Ensemble	indep. variables	statistical function	thermodynamic function
micro-canonical	E, V, N closed system	$\Omega(E,V,N)$	$S = k_B \ln \Omega$ tends to max.
canonical	T, V, N energy exchange w/ reservoir	$Z = \sum_n e^{-\beta E_n}$	$F = -k_B T \ln Z = E - TS$ tends to min.
grand canonical	T, V, μ energy + particle exchange w/ reservoir	$\mathcal{Z} = \sum_{r,s} e^{-\alpha N_r - \beta E_s}$ $\alpha = -\frac{\mu}{k_B T}$	$\Omega = -k_B T \ln \mathcal{Z}$ $= E - TS - \mu N$ tends to min.

Phys. 528 lecture 9

microcanonical ensemble

$$S = k_B \ln \Omega(E,V,N)$$

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

heat added

mechanical work

electrical/chemical work

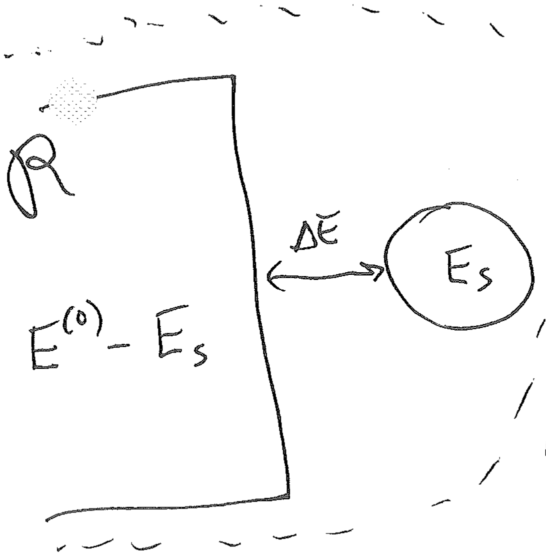
$$dS = \frac{dE}{T} + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN$$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N}$$

$$p = T\left.\frac{\partial S}{\partial V}\right|_{E,N}$$

$$\mu = -T\left.\frac{\partial S}{\partial N}\right|_{E,V}$$

Canonical ensemble



$$P_s \propto \Omega_R(E^{(0)} - E_s)$$

$$\ln \Omega_R(E^{(0)} - E_s) \simeq \ln \Omega_R(E^{(0)}) - \underbrace{\frac{\partial \ln \Omega_R}{\partial E}}_{\beta} E_s$$

$$P_s = C e^{-\beta E_s} = \frac{e^{-\beta E_s}}{Z}$$

$$1 = \sum_s P_s = C \sum_s e^{-\beta E_s} \qquad C = \frac{1}{Z}$$

$$Z = \sum_s e^{-\beta E_s}$$

$$S = -k_B \sum_s P_s \ln P_s = -k_B \langle \ln P_s \rangle$$

$$S = -k_B \langle -\beta E_s - \ln Z \rangle = \frac{E}{T} + k_B \ln Z$$

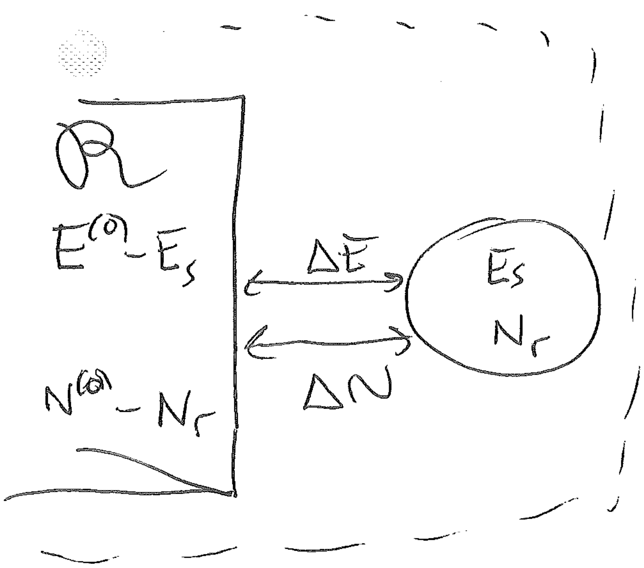
$$F = -k_B T \ln Z = E - TS$$

$$dF = dE - TdS - SdT = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT$$

$$P = -\frac{\partial F}{\partial V}\bigg|_{T,N} \qquad S = -\frac{\partial F}{\partial T}\bigg|_{N,V}$$

