THERMODYNAMICS PH332
& STATISTICAL MECHANICS

Feb 6, 2019

Thermodynamics
- macroscopic properties of systems P, V, T, etc
- used w/ systems that are large enough that microscopic fluctuations can be ignored

Stat mech
- individual states of atoms / microscopic states of particles in system & uses statistics to describe macroscopic behavior

- This course focuses on systems of large numbers of particles.
  - systems ?
  - large → how large?

Large? 1 mole → $N_A = 6.022 \times 10^{23}$ particles → Avogadro's #

- Why need statistics? → Ex Say we want to count # of particles in a mole of water.

$3\,\text{GHz} \rightarrow 3 \times 10^9\ s^{-1}$ count rate $\Rightarrow 2 \times 10^{14}\ s = 6.4 \times 10^6$ yrs.

→ needs stat models...

What is a mole? → A mole is the amount of matter that contains as matter as 12g of ^{12}C

Molar Mass M : mass of 1 mole of a substance in grams.

Ex $M_{^{12}C} = 12\,g/mol$ $M_{H_2O} = 18\,g/mol$

$M_{^4He} = 4\,g/mol$

Temperature → always use K. Don't use Fahrenheit.

Fahrenheit scale → freezing point of water: 32°F

Boiling point of water: 212°F

Celsius → 0°C

100°C

$$°F = 32 + \frac{9}{5}°C$$

$$\boxed{T_{(K)} = T_{(C)} + 273.15}$$

<u>What is temperature?</u>

$\boxed{\text{0th law of thermodynamics}}$

If A is in thermoequilibrium with B
but C is in thermo equilibrium with C
then A ... C
"thermoequilibrium" ≡ same T.

Ⓐ ↔ Ⓑ
Ⓑ ↔ Ⓒ
Ⓐ ↔ Ⓒ

<u>Temperature</u>: a measure of how likely it is for a system to give
energy to another system. Generally, higher T
→ more likely to give off energy

Feb 8, 2019

$\boxed{\text{Ideal Gas Law}}$ $PV = nRT$ vs $PV = NkT$

n : # of moles R : Gas constant 8.31 J/mol K

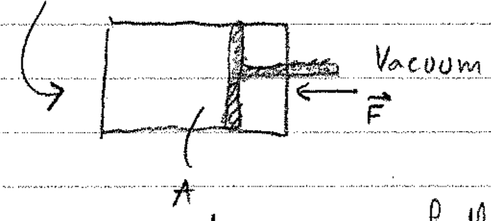
N : # of particles k_B : Boltzmann Constant = 1.38×10^{-23} J/K

so $\boxed{nR = Nk_B}$

<u>Note</u> $N = nN_A$ so $\boxed{R = N_A k_B}$ or $\boxed{k_B = \frac{R}{N_A}}$

<u>Assumptions</u>: point-like particles, don't interact

▨ How does temperature T of ideal gas relate to its KE?

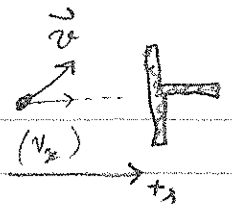


<u>Pressure</u> $= \frac{F}{A} = \frac{1}{A}\frac{dp}{dt} = \frac{1}{A}\frac{\Delta p}{\Delta t}$

★ assume perfectly elastic collisions

③

(1) Change in momentum of single particle.

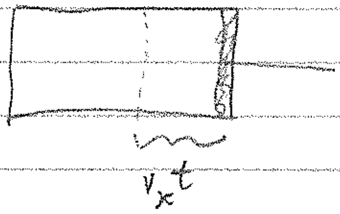


$$\Delta p = m v_f - m v_i$$

$$= -m v_x - m v_x = -2 m v_x$$

So $\Delta p_{\text{piston}} = 2 m v_x$

(2) # of collisions?



assume N molecules in volume V

$\rightarrow$ density $= \frac{N}{V} =$ ~~$\frac{N}{v_x t A}$~~

So # of collisions $= \frac{N}{V} \cdot (v_x t A)$

So # collision/sec $= \frac{N}{V}(v_x A)$

(3) Force on piston $\quad F = \frac{\Delta p}{\Delta t} = (2 m v_x)\left(\frac{N}{V} v_x A\right)$

$$= 2 m v_x^2 \frac{N}{V} A$$

So $\boxed{p = \frac{F}{A} = 2 m v_x^2 \frac{N}{V}}$

Now, corrections. Not all particles have the same v_x

$\rightarrow \langle v_x^2 \rangle$ instead of v_x. Also, ½ of particles are moving in the other direction $(-v_x)$ $\rightarrow$ divide by 2

So $p = m \langle v_x^2 \rangle \frac{N}{V}$

Now $v^2 = v_x^2 + v_y^2 + v_z^2$

$\Rightarrow \boxed{pV = m \langle v_x^2 \rangle N}$

$\Rightarrow$ Assume $\langle v_i^2 \rangle$ equal

$\Rightarrow \frac{1}{3}\langle v^2 \rangle = \langle v_x^2 \rangle$

So $PV = NkT = \frac{1}{3} m\langle v^2\rangle N = \frac{2}{3}\left[\frac{1}{2} m\langle v^2\rangle\right] N$

So $\boxed{kT = \frac{2}{3}\langle KE\rangle}$

$\hookrightarrow$ So $\boxed{\langle KE\rangle = \frac{3kT}{2}}$

<u>Average speed of the particles?</u>

<u>Naively</u> $\frac{1}{2} m\langle v^2\rangle = \frac{3}{2} kT$

$\to \langle v^2\rangle = \frac{3kT}{m}$ $\longrightarrow$ (g), not $M = m/N_A^{-1}$ $= mN_A$

So $\boxed{V_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}}$ $\longrightarrow$ But this is <u>NOT</u> $\langle v\rangle$

$\langle v\rangle = \sqrt{\langle v_x\rangle^2 + \langle v_y\rangle^2 + \langle v_z\rangle^2}$

<u>But</u> $\underbrace{\sqrt{\langle v^2\rangle}}_{v_{rms}} = \sqrt{\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle}$

We will (can) show that $\langle v\rangle = \sqrt{\frac{8kT}{\pi m}} < V_{rms}$

<u>Ex</u> Find rms v of N_2 molecules at room temp, ~ 300K

$v_{rms} = \sqrt{\frac{3k\cdot 300}{28/N_A}} \approx$

<u>or</u> $\boxed{V_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3nRT}{nM}} = \sqrt{\frac{3RT}{M}}} \approx \sqrt{\frac{3\cdot 8.31\,J/molK\cdot 300K}{28\,g/mol}}$

Now $28\,g/mol = 28\times10^{-3}\,kg/mol \to$ $V_{rms} \approx 517\,m/s$

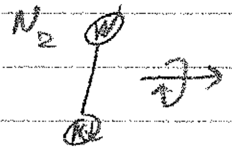
or internal

What's the total thermal energy of a gas?

$$\boxed{U = \frac{3}{2}kT\cdot N = \langle KE\rangle N}$$

→ but only true for "monotomic ideal gas"
↳ like noble gas.

Why? Degrees of freedom



→ other modes....

If translational motion is not the only contributing factor

↳ **Equipartition theorem**

↳ At some temp T, the average energy for every quadratic degree of freedom $= \frac{1}{2}kT$

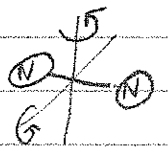
↑ Ex. $\frac{1}{2}m\langle v_x^2\rangle$

So $$\boxed{U_{thermal} = Nf\,\frac{1}{2}kT}$$ f = # of quadratic df.

Degrees of freedom?

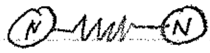
↳ . translational : x, y, z (3 df) → for a gas
. Rotational : how many axes of rotations introduce asymmetries?

Ex



→ (2 df)

Ex  → (3 df)

- Vibrational  → classical mech tells us that

$\langle KE \rangle = \langle PE \rangle$ for SHO → 2 degrees of freedom, both quadratic

at normal temp → quantum effect. Most diatomic molecules only have ⑤ df at typical room temp, as vibr. df are frozen out.

$$\rightarrow U_{\text{thermal } N_2} \cong N \cdot \left(\frac{3+2+0}{2}\right) kT$$

Feb 11, 2019

$\boxed{\text{Heat \& Work}}$ → Exchange in energy

Last time $U = \frac{f}{2} N kT$

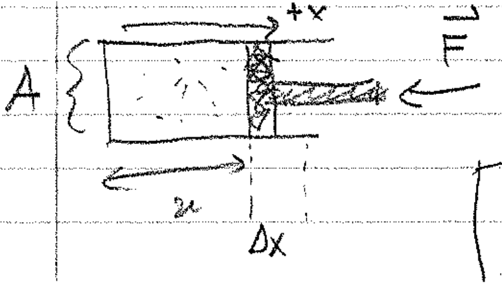
{ Heat (Q) → spontaneous flow of energy from one system to another due to a ΔT }

So $\boxed{\text{if } \Delta T \neq 0 \text{, then } Q \neq 0 \quad \text{(Heat) spontaneously}}$

{ Work → (W) non-spontaneous transfer of energy → need an "agent" to transfer energy }

Heat & Work are not intrinsic to system. → they're processes.

Compression work



$P = \frac{F}{A}$

positive, since $\Delta x < 0$

$$\boxed{W_{\text{on gas}} = \underbrace{-F\Delta x}_{} = -PA\Delta x = -P\Delta V}$$

So $\boxed{W_{on\,gas} = -P\Delta V}$

☒ Note Should use differentials, but they are not exact diff. because of path-dependence

$$W = \int_P \vec{F}\cdot d\vec{r}$$

A differential is exact if ∃ $f = f(x,y)$ such that

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

→ True for conservative vector fields $\vec{v} = \vec{\nabla} f$

☒ In other words, $df = A\,dx + B\,dy$ exact diff. if $\begin{cases} A = \frac{\partial f}{\partial x} \\ B = \frac{\partial f}{\partial y} \end{cases}$

$$\vec{\nabla} \times [A, B] = \begin{vmatrix} \partial/\partial x & \partial/\partial y \\ \frac{\partial f}{\partial x} & \frac{\partial f}{\partial y} \end{vmatrix} = \frac{\partial^2 f}{\partial x \partial y} - \frac{\partial^2 f}{\partial y \partial x} = 0$$

☒ Can use Euler's test to determine if we have an exact diff.

Let $df = A\,dx + B\,dy$

☒ Check if $\frac{\partial A}{\partial y} = \frac{\partial B}{\partial x}$ → Yes? → Exact

↘ No? → Not exact

☒ Inexact differentials are written as → $\boxed{đW \text{ or } đQ}$

↪ path-dependence!

▨ Inexact differentials can become exact by multiplying by some integrating factor.

e.g.

$$\begin{cases} \frac{đW}{P} = dV \longrightarrow \text{volume} & dV \rightarrow \text{exact diff} \\ \frac{đQ}{T} = dS \nearrow \text{entropy} & dS \rightarrow \text{exact diff} \end{cases}$$

▨ If Q & W are the only ways energy is transferred, then conservation of energy

$$\boxed{\Delta U = Q + W_{on}} \longrightarrow \text{1}^{st}\text{ law of thermody}$$

Q : heat added to system, W : work done on system

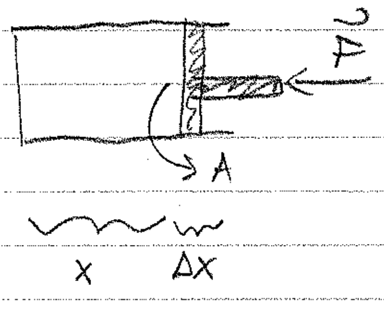
In differential $\longrightarrow$ $\boxed{dU = \delta Q + \delta W_{on} = \delta Q - \delta W_{by}}$

Units of energy $\rightarrow$ 1 J $\rightarrow$ 1 kg m^2/s^2

1 cal $\rightarrow$ 4.186 J

1 cal $\rightarrow$ # heat needed to raise 1g of H_2O by 1C or 1K

Compression Work



$$W_{on} = -F\Delta x \overset{?}{=} -P\Delta V$$

let $P \rightarrow P(V)$

Before, we assumed that P is constant over the process $\rightarrow$ assumed piston movement was slow

Quasi-static process → slow process, allow P to equilibrate

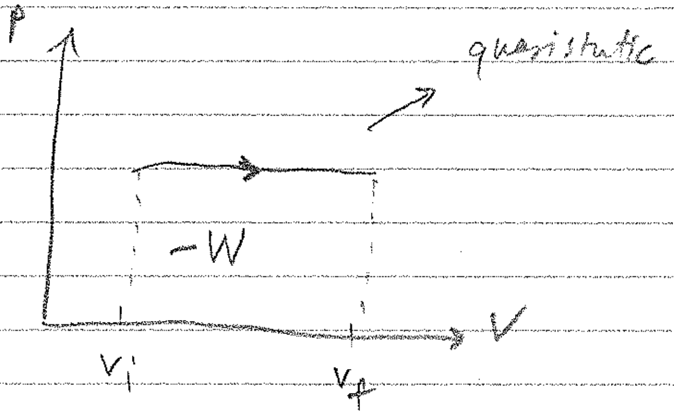
$\boxed{W_{on} = -P\Delta V}$ or $đW_{by} = P\,dV$

Note there is heat flow in quasi-static process

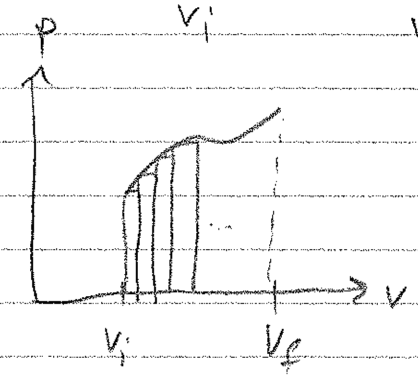
☒ We often consider infinitesimal changes that are each quasistatic & then integrate

$$\boxed{W_{on} = -\int_{V_1}^{V_2} P(V)\,dV}$$

☒ P-V diagrams



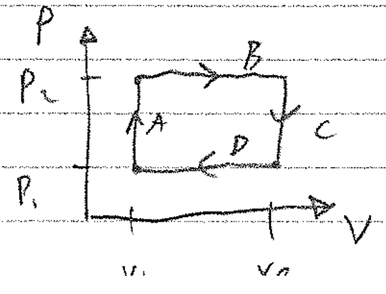
Non quasi-static



$$W_{on} = -\int_{V_i}^{V_f} P(V)\,dV$$

Example of PV diagram

Interpreting PV diagrams



An ideal diatomic gas (N_2)

For steps A → D, we want to determine W_{on}, Q_{add}, ΔU, and W_{total} and Q_{tot}

	A	B	C	D	Σ
W_{on}	0	$P_2(V_1-V_2)$	0	$P_1(V_2-V_1)$	<0
Q	$\frac{f}{2}V_1(P_2-P_1)$	$\frac{7}{2}P_2(V_2-V_1)$	$\vdots$	$\vdots$	>0
ΔU	$\frac{5}{2}V_1(P_2-P_1)$	$\frac{5}{2}P_2(V_2-V_1)$	$\vdots$	$\vdots$	0

A: $W = 0$, $\Delta U = \frac{f}{2}NkT = \frac{f}{2}Nk\frac{PV}{Nk} = \frac{f}{2}PV$

So $\Delta U_A = \frac{f}{2}V_i \Delta P$

$\Delta U = Q + W$

B $\Delta U = \frac{5}{2}P\Delta V = \frac{5}{2}P_2(V_2-V_1)$

$Q = \Delta U - W = \frac{5}{2}P_2(V_2-V_1) - P_2(V_1-V_2)$

Note $\left\{ \begin{array}{ll} W_{on,total} < 0 & \\ & Q > 0 \\ \Delta U = 0 & \end{array} \right\}$

Feb 12, 2019 Quasistatic review "slow" → so that system can equilibriate → pressure is uniform over system

$W_{on} = -F\Delta x \rightarrow -P\Delta V$

Not-quasistatic "fast" → pressure depends on position

Compression of an ideal gas

Isothermal compression → "slow" compression such that T = constant

Temp doesn't increase

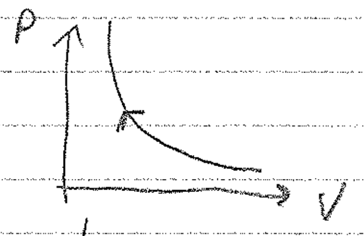
$\Delta U = W_{on} + Q_{add}$ → Q leaves system → $\Delta U = 0$

Adiabatic compression → "fast" compression. So fast that no heat can escape

$\boxed{Q=0}$ So $\Delta U = W_{on} + Q_{add} = W_{on}$.

→ $\boxed{\text{Temp increases}}$

P-V diagram



$\boxed{\text{Isothermal process → Quasistatic}}$

$$W_{on} = -\int_{V_i}^{V_f} P(V)\,dV = -\int_{V_i}^{V_f} \frac{NkT}{V}\,dV$$

↳ PV = const

$$= -NkT\int_{V_i}^{V_f} \frac{dV}{V}$$

$$\boxed{W_{on} = -NkT\ln\left(\frac{V_f}{V_i}\right)}$$

→ work done on system in isothermal compression.

Since T does not increase, how much heat is lost?

↳ $\Delta U = W_{on} + Q_{add} = 0$ or $W_{on} = Q_{out}$

$\Delta U \downarrow dT$

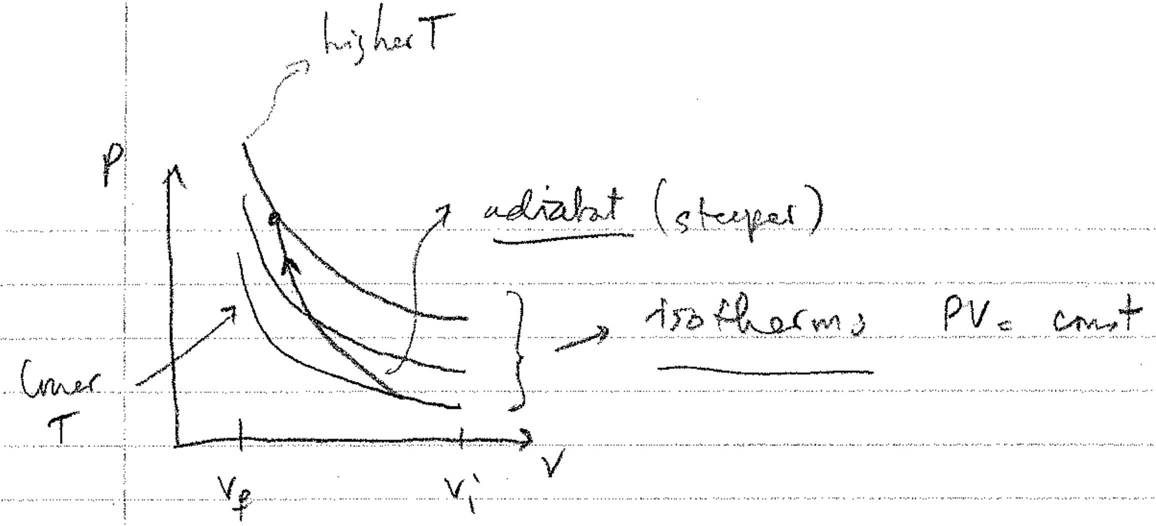
So $\boxed{Q_{add} = -W_{on} = NkT\ln\left(\frac{V_f}{V_i}\right)}$

$\boxed{\text{Adiabatic process → fast}}$

Assume quasistatic process ... $\Delta U = W_{on} + Q_{add}$

By definition of adiabatic → $Q = 0$

$\Big\}$ → $\Delta U = W_{on}$



▨ How different parameters change during adiabatic compression?

↳ Ideal gas $\Delta U = W_n + Q = W_n$

$$U = \frac{f}{2}NkT \longrightarrow dU = \frac{f}{2}Nk\,dT = dW = -P\,dV$$

So $\frac{f}{2}Nk\,dT = -\frac{NkT}{V}dV$

So $\int \frac{f}{2}\frac{dT}{T} = -\int \frac{dV}{V}$

So $\frac{f}{2}\ln\left(\frac{T_f}{T_i}\right) = -\ln\left(\frac{V_f}{V_i}\right)$

$$\left(\frac{T_f}{T_i}\right)^{f/2} = +\left(\frac{V_f}{V_i}\right)^{-1} \rightarrow V_i T_i^{f/2} = T_f^{f/2} V_f$$

So $\boxed{VT^{f/2} \rightarrow \text{constant}}$ → adiabatic compression/expansion of ideal gas

Can write this in volume & pressure

$T = \frac{PV}{Nk} \rightarrow V\cdot\left(\frac{PV}{Nk}\right)^{f/2} \rightarrow$ constant

$\rightarrow P^{f/2}V^{1+f/2} \rightarrow$ constant

$\rightarrow PV^{(1+f/2)/f/2} \rightarrow$ constant

$\Rightarrow PV^{1+2/f}$ = constant

Call $\gamma = 1+\frac{2}{f} = \frac{f+2}{f}$

$\rightarrow \boxed{PV^{\gamma} = \text{constant}}$

We call $\gamma \rightarrow$ "adiabatic exponent" $\gamma = \frac{f+2}{f}$

$$\gamma = \frac{f+2}{f} \quad \text{so} \quad \left\{ \begin{array}{l} PV^{\gamma} = \text{constant} \\ VT^{1/\gamma-1} = \text{constant} \end{array} \right\}$$

Now, pressure & temp.

$$\hookrightarrow \underline{V^{\gamma}P = \text{constant}} \qquad \downarrow \; \underline{V^{-\gamma}T^{-\gamma/\gamma-1} = \text{constant}}$$

$$\underline{\text{So}} \quad (V^{\gamma}P)(V^{-\gamma}T^{-\gamma/1-\gamma})$$

$$= PT^{-\gamma/1-\gamma} \quad \text{constant}$$

$$\underline{\text{So}} \quad \boxed{P^{1-\gamma}T^{\gamma} \quad \text{constant}}$$

Ex Diesel engine (no spark plugs ...)

↳ atm air is quickly compressed to 1/20 original volume

→ Estimate temp of air in cylinder...

Well $\frac{V_f}{V_i} = \frac{1}{20}$ & assume ideal gas (diatomic $\rightarrow f = 5$)

Ok $VT^{f/2} = \text{constant}$

$$\hookrightarrow \left(\frac{T_f}{T_i}\right)^{5/2} = \left(\frac{1}{20}\right)^{-1} = 20$$

$$\underline{\text{So}} \quad T_f = \sqrt[5/2]{20\,T_i^{5/2}} = \overbrace{\sqrt[5/2]{20}}^{\sim 3}\;\overset{\sim 300}{T_i}$$

$$\underline{\text{So}} \quad \boxed{T_f \approx 1000\text{K} > 700^{\circ}\text{C}}$$

→ hot enough to ignite Diesel without spark plug.

heat capacity

↳ The amnt of heat necessary to raise a substance by 1°C

$$\boxed{C \equiv \frac{Q}{\Delta T}} \qquad Q = C\Delta T = mc\Delta T$$

Specific heat capacity $\boxed{c \equiv \frac{C}{m}}$

But recall → $Q_{in} = \Delta U - W_{on}$. limiting case → $W = 0$
→ no change in V
get heat capacity at constant volume, C_V

not the most physical →
$$\boxed{C_V = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_{V\text{ constant}}}$$

Ex for 1g of H_2O $C_V = 1$ cal/K

Feb 13, 2019

Heat Capacity

limiting cases
→ $W = 0$, $\Delta V = 0$ → $C_V = \frac{\Delta U - W}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_{V\text{ const}}$
Constant volume
→ Constant pressure

Heat capacity at constant pressure

$$C_p = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} = \left(\frac{\Delta U - (-p\Delta V)}{\Delta T}\right)_{p\text{ const}}$$

$$\boxed{C_p = \left(\frac{\partial u}{\partial T} + p\frac{\partial V}{\partial T}\right)_{p\text{ const}}}$$

→ heat needed to compensate for expansion
(energy loss at work due to expansion)

Note $\left(\frac{\partial u}{\partial T}\right)_p \approx \left(\frac{\partial U}{\partial T}\right)_V$ →

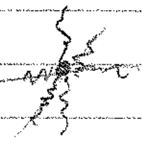
▨ Suppose we have a system that obeys equipartition theorem

$$U = \frac{f}{2} NkT$$

Then

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_{V\ \text{constant}} = \frac{f}{2} Nk}$$

→ if we can measure C_V then we can find f.

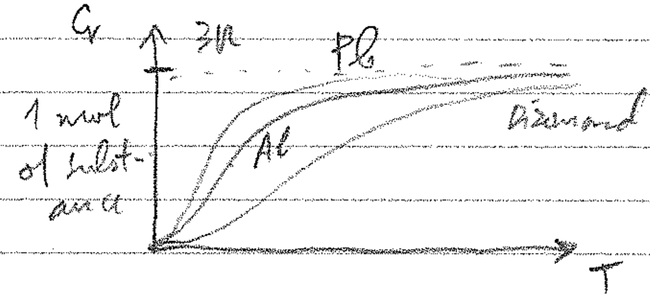


$\boxed{Ex}$

Consider solids/crystal
no rotation/translation
→ only df is vibration.

→ Solid should have $\underline{6}$ dfs

So $\boxed{C_V = \frac{6}{2} Nk = 3Nk = 3nR}$ → for solids



▨ Heat capacity at constant pressure for ideal gas.

↳ obeys eq. partition.

$$C_p = \left(\frac{\partial U}{\partial T}\right)_p + \left(p\frac{\partial V}{\partial T}\right)_p$$

$$= \frac{f}{2} Nk + p \frac{\partial}{\partial T}\left[\frac{NkT}{p}\right]$$

$$\boxed{\text{thus } nR = C_V + Nk = C_p} = \frac{f}{2} Nk + Nk$$

Recall $\gamma = \frac{f+2}{f} = 1 + \frac{2}{f}$

$$= \left(\frac{f}{2} + 1\right) Nk$$

$\rightarrow \gamma - 1 = \frac{2}{f}$

$$\boxed{C_p = \frac{\gamma}{\gamma - 1} Nk}$$

$\frac{f}{2} + 1 = \frac{1}{\gamma - 1} + 1$

Recall The Adiabatic exponent γ

Definition $\longrightarrow$ $\boxed{\gamma \equiv \frac{C_p}{C_V} = \frac{C_V + nR}{C_V} = \frac{f/2 + 1}{f/2} = \frac{2+f}{f}}$

Example of heat capacity

▨ Heat capacity of a star

Well $u_{pot} = \frac{-GMm}{r}$ $KE = \frac{1}{2}mv^2$ $v = \sqrt{\frac{GM}{r}}$

So $K = \frac{1}{2} m \frac{GM}{r}$

Virial Theorem } $\rightarrow$ $U_{tot} = U_{pot} + KE = \frac{1}{2} m \frac{GM}{r} - \frac{GMm}{r} = \frac{-1}{2}\frac{GMm}{r}$

$\downarrow$ $-2KE$ $\longrightarrow$ $U_{tot} = -K = \frac{-1}{2}\frac{GMm}{r}$

Star { H gas (3 df) $\rightarrow$ quadratic

obeys eq. part. thm $K = +\frac{1}{2}mv^2 = \frac{f}{2}NkT = \frac{3}{2}NkT$

So $\boxed{U_{tot} = \frac{-3}{2}NkT}$

So $\boxed{C_V = \left(\frac{\partial u}{\partial T}\right)_V = \frac{-3}{2}Nk}$ $\rightarrow$ negative heat capacity

$\hookrightarrow$ So, as a star radiates $\mathcal{E}$, it gets hotter.

☒ Latent heat → useful for phase transitions.

e.g. melting ice Solid → liquid → Vapor

Note temperature stays constant during phase transitions.

↳ need to know how much heat is needed to complete phase transition.

latent heat $\boxed{L \equiv \frac{Q}{m}}$

- Assume that P = constant over phase transitions
- Assume that no other work besides expansion/compression

Ex latent heat of fusion

H-Bonds! $\left\{ \begin{array}{lll} H_2O_{(s)} \longrightarrow H_2O_{(l)} & L_f = 333\ J/g >> C_p \\ H_2O_{(l)} \longrightarrow H_2O_{(g)} & L_v = 2260\ J/g >> C_p \end{array} \right.$

Ex 200g cup of tea that is @ boiling pt (212°F 100°C) & want to cool down to drink... 150°F ~65°C How much ice do we want?

$T_{ice,i} = -15°C$ $C_{ice} = 0.5$ cal/gC

$C_{H_2O(l)} = 1$ cal/gC $L_f = 80$ cal/g

$Q(\text{lost tea}) = m_{tea}\,\Delta T\,C_{H_2O} = 200\,(100-65)\ 1\,\text{cal} = 7000\ \text{cal}$

$$\overset{-15°C}{H_2O_{(s)}} \longrightarrow \overset{0°C}{H_2O_{(s)}} \longrightarrow \overset{0°C}{H_2O_{(l)}} \longrightarrow \overset{65°}{H_2O_{(l)}}$$

$7000\ \text{kcal} = m C_{ice} \Delta T + L \cdot m + m C \Delta T$

So $$m = \frac{7000 \text{ cal}}{C_{ice}(0-(-15)) + L + (65-0)\, C_{H_2O(l)}} \simeq 46 \text{ g of ice}$$

Feb 15, 2019 **Enthalpy** → total heat content of a system

$$\boxed{H \equiv U + PV} \rightsquigarrow \text{useful for constant P processes}$$

H is useful for constant-pressure processes.

Ex Add heat to a system at constant pressure. Then U, V, H change.

So $$H + \Delta H = U + \Delta U + P(V + \Delta V)$$

$$H + \Delta H = \underbrace{(U + PV)}_{H} + (\Delta U + P\Delta V)$$

So $$\boxed{\Delta H = \Delta U + P\Delta V} \longrightarrow \text{@ constant pressure.}$$

First law

if $$\Delta U = Q + \overset{\text{compression work}}{(-P\Delta V)} \longrightarrow + W_{\text{others}}$$

then $$\Delta H = \Delta U + P\Delta V = Q + W_{\text{others}}$$

So $$\boxed{\Delta H = Q_{\text{add}} + W_{\text{others}}} \rightsquigarrow \text{true for constant P processes.}$$

Heat capacity at constant pressure

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

☒ **Examples** ΔH for boiling H_2O (phase transitions...)

$$\Delta H = 40660\ J/mol \quad at\ 1\ atm,\ 298K$$

$$\Delta H = \frac{40\,660\ J/mol}{18\ g/mol} \approx 2260\ J/g = L_{H_2O}$$

↳ latent heat of vaporization

☒ How much work is needed to create space for the H_2O vapor.

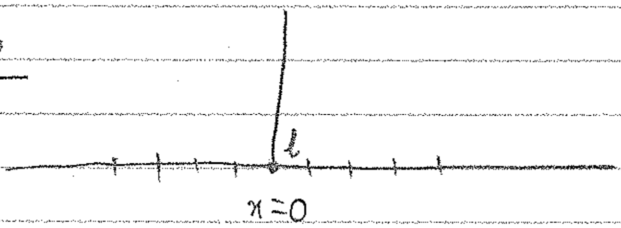
$$V_i \approx 0 \quad V_f \approx \frac{nRT}{P} = \frac{RT}{P} \quad (n=1)$$

$$\text{So } \Delta V = \frac{RT}{P} \rightarrow W = P\Delta V = RT = 8.314\ J/K \cdot 298K$$

$$\approx 3100\ J$$

Statistics

Random Walk problem



$$\begin{cases} P(\text{left}) = \cancel{P(\text{right})} = 1-p = q \\ P(\text{right}) = p \end{cases}$$

Final position $x = ml$ after N total steps where N, m are integers. $-N \le m \le N$

So $P_N(m)$ = Probability of finding our drunk at $x = ml$ after N steps.

Let n_R = # steps to R, n_L = # steps to L $\}$ $N = n_R + n_L$

And $m = n_R - n_L = n_R - (N - n_R) = -N + 2n_R$

☑ Probability of any sequence of steps (ass. independence) is

$$p^{n_R}(1-p)^{n_L} = p^{n_R}(1-p)^{N-n_R}$$ the products

☑ But there are many ways of taking N steps with n_R & n_L

The number of ways is called "Multiplicity", & Ω

↳ "# of microstates"

$$\boxed{\Omega = \frac{N!}{n_R!\,n_L!} = C^{N}_{n_R}}$$

Say there are N objects → N! permutations. But this is only true for distinguishable objects, since order matters

What abt the # of ways N objects can be arranged into n_R spaces? where $n_R < N$

$$\hookrightarrow P^{N}_{n_R} = (N)(N-1)\cdots\underset{\cdot(N-n_R+1)}{(N-n_R)} = \frac{N!}{(N-n_R)!}$$

If we have indistinguishable objects, we have all $n_R!$ ways of arranging N into n_R spaces are the same → divide them out

$$\rightarrow \frac{N!}{(N-n_R)!\,n_R!} = \frac{N!}{n_R!\,n_L!}$$

→ For indistinguishable objects, use combinations... Total multiplicity of outcomes

$$\Omega(n_R) = \frac{N!}{n_R!\,(N-n_R)!} = \binom{N}{n_R}$$

So $\boxed{P_N(n_R, n_L) = \binom{N}{n_R} p^{n_R}(1-p)^{N-n_R}}$

or other notation

$\boxed{W_N(n_R) = \binom{N}{n_R} p^{n_R}(1-p)^{N-n_R}}$ → same thing

Binomial distribution

☒ $\sum_{n=0}^{N} W_N(n) = 1$ ☒ $E(n_R) = Np$ ☒ $Var = Np(1-p)$

Feb 18, 2019

Binomial Distribution

$$P_N(n) = \binom{N}{n} p^n q^{N-n}$$

$$\sum_{n=0}^{N} P_N(n) = 1$$

More generally, $\sum_{n=0}^{N} W_N(n) = (p+q)^N$

Example Roll 4 dice

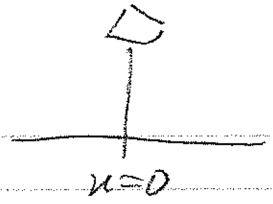
P(one of 4 is ⚀) $= \binom{4}{1}\left(\frac{1}{6}\right)^1\left(\frac{5}{6}\right)^{4-1} = 1-\left(\frac{5}{6}\right)^4 \approx 39\%$

Example Roll 2 1's, 4 dice

$$P_4(2) = \binom{4}{2}\left(\frac{1}{6}\right)^2\left(\frac{5}{6}\right)^{4-2} = \left(\frac{5}{6}\right)^2 \frac{1}{6} \approx 12\%$$

Note high multiplicity, but not likely outcome.

Random Walk



$x = ml$

What is the probability that we're back at $m = 0$ after N steps?

(a) If N is even?
(b) If N is odd?

$$P_N(m) = \frac{N!}{n_R!(N-n_R)!} p^{n_R}(1-p)^{N-n_R}$$

$N = n_R + n_L$
$m = n_R - n_L$
So $N = 2n_1 - m$

$$= \frac{(n_R+n_L)!}{n_R!\,n_L!} p^{n_R}(1-p)^{N-n_R}$$

$$= \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!} p^{\frac{N+m}{2}}(1-p)^{\frac{N-m}{2}}$$

Assume that $p = 1-p = \frac{1}{2}$

So

$$P_N(m) = \frac{N!}{\left(\frac{N+m}{2}\right)!\left(\frac{N-m}{2}\right)!}\cdot\left(\frac{1}{2}\right)^N$$

So

$$\boxed{P_N(m=0) = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\left(\frac{1}{2}\right)^N \Rightarrow \text{if } N \text{ even}}$$

if N is odd, then $m \neq 0$ since $\underset{\substack{\uparrow\\ \text{odd}}}{N} = \underset{\substack{\uparrow\\ \text{even}}}{2n_1} - \underset{\substack{\uparrow\\ \text{odd}}}{m}$

So $\boxed{P_N(m=0) = 0}$

Determination of mean values

Random walk with $N = 2$ steps. Let's say after 2 steps, drunk finds \$ and pick it up.

@ $x = -2l$ \$1
@ $x = 0$ \$5
@ $x = 2l$ \$20

Question on average, how much \$ would you pick up?

Well $P_2(-2l) = ?$ $P_2(2l) = ?$, $P_2(0) = ?$

$$\rightarrow \left\{ \begin{array}{l} P_2(0) = 1/2 \\ P_2(-2l) = P_2(2l) = 1/4 \end{array} \right\} \text{"by inspection"}$$

Let $f(x)$ be the amount of \$ at location x.

In general, $\langle x \rangle = E(x) = \sum_{i=0}^{\infty} x_i W_N(x_i)$

or

$$\boxed{\bar{x} = \frac{\sum_{x_i=0}^{\infty} P(x_i)\, x_i}{\sum_{x_i=1}^{\infty} P(x_i)}}$$

But since we're dealing w probabilities, ... $\sum_{0}^{\infty} P(x_i) = 1$

↳ Mean value of fn.

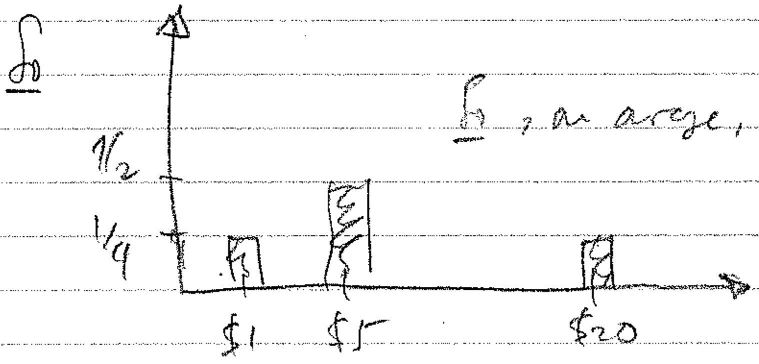
$$\boxed{E\left[f(x)\right] = \sum_{i=0}^{\infty} f(x_i) P(x_i)}$$

Note $E[f(u) + g(u)] = E(f(u)) + E(g(u))$

if $sE(f(u)) = E(sf(u))$, $s \in \mathbb{R}$

$\nleftarrow$

So



So, on average, $E(\$) = \frac{1}{4}\cdot 1 + \frac{1}{2}\cdot 5 + \frac{1}{2}\cdot 20$

$= \frac{1}{4} + \frac{5}{2} + 10$

$= \$\left(10 + \frac{11}{4}\right)$

$\boxed{\text{On average, how far away from the average are we?}}$

$\hookrightarrow E(u - E(u)) = ? = E(u) - \overline{E(u)} = 0$

What about $E((u - E(u))^2)$?

