IN-CLASS NOTES JAN 23, 2023

(1)

GOAL!

$$S(E,N,V) = k_B \ln \Omega(E,V,N)$$

1) Fundamental thermodyn. reln: (*) is always valid

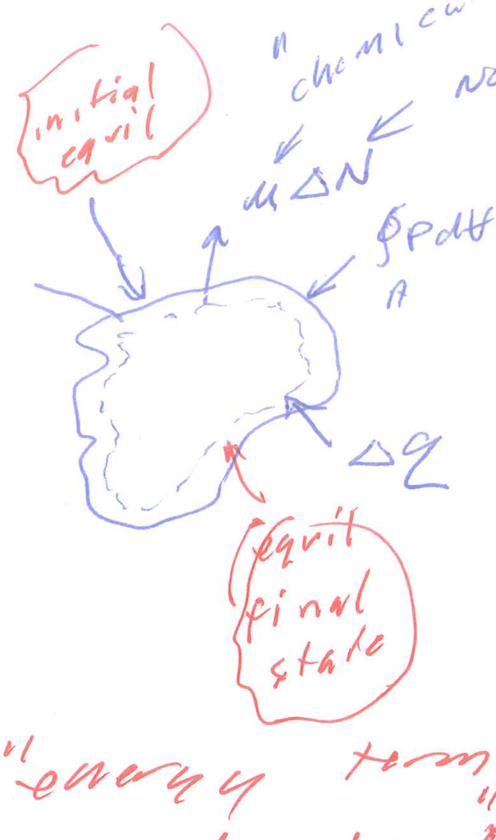
$$\boxed{dE = T\,dS - \underbrace{p\,dV}_{\text{diff'tl compn or expn}} + \underbrace{\mu\,dN}_{\text{loss of energy due to evaporation}}} \quad (1)$$

dE: Δ in internal energy

"chemical pot" = energy per ptcl

no of ptcls leaving over Δt

Fluid ptcl @ t



{ Δt = time increment }

A) "energy terms" (1) must correspond to "ex. terms" in 1st LAW:

$\Delta E \left(= E_{final} - E_{initial}\right) - P\Delta V$ (2)

$= \Delta Q - \oint_{A_{surf}} P\Delta V - \mu \Delta N$ (2)

FR

THIS GUY ALSO TRUE

$\therefore$ since (1) & (2) must both be true !

NOT TRUE

(+) $\boxed{\Delta Q \overset{~~must~~}{=} T\Delta S}$ (over dt)

(+) ~~This~~ this can't ~~be~~ in gen'l true

(+) (2) missing something ~~Frictional~~ heat

(3)

SO TdS term in (1)

1) subsumes & captures

& bypasses all irreversible

(small thermo)

(diff'l) processes that occur

during any/all

diff'l equil thermo processes

more ex. diffl thermo relationships

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1) (V.2) : Fund thermo Relationship

exact → $$\boxed{dS = \left(\frac{1}{T}\right) dE + \left(\frac{P}{T}\right) dV - \left(\frac{\mu}{T}\right) dN}$$ (1')

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} \qquad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} \qquad \frac{\mu}{T} = \left.\frac{\partial S}{\partial N}\right|_{V,E}$$

2) (1) or (1') apparently apply to small Δ's / diffl thermo processes that occur about some equil. state:

3) 2) since S is a "state thermo function" ⇒

(+) point fns ⟺ value of S, H, U, etc only depends on location in state

(+) Δ in thermo props path indep

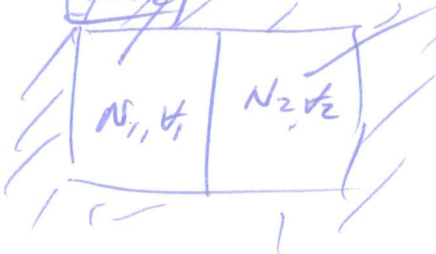
(+) mathly dS, dU etc are exact diffls

In our current problem: we want to calculate

$\boxed{\Delta S_1}$ & $\boxed{\partial S_2}$ due a fl'xn, $\boxed{\partial E_1}$

$\boxed{\Delta S_1} = \boxed{dS_1}$ $\qquad$ $\boxed{\partial S_2} = \boxed{dS_2}$

sys 1 $\qquad$ sys 2



When sys. (1) & sys (2) are in equil.

