Q Antenna cell, Working cell.

AC) $I \to II$: Q_{in} could, $E\uparrow$, $S\uparrow$ $T = 6000K = $ Const

$II \to III$ $E\downarrow$ $T = 300K = $ Const.

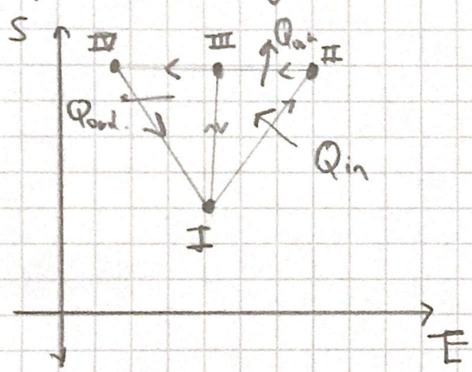
$III \to I$: $E\downarrow$ $S\downarrow$

WC) $I \to III$: $E\uparrow$

$III \to IV$: $\delta Q = 0$, $W \neq 0$

$IV \to I$: $E = $ Const $Q\downarrow$

a) Sketch cycle in SE diagram.



$$E = \frac{4\sigma}{c} V T^4$$
$$S = \frac{16\sigma}{3c} V T^3$$
$$\Rightarrow E = \frac{3}{4} T S$$

b) & c) $\eta = \frac{W}{Q}$, $x = \frac{(E_{II} - E_{III})}{(E_{II} - E_{IV})}$ [Fraction of useless vibrational energy]

Determine η as a func^n of x.

$\eta = \frac{W}{Q_{in}}$, $0 = \delta Q^* = dE + dW$

$$W_{III-IV} = -\int_{III}^{IV} dE = E_{III} - E_{IV}$$

$$\delta Q_{in} = TdS = \frac{4}{3} dE \Rightarrow Q_{in} = \frac{4}{3}\int_{I}^{II} dE = \frac{4}{3}(E_{II} - E_{I})$$

$$\Rightarrow \eta = \frac{E_{III} - E_{IV}}{E_{II} - E_{IV}} = \frac{3}{4}(1 - x)$$

$'' E_I$ (No E lost in between)

Rough

$dQ = -dE$

&

dW

$dE = dQ + dW$.

Rough : $x = \frac{E_{II} - E_{III}}{E_{II} - E_{IV}} \Rightarrow 1 - x = \frac{E_{II} - E_{IV} - (E_{II} - E_{III})}{(E_{II} - E_{IV})} = \frac{E_{III} - E_{IV}}{E_{II} - E_{IV}}.$

Antenna cell.

Q $\boxed{\text{I}}$ ✓ I → II: Adiabatic ↑ (Const S), II → III: Isochoric cooling (Const V), III → IV Adiabatic ↓ (Const S), IV → I: Isothermal (Const T)

$$PV = Nk_BT, \quad E = \frac{3}{2}PV = \frac{3}{2}Nk_BT \quad — \circledast$$

a) Show $PV = \text{cst}$ (Isotherm) & $PV^{5/3} = \text{Cst}$ on Adiabatics. Using $\circledast$ & $TdS = dE + PdV$

→ $PV = nk_BT$, $d(PV) = d(Nk_BT) = Nk_B \underset{0\,[\text{Isothermal}]}{dT} = 0$

$\therefore d(PV) = 0 \Rightarrow PV = \text{Constant}$ /

$N, k_B, T = \text{Const}$ so, $PV = Nk_BT = k = \text{Constant}$.

→ For Adiabatic: $\delta Q = 0$, $dE = \delta Q + \delta W \Rightarrow dE = \delta W$ $\quad \delta W = -PdV$

$\therefore dE = -PdV$ ← $\circledast$, $P = P(V)$

$$dE = \frac{3}{2}d(PV) = \frac{3}{2}(PdV + VdP) = \frac{3}{2}\left(PdV + V\frac{dP}{dV}dV\right)$$

$$= \frac{3}{2}\left(P + V\frac{dP}{dV}\right)dV$$

~~We know $d(PV) = 0$~~, We know, $dE + PdV = 0$ [From $\circledast$]

~~So, $0 = \frac{3}{2}\left(P + V\frac{dP}{dV}\right)dV$~~

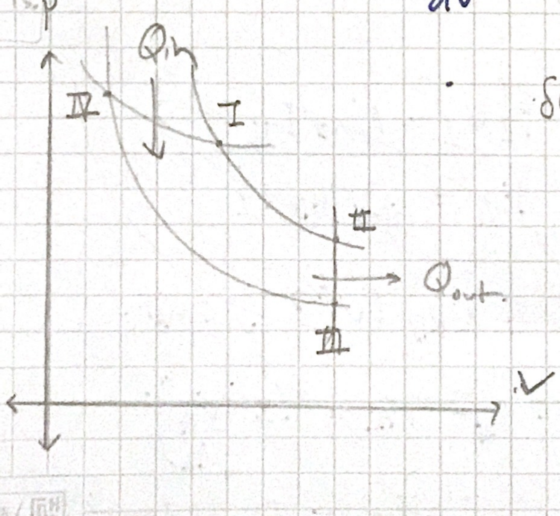
$$\therefore 0 = \frac{3}{2}d(PV) + PdV = \frac{3}{2}\left(P + V\frac{dP}{dV}\right)dV + PdV$$

$$= \underbrace{\left(\frac{5}{2}P + \frac{3}{2}V\frac{dP}{dV}\right)}_{=0}dV \Rightarrow \frac{5}{2}P + \frac{3}{2}V\frac{dP}{dV} = 0$$

{dV const, be 0 (adiabat)} ⇒ brackets is 0

$$V\frac{dP}{dV} = -\frac{5}{3}P \Rightarrow \left[PV^{\gamma} = \text{Const}\right] \quad \gamma = \frac{5}{3}$$

b)



$$\delta Q = dE + \delta W$$

$$\delta W = PdV$$

$$dE = \delta Q - PdV$$

c) ΔW in 1 cycle

$\delta Q = dE + \cancel{\delta A} + \delta W$

$\delta W = PdV$

$\delta Q = dE + PdV$

$\cancel{\delta W = \delta Q - dE}$

$PV = Nk_BT$

$P = \cancel{\frac{nRT}{V}} \frac{Nk_BT}{V}$

$$\Delta W = \left(\int_{I}^{II} + \int_{II}^{III} + \int_{III}^{IV} + \int_{IV}^{I}\right)\delta W$$

$$= \int_{I}^{II} \underbrace{\delta Q}_{0} - dE + 0 + \int_{III}^{IV} \underbrace{\delta Q}_{0} - dE + \int_{IV}^{I} \frac{nRT}{V}\, dV$$

$$= (E_I - E_{II} + E_{III} - E_{IV}) + Nk_BT \ln \frac{V_I}{\underbrace{V_{IV}}_{V'}} \quad (*)$$

d) ΔQ_{in}

$$\Delta Q_{in} = \int_{IV}^{I} \delta Q = \int_{IV}^{I} \underbrace{dE}_{0} + PdV = Nk_BT \ln \frac{V_I}{\underbrace{V_{IV}}_{V'}}$$

$\Rightarrow dE = Nk_B \underbrace{dT}_{0} = 0$

$$(*) = \frac{3}{2}Nk_B(T_{III} - T_{II}) + Nk_BT \ln V'$$

e

$$\eta = \frac{\Delta W}{\Delta Q_{in}} = \frac{\frac{3}{2}Nk_B(T_{III} - T_{II}) + Nk_BT_I \ln V'}{Nk_BT_I \ln V'}$$

$$= 1 - \frac{\frac{3}{2}\cancel{Nk_B}(T_{II} - T_{III})}{\cancel{Nk_B}T_I \ln V'} = \frac{1 - \frac{3}{2}\left[\left(\frac{V_I}{V_{II}}\right)^{2/3} - \left(\frac{V_{IV}}{V_{III}}\right)^{2/3}\right]}{\ln\left(\frac{V_I}{V_{IV}}\right)}$$

Rough:

$\cancel{PV = Nk_BT}$ $\quad P_IV_I = Nk_BT_I$

$\cancel{E = \frac{3}{2}Nk_BT}$ $\quad \cancel{E_I} = \frac{3}{2}Nk_BT_I$

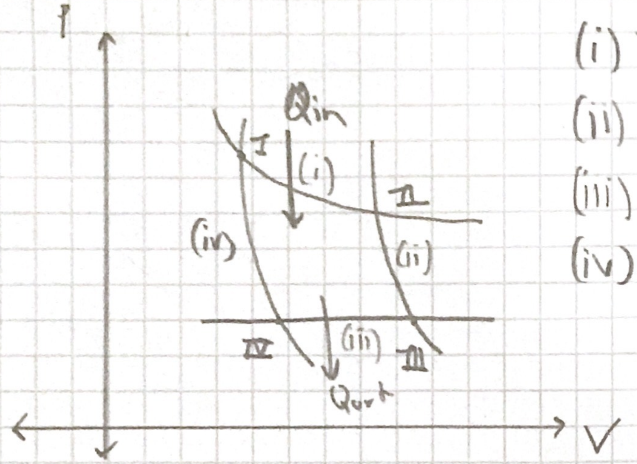
$$P = \frac{Nk_BT}{V} \Rightarrow PV^{5/3} = Nk_BTV^{2/3} = \text{const.}$$

$$\Rightarrow T_{II}V_{II}^{2/3} = T_IV_I^{2/3} \Rightarrow T_{II} = T_I\left(\frac{V_I}{V_{II}}\right)^{2/3}$$

$$T_{III} = T_I\left(\frac{V_{IV}}{V_{III}}\right)^{2/3}$$

Q3 c ...