$\hookrightarrow$ Second moment about the mean? → Variance

$\overline{\Delta u^2} = \sigma^2 = E[(u - E(u))^2]$

$= E(u^2) - 2E(u)\overline{E(u)} + E(E(u)^2)$

$$\boxed{Var(u) = E(u^2) - E^2(u)}$$

Standard deviation → $\boxed{\sqrt{var(u)} = \sigma_u = \sqrt{E(u^2) - E^2(u)}}$

(25)

Feb 19, 2019

Mean values: Random Walk problem

Recall

$$P_N(n_R) = \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

$$E\left[f(n_R)\right] = \sum_{n_R=0}^{N} f(n_R) P_N(n_R)$$

So

Average # steps to the right

$$E[n_R] = \sum_{n_R=0}^{N} n_R P(n_R) = \sum_{n_R=0}^{N} n_R \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

Notice $n_R p^{n_R} = p \frac{\partial}{\partial p}\left(p^{n_R}\right)$

So

$$E[n_R] = \sum_{n_R=0}^{N} \frac{N!}{n_R!(N-n_R)!} p \frac{\partial}{\partial p}\left(p^{n_R}\right) q^{N-n_R}$$

$$= p \frac{\partial}{\partial p} \sum_{n_R=0}^{N} \frac{N!}{n_R!(N-n_R)!} p^{n_R} q^{N-n_R}$$

$$= p \frac{\partial}{\partial p} (p+q)^N$$

$$= p \cdot N \cancel{\frac{\partial}{\partial p}} (p+q)^{N-1}$$ But $p+q = 1$

So $\boxed{E[n_R] = pN}$

Similarly $\boxed{E[n_L] = qN = N(1-p)}$

$$\left.\right\} \quad E[m] = E[n_R - n_L]$$

$$= E[n_R] - E(n_L]$$

$$= N(p-q)$$

So $\boxed{E(m) = N(p-q)}$

↳ If $p=q$, then $E(m) = 0$.

Variance

$$\mathrm{Var}(n_R) = E(n_R^2) - \overset{(pN)^2}{E(n_R)^2}$$

$$E(n_R^2) = \sum_{n_R=0}^{N} n_R^2 \, P(n_R)$$

$$= \sum_{n_R=0}^{N} n_R^2 \frac{N!}{n_R!\,(N-n_R)!} p^{n_R} q^{N-n_R}$$

→ Same trick as before .. $n_R^2 p^{n_R} = n_R p \frac{\partial}{\partial p} p^{n_R} = p\frac{\partial}{\partial p}\left(n_R p^{n_R}\right) = \left(p\frac{\partial}{\partial p}\right)^2 p^{n_R}$

So
$$E(n_R^2) = \sum_{n_R=0}^{N} \binom{N}{n_R} \left(p\frac{\partial}{\partial p}\right)^2 p^{n_R} q^{N-n_R}$$

$$= \sum_{n_R=0}^{N} \binom{N}{n_R} \left(p\frac{\partial}{\partial p}\right)^2 p^{n_R} q^{N-n_R}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 \sum_{n_R=0}^{N} \binom{N}{n_R} p^{n_R} q^{N-n_R}$$

$$= \left(p\frac{\partial}{\partial p}\right)^2 \left[p+q\right]^N$$

$$= \left[p\frac{\partial}{\partial p}\right]\left(p \cdot N\,(p+q)^{N-1}\right)$$

$$q+p=1 \longrightarrow \quad = p\left[N\,(p+q)^{N-1} + pN\,(N-1)\,(p+q)^{N-2}\right]$$

$$= pN + p^2 N(N-1) = pN + (pN)^2 - p^2 N$$

So $Var(n_R) = pN + \cancel{(pN)^2} - p^2N - \cancel{(pN)^2}$

$$= pN(1-p)$$

$$\boxed{Var(n_R) = Npq}$$

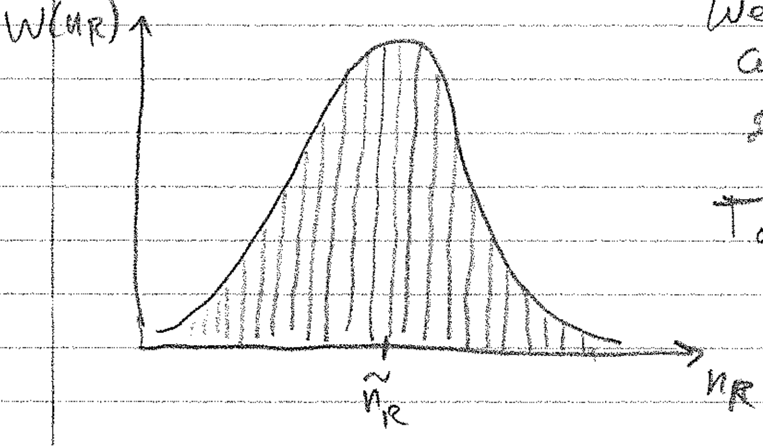
▨ Relative width of a distribution

▨ $\frac{\sigma_{n_R}}{\bar{n}_R} = \frac{\sigma_{n_R}}{E(n_R)} = \frac{\sqrt{Npq}}{Np} = \frac{\sqrt{q}}{\sqrt{Np}} = \boxed{\sqrt{\frac{q}{Np}}}$

when $p = q$, $\boxed{\frac{\sigma_{n_R}}{E(n_R)} = \frac{1}{\sqrt{N}}}$

$\Rightarrow$ So relative width is $\propto \frac{1}{\sqrt{N}}$ ($p \neq q$ in general)

▨ For large N, there's a well defined peak is a well-defined peak in $W_N(n_R)$ @ $n_R = \tilde{n}_R$, where $\tilde{n}_R$ is the most likely value.



We can treat this as a continuous function as N, n_R get large.

To find $\tilde{n}_R$ as a fn of N, p, q, we need to look for where $\frac{\partial W(n_R)}{\partial n_R} = 0$

▨ Instead of evaluating $\frac{dW}{dn_R}$, we'll do $\frac{d}{dn_R}\ln(W(n_R))$ since it has the same $\tilde{n}_R$ & is a more gradually vary fn of n_R

$$\frac{dW_{n_R}}{dn_R} = 0 = \frac{d\ln(W(n_R))}{dn_R}$$

☒ Taylor series expansion around "a"

$$f(x) \simeq f(a) + \frac{f'(a)}{1}(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \dots$$

We want to expand $\ln W(n_R)$ around $\tilde{n}_R$.

$$n_R = \tilde{n}_R + \varepsilon \qquad (\varepsilon << \tilde{n}_R) \qquad \text{Let's write } n \Leftrightarrow n_R$$

▨ $$\ln(W(n)) = \ln(W(\tilde{n})) + \underbrace{\cancel{\frac{d}{dn}\ln(W(n))\Big|_{\tilde{n}}}}_{0 \text{ since } \tilde{n} \text{ most likely...}} \varepsilon + \frac{1}{2}\frac{d^2}{dn^2}\ln(W(n))\Big|_{\tilde{n}}\varepsilon^2 + \dots$$

$$= \ln(W(\tilde{n})) + \frac{1}{2}\frac{d^2}{dn^2}\ln W(n)\Big|_{\tilde{n}}\varepsilon^2$$

So $$W(n) \simeq W(\tilde{n}) \cdot \exp\left[\frac{1}{2}\frac{d^2}{dn^2}\ln W(n)\Big|_{\tilde{n}}\varepsilon^2\right]$$

Next $$\frac{d\ln W(n)}{dn} = \frac{d}{dn}\left(\ln\left[\binom{N}{n}p^n q^{N-n}\right]\right)$$

$$= \frac{d}{dn}\Big[\ln(N!) - \ln(n!) - \ln((N-n)!) + n\ln p + (N-n)\ln q\Big]$$

- **Note that** $\boxed{\frac{d}{dx}\ln x! \simeq \ln x}$ for large x

So $$\frac{d}{dn}\ln(W(n))\Big|_{\tilde{n}} = -\ln\tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q$$

Feb 20
2019

Recall

$$W(n) = W(\tilde{n}) \exp\left[\frac{1}{2}(n-\tilde{n})^2 \left.\frac{d^2 \ln W}{dn^2}\right|_{\tilde{n}} \right]$$

$$\left.\frac{d \ln W}{dn}\right|_{\tilde{n}} = -\ln \tilde{n} + \ln(N-\tilde{n}) + \ln p - \ln q$$

$e^{0} =$ ~~$(-p) * (N-\tilde{n}) \times q \times q$~~

$$e^{0} = e^{\ln\left(\frac{(N-\tilde{n})p}{\tilde{n} q}\right)}$$

$$\text{So} \quad 1 = \frac{(N-\tilde{n})p}{\tilde{n} q} \Rightarrow \boxed{\tilde{n} = \frac{Np}{p+q} = Np} \nearrow = E(n)$$

Now, evaluate $\left.\frac{d^2 \ln W}{dn^2}\right|_{\tilde{n}}$

$$\frac{d^2 \ln W}{dn^2} = \frac{d}{dn}\left(\frac{d \ln W}{dn}\right) = \frac{d}{dn}\left[-\ln n + \ln(N-n) + \ln p - \ln q\right]$$

$$= \left.\frac{-1}{n} - \frac{1}{N-n}\right|_{\tilde{n}} = \left.\frac{-N+n-n}{n(N-n)}\right|_{\tilde{n}}$$

$$\text{So} \quad \left.\frac{d^2 \ln W}{dn^2}\right|_{\tilde{n}} = \frac{-N}{\tilde{n}(N-\tilde{n})} = \frac{-N}{Np(N-Np)} = \frac{-1}{Np(1-p)}$$

$$\boxed{\left.\frac{d^2 \ln W}{dn^2}\right|_{\tilde{n}} = \frac{-1}{Npq}} \rightarrow < 0$$

Finally, we need $W(\tilde{n})$

$$\hookrightarrow W(\tilde{n}) = \frac{N!}{\tilde{n}!(N-\tilde{n})!} p^{\tilde{n}} q^{N-\tilde{n}} = ? \quad \text{For large } N\ldots$$

Use Stirling formula $\boxed{n! \simeq \sqrt{2\pi n}\; n^n e^{-n}}$ for $n >> 1$

So
$$W(\tilde{n}) = \frac{\sqrt{2\pi N}\; N^N e^{-N}}{\sqrt{2\pi Np}\,(Np)^{(Np)} e^{-Np} \cdot \sqrt{2\pi (N-Np)}\,(N-Np)^{N-Np} e^{-(N-Np)}} \cdot p^{Np} q^{Np}$$

$$= \ldots$$

$$\boxed{W(\tilde{n}) = \frac{1}{\sqrt{2\pi Npq}}} \rightarrow \text{max of a Gaussian of } \sigma^2 = Npq$$

Now
$$W(n) = W(\tilde{n}) \exp\left[\frac{1}{2}(n-\tilde{n})^2 \frac{d^2 \ln W}{dn^2}\Big|_{\tilde{n}}\right]$$

$$\boxed{W(n) = \frac{1}{\sqrt{2\pi Npq}}\, e^{-\frac{(n-Np)^2}{2Npq}}} \rightarrow \text{Gaussian Normal}$$

→ Random walk for large N.

$$W(n) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(n-E(n))^2/2\sigma^2}$$

Example large N. A penny is tossed 400 times
Find the probability of exactly 215 heads

$p = q = \frac{1}{2}$
$N = 400$
$n = 215$
$Np = 200$

$$W(215) = \frac{1}{\sqrt{2\pi\, 100}} \cdot \exp\left[-\frac{1}{2}\frac{(215-200)^2}{100}\right]$$

$$= 1.3\% \rightarrow \text{very unlikely?} \ldots$$

More generally,

$$\boxed{f(x)dx = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-\mu)^2}{2\sigma^2}} dx}$$

→ probability density function — PDF

$$\boxed{\int_a^b f(x)dx = P(a \le x \le b)}$$

If probability dist. that depends on more than 1 var

$P(u_i, v_i) = f(u_i) f(v_i)$ → as long as u, v independent

Gaussian integrals are difficult to evaluate analytically

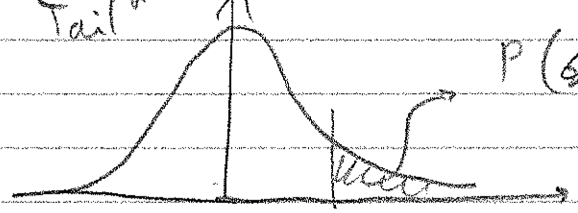
☒ But there 2 cases when we can have precise answers.

$$\int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

☒ But since it's symmetrical about $x = 0$

$$\hookrightarrow \int_0^{\infty} e^{-x^2} dx = \int_{-\infty}^{0} e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

☒ "Tail"



$$P(\overset{0 \le x \le u}{\cancel{x \le a}}) = erf(x) = \int_0^a e^{-x^2} dx \cdot \frac{2}{\sqrt{\pi}}$$

$$\Phi(x \ge a) = \cancel{\Phi} \; 1 - \Phi(a) = 1 - \int_{-\infty}^{a} \phi(u) dx$$

$\boxed{\text{Ex}}$ Town A has 2000 customers and they want to talk to town B. What is the minimum # lines needed such that at most 1% of town A's customers fail to have access to a line during the busiest hour of the day?

↳ Assume each caller is on the line for 2 mins in that hr randomly dist.

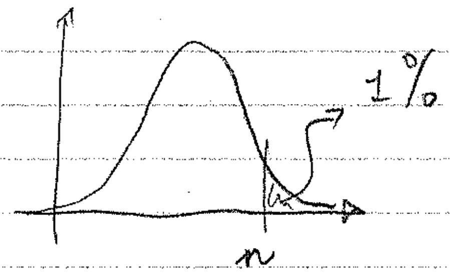
$N = 2000$ $\quad p = P(\text{line in use}) = \frac{2}{60} = \frac{1}{30}$

$n = \ ?$

$q = \frac{29}{30}$

$$W(n) = \frac{1}{\sqrt{2\pi Npq}} \exp\left[-\frac{1}{2}(n-Np)^2 \Big/ Npq\right]$$

Want



let $x = \left(\frac{1}{2}\frac{(n-Np)^2}{Npq}\right)^{1/2}$

$$\frac{dx}{dn} = \frac{d}{dn}\left[\frac{1}{\sqrt{2}}\frac{n-Np}{\sqrt{Npq}}\right]$$

$(n \simeq 85)$

Feb 22 2019

Back to Schroeder, Chap 2.

Terminology → $\boxed{\text{microstate}}$ → any individual outcome

↳ state of each individual particle in the system (order matters). $\Omega = 1$

↑ multiplicity

$\boxed{\text{Macrostate}}$ → more general description of the system

Has some multiplicity. Some microstates are indistinguishable

→ $\boxed{\text{multiplicity } \Omega}$ → the number of microstates in a macrostate

▨ Example

4 dice rolled ⇒ outcome $\underbrace{1\ 3\ 1\ 5}_{\text{microstate}}$

Macrostate could be system where we roll two 1s in 4 dice

multiplicity → $\Omega = \binom{4}{2} = 6$

▨ Note that small multiplicity implies highly ordered system.

vv large multiplicity implies disorder.

$\boxed{\text{Second Law of Thermodynamics}}$

↳ systems tend towards more disorder because multiplicity is higher

→ because these macrostates are more likely ...(?)

$\boxed{\Omega \text{ is related to Entropy}}$

▨ Two physical systems where we can count individual microstate

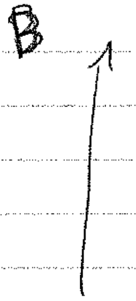
Ex (1) Two-state paramagnet → material in a $\vec{B}$ field

Individual dipoles line up in 1 or 2 states: aligned or anti-aligned.

Microstate → specified by stating direction of all individual dipoles.

macrostate → total # of dipoles that point up, $N_\uparrow$

$N = N_\uparrow + N_\downarrow$



dipoles

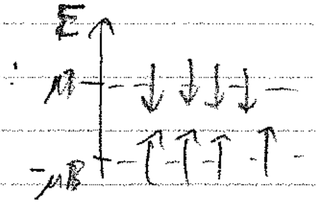
↑ ↑ ↓ ↓ ↑ ⤳ microstates..

↑ ↓ ↑ ↓ ↓ ⤴

Macrostates 5↓ + 5↑

μ → magnetic moment of individual dipole

only 2 allowed energy levels:



Total magnetic dipole moment

$$\hookrightarrow \vec{M} = \vec{\mu}\,(N_\uparrow - N_\downarrow)$$

or
$$\boxed{\vec{M} = \vec{\mu}\,(N_\uparrow - N + N_\uparrow) = \vec{\mu}\,(2N_\uparrow - N)}$$

Energy of single dipole $= -\vec{\mu}_i \cdot \vec{B} = \varepsilon_i \rightsquigarrow -\mu B$ for $\vec{\mu} \parallel \vec{B}$

So energy of paramagnet is

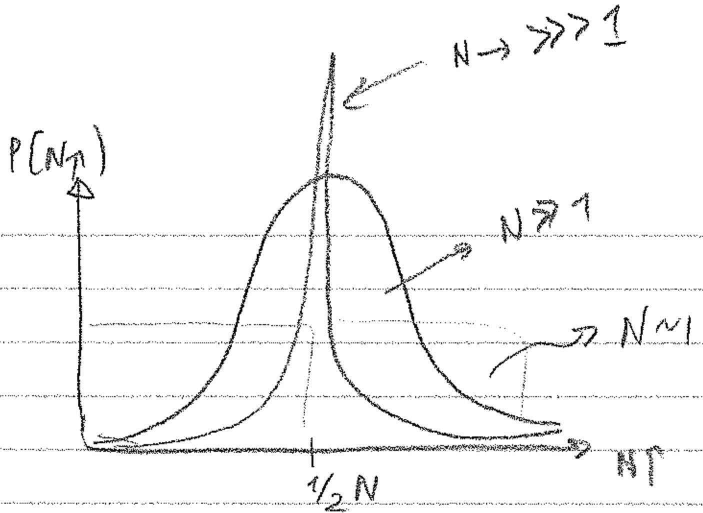
$$\boxed{U = -\vec{M} \cdot \vec{B} = \mu B\,(N_\downarrow - N_\uparrow)} \quad \nearrow \text{or } -2N_\uparrow + N$$

or
$$\boxed{U = \mu B\,(N - 2N_\uparrow)}$$

Calculate most probable energy $p = q = \frac{1}{2}$

$$\boxed{P(N_\uparrow) = \binom{N}{N_\uparrow} p^{N\uparrow} q^{N - N\uparrow} = \Omega(N\uparrow) \Big/ 2^N}$$

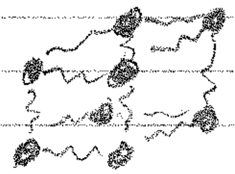
☒ As $N \to \infty$



So, random orientation of dipoles is most probable
$\rightarrow$ 2nd law of thermodynamics

there $P \propto \Omega$

▨ (2) Einstein's model of solid / bed spring model



N atoms which have 3N independent harmonic oscillators, which provide 6 degrees of freedom each. (per atom)
(1 KE + 1 PE) per spring."

Classical spring

$$U = \frac{1}{2}mv^2 + \frac{1}{2}kx^2 = KE + PE$$

$$= \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k(x^2 + y^2 + z^2)$$

↳ here we have "unlimited" energy spectrum", but a quantum oscillator → discrete energies that are allowed

$$\varepsilon_i = q_i hf = q_i \hbar\omega = q_i h\nu$$

- For N = 3 oscillators, the multiplicity of different energy levels

Osc	#1	#2	#3	ε	Ω
	0	0	0	0	1
	0	1	0	$h\nu$	3
	1	0	0	$h\nu$	
	0	0	1	$h\nu$	

# 1	# 2	# 3	ΣU	Ω
2	0	0	2hν	6
0	2	0		
0	0	2		
1	1	0		
1	0	1		
0	1	1		
	⋮		3hν	10
			~~4hν~~	

↳ General expression for multiplicity:

$\Omega \neq \binom{N}{q}$ Instead

$$\boxed{\Omega(\underset{\#\text{ oscillators}}{N},\underset{\text{units of energy}}{q}) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!}}$$

multiplicity of Einstein solid

//

eb 25, 2019

Heat flow & Irreversible Processes

Consider 2 Einstein solids that can interact

Solid A — Solid B

single atom{ $\underbrace{N_A = 3 \qquad N_B = 3}$ $\qquad U = qh\nu$

$$\left\{ \begin{array}{l} q = \text{total \# of energy quanta} = 6 = q_A + q_B \\ \text{So} \quad 0 \le q_A \le 6, \quad 0 \le q_B \le 6 \end{array} \right\}$$

$\boxed{\text{Multiplicity}}$ $\Omega = \binom{q+N-1}{q}$

Since A & B independent

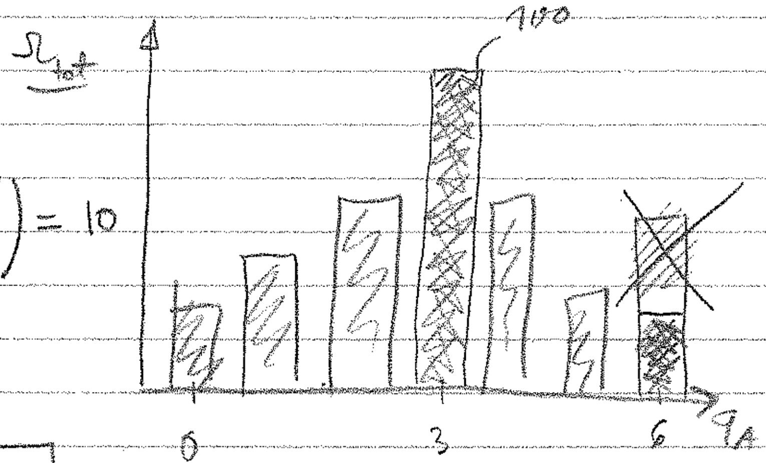
$\Omega_{tot} = \Omega_A \Omega_B$.

For A $\Omega_A = \binom{q_A+N_A-1}{q_A}$

For B

$\Omega_B = \binom{q_B+N_B-1}{q_B}$

☒ $\boxed{\Omega_{tot} = \Omega_A \Omega_B}$



$(q_A+q_B=6)$

$\boxed{\text{Ex}}$

$$\left.\begin{array}{l} \Omega_A(q_A=3) = \binom{3+3-1}{3} = 10 \\ \Omega_B(q_B=3) = 10 \end{array}\right.$$

$\boxed{\Omega_{tot} = \Omega_A \Omega_B = 100}$

☒ **Ex** $\Omega_A(q_A=6) = \binom{6+3-1}{6} = 28$

$\Omega_B(q_B=0) = \binom{0+3-1}{0} = 1$

So $\Omega_A \Omega_B = \Omega_{tot} = 28 \times 1 = 28$

Fundamental assumption in stat mech

{Any given microstate is equally probable. But some macrostates will be more probable than others because of higher multiplicity Ω}

☒ If you start out with a system near most likely macrostate, very unlikely that it will move far away from this distribution.

▨ **Ex** $N_A = 50$, $N_B = 50$, $q_{tot} = 50$

Case 1 $q_A = 50$, $q_B = 0$ $\longrightarrow \Omega_{tot} = \binom{100-1}{50}\binom{0+50-1}{0}$

Case 2 $q_A = q_B = 25$

$\hookrightarrow \Omega_{tot} \simeq \binom{25+50-1}{25}^2 = 1\times10^{39}$

$= \binom{99}{50}\binom{49}{0}$

$\simeq 5\times10^{28}$

So $q_A = 25 = q_B$ ← macrostate 20 billion times more probable than $q_A = 50$, $q_B = 0$.

Irreversible process

$\hookrightarrow$ energy flows from system A to system B, increasing the total Ω of the interacting system.

Restate 2nd Law of thermo

$\hookrightarrow$ { Systems in thermal equilibrium will be arranged with the highest amount of disorder }

(or)

{ Spontaneous flow of energy stops when a system is at or very near its most likely microstate greatest Ω }

irreversible
|||
not spontaneous

Large System

(s) • Small # → $(n<100)$

(l) • large # → Small # that are exponentiated 10^{23}

(L) • Very large # → large # that are exponentiated or large # in factorial ...

Ex $10^{10^{23}}$

Note some properties

(add) • $10^{23} + 23 \simeq 10^{23}$

(mult.) • $10^{10^{23}} \times 10^{23} = 10^{10^{23}+23} \simeq 10^{10^{23}}$

(Division) • $\dfrac{10^{10^{23}} \times 10^{23}}{10^{10^{23}}} = 10^{23}$

Manipulating large numbers $e^{10^{23}} \to \ln\left[e^{10^{23}}\right] = 10^{23}$

$$\to e^{10^{23}} \simeq 10^{4.34\times 10^{22}}$$

$e^{10^{23}}$ as $10^{x} \to 10^{23} = x\ln 10 \to x = 10^{23}/\ln(10) \sim 4.34\times 10^{22}$.

$\boxed{\text{Multiplicity of Einstein solid (large)}}$

↳ at high T $\Rightarrow q \gg N.$ ⇝ N large

$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \simeq \frac{(q+N)!}{q!\,N!}$$

Take the log

$$\ln\Omega = \ln\left[\frac{(q+N)!}{q!N!}\right] = \ln(q+N)! - \ln q! - \ln N!$$

☒ Use Stirling's formula: $N! \sim N^N e^{-N}\sqrt{2\pi N}$

↳ $\boxed{\ln(N!) \simeq N\ln N - N}$

So $\ln\Omega = (q+N)\ln(q+N) - (q+N) - [q\ln q - q] - [N\ln N - N]$

$=$

⟶ next page

So $\ln\Omega = (q+N)\ln(N+q) - N\ln N - q\ln q$

Rewrite $\ln(q+N) = \ln\left(q\left(1+\frac{N}{q}\right)\right) \rightarrow <<$

$= \ln q + \ln(1+N/q)$

$\simeq \ln q + \frac{N}{q}$

So
$$\ln\Omega \cong (q+N)\left[\ln q + \frac{N}{q}\right] - N\ln N - q\ln q \quad (q>>N)$$

$$= N\ln q + \cancel{\frac{N^2}{q}} - N\ln N + N \qquad \hookrightarrow \frac{N^2}{q} \simeq 0$$

So
$$\Omega = \exp\left[N\ln q - N\ln N + N\right]$$

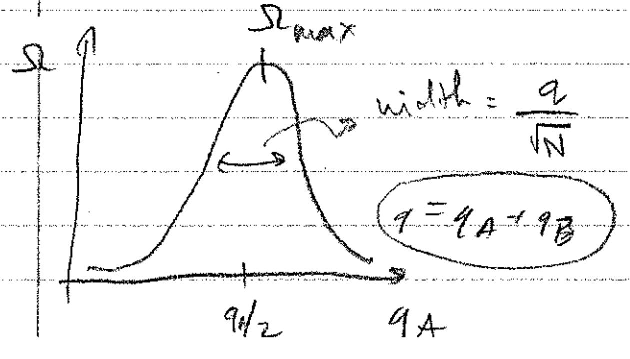
$$= \frac{e^{N\ln q}\,e^{N}}{e^{N\ln N}} = \frac{e^{N}\cdot q^{N}}{N^{N}} = \left(\frac{eq}{N}\right)^{N}$$

So
$(q>>N)$ $\boxed{\Omega = \left(\frac{eq}{N}\right)^{N}}$ ← total multiplicity of large Einstein solid in high temp limit, (like room temp)

Feb 26, 2019

$\rightarrow \Omega_{tot} = \Omega_A\Omega_B$

For interacting solids → $\boxed{\Omega = \Omega_{max}\, e^{-N(2x/q)^2}}$ ← Gaussian

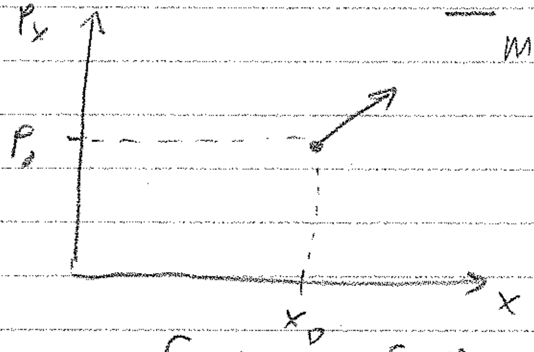


As N↑, the fluctuations away from the most likely macrostate become increasingly improbable.
→ Thermodynamic limit

Multiplicity of an ideal gas

★ Specify the state of a system in classical mechanics using phase space.

▨ If an object's position & momentum is known, we can predict it's position & momentum at any other time



Ex

$m\dot{x} = \vec{p} = cx$

We can determine $x(t)$ & $p(t)$ from initial conditions.

$$m\frac{dx}{dt} = cx \rightarrow \int_{x_0} \frac{m\,dx}{x} = \int c\,dt$$

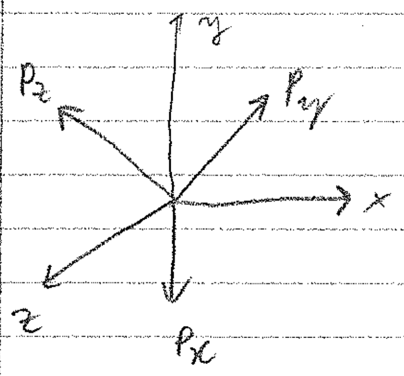
So $\ln\left(\frac{x}{x_0}\right) = \frac{c}{m}(t-t_0)$

So $\boxed{x(t) = x_0 e^{c/m(t-t_0)}}$

To get $p(t)$

$$\rightarrow p = m\dot{x} = m\cdot\frac{c}{m}x_0 e^{c/m(t-t_0)} = cx_0 e^{c/m(t-t_0)}$$

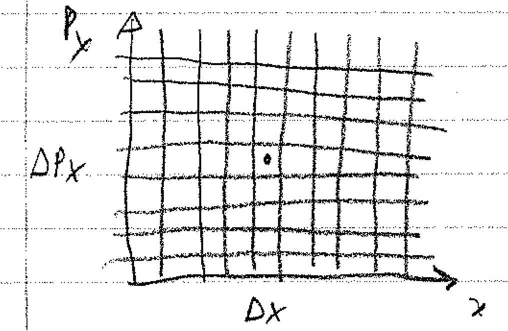
For particle in space



(x, y, z, p_x, p_y, p_z)

For N objects, we need 6N coordinates to describe its phase space.

☑ To describe state of system in phase space



particle located between x & $x+\Delta x$ and p_x & $p_x+\Delta p_x$

☑ Heisenberg Uncertainty principle

$$\Delta p\, \Delta x \geq \frac{\hbar}{2} \quad (?)$$

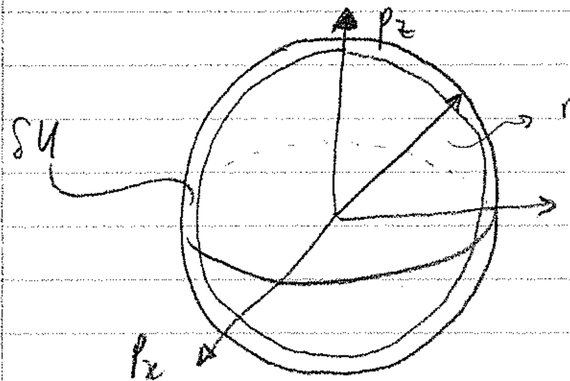
→ Let $\Delta x \Delta p = h$

☑ For a monatomic ideal gas, energy is all kinetic

$$U = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

So $\quad p = \sqrt{p_x^2 + p_y^2 + p_z^2} = \sqrt{2mU}$

→ In 3-D momentum space



inner radius $= \sqrt{2mU}$ outer radius $= \sqrt{2m(U+\delta U)}$

So

- $\Omega \propto V_x V_p$ → multiplicity of 1 particle

V_x: position volume; V_p: momentum volume

- And # states $\propto \dfrac{V_x}{\Delta x \Delta y \Delta z} \cdot \dfrac{V_p}{\Delta p_x \Delta p_y \Delta p_z}$

So

$$\boxed{\Omega(U) \propto \iiint_{U}^{U+\delta U} dx\, dy\, dz\, dp_x\, dp_y\, dp_z}$$

→ For N particles $\boxed{\Omega(U) \propto \int_{U}^{U+\delta U} \cdots\cdots \int d^3 r_1 \ldots d^3 r_N\, d^3 p_1 \ldots d^3 p_N}$

$d p_{Nx} d p_{Ny} d$ Pnz

Volume is independent, so

$$\Omega(u) \propto V^N \int_u^{u+\delta u} \cdots \int d^3p_1 \cdots d^3p_N$$

$$\propto V^N \int_{\sqrt{2mU}}^{\sqrt{2m(U+\delta U)}} \underbrace{p^{3N-1}}_{\text{"surface area"}} \cdot \underbrace{dp}_{\text{thickness}}$$

So $\Omega(u) \propto V^N \underbrace{\left(\sqrt{2mU}\right)^{3N-1}}_{\text{surface area}} \underbrace{\left[\sqrt{2m(U+\delta U)} - \sqrt{2mU}\right]}_{\text{thickness}}$

$$= V^N \sqrt{2mU}^{\,3N-1} \left[\sqrt{2mU}\sqrt{1+\frac{\delta u}{u}} - \sqrt{2mU}\right]$$

$$\Omega(u) \propto V^N \left(\sqrt{2mU}\right)^{3N} \left[\sqrt{1+\frac{\delta u}{u}} - 1\right]$$

- Taylor expand $(1+x)^n \sim 1 + nx \quad (x \ll 1)$

So $\Omega(u) \propto V^N \left(\sqrt{2mU}\right)^{3N} \cdot \left(\frac{\delta u}{2u}\right)$

So $\Omega(u) \propto V^N \left(\sqrt{2m}\right)^{3N} \cdot \frac{\delta u}{u}$

$$\Omega(u) \propto V^N u^{3N/2} \cdot (\delta u)\, u^{-1}$$

So $\Omega(u) \propto V^N u^{(3N/2 - 1)}\, \delta u$ → small number

· ignore u^{-1} as well...

So $\boxed{\Omega(u) \propto V^N u^{\frac{3}{2}N}}$

<u>More careful derivation gives</u>

$$\Omega(u) \simeq \frac{\pi^{3N/2}}{N!\, h^{3N} (3N/2)!} V^N \left(\sqrt{2mU}\right)^{3N}$$

→ multiplicity of monatomic ideal gas:

$\Omega \sim u^{(3/2)N}$

{ For general result → $\boxed{\Omega \sim u^{Nf/2}}$, f = # df for single particle }

Feb 27, 2019

Recall for monatomic ideal gas

$$\boxed{\Omega(u,V,N) \approx \frac{\pi^{3N/2}}{N!\; h^{3N}\;(3N/2)!}\, V^N \left(\sqrt{2mU}\right)^{3N}}$$

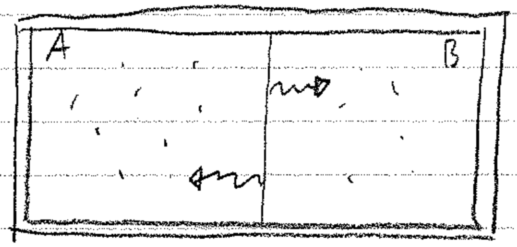
▨ Interacting ideal gas

{ assuming $A \neq B$ } ⇝

$$\boxed{\begin{aligned}\Omega_{tot} &= \Omega_A \Omega_B \\ &= [f(N)]^2 (V_A V_B)^N (u_A u_B)^{\frac{3N}{2}}\end{aligned}}$$

$\boxed{\text{3 ways to exchange multiplicity}}$

① Exchange energy



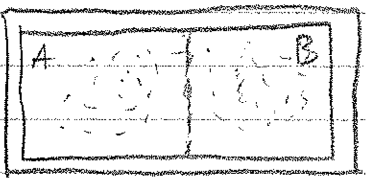
$(\Omega \sim u^{3N/2})$

▨ Width of peak in the multiplicity functions $\Omega_{tot} = \dfrac{u_{tot}}{\sqrt{3N/2}}$ and maximum u_{tot} is at $u_A = \frac{1}{2} u_{tot}$

② Exchange volumes via a movable partition

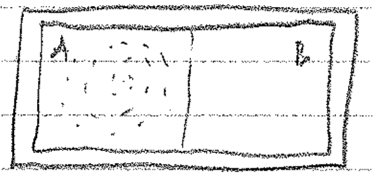
▨ Width of peak in $\Omega = \dfrac{V_{tot}}{\sqrt{N}}$ $(\Omega \sim V^N)$

③ Exchange particles via permeable membrane (membrane)



⇝ more complicated overall because of $f(N) = u(N)$

Consider specific case



Here $V_{tot} \downarrow \times 2$ → this reduces Ω_{tot} by 2^N

ENTROPY

$$\boxed{S \equiv k \ln \Omega}$$

where k is Boltzmann constant $= 1.38 \times 10^{-23}$ J/K
Ω is the multiplicity.

$$\boxed{2^{nd} \text{ Law of Thermodynamics}: \quad \Delta S \geq 0}$$

Note For interacting systems $\Omega_{tot} = \Omega_A \Omega_B$

$$S_{tot} = k \ln \Omega_{tot} = k \ln(\Omega_A \Omega_B)$$

$$= k \ln \Omega_A + k \ln \Omega_B$$

$$= S_A + S_B$$

So $\boxed{S_{tot} = S_A + S_B}$

☒ Spontaneous processes occur due to a net increase in entropy.

Entropy of an ideal gas

$$S = k \ln \Omega$$

$$= k \ln \left[\frac{\pi^{3N/2}}{N!\, h^{3N} (3N/2)!} V^N \left(\sqrt{2mU}\right)^{3N} \right]$$

Stirling's formula: $\ln N! \simeq N \ln N - N$

$$S = k \left[\frac{3N}{2} \ln \pi + N \ln V + \frac{3N}{2} \ln(2mU) - (N \ln N - N) - 3N \ln h - \left(\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right) \right]$$

$$= Nk \left[\frac{3}{2} \ln \pi + \ln V + \frac{3}{2} \ln(2mU) - (\ln N - 1) - 3 \ln h - \left(\frac{3}{2} \ln \frac{3N}{2} - \frac{3}{2} \right) \right]$$

$$\boxed{S = Nk \left\{ \ln \left[\frac{V}{N} \left(\frac{4\pi m U}{3Nh^2} \right)^{3/2} \right] + \frac{5}{2} \right\}}$$ → entropy of ideal monatomic gas

Sackur – Tetrode equation

300 K $\quad 10^5$ Pa

Ex Calc. S of 1 mole of He gas @ room temp & 1 atm.

