

Thermodynamics:

0th: \sim denotes thermal eq. Then $T_1 \sim T_2, T_2 \sim T_3 \Rightarrow T_1 \sim T_3$.
 1st: $E = \text{const.}$ for an isolated system. $dE = dQ + dW$
 2nd: A process whose sole effect is the transfer of E from cold to hot (heat flows $T_1 \to T_2$). $dS = dQ/T$.

3rd: As $T \rightarrow 0K$, the entropy approaches an absolute minimum. Absolute 0 is not possible. $\Rightarrow \eta_c < 1$.

Fundamental relation: $E = E(S, V, N)$. Rewrite for $S = S(E, V, N)$.

$$dE = TdS - PdV + \mu dN, \quad dS = \frac{1}{T}(dE + PdV - \mu dN)$$

- Can use this to get Maxwell relations. Ex:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V, N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S, N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S, V}$$

Ideal gases: $PV = Nk_B T = nRT$

$$E = \frac{1}{g-1} Nk_B T \text{ only depends on } T$$

$$C_p = Cv + Nk_B, \quad Cv = \frac{1}{g-1} Nk_B$$

$$\text{Mono: } \gamma = 5/3, \text{ Dia: } \gamma = \frac{7}{5} \text{ or } \frac{9}{4}$$

$$\gamma = 1 + \frac{2}{f}, f = \# \text{ of DeF. } n = N/V$$

- Entropy: To derive, integrate along coordinate

$$S(T, V, N) = \alpha_0 Nk_B + Nk_B \frac{f}{2} \ln \left[\frac{T}{n^{g-1}} \right]$$

- Usually set $\alpha_0 = 0$. Thermocarnt derive Φ_0 .

Thermodynamic potentials: Energies minimized, entropies max

Potential Differential Natural vars Name

$$E = dE = TdS - PdV + \mu dN$$

$$F = E - TS = -SdT - PdV + \mu dN$$

$$H = E + PV = TdS + VdP + \mu dN$$

$$G = E - TS + PV = -SdT + VdP + \mu dN$$

$$\Psi = F - TS - MN \quad d\Psi = -SdT - PdV - N\mu dN$$

Maxwell relations: fixed N | Inverting Legendre transforms:

$$\left(\frac{\partial T}{\partial S}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_S \quad (\text{E})$$

for all. Given $E = F + TS$, and

$$\left(\frac{\partial T}{\partial S}\right)_N = -\left(\frac{\partial F}{\partial S}\right)_V, \quad S = -(dF/dT)_V, \text{ so have:}$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \left(\frac{\partial V}{\partial P}\right)_S \quad (\text{H})$$

$$E = F - T\left(\frac{\partial T}{\partial S}\right)_P \Rightarrow E = -T^2 \frac{\partial (E/P)}{\partial (T/V)}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \quad (\text{F})$$

This gives you $E(T, V, N)$.

Note:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad (\text{G})$$

Rln w/ how C_v changes:

To get this, use:

$$\left(\frac{\partial C_V}{\partial T}\right)_N = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

(use $dE = 0 = dQ + dW$ and a Maxwell)

Heat engines: Cyclic \rightarrow returns to orig. state, $\Delta E = 0, Q_H = W + Q_L$

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

$$\eta_c = 1 - \frac{T_L}{T_H} \quad \text{Clausius} \quad \oint dQ = 0$$

$$W = Q = \oint PdV = \oint TdS$$

\therefore iff system reversible

Inexact differentials: Depend on path, $\oint dS$ not necessarily 0.

$$dF = \mu dT, \mu = \text{integrating factor}$$

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}$$

$$C_V = \left(\frac{\partial F}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial F}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

Heat capacity: $C_V = (dQ/dT)_V, \quad C_P = C_V + \frac{L}{\text{mole}}$

$$C_V = \left(\frac{\partial F}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial F}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

Adiabatic constant: $C_V = C_P / \gamma$

$$\gamma = \frac{1}{V} \left(\frac{\partial P}{\partial V}\right)_T, \quad K_T = \frac{1}{V} \left(\frac{\partial P}{\partial V}\right)_T, \quad K_S = -\frac{1}{V} \left(\frac{\partial P}{\partial S}\right)_T$$

\uparrow expansivity, \uparrow isothermal compressibility

Euler's Homogeneous function: S pure + w

$$f(\lambda x) = \lambda^n f(x) \text{ for } \lambda > 0, n = 0 \text{ intensive, } n = 1 \text{ extensive. Then:}$$

$$x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} = nf.$$

- Means extensive vars scale w/ each other, ie. S ext., so $S(E, V, N) = E \delta S / \delta E + \dots + N \delta S / \delta N$

- Usually set $\alpha_0 = 0$. Thermocarnt derive Φ_0 .