1) a)



(i) Isothermal (Const T) exp^n

(ii) Adiabatic exp^n

(iii) Isobaric (Const P) exp^n

(iv) Adiabatic compresson.

Q_{in} in (i) & Q_{out} in (iii)

b) We have, $PV = Nk_BT$, $E = \frac{3}{2}PV = \frac{3}{2}Nk_BT$ $\qquad \delta Q = dE + PdV$

$$\Delta W = \left(\int_{I}^{II} + \int_{II}^{III} + \int_{III}^{IV} + \int_{IV}^{I}\right) PdV$$

$$= \int_{I}^{II} \cancel{\delta Q - dE}^{\,PdV}\underbrace{}_{\substack{dE = 0 \\ \text{(Isothermal) } dT=0 \Rightarrow dE=0}} + \int_{II}^{III} \underbrace{\delta Q}_{= 0 \text{ (Adiabatic)}} - dE + \int_{III}^{IV} \underbrace{P}_{\substack{\text{Constant} \\ \text{(Isobaric)}}} dV + \int_{IV}^{I} \underbrace{\delta Q}_{= 0 \text{ (Adiabatic)}} - dE$$

$$= \int_{I}^{II} \frac{Nk_BT}{V}\, dV + \underbrace{P_{IV}}_{= P_{III}} (V_{IV} - V_{III}) + (E_{II} + E_{IV} - E_{III} - E_{I})$$

We have for adiabats: $PV^{5/3} = \text{Const} \Rightarrow V^{2/3}T = \text{Const}.$

$$\therefore \cancel{V_{IV}^{2/3} T_{IV} = V_{III}} \qquad V_{II}^{2/3} T_{II} = V_{III}^{2/3} T_{III} \quad (*)$$

$$P_{II} V_{II}^{5/3} = \underbrace{P_{III}}_{= P_{IV}} V_{III}^{5/3} \Rightarrow P_{IV} = P_{II}\left(\frac{V_{II}}{V_{III}}\right)^{5/3} = P_{II}\left(\frac{T_{III}}{T_{II}}\right)^{5/2}$$

From (*), $\frac{V_{II}}{V_{III}} = \left(\frac{T_{III}}{T_{II}}\right)^{3/2}$ & $\cancel{P_1V_1 = P_2V_2}$ $P_I V_I = P_{II} V_{II}$

$$\therefore P_{II} = \left(\frac{V_I}{V_{II}}\right) P_I$$

$$\therefore \Delta W = Nk_BT \ln \underbrace{v}_{= \left(\frac{V_{II}}{V_I}\right)} + E_{IV} - E_{III} + P_{III}(V_{IV} - V_{III})$$

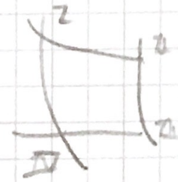
P_{II}

$$* \; E_{IV} - E_{III} = \frac{3}{2} N k_B (T_{III} - T_{II}) + \frac{N k_B}{V_{II}} \frac{T_{II}^{5/2}}{T_{II}^{3/2}} (V_{IV} - V_{III})$$

$$+ \frac{N k_B}{V_{II}} \frac{T_{II}^{5/2}}{T_{I}^{3/2}} \left(V_{IV} - \frac{T_{II}^{3/2}}{T_{III}^{3/2}} V_{II} \right)$$

$$P_{II} V_{II}^{5/3} = P_{III} V_{III}^{5/3}$$

$$= \frac{N k_B}{V_{II}} \frac{T_{II}^{5/2}}{T_{II}^{3/2}} V_{II}^{5/3}$$



$$T_{II} V_{II}^{2/3} = T_{III} V_{III}^{2/3}$$

$$\cancel{V_{IV}^{2/3} T_{IV} = V_{III}^{2/3} T_{III}}$$

$$\cancel{V_{IV} = V_{III}^{2/3} \frac{T_{III}}{T_{IV}}}$$

$$T_{II} V_{II}^{2/3} = T_{III} V_{III}^{2/3}$$

$$T_{IV} V_{IV}^{2/3} = T_{I} V_{I}^{2/3}$$

$$P_{III} = \frac{N k_B T_{II}^{5/3}}{V_I T_{II}^{3/2}}$$

$P_{III} = P_{IV}$

$P_I =$

$$E = \frac{3}{2} PV = \frac{3}{2} N k_B T$$

$$P_I V_I = P_{II} V_{II}$$

$$T_I V_I^{2/3} = T_{IV} V_{IV}^{2/3}$$

$$V_{IV} = \left(\frac{T_I}{T_{IV}} \right)^{3/2} V_I$$

$$T_I \left(\frac{P_{II} V_{II}}{P_I} \right)^{2/3} = T_{IV} V_{IV}^{2/3}$$

$$V_I \; \cancel{\frac{1}{A_I}} V_I \left(\frac{T_I}{T_{IV}} \right)^{3/2} \frac{\cancel{P_I V_I}}{\cancel{P_I}} = T_I \, V_{IV}$$

$$P_I V_I = P_{II} V_{II}$$

$$T_I = T_{II}$$

$$\cancel{V_{IV} = V_I}$$

$$V_I = \frac{P_{II}}{P_I} V_{II}$$

$=$

$$+ \frac{N k_B}{V_{II}} \frac{T_{III}^{5/2}}{T_{II}^{3/2}} \Big($$

$$P V_I = nRT_I$$

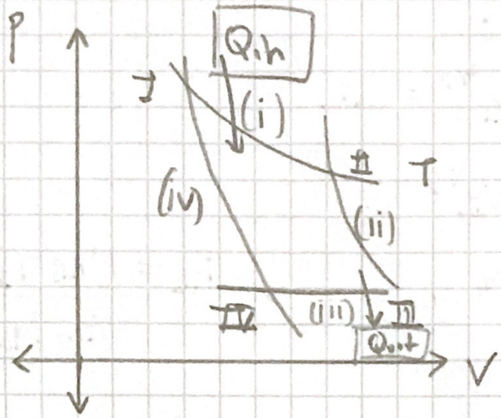
$$P V_{II} = nRT_{II}$$

Q) Consider the following P-V diagram, ✓ → finish d)

$I \to II$: Isotherm ↑, $II \to III$ Adiabatic ↑, $III \to IV$ Isobaric ↓, $IV \to I$ Adiabatic ↓.

$PV = Nk_BT$ & $E = \frac{3}{2}PV \equiv \frac{3}{2}k_BT$

a) Sketch (P,V)!



→ Diagram (That's why pencil)

(i): $dT = 0$

(ii): $\delta Q = 0$

(iii): $dP = 0$

(iv): $\delta Q = 0$

b) Work ΔW in one cycle.