From (i')

1) $$dS_1 = \left.\frac{\partial S_1}{\partial E_1}\right|_{N_1,V_1} \cancel{\partial E_1}\, dE_1$$

$$dS_2 = \left.\frac{\partial S_2}{\partial E_2}\right|_{N_2,V_2} \cancel{\partial E_2}\, dE_2 \qquad (3)$$

2) $\therefore$ $$\frac{dS_1}{dE_1} = \left.\cancel{\frac{\partial S_1}{\partial E_1}}\right|_{N_1,V_1} \left(\frac{1}{T_1}\right) \qquad \text{@ equil'l}$$

$$\frac{dS_2}{dE_2} = \left.\cancel{\frac{\partial S_2}{\partial E_2}}\right|_{N_2,V_2} \left(1/T_2\right) \qquad (3a) \qquad ''$$

3) From last time

(@ equil) i

tables

a) $\boxed{\left(\frac{d\ln\Omega_1}{dE_1}\right) = \beta_1}$

b) $\boxed{\left(\frac{d\ln\Omega_2}{dE_2}\right) = \beta_2}$ (4)

b) @ equil, i

$$\frac{d\ln\Omega_1}{dE_1} = \frac{d\ln\Omega_2}{dE_2}$$

(5) or $\boxed{\beta_1 = \beta_2}$ @ equil

4) collecting results

$$\frac{dS_1/dE_1}{d\ln\Omega_1/dE_1} = \frac{\cancel{1/T_1}\ \tfrac{1}{T}}{\cancel{\beta_1}\ \beta} \quad (6)$$

$$\frac{dS_2/dE_2}{d\ln\Omega_2/dE_2} = \frac{\cancel{1/T_2}\ 1/T}{\cancel{\beta_2}\ \beta}$$

MACRO O's

CONST = k_B

5) ~~(6)~~ (7) $\boxed{\frac{dS_1}{d(\ln\Omega_1)} = \frac{dS_2}{d\ln\Omega_2} = \frac{1}{\beta T}}$ @ equil

G1

Since system ① & ②
can be any combo
of gas, liq, solid
plasma

~~dS for any S and~~

the ratio of Δ in
system $\boxed{S}$ (macro)
to no system Q-states
(micro) due to a
random flxn in S
about equil must =
a const:

$$\boxed{\frac{dS}{d\ln\Omega} = k_B} \quad (8)$$

⊕ diff'l version of
Bridge reln

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ΔS $\therefore$ $\Delta S_1 + \Delta S_2 + \ldots \Delta S_n$

$$\overset{\text{must}}{=} k_B \left[\Delta(\ln \Omega_1) + \Delta(\ln \Omega_2) + \ldots + \Delta \ln \Omega_n \right]$$

or $\displaystyle\int_{S_{\text{initial}}}^{S_{\text{final}} = S} dS = k_B \int_{\ln \Omega_{\text{init}}}^{\ln \Omega_{\text{final}}} d\ln \Omega$

$$\Rightarrow \boxed{S - \overset{0}{\cancel{S_{\text{initial}}}} = k_B \ln \Omega - k_B \ln \overset{1}{\cancel{\Omega_{\text{initial}}}}}$$

$\oplus$ always

Finally choose initial state as the ground state for substance @ $\boxed{T = 0\,K}$

$\oplus$ For perfect crystals @ 0K $\Rightarrow$ $\boxed{\Omega_1 = 1}$ (i.e. ground state).

$\oplus$ let's define entropy @ 0K as $\boxed{0 = S(0K)}$

∴ Finally we arrive

@ Boltzmann's relationship:

$$\boxed{S(E,V,N) = k_B \ln \Omega(E,V,N)}$$

(f) second law thermo

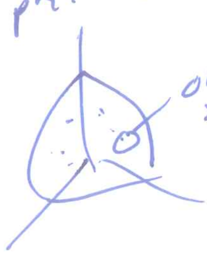
PREP NOTES JAN 23, 2023

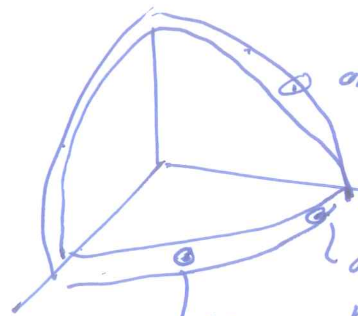
during any short time interval and at equil:

Claim 1 : $\Omega^0 = \Omega_1 \cdot \Omega_1$

A)