Legendre Transforms: $f(x, y, z)$, let $a = (df/dx)y, z$

$$so df = adx + bdy + cdz. \text{ Then let:}$$

$$L(a, y, z) = f - a \cdot x, \text{ so } dL = -xdx + bdy + cdz$$

- Swaps the role of x and a , but derivatives the same.

Gibbs-Helmholtz mns: \uparrow swaps convexity of f .

$$f = -a^2 \frac{\partial}{\partial a} \left(\frac{L}{a} \right), \quad L = -x^2 \frac{\partial}{\partial x} \left(\frac{f}{x} \right)$$

- Inverse: Given L , how to get f ? Can use L , also.

$$f = L + ax = L - a \frac{\partial L}{\partial a} \text{ as } x = -\left(\frac{\partial L}{\partial a}\right)_{y, z}$$

Ex: $f(x) = e^x$. Then $a = f'(x) = e^x, x = \ln(a)$, so

$$L = f - a \cdot x = e^x(1-x) \Rightarrow L = a(1 - \ln(a)).$$

To derive Maxwell mns, equate mixed partials. Ex:

$$\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T, \quad \left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial V}\right)_P$$

why can't we Legendre transform $G(T, P, N)$ all 3 variables? If $\Gamma = E - TS + PV$ and 4 (T, V, μ) are extensive, but only

\downarrow $A = E - TS + PV - \mu N$, $\Delta A = 0$ then $\Gamma = \Gamma(T, P, \mu)$, but T, P, μ are intensive: you can't invert!

\downarrow $G = f(T, P, N) - g(T, \mu, V)$, so must be extensive.

Gibbs-Duhem relation: \downarrow $f = (dG/dV)_T = \mu$ and $g = (dG/d\mu)_V = -PV$

Physical free energies are the convex hulls of given free energies during phase transitions.

Heat engines on PV diagrams run clockwise.

VanderWaals gas:

$$(P + \frac{N^2}{V^2})(V - Nb) = Nk_B T$$

$$E_{\text{mono}} = \frac{3}{5} Nk_B T - aN^2/V$$

Some relations you can get: To derive: $dE = (\partial E/\partial T)_V dT +$

$$\left(\frac{\partial E}{\partial V}\right)_T dV = -(\partial E/\partial V)_T dV + P dV = TdS - PdV,$$

so $\Delta S = \text{const.}$, divide by dV .

$$\left(\frac{\partial P}{\partial V}\right)_T = -C_P \left(\frac{\partial T}{\partial V}\right)_P, \quad C_V \left(\frac{\partial T}{\partial P}\right)_V$$

then factor out $(\partial T/\partial V)_P$ to get C_P .

$$\left(\frac{\partial P}{\partial V}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Use cyclic rule

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

Plug in defn and use previous 2 eqns.

$$K_S / K_T = C_V / C_P = 1/\gamma$$

This gives: $\left(\frac{\partial C_V}{\partial T}\right)_P = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$

Equal size blocks of undeteriorated, $T_1 \leq T_2$, $C_V(T) = \alpha T^2$. First assume infinite heat sources.

a) Equilibrium temp: ΔQ is the same, and $\Delta Q = C_V \Delta T$, so:

$$\Delta Q = \int_{T_1}^{T_2} C_V dT = \int_{T_1}^{T_2} C_V dT \Rightarrow T_F = \left(\frac{T_1 + T_2}{2} \right)^{1/4}$$

Alternatively, $E_F = \frac{1}{4} \alpha (T_1^4 + T_2^4)$, $E_F = \frac{1}{4} 2\alpha T_F^4$.