$\Delta W = \oint \delta W$, $\delta W = -PdV$, $dE = \delta Q + \delta W = \delta Q - PdV$

Side calc^n

$\delta Q = dE + PdV$

$\therefore dE = -PdV$ for adiabatic

$P = \frac{Nk_BT}{V}$

$$\Delta W = \int_I^{II} + \dots + \int_{IV}^{I} dW$$

$$= \int_I^{II} PdV + \int_{II}^{III} \underset{\overset{\parallel}{0}}{\delta Q} - dE + \int_{III}^{IV} PdV + \int_{IV}^{I} \underset{\overset{\parallel}{0}}{\delta Q} - dE$$

$$= Nk_BT\left[\ln V\right]_I^{II} - \int_{II}^{III} dE - \int_{IV}^{I} dE + \int_{III}^{IV} PdV$$

$$= Nk_BT \ln \frac{V_{II}}{V_I} - E_{III} + \underbrace{E_{II} - E_I}_{=0} + E_{IV} + P_{III}(V_{IV} - V_{III})$$

$\hookrightarrow E = \frac{3}{2}Nk_BT \to$ Isotherm $dT = 0 \Rightarrow E = 0$

$dE = Nk_B \underset{\overset{\parallel}{0}}{dT} \frac{3}{2}$, $\underset{\overset{\parallel}{0}}{dE}$

$$= Nk_BT_I \ln \frac{V_{II}}{V_I} + E_{IV} - E_{III} + P_{III}(V_{IV} - V_{III})$$

c) Find ΔQ_{in}

$$\Delta Q_{in} = \int_I^{II} dE + \delta W, \quad dE = \frac{3}{2}Nk_B dT$$

$$= \int_I^{II} PdV = Nk_BT_I \ln\left(\frac{V_{II}}{V_I}\right)$$

d) Find η,

$$\eta = \frac{\Delta W}{\Delta Q_{in}} = 1 + \frac{\overbrace{E_{IV} - E_{III}}^{-ve} + P_{III}\overbrace{(V_{IV} - V_{III})}^{-ve}}{\underbrace{N k_B T_{II} \ln\left(\frac{V_{II}}{V_I}\right)}_{>0}} \leq 1$$

For adiabatic, $PV^{5/3} = \text{Const}$.

$$P_{III} = \frac{N k_B T_{III}}{V_{III}}$$

$$P_{III} V_{III}^{5/3} = N k_B T_{III} V_{III}^{2/3} = \text{Const}.$$

$$\Rightarrow T_{III} V_{III}^{2/3} = T_{II} V_{II}^{2/3}$$

$$\Rightarrow V_{III} = \left(\frac{T_{II}}{T_{III}}\right)^{3/2} V_{II} \quad \Rightarrow \quad P_{III} = \frac{N k_B T_{III}^{5/2}}{V_{II} T_{II}^{3/2}}$$

b, c, d in terms of T_I, T_{IV} & $v = \frac{V_{II}}{V_I}$

b*) $\Delta W = N k_B \left[T_I \ln(v) + \frac{5}{2}(T_{IV} - T_{III})\right]$

c*) $\Delta Q_{in} = N k_B T_I \ln v$

d*) $$\eta = \frac{\Delta W}{\Delta Q_{in}} = \cancel{1 + \frac{5}{2}} \frac{N k_B \left[T_I \ln(v) + \frac{5}{2}(T_{IV} - T_{III})\right]}{N k_B T_I \ln(v)}$$

$$= 1 + \frac{5}{2} \frac{(T_{IV} - T_{III})}{T_I \ln(v)}.$$

Rough:

$$\frac{N k_B T_I \ln\left(\frac{V_I}{V_2}\right) + E_{IV} - E_{III} + P_{III}(V_{IV} - V_{III})}{N k_B T_I \ln\left(\frac{V_{II}}{V_2}\right)}$$

$\cancel{A}$ $PV = N k_B T$, $PV^{5/3} = \text{Const}$ $\frac{5}{3}$

$V^{2/3} N k_B \cancel{T} T = \text{Const}$ (For adiabatic

$V^{2/3} T = \text{Const}$ $T_{II} V_{II}^{2/3} = T_{III} V_{III}^{2/3}$.

Q $TdS = dE + PdV - \mu dN$ [I] , $dE = \delta Q + \delta W$

a) Microscopic def^n of entropy. w.r.t M.C Ensemble (classical)
What does it mean for S to be an extensive qty.

$\rightarrow S(W) = k_B \log W(E)$ where $W(E) = |\{E - \Delta E \le H(P,Q) \le E\}|$

$\rightarrow S = S(E,V,N,\dots) \xrightarrow{\text{Extensive}} S(\lambda E, \lambda V, \lambda N, \dots) = \lambda S(E,V,N,\dots) \quad \forall \lambda > 0.$

b) Derive the relations: $\left.\frac{\partial N}{\partial E}\right|_{V,S} = \frac{1}{\mu}$, $\left.\frac{\partial N}{\partial S}\right|_{V,E} = \frac{-T}{\mu}$, $\left.\frac{\partial N}{\partial V}\right|_{E,S} = \frac{P}{\mu}$

1st law ⇒

$\rightarrow \mu dN = dE + PdV - TdS \Rightarrow dN = \frac{1}{\mu} dE + \frac{P}{\mu} dV - \frac{T}{\mu} dS$ — (*)

We know, $N(E,V,S) \Rightarrow dN = \frac{\partial N}{\partial E} dE + \frac{\partial N}{\partial V} dV + \frac{\partial N}{\partial S} dS$? — (*)'

∴ From (*) & (*)', $\frac{\partial N}{\partial E} = \frac{1}{\mu}$, $\frac{\partial N}{\partial V} = \frac{P}{\mu}$, $\frac{\partial N}{\partial S} = -\frac{T}{\mu}$ □

c) Introduce free energy $F = E - TS$, $F = F(T,N,V)$ Write 1st law in F.

$\rightarrow F = E - TS$, $F = F(T,N,V)$

$dF = dE - \cancel{d(TS)} - TdS - SdT = \cancel{TdS} - PdV + \mu dN - SdT - \cancel{TdS}$

$\boxed{dF = -PdV + \mu dN - SdT}$ ↳ 1st law in terms of F

d) $dS = \frac{1}{T} dE + \frac{1}{T} p dV - \frac{1}{T} \mu dN$

$0 = d\left(\frac{1}{T}\right) dE + d\left(\frac{P}{T}\right) dV - d\left(\frac{\mu}{T}\right) dN$

$$* \begin{cases} d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT = -\frac{1}{T^2}\left(\frac{\partial T}{\partial E} dE + \frac{\partial T}{\partial V} dV + \frac{\partial T}{\partial N} dN\right) \\ d\left(\frac{P}{T}\right) - \frac{1}{P} dP - \frac{P}{T^2} dT = \frac{1}{T}\left(\frac{\partial P}{\partial E} dE + \frac{\partial P}{\partial V} dV + \frac{\partial P}{\partial N} dN\right) + P \end{cases}$$

$0 = \left(\frac{1}{T}\frac{\partial P}{\partial E} - \frac{P}{T^2}\frac{\partial T}{\partial E}\right) dE + \left(\frac{1}{T}\frac{\partial P}{\partial V} - \frac{P}{T^2}\frac{\partial T}{\partial V}\right) dV + \left(\frac{1}{T}\frac{\partial P}{\partial N} - \frac{P}{T^2}\frac{\partial T}{\partial N}\right) dN$

Collect terms $dE, dV, dEdN, dNdV$

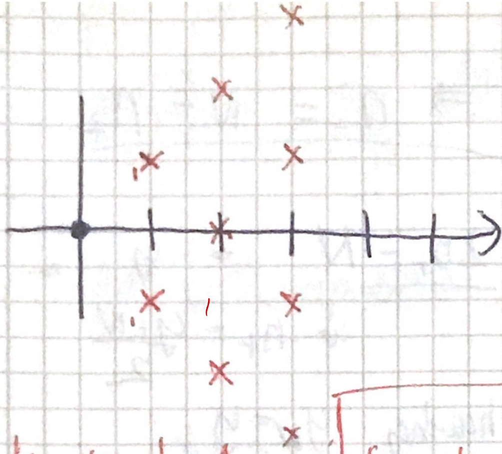
$\underline{dVdE}$: $+\frac{1}{T^2}\frac{\partial T}{\partial V} dE\, dV + \left(\frac{1}{T}\frac{\partial P}{\partial E} - \frac{P}{T^2}\frac{\partial T}{\partial E}\right)$ | $\left(-\frac{1}{T^2}\frac{\partial T}{\partial V} dVdE = \frac{1}{T^2}\frac{\partial T}{\partial V} dEdV\right)$

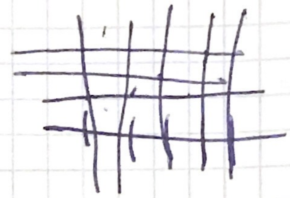
$\Rightarrow 0 = \frac{1}{T^2}\frac{\partial T}{\partial V} + \frac{1}{T}\frac{\partial P}{\partial E} - \frac{P}{T^2}\frac{\partial T}{\partial E} \quad dEdV$

$\Rightarrow 0 = \frac{\partial T}{\partial V} + T\frac{\partial P}{\partial E} - P\frac{\partial T}{\partial E}$

M1

1 VI





III : $\boxed{x_i - x_{i-1} = 1}$

$|y_i - y_{i-1}| = 1 \Rightarrow \boxed{(y_i - y_{i-1}) \begin{cases} 1 \\ -1 \end{cases}} \rightarrow 1 \quad 1 = 1$

Polymer oriented in x-dir^n.   N+1

(a) Determine the total no of microstates W

$$W \Rightarrow \begin{array}{cccccc} 0 & 1 & 2 & 3 & \cdots & N \\ \bullet & \bullet & \bullet & \bullet & \cdots & \bullet \\ \times & 2 & 2 & 2 & & 2 \end{array}$$

← Particle

← No of ways to arrange

1 2

~~Total particles~~: $\boxed{W = 2^N}$ → 0^{th} particle fixed.

