M0

Summarizing the canonical ensemble

Equilibrium

$$\frac{\partial}{\partial p_k}\left[\sum -k_B\, p_k \ln p_k + \Lambda_1\left(U-\sum_k p_k E_k\right) + \Lambda_2\left(1-\sum_k p_k\right)\right]=0$$

$$\Rightarrow \quad -k_B\left(\ln p_k + 1\right) - \Lambda_1 E_k - \Lambda_2 = 0$$

$$p_k = \underbrace{e^{-\frac{\Lambda_1}{k}E_k}}_{\substack{\text{adjusts}\\ \langle E\rangle}}\ \underbrace{e^{-\frac{\Lambda_2}{k}-1}}_{\substack{\text{Normalization}\\ =1/Z}}$$

$$p_k = e^{-\beta E_k}/Z \quad ; \quad Z=\sum_k e^{-\beta E_k}$$

$$U=\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{\sum_k E_k e^{-\beta E_k}}{\sum_k e^{-\beta E_k}}$$

$$C_V=\frac{\partial U}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial}{\partial\beta}U = +\frac{1}{k_B T^2}\left[\frac{\sum_k E_k^2 e^{-\beta E_k}}{\sum_k e^{-\beta E_k}} - \frac{\left(\sum E_k e^{-\beta E_k}\right)^2}{\left(\sum_k e^{-\beta E_k}\right)^2}\right]$$

$$=\frac{1}{k_B T^2}\left[\langle E^2\rangle - \langle E\rangle^2\right]$$

$$=\frac{1}{k_B T^2}\left\langle\left(E-\langle E\rangle\right)^2\right\rangle \geq 0$$

Fluctuation in Energy

$$S=-k_B\sum_k p_k\ln p_k = -k_B\sum_k p_k\left[-\beta E_k - \ln Z\right]$$

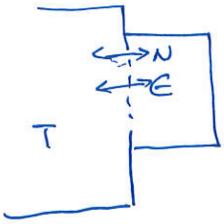
$$=+k_B\underbrace{\beta}_{\frac{1}{T}}\underbrace{\langle E\rangle}_{U} + k_B\ln Z$$

$$-k_B T\ln Z = U-TS = A$$

The chemical potential and the Grand Canonical Ensemble.

We now allow for the possibility of fluctuation in number of particles

μ_1



Then we have for 1st Law,

$$dU = \underbrace{T\,dS}_{\text{"}dQ\text{"}} - P\,dV + \mu\,dn$$

more formally, extensivity:

$$S(\lambda U, \lambda V, \lambda n) = \lambda S(U,V,n)$$

$$\frac{\partial}{\partial\lambda} \Rightarrow$$

$$\frac{\partial S(\lambda U ..)}{\partial \lambda U}\frac{\partial \lambda U}{\partial \lambda} + \frac{\partial S(\lambda V ..)}{\partial \lambda V}\frac{\partial (\lambda V)}{\partial \lambda} + \dots = S$$

$$\frac{1}{T}U + \frac{P}{T}V - \frac{\mu}{T}n = S$$

For $S = S(U,V,n)$

$$dS = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial n}dn$$

$$= \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn$$

$$\Rightarrow S = \frac{U}{T} + \frac{PV}{T} - \frac{\mu n}{T}$$

$$\Rightarrow U - TS = PV - \mu n$$

prob of k'th state with n particles $P_{n,k}$

$$S = -k_B \sum_{n,k} P_{n,k} \ln P_{n,k}$$

For fixed m, must reduce to canonical for $\Lambda_3 = 0$

Equilibrium:

$$0 = \frac{\partial}{\partial P_{m,k_m}}\left[S + \Lambda_1\left(U - \sum P_{n,k_n}E_{n,k_n}\right) + \Lambda_2\left(1 - \sum P_{n,k_n}\right) + \Lambda_3\left(N - \sum_{n,k_n} n P_{n,k_n}\right)\right]$$

$$-k_B \ln P_{m,k_m} - k_B - \Lambda_1 E_{m,k_m} - \Lambda_2 - \Lambda_3 m = 0$$

$$P_{m,k_m} = e^{-\frac{\Lambda_1}{k_B}E_{m,k_m}}\; \underbrace{e^{-\frac{\Lambda_2}{k_B} - 1}}_{\frac{1}{Z}}\; e^{-\frac{\Lambda_3}{k_B}m}$$

