{\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\} \qquad q\text{-potential}$$

$$\Omega = -RTq \qquad \text{Landau or grand-potential.}$$

↳ This is NOT the number of microstates despite the fact that the same notation is used!!!

Notice that $q = q(\alpha, \beta, E_s)$

$$dq = \frac{\partial q}{\partial \alpha} d\alpha + \frac{\partial q}{\partial \beta} d\beta + \frac{\partial q}{\partial E_s} dE_s =$$

$$= -\bar{N}\, d\alpha - \bar{E}\, d\beta + \frac{\sum_{r,s} (-\beta)\, e^{-\alpha N_r - \beta E_s}\, dE_s}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}} \Rightarrow \qquad \frac{\langle n_{r,s} \rangle}{N}$$

$$d \, dq = -\bar{N}\, d\alpha - \bar{E}\, d\beta - \frac{\beta}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, d\epsilon_s$$

Since

$$d(\bar{N}\alpha) = \bar{N}\, d\alpha + \alpha\, d\bar{N}$$

$$d(\bar{E}\beta) = \bar{E}\, d\beta + \beta\, d\bar{E}$$

$$d(q + \bar{N}\alpha + \bar{E}\beta) = \alpha\, d\bar{N} + \beta\, d\bar{E} - \frac{\beta}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, d\epsilon_s =$$

$$= \beta\left(\frac{\alpha}{\beta}\, d\bar{N} + d\bar{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, d\epsilon_s\right)$$

$$\therefore \; kT\, d(q + \bar{N}\alpha + \bar{E}\beta) = \frac{\alpha}{\beta}\, d\bar{N} + d\bar{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle \, d\epsilon_s \qquad (1)$$

From the First law of thermodynamics:

$$d\bar{E} = \delta Q - \delta W + \mu\, d\bar{N}$$

$$\therefore\ \delta Q = d\bar{E} + \delta W - \mu\, d\bar{N} \quad (2)$$

δW and δQ are not exact differentials

Comparing (1) and (2)

$$\frac{\alpha}{\beta} = -\mu \quad \therefore \boxed{\alpha = -\mu/kT} \qquad \boxed{\beta = (kT)^{-1}}$$

$$\delta W = -\frac{1}{N} \sum_{r,s} \langle n_{r,s} \rangle\, d\bar{E}_s$$

$$\delta Q = kT\, d(q + \bar{N}\alpha + \bar{E}\beta)$$

$$\therefore\ d(q + \bar{N}\alpha + \bar{E}\beta) = \beta\,\delta Q = \frac{\delta Q}{kT} \equiv \frac{dS}{k} = d(S/k)$$

dS

$$\therefore \boxed{q} = \frac{S}{k} - \bar{N}\alpha - \bar{E}\beta = \frac{TS + \bar{N}\mu - \bar{E}}{kT} = \frac{\cancel{TS} + \cancel{\bar{E}} - \cancel{TS} + PV - \cancel{\bar{E}}}{kT}$$

$$\bar{N}\mu = G = E - TS + PV$$

$$= \boxed{\frac{PV}{kT}}$$

for all systems with P, V, T (not true for magnetic systems with $E \propto HM$ or for systems with any additional energy terms.

Also noticed that

$$\boxed{\Omega} = -kTq = -kT\frac{PV}{kT} = \boxed{-PV}$$

Define $z = e^{-\alpha} = e^{\mu/kT}$ fugacity

Then:

$$\boxed{q} = \ln\left\{\sum_{r,s} e^{-\alpha N_r} e^{-\beta \epsilon_s}\right\} =$$

$$= \ln\left\{\sum_{r,s} z^{N_r} e^{-\beta \epsilon_s}\right\} =$$

$$= \ln\left\{\sum_{N_r=0}^{\infty} z^{N_r} \underbrace{\sum_{s} e^{-\beta \epsilon_s}}_{Z_{N_r}(V,T)}\right\} \qquad Z_0 = 1$$

$Z_{N_r}(V,T)$ canonical partition function for N_r particles.

$$= \ln\left\{\underbrace{\sum_{N_r=0}^{\infty} z^{N_r} Z_{N_r}(V,T)}_{\mathcal{Z}(z,V,T)}\right\} =$$

$$= \boxed{\ln \mathcal{Z}}$$

grand-partition function.