(a) # of particles : $(N+1)$

But 1st particle is fixed & N particle have 2 choices

gives us $\boxed{W = 2^N}$

(b) * $y_N = \sum_i \sigma_i = n_+ - n_- = y.$

n_+ ↓ Number of time $\sigma_i = +1$

n_- ↓ Number of time $\sigma_i = -1$.

$\sigma_i = y_i - y_{i-1} = \begin{cases} +1 & \text{if } \nearrow \\ -1 & \text{if } \searrow \end{cases}$

$$n_+ + n_- = N \Rightarrow n_- = N - n_+$$

$$y_n = n_+ - n_- = 2n_+ - N = y$$

$$\Rightarrow n_+ = \frac{y+N}{2}$$

$\Rightarrow$ Number of microstates having $y_N = y$,

$$^N C_{n_+} = {}^N C_{\frac{y+N}{2}} = W(y)$$

c) Calc the typical dist^n of the end chain.

$$\langle y_N^2 \rangle = \frac{\sum_y y^2 W(y)}{\sum_y W(y)}$$

$$\rightarrow Z(\beta) = \sum_y e^{\beta y} W(y)$$

$$\rightarrow \frac{(\ ?\ )}{Z(0)}$$

$\ln \frac{\partial}{\partial \beta}$

$$Z''(\beta) = \frac{\partial^2 Z(\beta)}{\partial \beta^2} = \sum_y e^{\beta y} y^2 W(y)$$

$$Z''(0) = \sum y^2 W(y)$$

$$\langle y_N^2 \rangle = \frac{Z''(0)}{Z(0)}$$

$Z(\beta) = \sum_y e^{\beta y} W(y)$ $\qquad y = 2n_+ - N$

→ ~~All y corresponds to all n_+.~~

$= \cancel{\sum_y e}$

→ All y are ~~compound~~ corresponds to all n_+.

$\boxed{{}^{n}C_r = \frac{n!}{r!(n-r)!}}$

$$Z(\beta) = \sum_{n_+} e^{\beta(2n_+ - N)}\ {}^{N}C_{n_+}$$

$$= \cancel{\sum_{n_+} (e^{\beta})^{n_+} (e}$$

$$= \sum_{n_+} e^{\beta(n_+ + n_+ - N)}\ {}^{N}C_{n_+}$$

$$= \sum_{n_+} (e^{\beta})^{n_+} (e^{\beta})^{n_+ - N}\ {}^{N}C_{n_+}$$

$$= \sum_{n_+} (e^{\beta})^{n_+} (e^{\beta})^{-(N - n_+)}\ {}^{N}C_{n_+}$$

$$= \sum_{n_+} (e^{\beta})^{n_+} (e^{-\beta})^{N - n_+}\ {}^{N}C_{n_+}.$$

$$(a+b)^n = \sum_{k=0}^{n} {}^{n}C_k\, a^{n-k} b^k$$

$$(a+b)^2 = \sum_{k=0}^{2} (\quad) = {}^{2}C_0\, a^2 b^0 + {}^{2}C_1\, a^1 b^1 + {}^{2}C_2\, a^0 b^2$$

$$= \frac{2!}{0!(2-0)!} a^2 + 2ab + b^2$$

$$= \sum_{n_+} (e^{\beta})^{n_+} (e^{-\beta})^{N-n_+} \, {}^N C_{n_+}$$

If $e^{\beta} = a$, $e^{-\beta} = b$, $n_+ = K$.

We can write this as

$$\sum_K (a)^K (b)^{N-K} \, {}^N C_K$$ we get the binomial formula.

$$= (a+b)^{N}$$

$$= (e^{\beta} + e^{-\beta})^{N}$$

$$\cosh x = \frac{e^{\beta}+e^{-\beta}}{2}, \quad \sinh x = \frac{e^{\beta}-e^{-\beta}}{2}$$

① $2\cosh x = e^{\beta}+e^{-\beta}$

②

$$(2\cosh(\beta))^N$$

$$Z(\beta) = 2^N \cosh^N(\beta)$$

$$\cancel{Z'(\beta) = 2^N \sinh^N(\beta)}$$

$$\cancel{Z'(\beta) = 2^N \frac{d}{d\beta}(\sinh(\beta))^N}$$

$$\cancel{2^N \sinh\beta}$$

$$Z'(\beta) = 2^N \frac{\partial}{\partial \beta} (\cosh(\beta))^N$$

$$= 2^N \left[N (\cosh(\beta))^{N-1} \cdot \sinh(\beta) \right]$$

$$\rightarrow Z''(\beta) = 2^N \frac{\partial}{\partial \beta} [\dots]$$

why? Squared

$$= 2^N \left[N(N-1)(\cosh(\beta))^{N-2} \sinh^2(\beta) + N(\cosh(\beta))^{N-1} \cdot \cosh(\beta) \right]$$

?

$$= 2^N (\cosh(\beta))^{N-2} N \left[(N-1)\sinh^2(\beta) + \cosh^2(\beta) \right]$$

$$Z(0) = 1 \, 2^N,$$

$$Z''(0) = 2^N (1) N [0 + 1]$$

$$= 2^N N.$$

$$\Rightarrow \langle y_N^2 \rangle = \frac{Z''(0)}{Z(0)} = \frac{2^N N}{2^N} = N$$

Q Hamiltonian of N classical, relativistic particles moving in 1D is

$$H(q_1,\dots,q_N,p_1,\dots,p_N) = \sum_{i=1}^{N}\{c|p_i| + U(q_i)\}$$

$(p_1,\dots,p_N)$ are momenta of the particles & $(q_1,\dots,q_N)$ the positions (i.e. $q_i, p_i \in \mathbb{R}$ for all $i=1,\dots,N$). Pot $U(q)=0$ if $q\in[0,L]$ & $=\infty$ otherwise, Interval is $[0,L]$

a) The MC part^n function for distinguishable particles is $W(E,L,N) = h^{-N}\int_{E\le H(\{p_i\},\{q_i\})\le E+\Delta E} dq_1 \dots dq_N\, dp_1 \dots dp_N$

Perform the 1st q_i integrals.

q integral: $q \in [0,L] \Rightarrow \int dq_1 \dots dq_N = L^N$

$$\Rightarrow W = \frac{L^N}{h^N}\int dp_1 \dots dp_N.$$

b) Now perform p_i assuming $\Delta E \ll E$. May use Volume of a layer of thickness $\delta \ll R$ surrounding the surface of an N-dim hyperpyramid ($\{x_i \ge 0, \sum_i^N x_i \le R\}$) is given by $\sim \delta\sqrt{N}R^{N-1}/(N-1)!$ Take into account that each p_i is +ve/−ve.

p integral: Find volume of phase space between E & E+ΔE.

Using $\sum_{i=1}^{N} x_i \le R$, $V = \frac{\delta\sqrt{N}R^{N-1}}{(N-1)!}$, $\sum_{i=1}^{N}|p_i| \le \frac{E}{c}$ ← [U doesn't depend on p_i]

$$\Rightarrow V = \left(\frac{\Delta E}{c}\right)\frac{\sqrt{N}}{(N-1)!}\left(\frac{E}{c}\right)^{N-1} \cancel{\left(\frac{\Delta E}{c}\right)}$$ [In our case $\delta = \frac{\Delta E}{c}$]

$$\Rightarrow W = \frac{L^N}{h^N}\frac{\sqrt{N}}{(N-1)!}\left(\frac{E}{c}\right)^{N-1}\frac{\Delta E}{c} \Rightarrow W = \left(\frac{2L}{h}\right)^N \frac{\sqrt{N}}{(N-1)!}\left(\frac{E}{c}\right)^{N-1}\frac{\Delta E}{c}$$

Taking into account each p_i can be +ve/−ve.

c) How to modify partition function W if particles are indistinguishable?