Need V, N, U, m_{He}

$N \sim 10^{23}$

$V \sim \frac{RT}{P} \simeq 25\,\ell$

$m_{He} =$

$$U = \frac{3}{2} NkT = \frac{3}{2} \overset{1}{n} TR = 3700\ \text{J}$$

Got $\boxed{S_{He} \simeq 126\ \text{J/K}}$

☒ If we hold N & U fixed and allow V to change

$\rightarrow \quad S \sim Nk\ln(V) \qquad \Delta S = Nk\ln\left(\frac{V_f}{V_i}\right)$

So $\boxed{\Delta S = Nk\ln\frac{V_f}{V_i}}$ ⟿ { quasi-static isothermal expansion/compression }

Note $\boxed{\text{if } Q\uparrow \text{, then } \Delta S > 0}$

Mar 1, 2019

How entropy is related to the heat input to system Q?

Heat in = work done by system
= − work done on system.

$\Delta U = 0$ (isothermal) $\quad Q_{add} = W_{by} = -W_{on}$

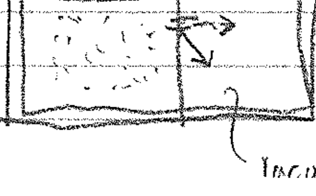
$$Q_{add} = -W_{on} = \int_{V_i}^{V_f} P(V)\,dV$$

$$= \int_{V_i}^{V_f} \frac{NkT}{V}\,dV = NkT\ln\left(\frac{V_f}{V_i}\right) = T\Delta S$$

So $\boxed{\Delta S = \frac{Q_{add}}{T}}$ ⇒ quasistatic isothermal

↳ more precisely $\boxed{dS = \frac{đQ}{T}}$

Free expansion – non quasistatic



n, T constant → $\Delta U = 0 = Q_{add} + W_{on}$

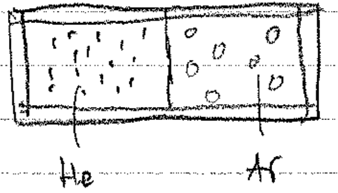
$Q_{add} = 0$ because no heat enters or leave system. So $W = 0$.

But there's an increase in entropy. Note can't use

$\Delta S = Q/T$ because the eq describes quasistatic isothermal

☒ $\boxed{\text{Entropy of mixing}}$

↳ Consider



Know $S_{tot} = S_A + S_B$

- Now, remove partition & let gases mix. How does S change?

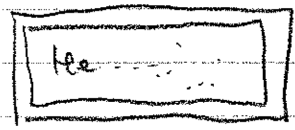
Back to S-T eqn: $S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$

$$\begin{cases} \text{He: } N \text{ const}, \ U \text{ const}, \ V' = 2V \\ \text{Ar: same thing.} \end{cases}$$

$$\Delta S = Nk\ln(2)\big|_{He} + Nk\ln(2)\big|_{Ar}$$

$\boxed{\Delta S = 2Nk\ln(2)}$ ← entropy of mixing (different gases

Consider (same gas)



Adding Ar to cylinder... with same N & U as He
→ expect $S\uparrow$ by a factor of 2

If we add He instead (at same energy) → same temperature

$$\left.\begin{aligned} &S = Nk\left[\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2} + \frac{5}{2}\right] \\ &V \text{ const} \quad N' = 2N \\ &U = \frac{3}{2}kNT \to U' = 2U \end{aligned}\right\}$$

$$S' = 2S_{He} + 2Nk\ln\left(\frac{1}{2}\right)$$

$$= 2S_{He} + \underbrace{\left(-2Nk\ln(2)\right)}$$

$$\boxed{S' = 2S_{He} \quad \Delta S_{mixing}}$$ → don't just get $S' = 2S$

Gibbs's PARADOX → why does distinguishability matter?

solution:
particle have
to be distinguishable

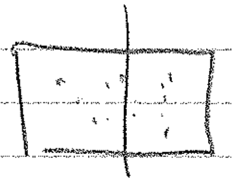
Recall
$$\Omega_N \simeq \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}\left(\sqrt{2m\theta}\right)^{3N}$$

$$\hookrightarrow \ln\Omega_N \sim \ln\left(1/N!\right) \rightsquigarrow -(N\ln N - N)$$

What if we're able to distinguish particles in gas → no $\frac{1}{N!}$
because order matters

$$\boxed{S = Nk\ln\left[V\left(\frac{4m\theta}{3Nh^2}\right)^{3/2} + \frac{3}{2}\right]}$$ → distinguishable

Consider



container with indistinguishable particles. Add a partition,

$N\downarrow \times 2$, $V\downarrow \times 2$, $V\downarrow \times 2$

So $\frac{1}{2}S^{new} = \frac{1}{2}S_{original} + \frac{1}{2}Nk\ln(1/2)$

$\frac{1}{2}S^{new} = \frac{1}{2}S_{original} - \frac{1}{2}Nk\ln(2)$ → decrease in entropy

↳ get decrease in entropy

Reversible vs Irreversible process

- ○ A process is irreversible if $\Delta S > 0$
- ○ A process is reversible if $\Delta S = 0$

→ need to be Quasistatic process.

↳ can be reversible, but don't have to be.

☒ All reversible processes are quasistatic. But not all quasistatic processes are reversible

$[\text{Reversible} \subsetneq \text{Quasistatic}]$

☒ Spontaneous heat flow is always irreversible

$\Omega\uparrow \quad S\uparrow$

☒ "Reversible heat flow"

System in $\Omega_{max} \exists$ thermo equilibrium

ΔT → Infinitesimal change in temperature.

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Mar 4, 2019

CHAPTER 3: RELATIONSHIP BETWEEN ENTROPY , TEMPERATURE

☒ Simple interacting system of 2 Einstein solids

N_A = 3 oscillators
$N_B = 2$
$q = 6$

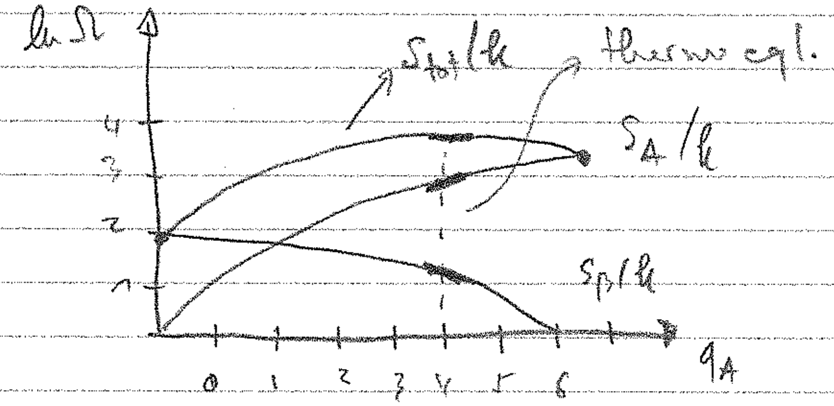
$$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!\,(N-1)!}$$

$$S = k \ln \Omega$$

So $\frac{S}{k} = \ln \Omega$

	$N_A = 3$			$N_B = 2$			
q_A	Ω_A	S_A/k	q_B	Ω_B	S_B/k	Ω_{tot}	S_{tot}/k
0	1	0	6	7	1.9	7	1.9
1	3	1.1	5	6	1.8	18	2.9
2	6	1.8	4	5	1.6	30	3.4
3	10	2.3	3	4	1.4	40	3.7
4	15	2.7	2	3	1.1	45	3.8
5	21	3.0	1	2	0.7	42	3.7
6	28	3.3	0	1	0	28	3.3

☒ Plot of $\ln \Omega$ versus E.



$\frac{\partial S_{tot}}{\partial q_A} = 0$, then we get maximum entropy

$\rightarrow$ condition for thermodynamic equilibrium

Recall $U_A = q_A \cdot (\text{constant})$

So $\frac{\partial S_{tot}}{\partial q_A} = 0 \leftrightarrow \frac{\partial S_{tot}}{\partial U_A} = 0$ at eql.

Now, $S_{tot} = S_A + S_B \Rightarrow \partial S_{tot} = \partial S_A + \partial S_B$

So $\frac{\partial S_{tot}}{\partial U_A} = \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0$ So $\boxed{\frac{\partial S_A}{\partial U_A} = \frac{-\partial S_B}{\partial U_A} \text{ at eq.}}$

Note $U_{tot} = u_A + u_B$ ← U_{tot} is conserved

$$\rightarrow \partial u_{tot} = 0 = \partial u_A + \partial u_B \rightarrow \partial u_A = -\partial u_B$$

So, we get $\boxed{\frac{\partial S_A}{\partial u_A} = \frac{\partial S_B}{\partial u_B}}$

Note when q_A is small ⇒ $\frac{\partial S_A}{\partial u_A}$ steep. → entropy of system A is increasing faster than entropy of B is decreasing

→ Spontaneous ~~heat~~ energy flow.

Energy flows to object with steeper S vs U slope

The steeper the slope the lower the temperature.

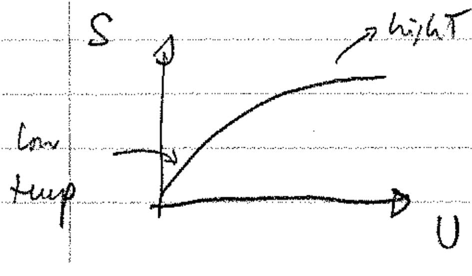
Units of S → J/K
Units of U → J } $T = \frac{\Delta U}{\Delta S} \equiv \frac{\partial U}{\partial S}$

Definition of temperature

$$\boxed{T^{-1} = \frac{\partial S}{\partial U}}$$ → N, V constant

* * *

Patterns in S vs U graphs.



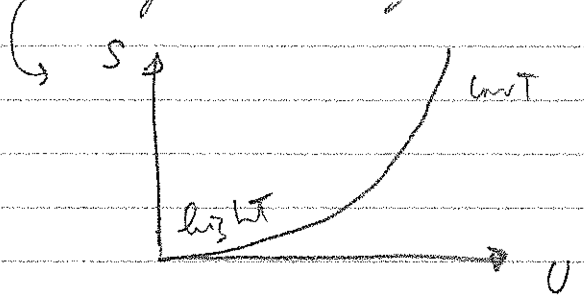
concave down → In most systems, as U↑, T↑ which means ... slope of $\left(\frac{\partial S}{\partial u}\right)_{N,V}$ decreases

Recall $\Delta U = Q_{add} + \cancel{W_{on}}$ (assume V constant)

$q_{add} = C\Delta T$

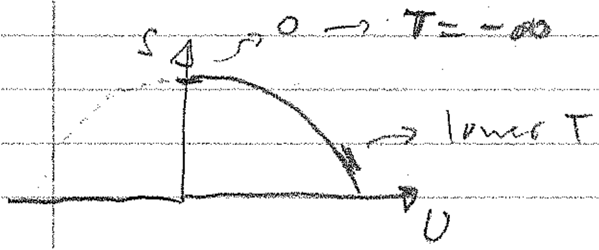
So $\Delta U = C\Delta T$ ⇝ makes sense

▨ However, there are systems with negative heat capacity (gravitationally bound)



concave up S-U graph

▨ **Ex** Concave down with negative slope ...



Ex paramagnet. $U = \mu B(N_\downarrow - N^\uparrow)$

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \text{negative} \rightarrow \boxed{\text{negative temperature}}$$

▨ **Example** Relationship between S, U, T

① large Einstein solid at high temp limit ⇝ $q \gg N \gg 1$

$$\Omega = \left(\frac{eq}{N}\right)^N$$

So $S = k\ln\Omega = Nk\ln\left(\frac{qe}{N}\right) = Nk + Nk\ln\left(\frac{q}{N}\right)$

Let $u = \varepsilon_0 q$

So $S = Nk\left[\ln\left(\frac{u}{N\varepsilon}\right) + 1\right]$

$= Nk\ln\left(\frac{u}{N\varepsilon}\right) + Nk$

$= Nk\ln u - Nk\ln(\varepsilon N) + Nk$

$\to \frac{1}{T} = \left(\frac{\partial S}{\partial u}\right)_{N,V} = \frac{Nk}{u} - 0 + 0$

So $T = \frac{u}{Nk}$ Recall $u = \frac{f}{2}NkT$

or $\boxed{u = NkT}$ $f = 2$ because SHO has 2 dofs.

② Ideal gas (monatomic)

$S = Nk\left(\ln\left[\frac{V}{N}\left(\frac{4\pi m u}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right)$ → constants kill by ln( )

$T = \left(\frac{\partial S}{\partial u}\right)^{-1}_{N,V} = \left[Nk \cdot \cancel{\frac{V}{N}}\cancel{\left(\frac{4\pi m}{3Nh^2}\right)^{3/2}} \cdot \frac{3}{2}\frac{1}{u}\right]^{-1}$

$T = \left(\frac{3}{2}Nk\frac{1}{u}\right)^{-1} \to \boxed{u = \frac{3}{2}NkT}$

Entropy & Heat Capacity

Mar 5, 2019

Recall: $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N}$

$$\left.\begin{aligned} &1^{st}\text{ law}\quad \Delta U = Q_{add} + W_{on} \\ &\text{if } V \text{ constant} \rightarrow W_{on} = 0 \end{aligned}\right\} \Rightarrow \Delta U = Q_{add}$$

Now $T = \left(\frac{\partial S}{\partial U}\right)^{-1} \Rightarrow dS = \frac{dU}{T}$ with constant volume

$$= \frac{Q}{T} \quad \text{so} \quad \boxed{dS = \frac{dQ}{T}}$$

But recall $dQ = C_V dT$

So $\boxed{dS = C_V \frac{dT}{T}} \rightarrow \int dS = \int C_V \frac{dT}{T}$ / if temp range is small → C_V constant

$$\Rightarrow \boxed{\Delta S = C_V \ln\left(\frac{T_f}{T_i}\right)}$$

☑ Example 6 Heat a cup of H_2O (200g) from 20°C to 100°C. Calculate how much entropy increases? $c_V = 1\,cal/gK = 4.186\,J/gK$

$$\Delta S = 4.186 \frac{J}{gK} \cdot (200g) \ln\left(\frac{373}{293}\right)$$

$$\simeq 200\, J/K$$

In terms of $\frac{\Omega_2}{\Omega_1} \rightarrow \Delta S = k \ln \frac{\Omega_2}{\Omega_1} \rightarrow \Omega_2 = e^{S/k}\Omega_1$

$$\rightarrow \Omega_2 = e^{200 J/K / 1.38\times10^{-23} J/K}\,\Omega_1$$

$$\boxed{\Omega_2 = e^{1.5\times10^{25}}\,\Omega_1}$$

☒ Total entropy of the system

$$\Delta S = S_f - S_{(T=0)} = \int_0^{T_f} \frac{C_v}{T}\,dT$$

But we need C_v at $T=0$. Guess that $S(0) \to 0$

$$\boxed{\text{Third Law of Thermodynamic}}$$

↳ Planck's Formalism. As $T \to 0$, entropy goes to its minimum value

↳ Note this is only true for crystalline solids

Another way to state 3rd law $\boxed{\text{As } T \to 0,\ C_v \to 0}$

Ex ideal gas $C_v = \frac{3}{2}Nk \to 0$ as $T \to 0$

☒ Macroscopic view of Entropy $\Rightarrow \boxed{dS = \frac{dQ}{T}}$

☆ Example The sun heating the surface of the Earth

~1000 W/m². $T_\odot = 6000K$

$T_\oplus = 300K$

Estimating entropy created in 1 year by the flow of heat to the Earth's surface.

$$\Delta S_\odot = \frac{Q}{T} = \frac{(-1000 J/s)(60^2)(24)(365)}{6000K \cdot 1m^2} = -1.75 \times 10^6 J/K$$

$$\Delta S_\oplus = \frac{Q}{T} = \frac{(-1000J/s)(60^2)(24)(765)}{300K \cdot 1m^2} = +3.5 \times 10^7 J/K$$

$$\Delta S_{tot} = \Delta S_{\odot} + \Delta S_{\oplus} \simeq 7.3 \times 10^{7}\ J/K\,m^2$$

▨ Suppose we plant grass on this 1 m^2 area. Does the decrease in entropy violate the 2nd law?

On 1 m^2 → maybe 10kg of grass. Let's say grass = C
$M = 12 g/mol$

Say 1200 g of grass

→ $N = 1000 N_A$ C atoms/m^2

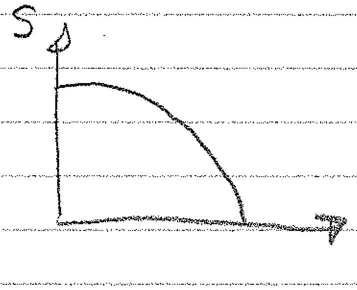
To assemble grass out of smaller molecules.

$$S \sim Nk \sim nR = 1000R \simeq 1000\,\text{mol} \cdot 8.31\ J/mol\,K$$

$$\rightarrow S \cong 10^4\ J/K \ll \Delta S_{\oplus}$$

▨ Paramagnetism 1) Ω 2) S 3) T 4) $U(T)$ 5) C_V

Recall



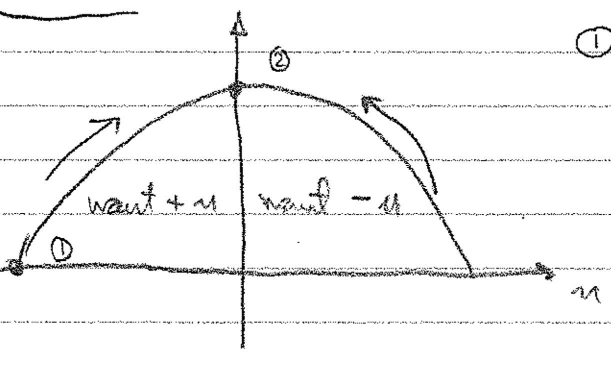
For paramagnets

$$U = \mu B(N_{\downarrow} - N_{\uparrow})$$
$$= \mu B(2N_{\downarrow} - N)$$

Question: how do U, M depend on temperature

$$M = \mu(N_{\uparrow} - N_{\downarrow}) = \frac{-U}{B}$$

(★) (1) Get Ω



① all N are $N_{\uparrow}$ } ⇒ low T, positive
S vs U → steep }
→ wants to absorb U

② $N_{\downarrow} = N_{\uparrow} = \frac{1}{2}N$. Max entropy
$U = 0$. If it absorbs U
→ S vs U has (−) slope

Temp of paramagnet ① $u =$ negative but $\frac{\partial S}{\partial u} =$ positive

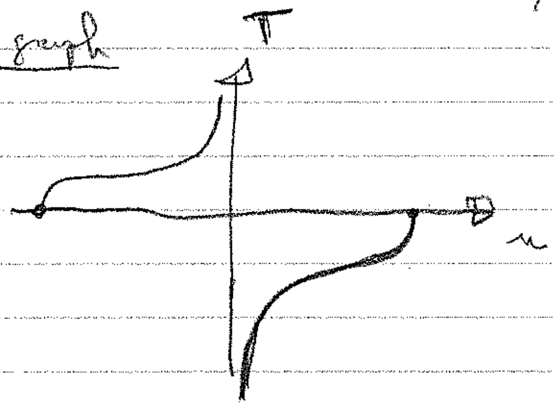
$T\uparrow$ as $u\uparrow$

② $u =$ positive but $\frac{\partial S}{\partial u} =$ negative

$T\downarrow$ as $u\uparrow$

→ system wants to give off energy

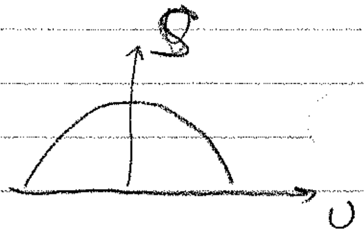
Temp graph



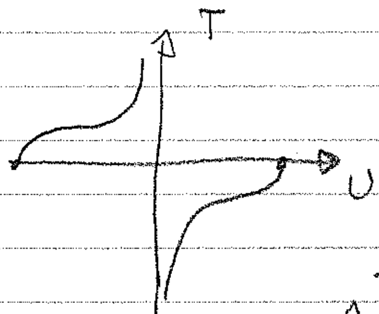
$$\boxed{\text{Recall } \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}}$$

Mar 6, 2019

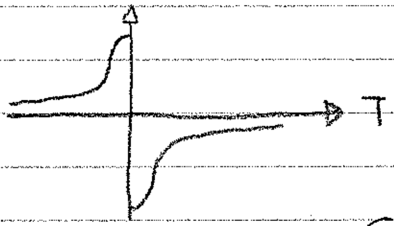
Recall paramagnet has a "weird" S-U graph:



So T vs U looks like

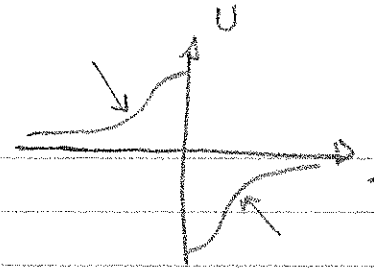


Flip the axes →



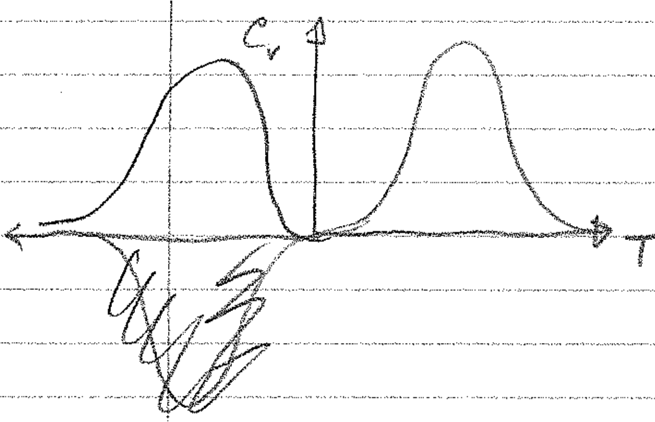
Recall $\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}}$ → **So**

$$\begin{cases} C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = 0 \text{ when } T = 0 \\ C_V = 0 \text{ when } T = \pm\infty \end{cases}$$



▨ There's also an inflection points

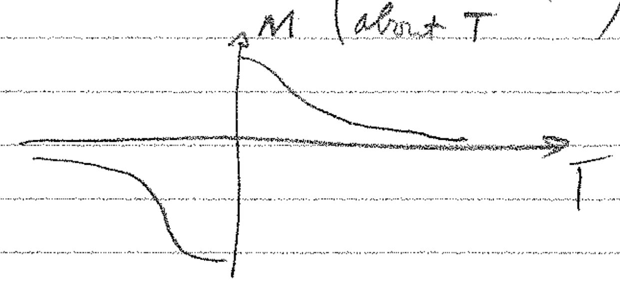
- Consider (positive) temperatures only



magnetism

And recall $M \propto -U$ (reflection of U about T)

So



Analytic solutions to paramagnets

Recall

$$\Omega = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!} \quad \text{assume } N >>> 1$$

$$S = k\ln\Omega = k\left(\ln(N!) - \ln(N_\uparrow!) - \ln((N-N_\uparrow)!)\right)$$

Stirling's approx $\ln N! \sim N\ln N - N$

So
$$\frac{S}{k} = (N\ln N - \cancel{N}) - (N_\uparrow \ln N_\uparrow - \cancel{N_\uparrow}) - (\cancel{N}-N_\uparrow)\ln(N-N_\uparrow) + (\cancel{N} - \cancel{N_\uparrow})$$

$$= N\ln N - N_\uparrow \ln N_\uparrow - (N-N_\uparrow)\ln(N-N_\uparrow)$$

Now $\left(\frac{1}{T}\right) = \left(\frac{\partial S}{\partial U}\right)_{N,B}$ and $U = \mu B(N - 2N_\uparrow)$

So
$$\left(\frac{\partial S}{\partial U}\right) = \left(\frac{\partial S}{\partial N_\uparrow}\right)\left(\frac{\partial N_\uparrow}{\partial U}\right) = (-2\mu B)^{-1}\left(\frac{\partial S}{\partial N_\uparrow}\right) = \frac{-1}{2\mu B}\left(\frac{\partial S}{\partial N_\uparrow}\right)$$

Now
$$\left(\frac{\partial S}{\partial N_\uparrow}\right) = k\left[-\ln N_\uparrow - \cancel{1} + \ln(N-N_\uparrow) + \cancel{\frac{N-N_\uparrow}{N-N_\uparrow}}\right]$$

$N_\uparrow = \frac{1}{2}\left(N - \frac{u}{\mu B}\right)$

So $$\left(\frac{\partial S}{\partial N_\uparrow}\right) = k\left[-\ln\left(\frac{1}{2}\left(N - \frac{u}{\mu B}\right)\right) + \ln\left(N - \frac{1}{2}N + \frac{u}{2\mu B}\right)\right]$$

$$= \ldots$$

$$\boxed{\frac{\partial S}{\partial N_\uparrow} = k \ln\left(\frac{N + u/\mu B}{N - u/\mu B}\right)}$$

So $$\left(\frac{\partial S}{\partial U}\right) = \frac{\partial S}{\partial N_\uparrow}\frac{\partial N_\uparrow}{\partial U} = \frac{k\ln}{-2\mu B}\left(\frac{N + u/\mu B}{N - u/\mu B}\right) = \frac{1}{T}$$

So $$\boxed{\frac{1}{T} = \frac{k}{2\mu B}\ln\left(\frac{N - u/\mu B}{N + u/\mu B}\right)} \qquad T(u)$$

So we can solve for $u(T)$

$$\frac{2\mu B}{kT} = \ln\left(\frac{N - u/\mu B}{N + u/\mu B}\right)$$

$$e^{2\mu B/kT} = \frac{N - u/\mu B}{N + u/\mu B} = \frac{1 - u/N\mu B}{1 + u/N\mu B}$$

So $$e^{2\mu B/kT} + \frac{u}{N\mu B}e^{2\mu B/kT} = 1 - \frac{u}{N\mu B}$$

So $$\frac{u}{N\mu B}\left(e^{2\mu B/kT} + 1\right) = 1 - e^{2\mu B/kT}$$

So $$u(T) = N\mu B\,\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}}$$

Now, simplify $\longrightarrow$ use $\sinh(x) = \frac{1}{2}(e^{x} - e^{-x})$, $\cosh(x) = \frac{1}{2}(e^{x}+e^{-}$

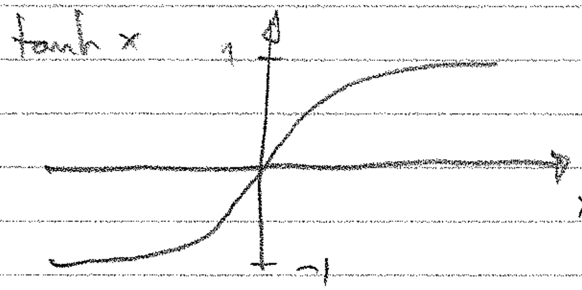
So $\tanh x = \frac{e^{x}-e^{-x}}{e^{x}+e^{-x}} = -\left(\frac{1-e^{-2x}}{1+e^{-2x}}\right)$

So $-\tanh x = \frac{1-e^{-2x}}{1+e^{-2x}}$

So let $x = \left(\frac{\mu B}{kT}\right)$, then

$$\boxed{\begin{aligned} U(T) &= -\mu B N \tanh\left(\frac{\mu B}{kT}\right) \\ M(T) &= +N\mu \tanh\left(\frac{\mu B}{kT}\right) \end{aligned}}$$

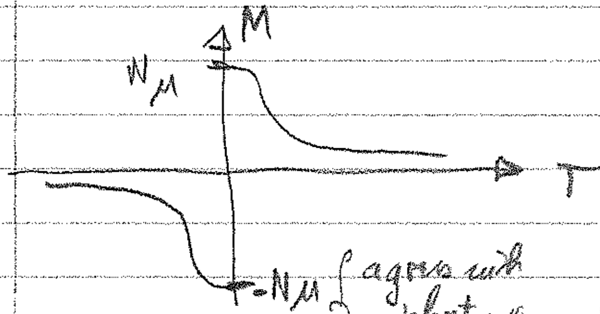
with $M = -\frac{U}{B}$



as $x \to 0$, $\tanh x \to 0$

☐ $x = \frac{\mu B}{kT}$, $T \to \pm\infty$

$\to$ $M, U \to 0$



☐ $x \to \infty$, $\to T \to 0_{+}$

$\tanh x \to 1$ $\to$ $M = N\mu$

☐ $x \to -\infty$, $T \to 0_{-}$

$\tanh x \to -1$ $\to$ $M = -N\mu$

{ agrees with what we predicted...

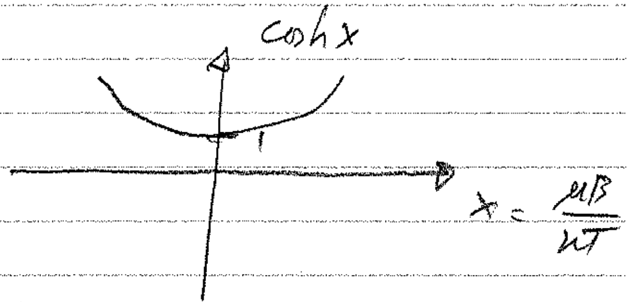
$\boxed{\text{What about heat capacity of paramagnet?}}$

$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B}$. Now, $U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$

Recall $\frac{d}{dx}\tanh(u) = \operatorname{sech}^2(u)\cdot\frac{du}{dx} = \frac{1}{\cosh^2(u)}\frac{du}{dx}$ $\Bigg\} \Rightarrow$

$$\left(\frac{\partial U}{\partial T}\right)_{N,B} = -N\mu B \,\mathrm{sech}^2\left(\frac{\mu B}{kT}\right)\left(\frac{-\mu B}{kT^2}\right) = C_B$$

So
$$\boxed{C_B = \frac{Nk\left(\frac{\mu B}{kT}\right)^2}{\cosh^2\left(\frac{\mu B}{kT}\right)}}$$

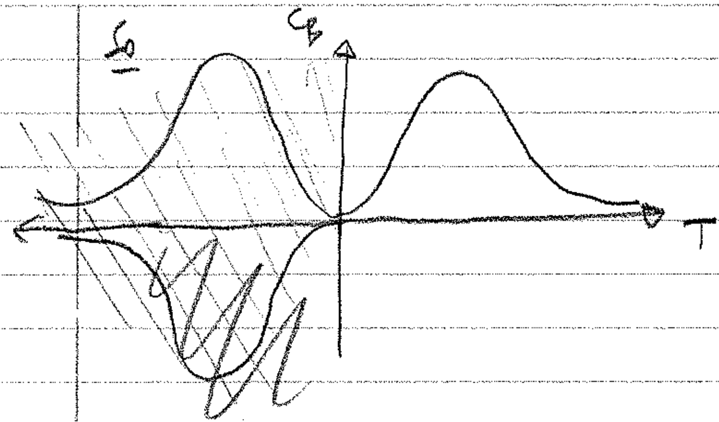


⊙ as $x \to 0$, $T \to \pm\infty$ $\cosh(x) = 1$
$\to \boxed{C_B \Rightarrow 0 \text{ as } T \to \pm\infty}$

⊙ as $x \to \infty$, $T \to 0_+$, $\cosh(x) \to +\infty$ (faster)

So $\boxed{C_B \to 0 \text{ as } T \to 0}$

So



Ex Consider two-state paramagnet.

Let $\mu = \mu_B$ Bohr magneton $\mu_B = \frac{eh}{4\pi m_e} = \frac{e\hbar}{2m_e}$

Let $\vec{B} = 1\,T$

$\simeq 5.788\ eV/T$

$\simeq 9.274 \times 10^{-24} J/T$

Then $M = ?$
$$\left.\begin{array}{l}\mu B = 5.8 \times 10^{-5}\ eV \\ kT = \frac{1}{40}\ eV\end{array}\right\} \to \frac{\mu B}{kT} \ll 1$$

Now $\tanh(x) \simeq x$ for small x

$\to \boxed{M \simeq (N\mu)\left(\frac{\mu B}{kT}\right) = \frac{N\mu^2 B}{kT}}$ → true in "high-temperature" limit.

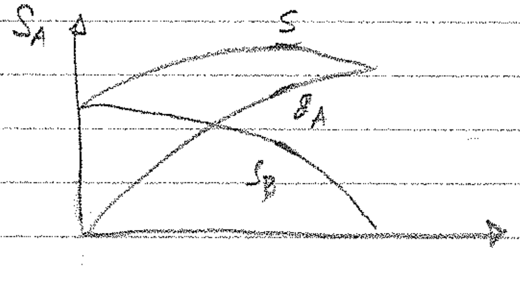
$\boxed{\text{Get}}$ $M \propto \frac{1}{T}$ → Curie's Law (Pierre Curie)
(high temp limit)

$\boxed{\text{Get}}$ $C_B \propto \frac{1}{T^2}$ → (high temp limit)

Mar 8, 2019

MECHANICAL EQUILIBRIUM

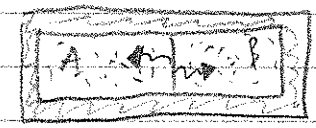
we're been discussing dU and dS



So get

at thermal Eq $\frac{\partial S_{tot}}{\partial U} = 0 \Rightarrow \boxed{\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}}$ ↗ conserved U

Consider some interacting system that can exchange volume as well as energy



→ changes in V governed by changes in P

→ changes in U governed by change in T

as $U\uparrow, \Omega\uparrow, S\uparrow$
$V\uparrow, \Omega\uparrow, S\uparrow$

Goal develop a relationship between $\frac{\partial S}{\partial V}$ and P

Just like dS_{tot}/dU gives thermal equilibrium

$\boxed{\frac{\partial S_{tot}}{\partial V} = 0}$ → mechanical equilibrium

So $\frac{\partial S_{tot}}{\partial V_A} = 0 \Rightarrow \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$

$\Downarrow$ $\qquad\qquad\qquad \Uparrow$

$\frac{\partial S_{A}}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0$, but $\partial V_A = -\partial V_B$

} volume is conserved

mech. equil.

What are being held constant $\Rightarrow \boxed{\left(\frac{\partial S_A}{\partial V_A}\right)_{U_A,N_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{U_B,N_B}}$

Dimensional analysis.

$$\frac{[S]}{[V]} = \frac{J/K}{[m^3]} = \frac{N\cdot m/K}{m^3} = \frac{N}{m^2}\cdot\frac{1}{K} = \frac{[P]}{[T]}$$

Guess $\boxed{\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}}$

☑ Look at ideal monatomic gas ... $\Omega = f(N)\,V^N U^{3N/2}$

$$S = k\ln\Omega = k\left[\ln f(N) + \ln V^N + \ln U^{3N/2}\right]$$

$$= k\left[\ln f(N) + N\ln V + \frac{3N}{2}\ln U\right]$$

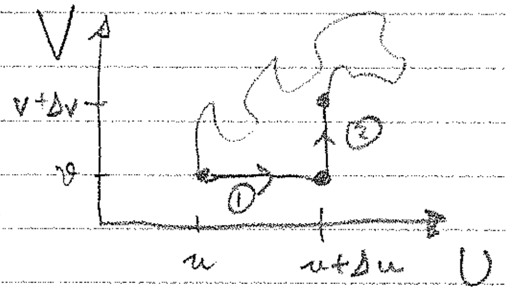
if $P \overset{?}{=} T\left(\frac{\partial S}{\partial V}\right)_{U,N}$, then

$$\overset{?}{=} T\,k\,.\,N\,.\,\frac{1}{V}$$

$\Rightarrow P \overset{?}{=} \frac{NkT}{V}$ works ...

$\boxed{PV = NkT}$ ✓

We'd like to combine both of these relations for thermal and mechanical equilibrium.



$\boxed{\text{Entropy is an exact differential}}$

↳ path independent.

$$\Delta S_{tot} = \Delta S_1 + \Delta S_2$$

① Isochoric process → volume constant ...

② Isothermal process → temp constant or energy ...

$$\boxed{\Delta S_{tot} = \left(\frac{\partial S}{\partial U}\right)\Delta U + \left(\frac{\partial S}{\partial V}\right)\Delta V}$$

So $S(\underset{\substack{\uparrow \\ T}}{U}, \underset{\substack{\uparrow \\ \text{vol}}}{V}, \underset{\substack{\uparrow \\ \#\,\text{part.}}}{N})$

$$\partial S_{tot} = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV$$

$$= \frac{1}{T}\,dU + \frac{P}{T}\,dV$$

So

$$\boxed{dU = TdS - PdV} \longrightarrow \text{thermodynamic identity}$$

↑ as long as N is constant.

Note this is just the first law of thermo.

$$dU = dW_{on} + dQ$$

{ For quasi-static processes → $W_{on} = -PdV$

{ For quasi-static isothermal process → $\Delta S = \dfrac{Q}{T} \rightarrow dQ = TdS$

So $\boxed{Q = TdS}$ → for any quasi-static process. <u>Not just</u> isothermal

$$dU = TdS - PdV$$ ← more fundamental.

☑ Now, if $u = u(S,V)$ and dU exact, then

$$\frac{\partial^2 u}{\partial V \partial S} = \frac{\partial^2 u}{\partial S \partial V}$$ order of diff. doesn't matter.

<u>Then</u> $$du = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_{S} dV$$

$$du = TdS - PdV$$

<u>Then</u> $$\left(\frac{\partial}{\partial V}\right)_S \underbrace{\left(\frac{\partial u}{\partial S}\right)_V}_{T} = \left(\frac{\partial}{\partial S}\right)_V \underbrace{\left(\frac{\partial U}{\partial V}\right)_S}_{-P}$$

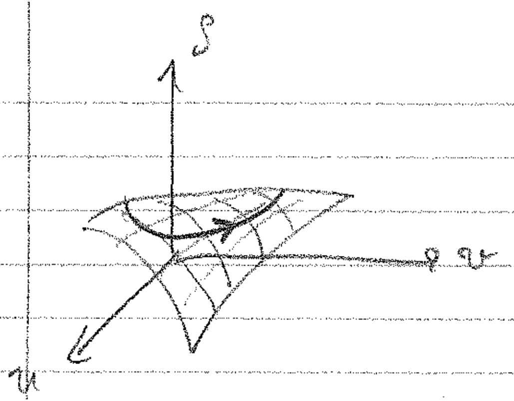
<u>So</u> $$\boxed{\left(\frac{\partial}{\partial V}\right)_S T = -\left(\frac{\partial}{\partial S}\right)_V P}$$ ← maxwell's relation

☑ $\boxed{\text{Constant Entropy process?}}$

If we have <u>quasi-static</u> process & <u>adiabatic process</u> (no heat
(P equilibrates) leave system)

→ no change in Entropy

$Q = TdS = 0$ } → "Isentropic" { quasi static
adiabatic



$$dU = TdS - PdV$$

$$\boxed{TdS = 0 = dU + PdV}$$

$dS_{tot} = 0$ but $\frac{\partial S}{\partial U} \neq 0 \neq \frac{\partial S}{\partial V}$

☑ Recall $C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{V,N}$

$$Q = C_V \Delta T = TdS$$

So $\Delta S = \int \frac{C_V}{T} dT$ But we want to look at constant pressure processes

$\boxed{(\Delta S)_P = \int \frac{C_P}{T} dT}$ → more useful in many cases...