$\frac{\Lambda_1}{k_B}$: β adjusts temp

$\frac{\Lambda_3}{k_B}$: ? adjusts # of particles choose as $\mu\beta$

$$= e^{-\beta E_{m,k_m}}\, e^{\beta\mu m} / Z$$

The Grand Canonical partition function: μ_2

$$\mathcal{Z} = \sum_{n,k_n} e^{-\beta \epsilon_{n,k_n} + \beta\mu n} = \sum_n e^{\beta\mu n} \underbrace{\sum_{k_n} e^{-\beta \epsilon_{n,k_n}}}_{Z_n(\beta, V)}$$

$U = \langle E \rangle$

$N = \langle n \rangle$

$$-\frac{\partial}{\partial\beta} \ln \mathcal{Z} = \langle E - \mu n \rangle = U - \mu N$$

$$\frac{1}{\beta}\frac{\partial}{\partial\mu} \ln \mathcal{Z} = \langle n \rangle = N$$

← This equation gives N for a certain value of μ.

Eliminate μ ~~from~~ using this eqn. in favor of N

$$S = -k_B \sum_{n,k_n} p_{n,k_n} \ln p_{n,k_n}$$

$$= -k_B \sum_{n,k_n} p_{n,k_n} \left[-\beta \epsilon_{n,k_n} + \beta\mu n - \ln \mathcal{Z} \right]$$

$$= k_B \underbrace{\beta}_{1/k_B T} \langle E \rangle - k_B \beta\mu \langle n \rangle + k_B \ln \mathcal{Z}$$

$$ST = U - \mu N + k_B T \ln \mathcal{Z} = U + PV - \mu N$$

$$\Rightarrow + k_B T \ln \mathcal{Z} = PV$$

Example: Classical ideal gas.

$$Z_n = Z_1^n \frac{1}{n!} \leftarrow \text{non interacting particles}$$

$$= \left[\frac{\int d^3p \int d^3q}{h^3} \; e^{-\beta \frac{p_x^2}{2m} - \beta \frac{p_y^2}{2m} - \beta \frac{p_z^2}{2m}} \right]^n \frac{1}{n!}$$

$$= \left[V \left(\frac{\pi \, 2m}{\beta} \right)^{3/2} \right]^n \cdot \frac{1}{n!}$$

$$\mathcal{Z} = \sum_n e^{\beta \mu n} \left[V (2mkT)^{3/2} \right]^n \frac{1}{n!}$$

$$= \exp\left[e^{\beta\mu} (2mkT)^{3/2} V \right]$$

$$\ln \mathcal{Z} = e^{\beta\mu} (2m k_B T)^{3/2} V$$

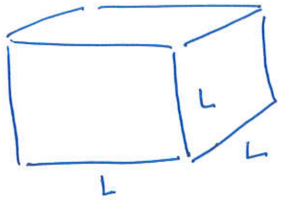
$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \ln \mathcal{Z}$$

$$k_B T \ln \mathcal{Z} = N k_B T = PV \checkmark$$

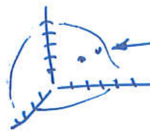
$$U - \mu N = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} = \underbrace{-\mu \ln \mathcal{Z}}_{\text{derivative of } e^{\beta\mu}} + \frac{3}{2} \frac{1}{\beta} \ln \mathcal{Z}$$

$$U = \frac{3}{2} N k_B T \checkmark$$

Fermions



$k_x = \frac{n_x \pi}{L}$, $k_y = \frac{n_y \pi}{L}$, $k_z = \frac{n_z \pi}{L}$ μ4



(n_x, n_y, n_z) : single particle states

Each state may be occupied by an e^- in $|\uparrow_z\rangle$ or $|\downarrow_z\rangle$ state

$(k_x, k_y, k_z)|\text{spin}\rangle = $ "k", $n_k = 0, 1$ $\epsilon_k = \frac{\hbar^2 k^2}{2m}$

\# of states with k between k and $k+dk$:

corresponding to energy $\frac{\hbar^2 k^2}{2m}$

$$\frac{4\pi k^2}{8\left(\frac{\pi}{L}\right)^3} \cdot dk \times \underbrace{2}_{\text{spin degeneracy}} = \frac{V k^2 dk}{\pi^2} \Rightarrow \sum_k f(k) = \int \frac{V k^2 dk}{\pi^2} f(k)$$

Canonical partition function

$$Z_N = \underbrace{\sum_{n_k=0,1} \cdots \sum_{n_2=0,1} \sum_{n_1=0,1}}_{\substack{\text{with constraint} \\ \sum_k n_k = N}} e^{-\beta \sum_k n_k \epsilon_k} \quad \leftarrow \text{difficult summation}$$

$E = \sum_k n_k \epsilon_k$

$n_k = 0$ if state is empty

$n_k = 1$ if state is occupied.