Divide W by N!

d) Compute entropy $S = k_B \log W$ in the MCE for indistinguishable particles & verify $S = Nk_B\log\left(\frac{2e^2LE}{hcN^2}\right)$ up to subleading terms in the large N limit ($N! \sim N^N e^{-N}$)

$$W = \left(\frac{2L}{h}\right)^N \frac{\sqrt{N}}{(N-1)!\,N!}\left(\frac{E}{c}\right)^{N-1}\left(\frac{\Delta E}{c}\right),$$

Large N limit → $N-1 \simeq N$, $\frac{\Delta E}{c}$ → Neglect, $\sqrt{N} \ll N!$

$$\Rightarrow W(E,L,N\gg1) = \left(\frac{2L}{h}\right)^N \frac{1}{(N!)^2}\left(\frac{E}{c}\right)^N = \left(\frac{2LE}{hc}\right)^N \frac{1}{(N!)^2}$$

$$S = k_B \log W = k_B\left[N\log\left(\frac{2LE}{hc}\right) - 2\left(N(\log N - 1)\right)\right]$$

$$= k_B\left[N\log\left(\frac{2LE}{hc}\right) - \underbrace{2N\log N}_{N\log N^2} + \underbrace{2N}_{N\log e^2}\right] = k_B N \log\left[\frac{2e^2LE}{hcN^2}\right]$$

e) Use d) & 1^{st} law to derive $P = Nk_B T/L$ for pressure.

$$dE + PdV = TdS = T\left(\frac{\partial S}{\partial L}dL + \frac{\partial S}{\partial E}dE\right)$$

$$\rightarrow P = T\frac{\partial S}{\partial E}, \quad \frac{1}{T} = \frac{\partial S}{\partial E}$$

$$P = T\frac{\partial}{\partial L}\left(k_B N \log\left(\frac{2e^2 LE}{hcN^2}\right)\right) = T\frac{k_B N}{L}$$

f) Similarly derive $1/T = Nk_B/E$

$$\frac{1}{T} = \frac{\partial}{\partial E}\left(k_B N \log\left(\frac{2e^2 LE}{hcN^2}\right)\right) = \frac{k_B N}{E}.$$

g) Argue that probab density $\rho(p)$ for finding a particle with mom p is given by $\rho(p) = \frac{L}{Nh}\frac{W(E-c|p|, L, N-1)}{W(E,L,N)}$

→ Fix 1^{st} particle momentum p. Remaining particles: $N-1$. Energy $E-c|p|$

Probab of finding particle with momentum ~~p~~ is given by:

$$\rho(p) = \frac{W(E-c|p|, L, N-1)}{W(E,L,N)} \Rightarrow \rho(p) = \frac{L}{Nh}\frac{W(E-c|p|, ~~N-1~~ L, N-1)}{W(E,L,N)}$$

Multiply by volume of 1 phase space element: $\frac{L}{Nh}$

$$W(N \gg 1) = \left(\frac{2LE}{hc}\right)^N \frac{1}{(N!)^2}$$

$$\rho(p) = \frac{L}{Nh}\left[\left(\frac{2L(E-c|p|)}{hc}\right)^{N-1}\frac{1}{[(N-1)!]^2}\right]\left[\left(\frac{hc}{2LE}\right)^N \cdot (N!)^2\right]$$

$$= \left(\frac{2(E-c|p|)}{c}\right)^{N-1}\underbrace{\left(\frac{c}{2E}\right)^N}_{\left(\frac{c}{2E}\right)^{N-1}\cdot\frac{c}{2E}} \cdot \underbrace{\frac{N}{(N-1)!}}_{N}$$

$$\rho(p) = \frac{cN}{2E}\left(\frac{E-c|p|}{E}\right)^{N-1} \qquad (\text{sub } E = Nk_B T)$$

$$\rho(p) = \frac{cN}{2Nk_B T}\left(1 - \frac{c|p|}{Nk_B T}\right)^{N-1} \approx \frac{c}{2k_B T}e^{-\frac{c|p|}{k_B T}}$$

using $\left(1+\frac{a}{N}\right)^N \sim e^a$ for $N \gg 1$.

II

P.4) Lagrange multipliers:

1) Function to maximize: $S = -k_B \sum_n p_n \log p_n$

2) Constraints:

i) $U = \sum E_n p_n$

ii) $v = \sum n p_n$

iii) $\sum p_i = 1$

3) Define:

$$\mathcal{L} = -k_B \sum p_n \log p_n - \lambda_1 \left(\sum p_n E_n - U \right) - \lambda_2 \left(\sum n p_n - v \right) - \lambda_3 \left(\sum p_n - 1 \right)$$

$$\longrightarrow \frac{\partial \mathcal{L}}{\partial p_n} = 0.$$

extrem

$$\frac{d}{dp_n}\Big(-k_B \sum p_n \log p_n - \lambda_1 \left(\sum p_n E_n - U \right) - \lambda_2 \left(\sum n p_n - \cancel{v} \right) - \lambda_3 \left(\sum p_n - 1 \right) \Big) = 0$$

→ Note: all sums vanish.

$$\Rightarrow \frac{\partial \mathcal{L}}{\partial p_n} = -k_B \left(\log(p_n) + 1 \right) - \lambda_1 (E_n) - \lambda_2 (n) - \lambda_3 = 0.$$

→ Solve for $\log(p_n)$ ⇒ then for p_n

$$-k_B \log(p_n) = \frac{k_B + \lambda_1 E_n + \lambda_2 n + \lambda_3}{k_B}$$

$$\Rightarrow \log(p_n) = 1 - \frac{1}{k_B} \left(\lambda_1 E_n + \lambda_2 n + \lambda_3 \right)$$

$$P_n = e^{1-\frac{1}{k_B}(\lambda_1 E_n + \lambda_2 n + \lambda_3)} =$$

$\hookrightarrow$ compare with $p_n = \frac{1}{y} e^{-\beta(E_n - \mu n)}$

$$= e^{-\frac{1}{k_B}(\lambda_1 E_n + \lambda_2 n)} \cdot \underbrace{e^{-\frac{\lambda_3}{k_B}+1}}_{\text{all const}} \Rightarrow y' = \frac{1}{y}$$

$$P_n = e^{-\frac{1}{k_B}(\lambda_1 E_n + \lambda_2 n)} \cdot \frac{1}{y}$$

compare further (expand brackets):

$$\frac{1}{y} \cdot e^{\left(-\frac{\lambda_1 E_n}{k_B} - \frac{\lambda_2 n}{k_B}\right)} \quad \Big/ \quad \frac{1}{y} \cdot e^{\left(-\frac{E_n}{k_B T} + \frac{\mu n}{k_B T}\right)}$$

$$-\frac{\lambda_1}{\cancel{k_B}} = -\frac{1}{\cancel{k_B} T} \Rightarrow \lambda_1 = \frac{1}{T}$$

$$-\frac{\lambda_2}{\cancel{k_B}} = \frac{\mu}{\cancel{k_B} T} \Rightarrow \lambda_2 = -\frac{\mu}{T}$$

for this λ_1, λ_2:

$\Rightarrow p_n = \dots$

<u>Verify:</u>

$\Rightarrow$ ~~$P_n = \frac{1}{y} e^{-\beta}$~~

$$\Rightarrow P_n = \frac{1}{y} \cdot e^{\left(-\frac{E_n}{k_B} \cdot \frac{1}{T} + \frac{\mu}{T} \frac{n}{k_B}\right)}$$

$$= \frac{1}{y} \cdot e^{-\frac{1}{k_B T}(E_n - \mu n)}$$

$$= \frac{1}{y} \cdot e^{-\beta(E_n - \mu n)} \quad \square.$$

Q5. 1D lattice of N+1 atoms, each with spin $\sigma_i = \pm 1$, $i = 0, \dots, N$

$H(\{\sigma_i\}) = -J \sum_{i=1}^{N} \sigma_i \sigma_{i-1}$

a) Neighbouring spins can have same/diff signs ⇒ "↑↑" or "↑↓". ν: # of ↑↓ pair in $\{\sigma_i\}$. Express energy in terms of ν. Count no. of state with ν anti-∥ pair $W(E)$? for $\{\sigma_i\}$ having $H\{\sigma_i\} = E$?

→ ν: # anti-∥ pair, $H(\nu) = ?$, $W(\nu)$ = # of configs.

