Grand-canonical potential and Gibbs distribution

Reminder: we considered the dependence of thermodynamic functions on the number of particles N and introduced the chemical potential

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

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

In order to have some potential which has μ as an external parameter we introduced the differential of another potential, $F - \mu N$, in a given volume

$$d\Omega = -S\,dT - N\,d\mu \qquad \Big| \; N = -\frac{\partial \Omega}{\partial \mu}$$

Also, we've shown that $\varphi = \mu N$, so

$\Omega = F - \varphi = -PV$

but note: it has to take μ and T as variables!!!

Gibbs distribution

$$w_{nN} = \frac{e^{\frac{\mu N - \varepsilon_{nN}}{T}}}{\Xi}$$ – Grand-canonical ensemble

$$w_{nN} = \frac{e^{\quad T}}{\tilde{Z}}$$ – Grand-canonical ensemble

$$\tilde{Z} = \sum_{n,N} e^{\frac{\mu N - \varepsilon_{nN}}{T}}$$ – Grand canonical partition function

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Generalise the definition of entropy

$$S = -\langle \ln w_{nN} \rangle \equiv -\sum_{nN} w_{nN} \ln w_{nN} \qquad (*)$$

We may also introduce a „more quantum" representation for it: $\tilde{Z} = \mathrm{Tr}\left(e^{\frac{\mu \hat{N} - \hat{H}}{T}}\right)$

Let's use (*) with the grand-canonical Gibbs distribution

$$S = -\left\langle \ln \frac{1}{\tilde{Z}} + \frac{\mu N - \varepsilon_{nN}}{T} \right\rangle =$$

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

$$\rightarrow -T \ln \tilde{Z} = E - ST - \mu N$$

since $E - ST - \mu N \equiv F - \mu N = \Omega$

$$\boxed{-T \ln \tilde{Z} = \Omega}$$

Once more,

$$\boxed{\Omega = -T \ln \sum \left[e^{\frac{\mu N}{T}} \sum e^{-\frac{E_{nN}}{T}} \right]}$$

$$\boxed{\Omega = -T \ln \sum_N \left[e^{\frac{\mu N}{T}} \sum_n e^{-\frac{E_{nN}}{T}} \right]}$$

It's also convenient to write the grand-canonical distribution in the form

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