Grand canonical partition function

$$\mathcal{Z} = \sum_{N=0} e^{\beta\mu N} Z_N = \sum_{n=0}^{\infty} e^{\beta\mu n} \underbrace{\sum_{n_k=0,1} \cdots \sum_{n_1=0,1}}_{\sum n_k = n} e^{-\beta \sum_k n_k \epsilon_k}$$

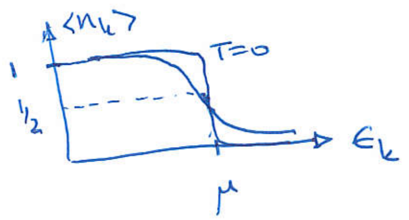
$e^{\beta\mu n} = e^{\beta \sum_k \mu n_k}$

$$= \underbrace{\sum_{n_k=0,1} \cdots \sum_{n_1=0,1}}_{\text{No restrictions}} e^{-\beta n_k(\epsilon_k - \mu)}$$

$$= \prod_k 1 + e^{-\beta(\epsilon_k - \mu_k)}$$

$$\ln \mathcal{Z} = \sum_k \ln\left(1 + e^{-\beta(\epsilon_k - \mu_k)}\right)$$

$$N = \langle n \rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu} \ln \mathcal{Z} = \sum_k \frac{e^{-\beta(\epsilon_k-\mu)}}{1 + e^{-\beta(\epsilon_k-\mu)}} = \sum_k \underbrace{\frac{1}{e^{\beta(\epsilon_k-\mu)} + 1}}_{\langle n_k \rangle}$$



Define $\mu = \epsilon_F$: Fermi Energy

Using the $T=0$ form,

$$N = \int_0^{k_F} \frac{V k^2 dk}{\pi^2} = \frac{V}{\pi^2}\frac{k_F^3}{3}$$

$$= \frac{V}{3\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{1/3}$$

$\frac{\hbar^2 k_F^2}{2m} = \epsilon_F$

$k_F = \left(\frac{2m\epsilon_F}{\hbar^2}\right)^{1/3}$

$$\left(3\pi^2 N/V\right)^3 \frac{\hbar^2}{2m} = \epsilon_F$$

Remember

$$-\frac{\partial}{\partial\beta}\ln\mathcal{Z} = U-\mu N$$

$$=\sum_k \frac{(\epsilon_k-\mu)\,e^{-\beta(\epsilon_k-\mu)}}{1+e^{-\beta(\epsilon_k-\mu)}} = \sum_k \frac{(\epsilon_k-\mu)}{e^{\beta(\epsilon_k-\mu)}+1} = \sum_k(\epsilon_k-\mu)\langle n_k\rangle$$

$$U=\sum_k \epsilon_k\langle n_k\rangle$$

For $T=0$ case $\quad U=\int_0^{k_F}\frac{Vk^2dk}{\pi^2}\cdot\frac{\hbar^2k^2}{2m} = \frac{V\hbar^2}{2\pi^2m}\cdot\frac{k_F^5}{5}$

$c_V\sim\frac{\partial U}{\partial T}\propto T$ for low T

The general problem

Use $\quad N=\int_0^{\infty}\frac{V\,k^2dk}{\pi^2}\;\frac{1}{e^{\beta(\hbar^2k^2/2m-\mu)}}$ $\quad$ to find $\mu(T,N)$

Substitute in

$$PV=\frac{1}{\beta}\ln\mathcal{Z}=\frac{1}{\beta}\int_0^{\infty}\frac{Vk^2dk}{\pi^2}\ln\left(1+e^{-\beta(\hbar^2k^2/m-\mu)}\right)$$

To find the eqn. of state