Def: $S_i = \sigma_i \sigma_{i-1}$ $\begin{cases} +1 & \text{for } \uparrow\uparrow \\ -1 & \text{for } \downarrow\uparrow / \uparrow\downarrow \text{ spins.} \end{cases}$

$$H = -J \sum_{i=1}^{N} S_i = -J(\# \uparrow\uparrow - \# \uparrow\downarrow) = -J((n-\nu) - \nu) = 2J\nu - Jn$$

$$\nu(E) = \frac{N}{2} + \frac{E}{2J}$$

# of config with ν anti-∥: $W(\nu) = 2 \dfrac{N!}{\nu(E)!(N-\nu(E))!} = 2 \dfrac{N!}{\left(\frac{N+E/J}{2}\right)! \left(\frac{N-E/J}{2}\right)!}$

b) Use a) to calc $Z(\beta) = \sum_{\{\sigma_i\}} e^{-\beta H(\{\sigma_i\})}$

$$Z = \sum_{\{\sigma_i\}} e^{-\beta H(\{\sigma_i\})} = \sum_{\nu=0} e^{-\beta(2J\nu - JN)}$$

→ Missing the no of config with a given, $\dfrac{2N!}{\nu!(N-\nu)!}$,

$$= \sum_{\nu=0}^{N} \frac{2N!}{\nu!(N-\nu)!} e^{-\beta(2J\nu - JN)} = 2e^{JN\beta} \sum_{\nu=0}^{N} \frac{N!}{\nu!(N-\nu)!} \left(e^{-2\beta J}\right)^{\nu}$$

$$= 2(e^{\beta J} + e^{-\beta J})^N = 2(2\cosh(\beta J))^N$$

c) Calc free energy F/N per spin & the entropy per spin in the can & mce for large N

$\dfrac{F}{N}$: $F = -\beta^{-1} \log Z$; $\dfrac{F}{N} = \dfrac{-\beta^{-1}}{N}[N \log(2\cosh \beta) + \log 2]$

$N \to \infty$: $\dfrac{F}{N} = -\beta^{-1} \log(2\cosh \beta J)$

S in Can. E. : $S = -\dfrac{\partial F}{\partial T} \Rightarrow \dfrac{S}{N} = -\dfrac{\partial (F/N)}{\partial T}$

$$= \frac{\partial}{\partial T}\left(k_B T \log\left(2\cosh \frac{J}{k_B T}\right)\right) = k_B \log\left(2\cosh \frac{J}{k_B T}\right) + k_B T \frac{1}{2\cosh J/k_B T} 2\sinh J/k_B T \left(\frac{-J}{k_B T^2}\right)$$

$$= k_B \left[\log(2\cosh J/k_B T) - \frac{J}{k_B T} \tanh\left(\frac{J}{k_B T}\right)\right]$$

$$S = -\frac{\partial F}{\partial T}(T, V, N)$$

→ M.C.E.

$$S = k_B \log \underbrace{W(E)}_{\text{\# of config for a given energy.}} = k_B \left[\log N! - \log \left(\frac{N + E/J}{2} \right)! - \log \left(\frac{N - E/J}{2} \right)! + \log 2 \right.$$

Stirling's formula.

$$= k_B \left[N(\ln(N) - \cancel{1}) - \left(\frac{N + E/J}{2} \right) \left(\ln \left(\frac{E/J + N}{2} \right) - \cancel{1} \right) - \left(\frac{N - E/J}{2} \right) \left(\ln \left(\frac{N - E/J}{2} \right) - \cancel{1} \right) \right]$$

$$+ O(\ln N)$$

$$\frac{S}{N} = k_B \left[\frac{1 + \varepsilon/J}{2} \ln \left(\frac{1 + \varepsilon/J}{2} \right) + \frac{1 - \varepsilon/J}{2} \ln \left(\frac{1 - \varepsilon/J}{2} \right) \right]$$

$\varepsilon := E/N$ → Energy per spin.

Q. Given → $\hat{H}|n_+,n_-\rangle = E_{n_+,n_-}|n_+,n_-\rangle$, $\hat{Q}|n_+,n_-\rangle = q(n_+-n_-)|n_+,n_-\rangle$ — (*)

$\rho = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}|n_+,n_-\rangle\langle n_+,n_-|$, $\mathrm{Tr}\,\rho = 1$

$\langle A\rangle = \mathrm{Tr}(A\rho) = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}\langle n_+,n_-|\hat{A}|n_+,n_-\rangle$, $S(\rho) = \cancel{-k_B \log\rho}$ $\neq$

$S(\rho) = -k_B\,\mathrm{Tr}(\log\rho) = -k_B \sum_{n_+,n_-\geq 0} p_{n_+,n_-}\log p_{n_+,n_-}$ [By defn]

From (*)
$$\begin{cases} E = \langle\hat{H}\rangle = \mathrm{Tr}(\rho\hat{H}) = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}\langle n_+,n_-|\hat{H}|n_+,n_-\rangle = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}E_{n_+,n_-} \\ Q = \langle\hat{Q}\rangle = \mathrm{Tr}(\rho\hat{Q}) = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}\langle n_+,n_-|\hat{Q}|n_+,n_-\rangle = \sum_{n_+,n_-\geq 0} p_{n_+,n_-}q_{n_+,n_-}(n_+-n_-) \end{cases}$$

a) Show density matrix that maxes $S(\rho)$ for fixed E, Q is $p_{n_+,n_-} = \frac{1}{Y}\exp\left(-\beta\left[E_{n_+,n_-} + \phi q(n_+-n_-)\right]\right)$
or $\rho = \frac{1}{Y}\exp[-\beta(\hat{H}+\phi\hat{Q})]$ $\beta, \phi, Y \Rightarrow$ Const.

→ Lagrange multiplier for $S(\rho)$ with 3 constraints: i) $\mathrm{Tr}(\hat{H}\rho) = E$ ii) $\mathrm{Tr}(\hat{Q}\rho) = Q$ iii) $\mathrm{Tr}\,\rho = 1$

So, ($S(\rho) = -k_B\mathrm{Tr}(\rho\log\rho)$)

$L = -k_B\mathrm{Tr}(\rho\log\rho) + \lambda_1(\mathrm{Tr}(\hat{H}\rho) - E) + \lambda_2(\mathrm{Tr}(\hat{Q}\rho) - Q) + \lambda_3(\mathrm{Tr}\,\rho - 1)$

→ $\lambda_1, \lambda_2, \lambda_3$ → Lagrange multipliers.

$= -k_B\sum p_{n_+,n_-}\log p_{n_+,n_-} + \lambda_1\left(\sum p_{n_+,n_-}E_{n_+,n_-} - E\right) + \lambda_2\left(\sum p_{n_+,n_-}q_{n_+,n_-}(n_+-n_-) - Q\right) + \lambda_3\left(\sum p_{n_+,n_-} - 1\right)$

[All sums over $n_+,n_-\geq 0$]

→ Take derivative of L ~~with~~ w.r.t p_{n_+,n_-} & equate to zero! [Note how the sums vanish]

$$\frac{\partial L}{\partial p_{n_+,n_-}} = -k_B\left(\cancel{p_{n_+,n_-}}\cdot\frac{1}{\cancel{p_{n_+,n_-}}} + \log p_{n_+,n_-}\right) + \lambda_1 E_{n_+,n_-} + \lambda_2 q_{n_+,n_-} + \lambda_3 = 0$$

$$\Rightarrow \log p_{n_+,n_-} = \frac{\lambda_1 E_{n_+,n_-} + \lambda_2 q_{n_+,n_-} + \lambda_3}{k_B} - 1$$

$$p_{n_+,n_-} = \exp\left[\frac{1}{k_B}(\lambda_1 E_{n_+,n_-} + \lambda_2 q_{n_+,n_-} + \lambda_3) - 1\right]$$

$$= \exp\left[\frac{1}{k_B}(\lambda_1 E_{n_+,n_-} + \lambda_2 q_{n_+,n_-})\right]\exp\left[\frac{\lambda_3}{k_B} - 1\right] = \frac{1}{Y}\exp\left[\frac{1}{k_B}(\lambda_1 E_{n_+,n_-} + \lambda_2 q_{n_+,n_-})\right]$$

when $Y = \exp\left[1 - \frac{\lambda_3}{k_B}\right]$ & if $\lambda_1 = -\frac{1}{T}$ & $\lambda_2 = -\frac{\phi}{T}$;

We can write,

$$p_{n_+,n_-} = \frac{1}{Y}\exp(-\beta[E_{n_+,n_-} + \phi q_{n_+,n_-}(n_+-n_-)])$$

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March 18 $\hat{H}, \hat{Q}$ 1/2

$$\rho = \sum_{n_+,n_- \geq 0} \rho_{n_+,n_-} |n_+,n_-\rangle\langle n_+,n_-|$$

$$= \sum_{n_+,n_- \geq 0} \frac{1}{Y} \exp\left(-\beta\left[E_{n_+,n_-} + \phi\, q_{n_+,n_-}(n_+ - n_-)\right]\right) \cdot |n_+,n_-\rangle\langle n_+,n_-|$$

$$= \frac{1}{Y} \exp\left(-\beta\left[\hat{H} + \phi\hat{Q}\right]\right) \quad [\text{By} \circledast]$$

b) Define $G = -k_B T \log Y(T,\phi)$, $\beta^{-1} = k_B T$. Using $Y = \mathrm{Tr}\exp\left[-(\hat{H} + \phi\hat{Q})/k_B T\right]$

Show $S = -\frac{\partial G}{\partial T}\Big|_\phi$ & $Q = -\frac{\partial G}{\partial \phi}\Big|_T$

→ $G = -k_B T \log Y(T,\phi)$, $Y = \mathrm{Tr}\left[\exp\left(\left[-\hat{H} + \phi\hat{Q}\right]/k_B T\right)\right]$

