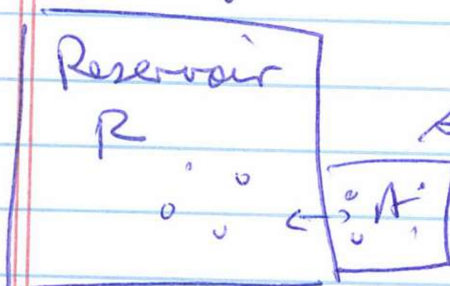
More on
Chap. 9

Grand Canonical Ensemble



system

particles (heat) flow in or out

N can change

Definitions:

$$\frac{1}{T} = k_B \left(\frac{\partial}{\partial U_R} \ln W_R\right)_{N_R} = \frac{\partial S}{\partial U}$$

$$\mu = -k_B T \frac{\partial}{\partial N_R}\left(\ln W_R\right)_{U_R} = -T\frac{\partial S}{\partial N}$$

μ & T <u>constant</u>
for large reservoir

Solve above.

$$\ln W_R = \underset{\text{constant}}{K} + \frac{U_R - \mu N_R}{k_B T}$$

$$W_R \propto \exp\left(\frac{U_R - \mu N_R}{k_B T}\right)$$

$$W_R(U_R, N_R) = \gamma\, e^{(U_R - \mu N_R)/k_B T}$$

$$W(U_R, N_R) = \gamma\, e^{(U_R - \mu N_R)/k_B T}$$

$$W(U_A, N_A) = W_A(U_A)\, W_R(U_R, N_R)$$

single qu. state $|E_i\rangle, N_i$

$$W(E_i) = 1 * W_R(\underbrace{U_T - U_A}_{E_i},\ \underbrace{N_T - N_A}_{\mu N_i})$$

Then $$W(E_i, N_i) = \gamma\, e^{(U_T - \mu N_T)/k_B T} * e^{-(E_i - \mu N_i)/k_B T}$$

$$= \xi\, e^{-(E_i - \mu N_i)/k_B T}$$

Prob. of realizing state $|E_i, N_i\rangle$

$$p_i \propto e^{-(E_i - \mu N_i)/k_B T}$$

Total number of states $W = \sum_i W_i$

$$p_i = \frac{W_i}{W} = \frac{e^{-(E_i - \mu N_i)/k_B T}}{\sum_i e^{-(E_i - \mu N_i)/k_B T}}$$

Now consider ensemble of replicas of E_i, N_i

- both energy and particle number flowing

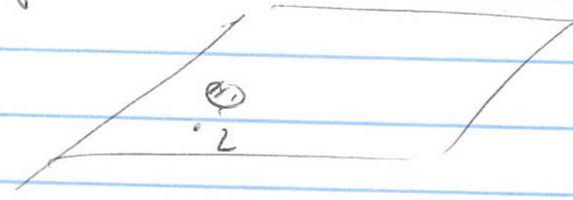
$\longrightarrow$ grand canonical ensemble

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

Example: particles on a surface

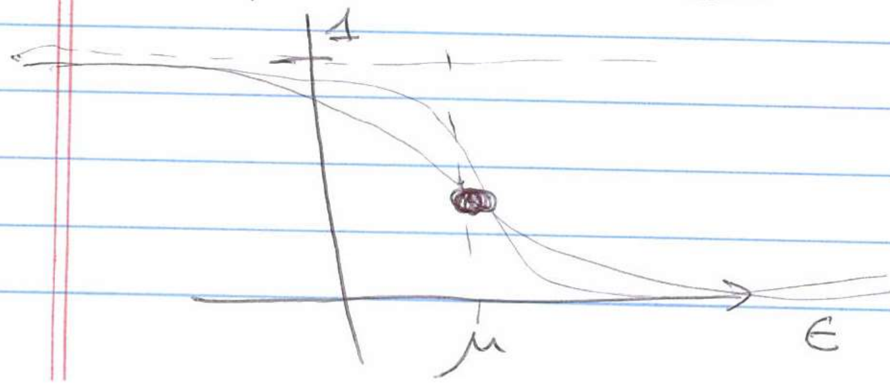
$n_i = 1$ or 0

$E_i = \epsilon_i$ $\quad 0$



$$\mathcal{Z} = 1 + e^{-(\epsilon_i - \mu)/k_B T}$$

$$p_{\text{site occupied}} : p = \frac{e^{-(\epsilon_i - \mu)/k_B T}}{\mathcal{Z}} = \frac{1}{e^{(\epsilon_i - \mu)/k_B T} + 1}$$



Average number

$$\bar{n} = \sum_i n_i p_i \qquad n_i = 0 \text{ or } 1, \quad p_i = 1-p \quad p$$

$$= 0 * (1-p) + 1 * p$$

$$= \frac{1}{e^{(\epsilon-\mu)/k_BT} + 1}$$

Link to thermodynamic functions

Entropy $\quad S = -k_B \sum_i p_i \ln p_i$

$$p_i = e^{-(E_i-\mu N_i)/k_BT} / Z$$

Hence

$$S = -k_B \sum_i \left\{ p_i \left[\left[\frac{-(E_i-\mu N_i)}{k_BT} \right] - \ln Z \right] \right.$$

$$= \frac{\bar{U}_i}{T} - \frac{\mu\bar{N}}{T} + k_B \ln Z$$

$\boxed{\text{Grand Potential}}$

$$\boxed{\Phi_G = -k_BT \ln Z = \bar{U} - \mu\bar{N} - TS}$$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{V,U} dN.$$

$$= \frac{d\bar{U} + PdV - \mu\, dN}{T}$$

$$\boxed{d\bar{U} = -PdV + \mu dN + TdS}$$

$$\Phi_G = \bar{U} - \mu N - TS \qquad \text{by definition}$$

Thus
$$d\Phi_G = d\bar{U} - d(\mu N) - d(TS).$$
$$= -PdV - \bar{N}\, d\mu - SdT$$

$$\boxed{\begin{aligned} S &= -\left(\frac{\partial \Phi_G}{\partial T}\right)_{V,\mu} = \frac{\partial}{\partial T}\left(k_B T \ln Z\right)_{V,\mu}. \\ P &= \frac{\partial}{\partial V}\left(k_B T \ln Z\right)_{T,\mu} \\ \bar{N} &= \frac{\partial}{\partial \mu}\left(k_B T \ln Z\right)_{T,V}. \end{aligned}}$$

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example : Surface $\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/k_BT}$

$$\bar{N} = k_BT \frac{\partial}{\partial\mu} \ln \mathcal{Z} = \frac{e^{-(\epsilon-\mu)/k_BT}}{1+e^{-(\epsilon-\mu)/k_BT}}$$

$$\bar{N} = \frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$$

A Note

$$Z_N = \frac{Z_1^N}{N!}$$ ordinary partition fn

$$F = -k_BT \ln Z_N = -k_BT\left(N \ln Z_1 - N\ln N + N\right)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_BT\left(\ln Z_1 - \ln N\right)$$

$$= -k_BT \ln \frac{Z_1}{N}.$$

$$e^{-\beta\mu} = \frac{Z_1}{N}. \qquad \boxed{e^{\beta\mu} = \frac{N}{Z_1}}$$