☑ Example 1L of air (N_2 & O_2) at 1 atm. Heat air until it doubles in volume —
What is ΔS?

Diatomic gas $C_V = \frac{f}{2} Nk$

$$C_P = C_V + Nk$$

For diatomic gas at room temp. $f = 5$

So $C_P = \frac{7}{2} Nk$

Ideal gas law → $PV = NkT$ → $Nk = \frac{PV}{T} = \frac{(10^5\,\text{Pa})(1 \times 10^{-3}\,\text{m}^3)}{300\,\text{K}}$

$= \frac{1}{3}$ J/K

$P\overset{\uparrow \times 2}{V} = NkT$

So $T' = 2T$

So $(\Delta S)_p = \int \frac{C_p}{T} dT = C_p \ln \frac{T_f}{T_i} = C_p \ln(2)$

So $(\Delta S)_p = C_p \ln(2) = \left(\frac{7}{2}Nk\right) \ln(2) \simeq 0{,}81$ J/k

Another way to do this

↳ $dU = TdS - PdV$

↓

$$\frac{5}{2}kN\,dT = TdS - \frac{NkT}{V}dV$$

~~$\frac{5}{2}kN = T\frac{dS}{dT} - NkT$~~

$$\frac{5}{2}kN\frac{dT}{T} = dS - \frac{Nk}{V}dV$$

So

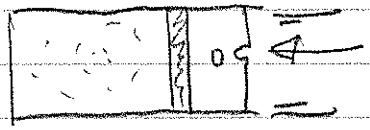
$$\Delta S = \frac{5}{2}kN \ln\frac{T_f}{T_i} + Nk\ln\left(\frac{V_f}{V_i}\right)$$

$$\boxed{(\Delta S)_p = \frac{7}{2}kN\ln(2)}$$

Nov 11, 2019

Recall $\boxed{dU = TdS - PdV}$ → can be used for non-quasi-static processes

① Fast compression



$dV \sim 0$. We have done work but work is greater than $-PdV$

$$dU = TdS - PdV = Q + W$$

So $Q < TdS$ → $\boxed{dS > \frac{Q}{T}}$ → added entropy

② Free-expansion

→ vacuum → allow gas expand into vacuum

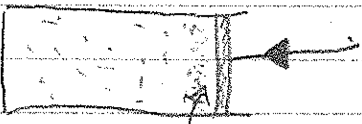
$W = 0$, $Q = 0$ so $dU = 0$ ↓ unquasi static

but $dU = TdS - PdV = 0 \Rightarrow TdS = PdV > 0$ $(W \neq PdV)$

↳ we added entropy

Example Fast compression of air at $P = 1\,atm$, $T = 300K$

$= 10^5\,Pa$



$F = 2000N$

$n = \frac{1}{25}\,mol$

$A = 0.01\,m^2$ $V = 1L$

Say piston moves 1mm before it stops...

- If this is quasi-static $W = \int PdV = \int -\frac{NkT}{V}\,dV = NkT\ln\frac{V_i}{V_f}$

$$W = nR\ln\frac{V_i}{V_f}$$

$V_i = \frac{1.00\,L}{1000}$, $V_f = \frac{1.00}{1000} - (0.001)(0.01)$

Work actually done

$$W = Fd = (2000N)\,(0.001)m = 2\,J$$

$> -PdV$

Fast compression Adiabatic → $Q = 0$

$$\rightarrow \Delta U = Q + W = 0 + W = 2J$$

How does S change? $dU = TdS - PdV$

$$\Delta S = dS = \frac{dU + PdV}{T} = \frac{2J + (10^5\,Pa)(-0.01\,m^2)(0.001\,m)}{300\,K} \simeq \frac{1}{300}\frac{J}{K}$$

Diffusive Equilibrium

Thermal equil → T same
Mech equil → P same
Diffusive equil → N same (μ)

assume <u>same gas</u>

Assume V constant. Assume that gases can exchange energy and particles. Assume same gas on both sides...

$$U_{tot} \; \& \; N_{tot} = \text{fixed}$$

$$S_{\cancel{tot}} = S(U_A, N_A)$$

<u>Before</u>

- $\left(\frac{\partial S_{tot}}{\partial U_A}\right)_{N,V} = \left(\frac{\partial S_{tot}}{\partial U_B}\right)_{N,V} = 0$ at thermal equilibrium.

- $\left(\frac{\partial S_{tot}}{\partial N_A}\right)_{U,V} = \left(\frac{\partial S_{tot}}{\partial N_B}\right)_{U,V} = 0$ at diffusive eql.

- $\left(\frac{\partial S_A}{\partial N_A}\right)_{U,V} = \left(\frac{\partial S_B}{\partial N_B}\right)_{U,V} = 0$ at equilibrium.

<u>Rather</u> not N, but μ

→ $\boxed{\mu : \text{Chemical potential } (\mu) \text{ has units of energy } [J]}$

Relating $\underset{\uparrow \atop J/K/\#}{\frac{\partial S}{\partial N}}$ to $\underset{\uparrow \atop J}{\mu}$

$\underline{\delta}$ $\left(\frac{\partial S}{\partial n}\right)$ multiply by temperature + set μ

$$\boxed{\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}}$$

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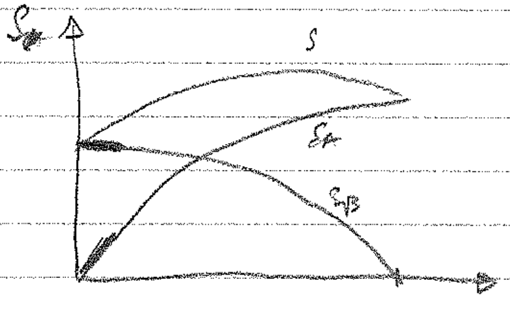
At equilibrium $\mu_A = \mu_B$. Consider S vs. N



→ particles will flow from system with lower $\partial S/\partial N$ to high $\frac{\partial S}{\partial N}$

Since, Larger $\left(\frac{\partial S}{\partial N}\right)$ → smaller μ.

→ particles flow from system with high to low μ

μ → concentration / density of gas...

Generalized Thermodynamic Identity

$S = S(U,N,V)$

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV$$

$$= \frac{1}{T} dU + \frac{-\mu}{T} dN + \frac{P}{T} dV$$

So $TdS = dU - \mu dN + PdV$

So $$\boxed{dU = TdS + \mu dN - PdV}$$

if quasi-static... → "heat" "chem work" "mech work"

When U, V constant → $\mu = -T\left(\frac{\partial S}{\partial N}\right)$ } ΔE due to change in N

When, S, V constant → $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$

Normally, to keep $\Delta S = 0$, if we $\uparrow N$, need to $\downarrow U$

e.g. Einstein solid w/ $N = 3$, $q = 3$

$$\Omega = \binom{3+2-1}{3} = 10$$

Then

$S = k \ln \Omega$. If we $\uparrow N$ by 1, $N = 4$

$$\text{Then } \Omega' = \binom{4+3-1}{3} = 20 \qquad S'' = k \ln 20 > S.$$

to keep S constant $\rightarrow$ need to decrease q $\rightarrow q = 2$

$$\Omega'' = \binom{4+2-1}{2} = 10 \text{ so that } S'' = S$$

$$\left.\begin{array}{l} \Delta U = q_f \varepsilon - q_i \varepsilon = 2\varepsilon_i - 3\varepsilon_i = -\varepsilon \\ \Delta N = 1 \end{array}\right\} \text{ So } \frac{\partial U}{\partial N} = -1$$

$$\text{So } \mu = -\left(\frac{\partial U}{\partial N}\right)_{S,V} = \frac{-1\varepsilon}{1} = -\varepsilon$$

Mar 18, 2019

$\boxed{\text{Chemical potential of ~~ideal~~ gas}}$ (monatomic)

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \qquad S = Nk\left[\ln\left(V\left(\frac{4\pi m U}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right]$$

$$\mu = -T\left\{k\left[\ln\left(V\left(\frac{4\pi m U}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \cancel{\frac{5}{2}}\right] + \cancel{Nk}\left[0 - \cancel{\frac{5}{2}}\frac{1}{\cancel{N}}\right]\right\}$$

$$\boxed{\mu = -Tk \ln\left[\frac{V}{N}\left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right]} \qquad \text{But } U = \frac{3}{2}NkT$$

So $$\boxed{\mu = -Tk \ln\left[\underbrace{\frac{V}{N}}_{\downarrow\ \frac{kT}{P}}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]}$$

Ex for He at room temp ~ 1 atm. → $\boxed{\mu = -0.32\ \text{eV}}$

higher μ → higher concentration → more likely to give off particles

What about for a mixture of gases?

$$\mu_1 = -T\left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2} \rightarrow S_{total}$$

$$\mu_2 = -T\left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1}$$

Thermo identity ⇒ $\boxed{dU = TdS - PdV + \sum_i \mu_i dN_i}$

In diffusive equilibrium → $\mu_{1A} = \mu_{1B}$, $\mu_{2A} = \mu_{2B}$, ...
where { A, B → systems
1, 2, ... → species of atoms/molecules

Notes Chemists use $\mu = -T\left(\frac{\partial S}{\partial n}\right)_{U,V}$ → # moles $n = N/N_A$

▨ In a mixture of ideal gases, each μ_i behaves as if the other species weren't present. At constant partial pressure

$$\boxed{P_i = x_i P}$$

Define mole fraction → $x_i = \frac{N_i}{N_{tot}}$

Now $P_i = x_i P = x_i \dfrac{N_{tot} kT}{V} = \dfrac{N_i}{N_{tot}} \dfrac{N_{tot} kT}{V} = \boxed{N_i \dfrac{kT}{V} = P_i}$

☒ Now, consider 2 gases A & B → mixture occupying the same volume V

$$S_{tot} = S_A + S_B = S(U_A, V, N_A) + S(U_B, V, N_B)$$

if we hold U constant at equilibrium, then this is the same as holding U_A & U_B constant.

$$\boxed{\mu_A = -T\left(\frac{\partial S_{tot}}{\partial N_A}\right)_{U,V,N_B} = -T\left(\frac{\partial S_A}{\partial N_A}\right)_{U,V}} \qquad (\text{since } \partial S_B = 0)$$

same as if B not present

Chemical Potential of A Large Einstein Solid

(a) $$\Omega = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} = \frac{(q+N)!\,N}{(q+N)\,N!\,q!}$$

note $(N-1)! = \dfrac{N!}{N}$

Stirling's approximation → $N! \simeq N^N e^{-N}\sqrt{2\pi N}$

$$\Omega \simeq \frac{(q+N)^{q+N} \cancel{e^{-q-N}} \sqrt{2\pi(q+N)}}{(q+N)} \cdot \frac{N}{q^q \cancel{e^{-q}} \sqrt{2\pi q}\, N^N \cancel{e^{-N}} \sqrt{2\pi N}}$$

$$\simeq \frac{(q+N)^{q+N}}{q^q N^N} \sqrt{\frac{N}{2\pi q(q+N)}}$$

$\simeq 1$

$$\simeq \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N \sqrt{} \simeq \boxed{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}$$

$\simeq$

So $S = k\ln\Omega = q\cancel{k}\ln\left(\frac{q+N}{q}\right) + Nk\ln\left(\frac{q+N}{N}\right)$

$$\boxed{S = kq\ln\left(1+\frac{N}{q}\right) + Nk\ln\left(\frac{q}{N}+1\right)}$$

So $\frac{\partial S}{\partial N} = kq\frac{1}{1+N/q}\cdot\frac{1}{q} + k\ln\left(\frac{q}{N}+1\right) + Nk\frac{1}{1+\frac{q}{N}}\cdot\left(\frac{-q}{N^2}\right)$

$$\boxed{\frac{\partial S}{\partial N} = k\ln\left(1+\frac{q}{N}\right)}$$

↗ chemical potential of a large Einstein solid

Now $$\boxed{\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = -kT\ln\left(1+\frac{q}{N}\right)}$$

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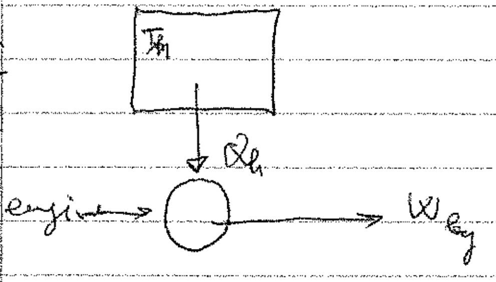
ur 15, 2019

Ch. 4 HEAT ENGINE & REFRIGERATOR

Concept → absorb Q & convert to mechanical W

Consider



Design considerations

① ↳ Want to start & end at the same macrostate (energy)

⟹ Cyclic on PV diagram

So $\Delta U = 0$

② Must obey 1st law of Thermodynamics

$$\boxed{\Delta U = Q_{absorb} - W_{by}}$$

③ Must obey 2nd law of of thermodynamics $\boxed{\Delta S \geq 0}$

- It turns out that it is impossible to convert 100% of absorb Q into usable work because we have heat flow.

→ Look at entropy of system

For reversible engine, want $\Delta S_{engine} = 0$

$$\Delta S_{reservoir} = \frac{-Q_h}{T_h} \geq 0$$

1st law

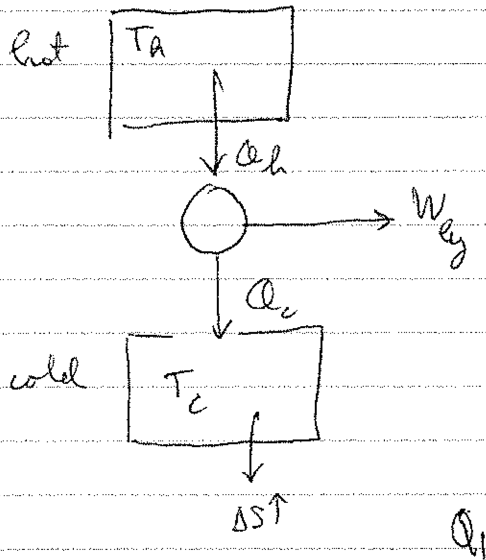
$$\underbrace{\Delta U}_{0} = Q_{abs} - W_{by} \Rightarrow Q_{abs} = W_{by}$$

So $\Delta S_{system} = \Delta S_{engine} + \Delta S_{reservoir} = -\frac{Q_h}{T_h} = \frac{-W_{by}}{T_h} \geq 0$

But then W_{by} has to be negative ...

→ Result: cannot build an engine with a single reservoir that converts heat into work

☒ To fix this



- Assume cyclic engine $\Delta U = 0$

Then $\underbrace{\Delta U_h}_{} - \underbrace{\Delta U_c}_{} = 0$

$$Q_h - Q_c - W_{by} = 0$$

So $\boxed{W_{by} = Q_h - Q_c}$ → work done by the engine.

Q_h = Q absorbed by the ~~heat~~ engine
W_{by} = W done by engine.
Q_c = Q expelled by the engine

Efficiency

$$\boxed{e = \frac{W_{by}}{Q_{abs}} = \frac{W_{by}}{Q_h}}$$

Recall

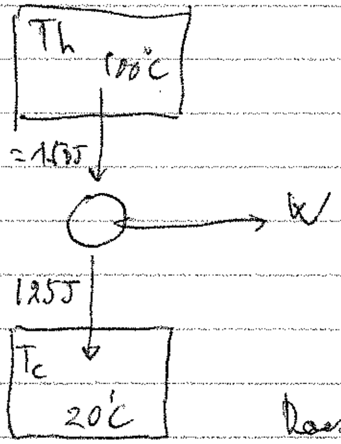
$$\boxed{e = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}}$$

$$\Delta S_{\substack{hot\\res}} = \frac{-Q_h}{T_h}, \quad \Delta S_{\substack{cold\\res}} = \frac{Q_c}{T_c}$$

So $\boxed{\frac{Q_c}{T_c} \geq \frac{+Q_h}{T_h}}$ for $\Delta S \geq 0$

So $\boxed{e \leq 1 - \frac{T_c}{T_h}}$

Example



Assume $\Delta u = 0$

$W = \underbrace{150J - 125J}$ = 25J

$Q_{abs} = Q_h - Q_c$

$e = \frac{W_{by}}{Q_h} = \frac{25}{150} = \frac{1}{6}$

Does this engine reach maximum eff.?

Max $e = 1 - \frac{T_c}{T_h} = 1 - \frac{20+273}{100+273} = 21.4\%$

So

No, doesn't reach maximum efficiency.

Carnot Cycle → towards a more efficient engine

- To avoid creating excess entropy in an engine.

  $T_{engine} = T_h$ → not possible.

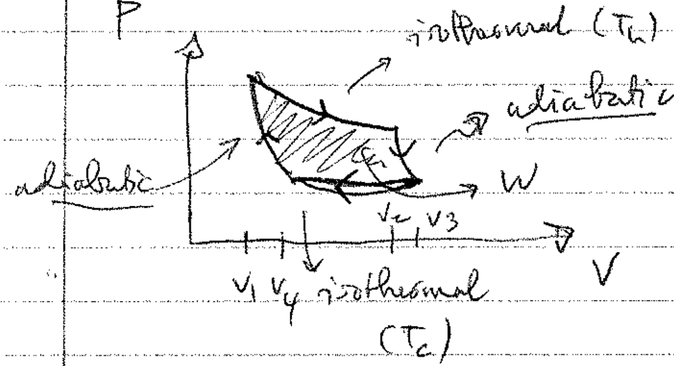
Instead, we want ~~T_{engine}~~ just slightly below T_h

⇒ Let it expand isothermally to keep $T_{engine} \sim$ constan

- after isothermal expansion → bring temp of engine down to ~~T_c~~ ↘ ($T_{engine} > T_c$ slightly)

→ Want [adiabatic expansion] (to avoid additional heat flow)

↳ expel waste heat during an isothermal compression.



Carnot Cycle

(1) Isothermal expansion @ T_h
(2) Adiabatic expansion to get T_c
(3) Isothermal compression @ T_c (waste heat dump)
(4) Adiabatic compression to bring engine back to T_h.

(1) $Q_h = W_{by} = \int_{V_1}^{V_2} P\,dV = \int_{V_1}^{V_2} \frac{NkT_h}{V}\,dV = NkT_h \ln \frac{V_2}{V_1}$

$(V_3 > V_4)$ $Q_c = -\int_{V_3}^{V_4} P\,dV = -NkT_c \ln\left(\frac{V_4}{V_3}\right) = NkT_c \ln\left(\frac{V_3}{V_4}\right)$

So $e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)} \cdot \frac{T_c}{T_h}$

Now, for adiabatic processes

$\hookrightarrow VT^{f/2} = \text{constant}$

So $V_3 T_c^{f/2} = V_2 T_h^{f/2}$ & $V_4 T_c^{f/2} = V_1 T_h^{f/2}$

So $\frac{V_3 T_c^{f/2}}{V_4 T_c^{f/2}} = \frac{V_2 T_h^{f/2}}{V_1 T_h^{f/2}} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \frac{\ln(V_3/V_4)}{\ln(V_2/V_1)}$

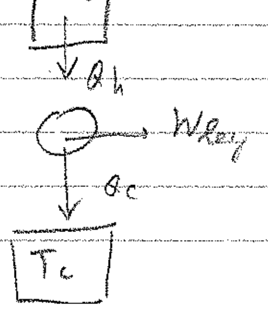
So $\boxed{e = 1 - \frac{T_c}{T_h}}$ ⤳ assuming adiabatic.

→ Carnot cycle produces max efficiency.

* * *

Nov 18, 2019 **Heat Engines**

Recall



Cyclic process → $\Delta U = 0$

$W_{by} = Q_{in} - Q_{out}$

$e = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{W_{by}}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$

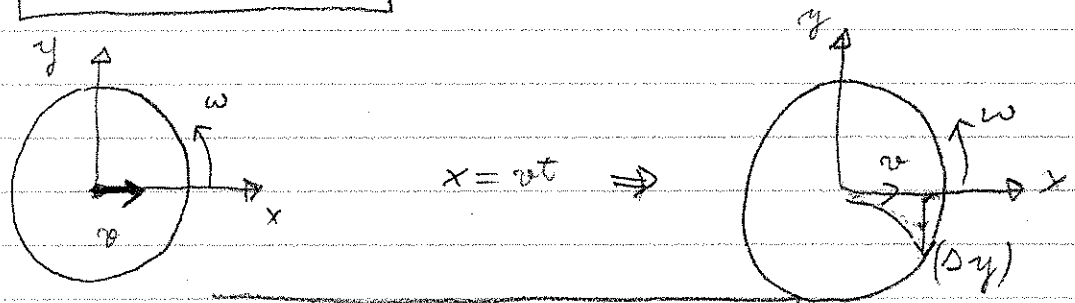
Since $\Delta S \geq 0$, so $e \leq 1 - \frac{T_c}{T_h}$ equality holds when Carnot engine

Hurricanes as Heat Engines

Hot reservoir → ocean surface
Cold reservoir → atmosphere.

→ Low pressure system with circulation due to Coriolis effect

$$\boxed{F_c = 2mv \times \omega}$$



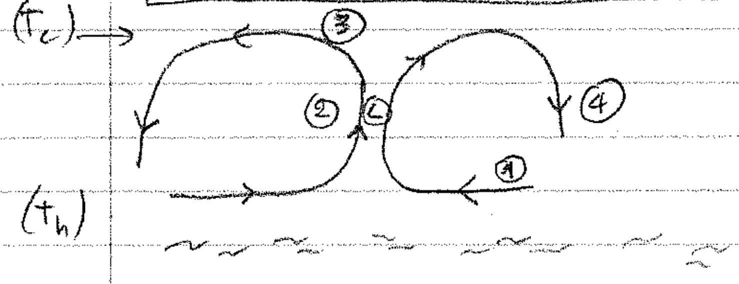
if $v \perp \omega$, then
$$\Delta y = (\omega t)\, x$$

Coriolis acceleration

But since $x = vt$ → $\boxed{\Delta y = \omega v t^2 = \frac{1}{2}\underbrace{(2\omega v)} t^2 = \frac{1}{2} a_c t^2}$

Steps of Hurricane engine

→ same as Carnot's...



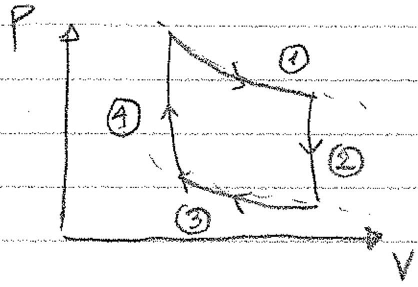
(1) Isothermal expansion of air over hot ocean ($T \simeq 300K$)

(2) Adiabatic expansion
→ air moves rapidly up eyewall up to tropopause

(3) Isothermal compression in tropopause ($T \simeq 200K$)

(4) Adiabatic compression of dry air

On PV diagram



Work produced by Hurricane dissipated by friction

$$\boxed{W = F_{drag} \cdot x} \longrightarrow \propto v^2 \text{ (turbulent flow)}$$

So $\frac{dW}{dt} = (av^2)v \simeq av^3$

Heat transfer from the ocean by forced convection. $Q_h \propto v$

So Total: $Q_h = \underbrace{av^3}_{Q \text{ due to friction}} + bv \rightsquigarrow Q_{ocean}$

So

$$\boxed{e = \frac{W_{by}}{Q_{abs}} = \frac{av^3}{av^3+bv} = 1 - \frac{T_c}{T_h}} \rightsquigarrow \text{Carnot engine}$$

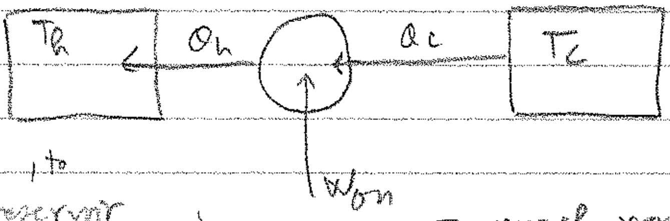
⇒ Can solve for v.

$$\frac{av^2}{av^2+b} = 1-\frac{T_c}{T_h} \Rightarrow av^2 = (av^2+b)\left(1-\frac{T_c}{T_h}\right) = av^2\left(1-\frac{T_c}{T_h}\right) + b\left(1-\frac{T_c}{T_h}\right)$$

$$\text{So} \quad av^2\left(\frac{T_c}{T_h}\right) = b\left(1-\frac{T_c}{T_h}\right)$$

$$\boxed{v = \sqrt{\frac{b}{a}\left(\frac{T_h}{T_c}-1\right)}}$$

Refrigerator



Work done on substance, to pull heat out of cold reservoir → expel waste heat to heat reservoir.

Now, $\Delta U = 0 \Rightarrow \boxed{\underbrace{Q_c + W_{on}}_{\text{compression work.}} = Q_h}$

Coefficient of Performance

$$\boxed{COP = \frac{Q_c}{W_{on}}} \quad \text{replace } W_{on} = Q_h - Q_c$$

So $$\boxed{COP = \frac{Q_c}{Q_h - Q_c} = \frac{1}{Q_h/Q_c - 1}} \geq 1$$

☒ By 2nd law, $\Delta S \geq 0 \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0$ So, $\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c}$

So $$\boxed{COP = \frac{1}{Q_h/Q_c - 1} \leq \frac{1}{T_h/T_c - 1}}$$

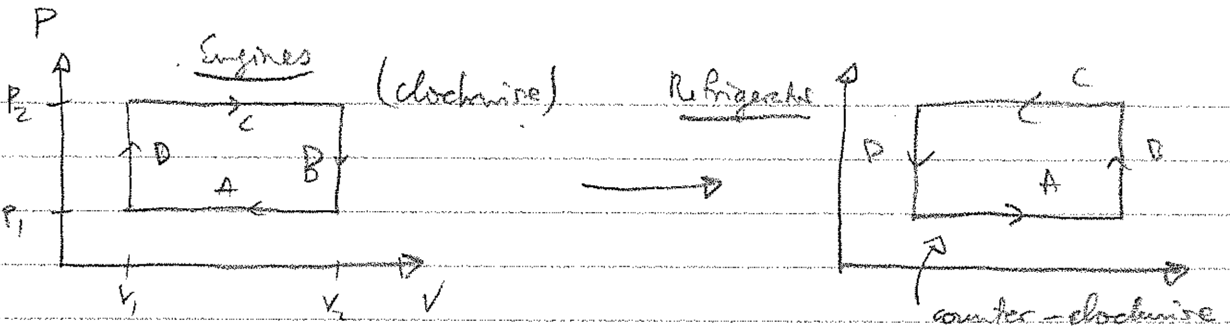
☒ Carnot cycle once again creates the most efficient refrigerator

Need $\begin{cases} T \geq T_h & \text{during heat expulsion} \\ T \leq T_c & \text{during heat absorption} \end{cases}$

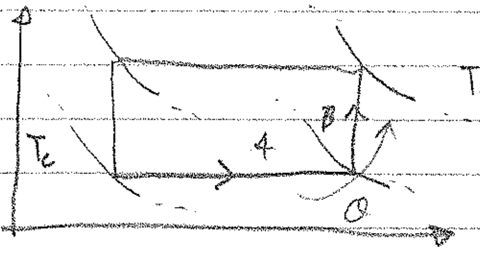
Example What is the max possible COP for a standard AC unit?

Let $T_{in} = 22^\circ C$, $T_{out} = 30^\circ C$ Then $COP_{max} = \frac{1}{\frac{30+273}{22+273} - 1} \simeq 36.9$

PV diagram



But



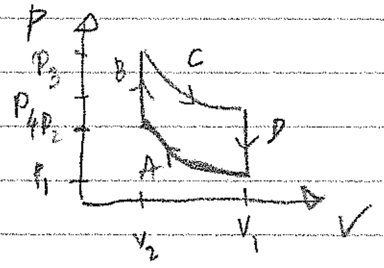
Need $T_c > T_h$ for heat flow A, B } not going to work
and $T_h < T_c$ for heat flow C, D

⇒ Need adiabatic processes.

Nov 19, 2019

Real Heat Engines

Example Internal Combustion Engine (Otto cycle)



A, C → adiabats.

A: adiabatic compression of air + fuel
B: spark plug ignites the mixture, increasing T, P, holding V constant
C: adiabatic expansion inside cylinder due to high pressure
D: Hot exhaust is expelled and replaced by new mixture at lower temperature

Efficiency of this engine?

$$e = 1 - \frac{Q_c}{Q_h}$$ Steps A & C are adiabatic $\rightarrow Q = 0$

B $\rightarrow Q_h$

D $\rightarrow Q_c$

Step B $\Delta U_B = Q + \cancelto{0}{W} \Rightarrow Q = \frac{f}{2} NkT = \frac{f}{2} PV = \frac{f}{2} V_2 (P_3 - P_2)$

Step D $\Delta U_D = Q_c + \cancelto{0}{W} = -\frac{f}{2} NkT \Rightarrow Q_c = \frac{f}{2} V_1 (P_4 - P_1)$

So, $\boxed{e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{V_1 \; (P_4 - P_1)}{V_2 \; (P_3 - P_2)}}$

But more convenient with temperatures...

Adiabatic $\Rightarrow P_4 V_1^\gamma = P_3 V_2^\gamma$ & $P_1 V_1^\gamma = P_2 V_2^\gamma$

So $(P_4 - P_1) V_1^\gamma = (P_3 - P_2) V_2^\gamma$

So $$\frac{P_4 - P_1}{P_3 - P_2} = \frac{V_2^\gamma}{V_1^\gamma} = \left(\frac{V_2}{V_1}\right)^\gamma$$

So
$$e = 1 - \frac{V_1 V_2^\gamma}{V_2 V_1^\gamma} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$$

So $$\boxed{e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1}}$$

Compared to Carnot engine: $\boxed{e = 1 - \frac{T_c}{T_h} = e = 1 - \frac{T_1}{T_3}}$

Remember that $TV^{\gamma - 1}$ = constant for an adiabat $\Rightarrow \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma - 1}$

$\rightarrow \boxed{e = 1 - \frac{T_1}{T_2}}$

or, another adiabat → $T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$

So $\frac{T_4}{T_3} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$ So $\boxed{e = 1 - \frac{T_4}{T_3}}$

Note $\frac{T_1}{T_3} < \frac{T_1}{T_2}$ and $\frac{T_1}{T_3} < \frac{T_4}{T_3}$

So $\boxed{e_{Otto} < e_{Carnot}}$

So { Otto cycle will always be less efficient than Carnot engine
use the same T }

▨ Revisiting 3rd law

↳ "Planck's statement → " as $T \to 0$, $S \to S_{min}$, $S_{min} = 0$
for pure crystalline solids."

Einstein statement

↳ "As $T \to 0$, S remains finite"

$$\text{So} \quad S = \int_0^{T_f} \frac{c_v}{T}\, dT \quad \text{if } C_v \not\to 0 \text{ then } S \to S_{min} = -\infty$$

Nernst unattainability principle

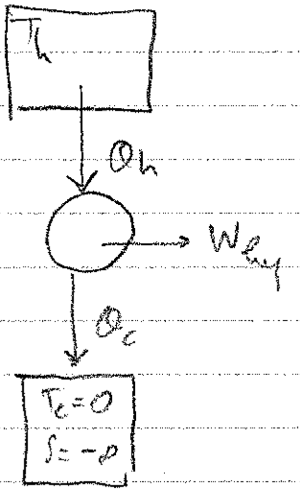
↳ "Any thermo-dynamic process cannot reach absolute zero in a finite number of steps in a finite amount of time"

▨ 1st law tells us we can't get work for free

▨ 2nd law tells us we can't build a monothermal heat engine

▨ 3rd law tells us we can't get 100% conversion of heat to work even if $\Delta S = 0$

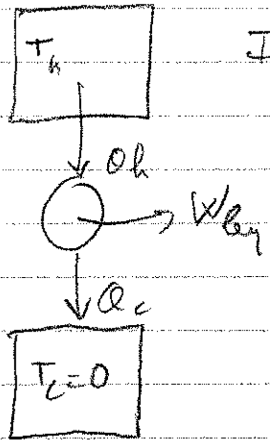
Einstein



$Q_h = W_{by}$. Einstein statement

→ S finite at $T=0$

Nernst



If you want $\Delta S=0$, Nernst says can't get engine to $T=0$ in finite time

---

$$\boxed{\text{ch 5} \rightarrow \text{FREE ENERGY}}$$

▨ Enthalpy → useful at constant P

$$H \equiv U + PV \Rightarrow dH = dU + PdV$$

or
$$\boxed{\Delta H = \underbrace{\Delta U}_{Q + \underbrace{W_{on}}_{-P\Delta V + W_{other}}} + P\Delta V}$$

So
$$\boxed{\Delta H = Q + W_{other}}$$

$\boxed{\text{Helmholtz free energy } (F)}$

↳ useful for constant T processes.

$$\boxed{F \equiv U - TS} \rightarrow \text{create system out of nothing}$$

$Q = T\Delta S$, quasistatic

↓

$S_{\text{final}} - 0$

$\boxed{\text{Gibbs free energy } (G)}$

↳ useful for constant T & P

$$\boxed{G \equiv U - TS + PV = H - TS}$$

Nov 20, 2019 Recall Thermodynamic Potential U, H, F, G

▨ Look at changes in these: $F \equiv U - TS \Rightarrow dF = dU - SdT - TdS$

For F, T constant $\rightarrow$ $\boxed{\Delta F = \Delta U - T\Delta S}$ can rewrite...

$\boxed{\Delta F = Q_{in} + W_{on} - T\Delta S}$ Now $Q_{in} \leq T\Delta S$ (in general)

↳ $\boxed{\Delta F \leq W_{on}}$ (constant T, equality when quasi static)

↑ can be expansion / compression work $= \int PdV$ + others.

▨ Gibbs free energy $\Rightarrow G \equiv U - TS + PV \Rightarrow dG = dU - TdS - \cancelto{0}{SdT} + PdV + \cancelto{0}{VdP}$

↳ constant $T, P \rightarrow$ $dG = \underbrace{dU}_{Q_{in} + W_{on}} - TdS + PdV$

$Q_{in} + W_{on}$, $Q_{in} \leq TdS$, $W_{on} = -P\Delta V + W_{other}$

So

$$\boxed{\Delta G \leq W_{other}}$$

Also $\Delta H = \underbrace{\Delta U}_{Q_{in} + W_{on}} + P\Delta V = Q_{in} + W_{other}$ So $\boxed{\Delta G = \Delta H - T\Delta S}$

Ex of using ΔG

☒ Electrolysis of water $1H_2O_{(l)} \rightarrow 1H_2 + \frac{1}{2}O_2$

$$\Delta H_f = -286 \text{ kJ/mol}$$

How much work do we need to supply to get reaction to proceed?

☒ Change in S: $S_{H_2O(l)} = 70 \text{ J/K}$

$S_{H_2(g)} = 131 \text{ J/K}$

$S_{O_2(g)} = 205 \text{ J/K}$

$$\cdot\ \Delta S = \left(131 \text{ J/K} + \frac{1}{2}\cdot 205 \text{ J/K}\right) - 70 \text{ J/K} = 163 \text{ J/K}$$

Max amount of heat that can enter system = $T\Delta S = 49$ kJ

$$\Delta G = \Delta H - T\Delta S = 286 \text{ kJ} - 49 \text{ kJ} = \boxed{\Delta G = 237 \text{ kJ}}$$

Thermodynamic identities

$$dU = TdS - PdV\ (+\mu dN) \Rightarrow u(s,v)$$

So $$dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial u}{\partial V}\right)_{S,N} dV$$

So $$\frac{\partial^2 u}{\partial v \partial s} = \frac{\partial^2 u}{\partial s \partial v} \Rightarrow \frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial S}\right)_{V,N}\right]_{S,N} = \frac{\partial}{\partial S}\left[\left(\frac{\partial U}{\partial V}\right)_{S,N}\right]_{V,N}$$

① $$\boxed{\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}}$$ ⇝ independent variables S, V

Maxwell's relation #1

② $$dU = TdS - PdV = TdS - d(PV) + VdP \rightarrow d(U+PV) = TdS + VdP$$

So $\boxed{dH = TdS + VdP}$ ⇝ how to get ΔH at non-standard P, T ...

$+\mu dN$

■ $H = H(S,P)$

So $$\boxed{dH = \underbrace{\left(\frac{\partial H}{\partial S}\right)_{P,N}}_{T} dS + \underbrace{\left(\frac{\partial H}{\partial P}\right)_{S,N}}_{V} dP}$$

So $$\boxed{T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \quad ; \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}}$$

Now $$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_{P,N} = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_{S,N}$$

So $$\boxed{\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}}$$ → Maxwell's relation #2

③ Independent variables T, V

$$dU = TdS - PdV$$

$$= d(TS) - SdT - PdV$$

So $$d(U - TS) = -SdT - PdV$$

$$\boxed{dF = -SdT - PdV}$$

Here $F(T,V)$

So $$dF = \underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,N}}_{-S} dT + \underbrace{\left(\frac{\partial F}{\partial V}\right)_{T,N}}_{-P} dV$$

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

Eg, $$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)$$

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

So $$\boxed{\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}}$$

④ Independent variables : T & P

$$dU = TdS - PdV = d(TS) - SdT - d(PV) + VdP$$

So $$d(U - TS + PV) = -SdT + VdP$$

$$\boxed{dG = -SdT + VdP}$$

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

and $$\boxed{\left(\frac{\partial V}{\partial T}\right)_{P,N} = \left(\frac{\partial S}{\partial P}\right)_{T,N}}$$

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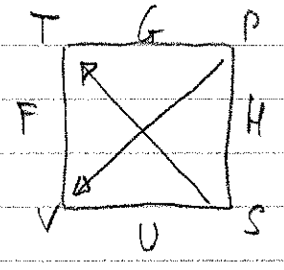
Mar 22, 2019

Thermodynamic Potentials U, H, F, G → "good physicists have studied under very fine teachers"

Ufe square



$$dH = VdP + TdS + \mu dN$$
$$dU = TdS - PdV + \mu dN$$

Write potentials as fn of vars on that side of square { coeffs diagonal
signs + arrows
pt to (-) diffs,

Maxwell's Relations

$$\llcorner = \lrcorner \longrightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

arrows point to minus sign for the constant variable.

