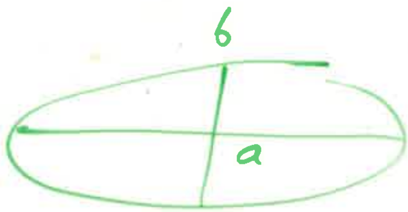
One-dimensional chain w/ massless link

Tension in chain? $\tau = Mg$



At temp T, what is $\underline{L}$?

Energy states of one link.

$$0 \qquad\qquad \tau(a-b)$$

$$-\tau a \qquad\qquad -\tau a$$

$$E_1 = -\tau a \qquad\qquad E_2 = -\tau b$$

Partition function for one link

$$z = e^{-\beta(-\tau a)} + e^{-\beta(-\tau b)} = e^{\beta\tau a} + e^{\beta\tau b}$$

$$Z = z^N = \left(e^{\beta\tau a} + e^{\beta\tau b}\right)^N$$

$$\ln(Z) = N\ln\left(e^{\beta\tau a} + e^{\beta\tau b}\right)$$

What thermo. potential should we calculate

$$U = -\frac{\partial}{\partial\beta}\ln(Z) \quad ; \quad F = -\frac{1}{\beta}\ln(Z)$$

Expect $\langle L \rangle = \pm \left.\frac{\partial(\text{Potential})}{\partial(\text{variable})}\right|_{x,y}$

$$dF = -S\,dT + \underline{\tau\, dL} + \cancel{\mu\, dN}^{\,0}$$

$\Rightarrow$

$$dF = \left(\frac{\partial F}{\partial T}\right)\bigg|_{LN} dT + \left(\frac{\partial F}{\partial L}\right)\bigg|_{TN} dL + (\cdot)$$

$$\Rightarrow S = -\left.\frac{\partial F}{\partial T}\right|_{LN} \quad , \quad \tau = \left.\frac{\partial F}{\partial L}\right|_{TN}$$

gas

$\boxed{F + PV = G}$

but we want $\langle L \rangle$, not $\langle \tau \rangle$

$F - L\tau = G$

(Legendre Transformation)

$$dG = -S\,dT - \underline{L\,d\tau}$$

$U - TS = F$

$U - TS + PV = G$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{\tau,N} dT + \left(\frac{\partial G}{\partial \tau}\right)_{T,N} d\tau + (\cdot)$$

$$\Rightarrow \langle L \rangle = -\left(\frac{\partial G}{\partial \tau}\right)_{T,N}$$

How do we get G? – Already have it.

Z is not the canonical partition function.

$-\tau a$, $-\tau b$ are not E_1 & E_2

$-\tau a = H_1$, $-\tau b = H_2$ enthalpies

script Z

$$\mathcal{Z} = e^{-\beta H_1} + e^{-\beta H_2} \leftarrow \text{Gibbs partition function}$$

$$\Rightarrow G = -\frac{1}{\beta} \ln(\mathcal{Z}) = -k_B T \ln(\mathcal{Z})$$

Gibbs

$$\Rightarrow F = -k_B T \ln(Z)$$

canonical

$$\mathcal{Q} = \sum_i e^{-\beta(E_i - \mu N_i)} \leftarrow \text{grand partition function}$$

Gibbs sum

$$\Rightarrow \Phi = -k_B T \ln(\mathcal{Q})$$

grand potential

$\mathcal{G}$ – script G

Ω –

$$\mathcal{Z} = \left(e^{+\beta\tau a} + e^{+\beta\tau b}\right)^N$$

$$G = -k_B T \ln(\mathcal{Z}) = -k_B T N \ln\left(e^{\beta\tau a} + e^{\beta\tau b}\right)$$

$$\langle L \rangle = -\left(\frac{\partial G}{\partial \tau}\right)\Big|_{T,N} = -\frac{\partial}{\partial \tau}\left[-k_B T N \ln\left(e^{\beta\tau a} + e^{\beta\tau b}\right)\right]$$

$$\langle L \rangle = \frac{\cancel{k_B} T N \cancel{\beta}\left[a e^{\beta\tau a} + b e^{\beta\tau b}\right]}{e^{\beta\tau a} + e^{\beta\tau b}}$$

$$\langle L \rangle = \frac{N\left[a e^{\beta\tau a} + b e^{\beta\tau b}\right]}{e^{\beta\tau a} + e^{\beta\tau b}}$$

Low T, High β: Na ✓

High T, Low β: $\dfrac{N(a+b)}{2}$ ✓

Find chemical potential μ for an ideal gas.

$$Z = \left[\frac{eV}{N}\left(\sqrt{2\pi m k_B T}\right)^3\right]^N$$

Get a potential

$$F = -k_B T \ln(Z)$$

$$dF = -S\,dT - p\,dV + \mu\,dN$$

$$= \left(\frac{\partial F}{\partial T}\right)_{VN} dT + \left(\frac{\partial F}{\partial V}\right)_{TN} dV + \left(\frac{\partial F}{\partial N}\right)_{TV} dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{TV} = \frac{\partial}{\partial N}\left[N \ln\left(\frac{eV}{N}\left(\underbrace{\sqrt{2\pi m k_B T}}_{h}\right)^3\right)\right]$$

$$\lambda_Q(T) = \frac{h}{\sqrt{2\pi m k_B T}} = \sqrt{\frac{\hbar\beta}{m}}$$

de Broglie wavelength $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$

$$\mu = \frac{\partial}{\partial N}\left\{N \ln\left[\frac{eV}{N}\frac{1}{\lambda_Q^3}\right]\right\} = k_B T \ln\left(\frac{N \lambda_Q^3}{V}\right)$$

λ_Q^3 = quantum volume.