$S = -k_B \,\mathrm{tr}\,\rho \log\rho$, $\rho = \frac{1}{Y} e^{-\beta(\hat{H}+\phi\hat{Q})} \equiv \frac{1}{Y} e^{-\beta\hat{A}}$ — $\hat{A} = (\hat{H} + \phi\hat{Q})$

$\log\rho = \cancel{-k} - \log Y - \beta\hat{A}$

$\frac{\partial G}{\partial T} = -k_B \log Y - k_B T \frac{1}{Y}\frac{\partial Y}{\partial T}$, — $\circledast'$

Lets have a look at $S(\rho)$,

$$S = -k_B \mathrm{tr}\,\rho\log\rho = -k_B \mathrm{tr}\left[\left(\frac{1}{Y}e^{-\beta\hat{A}}\right)\log\left(\frac{1}{Y}e^{-\beta\hat{A}}\right)\right]$$

$$= -k_B \frac{1}{Y} \mathrm{Tr}\left[e^{-\beta A}\left(\log\frac{1}{Y} - \beta\hat{A}\right)\right]$$

$$= -k_B \frac{1}{Y}\left[\mathrm{Tr}\left(e^{-\beta\hat{A}} \log\frac{1}{Y}\right) - \cancel{\beta A}\, \mathrm{Tr}\left(e^{-\beta\hat{A}}\beta\hat{A}\right)\right]$$

$$= -k_B \frac{1}{Y}\left[\log\frac{1}{Y} \underbrace{\mathrm{Tr}\, e^{-\beta A}}_{=Y} - \beta\, \mathrm{Tr}\left(\hat{A} e^{-\beta\hat{A}}\right)\right]$$

$$= -k_B \frac{1}{Y}\left[Y \log\frac{1}{Y} - \cancel{\beta} \frac{1}{k_B T} \mathrm{Tr}\left(\hat{A} e^{-\beta\hat{A}}\right)\right]$$

$$= -k_B \log\frac{1}{Y} + \frac{1}{T}\mathrm{Tr}\left(\hat{A}e^{-\beta\hat{A}}\right) = k_B \log Y + \frac{1}{TY}\mathrm{Tr}\left(\hat{A} e^{-\beta\hat{A}}\right) \quad \cancel{\circledast}$$

~~Compare $\circledast$ & $\circledast'$,~~

$\cancel{\frac{\partial G}{\partial T} = -S \;\square}$

$\therefore \left[S = k_B \log Y + \frac{1}{TY}\mathrm{tr}\left(\hat{A}e^{-\beta\hat{A}}\right)\right] \to \circledast''$

→ Now lets ~~look at $\frac{\partial G}{\partial T}$,~~

$\cancel{\frac{\partial G}{\partial T} =}$

PTO.

Now lets look at $\frac{\partial G}{\partial T}$,

$$\frac{\partial G}{\partial T} = -k_B \log Y - \frac{k_B T}{Y}\underline{\underline{\frac{\partial Y}{\partial T}}}$$ — From ($*$)'

$$\rightarrow \frac{\partial Y}{\partial T} = \frac{\partial}{\partial T} tr(e^{-\beta A}) = tr\left(\frac{\partial}{\partial T} e^{-\beta \hat{A}}\right) = tr\left(\frac{\partial}{\partial T} e^{-\hat{A}/k_B T}\right)$$

$$= tr\left(\cancel{\frac{\partial}{\partial T}} e^{-\hat{A}/k_B T} \frac{\hat{A}}{k_B T^2}\right) = \frac{1}{k_B T^2} tr\left(\hat{A} e^{-\hat{A}/k_B T}\right) = \frac{1}{k_B T^2}\left(\hat{A} e^{-\beta \hat{A}}\right)$$

→ Plug in ($*$)'

$$\rightarrow \frac{\partial G}{\partial T} = -k_B \log Y - \frac{\cancel{k_B T}}{Y} \frac{1}{\cancel{k_B} T^{\cancel{2}}}\left(e^{-\hat{A}\beta} \hat{A}\right)$$

$$\Rightarrow \frac{\partial G}{\partial T} = \cancel{\log} -k_B \log Y - \frac{1}{TY} tr\left[\hat{A} e^{-\beta \hat{A}}\right]$$ — ($*$)'''

Compare ($*$)''' & ($*$)'', $\Rightarrow$ $S = -\frac{\partial G}{\partial T}$

Now for $\frac{\partial G}{\partial \phi}$,

$$\frac{\partial G}{\partial \phi} = \frac{\partial}{\partial \phi}\left(-k_B T \log Y(T,\phi)\right) = -k_B T \frac{1}{Y} \underline{\underline{\frac{\partial Y}{\partial \phi}}}$$

$$\frac{\partial Y}{\partial \phi} = \cancel{\frac{\partial}{\partial \phi} tr[\exp[\hat{A}+\phi\hat{Q})}\ \frac{\partial}{\partial \phi}\left(tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta}\right)\right)$$

$$= tr\left(\frac{\partial}{\partial \phi} e^{-[\hat{A}+\phi\hat{Q}]\beta}\right) = tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta} . (-1) . \hat{Q}\beta\right)$$

$$= -\beta\, tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta} \hat{Q}\right)$$

Plug in

$$\Rightarrow \frac{\partial G}{\partial \phi} = +k_B T \frac{1}{Y} \beta\, tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta} \hat{Q}\right) = \frac{tr}{Y}\left(e^{-[\hat{A}+\phi\hat{Q}]\beta} \hat{Q}\right)$$

We know, $\rho = \frac{1}{Y} tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta}\right)$ & $\langle\hat{Q}\rangle = tr\langle\rho\hat{Q}\rangle$

$$= \frac{1}{Y} tr\left(e^{-[\hat{A}+\phi\hat{Q}]\beta} \hat{Q}\right)$$

$\therefore \frac{\partial G}{\partial \phi} = Q.$

[right]

c) For a charged gas at fixed volume, 1^{st} law is $TdS = dE - \phi dQ$. What is meaning of Φ? Show that if we define $G = E - TS - \phi Q$, then $G = G(T, \phi)$ satisfies $dG = -SdT - Qd\Phi$.

→ 1^{st} law: $dE = TdS + \phi dQ$. ↳ ϕ → Electric potential.

$$G = E - TS - \phi Q,$$

$$dG = dE - TdS - SdT - \phi dQ - Qd\phi$$

$$= \cancel{TdS} - \cancel{TdS} + \cancel{\phi dQ} - SdT - \cancel{\phi dQ} - Qd\phi$$

$$= -SdT - Qd\phi. \quad \square$$

d) Verify relation in b) $S = -\frac{\partial G}{\partial T}\Big|_{\phi}$, $Q = -\frac{\partial G}{\partial \phi}\Big|_T$ ~~~~ using $dG = -SdT - Qd\phi$

We have, $G(T, \phi) \Rightarrow dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial \Phi} d\Phi$ &

$$dG = -S\,dT - Q\,d\phi$$

$$\therefore \frac{\partial G}{\partial T} = -S, \quad \frac{\partial G}{\partial \phi} = -Q.$$

Q1) Polymer $i = (0, 1, \ldots, N)$ pos $(x_i, y_i) \in \mathbb{Z}^2$. Atom at origin $x_0 = y_0 = 0$

other atom $x_i - x_{i-1} = 1$, $|y_i - y_{i-1}| = 1$

a) Determine no. of microstates

$\rightarrow$ 2^N (Yes/No chain of length N)

b) Determine no. of microstates having prop $y_N = y$

$$\sigma_i = y_i - y_{i-1} \Rightarrow Y_1 = \sigma_1, \; Y_2 = \sigma_1 + \sigma_2, \; Y_N = \sum_{n=0}^{N} \sigma_n = n_+ - n_-$$

$$\Rightarrow Y_N = 2n_+ - N \qquad \Rightarrow n_+ = \frac{Y_N + N}{2}$$

$$\Rightarrow \binom{N}{n_+} = \binom{N}{\frac{Y_N + N}{2}} = \cancel{W(Y)} \; W(n_+) \quad - \text{ \# microstates with } n_+ \text{ steps.}$$

c) Deflection at chain end $\langle Y_N^2 \rangle$

$$\langle Y_N^2 \rangle = \frac{\sum_Y Y^2 W(Y)}{\sum_Y W(Y)}, \qquad Z(\beta) = \sum_Y e^{\beta Y} W(Y)$$

$$Z''(\beta) = \sum_Y Y^2 e^{\beta Y} (W(Y))$$

$$\Rightarrow \frac{Z''(0)}{Z(0)} = \frac{\sum_Y Y^2 W(Y)}{\sum_Y W(Y)} = \underline{\langle Y_N^2 \rangle}$$

We need to find $Z''(0)$ & $Z(0)$.

$$2n_+ - N = n_+ - n_-$$

$$Z(\beta) = \sum_{n_+=0}^{N} e^{\beta(2n_+ - N)} \binom{N}{n_+}$$

$$= \sum_{n_+=0}^{N} (e^{\beta})^{n_+} (e^{-\beta})^{N-n_+} \binom{N}{n_+} \overset{\text{Binomial}}{=} (e^{\beta} + e^{-\beta})^N = 2^N \cosh^N(\beta)$$

$$Z'(\beta) = 2^N N \cosh^{N-1}(\beta) \sinh(\beta) \Rightarrow Z''(\beta) = 2^N N(N-1) \cosh^{N-2}(\beta) \sinh^2(\beta)$$
$$+ 2^N N \cosh^{N-1} \cosh(\beta)$$

$$\Rightarrow \langle Y_N^2 \rangle = \frac{\sum_Y Y^2 W(Y)}{\sum_Y W(Y)} = \frac{Z''(0)}{Z(0)} = \frac{2^N N}{2^N} = \underline{\underline{N}}.$$

BRUNNEN

Qs. 1-D Ising spin chain with periodic. B.C.