Definitions of Potentials From squares

$H = U + PV$ ↺, against arrow → (+)

$G = H - TS$

$= U + PV - TS$

Usefulness of Maxwell's Relations

↳ Can derive a relationship between C_p & C_v for any substance

Reminder $C_v \equiv \left(\frac{\partial U}{\partial T}\right)_V$

$$C_p \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

① Start by writing S in terms of T, V

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_V}\, dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \left(\frac{C_v}{T}\right) dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Express $V = V(T, P)$ @ consider constant pressure

$$(dV)_P = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = \left(\frac{\partial V}{\partial T}\right)_P (dT)_P$$

So $(dS)_P = \left(\frac{C_v}{T}\right)(dT)_P + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P (dT)_P$

So $$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

For C_p, use identity for enthalpy – $dH = TdS + VdP$

At constant pressure $\Rightarrow$ $(dH)_p = (TdS)_p$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{So} \quad \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

So

$$T\left(\frac{\partial S}{\partial T}\right)_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

So $$C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

Use maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

So

$$\boxed{C_p = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$$

- Let $\boxed{\beta \equiv \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p}$ ⇝ "thermal volume coefficient of expansion"

- Let $\boxed{\kappa_T \equiv \left(-\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T}$ ⇝ "isothermal compressibility"

To write $C_p - C_V$ in terms of β & κ_T, more partial derivatives manipulation is required.

$$\boxed{z = z(x,y) \text{, then } \left(\frac{\partial x}{\partial y}\right)_z = \frac{-(\partial z/\partial y)_x}{(\partial z/\partial x)_y}}$$

Proof $\partial z = \left(\frac{\partial z}{\partial y}\right) dy + \left(\frac{\partial z}{\partial x}\right) dx$

when z constant → $dz = 0$

So $\left(\frac{\partial z}{\partial x}\right) dx = -\left(\frac{\partial z}{\partial y}\right) dy \qquad (dz = 0)$

So

$$\left(dx\right)_z = \frac{-(\partial z/\partial y)(dy)_z}{(\partial z/\partial x)}$$

So $$\left(\frac{dx}{dy}\right)_z = \frac{-(\partial z/\partial y)_x}{(\partial z/\partial x)_y}$$

So back to deriv's...

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

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

$$= -T(V\beta)^2 \frac{-1}{K_T V}$$

So $$\boxed{C_p - C_V = \frac{T\beta^2 V}{K_T}}$$ ⇝ true for any substance

Ex For ideal gas → $C_p - C_V = nR = Nk$

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

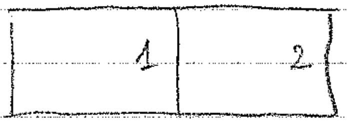
$= \frac{1}{V}\left(\frac{Nk}{P}\right)$, $= \frac{-1}{V}\left(\frac{-NkT}{P^2}\right) = \frac{NkT}{PVP} = \frac{1}{P}$

$\beta = \frac{1}{T}$ **So** $$\boxed{C_p - C_V = \frac{T(T)^{-2} V}{P^{-1}} = \frac{PV}{T} = Nk = nR}$$

April 1, 2019

Extensive vs. Intensive parameters

Say we have a homogeneous system



① if $y_1 + y_2 = y$ then y is an extensive parameter,
② if $y_1 = y_2 = y$ then y is an intensive parameter.

▨ Extensive { volume (V), mass (m), # particles (N), internal energy (U), Entropy (S)
Enthalpy (H), (F), (G)

▨ Intensive { Temp (T), Pressure (P), density (ρ), chemical potential (μ)

▨ Rules of multiplication & addition:

① $(\text{Ext}) \cdot (\text{Int}) = (\text{Ext})$ Ex $V \times \rho = m$

② $\dfrac{[\text{Ext}]}{[\text{Ext}]} = [\text{Int}]$ Ex $\dfrac{m}{V} = \rho$

or $\dfrac{C_V}{\text{mass}} = c_V$

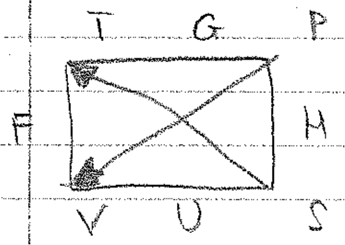
③ $(\text{Ext} \cdot \text{Ext}) \Rightarrow$ neither (extensive) nor (intensive)

④ $[\text{Ext}] + [\text{Ext}] = [\text{Ext}]$

⑤ Not allowed $\cancel{[\text{Ext}] + [\text{Int}]}$

Ex G has units of J But $G+\mu$ does not make sense
μ has units of J

▨ Gibbs free energy & chemical potential



$$dG = VdP - SdT + \mu dN$$

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

Now,

$$\underset{\text{int}}{\mu} = \left(\frac{\overset{\text{ext}}{\partial G}}{\underset{\text{ext}}{\partial N}}\right)_{\underset{\text{intensive}}{P,T}}$$

$$\boxed{@ \text{ constant } P,T \rightarrow G = \mu N}$$ as $N\uparrow$, $G\uparrow$ proportionally

for a system with only 1 type of particles, $\boxed{\mu = G/N}$

▨ Helmholtz free energy & chemical potential

$$dF = -SdT - PdV + \mu dN$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{\underset{\text{int}}{T},\underset{\text{ext}}{V}} \rightarrow \boxed{F = N\mu(v)}$$

▨ Derivation of chemical potential of ideal gas

Before, $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

Now,

$$G = \mu N \quad \text{or} \quad \mu = \frac{G}{N}$$

Consider a fixed amount of gas (N) at const (T) and allow P to vary

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,N} = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial N}\right)_{T,N} = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{V}{N}$$

So $\displaystyle\int d\mu_{T,N} = \int \left(\frac{V}{N}\right) dP_{T,N} \Rightarrow \Delta\mu = \int_{P_i}^{P_f} \frac{kT}{P}\,dP = kT\ln\left(\frac{P_f}{P_i}\right)$

So $$\boxed{\mu(T,P_f) - \mu(T,P_i) = kT\ln\left(\frac{P_f}{P_i}\right)}$$

write $\mu(T,\underset{\substack{\uparrow\\ 1\text{ atm}}}{P_i}) = \mu^{\circ}(T) \Rightarrow \boxed{\mu(T,P) = \underset{(T)}{\mu^{\circ}} + kT\ln\left(\frac{P}{\underset{\substack{\uparrow\\ \text{typically, 1 atm}}}{P_0}}\right)}$

- P is the partial pressure

Ex $\boxed{He, H}$ $\mu_{He}(T,P) = \mu^{\circ}_{He}(T) +$ [illegible] $+ kT\ln\left(\frac{P_{He}}{P^{o}}\right)$

▨ Test vs μ derived for a monatomic ideal gas

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

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\overset{\pi}{\wedge}m kT}{h^2}\right)^{3/2}\right]$$

$$= -kT\ln\left[\frac{P^{0}}{P^{0}}\frac{kT}{P}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]$$

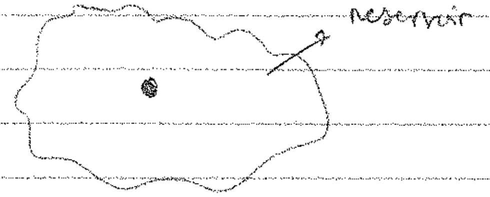
$$= -kT\ln\left[\frac{kT}{P^{0}}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right] + kT\ln\left(P/P^{0}\right)$$

$$\boxed{\mu = \underbrace{-kT\ln\left[\frac{kT}{P^{0}}\left(\frac{2\pi m kT}{h^2}\right)^{3/2}\right]}_{\mu^{\circ}(T)} + kT\ln\left(P/P^{0}\right)}$$

Free Energy as a Force Towards Equilibrium

- For isolated system → $S \uparrow$
- For interacting system → $S_{tot} \uparrow$

Assume environment is a reservoir of constant T, V, N



$$S_{tot} = S_{system} + S_{reservoir}$$

$$dS_{tot} = dS_{sys} + dS_{res}$$

▨ For reservoir, $TdS = dU + PdV - \mu dN$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

✿ if T, N, V constant, then $dS_{res} = \frac{1}{T_{res}} dU_{res}$

So $dS_{tot} = dS_{sys} + \frac{1}{T_{res}} dU_{res}$

In eq., $T_{sys} = T_{res}$, $dU_{sys} = -dU_{res}$

So $dS_{tot} = dS_{sys} - \frac{1}{T_{sys}} dU_{sys}$

So

$$dS_{tot} = -\frac{1}{T}\Big(\underbrace{dU - TdS}_{dF}\Big)$$ ⟶ dropping sys. subscript

So $\boxed{dS_{tot} = -\frac{dF}{T}}$

if $dF < 0$ → spontaneous flow towards equilibrium

✿ Now, let V vary, holding P, T, (& N) constant

$$dS_{tot} = dS_{sys} + \frac{1}{T_{res}} dU_{res} + \frac{P_{res}}{T_{res}} dV_{res} - \cancelto{0}{\frac{\mu_{res}}{T_{res}} dN_{res}}$$

At equilibrium, $P_{res} = P_{sys}$, $T_{res} = T_{sys}$, $dU_{res} = -dU_{sys}$

$dV_{res} = -dV_{sys}$

So

$$dS_{tot} = dS - \frac{1}{T}dU - \frac{P}{T}dV$$

So

$$dS_{tot} = \frac{-1}{T}\Big(\underbrace{dU - TdS + PdV}_{dG}\Big)$$

So

$$\boxed{dS_{tot} = \frac{-dG}{T}} \rightarrow dG = dG_{sys}, \quad T = \text{equilibrium } T$$

So

For fixed P, T, N $\Rightarrow$ $\boxed{G \text{ tends to decrease}}$

(if $\Delta G < 0$ → spontaneous process)

Example use of free energy to calculate whether a reaction is spontaneous or not

Crystallized ammonium nitrate NH_4NO_3

$$NH_4NO_{3(s)} + H_2O_{(l)} \longrightarrow NH^+_{4(aq)} + NO^-_{3(aq)} + H_2O(l)$$

look up $\Delta_f H$, $\Delta_f S$

	$\Delta_f H$	$\Delta_f S$
$NH_4NO_3(s)$	-365.56	151.08
NH_4^+ (aq)	-132.51	113.4
NO_3^- (aq)	-205.0	146.4

@ eq, $\Delta G = 0$

$\Delta G = \Delta H - T\Delta S = -4.4$ kJ < 0 → spontaneous

@ constant T

In general, $H = U + PV$ for constant P process, $\Delta H = \Delta U + P\Delta V$

$\Delta H = \Delta U + P\Delta V = Q_{alo}$

$$\boxed{\begin{array}{l} \Delta H < 0 \Rightarrow \text{exothermic rxn} \\ \Delta H > 0 \Rightarrow \text{endothermic rxn} \end{array}}$$

if $\Delta H < 0, \Delta S > 0 \Rightarrow \Delta G < 0$ spontaneous
$\Delta H > 0, \Delta S < 0 \Rightarrow \Delta G > 0$ not spontaneous process.

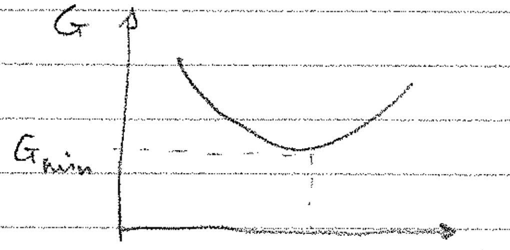
▨ Summary

Reservoir	System
• At constant U, V	S↑
• At const T, V	F↓
• At const T, P	G↓

▨ Stability against temperature fluctuations

Consider a system. Let T, V be independent parameters that describe system

1^{st}, hold V fixed & allow T to vary
Interacting with respect to constant T, P, N



min of G occurs @ T_0

• Expand G around eq. value $\Delta G = G - G_{min} = \left(\frac{\partial G}{\partial T}\right)_V \Delta T + \frac{1}{2}\left(\frac{\partial^2 G}{\partial T^2}\right)_V (\Delta T)^2$

$+ \cdots$

where $\Delta T = T - T_0$

Evaluate derivs at $T = T_0$

$$\left(\frac{\partial G}{\partial T}\right)_V \Bigg|_{T_0 \leq \infty} = 0 \; , \qquad \left(\frac{\partial^2 G}{\partial T^2}\right)_V \Bigg|_{T_0} > 0$$

- $G = U - TS + PV \qquad G_0 \;@\; T_0, P_0$
- $G_0 = U - T_0 S + P_0 V$

So

$$\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0\left(\frac{\partial S}{\partial T}\right)_V = 0 \quad @\; T = T_0$$

$$dU = TdS - P\,\cancel{dV}_{\to 0} \quad \text{So} \quad \left(\frac{dU}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial G}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V - T_0\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right]$$

$$\boxed{\left(\frac{\partial G_0}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left[1 - \frac{T_0}{T}\right]}$$

- Evaluate $\left(\frac{\partial^2 G_0}{\partial T^2}\right)_V = \left(\frac{\partial}{\partial T}\right)\left(\frac{\partial G_0}{\partial T}\right) = \frac{T_0}{T^2}\left(\frac{\partial U}{\partial T}\right)_V + \left(1 - \frac{T_0}{T}\right)\left(\frac{\partial^2 U}{\partial T^2}\right)_V > 0$

at $T = T_0$

So

$$\frac{T_0}{T^2}\left(\frac{\partial U}{\partial T}\right)_V > 0$$

$$\text{So} \quad \boxed{\left(\frac{\partial U}{\partial T}\right)_V > 0} \rightarrow \boxed{C_V > 0}$$

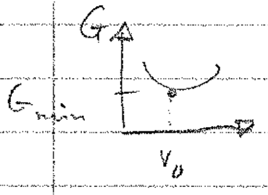
→ if heat cap > 0, then stable around δT

Le Châtelier's Principle

pril 3, 2019

☒ $\Big\{$ When a system in eq. is disturbed, it will respond in a (stable) way to restore itself back to equilibrium $\Big\}$

☒ Result for V fluctuations



$$\left(\frac{\partial^2 G}{\partial V^2}\right)\Bigg|_{T=T_0} = -\left(\frac{\partial P}{\partial V}\right)_T > 0$$

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

$\frac{1}{K_T} > 0$ or simply $\boxed{K_T > 0}$

Chemical Equilibrium

Can use Gibbs to determine equilibrium condition...

e.g. $H_2O \rightleftharpoons H^+ + OH^-$

Mixture of H_2O + ions is most stable state (lower G)

$G = U - TS$

@ Eq... $\Delta G = 0$. Ions have a higher entropy. But additional entropy of mixing makes the mixture more stable.

@ Eq, $dG = 0 = dH - TdS = \mu N \ldots = \sum_i \mu_i dN_i = \sum_i \mu_i dN_i$

For this rxn, $H_2O \rightleftharpoons H^+ + OH^-$

$dN_{H_2O} = -1$, $dN_{H^+} = +1$, $dN_{OH^-} = +1$ So @ eq, $dG = 0 = \sum_i \mu_i dN_i$

So $-\mu_{H_2O} + \mu_{OH^-} + \mu_{H^+} = 0$

So $\boxed{\mu_{OH^-} + \mu_{H^+} = \mu_{H_2O}}$

More generally, $\nu_1 X_1 + \nu_2 X_2 + \dots \rightleftharpoons \nu_3 X_3 + \nu_4 X_4 + \dots$

$\nu_i \to$ stoichiometric coefficient of species i

In eq, $\boxed{\nu_1 \mu_1 + \nu_2 \mu_2 + \dots = \nu_3 \mu_3 + \nu_4 \mu_4 + \dots}$

The rxn $H_2O \rightleftharpoons H^+ + OH^-$ produces a solution, which is a mixture of a solvent (primary component) + solute (secondary comp)

☒ Dilute solution { # of solute molecules << # of solvent molecules and solute molecules don't interact with each other

→ can treat them as an ideal gas!

☒ Need to calculate μ for solvent & solute in order to predict eq.

Suppose we have pure water... 100% H_2O ... solvent, A

$$G = N_A \mu_A = N_A \mu_A^0(T,P)$$ "pure" μ_A^0: chem. pot. of pure solvent...

Add a single B molecule (solute), holding T, P fixed

$$dG = \underbrace{dU}_{\text{indep of } N_A \text{, only dep on } N_B} + \underbrace{PdV} - \underbrace{TdS}_{\text{dep on } N_A \ (\Omega \sim N_A)}$$

$dS = k \ln N_A$ + additional terms indep of N_A...

So $\boxed{dG = -kT \ln N_A + \underbrace{f(T,P)}_{\text{indep of } N_A}}$ for adding 1 molecule

Adding 2 B molecules...

$$\text{Guess} \rightarrow dG' = 2\,dG = 2\left[f(T,P) - kT\ln N_A\right] \quad \otimes$$

But B molecules indistinguishable.

↳ I needs to be divided by $2!$ → indistinguishable

So...

$$dG' = 2f(T,P) - T\left[2k\ln N_A - k\ln 2\right]$$

$$= 2f(T,P) - 2kT\ln N_A + kT\ln 2$$

Generalizing... (for N_B molecules...)

$$\boxed{dG = N_B f(T,P) - N_B kT\ln N_A + \overbrace{kT\ln(N_B!)}^{kTN_B\ln N_B - kTN_B}}$$

Pure Solvent

$$G = N_A\mu^0(T,P)$$

Dilute Solution $G + dG$

Solution

$$\boxed{\begin{aligned} G = {} & N_A\mu^0(T,P) + N_B f(T,P) - N_B kT\ln N_A \\ & + N_B kT\ln N_B - N_B kT \end{aligned}}$$

↑ valid if $N_B \ll N_A$ (dilute solution...)

Since, $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$ we can solve for μ_A & μ_B

$$\boxed{\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} = \mu^0(T,P) - N_B kT/N_A}$$

→ chem pot of solvent

chem pot of solute

$$\boxed{\begin{aligned} \mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A} & = f(T,P) - kT\ln N_A - \cancel{kT} + \cancel{kT} + kT\ln N_B \\ & = f(T,P) + kT\ln\frac{N_B}{N_A} \end{aligned}}$$

<u>April 5, 2019</u> **Recall** ① Started with G for pure solvent (A)

$$G = \mu^\circ(T,P)\,N_A$$

② Add solute particles (B) to this

$$dG = \underbrace{dU + PdV}_{f(T,P) \text{ independent of } N_A} - TdS \longrightarrow \begin{array}{l}\text{some terms dep. on } N_A \\ \text{some indep of } N_A\end{array}$$

$$\Omega = \frac{N_A!}{N_B!\,(N_A-N_B)!} \text{, and since } N_A \gg N_B \Rightarrow \Omega \simeq \frac{N_A^{N_B}}{N_B!}$$

So

$$S = k\ln\Omega = k\ln\left[\frac{N_A^{N_B}}{N_B!}\right] = k\ln\left(N_A^{N_B}\right) - k\ln(N_B!)$$

$$\simeq N_B\, k\ln(N_A) - N_B\, k\ln N_B + N_B\, k$$

Now,

$$G = G_A + dG$$

So

$$dG = N_B\, f(T,P) - N_B kT\ln N_A + kT\overset{N_B}{\ln} N_B - N_B kT$$

So

$$\boxed{G = \mu^\circ(T,P)\,N_A + N_B\, f(T,P) + N_B kT\ln\left(\frac{N_B}{N_A}\right) - N_B kT}$$

Now,

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \Rightarrow \left\{\begin{array}{l} \boxed{\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P} = \mu^\circ(T,P) - \frac{N_B kT}{N_A}} \\ \qquad\qquad\qquad\qquad \text{(solvent)} \\ \boxed{\mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P} = f(T,P) + kT\ln\frac{N_B}{N_A}} \\ \qquad\qquad\qquad\qquad \text{(solute)} \end{array}\right\}$$

Definition

"Molality" → # moles of solute per kg of solvent.

$$\boxed{m = \frac{\text{moles solute}}{\text{kg solvent}} \propto \frac{N_B}{N_A}}$$

☒ Re-writing μ_B in terms of m: $\longrightarrow$ absorbed ... extra term ...

* $\mu_B = f'(T,P) + kT\ln(m_B)$. (?)

* $\mu_B^0(T,P) \overset{\Delta}{\rightsquigarrow}$ standard condition for molality $= \underline{1} = m_B$

So when $m_B = 1 \rightarrow \boxed{\mu_B = \mu_B^0(T,P) + kT\ln(m_B)}$

Example Dissociation of water

$H_2O \longleftrightarrow H^+ + OH^-$ @ eq $\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-}$

Treat as dilute solution: solvent H_2O

$$\left.\begin{array}{l} ☒\ \mu_{H_2O} = \mu^0_{H_2O}(T,P) - \overset{\to 0}{\dfrac{N_{H^+}kT}{N_{H_2O}}} - \overset{\to 0}{\dfrac{N_{OH^-}kT}{N_{H_2O}}} \\ ☒\ \mu_{H^+} = \mu^0_{H^+}(T,P) + kT\ln m_{H^+} \\ ☒\ \mu_{OH^-} = \mu^0_{OH^-}(T,P) + kT\ln m_{OH^-} \end{array}\right\}$$

at room temp, $kT \sim 4\times10^{-21}\,J$

So $\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \Rightarrow \mu_{H_2O} - \mu_{H^+} - \mu_{OH^-} = 0$

$$\Rightarrow \mu^0_{H_2O} - \mu^0_{H^+} - \mu^0_{OH^-} = kT\ln(m_{H^+}) + kT\ln(m_{OH^-})$$

$$= kT\ln(m_{H^+}\cdot m_{OH^-})$$

So $\underbrace{-N_A\left[\mu^0_{H^+} + \mu^0_{OH^-} - \mu^0_{H_2O}\right]} = RT\ln(m_{H^+}\cdot m_{OH^-})$

$$\boxed{-\Delta G^0 = RT\ln(m_{H^+}\cdot m_{OH^-})}$$

☒ Ex ΔG^0 dissociation of water = 79.9 kJ/mol

Now

⇒ $m_{H^+} \cdot m_{OH^-} = \underbrace{e^{-\Delta G/RT}}_{K \text{ equilibrium constant}}$

For room temp & standard P,

$K_{H_2O} = 10^{-14}$

So $m_{H^+} \cdot m_{OH^-} = 10^{-14} = (m_{OH^-})^2 = (m_{H^+})^2$

So $\boxed{m_{H^+} = m_{OH^-} = 10^{-7}}$ → moles/kg H_2O

$\boxed{pH \equiv -\log_{10}(m_{H^+})}$ ⇒ pH = 7 for "pure" H_2O

{ if fewer H^+ conc. then Base, pH ↑
if more H^+ conc. then Acidic, pH ↓ }

* * *

☒ Ionization of H $\qquad H \rightleftharpoons p^+ + e^-$

partial pressure

Treat as ideal gas : $\boxed{\mu(T,P) = \mu^0(T) + kT\ln\left(P/P^0\right)}$

std. atm. pressure

$$\left(\mu^0_{p^+} + \mu^0_{e^-} - \mu^0_H\right) = kT\ln\left(\frac{P_H}{P^0}\right) - kT\ln\left(\frac{P_{p^+}}{P^0}\right) - kT\ln\left(\frac{P_{e^-}}{P^0}\right)$$

$$\Rightarrow \quad -\Delta G^0 = N_A kT\ln\left[\frac{P_H P^0}{P_{p^+} P_{e^-}}\right]$$

kT/P^0

So Recall, for ideal gas $\mu^0 = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$

But μ for H should be less than $-13.6\,eV$ when at rest $(KE = 0)$

So $$\boxed{\mu_H^0 = -kT\ln\left[\frac{kT}{p^0}\left(\frac{2\pi m_H kT}{h^2}\right)^{3/2}\right] - 13.6\,eV}$$

Also But p^+, e^- unbound $\rightarrow$

$$\rightarrow \quad \mu^0_{p^+} = -kT\ln\left[\frac{kT}{p^0}\left(\frac{2\pi m_p kT}{h^2}\right)^{3/2}\right]$$

$$\mu^0_{e^-} = -kT\ln\left[\frac{kT}{p^0}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2}\right]$$

Now, $m_H \simeq m_e$

So $$\mu^0_{p^+} + \mu^0_{e^-} - \mu^0_{H_e\,0} = -kT\ln\left(\frac{kT}{p^0}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2}\right) + 13.6\,eV$$

Therefore,

$$-\ln\left(\frac{P_H P^0}{P_{p^+} P_{e^-}}\right) = \ln\left(\frac{kT}{p^0}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2}\right) - \frac{13.6\,eV}{kT}$$

So $$\left(\frac{P_H P^0}{P_{p^+} P_{e^-}}\right)^{-1} = \frac{kT}{p^0}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \cdot e^{-13.6\,eV/kT}$$

So $$\frac{P_{H^+} P_{e^-}}{P_H} = kT\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \cdot e^{-13.6\,eV/kT}$$

So $$\boxed{\frac{P_{H^+}}{P_H} = \frac{kT}{P_{e^-}}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \cdot e^{-13.6\,eV/kT}}$$ Saha Eqn

$$\underbrace{\frac{P_{H^+}}{P_H}}_{N_{p^+}/N_H}$$

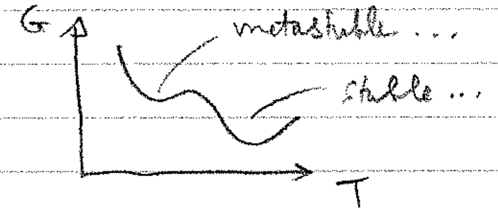
PHASE TRANSFORMATION

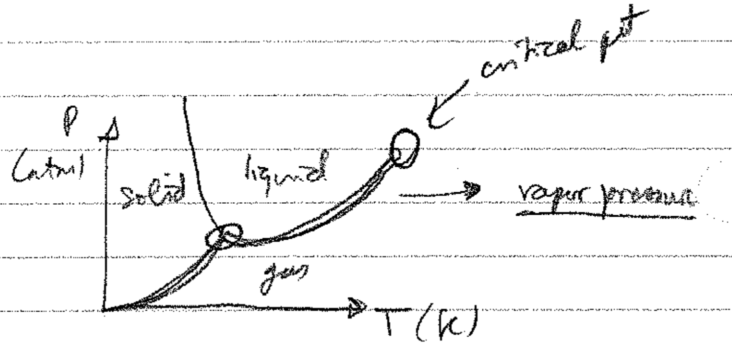
- def { A continuous change in property of matter as its environment changes infinitesimally. }

- Phases { different states of matter – or unique structural arrangement of atoms within matter.

- Can depend on many variables : eg: P, T, B, ...

↳ Gibbs free energy is key to understanding these...

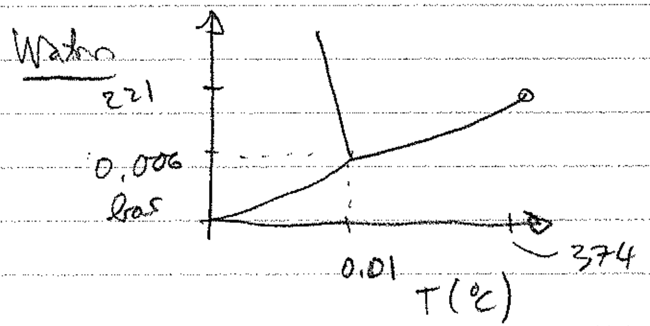


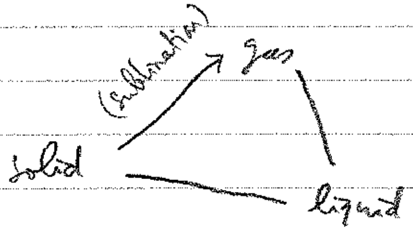


- Phase diagram for water

- Vapor pressure → pressure at which liquid or solid phase can coexist with gas

- Triple point → precise T, P at which all 3 phases (liquid, gas, solid) can coexist...

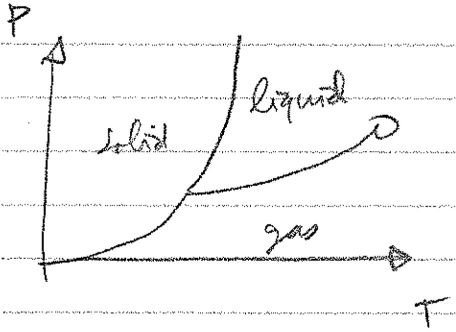




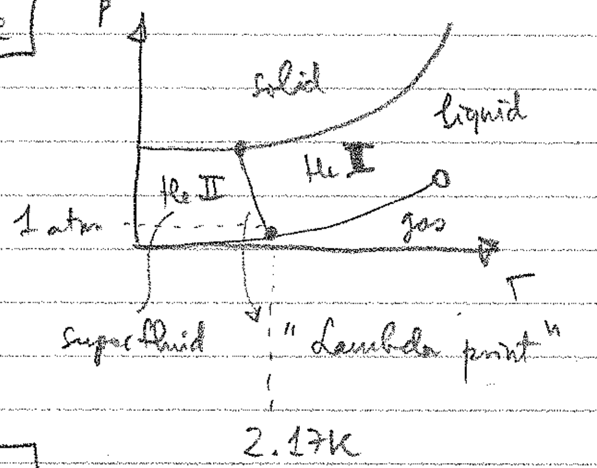
- Critical point As P or T increases, we reach a point where liquid & gaseous phases are indistinguishable.

Ex plasma...

Ex $\boxed{CO_2}$



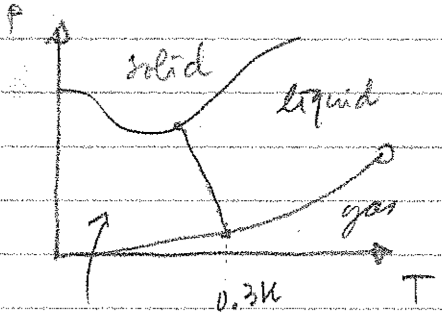
$\boxed{{}^4He}$



^4He is a superfluid below the Lambda point (@1atm, 2.17K)

$\boxed{\text{Superfluid}}$ → { zero viscosity
zero entropy
high conductivity

$\boxed{{}^3He}$



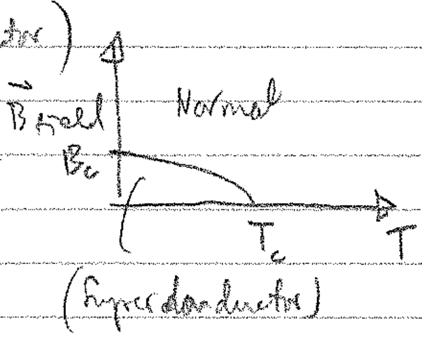
2 superfluid phases.

<u>Other variables that can cause phase change:</u>

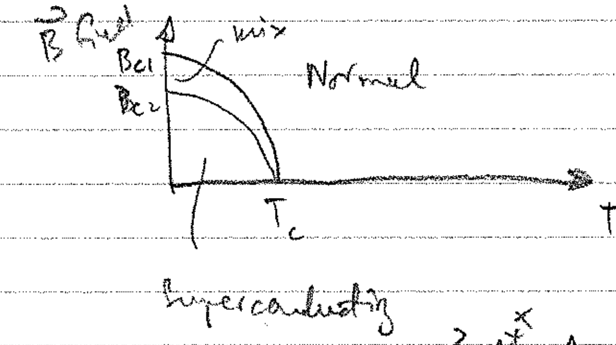
- Chemical composition:
- external $\vec{B}$ field strength → (Type I superconductor)
(0 resistivity)

(Type I Superconductor)

Typical $B_c \sim 0.01 - 0.1T$
$T_c \sim 10K$



Aside Type II - Superconductor



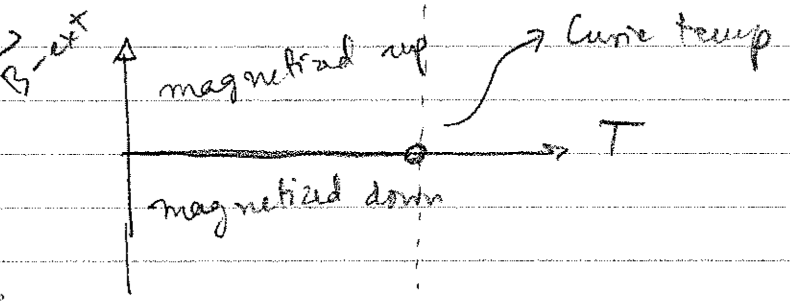
$B_{c2} \gg B_{c_1}$

|

25T

$T_c \sim 10K \sim 90K$

[Ferromagnets]



At T_c 1043K for Fe

→ magnetization disappears

→ behaves like paramagnet

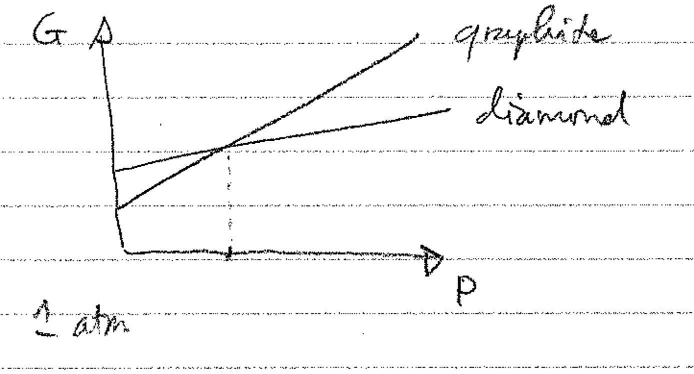
☒ Using Gibbs free energy to evaluate stable phase for substances

$$dG = -SdT + VdP + \mu dN$$

$$\text{So} \quad \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad ; \quad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

Ex Diamond vs Graphite, look up $\Delta_f G$ for both room T & 1 atm

$\Delta_f G_{graphite}$ is 2900 J less than $\Delta_f G_{diamond}$ @ 298K, 1 atm



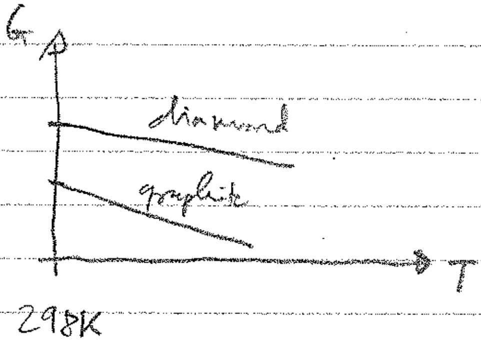
@ high pressures, diamond becomes the stable phase.

▨ Now look at T dependence

$\left(\frac{\partial G}{\partial T}\right) = -S$ as T↑, G↓

Entropy of diamond vs graphite.

↑ lower S ↑ higher S



Graphite is always more stable.

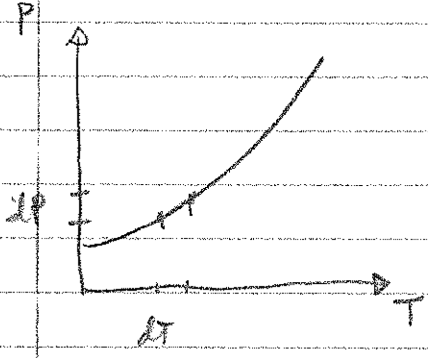
▨ Clausius - Clapeyron relation

Since $\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$, $\left(\frac{\partial G}{\partial P}\right)_{T,N} = +V$ then ~~shape~~ of the phase boundary line on P v. T diagram is related to S & V of the two phases...

Phase boundary between liquid & gas

→ assume 1 mole of substance

On the boundary $G_l = G_g$



increase P & T s.t. 2 phases remain in eq.

$$\cancelto{0}{dG} = -SdT + VdP + \cancelto{0}{\mu dN}$$

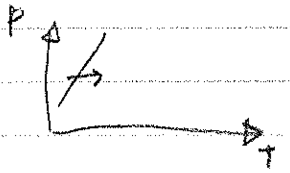
So $SdT = VdP$ ...

$$dG_l = -S_l dT + V_l dP$$
$$dG_g = -S_g dT + V_g dP$$ } equal

So $(V_g - V_\ell)\,dP = (S_g - S_\ell)\,dT$

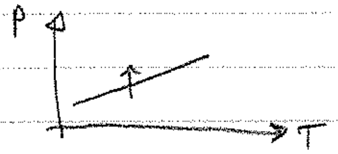
$$\boxed{\frac{dP}{dT} = \frac{S_g - S_\ell}{V_g - V_\ell}}$$

- if we have a large entropy difference between phases
  → steep slope...



dP/dT steep: Small T changes will change the phase...

- if large volume difference



$\frac{dP}{dT} \Rightarrow$ shallow. Small P change will change phase.

☒ <u>Reminder</u> $\Delta S = \frac{Q}{T} = \frac{L}{T}$

So $\boxed{\frac{dP}{dT} = \frac{L}{T\Delta V}}$ L: total latent heat of vaporization
$\Delta U = V_g - V_\ell$

Clausius - Clapeyron Eqn.

$L = l\,m$ → extensive
ΔV = extensive
} ⇒ ratio $\frac{L}{\Delta V}$ = intensive.

<u>Example</u> Use Clausius - Clapeyron to explain why H_2O has negative $\frac{dP}{dT}$ between solid - liquid phases.

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\Delta S}{\Delta V}$$

$\rho_{ice} = 917\ \text{kg/m}^3$, $\rho_{liq} = 1000\ \text{kg/m}^3$ → use 1000 kg of H_2O

$V_\ell = m/\rho = \frac{1000\,kg}{1000\,kg/m^3} = 1\,m^3$ $\quad V_{ice} = \frac{1000\,kg}{917\,kg/m^3} = 1.09\,m^3$

$(V_\ell - V_s) = -0.09\,m^3$

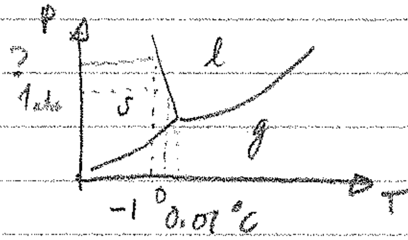
As we go from ice to water, $V\downarrow$, $S\uparrow$

So $\frac{dP}{dT}$ is negative

Assume L is constant with P, T: $\frac{dP}{dT} = \frac{333\,J/g \times 10^6\,g}{(273\,K)(-0.09\,m^3)}$

$= -1.35\times10^7\,Pa/K$

How much pressure is required to melt ice at $-1°C$?