E_1 angular w/in $\frac{1}{8}$ spher





$E_2 \approx$ fixed since $E_2(t=0) >> E_1(t=0)$

t = jot

$\Downarrow$

$$\Omega^0(jot) = \Omega_1(\ ) \cdot \Omega_2(\ )$$

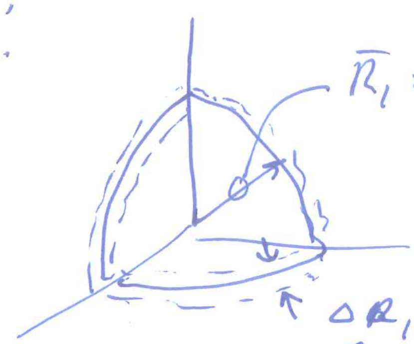
B) @ equil : a) $E_1^{(t)} + E_2^{(t)} = E^0$

b) $\bar{E}_1 \stackrel{\text{should}}{=} \bar{E}_2$

c) a) $\Rightarrow \overline{E_1(t)} + \overline{E_2(t)} = E_0$

d) a) $\Rightarrow \Delta E_1(t) = -\Delta E_2(t)$

$\therefore$

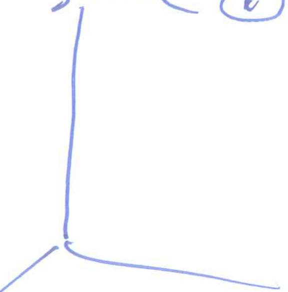


$R_1 = \frac{\sqrt{E_1}}{\sqrt{c}}$

$\Delta R_1 = \Delta\left(\sqrt{\frac{E_1}{c}}\right)$

$= \frac{1}{2\sqrt{E_1 c}} \Delta E_1$

same (2)

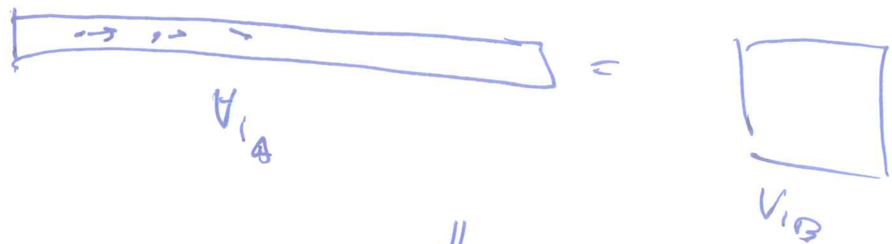


@ equil $\Omega_1 \cong$ vol $=$ ~~$R_1 \Delta R_1$~~ $\frac{4\pi R_1^2}{8} \Delta R_1$

$\cong \cancel{\sqrt{E_1/c}}\ \frac{4\pi}{8}\left(\frac{E_1}{c}\right) \frac{1}{\sqrt{E_1 c}} \Delta E_1$

(2)

text claims $\Omega_1 = \Omega_1(V_1, N_1, E_1)$



$\Downarrow$

dynamics A ~ 1-D
while dynamics B
3-D

$n_x^2 + n_y^2 + n_z^2 =$

$E_y \psi_y = -\frac{\hbar^2}{2m} \psi_y''$

$\Rightarrow \psi_y =$

III) Fund. thermo reln = q.
a) gives diff'l Δ's in
system U in terms of
diff'l Δ's in ~~of~~ terms S ~~...~~
~~thermo vbls~~ δS. and
other equil thermo state vbls.

b) seems to ~~be~~ correspond
to ~~as~~ a statement of
cons. energy: $dU_{sys} = \delta Q$

II) Fund. eqn in Thermo p-p. form

Since * For a system containing a single species that can be added/removed by chem. reactions / phase change

$$ * \quad dE = T\,dS - P\,dV + \mu\,dN $$

accommodates irreversible processes

during diff. proc.

+ only work form^n = compression/expansion work

+ TdS ⇐ interpreted as very slow/reversible heat add/removal to system

$G = H - TS$

$dG = dH - ~~TdS~~$

E = potential + kinetic energy + rotation + electric + vibration

Over all

+ $\mu\,dN$ represents addn/removal of

+ ~~[illegible]~~ related to/species

version of 2nd law

+ GIBBS subsumed all irrev. processes into TdS

Ru. b) ~~+ more~~ $~~dS = \frac{\partial S}{\partial E}\Big|_{N,V} dE + \frac{\partial S}{\partial V}~~$ more later

III) a) $$\boxed{dS = \left(\frac{1}{T}\right)dE + \left(\frac{P}{T}\right)dV - \frac{\mu}{T}\,dN} \quad \otimes$$

a) $\otimes \Rightarrow S = S(E, V, N)$

Since S is a point fn of any 3 thermo vbls, T, P, V, N, G, H, A, then

@ equil where AVG system props are $\bar{E}, \bar{V}, \bar{N}$

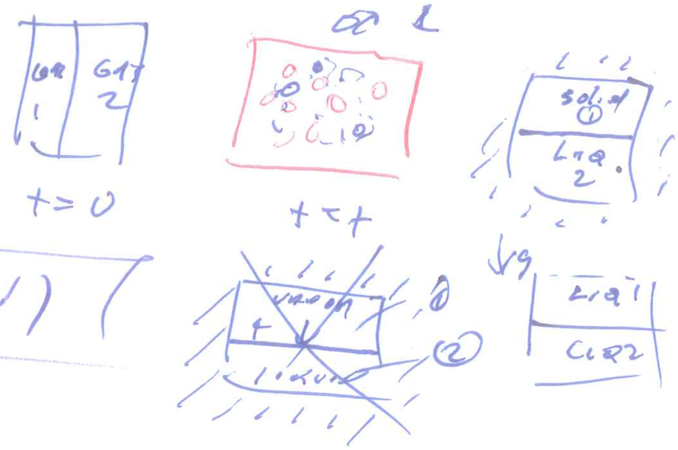
(2)