$\to n$ spins $\sigma_1, \dots, \sigma_n \in \{\pm 1\}$

$$H = -J(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \dots + \sigma_{n-1}\sigma_n + \sigma_n\sigma_1)$$

Probab dist^n: $p(\{\sigma_j\}) = \frac{1}{Z}\exp(-\beta H(\{\sigma_j\}))$

a) Draw a picture of the spin chain

$\to$ $H_{min} = -nJ$ $\quad \uparrow\uparrow\uparrow \dots \uparrow$ or $\downarrow\downarrow\downarrow \dots \downarrow$

$H_{max} = -J(-n) = nJ$ $\quad \uparrow\downarrow\uparrow\downarrow \dots \uparrow\downarrow$

} Periodic B.C

b) Show $Z = \sum_{\{\sigma_j\}} \exp(-\beta H(\{\sigma_j\}))$

$\to$ $\sum_i p(\{\sigma_i\}) = 1 \Rightarrow \sum_i p(\{\sigma_i\}) = \sum_i \frac{1}{Z}\exp(-\beta H(\{\sigma_i\}))$

$\therefore \quad 1 = \sum_i \frac{1}{Z} e^{-\beta H(\{\sigma_i\})} \Rightarrow 1 = \frac{1}{Z}\sum_i e^{-\beta H(\{\sigma_i\})}$

$\Rightarrow \quad Z = \sum_i e^{-\beta H(\{\sigma_i\})}$ $\square$

c) Show that Z can be written as: $Z = \sum_{\sigma_1=\pm1} \dots \sum_{\sigma_n=\pm1} T_{\sigma_1\sigma_2} T_{\sigma_2\sigma_3} \dots T_{\sigma_{n-1}\sigma_n} T_{\sigma_n\sigma_1}$

$= Tr(T^n)$

Where, $T_{\sigma\sigma'} = e^{\beta J\sigma\sigma'}$ or $T = \begin{bmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{bmatrix}$

$\to$ $Z = \sum_i e^{-\beta H(\{\sigma_i\})}$

Substituting $H = -J(\dots)$

$$= \sum_{\sigma_1=\pm1,\dots,\sigma_n=\pm1} e^{-\beta J \sum_{j=1} \sigma_j\sigma_{j+1}} = \sum \underbrace{\prod_{i=1}^{N} e^{\beta J\sigma_i\sigma_{i+1}}}$$

$$T_{\sigma_j\sigma_{j+1}} = \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix}$$

$$\begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix} = \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix},$$

We have,

$$|\sigma_j\rangle = \begin{cases} \begin{pmatrix}1\\0\end{pmatrix} & \text{if } \sigma_j = +1 \quad : |\uparrow\rangle \\ \begin{pmatrix}0\\1\end{pmatrix} & \text{if } \sigma_j = -1 \quad : |\downarrow\rangle \end{cases}$$

$$\sum_{\sigma_j=\pm1} |\sigma_j\rangle\langle\sigma_j| = \mathbb{1}$$

Ising

d) Diagonalize T & show it has eigenvalues
$\lambda_1 = 2\cosh(J\beta)$
$\lambda_2 = 2\sinh(J\beta)$ Use this and $Z = Tr(T^n)$
to show $Z = 2^n\left[(\cosh(\beta J))^n + (\sinh(\beta J))^n\right]$

→ Use everything in (c) &

$$\langle\sigma_j|T|\sigma_{j+1}\rangle = e^{\beta J \sigma_j \sigma_{j+1}} = T_{\sigma_j \sigma_{j+1}}$$

$$\Rightarrow Z = \sum_{\sigma_1=\pm1, \sigma_2=\pm1 \ldots} \langle\sigma_1|T|\underbrace{\sigma_2\rangle\langle\sigma_2}_{=1}|T|\underbrace{\sigma_3\rangle \ldots}_{=1} \langle\sigma_N|T|\sigma_1\rangle$$

$$= \sum_{\sigma_1=\pm1} \langle\sigma_1|T^n|\sigma_1\rangle = \underline{\underline{Tr(T^n)}}$$

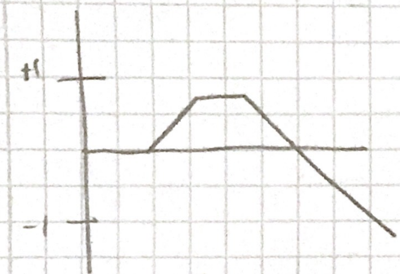
$$T = UDU^\dagger, \quad UU^\dagger = \mathbb{1}, \quad D = \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix}$$

$$\Rightarrow Tr(T^n) = Tr(UD\underbrace{U^\dagger U}_{\mathbb{1}}D\underbrace{U^\dagger \ldots}_{\mathbb{1}} UDU^\dagger)$$ → Unit matrix

$$= tr(UD^nU^\dagger) = tr(U^\dagger UD^n) = tr(D^n)$$

$$= \lambda_1^n + \lambda_2^n = 2^n\cosh^n(\beta J) + 2^n\sinh^n(\beta J)$$

$$= \cancel{2^n[\cosh^n(\beta J)}\ 2^n\left[(\cosh(\beta J))^n + (\sinh(\beta J))^n\right]$$



$x_i - x_{i-1} = 1$ & $x_0 = 0$

$\Rightarrow x_1 = 1,\ x_2 = 2$

$y_i - y_{i-1} \in \{0, 1, -1\}$ & $y_0 = 0$.

$y_1 = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$ if $y_1 = 1 \to y_2 = \begin{cases} 2 \\ 1 \\ 0 \end{cases}$

$y_1 = 0 \to y_2 = \begin{cases} 1 \\ 0 \\ -1 \end{cases}$

$y_1 = -1 \to y_2 = \begin{cases} 0 \\ -1 \\ -2 \end{cases}$

We have 3^N config but as x_0, y_0 is fixed $\#$ configs $= W = 3^{N-1}$

What is Y_N?

Let $N_+ = \#$ (+ deflections) & $N_- = \#$ (− deflections) & $N_0 = \#$ (0 deflections)

Deflections are present at 0 & $N = N_+ + N_- + N_0$

For our config $N_+ = 1$

$N_- = 3$

$N_0 = 1$

Let $Y_N = N_+ - N_-$, then $Y_N = -2$ for our config.

We want $\langle e^{-\beta Y_N} \rangle$

$$\langle e^{-\beta Y_N} \rangle = \frac{1}{3^{N-1}} \sum_{\substack{N_+ + N_- + N_0 \\ = N}} \frac{N!}{(N_+! N_-! N_0!)} \underbrace{e^{-\beta (N_+ - N_-)}}_{e^{-\beta N_+} e^{\beta N_-} (1)^{N_0}}$$

$$\left[\text{Trinomial} \quad (a+b+c)^n = \sum_{\substack{i,j,k \\ n = i+j+k}} \frac{n!}{i!\, j!\, k!} a^i b^j c^k \right]$$

$$\langle e^{-\beta Y_N} \rangle = \frac{1}{3^{N-1}} \left(e^{-\beta} + e^{\beta} + 1 \right)^N$$

$$\langle Y_N^2 \rangle = \frac{1}{3^{N-1}} \sum \frac{N!}{N_+! N_0! N_-!} Y_N^2 = \frac{d^2}{d\beta^2} \langle e^{-\beta Y_N} \rangle \Big|_{\beta = 0} = 2N$$

$$\& \quad \frac{d^2}{d\beta^2} \langle e^{-\beta Y_N} \rangle = \sum \frac{N!}{N_+!\, N_-! N_0!} Y_N^2 e^{-\beta Y_N}$$

Send $\beta \to 0$ to get wanted exp.