c) Find ΔS . Have: $dS = dQ/T = C_V dT/T$:

$$\Delta S = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C_V dT}{T} = \int_{T_1}^{T_2} \frac{\alpha T^2 dT}{T} = \Delta S_2 = \int_{T_1}^{T_2} \alpha T^2 dT$$

d) Suppose finite heat reservoirs. How much W can be extracted? Have:

$$\textcircled{1} \quad dW = \eta dQ_H \Rightarrow \frac{dQ_H}{dQ_L} = \frac{T_H}{T_L} \quad \text{Now } T_L, T_H \text{ will vary. Use}$$

$$\textcircled{2} \quad \textcircled{3} \quad \textcircled{4} \quad \textcircled{5}: \quad -T_H^2 dT_H = T_L^2 dT_L \Rightarrow T_L(T_H)$$

$$= \sqrt[3]{C - T_H^3}. \text{ To find } C, \text{ use }$$

To find T_F , know $T_L(T_F) = T_F$. Then get:

$$T_L(T_H = T_2) = T_1. \text{ Then get:}$$

$$T_L(T_H) = \sqrt[3]{T_1^3 + T_2^3 - T_H^3}$$

Finally to get W , can use:

$$W = \int dW = \int \eta dQ_H = \int_{T_2}^{T_F} \left(1 - \frac{T_L}{T_H} \right) dT_H^2 dT_H$$

$$= \frac{\alpha}{4} \left[T_H^4 + T_2^4 - 2 \left(\frac{T_1^3 + T_2^3}{2} \right)^{4/3} \right]$$

Easier way: $\Delta S_1 + \Delta S_2 = \Delta S = 0$ bc reversible, gives you T_F .

Then $\Delta Q = Q_1 + Q_2 = \int_{T_1}^{T_F} \alpha T^3 dT + \int_{T_2}^{T_F} \alpha T^3 dT$, and

$W = -\Delta Q$. Will get same answer

Ref problem: Want to find ΔE of something held at constant T w/ $\Delta V \neq 0$.

$dE = TdS - fV \delta P/dV$, want to find $(\partial E/\partial V)_T$.

Since we want $\delta P/\delta V \neq 0$, want to get $E(T, V)$. So

use $F = E - TS$. Then $(\partial E/\partial V)_T = (\partial F/\partial V)_T + T =$

$(\partial S/\partial V)_T + T$. But $\partial F = -SdT - fV \delta P/dV$, so $(\partial F/\partial V)_T =$

$-fV$. Then to get $(\partial S/\partial V)_T$, use a Maxwell reln:

$$\frac{\partial E}{\partial T} = -\left(\frac{\partial S}{\partial T}\right)_V = -fV \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = fV \left(\frac{\partial P}{\partial T}\right)_V$$

So we know to use F here bc we have $(\partial / \partial V)_T$.

Problem: Given C_p , C_p doesn't vary w/ temp. Find ΔG in

terms of S_0, T_0, C_p , and T for isobaric expansion.

Have $C_p = (\partial H/\partial T)_P$, and $H = G + TS$ so $C_p = (\partial G/\partial T)_P$

$$+ (\partial (TS)/\partial T)_P \Rightarrow \Delta G = \int dT (\partial G/\partial T)_P = C_p \Delta T - \int \frac{dS}{T} \Delta T = \int \frac{C_p}{T} dT$$

Integrate $\int \frac{dS}{T} (\partial S/\partial T) dT$ by parts to kill the $\int dS$, and get

$$\Delta G = C_p \Delta T + S_0 T_0 - ST$$

To find S_0 , $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$, and

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_P \Rightarrow dS = \frac{C_p}{T} dT \Rightarrow S = S_0 + C_p \ln(T/T_0)$$

Then:

$$\Delta G = (C_p - S_0) \Delta T - C_p T \ln(T/T_0)$$

Anytime you have multiple heat sources and different ways to run a combination of reversible engines, they necessarily must have the same efficiency, or else you could use the work from the more efficient one to run the other one backward and

Note for parts $a-c$, $\Delta S > 0$ and when will $U(T, V, N)$ be minimized? When

it is not reversible, To show $U(T, V, N) = -PV$ $dU = 0$, and $dU = -SdT - PdV - Ndu$,

This is b/c it is spontaneous heat flow, whereas $dU = \lambda dT + \lambda dV - \lambda du$, so when T, V, u are constant,

then $U(T, V, u) = \lambda T$. To show $F(T, V, N)$ is extensive, show that

$dU(T, V, N) = \lambda T$, so take a derivative:

$$\frac{\partial U}{\partial V} = \frac{\partial T}{\partial (V)} = \frac{\partial T}{\partial (N)} = \frac{\partial F}{\partial (V)}$$