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

Thermodynamic properties in the grand-canonical ensemble:

$$q = \frac{PV}{kT} \Rightarrow P = \frac{kTq}{V} = \frac{kT}{V} \ln \mathcal{Z}(z, V, T) = \quad (1)$$

$$= -\frac{\Omega}{V}$$

$$\therefore \boxed{\Omega = -kT \ln \mathcal{Z}(z, V, T)}$$

This is analogous to $F = -kT \ln Z$ in the canonical.

Now we will use $\bar{N} \equiv N$ and $\bar{E} \equiv U$

Let's obtain N and U from $\mathcal{Z}$:

$$N(z,V,T) = -\frac{\partial}{\partial\alpha}\left\{\ln\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right\} =$$

$$= z\frac{\partial}{\partial z} q(z,V,T)\Big|_{V,T} = z\,\frac{\sum_{N_r=0}^{\infty} N_r z^{N_r-1} Z_{N_r}(V,T)}{\mathcal{Z}} =$$

$$= \frac{\sum_{N_r=0}^{\infty} N_r z^{N_r} Z_{N_r}}{\mathcal{Z}} \equiv$$

$$\equiv kT\frac{\partial}{\partial\mu} q(\mu,V,T)\Big|_{V,T} = -\frac{\partial\Omega}{\partial\mu}\Big|_{V,T} \quad (2)$$

$\alpha = -\frac{\mu}{kT}$

$\partial\alpha = -\frac{\partial\mu}{kT}$

$\frac{\partial}{\partial\alpha} = -kT\frac{\partial}{\partial\mu}$

$z = e^{-\alpha}$

$\frac{\partial}{\partial\alpha} = \frac{\partial}{\partial z}\frac{\partial z}{\partial\alpha}$

$= -z\frac{\partial}{\partial z}$

Remember: $F(V,T,N) = E(V,S,N) - TS$ (gets rid of S as the external parameter and replaces it by T).

$$G(P,T,N) = F(V,T,N) + PV$$

$$H(P,S,N) = E(V,S,N) + PV$$

Then to get rid of N and replace it by μ you add $-\mu N$ to the known functions:

$$\Omega(V,T,\mu) = F(V,T,N) - \mu N$$

$$U(z,V,T) = -\frac{\partial q}{\partial \beta} = -\frac{\partial}{\partial \beta}\left\{ \ln \sum_{r,s} e^{-\alpha N_r - \beta E_s} \right\} =$$

$$= kT^2 \left[\frac{\partial q(z,V,T)}{\partial T} \right]_{z,V} \qquad (3)$$

$\beta = \frac{1}{kT}$

$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T}\frac{\partial T}{\partial \beta} = -kT^2 \frac{\partial}{\partial T}$

From ① and ②: getting rid of z we can obtain the equation of state, i.e. relationship between P, V and T.

From ② and ③ we can get $U = U(N, V, T)$ allowing to obtain $c_V = \frac{\partial U}{\partial T}\Big|_{N,V}$.

Helmholtz free energy:

$$\underbrace{\Omega}_{} = -kTq = -kT\ln \mathcal{Z}$$

$$F = E - TS = TS - PV + \mu N - TS = -PV + \underbrace{\mu N}_{} =$$

$$= NkT\ln z - kT\ln \mathcal{Z} =$$

$$= -kT\ln\left(\mathcal{Z}/z^N\right) \qquad ④$$

$$z = e^{-\alpha} = e^{\mu/kT}$$

$$\therefore \mu = kT\ln z$$

Also

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$$S = \frac{U-F}{T} = \frac{kT^{2}}{\cancel{T}}\frac{\partial q}{\partial T}\Big|_{z,V} - \frac{NK\cancel{T}}{\cancel{T}}\ln z + \frac{k\cancel{T}}{\cancel{T}}\underbrace{\ln Z}_{q} = kT\frac{\partial q}{\partial T}\Big|_{z,V} - Nk\ln z + kq$$