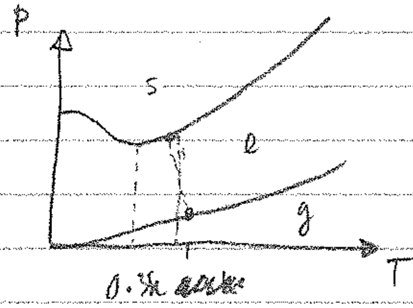
$\frac{dP}{dT} = -1.35\times10^7\,Pa/K$

$dP = (-1.35\times10^7\,Pa/K)(-1\,K)$

$dP = 1.35\times10^7\,Pa \cong 135\,atm$

$= 135\,bar$

▨ Ex ^3He



- At $T < 0.3K$, slope between solid – liquid is negative
- which phase is more dense? Remember that $\left(\frac{\partial G}{\partial T}\right)_{P,N} = V$

Solid ^3He is stable phase at high P, so it
must have smaller V. Shallower dG/dP
→ solid is more dense.

☒ Which phase has more entropy?

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} < 0 \quad @ \ T < 0.3K$$

if V↓ as we go $l \to s$, S↑ as we go from $l \to s$

↳ solid ^3He has more entropy.

☒ Q: What is the slope of the phase boundary at $T = 0$?

3rd law: As $T \to 0K$, $S \to$ minimum value.

↳ $\Delta S = 0$ between the phases @ $T = 0$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \Rightarrow \frac{dP}{dT} = 0 \Rightarrow$$ slope of phase boundary goes away..

April 10, 2019

The van der Waals model

Ideal gas: $PV = nRT = NkT$ → want to correct for finite volumes of molecules & attractive forces between particles

$$\boxed{\left(P + \frac{aN^2}{V^2}\right)\left(V - Nb\right) = NkT}$$ van der Waals equation.

Two modifications: ① $V \to V - V_0$ → can't compress gas to $V = 0$
"b" represents volume per particle
min volume $= Nb$ @ $P = \infty$

② $P \to P + \frac{aN^2}{V^2}$ accounts for <u>short range attractive</u> forces between molecules

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

Imagine being at $T=0$, frozen thermal motion. ⇒ no KE, but still has potential energy

$PE_{\text{single particle}} \propto N/V \Rightarrow PE_{\Sigma} \propto \frac{N}{V} \cdot N$

$\Rightarrow PE_{tot} = -\frac{aN^2}{V}$, negative since it works against KE

- "a" constant depending on type of molecules  vs. 
- To calculate P, $dU = T\,\overset{0}{\cancel{dS}} - PdV \underset{(T=0)}{} \Rightarrow P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$
- Contribution to P from PE

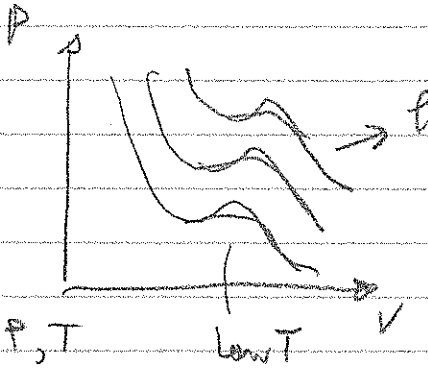
$$\hookrightarrow P = \frac{-\partial}{\partial V}\left(-\frac{aN^2}{V}\right)_{S,N} \Rightarrow \boxed{P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}}$$

Ex Molecular Interaction H_2O : $b \simeq 5\times10^{-24}\,\text{cm}^3 \sim (4\,\text{Å})^3$
N_2 similar

"a" varies between molecules... N_2 : $a \sim 2.5\,\text{eV}\,\text{Å}^3$
$H_2O \sim a_{N_2}$ due to dipole interaction
He : $a_{He} < a_{N_2}$ (monatomic)

Consequences of vdW model

For a given T, plot P v. V.



⇒ Multiple possible V's for a given P, T

Use G to find which volume is stable

$dG = -SdT + VdP + \mu dN$, for T & N ⇒ $\left(\frac{\partial G}{\partial V}\right)_{T,N} = V\left(\frac{\partial P}{\partial V}\right)_{T,N}$

$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}$ So,

$$V\left(\frac{\partial P}{\partial V}\right)_{T,N} = V\frac{\partial}{\partial V}\left[\frac{NkT}{V-Nb} - \frac{aN^2}{V^2}\right]$$

$$= V\left[\frac{-NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3}\right]$$

$$\rightarrow \left(\frac{\partial G}{\partial V}\right)_{T,N} = \frac{-NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

$$\underline{\text{So}} \quad \int dG = \int \left[\quad\right] dV$$

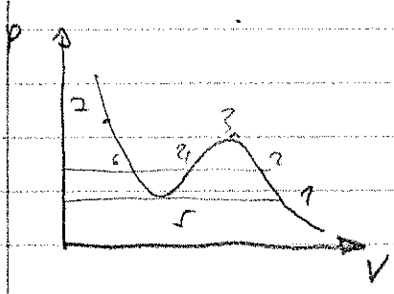
$$= \int \frac{-NkT(V-Nb+Nb)}{(V-Nb)^2} + \frac{2aN^2}{V^2}\, dV$$

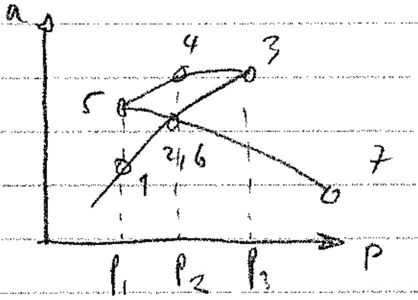
$$= \int \frac{-NkT(V-Nb)}{(V-Nb)^2} - \frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^2}\, dV$$

constant of int

$$\rightarrow G = -NkT\ln(V-Nb) + \frac{NkT(Nb)}{(V-Nb)} - \frac{2aN^2}{V} + c(T)$$

Want to know G vs. P





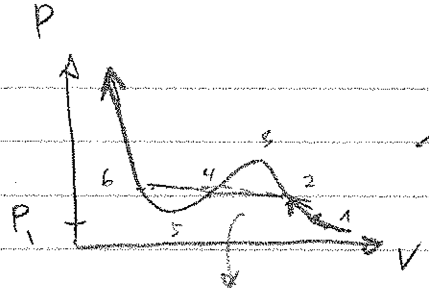
-]2 , 6[are unstable.
- Substance will go directly from vol @ 2 → vol @ 6 as it's compressed
- Discontinuity = phase change

ΔG around loop = 0 $\quad \oint_{\text{loop}} dG = 0$, $\left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow \int\left(\frac{\partial G}{\partial P}\right)_T dP = 0$

$$\underline{\text{So}} \quad \boxed{0 = \int_{\text{loop}} V\,dP}$$

April 12, 2019

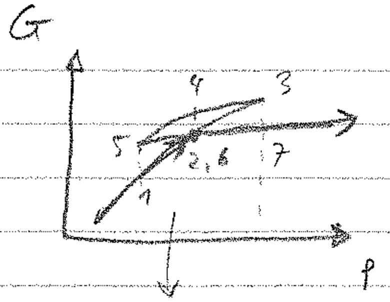
Recall, vdW



discontinuity

→ phase transition ...

⇝



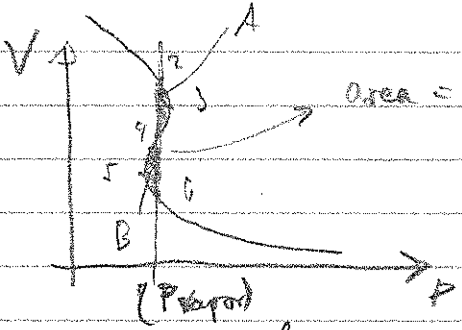
continuity

$$\int_{\text{Loop } 2-6} dG = 0 \quad = \int_{\text{Loop } 2-6} dG = 0 \quad \text{where } dG = -SdT + PdV$$

$$\hookrightarrow \left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

So $\displaystyle\int_{\text{Loop } 2-6} V dP_T = 0$

flip around ...

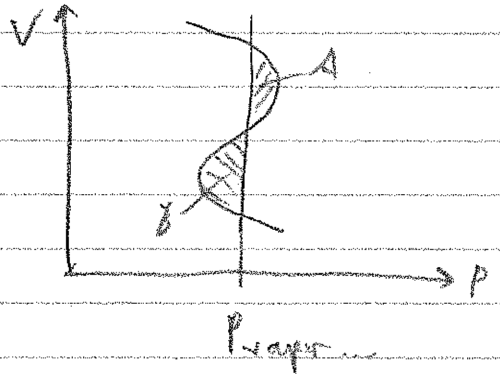


Area = 0 & A = B

→ area (A) = area (B) for $\displaystyle\int_{\text{Loop } 2-6} V dP_T = 0$

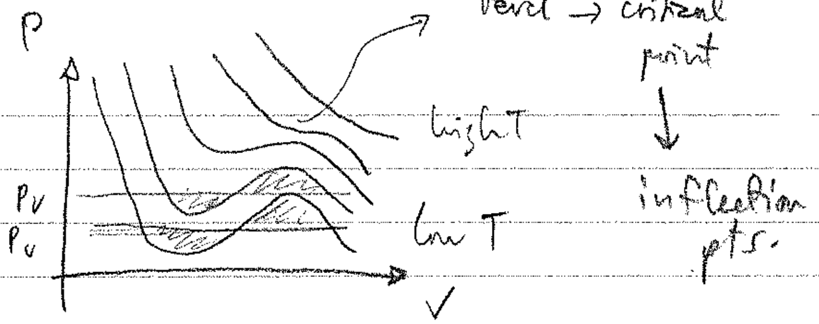
↳ "Maxwell's construction"

⇒ P of phase transformation occurs where vertical P divides the area in equal halves

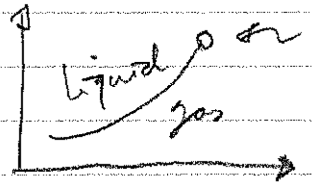


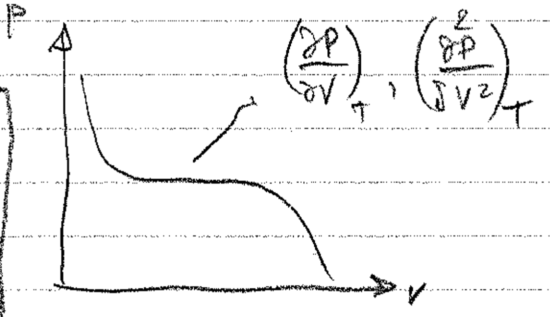
P_vapor ...

Isotherms @ different T



↳ By finding P_{vapor} based on Isotherms...

↳ 



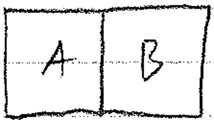
$$\boxed{(\text{Critical point}) \rightarrow \left\{ \begin{aligned} \left(\frac{\partial P}{\partial V}\right)_T &= 0 \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_T &= 0 \end{aligned} \right\}}$$

{ T_c = critical temp is where first & 2nd derivs of P wrt V are zero. }

PHASE TRANSFORMATION OF MIXTURES (§5.4)

Start with G $\quad G = U - TS + PV$

Consider a mixture of 2 substances A & B



in thermal & mech. equilibrium
$\rightarrow T_A = T_B$ & $P_A = P_B$

Then $G_{tot} = G_A + G_B$. Let $x = \frac{\# B}{\Sigma} \Rightarrow 1 - x = \frac{\# A}{\Sigma}$

Can write G_A° = Gibbs free energy of pure A $(x=0)$
G_B° = Gibbs free energy of pure B $(x=1)$

☒ Remove partition & let A & B mix

$G = U - TS + PV$, Assume these changes are small $^{\text{in } U, V}$

$$\Delta G = \Delta U - T\Delta S + P\Delta V$$

Initially , $G^{\circ}_{tot} = (1-x)\,G^{\circ}_A + x\,G^{\circ}_B$

Recall , $\Delta S_{mixing} = -Nk\left[x\ln x + (1-x)\ln(1-x)\right]$

So assuming $\Delta U = 0$, $\Delta V = 0$, then,

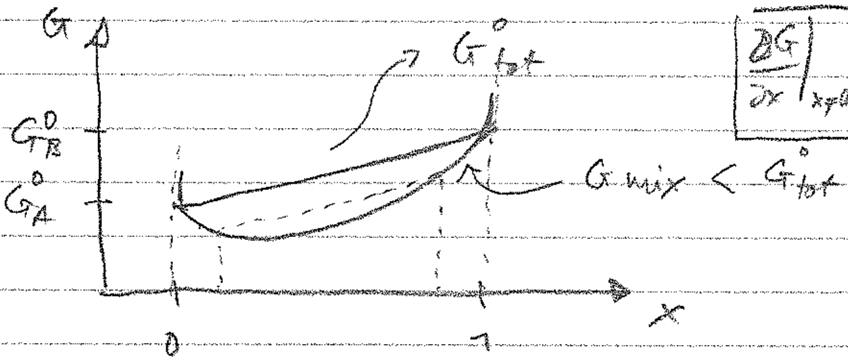
$$G_{mixed} = G^{\circ}_{tot} - T\Delta S$$

$$= G^{\circ}_{tot} + NkT\left[x\ln x + (1-x)\ln(1-x)\right]$$

So $$\boxed{G_{mixed} = (1-x)G^{\circ}_A + xG^{\circ}_B + nRT\underbrace{\left[x\ln x + (1-x)\ln(1-x)\right]}_{<0}}$$

↳ We call this an ideal mixture ⇒ derived from ideal gas...

$\boxed{\text{Plot } G \text{ vs } x}$



$$\boxed{\left.\frac{\partial G}{\partial x}\right|_{x\to 0,1} = \infty}$$

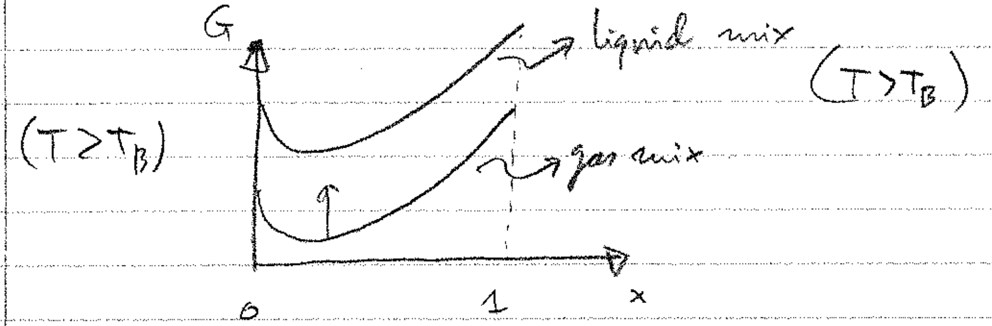
- slope of G vs. x @ 0, 1 is ∞
- impure (mixed) is always more stable b/c of entropy of mixing...

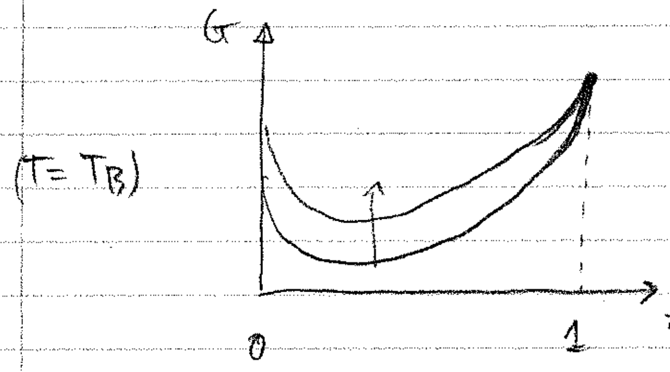
Phase changes of mixtures

e.g. $N_2 + O_2$

Let T_A = boiling point of pure substance A
T_B = boiling point of pure substance B

Let $T_B > T_A$. Then at high temp. $T > T_B > T_A$
→ stable phase is a gas regardless of composition...

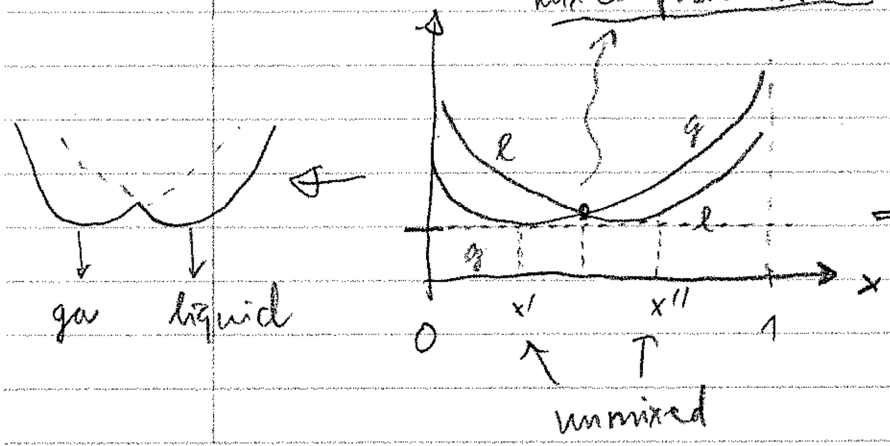




As we decrease T, G changes.

know $\left(\frac{\partial G}{\partial T}\right) = -S$

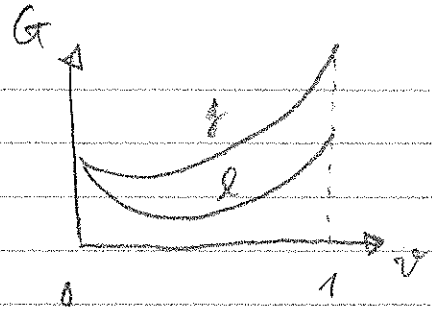
gas & liquid of pure B are in equilibrium.



$T_A < T < T_B$

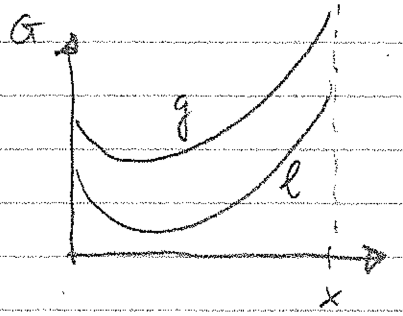
⇒ Unmixed combination of liquid & gas is more stable than mixed

Decrease T further...



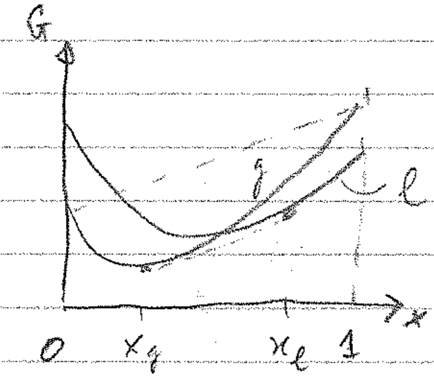
(~~[illegible]~~)

$T = T_A \Rightarrow$ liquid stable for <u>pure A</u>



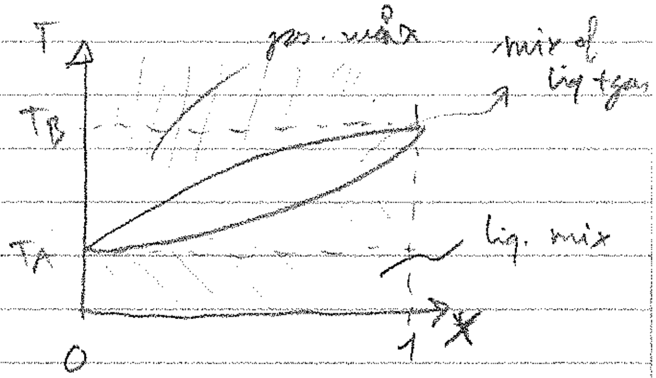
$T < T_A$ ⇝ liquid mixed is stable

pril 15, 2019

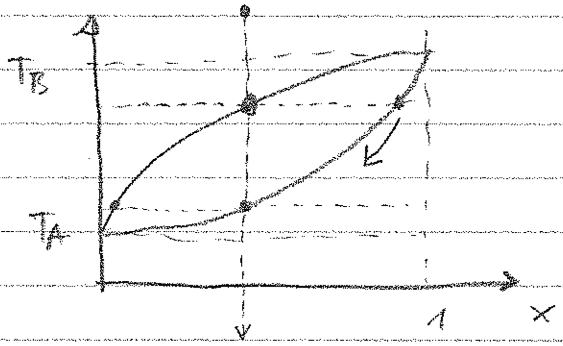


gas mix

⇝

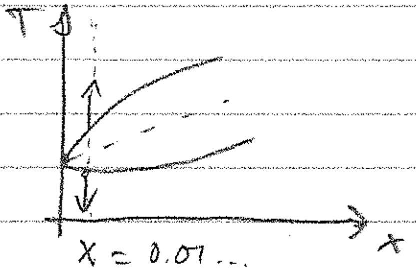


So



as we go down in temp

$\boxed{\text{For dilute solutions}}$, x is small. Means solute does not evaporate ~ gas is pure solvent



⇝ only need equilibrium condition for solvent.

A = solvent, B = solute

▨ $\mu_{A,liq}(T,P) = \mu_{A,gas}(T,P) \rightsquigarrow$ A in equili.

Solvent, $\mu_{A,liq}(T,P) = \mu_0(T,P) - \frac{N_B kT}{N_A}$

And so,

$$\mu_0(T,P) - \frac{N_B kT}{N_A} = \mu_{A,gas}(T,P)$$

Let T_0 be boiling point of pure solvent (A). Hold pressure steady, vary temperature around T_0 to see how μ changes...

$$\cancel{\mu_0(T_0,P)} + (T-T_0)\left(\frac{\partial \mu_0}{\partial T}\right) - \frac{N_B kT}{N_A} = \cancel{\mu_{gas}(T_0,P)} + (T-T_0)\left(\frac{\partial \mu_{gas}}{\partial T}\right)$$

↳ at $T=T_0$, by assumption $\mu_{A,gas}(T_0,P) = \mu_{0_{liq}}(T_0,P)$ @ eq.
(assuming gas is pure solvent)

So

$$(T-T_0)\left(\frac{\partial \mu_0}{\partial T}\right) - \frac{N_B kT}{N_A} = (T-T_0)\left(\frac{\partial \mu_{gas}}{\partial T}\right)$$

Also,

$$\mu = \frac{G}{N} \rightsquigarrow \partial\mu/\partial T = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_{V,N} = \frac{-S}{N}$$

So

$$(T-T_0)\left(\frac{-S_{liq}}{N_A}\right) - \frac{N_B kT}{N_A} = (T-T_0)\left(\frac{-S_{gas}}{N_A}\right)$$

So

$$(T-T_0)\left[\frac{S_{gas}}{\cancel{N_A}} - \frac{S_{liq}}{\cancel{N_A}}\right] = \frac{N_B kT}{\cancel{N_A}}$$

So

$$(T-T_0) = \frac{N_B kT}{S_{gas}-S_{liq}} = \frac{N_B kT}{\Delta S} = \frac{N_B kT}{Q/T_0} = \frac{N_B kT T_0}{L}$$

$Q = L$ = Latent heat

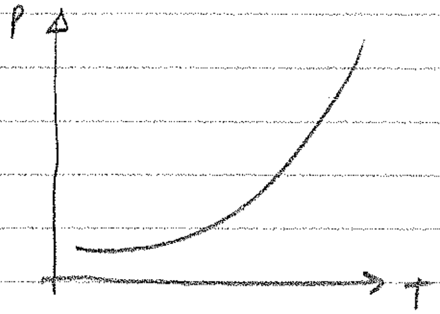
Assuming $T_0 \approx T$

$$\rightarrow \boxed{T-T_0 = \frac{N_B k T_0^2}{L}}$$

So, $\boxed{T-T_0 = \frac{n_B R T_0^2}{L}}$ → shift in boiling point of solvent due to n_B solute.

Shift in vapor pressure

... (derivation in book)



Raoult's law $\boxed{\frac{P}{P_0} = 1 - \frac{N_B}{N_A}}$

only for dilute solutions ...

#

Ch. 6 Boltzmann Statistics

<u>Goal</u>: Get multiplicity for more complicated systems

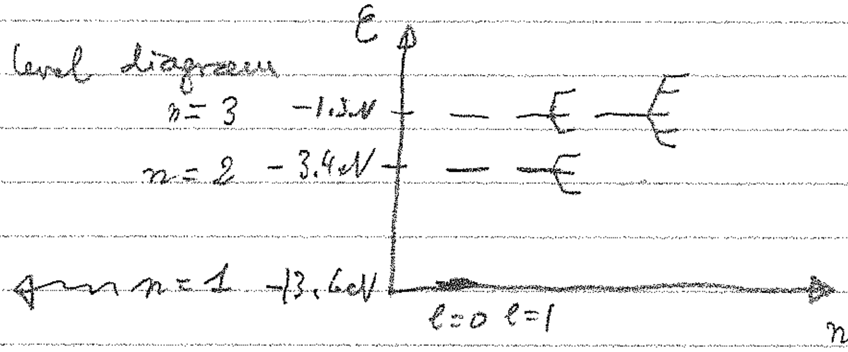
April 16, 2019

▨ "System" of a single atom in a reservoir of other atoms at some temperature T

- Macrostate = energy level. These energy levels are degenerate. → multiple microstates.

<u>Ex</u> Hydrogen atom, n, l, m_l, m_s.

- Energy level diagram



principal q. number.

n is # ≥ 1

l : orbital angular momentum. l is $0, 1, .. (n-1)$

m_l : z-component of orbital angular momentum $-l \leq m_l \leq l$

m_s : z-component of spin angular momentum $m_s = \pm\frac{1}{2}$ ..

▨ In general, for H, degeneracy is $\boxed{2n^2}$ for H

- Single atom exchanges energy with reservoir at temp T.
  Assumption → all microstates with in a given macrostate are equally probable.

- Macrostate of the atom + reservoir system with highest multiplicity should be most probable.

- Remember : $P(A) = \dfrac{\# A}{\# \Omega \to \Sigma}$

- Use ratios instead to avoid $\# \Omega$. Take 2 possible states of atom s_1 & s_2.

$E(s_1)$ = Energy of atom in s_1
$E(s_2)$ = Energy of atom in s_2
$P(s_1)$ = prob. in s_1
$P(s_2)$ = prob. in s_2

<u>Want</u> state with highest multiplicity in combined atom + reservoir system → most probable.

$\Omega_R(s_1)$ → multiplicity of reservoir when atom is in state s_1

$$P_R(s_1) \propto \Omega_R(s_1) \Rightarrow \frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} \qquad S = k \ln \Omega$$

$$S = k \ln \Omega \rightarrow \boxed{\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{\left(\underbrace{S_R(s_2) - S_R(s_1)}_{\text{infinitesimal change in entropy of reservoi}}\right)/k}}$$

$$dS_R = \frac{1}{T_R}\left[dU_R + P\,dV_R - \mu\, dN_R\right]$$

equal & opposite
to the atoms ...

$\rightsquigarrow P\,dV_R \rightarrow \sim (1\,\text{Å})^3$ at 1 atm $\rightarrow (10^5\,\text{Pa})(10^{-10})^3 \simeq 10^{-25}\,\text{J}$

$dU_R \sim$ few eV $\sim 10^{-19}\,\text{J}$

So $P\,dV_R \ll dU_R \rightarrow$ ignore. $\rightsquigarrow dV_R \simeq 0$

Also, $dN_R \simeq 0$

So,
$$\left[S_R(s_2) - S_R(s_1)\right] = \frac{1}{T_R}\left[U_R(s_2) - U_R(s_1)\right]$$

reservoir ...

atom ...

$$\left[S_R(s_2) - S_R(s_1)\right] = \frac{-1}{T_R}\left[E(s_2) - E(s_1)\right]$$

And so,
$$\frac{P(s_2)}{P(s_1)} = e^{-[E(s_2)-E(s_1)]/kT}$$

$$\boxed{\frac{P(s_2)}{P(s_1)} = \frac{e^{-E(s_2)/kT}}{e^{-E(s_1)/kT}}}$$

→ Boltzmann factor...

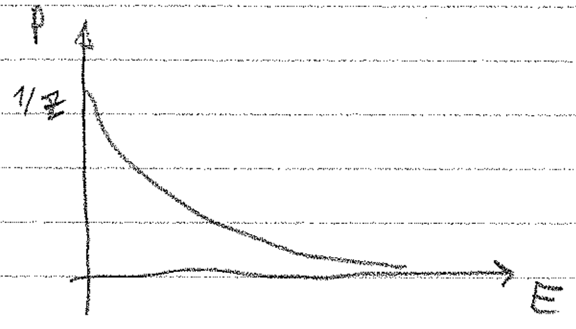
$e^{-E(s)/kT}$

So
$$\underset{\text{indep. of } s_1}{P(s_2)\,e^{E(s_2)/kT}} = \underset{\text{indep of } s_2}{P(s_1)\,e^{E(s_1)/kT}} \Rightarrow \text{must be constant.}$$

So
$$\frac{P(s_2)}{e^{-E(s_2)/kT}} = \frac{P(s_1)}{e^{-E(s_1)/kT}} = \text{constant} = \frac{1}{Z}$$

$$\boxed{P(s) = \frac{1}{Z}\,e^{-E(s)/kT}}$$

$\rightsquigarrow$ Boltzmann distribution (canonical distribution)



Z : The Partition Function

Total probability of finding an atom in some state or another = 1

$$1 = \sum_s P(s) = \sum_s \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z}\sum_s e^{-E(s)/kT}$$

So $\boxed{\underbrace{Z}_{\text{constant}} = \sum_s e^{-E(s)/kT}}$ ~ partition function...

April 17, 2019

Z → normalization factor that converts Boltzmann factor into a prob

Temp. dependence of Z

① Low T, @ room T, $kT \approx 0.0257$ eV

ground state energy = 0 eV

→ dominates partition function.

Ex Excited state $\underbrace{e^{-10.2\,eV/kT}}_{\text{tiny...}}$ while $e^{-0} = 1$

→ @ low T, $\boxed{Z = 1}$ ⟶ 1 possible state available...

② At high T $E < kT$

$$Z = e^{-0/kT} + e^{-E_2/kT} + \ldots$$

$$= 1 + (\text{order of unity}) + \ldots$$

So $Z \gg 1$

★ At high temp, there are many states available...


greetings

$\boxed{\text{Applications of Boltzmann factors}}$

☒ Thermal excitations of atoms in stellar atmospheres..

Consider H atom in atm of sun ($T \sim 5800K$).
What is the prob. of finding e^- in one of the first excited states compared to probability of finding e^- in ground state.

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-E_2/kT}}{e^{-E_1/kT}} = e^{-(E_2-E_1)/kT} \quad \&$$

For H, $E_2 - E_1 = \Delta E = -3.4\,\text{eV} - (-13.6\,\text{eV}) = 10.2\,\text{eV}$

And $kT = (8.62\times10^{-5}\,\text{eV/K})(5800\,\text{K}) = 0.50\,\text{eV}$

$$\frac{P(s_2)}{P(s_1)} = e^{-10.2\text{eV}/0.5\text{eV}} = 1.4\times10^{-9}$$

But we need to add "statistical weights" to account for degeneracy of energy levels...

$g_2 = 8 \quad (2n^2)$
$g_1 = 2$

$$\& \quad P(\varepsilon_2)/P(\varepsilon_1) = \frac{g_2}{g_1}\cdot e^{-\Delta E/kT}$$
$$= 4\left[2.4\times10^{-9}\right]$$
$$= 5.6\times10^{-9}$$

$\boxed{\text{Caveat}}$ At some temp T, we start ionizing atoms.

→ No more e^- for upwards transitions.

→ Boltzmann dist is only part of the story...

↑ (Excitation → need to add Saha equation to account for ionization. Saha eqn:

$$\text{pressure} \longrightarrow \frac{P_{H(\text{ionized})}}{P_{H(\text{neutral})}} = \frac{1}{n_e}\left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} e^{-E_I/kT}$$

~~4~~

$\boxed{\text{Average values}}$ § 6.2.

$$\boxed{p(s) = \frac{1}{Z} e^{-E(s)/kT} = \frac{1}{Z} e^{-\beta E(s)}}$$

where $\beta = 1/kT$

And so $Z = \sum_s e^{-E(s)/kT} = \sum_s e^{-\beta E(s)}$

Imagine we have an atom with 3 discrete energy levels...
0eV, 4eV, 7eV ...
Say we have 5 such atoms, 2 in ground, 2 in 1st state,
1, in 2nd state.

Average energy of all 5 atoms is:

$$\bar{E} = \frac{0\,\text{eV}\cdot 2 + 4\,\text{eV}\cdot 2 + 7\,\text{eV}\cdot 1}{5} = \frac{15\,\text{eV}}{5} = 3\,\text{eV}\ldots$$

or

$$\bar{E} = \left(\frac{2}{5}\,0\,\text{eV}\right) + \left(\frac{2}{5}\,4\,\text{eV}\right) + \left(\frac{1}{5}\cdot 7\,\text{eV}\right)$$

$$= P(|0\rangle)\cdot 0\,\text{eV} + P(|1\rangle) - \cdots$$

$\frac{1}{Z} e^{-\beta E(s)}$

$\boxed{\text{Generalize}}$

$$\boxed{\bar{E} = \frac{\sum_s E(s)\,N(s)}{N} = \sum_s E(s)\frac{N(s)}{N} = \sum_s E(s)P(s)}$$

So $\bar{E} = \frac{1}{Z}\sum_s E(s)\, e^{-\beta E(s)}$

Can do this for avg value of any property

$$\boxed{\overline{X} = \sum_s X(s)P(s) = \frac{1}{Z}\sum_s X(s)\,e^{-\beta E(s)}}$$

Also note that average values are additive...

if $\bar{E}$ is avg value of single atom, so in general,

$$\boxed{\langle u \rangle = N\bar{E}}$$ → avg energy of ensemble of N particles...

Calculate deviation about the mean

For our 5 atoms @ 3 energy level. $\bar{E} = 3eV$ ... then the difference from the mean

2 atoms @ 0eV : $\Delta E = E_1 - \bar{E} = 0 - 3eV = -3eV$
2 atoms @ 4eV : $\Delta E = E_2 - \bar{E} = 4eV - 3eV = 1eV$
'' $= 4eV$

$\overline{(\Delta E)^2}$ → average of the square deviation.

$$= \frac{(-3)^2 \cdot 2 + (1)^2 \cdot 2 + 4^2}{5} = 7.2\ eV^2$$

Then, $\sqrt{\overline{(\Delta E)^2}}$ = rms / stdev ... = $\sigma_E = \sqrt{7.2\,eV^2} = 2.7\,eV$

But we developed that

$$\sigma_E^2 = \overline{E^2} - \bar{E}^2$$

For any system in thermal equilibrium with reservoir at temp T, average value of the energy, $\overline{E}$:

$$\boxed{\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \quad \text{where } \beta = \frac{1}{kT}}$$

or equivalently

$$\boxed{\overline{E} = -\frac{\partial \ln(Z)}{\partial \beta}}$$

Proof

$$\frac{\partial Z}{\partial \beta} = \frac{\partial}{\partial \beta}\left[\sum_s e^{-\beta E(s)}\right] = \sum_s \frac{\partial}{\partial \beta} e^{-\beta E(s)} = \sum_s -E(s)\, e^{-\beta E(s)}$$

So

$$-\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{+1}{Z}\sum_s +E(s)\, e^{-\beta E(s)} = \sum_s \left(\frac{1}{Z}\right) E(s) \left(e^{-\beta E(s)}\right) = \sum E(s) \cdot P(s)$$

So $$\boxed{-\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \overline{E}}$$

Can also show that

$$\boxed{\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}}$$

How is work related to Z?

→ suppose we have a system characterized by a single param, x.

→ Quasi-static change in x, $x \to x + dx$

- Energy of state (s) changes by some small amount

$$\Delta_x E_s = \frac{\partial E_s}{\partial x}\, dx$$

- Work done on the system ⇒ $W = \int F \cdot dx$ or $\sum F \cdot \Delta x$
  where F → is change in Energy w.r.t x.

$$F = \frac{\partial E_s}{\partial x}$$

- Work done on system $$W = \frac{\sum_s \frac{\partial E_s}{\partial x}\, e^{-\beta E(s)}\, \Delta x}{\sum_s e^{-\beta E(s)}}$$

Re-write numerator $\sum_s e^{-\beta E(s)} \frac{\partial E(s)}{\partial x} = -\frac{1}{\beta}\frac{\partial}{\partial x}\left(\sum_s e^{-\beta E(s)}\right)$

So

$$\sum_s e^{-\beta E(s)}\frac{\partial E(s)}{\partial x} = \frac{-1}{\beta}\frac{\partial}{\partial x}\left(\underbrace{\sum_s e^{-\beta E(s)}}_{Z}\right) = \frac{+1}{-\beta}\frac{\partial Z}{\partial x}$$

So,

$$W = \frac{-1}{\beta}\frac{\partial Z}{\partial x}dx \Big/ Z$$

So

$$W = \frac{-1}{\beta}\frac{\frac{\partial Z}{\partial x}dx}{Z} = \frac{-1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{-1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

So

$$\boxed{W_{on} = \frac{-1}{\beta}\frac{\partial \ln Z}{\partial x}dx}$$

▨ For example, $x = V$ (volume)

$$W_{on} = -\bar{P}\,dV = \frac{-1}{\beta}\frac{\partial \ln Z}{\partial V}dV$$

So

$$\boxed{\bar{P} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}}$$

▨ How is Z related to S?

$Z = Z(\beta, x)$. For small changes in Z,

$$d\ln Z = \underbrace{\frac{\partial \ln Z}{\partial x}dx}_{} + \underbrace{\frac{\partial \ln Z}{\partial \beta}}_{}d\beta$$

So

$$\boxed{d\ln(Z) = -\beta \underset{\substack{\uparrow \\ dW_{on}}}{W_{on}} + -\bar{E}\,d\beta}$$

Re-writing $d\ln z = -\beta dW - d(\bar{E}\beta) + \beta d\bar{E}$

So $d(\ln z + \bar{E}\beta) = \beta(\underbrace{d\bar{E} - dW_m}_{dQ \text{ (first law)}}) = \beta dQ = \frac{dQ}{kT} = \frac{1}{k}ds$

So $d(\ln z + \bar{E}\beta) = \frac{dS}{k}$ Now, $S = k\ln\Omega$

So $\boxed{S = k(\ln z + \beta\bar{E})}$

So $\ln z + \beta\bar{E} = \ln\Omega$

So $\boxed{\ln z = \ln\Omega - \beta\bar{E}}$

Example of paramagnetism

Before: ① $\Omega(N_\uparrow) = \binom{N}{N\uparrow} = \frac{N!}{N_\uparrow!\,N_\downarrow!}$

② $S = k\ln\Omega$ (use Sterling approximation)

③ $\frac{1}{T} = \left(\frac{\partial S}{\partial u}\right)$

④ $U = U(T) \rightarrow u = -N\mu B\tanh\left(\mu B/kT\right)$

⑤ $M = -\frac{u}{B}$

⑥ $C_B = \left(\frac{\partial U}{\partial T}\right)_B$

Now, we'll redo this with Boltzmann statistics... Two possible energy states...

