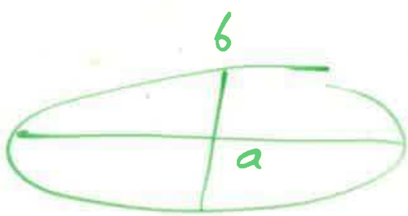
One-dimensional chain w/ massless link

Tension in chain? $\tau = Mg$



At temp T, what is L?

Energy states of one link.

$0 \quad\quad \tau(a-b)$ ~~[illegible]~~

$-\tau a \quad\quad -\tau a$

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

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

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

$\Rightarrow$

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

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

gas

$$\boxed{F + pV = G}$$

$$F - L\tau = G$$

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

(Legendre Transformation)

$$U - TS = F$$

$$U - TS + pV = G$$

$$dG = -S\,dT - L\,d\tau$$

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

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

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 –

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

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

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

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

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

Low T, High β : Na ✓

High T, Low β : $\frac{N(a+b)}{2}$ ✓

Find the chemical potential μ for an ideal gas.

$$Z = \left[\frac{eV}{N}\left(\frac{\sqrt{2\pi m k_B T}}{h}\right)^3\right]^N$$ cf. Lect 16

See Schroder p. 118 for the hard way.

Get a potential: $F = -k_B T \ln(Z)$

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

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

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

Define:

Thermal de Broglie Wavelength $\quad \lambda_Q \equiv \dfrac{h}{\sqrt{2\pi m k_B T}}$

in analogy with the de Broglie wavelength $\quad \lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mE}}$

Further, define the quantum volume $v_Q \equiv \lambda_Q^3$

intensive volume per "particle"

$$\mu = -k_B T \frac{\partial}{\partial N}\left\{N \ln\left[\frac{eV}{N v_Q}\right]\right\}_{TV}$$

$$= -k_B T\left\{\ln\left[\frac{eV}{N v_Q}\right] + N\frac{\partial}{\partial N}\left[\cancel{\ln e} + \cancel{\ln V} - \ln N - \cancel{\ln v_Q}\right]_{TV}\right\}$$

$$= -k_B T\left\{\ln\left[\frac{eV}{N v_Q}\right] + N\left[-\frac{1}{N}\right]\right\}$$

$$= -k_B T\left\{\ln e + \ln\left[\frac{V}{N v_Q}\right] - 1\right\}$$

$$= -k_B T \ln\left[\frac{V}{N v_Q}\right]$$ Schroder Eq. 3.63

Call $\frac{V}{N} = v$ $\left(\frac{\text{extensive}}{\text{extensive}} = \text{intensive}\right)$

$$\mu = k_B T \ln\left(\frac{v_Q}{v}\right)$$ for ideal gas