$$\mu = \frac{\partial F}{\partial N}\bigg|_{T,V} \equiv F(N,T,V) - F(N-1,T,V)$$

Grand Canonical Ensemble



$$P_{r,s} \propto \Omega_{\mathcal{R}}(N^{(0)} - N_r, E^{(0)} - E_s)$$

$$\ln \Omega_{\mathcal{R}}(N^{(0)} - N_r, E^{(0)} - E_s)$$

$$\simeq \Omega_{\mathcal{R}}(N^{(0)}, E^{(0)}) - \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial N} N_r$$

$$- \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial E} E_s$$

$$P_{r,s} = C e^{-\alpha N_r - \beta E_s}$$

$$P_{r,s} = \frac{e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}}$$

$$\mathcal{Z} = \sum_{r,s} e^{-\alpha N_r - \beta E_s}$$

$$\left.\begin{aligned} \beta &= \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial E} = \frac{1}{k_B T_{\mathcal{R}}} \\ \alpha &= \frac{\partial \ln \Omega_{\mathcal{R}}}{\partial N} = -\frac{\mu_{\mathcal{R}}}{k_B T_{\mathcal{R}}} \end{aligned}\right\} \text{drop subscript } \mathcal{R}$$

$$S = -k_B \sum_{r,s} P_{r,s} \ln P_{r,s} = -k_B \langle \ln P_{r,s} \rangle$$

$$= -k_B \langle -\alpha N_r - \beta E_s - \ln \mathcal{Z} \rangle$$

$$S = -\frac{\mu}{T} N + \frac{E}{T} + k_B \ln \mathcal{Z}$$

$$\Omega = -k_B T \ln \mathcal{Z} = E - TS - \mu N$$

$$d\Omega = (\cancel{TdS} - p\,dV + \cancel{\mu dN}) - \cancel{TdS} - S\,dT - \cancel{\mu dN} - N\,d\mu$$

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

$$p = -\left.\frac{\partial \Omega}{\partial V}\right|_{T,\mu} \qquad S = -\left.\frac{\partial \Omega}{\partial T}\right|_{V,\mu}$$

$$N = -\left.\frac{\partial \Omega}{\partial \mu}\right|_{T,V}$$

Fluctuations in GCE

$$\langle N \rangle = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}}$$

$$\left.\frac{\partial \langle N \rangle}{\partial \alpha}\right|_{\beta} = -\frac{\sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}}$$

$$- \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}} \frac{\frac{\partial \mathcal{Z}}{\partial \alpha}}{\mathcal{Z}}$$

$$= -\langle N^2 \rangle + \langle N \rangle^2$$

$$\alpha = -\beta \mu$$

$$\langle (\Delta N)^2 \rangle = k_B T \left.\frac{\partial \langle N \rangle}{\partial \mu}\right|_{T,V}$$

addition spectrum

$$\langle E \rangle = \frac{\sum_{r,s} E_s e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}}$$

$$\left.\frac{\partial \langle E \rangle}{\partial \beta}\right|_{\alpha,V} = -\frac{\sum_{r,s} E_s^2 e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}}$$

$$- \frac{\sum_{r,s} E_s e^{-\alpha N_r - \beta E_s}}{\mathcal{Z}} \left.\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right|_{\alpha,V}$$

$$= -\langle E^2 \rangle + \langle E \rangle^2$$

$$\langle (\Delta E)^2 \rangle \equiv \langle E^2 \rangle - \langle E \rangle^2 = -\left.\frac{\partial \langle E \rangle}{\partial \beta}\right|_{\alpha,V}$$

$$= k_B T^2 \left.\frac{\partial \langle E \rangle}{\partial T}\right|_{\alpha,V}$$

$$\left.\frac{\partial E}{\partial T}\right|_{\alpha,V} = \left.\frac{\partial E}{\partial T}\right|_{N,V} + \left.\frac{\partial E}{\partial N}\right|_{T,V} \left.\frac{\partial N}{\partial T}\right|_{\alpha,V}$$