(*) ⇒

$$\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{\bar{N}, \bar{V}, \bar{E}}$$

$$\frac{P}{T} = \frac{\partial S}{\partial V}\Big|_{E, N, \bar{V}}$$

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}\Big|_{E, V, \bar{N}}$$



Fund reln ⇒

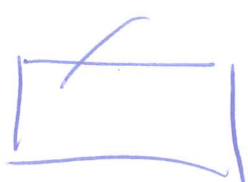
then $\boxed{S = S(E, V, N)}$

IV) For our problem, we're interested

a) in find ΔS_1 produced by flucs, ΔE_1 @ about $\bar{E}_1$ @ equil.

1st problem: N's, V's fixed

⊕



$E_0^u = E_1 + E_2$ @ any t

$E_0 = \bar{E}_1 + \bar{E}_2$

$\Rightarrow dE_1 = -dE_2$ " t

$dN_1 = 0 \; (= dN_2)$

$dV_1 = dV_2 = 0$

b) ∴ $$dS_1 = \frac{\partial S_1}{\partial E_1}\Big|_{N_1, V_1, \bar{E}_1} \Delta E_1$$

$$dS_2 = \frac{\partial S_2}{\partial E_2}\Big|_{N_2, V_2, \bar{E}_2} \Delta E_2$$

(5)

c) c1) $$\frac{dS_1/dE_1}{d\ln\Omega_1/dE_1} = \frac{(\partial S_1/\partial E_1)|_{N,V_1}}{\partial \ln\Omega/\partial E_1|_{N,V}} = \frac{(1/T_1)}{(\beta_1)}$$

c2) $$\frac{dS_2}{d\ln\Omega_2} = \frac{(\quad)}{(\quad)} = \frac{1/T_2}{\beta_2}$$

d) But @ equil, we know already

$\boxed{T_2 = T_1}$ $(= T)$

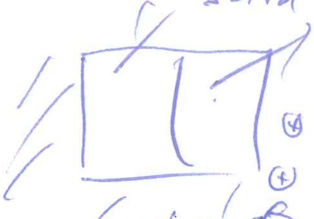
and showed

$\boxed{\beta_1 = \beta_2}$ $(= \beta)$

e) ∴ ⇒ c1) & c2) ⇒

(5a) $$\boxed{\frac{dS_1}{d\ln\Omega_1} = \frac{dS_2}{d\ln\Omega_2} = \frac{1}{\beta T}}$$

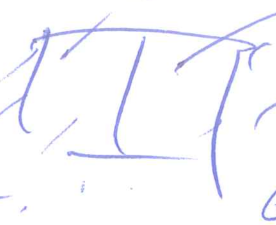
f) since (5a) applies to



⊕ $\Delta E_1 = -\Delta E_2$

⊕ Ω^0 maxed $T_1 = T_2$

mix of non-reacting (1) (2) liqs and gases etc



⊕ $\Delta E_1 = -\Delta E_2$

⊕ Ω^0 maxed

⊕ ⇒ $\frac{\partial \ln\Omega}{\partial E} = \frac{\partial \ln\Omega}{\partial E}$

$\nabla T_1 = T_2$ equil @ ~~then~~

then random small flucts in energy? (10)

$\Rightarrow$ in (5*) $\boxed{\frac{1}{\beta T} = \text{const} = k_B}$ $\Rightarrow$

$\therefore$ $\boxed{dS = k_B\, d(\ln \Omega)}$ (6*)

diff'tl Δ in state fixed mass, non-reacting system's entropy produced by ΔT.

diff'tl Δ in $\ln \Omega$ small

=

$\therefore \quad S(E, V, N) - S(E = T = 0K, V, N)$

$= k_B \ln \Omega(\,) - k_B \ln \Omega(0K)$

$\therefore \quad \boxed{S(E, V, N) = k_B \ln \Omega(\,)}$

(1) 2nd Law Thermo
isolated system w/
S for spontaneous process
is maximized. (=) consistent w/ $\Omega \to$ maxd

initial $\downarrow$ fin equil

(2) 3rd Law Thermo

S @ T = 0 = 0 or fixed
crystal having single Q ground
glassy matl