Gibbs free energy of an ideal gas w/

$$\Rightarrow V \left(\frac{\partial U}{\partial V}\right)_T = T \text{ (at } \lambda = 1\text{)}$$

given. Have $E = \frac{1}{8} Nk_B T$, so $H = E + PV$ use $P = -(\partial F/\partial V)_{T,N}$. To find $E(T, V, N)$,

and write $H = H(T, P, N)$. Then do $G = H - TS$ For a non-ideal gas, isotherm does not

necessarily imply $dE = 0$; E could be a fn of V .

Free expansion: $dF = 0$, $dU = 0$, $dW = 0$, but

Derive S for ideal gas. Use $S(T, P, N)$: Maxwell reln $\frac{\partial S}{\partial T} = \frac{\partial F}{\partial P}$, $\frac{\partial S}{\partial P} = \frac{\partial F}{\partial T}$, $\frac{\partial S}{\partial N} = \frac{\partial F}{\partial V}$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial N}\right)_V dN = \frac{1}{T} C_p dT - \left(\frac{\partial F}{\partial P}\right)_T dP - \frac{1}{N} dN$$

$\Rightarrow S(T, P, N) = C_p \ln T - Nk_B \ln P - f(N) = Nk_B \ln \left[\frac{T}{P} \right] - \frac{f(N)}{P}$ don't know μ Gibbs-Helm.

Another way: $\frac{\partial Q}{\partial T} = dS = \frac{dE}{dT} + \frac{PdV}{dT}$. Derive $\left(\frac{\partial E}{\partial T}\right)_{P,V} = T \left(\frac{\partial P}{\partial T}\right)_{V,N} - P$ rln between G and H :

$$\text{Use } dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV, \text{ so you get } W = F(T, V, N). \text{ Use:}$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \frac{1}{T} (P + \left(\frac{\partial P}{\partial V}\right)_T) dV \quad \left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial F}{\partial V}\right)_T + \left(\frac{\partial V}{\partial T}\right)_{P,N} \quad \left(\frac{\partial H}{\partial T}\right)_P = V - T \left(\frac{\partial V}{\partial T}\right)_P$$

$$= \frac{1}{T} C_p dT + Nk_B \frac{dV}{V} \Rightarrow S = C_p \ln T + Nk_B \ln V$$

+ So, but need S to be extensive, so $= P + T \left(\frac{\partial P}{\partial V}\right)_T \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T$ (maxwell)

plug in and introduce $f(N)$ $\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T$ w/ $G = H - TS$

Clausius inequality: Note reversible engines have $Q_L/Q_H = T_L/T_H$

$$\text{Given } F(T, V, N) = 3Nk_B T \ln \left[\frac{P \cdot b}{T} \right] \quad \delta Q \leq 0$$

$$E = -T^2 \left(\frac{\partial F}{\partial T} \right)_V = +T^2 3Nk_B \frac{2}{T} \ln T$$

$= 3Nk_B T$ (note ln(...)) derive are easy!

Now to express $E(T, V, N)$ as $E(S, V, N)$: so $1Q_H/V_T = -1Q_L/V_T \leq 0$

Solve for $T(S, V, N)$ by inverting $S(T, V, N)$ w/ equality iff reversible.

Maximize $S = \min E$. If S was max and E not min,

could extract W and add it back in a heat engine, returning the system to its original energy.

Then S is maximal, so

$$dS = \left(\frac{\partial S}{\partial E}\right)_T dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$= 0$, but $dE = -dE_2$

$$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_T = \left(\frac{\partial S}{\partial E_2}\right)_T$$

$\Rightarrow 1/T_1 \geq 1/T_2 \Rightarrow T_1 \leq T_2$

Carries the same w/ P ,

$1/V_1 \geq 1/V_2 \Rightarrow V_1 \leq V_2$ when entropy is extermized.