Now $N = -\left.\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\right|_{\beta,V}$, $E = -\left.\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right|_{\alpha,V}$

so $\left.\frac{\partial N}{\partial \beta}\right|_{\alpha, V} = \left.\frac{\partial E}{\partial \alpha}\right|_{\beta, V}$

$$\left.\frac{\partial N}{\partial T}\right|_{\alpha, V} = \frac{1}{T}\left.\frac{\partial E}{\partial \mu}\right|_{T, V}$$

$$\langle (\Delta E)^2 \rangle = k_B T^2 C_V + k_B T \left.\frac{\partial E}{\partial N}\right|_{T, V} \left.\frac{\partial E}{\partial \mu}\right|_{T, V}$$

$$= \langle (\Delta E)^2 \rangle_{can.} + \left(\left.\frac{\partial E}{\partial N}\right|_{T, V} \right)^2 \langle (\Delta N)^2 \rangle$$

Examples

1) <u>single fermionic orbital</u>

$\mathcal{Z} = 1 + e^{-\beta(\varepsilon - \mu)}$, ε = orbital energy

$$\langle N \rangle = \frac{e^{-\beta(\varepsilon - \mu)}}{1 + e^{-\beta(\varepsilon - \mu)}} = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

Fermi-Dirac distribution

$$\langle (\Delta N)^2 \rangle = k_B T \left.\frac{\partial \langle N \rangle}{\partial \mu}\right|_{T,V}$$

$$= k_B T \frac{\partial}{\partial \mu}\left(e^{\beta(\varepsilon-\mu)}+1\right)^{-1}\Big|_{\beta,\varepsilon}$$

$$= \frac{e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)}+1\right)^2} = \langle N \rangle \left(1-\langle N \rangle\right)$$

2) <u>single bosonic orbital</u>

$$\mathcal{Z} = \sum_{n=0}^{\infty}\left[e^{-\beta(\varepsilon-\mu)}\right]^n = \frac{1}{1-e^{-\beta(\varepsilon-\mu)}}$$

$$\langle N \rangle = -\left.\frac{\partial \ln \mathcal{Z}}{\partial \alpha}\right|_{\beta,V} = k_B T \left.\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right|_{\beta,V}$$

$$= +\frac{\partial}{\partial \alpha}\ln\left(1-e^{-\alpha-\beta\varepsilon}\right)\Big|_{\beta,V}$$

$$= \frac{e^{-\alpha-\beta\varepsilon}}{1-e^{-\alpha-\beta\varepsilon}} = \frac{1}{e^{\beta(\varepsilon-\mu)}-1} = \langle N \rangle$$

<u>Bose-Einstein distribution</u>

$$\langle (\Delta N)^2 \rangle = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_{T,V}$$

$$= k_B T \frac{\partial}{\partial \mu} \left(e^{\beta(\varepsilon - \mu)} - 1 \right)^{-1} \Big|_{\beta, \varepsilon}$$

$$= \frac{e^{\beta(\varepsilon-\mu)}}{\left(e^{\beta(\varepsilon-\mu)} - 1\right)^2} = \langle N \rangle \left(1 + \langle N \rangle \right)$$

$$\langle (\Delta N)^2 \rangle = \langle N \rangle \left(1 \pm \langle N \rangle \right)$$

for bosons / fermions

Fluctuations due to random (uncorrelated) processes would yield

$$\langle (\Delta N)^2 \rangle \Big|_{\text{classical}} = \langle N \rangle$$

Remark For a single orbital,

$$\mathcal{Z}_{\text{fermion}} = 1 + e^{-\beta(\varepsilon-\mu)}$$

$$\mathcal{Z}_{\text{boson}} = \sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu)n} = \frac{1}{1-e^{-\beta(\varepsilon-\mu)}}$$

$$\mathcal{Z}_{\text{classical}} = \sum_{n=0}^{\infty} \frac{Z_1^n}{n!} e^{\beta\mu n} = \sum_{n=0}^{\infty} \frac{(e^{\beta\mu} Z_1)^n}{n!}$$

$$= e^{Z_1 e^{\beta\mu}},$$ where Z_1 = 1-body partition function for a single cell of volume h^f in phase space.

The classical "calculation" overestimates n compared to fermions, but underestimates n compared to bosons. This is due to the Gibbs correction, which should not be applied to a single quantum state.