"up" $u = -\mu B$
"down" ~~μ~~ $u = \mu B$ } then $z = \sum_s e^{-\beta E(s)} = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)}$

$= e^{\mu\beta B} + e^{-\mu\beta B}$

So $\boxed{z = 2\cosh(\mu\beta B)}$

☒ Probability of finding m up / down direction.

$$P_\uparrow = \frac{e^{\beta\mu B}}{2\cosh(\mu\beta B)}, \quad P_\downarrow = \frac{e^{-\beta\mu B}}{2\cosh(\mu\beta B)}, \quad P_\downarrow + P_\uparrow = 1$$

Average energy of a dipole

$$\bar{E} = \sum_i E(i)P(i) = (-\mu B)\frac{e^{\beta\mu B}}{2\cosh(\mu B\beta)} + (\mu B)\frac{e^{-\mu B\beta}}{2\cosh(\mu B\beta)}$$

$$= (-\mu B)\frac{2\sinh(\mu B\beta)}{2\cosh(\mu B\beta)}$$

$$= -\mu B\tanh(\beta\mu B)$$

So $\bar{E} = -\mu B\tanh(\mu B\beta)$

So $$\boxed{\bar{E}_{tot} = -N\mu B\tanh(\beta\mu B) = -N\mu B\tanh\left(\frac{\mu B}{kT}\right)}$$

Alternate approach

$$\bar{E} = \frac{-1}{z}\frac{\partial z}{\partial\beta}$$

$$= \frac{-1}{z}\frac{\partial}{\partial\beta}\left[2\cosh(\beta\mu B)\right]$$

$$= \frac{-1}{z}\cdot 2\left(\mu B\sinh(B\mu\beta)\right)$$

$$= (2\mu B)\frac{-1}{2\cosh(\mu B\beta)}\sinh(B\mu\beta)$$

$$= -\mu B\tanh(\mu B\beta)$$

So $$\boxed{\bar{E}_{tot} = -N\mu B\tanh(\mu B\beta)}$$

Magnetization $\Longrightarrow$ $M = N\bar{\mu}_z$, $\bar{\mu}_z = \sum \mu_s P(s) \ldots$

$$= +\mu P_\uparrow + (-\mu)P_\downarrow$$

April 22, 2019

The Equipartition Theorem

↳ applies to systems with quadratic degrees of freedom.

$E = p^2/2m$

$E = cq^2$ where q = position or momentum coordinates...

• $Z = \sum_q e^{-\beta c q^2}$, and assuming that the spacing Δq is constant and small...

So $Z = \frac{1}{\Delta q}\sum_q e^{-\beta c q^2}\Delta q$

$$= \frac{1}{\Delta q}\int_{-\infty}^{\infty} e^{-\beta c q^2}\,dq$$

Change of variables: Let $x = \sqrt{\beta c}\cdot q \rightarrow x^2 = \beta c q^2$

$$dq = \frac{dx}{\sqrt{\beta c}}.$$

So

$$Z = \frac{1}{\Delta q}\int_{-\infty}^{\infty} e^{-x^2}dx \cdot \frac{1}{\sqrt{\beta c}} = \frac{1}{\Delta q}\frac{1}{\sqrt{\beta c}}\int_{-\infty}^{\infty} e^{-x^2}dx$$

assumption...

(*) As long as $\Delta q \ll kT$, then equipartition holds (high temp)

$$Z = \frac{\sqrt{\pi}}{\Delta q\sqrt{\beta c}}$$

So $\boxed{Z = \frac{1}{\Delta q}\sqrt{\frac{\pi}{\beta c}}}$

Or, equivalently, $\boxed{Z = C\beta^{-1/2}}$ ⇝ C is some constant...

So, $\bar{E} = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-1}{C\beta^{-1/2}}\left(\frac{-1}{2}C\beta^{-3/2}\right) \Rightarrow \bar{E} = \frac{1}{2}\beta^{-1}$

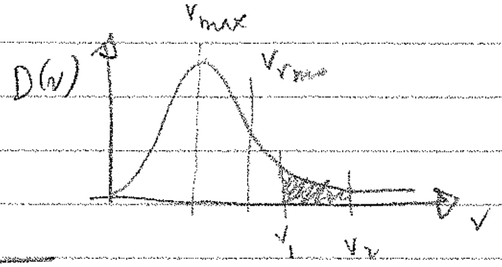
So $\boxed{\bar{E} = \frac{1}{2}kT}$ → Eq. partition theorem for sgle df.

Note **Conditions**

▨ Equipartition doesn't hold for quantum mechanical systems, since it requires a continuum of Δq...

▨ Equipartition holds if $\Delta q \ll kT$ (high temp)

The Maxwell's Speed Distribution



▨ From equipartition, can imagine:

$\overline{\frac{1}{2}mv^2} = \frac{3}{2}kT$, then $v_{rms} = \sqrt{\frac{3kT}{m}}$

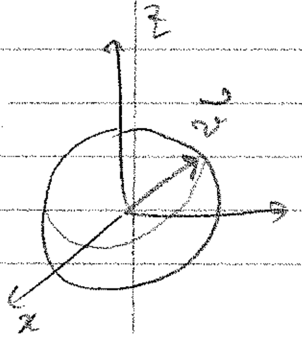
$P(v_1 < v < v_2) = \int_{v_1}^{v_2} \underbrace{D(v)\,dv}_{\text{pdf.}}$, where $D(v)$ is the dist. function...

▨ What is $D(v)$? → $D(v) \propto$ prob that a molecule will have ~~velocity $\vec{v}$~~ - a # of vectors, $\vec{v}$ corresponding to speed $\vec{v}$.

$$D(v) \propto \underbrace{\begin{pmatrix}\text{prob. of molecule} \\ \text{w/ velocity } \vec{v}\end{pmatrix}}_{\boxed{?}} \times \underbrace{\begin{pmatrix}\text{\# of vectors, } \vec{v} \\ \text{corresponding to speed } v\end{pmatrix}}_{\sim\Omega \quad \boxed{??}}$$

Know, $\boxed{?} \propto$ Boltzmann factor... $E = \frac{1}{2}mv^2 \rightarrow = \boxed{e^{-mv^2/2kT}}$

$\boxed{??} \propto 4\pi v^2$



→ Larger v, more surface area, higher Ω for $\vec{v}$.

So $\boxed{D(v) = C\,(4\pi v^2)\, e^{-mv^2/2kT}}$

$$1 = \int_0^\infty D(v)\,dv = 4\pi C \int_0^\infty v^2 e^{-mv^2/2kT}\,dv$$

Change of vars, $x = v\sqrt{\frac{m}{2kT}}$, then...

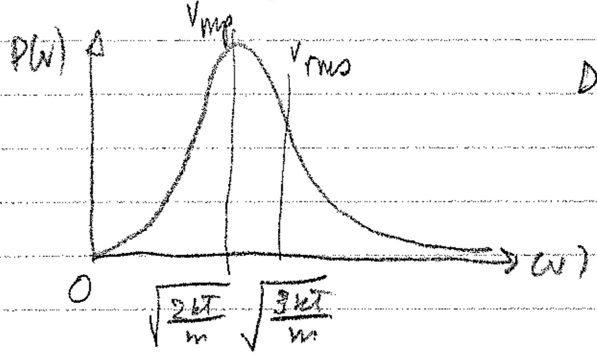
$$1 = 4\pi C \int_0^\infty x^2 e^{-x^2}\,dx \left(\sqrt{\frac{2kT}{m}}\right)^3$$

$$= 4\pi C \cdot \left(\frac{2kT}{m}\right)^{3/2} \underbrace{\int_0^\infty x^2 e^{-x^2}\,dx}_{\sqrt{\pi}/4}$$

So $\boxed{C = \left(\frac{m}{2\pi kT}\right)^{3/2}}$

Maxwell's speed distribution...

Thus, $\boxed{D(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{\frac{-mv^2}{2kT}}}$



$D(v) = 0$ @ $v = 0$ & $v \to \infty$

☒ Calculate V_{mp} (most probable)

$$0 = \frac{d}{dv} D(v) = 0 \rightarrow 0 = \frac{d}{dv}\left[v^2 e^{-mv^2/2kT}\right]$$

So $0 = 2v\,\cancel{e^{-mv^2/2kT}} + v^2 \cdot \left(\frac{-mv}{kT}\right)\cancel{e^{-mv^2/2kT}}$

$$= 2v + \frac{-mv^3}{kT} \Rightarrow 0 = 2 - \frac{mv^2}{kT} \Rightarrow \boxed{V_{mp} = \sqrt{\frac{2kT}{m}}}$$

$\boxed{\text{Calculate } \bar{v}}$

$$\bar{v} = E(v) = \int_0^\infty v\, D(v)\, d_N = \int_0^\infty 4\pi v^3 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}}\, dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 e^{-mv^2/2kT}\, dv$$

$$\bar{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} (4\pi) \cdot \frac{1}{2}\left(\frac{2kT}{m}\right)^2$$

So $\bar{v} = \left(\frac{2kT}{m}\right)^{1/2} \cdot \frac{2}{\sqrt{\pi}}$

So $\boxed{\bar{v} = \left(\frac{8kT}{m\sqrt{\pi}}\right)^{1/2}}$

$M = mN_A$.

Ex N_2 in air @ room temp... $T \sim 298K$, $m_N = 14\ g/mol$

$m_{N_2} = 28 g/mol$

$$v_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2(1.38\times10^{-23})(298K)}{28\times10^{-3} kg/mol / 6.023\times10^{-23}}} \simeq \boxed{420.5\ m/s}$$

April 23, 2019

$\boxed{\text{PARTITION FUNCTION \& FREE ENERGY}}$

$\Omega(u)$ @ const $u \Rightarrow S$ tends to T, $S = k\ln\Omega$

$Z(T) \Leftrightarrow F$ @ constant T

Recall $F \equiv U - TS \longrightarrow \frac{F-U}{T} = -S$

$$dF = -PdV - SdT + \mu dN \rightarrow \left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$$

So, $\left(\frac{\partial F}{\partial T}\right)_{V,N} = \frac{F-U}{T}$ ①

Guess $\tilde{F} = -kT\ln Z \Rightarrow Z = e^{-\tilde{F}/kT}$

Check deriv w.r.t T: $\frac{\partial}{\partial T}\tilde{F} = \frac{\partial}{\partial T}\left(-kT\ln Z\right)$

$$= -k\ln Z - kT\frac{\partial}{\partial T}\ln Z$$

$$= -k\ln Z - kT\underbrace{\frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta}\ln Z}_{\frac{-1}{kT^2}\underbrace{\frac{1}{Z}\frac{\partial Z}{\partial\beta}}_{-U}}$$

$$\rightarrow \frac{\partial\tilde{F}}{\partial T} = -k\ln Z - \frac{U}{T}$$

$\frac{\partial\tilde{F}}{\partial T} = \frac{\tilde{F}}{T} - \frac{U}{T} = \frac{\tilde{F}-U}{T}$, same as ①, so we know guess was correct, except there might be a constant

<u>Check initial condition</u> (to determine constant)

$F = U - TS$ Let's use $T=0$, then $F(T=0) = U_0$

$\uparrow$ Lowest possible energy.

$Z(@T=0) = \cancel{U_0}\sum_s e^{-E(s)/kT}$

$= e^{-U_0/kT}$ + high order terms, negligible because $U \gg kT$

So $\tilde{F}(T=0) = -kT\ln Z = -kT(-u_0/kT) = -U_0$

<u>So</u> $\tilde{F}(T=0) = U_0$ no constant!

<u>So</u> $\boxed{F = -kT\ln Z}$

$dF = -PdV - SdT + \mu dN$

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

<u>Example</u> $\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S$ $F = -kT\ln Z$, $S = \frac{-\partial}{\partial T}\left(-kT\ln Z\right)$

$$S = \frac{-\partial}{\partial T}\left(-kT\ln Z\right) = k\ln Z + \frac{\partial\beta}{\partial T}\frac{\partial}{\partial\beta}\ln Z$$

$$= k\ln Z + \frac{\bar{E}}{T}$$

So $\boxed{S = k\left(\ln Z + \beta\bar{E}\right)}$ ✓ Same as before

or $\ln Z = \frac{S}{k} - \beta\bar{E}$

Partition Function for Composite System

Goal: write an expression for Z for an ideal gas

1st: Determine how Z_{tot} depends on Z for each individual particle...

Start w/ system ~~of~~ 2 particles. If they do not interact, total ~~energy~~

$$E_{tot} = E_1 + E_2$$

$$Z_{tot} = \sum_s e^{-\beta[E_1(s)+E_2(s)]} = \sum_s e^{-\beta E_1(s)}e^{-\beta E_2(s)}$$

If we also assume that states of individual particles are independent of each other:

$$Z_{tot} = \underbrace{\sum_{s_1} e^{-\beta E_1(s)}}_{Z_1}\ \underbrace{\sum_{s_2} e^{-\beta[E(s)]}}_{Z_2} \Rightarrow \boxed{Z_{tot} = Z_1 Z_2}$$

(non-interacting distinguishable ~~system~~ particles)

If particles are indistinguishable, we have double counted states.

↳ $Z_{tot} \approx \frac{1}{2} Z_1 Z_2$

Generalize this to N particles → $Z_{tot} = Z_1 Z_2 \ldots Z_N$ distinguishable → or $Z_{tot} = Z_1^N$

For distinguishable, $\boxed{Z_{tot} = \frac{1}{N!} Z_1^N}$

April 26, 2019

Working towards Z for ideal gas.

$$Z_{tot} = \frac{1}{N!} Z_1^N$$

$$E_{tot} = E_{tr} + \underset{\sim}{E_{int}}$$

E_{tr} ↓ (translation) (KE) or thermal energy

E_{int}: internal states (rotation/vibration)

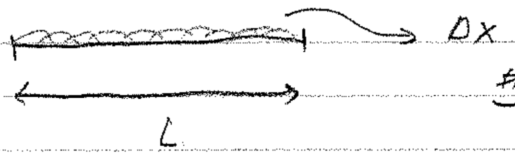
$$\boxed{\text{Boltzmann factor}} \rightarrow e^{-E_{tot}(s)/kT} = e^{-(E_{tr})/kT} \cdot e^{-(E_{int})/kT}$$

So $Z_1 = Z_{tr} Z_{int}$

$$Z_{tr} = \sum_{tr} e^{-E_{tr}(s)/kT} \quad \& \quad \overbrace{Z_{int} = \sum_{int} e^{-E_{int}(s)/kT}}^{\text{ignore this one for now ...}}$$

☒ When we counted states before:

1D:



$$\underline{\text{\# Position states}} = \frac{L}{\Delta x}$$

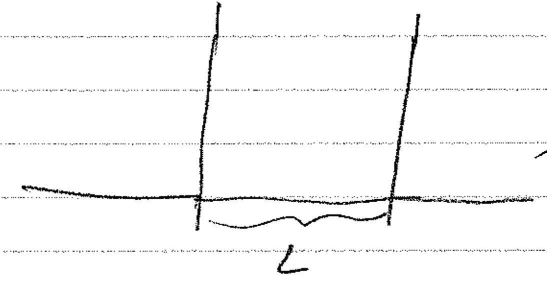
$$\underline{\text{\# Momentum states}} = \frac{L_p}{\Delta p}$$

Total # of states

$$\frac{L}{\Delta x} \cdot \frac{L_p}{\Delta p} \cong \frac{L L_p}{h}$$

☒ More rigorously,

↳ Count all independent, definite energy states or wave function



→ infinite square well

$$\text{Potential energy} \begin{cases} 0 & \text{inside box} \\ \infty & \text{outside the box} \end{cases}$$

$$\rightarrow KE = \begin{cases} 0, & \text{outside} \\ \text{something}, & \text{inside} \end{cases}$$

$$\boxed{KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}}$$ → only certain wavelengths are allowed

$\rightarrow \lambda_n = \frac{2L}{n}$, $n = 1, 2, 3 \ldots$

So $\boxed{p = \frac{h}{\lambda} = \frac{hn}{2L}}$ → allowed momenta

So $\boxed{E_n = \frac{p^2}{2m} = \left(\frac{hn}{2L}\right)^2 \frac{1}{2m} = \frac{h^2 n^2}{8mL^2}}$ → allowed independent energies..

So, $Z_{k\,(1\text{-}D)} = \sum e^{-E_n(s)/kT}$

$$= \sum_n \exp\left[\frac{-h^2 n^2}{8mL^2} \cdot \beta\right]$$

assume large T, L → $\simeq \int_0^\infty \exp\left[\frac{-h^2 n^2}{8mL^2 kT}\right] dn$

$\boxed{\Delta n = 1}$

Let $x = \frac{hn}{\sqrt{8mL^2 kT}} \rightarrow \frac{dx}{dn} = \frac{h}{\sqrt{8mL^2 kT}}$

So, $Z_{1D} = \frac{\sqrt{8mL^2 kT}}{h} \int_0^\infty e^{-x^2} dx$

$$= \sqrt{\frac{8mL^2 kT}{h^2}} \cdot \sqrt{\frac{\pi}{2^2}}$$

$$\boxed{Z_{1D} = \frac{\sqrt{2\pi mkT}}{h} L = \frac{L}{l_Q}}$$ → l_Q = "quantum length"

- The quantum length, l_Q is roughly the de Broglie λ of a particle of mass m & energy kT...

$= \frac{h}{\sqrt{2\pi mkT}}$

$\lambda = \frac{h}{p}$, $E = kT = \frac{p^2}{2m} \rightarrow p = \sqrt{2mkT}$, then $\boxed{\lambda = \frac{h}{\sqrt{2mkT}}}$

$l_Q \cdot \sqrt{\pi}$

$\shortparallel$

So $l_Q \sim$ roughly the size of a particle... ~~For N_2~~:

☒ Ex For N_2 @ $T = 298K$, $l_Q \simeq 1.9\times10^{-11}$ m

$\Rightarrow \frac{L}{l_Q}$ is large.

$\boxed{\text{In three dimensions}}$

$$E_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$ independent

each $p_{i,n} = \frac{hn_i}{2L}$

So

$$E_{tr} = \sum_s e^{-E(s)/kT} = \sum_{n_x n_y n_z} e^{\frac{-h^2n_x^2}{8mL_x^2kT}} e^{\frac{-h^2n_y^2}{8mL_y^2kT}} e^{\frac{-h^2n_z^2}{8mL_z^2kT}}$$

$$= \dots$$

$$= \frac{L_x}{l_Q}\cdot\frac{L_y}{l_Q}\cdot\frac{L_z}{l_Q}$$ For each atom.

So

$$\boxed{Z_{tr} = \frac{V}{l_Q^3} = \frac{V}{v_Q}}$$ "quantum volume"

☒ $$v_Q = l_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3$$

So

$$Z_{tot} = \frac{1}{N!}Z_1^N = \frac{1}{N!}\left(Z_{tr}\cdot Z_{int}\right)^N$$ ignore this

$$\boxed{Z_{tot} = \frac{1}{N!}\left(\frac{V}{v_Q}\cdot Z_{int}\right)^N}$$

Sometimes, log of Z is more useful...

$$\underbrace{}_{}$$
Stirling's approx

$$\boxed{\ln Z_{tot} = N\left(\ln V + \ln Z_{int} - \ln V_Q\right) - N\ln N + N}$$

So, $\boxed{\ln Z_{tot} = N\left[\ln V + \ln Z_{int} - \ln V_Q - \ln N + 1\right]}$

log of partition function for ideal gas...

Now we can predict the thermodynamic properties of ideal gas

- Average energy of ideal gas → expect $\bar{E} = \frac{3kTN}{2}$

↳ $\ln Z_{tot} = N\left[\ln V + \ln Z_{int} - \ln V_Q - \ln N + 1\right]$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial \ln Z}{\partial\beta}$$

Note: V is independent of T, β

N is also independent of T, β

Z_{int}, V_Q depend on β.

So,

$$\bar{E} = -N\left[\frac{\partial}{\partial\beta}(\ln Z_{int}) - \frac{1}{V_Q}\frac{\partial V_Q}{\partial\beta}\right]$$

$$= -N\left[-\bar{E}_{int} + \frac{1}{V_Q}\frac{\partial}{\partial\beta}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right]$$

$$= N\bar{E}_{int} + \frac{1}{V_Q}\left(\frac{h^2}{2\pi m}\right)^{3/2}\frac{\partial}{\partial\beta}\left(\beta^{3/2}\right)$$

$$= N\bar{E}_{int} + \frac{1}{V_Q}\left(\frac{h}{\sqrt{2\pi m}}\right)^{3}\frac{3}{2}\beta^{1/2}$$

$$= N\bar{E}_{int} + N\left(\frac{\sqrt{2\pi mkT}}{h}\right)^{3}\left(\frac{h}{\sqrt{2\pi m}}\right)^{3}\cdot\frac{3}{2}\sqrt{\beta}$$

$$= N\bar{E}_{int} + \frac{3}{2}N\beta^{-1} \quad \text{So} \quad \boxed{\bar{E} = N\bar{E}_{int} + \frac{3}{2}NkT}$$

→ if assume no internal energy, $\bar{E} \to \frac{3}{2}NkT$

→ E_{int} depends on Eq. Partition Thm

Heat Cap $\boxed{C_V = \left(\frac{\partial U}{\partial T}\right) = \left(\frac{\partial U_{int}}{\partial T}\right) + \frac{3}{2}Nk}$

April 29, 2011

Ch 7: QUANTUM STATISTICS

↳ We'll use Gibbs factors instead of Boltzmann factor...

☒ Think about system that can exchange energy & particles...

↳ Look at ratio of probabilities $\frac{P(s_2)}{P(s_1)} = \Omega_R(s_2)/\Omega_R(s_1) = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}}$

So,

$$\frac{P(s_2)}{P(s_1)} = e^{(S_R(s_2) - S_R(s_1))/k}$$

$$dS_R = \frac{1}{T}\left[dU_R + PdV_R - \mu dN_R\right]$$

- Assume that $dV_R = 0$
- keep μdN terms this time

So,

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}\left[\overbrace{\left(E(s_2) - E(s_1)\right)}^{dU_{sys}} - \overbrace{\left(\mu dN(s_2) - \mu dN(s_1)\right)}^{\mu dN_{sys}}\right]$$

$$= -\Delta S_R$$

So

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-[(E(s_2) - \mu N(s_2))]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}$$

So, instead of Boltzmann factor, we get this factor → Gibbs

$$\boxed{e^{-(E(s) - \mu dN)/kT}}$$

To get absolute probability → need constant at front

$$\boxed{P(s) = \frac{1}{\mathcal{Z}} e^{-(E(s)-\mu N(s))/kT}}$$

$\mathcal{Z}$ ⇒ "grand partition function" or "Gibbs sum"

So that $\sum_s P(s) = 1 \rightarrow \boxed{\mathcal{Z} = \sum_s e^{-(E(s)-\mu N(s))/kT}}$

Sum over all Gibbs factors...

If you have more than 1 types of particles, then sum over all species $\mu_i dN_i$

Ex 2 particles.. Gibbs factor : $e^{-(E(s)-\mu_A N_A(s)-\mu_B N_B(s))/kT}$

BOSONS + FERMIONS

Quantum statistics → important for high density + low temp systems...

In this case, derivation of

$$Z_{tot} = \frac{1}{N!} Z_1^N$$ breaks down @ high density, low temperature..

⇝ $\frac{1}{N!}$ is not quite correct here.

Ex 2 interacting particles, each with 5 available states in the ground state energy, $E=0$.

☐ ☐ ☐ ☐ ☐ $E = 0$

Boltzmann factor $= e^{-0} = 1 \Rightarrow Z = 5$ so $Z = \Omega$

<u>But</u> • If distinguishable $\Rightarrow \Omega = 5 \times 5 = 25 = Z$

so $\boxed{Z_{tot} = Z_1^N}$

• If indistinguishable $\Rightarrow \Omega = \binom{5}{2} = 10$

<u>so</u> $\boxed{Z = 10}$

Previous assumption for indistinguishable particles

$$Z_{tot} = \frac{1}{N!} Z_1^N = \frac{25}{2!} = 12.5$$ → does not make sense...

(Fermions) # states for indistinguishable particles ⇒ ⑩, no 2 particles are occupying the same states.

(Bosons) ☒ But if we allow them to be in the same state ⇒ ⑮ for indistinguishable particles that <u>can</u> be in the same state → boson.

⇒ And so 12.5 → average between bosons & Fermions

☒ $\underbrace{\frac{1}{N!} Z_1^N}$ correctly cuts down 20 states for distinguishable particles to 10 for indistinguishable particles. But also cuts down 5 → 2.5 incorrectly.

$\boxed{\text{Bosons}}$ → can share the same (quantum) states (Ex; photons, pions, ^{4}He nuclei). integer spin: 0, 1, 2, ħ

$\boxed{\text{Fermions}}$ → cannot occupy the same (q) states $(e^-, p^+, n, \nu, ..)$

↳ half-integer spin $\frac{\hbar}{2}, \frac{3\hbar}{2}, \ldots$)

$\boxed{\text{Pauli exclusion principle}}$ → Fermions

So $Z_{tot} = \frac{1}{N!} Z_1^N$ interpolates between correct value for indistinguishable bosons & fermions...

▨ Bosons → governed by Bose-Einstein statistics.

▨ Fermions → governed by Fermi-Dirac statistics.

$\boxed{?}$ When do we need to use B-E & F-D stats rather than Boltzmann stats?

↳ when # of single particle states >> # of particles, then it doesn't matter if we have bosons or fermions, use Boltzmann statistics

→ if $Z_1 \gg N$

▨ Think back to Ideal gas: $Z_1 = \frac{V}{V_Q} Z_{int}$, where

$$V_Q = \left(\frac{h}{\sqrt{2\pi m kT}}\right)^{3}, \text{ for } Z_1 \gg N$$

$\frac{V}{V_Q} \gg N$, And so, $\frac{V}{N} \gg V_Q$ → average distance between particles is >> de Broglie wavelengths.

⊛ when $\frac{V}{N} \sim V_Q$, then it matters whether we have Bosons or Fermions. → use Quantum Statistics either B-E or F-D.

At high temperature, $Z_1 \gg N \rightarrow$ more Boltzmann statistics.

$$\boxed{\text{Single-particle state of a system}}$$

- System → particular state of particle.
- "Reservoir" → all the possible states.

April 10, 2019

DISTRIBUTION FUNCTIONS

- System ⇒ single-particle quantum state
- Reservoir ⇒ all other possible states

~ If state is occupied, it has energy ε
  If unoccupied, energy 0

If state can be occupied by N particles → Energy $N\varepsilon$

☒ Probability of being occupied by N particles

$$P(N) = \frac{1}{Z} e^{-(N\varepsilon - N\mu)/kT}$$

So

$$\boxed{P(N) = \frac{1}{Z} e^{-N(\varepsilon-\mu)/kT}}$$

For Fermions, $n = 0$ or 1

$$Z_F = e^{0(\cdots)/kT} + e^{-1(\varepsilon-\mu)/kT} = 1 + e^{-(\varepsilon-\mu)/kT}$$

So Fermions: $\boxed{Z_F = 1 + e^{-(\varepsilon-\mu)/kT}}$

Determine the average # of particles in a state, or the occupancy of the state

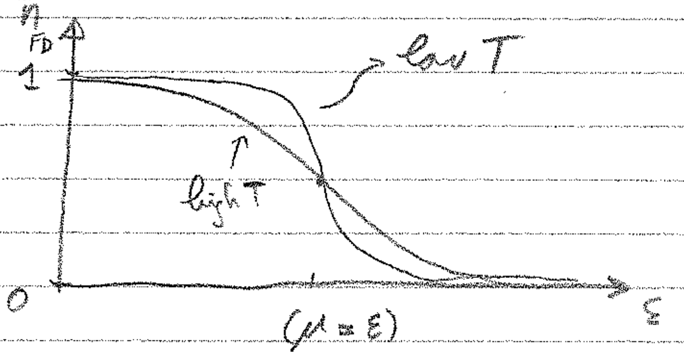
Fermions

$$\bar{n} = \sum_n n P(n) = 0 \cdot P(0) + 1 \cdot P(1)$$

$$= \frac{e^{-(\varepsilon-\mu)/kT}}{1+e^{-(\varepsilon-\mu)/kT}}$$

So $\boxed{\bar{n}_{FD} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}}$ ⇝ Fermi-Dirac distribution

- ▨ If $\boxed{\varepsilon \gg \mu}$ $\bar{n} \to 0$
- ▨ If $\boxed{\varepsilon \ll \mu}$ $\bar{n} \to 1$
- ▨ If $\boxed{\varepsilon = \mu}$ $\bar{n} \to 1/2$ ⇝ 50% chance of being occupied.



$\boxed{\text{Bosons}}$ → $n \in \mathbb{N}$ 0, 1, 2, ...

Then

$$\mathcal{Z} = 1 + e^{-(\varepsilon-\mu)/kT} + e^{-2(\varepsilon-\mu)/kT} + \dots$$

But $\frac{1}{1-x} = 1 + x + x^2 + x^3 + \dots$ (geometric series)

So $\boxed{\mathcal{Z} = \frac{1}{1-e^{-(\varepsilon-\mu)/kT}}}$

So, partition functions for bosons,

$$\boxed{\mathcal{Z}_B = \frac{1}{1-e^{-(\varepsilon-\mu)/kT}}}$$

☒ Average occupancy: $\bar{n} = \sum_n n P(n)$. Let $x = \frac{\varepsilon-\mu}{kT}$

then $$\bar{n} = \sum_n n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \sum_n \frac{d}{dx} e^{-nx}$$

$$= \frac{-1}{\mathcal{Z}} \frac{d}{dx} \sum_n e^{-nx}$$

$$\boxed{\bar{n}_B = \frac{-1}{\mathcal{Z}} \frac{d}{dx} \mathcal{Z}}$$

So $$\bar{n}_B = -\left(1-e^{-x}\right) \cdot \frac{d}{dx} \left(1-e^{-x}\right)^{-1}$$

$$= \frac{1-e^{-x}}{(1-e^{-x})^2} \cdot (e^{-x})$$

$$= \frac{e^{-x}}{1-e^{-x}}$$

$$\bar{n}_B = \frac{1}{e^{x}-1}$$

Bose-Einstein dist.

So $$\boxed{\bar{n}_{BE} = \frac{1}{e^{+(\varepsilon-\mu)/kT}-1}}$$

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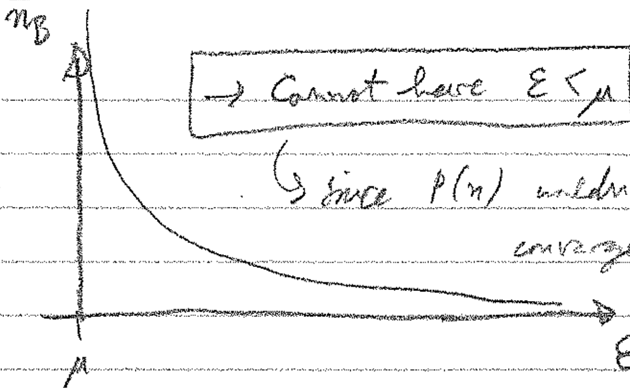
☒ If $\boxed{\varepsilon >> \mu} \rightsquigarrow \bar{n} \to 0$

☒ If $\boxed{\varepsilon << \mu} \longrightarrow \bar{n} \to -1$ (X)

☒ If $\boxed{\varepsilon \to \mu} \longrightarrow \bar{n} \to \infty$



→ Cannot have $\varepsilon < \mu$

↳ since $P(n)$ wouldn't converge...

☒ Consider particles obeying Boltzmann statistics

$P(s) = \frac{1}{Z_1} e^{-E(s)/kT}$. If we have N particles, then

$$\boxed{\bar{n}_\beta = \frac{N}{Z_1} e^{-E(s)/kT} = \frac{N}{Z_1} e^{-\varepsilon/kT}}$$

Boltzmann distribution.

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad \& \quad F = -kT \ln Z$$

So,

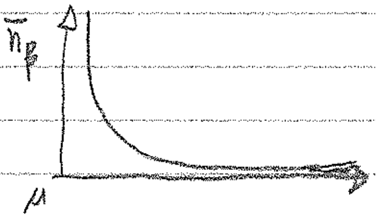
$$\mu = -kT \ln\left(\frac{Z_1}{N}\right)$$

So

$$e^{-\mu/kT} = \frac{Z_1}{N} \quad \text{So} \quad \bar{n}_{Boltz} = e^{\mu/kT} e^{-\varepsilon/kT} = e^{-(\varepsilon-\mu)/kT}$$

So

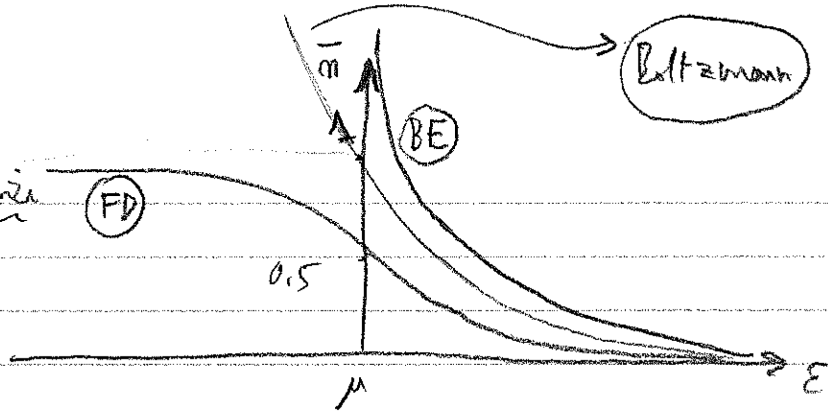
$$\boxed{\bar{n}_\beta = \frac{1}{e^{(\varepsilon-\mu)/kT}}}$$



So

$$\bar{n}_F = \frac{1}{e^x+1}, \quad \bar{n}_B = \frac{1}{e^x-1}, \quad \bar{n}_\beta = \frac{1}{e^x}$$

So, summarize



DEGENERATE FERMI GASES

☒ Consider a gas of Fermions at low T, or $\frac{V}{N} \not\gg V_Q$

Ex: for an electron at room temp:

$$V_Q = \left(\frac{h}{\sqrt{2\pi m_e kT}}\right)^3 = (4.3\ nm)^3$$

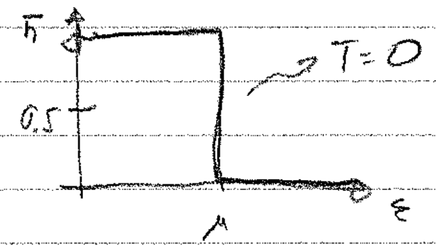
Typical conductor supplies 1 free e^- for every atom

↳ 1 e^- per atom → $V \sim (\text{size of atom})^3 \sim (0.2nm)^3$

May 1, 2012

Recall

$$\bar{n}_F = \frac{1}{e^{(\varepsilon-\mu)/kT}+1} \rightarrow$$



@ T=0 all $\varepsilon < \mu$ will be occupied. All $\varepsilon > \mu$ unoccupied

→ $\boxed{\text{"Degenerate Fermi gas"}}$

$\boxed{\text{At } T=0}$ at $\mu(T=0) = \varepsilon_F$ ⇐ Fermi Energy

$\boxed{\text{Goal}}$ Calculate → total & average energy of Fermi gas

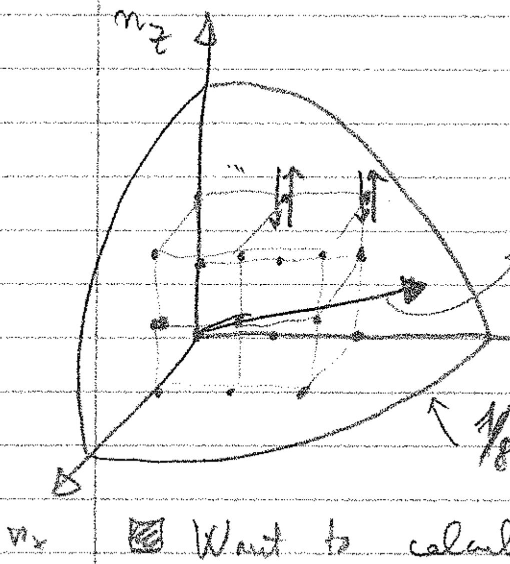
↳ degeneracy pressure. (whenever there's degenerate Fermi gas ...)

▨ Consider packing electrons into some 3D volume (infinite square well)

Allowed wavefunctions give $\lambda_n = \frac{2L}{n}$ & $p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$

$$p_x = \frac{hn_x}{2L_x}, \quad p_y = \frac{hn_y}{2L_y}, \quad p_z = \frac{hn_z}{2L_z}$$

n_x, n_y, n_z are integers ... independent of each other ...



Allowed energies: $E = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{2m\,\underset{(2L)^2}{\downarrow}}\left[n_x^2 + n_y^2 + n_z^2\right]$

$$\boxed{n_{max} = \sqrt{n_x^2 + n_y^2 + n_z^2}}$$

▨ Each point represents 2 electrons (spin $\pm 1/2$)

1/8 of a sphere of radius n_{max}

▨ Want to calculate $\boxed{\mathcal{E}_F = \text{max energy}}$

$$\mathcal{E}_F = \frac{h^2}{2m} \cdot \frac{1}{4L^2} = \frac{h^2}{8mL^2} n_{max}^2$$

Total # of electrons = 2. Volume of 1/8 sphere

$$N = 2 \cdot \left[\frac{1}{8} \frac{4}{3} \pi \cdot n_{max}^3\right]$$

$$N = \frac{1}{3}\pi \left[\sqrt{n_x^2 + n_y^2 + n_z^2}\right]^3$$

Solve for n_{max}

$$n_{max} = \left(\frac{3N}{\pi}\right)^{1/3} \quad \& \quad \mathcal{E}_F = \frac{h^2}{2m}(n_{max})^2 \cdot \frac{1}{4L^2}$$

&

$$\boxed{\mathcal{E}_F = \frac{h^2}{8mL^2}\left(\frac{3N}{\pi}\right)^{2/3}}$$ ← Fermi energy.