ΔQ

ΔS

ΔS_2

ΔT

ΔT_2

ΔT_1

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Problems: 1D Ising model; $L=0$. Then

$$\chi = -J \sum_{j=1}^N \sigma_j \sigma_{j+1}, \text{ so } \chi = -\frac{1}{2} m \Omega^2 r^2 \text{ so } \mu_j = k_B T \ln(n_j/n)$$

$\chi = \sum_{i,j=1}^N \sigma_i \sigma_j \sum_{n=1}^{\infty} e^{-\beta E_n}$, $\sum_{n=1}^{\infty} e^{-\beta E_n} = \text{const.}$ Solve for $n(r)$, then set

$$\sum_{n=1}^{\infty} e^{-\beta E_n} = 2 \cosh(\beta J \omega_{n-1}) = 2 \cosh(\beta J) \quad n(r) = N \left[\frac{m \Omega^2 r^2}{2 \pi L} \exp(-\beta m \Omega^2 r^2) \right]$$

Likewise, get $\chi = (2 \cosh(\beta J))^N - 1$. For $N \gg 1$, fraction of N particles are of species 1

$$F = -\frac{1}{2} \ln \chi = -N k_B T \ln(2 \cosh(\beta J))$$

Greenhouse temp. of Earth:

$$P_{\text{out}} = 4\pi R_s^2 \sigma_0 \epsilon T_s^4 \quad P_{\text{in}} = \sigma \cdot F_{\text{out}} \cdot \frac{T_s^4}{4\pi R_s^2} = 4\pi R_s^2 \sigma T^4$$

$$R_s \epsilon = 1, R_s \epsilon_{\text{Earth}} = T^4 = \frac{1}{4} (R_s)^2 T_s^4 \quad J_o = \sigma (T_s^4 - (1-r)T^4)$$

$$\text{black} \rightarrow \text{reflected} \rightarrow \text{emitted} \rightarrow \text{reflectivity} r$$

$$\text{For } j, j+1 \text{ need to sum a series, } \sum_{n=1}^{\infty} \sigma_{n-1} \sigma_j = \frac{1}{4\pi r}$$

$$J_j^{(1)} = \sigma \{ T_j^4 - r T_j^4 + r T_{j+1}^4 \} = \sigma T_{j+1}^4 (1-r)$$

$$J_j^{(2)} = \sigma \{ -T_{j+1}^4 + r T_{j+1}^4 - r T_j^4 + r T_{j+2}^4 \} = -\sigma T_{j+2}^4 (1-r)$$

$$\text{New we need } J_j = \frac{1}{r+1} \sigma (1-r) (T_j^4 - T_{j+1}^4)$$

$$\text{we need } J_j = k_B T \text{ for steady state. So add them: } \sigma T^4$$

$$E = 2E_1 + 2E_2 + 2E_3 + 2E_4 \quad \text{FD dist} \bar{n} = \frac{\partial E}{\partial T}$$

$$\text{Ex: BE @ } 4E, \text{ can have } (1,3), (2,2) \text{ etc. But } J = \sigma (1-r) (T_s^4 - T^4) = \sigma (1-r) (T_s^4 - T^4), \text{ so plugin}$$

$$(1,1), (1,2), (2,2). \text{ Note } (1,3) = (3,1), \text{ for } T_s^4, T^4 \text{ to get } J = \frac{5}{2}(1-r)(T_s^4 - T^4)$$

$$(1,2) = (2,1), \text{ so we have 2 less than classical FD @ } 4E, \text{ like BE, but } (1,1), (2,2) \text{ not allowed. FD @ } 2E \text{ is easier b/c you don't forget polarizations}$$

$$\text{BE condensate: } N \text{ atoms, spin } 0. \text{ Let } T < T_c. \text{ In } N \text{ spin } 1/2 \text{ atoms in fd}$$

$$\beta \mu \sim 0, \text{ so } E = \int_0^{\infty} \epsilon dE \cdot D(E) = \frac{m^3 \epsilon^3 V}{2 \pi k^3} \int_0^{\infty} \epsilon^{3/2} dE$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V \text{ where in fd state have } \epsilon = 0, \text{ so don't count}$$

$$dS = \frac{C_v dT}{T} \Rightarrow S = S_0 + \int_0^T C_v dT \text{ Note atoms in fd state act like they aren't there!}$$

$$\text{Calculate } H_c(T) \text{ for } H_2 \rightleftharpoons 2H$$

$$V_H = 2, V_{H_2} = 1. H_2 \text{ has } Z_H = 2, Z_{H_2} = 1, N_2 O_4 \rightleftharpoons 2NO_2. \text{ Calculate fraction of dissociated } NO_2,$$

$$\text{has } Z_{NO_2} = 1 \text{ (R=rotation, V=vib). treat classically, so already have calculated } Z_{NO_2}$$

$$\text{Then fd } f_k = n_k(T) \frac{Z_k}{Z_{NO_2}} \quad K_c(T) = \frac{n_c(T) m_H}{(n_H(T) 2m_H) \frac{Z_H}{Z_{NO_2}}}$$

$$\text{Given latent heat } L_{\text{vap}}, L_{\text{fusion}} \text{ @ triple point, how to find } L_{\text{sublim}}? \quad Z = \sum_{k=1}^{\infty} e^{-\beta c(n_k^2 + n_k^2)/L}$$

$$\text{Need } L_{\text{sublim}} = L_{\text{vap}} + L_{\text{fusion}} \text{ b/c if not, could go solid } \rightarrow \text{gas } \rightarrow \text{liquid!}$$

$$\text{and generate energy } = \text{polar.} = k_B T \ln(N/n_A) \quad \text{BE gas, } N \text{ spin } 0 \text{ atoms, twice as many particles}$$

$$3D \text{ box w/ 2D surface atoms can bond to } 1 \text{ O state as } 1 \text{ state. Find } T_c. N_H = 2N_p$$

$$\frac{N_H}{V} = \frac{P}{k_B T} \Rightarrow V = \frac{k_B T}{P} \text{ so } L \sim V^{\frac{1}{2}} = \left(\frac{k_B T}{P} \right)^{\frac{1}{2}}$$

$$\text{Calculate } \mu_2 \text{ on the 2D wall. Diffusive eqn, so } \mu_2 = \mu_{\text{gas}}. Z_g = Z_g^{\text{int}} V^{\frac{1}{2}} \text{ b/c } Z_g^{\text{int}} = \frac{1}{N} \text{ ideal gas}$$

$$Z_g = \frac{1}{N} \left(\frac{2\pi m}{\lambda k_B T} \right)^{\frac{1}{2}}. \text{ Plug in for } F, \mu = \partial F / \partial N, \text{ so } \mu_2 = k_B T \ln \left[\frac{1}{N_2} \left(\frac{2\pi m}{\lambda k_B T} \right)^{\frac{1}{2}} \right] + \epsilon = \mu_2$$

$$\mu_2 = \mu_{\text{gas}} + k_B T \ln \left[\frac{1}{N_2} \left(\frac{2\pi m}{\lambda k_B T} \right)^{\frac{1}{2}} \right]. \text{ Can get another expr. for } \mu_2 \text{ by considering it as a 2D ideal gas w/ binding energy.}$$

$$\mu_2 = k_B T \ln \left[\frac{1}{N_2} \left(\frac{2\pi m}{\lambda k_B T} \right)^{\frac{1}{2}} \right] - \epsilon = \mu_2$$

$$\text{Partition function: Let } -\eta N = V_0 + \frac{1}{2} \sum_{k=1}^{\infty} = D(E) SE, \text{ so } S = k_B \ln W$$

$$\ln Z \sim BN^2 - \int_0^{\infty} dw g(\omega) \ln(1 - e^{-\beta \omega})$$

$$S = k_B \ln(D(E) SE)$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right) = k_B \frac{D'(E) SE}{D(E) SE} = k_B \frac{D'(E)}{D(E)}$$

$$\text{constant}$$

$$\text{1st order: } \frac{\partial S}{\partial E} \text{ is } \frac{\partial^2 F}{\partial T^2} \text{ not smooth.}$$

$$\text{2nd order: Jump in 2nd derivative of } S$$

$$\text{Lower } T \text{ stable, } m=0 \text{ or } m=1$$

$$\text{Higher } T \text{ unstable, } m=0 \text{ or } m=1$$

$$\text{Latent heat } L = T_{\text{cav}} \Delta S, \text{ to get } \Delta S, \text{ use } S = -\frac{\partial F}{\partial T}$$

$$\text{Find } \frac{\partial F}{\partial T} @ m=0 \text{ and the next minimum.}$$

$$\text{Change in } m \text{ is smooth.}$$

$$\text{No longer a discontinuity in } m. \text{ In first order, } m \text{ abruptly changes from new}$$

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