Since $V = L^3 \Rightarrow L^2 = V^{2/3}$

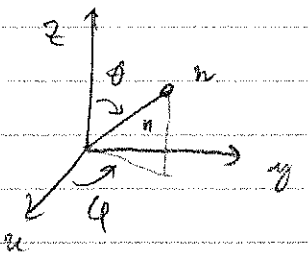
So $$\boxed{\varepsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}}$$ $\Leftarrow$ Fermi energy...

number density... intensive property...

■ Total energy of degenerate Fermi gas

$$U_{tot} = 2\int_0^\infty\int_0^\infty\int_0^\infty \varepsilon(n)\, dn_x\, dn_y\, dn_z$$ → assuming large # states...

Convert to spherical coordinates...



$n^2 dn$ $$\boxed{dV = dn_x\, dn_y\, dn_z = n^2 \sin\theta\, d\varphi\, d\theta\, dn}$$

So
$$U_{tot} = 2\int_0^{n_{max}}\int_0^{\pi/2}\int_0^{\pi/2} \varepsilon(n)\, n^2 \sin\theta\, d\varphi\, d\theta\, dn$$

$$= 2\left(\frac{4\pi}{8}\right)\int_0^{n_{max}} \varepsilon(n)\, n^2\, dn$$

$$= \pi\int_0^{n_{max}} \varepsilon(n)\, n^2\, dn$$

$$= \pi\int_0^{n_{max}} \frac{h^2 n^2}{8mL^2}\, n^2\, dn$$

$$= \frac{h^2\pi}{8mL^2}\int_0^{n_{max}} n^4\, dn$$

$$= \frac{h^2\pi}{8mL^2}\cdot\frac{1}{5}n_{max}^5 \Rightarrow \boxed{U_{tot} = \frac{h^2\pi}{40mL^2}\cdot n_{max}^5}$$

In terms of $\varepsilon_F = \frac{h^2}{8mL^2} \cdot n_{max}^2$, $n_{max} = \left(\frac{3N}{\pi}\right)^{1/3}$

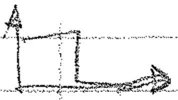
$$U_{tot} = \frac{\pi \varepsilon_F}{5} n_{max}^3$$

So

$$\boxed{U_{tot} = \frac{3}{5} N \varepsilon_F} \text{ at } T=0$$

temp-ind.

average energy as expected, a little bit $> \frac{1}{2}\varepsilon_F$



So, average energy per particle .. $\boxed{\bar{U} = U_{tot}/N = \frac{3}{5}\varepsilon_F}$

If $\boxed{\varepsilon_F \gg kT \rightsquigarrow \text{degenerate gas}}$

Fermi Temperature ⇝ temp. at which characteristic thermal energy = Fermi energy

$kT = \varepsilon_F \Rightarrow \boxed{T_F = \frac{\varepsilon_F}{k}}$ ⇝ need T lower than T_F to set degenerate Fermi gas

Pressure of degenerate Fermi gas (due to Pauli's exclusion principle)

$$dU = \overset{0}{\cancel{T dS}} - P dV + \overset{0}{\cancel{\mu dN}}$$

So $\left(\frac{dU}{dV}\right)_{S,N} = -P \rightsquigarrow P = -\left(\frac{\partial U}{\partial V}\right)_{S,N}$

So $P_F = -\frac{\partial}{\partial V}\left[\frac{3}{5} N \frac{h^2}{8m}\left(\frac{3N}{\pi}\right)^{2/3} \cdot V^{-2/3}\right]$

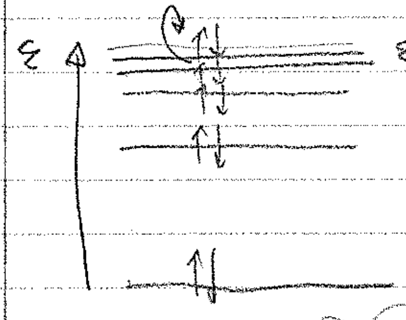
$= \frac{3}{5} N \frac{h^2}{8m}\left(\frac{3N}{\pi}\right)^{2/3} \cdot \left(\frac{-2}{3}\right) V^{-5/3}$ So $\boxed{P_F = \frac{2}{5}\frac{N}{V}\varepsilon_F}$

In terms of U_{tot} ⇒ $\boxed{P = \frac{2}{3}\frac{U_{tot}}{V}}$ → $\frac{2}{3}$ of energy density of degenerate Fermi gas

temperature - independent

$\boxed{P > 0 \rightarrow \text{pushing outwards}}$ → Ex white dwarf star.. prevents collapse due to gravity...

▨ Consider small, non zero temp



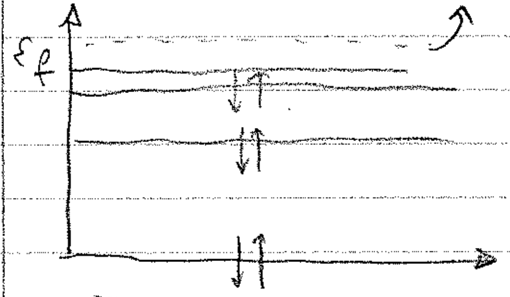
▨ total energy gained by degenerate gas

$$\text{is proportional to } \underbrace{(\#\text{ of } e^-)}_{\propto NkT} \cdot \underbrace{\begin{pmatrix}\text{E gained}\\ \text{per electron}\end{pmatrix}}_{\propto kT}$$

So $U_{gained} \propto N(kT)^2$

May 6, 2019

Degenerate Fermi Gas at small non-zero temps



if ΔT > 0, small, e^- ⇒ ΔE = kT

$$\boxed{\text{Energy gained by degenerate Fermi-gas}} \propto \cancel{N(kT)}^2$$

$$\underbrace{\begin{pmatrix}\#\text{ e that}\\ \text{can jump}\end{pmatrix}}_{(NkT)} \times \underbrace{\begin{pmatrix}\text{energy}\\ \text{gained}\end{pmatrix}}_{\sim(kT)}$$

So $\boxed{U_{gained} \sim N(kT)^2}$ → when ΔT > 0, small

So, since $U_{gained} \propto N(kT)^2$

units of constants $= \left(\frac{1}{\text{energy}}\right)$

Guess ⇒ $\frac{1}{\varepsilon_F}$

Additional constant of proportionality ⇒ $\frac{\pi^2}{4}$

So $\boxed{U_{gained} = \frac{\pi^2}{4\varepsilon_F} N(kT)^2}$

So

$$U_{tot} = U(T=0) + U(\Delta T)$$

$$\boxed{U_{tot} = \frac{3}{5}N\varepsilon_F + \frac{\pi^2}{4}\frac{N}{\varepsilon_F}(kT)^2}$$

→ energy of degenerate gas...

this true for any temperature...

$\boxed{kT \ll \varepsilon_F}$

Heat capacity

↳ at constant volume ⇒ $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

So $C_V = \frac{\partial}{\partial T}\left(\frac{\pi^2}{4}\frac{N}{\varepsilon_F}(kT)^2\right)$

$$\Rightarrow \boxed{C_V = \frac{\pi^2 N k^2 T}{2\varepsilon_F}}$$

↳ as $T \to 0$, $C_V \to 0$, as expected...

↳ Note $\boxed{C_V \propto T}$ (linearly in temp)

Density of States

$$U = \underset{(\downarrow\uparrow)}{2} \int_0^{n_{max}} n^2 \varepsilon(n)\, dn \underbrace{\int_0^{\pi/2} d\varphi \int_0^{\pi/2} \sin\theta\, d\theta}_{(\pi/2)}$$

$$\boxed{U = \pi \int_0^{n_{max}} n^2 \varepsilon(n)\, dn} \longrightarrow \text{integrating over all states} \ldots$$

What about integrating over all energies...

$$\varepsilon = \frac{h^2}{8mL^2} n^2 \implies n = \sqrt{\frac{8mL^2}{h^2}} \sqrt{\varepsilon}$$

So $\quad dn = \sqrt{\frac{8mL^2}{h^2}} \frac{1}{2\sqrt{\varepsilon}}\, d\varepsilon \qquad (n_{max} \sim \varepsilon_F)$

So,

$$\cancel{U = \pi \int_0^{\varepsilon_F} \varepsilon \cdot \sqrt{\frac{8mL^2}{h^2}} \frac{1}{2\sqrt{\varepsilon}}\, d\varepsilon}$$

$$U_{tot} = \pi \int_0^{\varepsilon_F} \varepsilon \left[\left(\frac{8mL^2}{h^2} \right) \varepsilon \left(\frac{8mL^2}{h^2} \right)^{1/2} \frac{1}{2\sqrt{\varepsilon}} \right] d\varepsilon$$

Call Density of states

$$\boxed{g(\varepsilon) = \pi \left(\frac{8mL^2}{h^2} \right)^{3/2} \cdot \frac{\sqrt{\varepsilon}}{2} = \pi \left(8m \right)^{3/2} \cdot \frac{V\sqrt{\varepsilon}}{2h^3}}$$

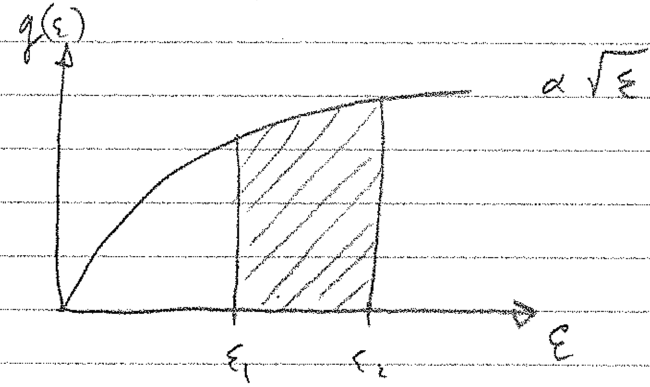
▨ $g(\varepsilon)$ ⤳ probability density, or total # of states with energy ε

- Now, $$\boxed{\varepsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}}$$ $$\boxed{g(\varepsilon) = \frac{\pi(8m)^{3/2}}{2h^3}V\sqrt{\varepsilon}}$$

So $$\boxed{g(\varepsilon) = \frac{3N}{2\varepsilon_F^{3/2}}\sqrt{\varepsilon}} \longrightarrow //$$

▨ **Note:** $g(\varepsilon) \propto V$, independent of N
$\propto \sqrt{\varepsilon}$

▨ Now



▨ At T = 0, then, all e^- are below ε_F, then

$$\left\{\begin{aligned} &P(\text{occupied} \mid \varepsilon < \varepsilon_F) = 1 \\ &P(\text{occupied} \mid \varepsilon > \varepsilon_F) = 0 \end{aligned}\right\}$$

▨ So $$\boxed{N(T=0) = \int_0^{\varepsilon_F} g(\varepsilon)\,d\varepsilon}$$

▨ For non-zero temperature...

$$\boxed{N(T=t) = \int_0^{\infty} g(\varepsilon)\cdot P(\varepsilon)\,d\varepsilon}$$

$\frac{e^{-E/kT}}{Z}$ were Fermi-Dirac dist

$$N = \int_0^\infty g(\varepsilon)\; P(\varepsilon)\; d\varepsilon \longrightarrow \bar{n}_{FD} = \frac{1}{e^{(\varepsilon-\mu)/kT}+1}$$

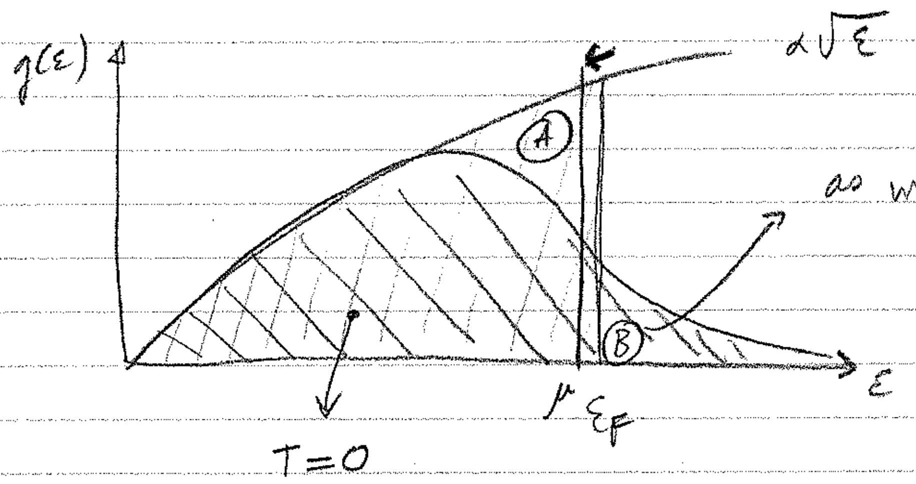
So

$$N = \int_0^\infty g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon$$

So, total energy ...

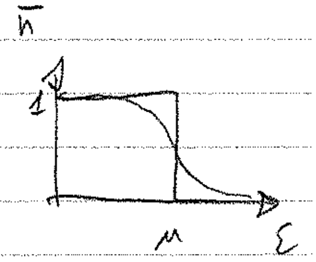
(..stuff)

$$\boxed{U_{tot} = \int_0^\infty \varepsilon\, g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/kT}+1}\,d\varepsilon}$$



$$\boxed{(\text{Area } A) = (\text{Area } B)}$$

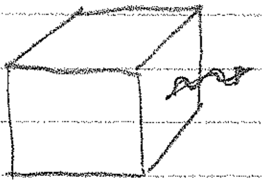
At $T=0$, $\varepsilon_F = \mu$



At $T>0$, μ decreases...

(concentration drops)

Black-body radiation



Inside box... definite energy wavefunctions

$$\lambda = \frac{2L}{n}$$

- Each wave has frequency $\nu = \frac{c}{\lambda}$
- Each wave has 2 df ↗ eq. partition
- Average thermal energy $= 2\cdot\left(\frac{1}{2}kT\right) = kT$

$\boxed{\text{Ultraviolet Catastrophe}}$ → too much radiation is predicted at short λ....

Solution comes from QM → energy is quantized..

$$E_n = 0,\ \hbar\omega,\ 2\hbar\omega,\ 3\hbar\omega,\ \ldots$$

then $Z = \sum_n e^{-E_n/kT} = 1 + e^{-\varepsilon_n/kT} + \left(e^{-\varepsilon_n/kT}\right)^2 + \ldots$

$$= \frac{1}{1-e^{-\beta h\nu}}$$

So $$\boxed{Z = \frac{1}{1-e^{-\beta h\nu}} = \frac{e^{\beta h\nu}}{e^{\beta h\nu}-1}}$$

So $$\boxed{\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{h\nu}{e^{h\nu/kT}-1}}$$

Energy comes in units of $h\nu = \hbar\omega$.

Then average # of units $= \dfrac{\text{Avg. Energy}}{h\nu}$

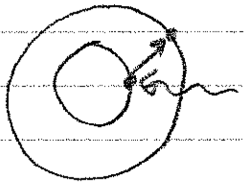
So $\boxed{\bar{n}_{Pl} = \dfrac{\bar{E}}{h\nu} = \dfrac{1}{e^{+h\nu/kT}-1}}$ → Planck's distribution ...

Planck

Note NOT the same as Bose-Einstein dist where

$$\bar{n}_{BE} = \frac{1}{e^{(\epsilon-\mu)/kT}-1}$$

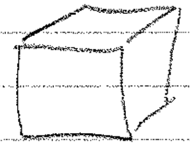
So $\boxed{\mu = 0 \text{ for photons}}$ → $\boxed{\#\gamma \text{ not conserved ...}}$ photons created & destroyed all the time



$$e^- + \gamma \longrightarrow e^-$$

So $\cancel{\mu_{e^-}} + \mu_\gamma = \cancel{\mu_{e^-}}$ so $\mu_\gamma = 0$

May 7, 2019 → $\boxed{\text{Blackbody Radiation}}$



→ what is the total energy inside the box

Reminder Planck's distribution gives the average "occupancy" of an energy mode

$$\bar{n}_{Pl} = \frac{1}{e^{\epsilon/kT}-1}$$

Allowed wfn → $\lambda = \dfrac{2L}{n}$, $p = \dfrac{hn}{2L}$ → allowed energies ..?

Allowed energies: $\Rightarrow E = pc$, not $p^2/2m$ $\Rightarrow$ $\boxed{E_n = \frac{hcn}{2L}}$

In 3D, $\mathcal{E} = cp = c\sqrt{p_x^2 + p_y^2 + p_z^2}$

$$= \frac{hc}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2}$$

Average energy per mode, then

$$= \mathcal{E} \times \underbrace{(\text{occupancy of mode})}_{\text{Planck's distribution, } \bar{n}_{Pl}} =$$

So

total energy $\Rightarrow$ $\boxed{U = 2\sum_{n_x}\sum_{n_y}\sum_{n_z} \mathcal{E}_{\text{mode}} \cdot \bar{n}_{Pl}(\mathcal{E})}$

2 independent polarization states for photons.

So, $\boxed{U = \sum_{n_x, n_y, n_z} \frac{hcn}{L} \cdot \frac{1}{e^{hcn/2LkT} - 1}}$

Convert this to an integral in spherical coordinates.

$$U = \int_0^\infty n^2 \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}\, dn \int_0^{\pi/2} d\varphi \int_0^{\pi/2} \sin\theta\, d\theta$$

$$= \left(\frac{\pi}{2}\right) \cdot \left[\text{change of variables}\right]$$

$\varepsilon = \frac{hcn}{2L} \Rightarrow n^2 = \frac{4\varepsilon^2 L^2}{h^2 c^2}$

$d\varepsilon = \frac{hc}{2L}\, dn$

$$= \frac{\pi}{2} \int_0^\infty \frac{4\varepsilon^2 L^2}{h^2 c^2} \cdot 2\left(\frac{\varepsilon}{1}\right) \cdot \frac{1}{e^{\varepsilon/kT} - 1} \left(\frac{2L}{hc}\right) d\varepsilon$$

So, $U = \frac{8\pi L^3}{(hc)^3}\int_0^\infty \frac{\varepsilon^3}{e^{\varepsilon/kT}-1}\, d\varepsilon$. Call $L^3 = V$

then $$\boxed{\frac{U}{V} = \int_0^\infty \underbrace{\frac{8\pi}{(hc)^3}\,\frac{\varepsilon^3}{e^{\varepsilon/kT}-1}}\, d\varepsilon}$$ → total energy density (per unit volume)

⟨energy density per unit photon energy.⟩

↳ $\boxed{\text{spectrum of photons}}$ → called $u(\varepsilon)$

Spectrum

$$\boxed{u(\varepsilon) = \frac{8\pi}{(hc)^3}\,\frac{\varepsilon^3}{e^{\varepsilon/kT}-1}}$$ → $\boxed{\text{PLANCK'S SPECTRUM}}$

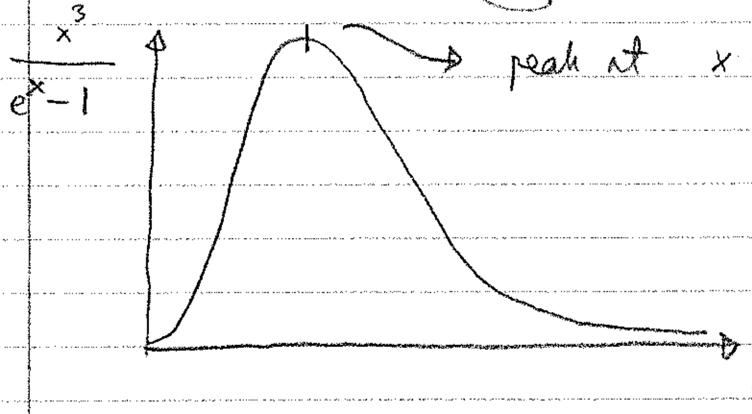
(careful when convert to λ since $d\varepsilon \neq d\lambda$ ...)

Next, evaluate the integral ...

$x = \varepsilon/kT$, so $dx = \frac{1}{kT}\, d\varepsilon$

$$\boxed{\frac{U}{V} = \frac{8\pi}{(hc)^3}\cdot (kT)^4 \underbrace{\int_0^\infty \frac{x^3}{e^x-1}\, dx}}$$

peak energy of spectrum of γ



→ peak at $x = 2.82$ or $\boxed{\varepsilon = 2.82\, kT}$

(one version of Wien's law)

$\lambda = 2.9\times10^{-3}\,[\text{m K}]/T[\text{K}]$

▨ $$\int_0^\infty \frac{x^3}{e^x-1}\,dx = \frac{\pi^4}{15}$$ (Appendix B)

So $$\boxed{\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15(hc)^3}} \rightarrow$$ electromagnetic energy density

Entropy of Photon gas

▨ First calculate heat capacity, C_V

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aT^3 \quad \text{where} \quad a = \frac{8\pi^5 k^4 V}{15(hc)^3}}$$

▨ Entropy...

$$S = \int_0^T \frac{C_V}{T'}\,dT' = \int_0^T 4a\,\frac{(T')^3}{T'}\,dT' = \int_0^T 4a(T')^2\,dT' = \frac{4}{3}aT^3$$

So $$\boxed{S = \frac{32\pi^5}{45} V \left(\frac{kT}{hc}\right)^3 \cdot k} \rightarrow$$ entropy of photon gas...

▨ Pressure of a photon gas...

$$dU = TdS - PdV + \mu dN$$

$$\Rightarrow P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \rightarrow$$ need $U = U(V,S)$ if S constant, N = constant...

$$\frac{U}{V} = \frac{8\pi^5}{15(hc)^3}(kT)^4 \quad \& \quad S = \frac{32\pi^5}{45}\left(\frac{kT}{hc}\right)^3 k \cdot V$$

So want to eliminate temperature...

⊛ Let $\boxed{\alpha = \frac{8\pi^5 k^4}{15(hc)^3}}$, then $U = \alpha V \cdot T^4$, $S = \frac{4}{3}\alpha V T^3$

⇒ Solve for temperature... $T = \left(\frac{3S}{4}\right)^{1/3} \cdot (\alpha V)^{-1/3}$

So

$$U = (\alpha V)\left(\frac{3S}{4}\right)^{4/3} \cdot (\alpha V)^{-4/3}$$

$$\boxed{U = \left(\frac{3S}{4}\right)^{4/3} \cdot (\alpha V)^{-1/3}}$$

So,

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{\partial}{\partial V}\left[\left(\frac{3S}{4}\right)^{4/3} \cdot (\alpha V)^{-1/3}\right]_{S,N}$$

$$= \left(\frac{3S}{4}\right)^{4/3} \cdot \frac{1}{3}\alpha^{-1/3} V^{-4/3}$$

$$= \frac{1}{3}\left(\frac{3}{4}\left[\frac{4}{3}\alpha V T^3\right]\right)^{4/3} \alpha^{-1/3} V^{-4/3}$$

So $\boxed{P = \frac{1}{3}\alpha T^4}$

or in terms of U/V ... ⇒ $\boxed{P = \frac{1}{3}\frac{U}{V}}$

Compare this pressure of Ideal gas ... Monatomic

$$PV = NkT \quad \& \quad U = \frac{f}{2}NkT = \frac{3}{2}NkT$$

So $PV = \frac{2}{3}U$

So $\boxed{P = \frac{2}{3}\frac{U}{V}}$

$\boxed{\text{Ex}}$ CMB — Cosmic Microwave Background radiation...

$T = 2.73K$. Peak $\lambda = \frac{2.93\times10^{-3}}{2.73} \simeq 1\,mm$

Total energy density in CMB...

$$\frac{U}{V} = 8\pi^5 (kT)^4 \Big/ 15(hc)^3 = \boxed{0.26\ MeV/m^3}$$

ordinary matter 1 proton/m^3 → $\boxed{1\ GeV/m^3}$

→ photon density energy pretty low...

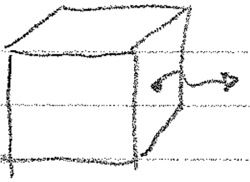
Entropy of CMB ⇒ $S = \frac{32\pi^5}{45} V \cdot \left(\frac{kT}{hc}\right)^3 \cdot k \simeq$

$$\Rightarrow \boxed{\frac{S}{V} \simeq 2.89\times10^9 k} \rightarrow \text{much higher}$$

ordinary matter .. $S/V \sim Nk \sim k$.

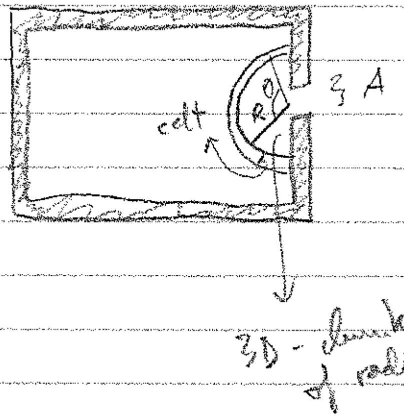
May 8, 2019

Radiation emitted by a Blackbody



{Spectrum of the emitted radiation is the Planck spectrum.}

How much energy escapes from hole?



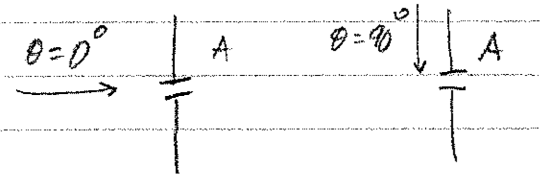
Volume of chunk of radiation that could escape

$$= (R\,d\theta)(R\sin\theta\,d\phi)(c\,dt)$$

Energy density of chunk $= \frac{U}{V} = \frac{8\pi^5}{15}\frac{(kT)^4}{(hc)^3}$

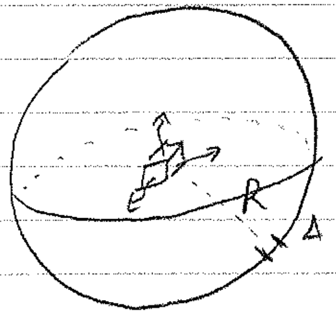
$$\boxed{\text{Total energy of chunk} = \frac{8\pi^5}{15}\frac{(kT)^4}{(hc)^3}\, R^2 c \sin\theta\, d\theta\, d\varphi\, dt}$$

Project hole size depend on angle of photon wrt hole ...



$$\Rightarrow \boxed{\text{Size of hole} = A\cos\theta}$$

Now



probability of photon exiting hole $\Big\} \Rightarrow \boxed{\dfrac{A\cos\theta}{4\pi R^2} = \dfrac{\text{hole size}}{\text{total area}}}$

Energy that escapes hole

$$u = \frac{U}{V} \times \cancel{R^2} c \sin\theta\, d\theta\, d\varphi\, dt \cdot \frac{A\cos\theta}{4\pi \cancel{R^2}}$$

So

$$u_{tot} = \int_0^{\pi/2} d\varphi \int_0^{\pi/2} d\theta \sin\theta\cos\theta \cdot \left(\frac{A}{4\pi}\right) \cdot c\left(\frac{u}{V}\right)\cancel{R^2}\, dt$$

$$= 2\pi \cdot \frac{A}{4\pi}\frac{u}{V}\, c\,dt \underbrace{\int_0^{\pi/2} \cos\theta \sin\theta\, d\theta}_{1/2}$$

$$\boxed{u_{tot} = \frac{A}{4}\left(\frac{u}{V}\right) c\, dt}$$

Energy per unit time gives power → "luminosity"

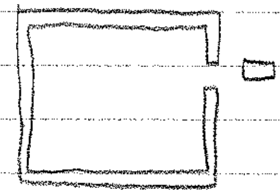
$$P = \frac{U_{tot}}{dt} \longrightarrow \boxed{\text{Flux} = \frac{\text{Power}}{\text{Area}} = \frac{uc}{4V}}$$

So
$$\boxed{\text{Flux} = \frac{c}{4}\left(\frac{u}{V}\right) = \frac{c}{4}\left(\frac{2\pi^5}{15}\right)\frac{(kT)^4}{(hc)^3} = \frac{2\pi^5}{15}\frac{(kT)^4}{h^3c^2} = \sigma T^4 \qquad \sigma = \frac{2\pi^5 k^4}{15h^3c^2} = 5.67\times10^{-8}\ W/m^2K^4}$$

Stefan-Boltzmann Constant

{ Stefan-Boltzmann Law

$\boxed{\text{Why is this blackbody radiation?}}$



What if an object is not black?

↳ Some λ are reflected rather than absorbed

Refine Emissivity, e

↳ = amount of radiation absorbed

If $e=1 \Rightarrow$ blackbody

If $e=0 \Rightarrow$ perfect reflector

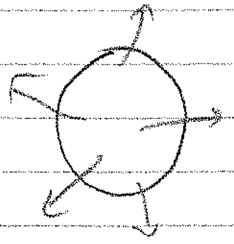
Note e is λ-dependent.

So $\boxed{\frac{\text{Power}}{\text{Area}} = \text{Flux} = \sigma e T^4}$

$$\boxed{\text{Power} = \sigma e A T^4} \rightarrow \text{luminosity}$$

Example $\boxed{\text{Sun}}$ assume $e = 1$

Solar luminosity $= \frac{\text{Power}}{1} \Rightarrow \boxed{L_\odot = 3.8\times10^{26}\,W}$



$A = 4\pi R_\odot^2$, $F_{\text{at surface}} = \frac{L}{A} = \frac{L}{4\pi R_\odot^2} = F_\odot = e\sigma T^4$

$$\text{So} \quad T = \sqrt[4]{\frac{L}{4\pi R_\odot^2 e\sigma}} = \sqrt[4]{\frac{L}{4\pi R_\odot^2 \sigma}} \cong \boxed{5800\,K}$$

- Can also use Wein's law

$$\lambda_{peak} = \frac{2.9\times10^{-3}}{T} \rightarrow \text{get } T \rightarrow \text{get } R \ldots$$

- Can do the same thing for the Earth...

May 10, 2009

BOSE - EINSTEIN CONDENSATES

Now, dealing with ordinary bosons. $\mu \neq 0$, $\mu = \mu(T,P)$

- Phenomenon $\Rightarrow$ a gas of bosons will abruptly "condense" into the ground state energy as T goes below critical value.

1st consider $T \to 0$ Every boson in ground state

$$\varepsilon_0 = \frac{h^2}{8mL^2}(1^2+1^2+1^2) = \frac{3h^2}{8mL^2}$$

Avg # of atoms in ground state at temp T

$$N_0 = \bar{n}_{BE} = \frac{1}{e^{(\varepsilon-\mu)/kT}-1}$$. At low T, $N_0 \to$ large

$$\underbrace{e^{(\varepsilon_0-\mu)/kT}}_{\text{close to } 1} - 1 \longrightarrow \text{small } \# \quad \text{since } \frac{\varepsilon_0-\mu}{kT} \ll 1$$

Now, $e^x \simeq 1+x$

So $N_0 \simeq \dfrac{1}{1+\frac{\epsilon_0-\mu}{kT} - 1} \simeq \dfrac{kT}{\epsilon_0-\mu}$ → large # at low T

at $T=0$, $\mu = \epsilon_0$

& $T \gtrsim 0$, $\mu \leq \epsilon_0$ to keep $N_0 \sim$ constant

☐ How low does T need to be for N_0 to be large?

$N_{tot} = \sum_i \dfrac{1}{e^{(\epsilon(i)-\mu)/kT}-1}$. If $kT \gg \epsilon_0$, convert sum to integral

$$\Rightarrow \boxed{N_{tot} = \int_0^\infty \underset{\uparrow}{g(\epsilon)} \frac{1}{e^{(\epsilon-\mu)/kT}-1}\, d\epsilon}$$

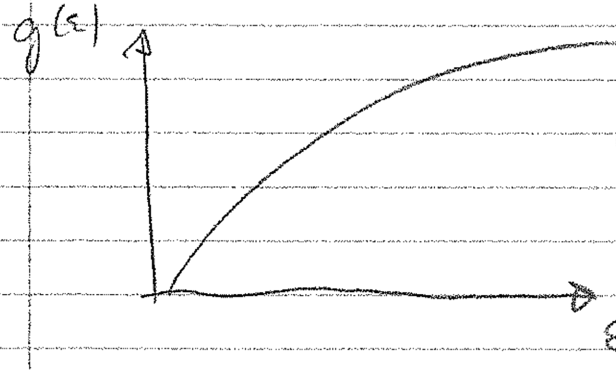
density of states – multiplicity

For fermions

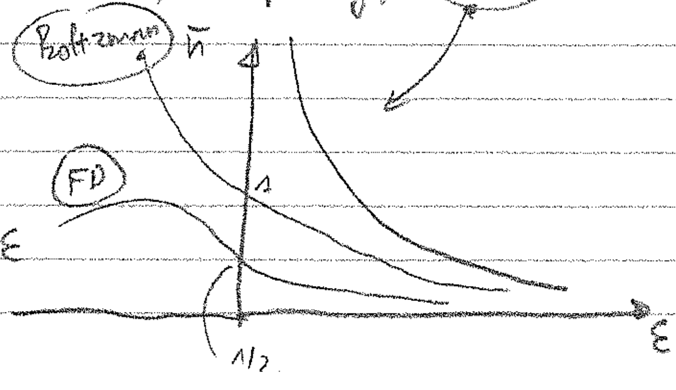
$$g(\epsilon) = \frac{\pi (8m)^{3/2}}{2h^3} V\sqrt{\epsilon} \quad \text{(fermions)}$$

For bosons, divide by 2 (since there's only one spin)

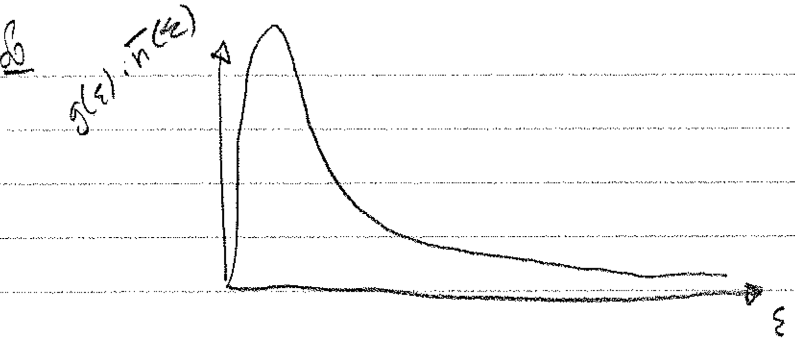
So $\boxed{g(\epsilon) = \dfrac{2}{\sqrt{\pi}}\left(\dfrac{2\pi m}{h^2}\right)^{3/2} \cdot V\sqrt{\epsilon}}$ ← density of states for bosons



Now, occupancy,



So



Total # of particles...

$$N_{tot} = \int_0^\infty g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/kT}-1}\,d\varepsilon$$

<u>guess values for μ . 1st guess $\mu = 0$</u>

So
$$N_{tot} = \int_0^\infty \frac{2}{\sqrt{\pi}}\left(\frac{2\pi m}{h^2}\right)^{3/2}\cdot V\sqrt{\varepsilon}\,\frac{1}{e^{\varepsilon/kT}-1}\,d\varepsilon$$

$$= \frac{2}{\sqrt{\pi}}\left(\frac{2\pi m}{h^2}\right)^{3/2} V\int_0^\infty \sqrt{\varepsilon}\cdot\frac{1}{e^{\varepsilon/kT}-1}\,d\varepsilon$$

change of variable → $x = \frac{\varepsilon}{kT}$, $dx = \frac{1}{kT}\,d\varepsilon$

So
$$N_{tot} = \frac{2}{\sqrt{\pi}}\left(\frac{2\pi mkT}{h^2}\right)^{3/2} V\underbrace{\int_0^\infty \frac{\sqrt{x}}{e^x-1}\,dx}_{(2.315)}$$

So
$$\boxed{N_{tot} = (2.612)\left[\frac{2\pi mkT}{h^2}\right]^{3/2}\cdot V}$$
→ but if $T\uparrow$, $N\uparrow$
→ wrong...

But At $T = T_c$ → condensation temperature, this is <u>true</u>

So
$$\boxed{N_{tot} = (2.612)\left[\frac{2\pi mkT_c}{h^2}\right]^{3/2}\cdot V}$$

So $\boxed{kT_c = 0.527 \left(\frac{h^2}{2m\pi}\right)\left(\frac{N}{V}\right)^{2/3}} \rightarrow$ (density)

At $\boxed{\text{high temperatures } T, \ (T > T_c)}$

expect very few bosons in the ground state ...

↳ large $e^{(\varepsilon_0-\mu)/kT} \rightarrow$ large $\frac{\varepsilon_0-\mu}{kT} \rightarrow \boxed{\text{need } \mu < 0}$

$\boxed{\text{At low } T, \ (T < T_c)}$

$kT \not\gg \varepsilon_0-\mu$, i.e. $kT \not\gg \varepsilon_0 \rightarrow$ can convert the sum to an integral

☒ So, just consider excited states where $kT \gg \varepsilon_0 \rightarrow$ have integral again.

So, $\boxed{\#\text{excited} = (2.612)\left(\frac{2\pi m kT}{h^2}\right)^{3/2} \cdot V}$

And $\boxed{N_{tot} = (2.612)\left(\frac{2\pi m kT_c}{h^2}\right)^{3/2} \cdot V}$

low temp ↓

And so,

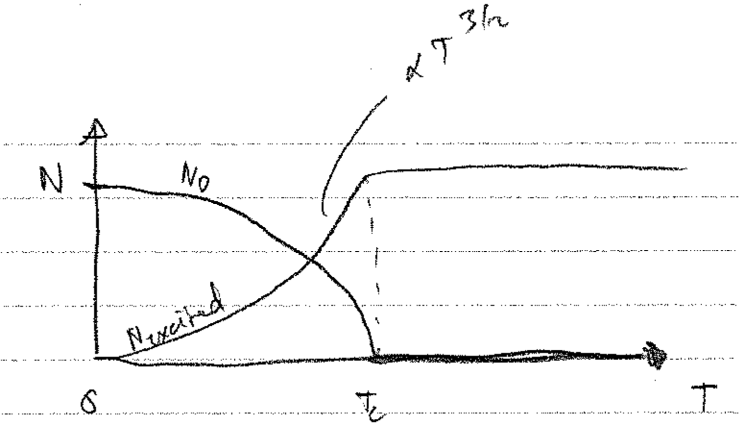
$$N_{excited} = N_{tot}\left(\frac{T}{T_c}\right)^{3/2}$$

$* \ T < T_c$

→ the rest must be in the ground state ... ↗ low temp ...

$$N_0 = N_{ground} = N_{tot} - N_{excited} = \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right] N_{tot}$$

- [illegible]



$$\boxed{T_c \text{ is approximately when } \frac{V}{N} \simeq V_Q} \qquad \left(\frac{2\pi m k T_c}{\hbar^2}\right)^{3/2} \cdots$$

* * *

THE END