Statistical Physics

Isolated system: no exchange of energy or particles with outside world.

Assume QM, but applied to classical phys (Σ - $\int$ phase space)

E, N, ...

finite no. of states

finite V

TISE: $\underbrace{\hat{H}\psi = E}_{\text{eval}}\overbrace{\psi}^{\text{estate}}$.

Def^n Microstate is the actual (quantum) state of system. It has max. info allowed by QM.

Def^n A macrostate specify a few macroscopically observable quantities, e.g. energy E, volume V, temp. T, # particles N, ...

1 macrostate $\longleftrightarrow$ many microstates

$N \sim 10^{23}$ d.o.f. $\Rightarrow$ impossible to solve, microstate is always changing

Mixed state: prob $p(n)$ for state $|n\rangle$ (in some basis)

Expectation values is

$$\langle \hat{O} \rangle = \sum_n p(n) \langle n | \hat{O} | n \rangle .$$

Density matrix

$$\rho = \sum p(n) \, |n\rangle\langle n| .$$

This combines classical and QM uncertainty.

Def^n A system is at equilibrium if prob. distribution $p(n)$, (or ρ) is time-independent.

Fundamental Assumption : for isolated system in eqm, all accesible microstates are equally likely.

(for now) some energy E, more precisely $E < E_n < E + \Delta E$.

Defⁿ (Microcanonical Ensemble) $\Omega(E)$ = no. of states with energy E, then

$$p(n) = \begin{cases} 1/\Omega(E) & \text{if } |n\rangle \text{ satisfies } E<E_n<E+\Delta E \\ 0 & \text{o/w.} \end{cases}$$

- $\Omega(E, \Delta E)$ is huge !

10^{23} particles, each of them with only 2 states, $\Rightarrow 2^{(10^{23})}$

- Although E level discrete, $N \sim 10^{23}$ particles $\Rightarrow$ very finely spaced $\Rightarrow$ almost continuum.

- level spacing $\ll \Delta E \ll$ measurement accuracy. Choice doesn't matter much!

Defⁿ Boltzmann entropy of system (macrostate) is

$$S(E) = k_B \log \Omega(E).$$

k.

where $k_B = 1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ is the Boltzmann constant.

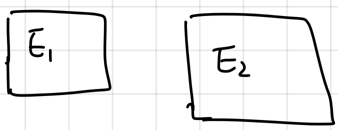
e.g. For 2-state particles, $\Omega = 2^N \Rightarrow S = kN \log 2$.

e.g. gas of 10^{23} particles, $\frac{S}{k} \sim 10^{23}$, $\Omega = e^{S/k} \sim 10^{(10^{23})}$.

If $\Delta E \mapsto 10^6 \Delta E$, then

$$S \longrightarrow S + k \ln 10^6 \approx S.$$

- S is additive : consider 2 systems



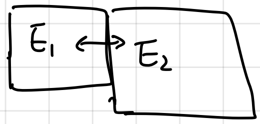
$\Rightarrow \Omega(E_1, E_2) = \Omega(E_1)\,\Omega(E_2)$

$\Rightarrow S(E_1, E_2) = S(E_1) + S(E_2)$.

Bring the two systems together, they exchange energy

$$E_1^{old} \to E_1, \quad E_2^{old} \to E_2,$$

$$E_{tot} = E_1^{old} + E_2^{old} = E_1 + E_2.$$



$$\Omega(E_{tot}) = \sum_{\substack{\{E_i\} \\ \text{disjoint}}} \Omega_1(E_i)\,\Omega_2(E_{tot}-E_i) = \sum_{\{E_i\}} \exp\left(\frac{S_1(E_i)}{k} + \frac{S_2(E_{tot}-E_i)}{k}\right)$$

For $N \sim 10^{23}$, system is <u>dominated</u> by max S. $\Rightarrow$ maximise S

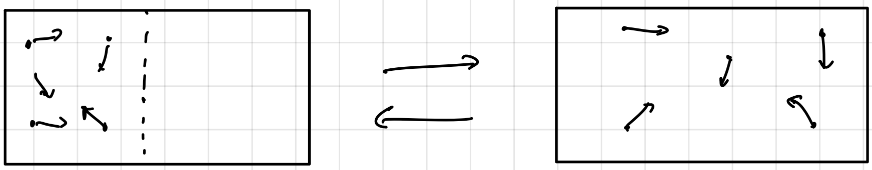
$$\Rightarrow \Delta S \geq 0.$$

This is the <u>second law of thermodynamics</u>.

<u>Note</u>: for non-isolated system, e.g. <u>Earth</u>. S can leave, but total entropy (including env't) increases.

Why entropy increases? Is it because many more high S state than low S? No! Can't get a time asymmetric conclusion without a time asymmetric assumption.

Micro-laws of physics are reversible. Can play backwards, and still make sense.



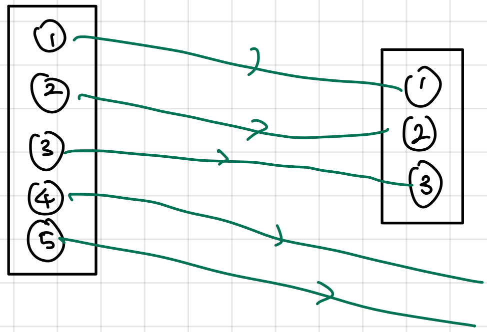
S_1 $\qquad\qquad$ $S_2 = S_1 + kN\log 2.$

Time reverse obeys the same laws (except weak force, which does not matter).

To justify 2^{nd} law, need to assume universe began in low S state. Observationally true in Big Bang Cosmology. This time asymmetry + micro-reversibility $\Rightarrow$ 2^{nd} law probable.

Suppose I claim: microstate $M_1 \longrightarrow$ microstate M_2 after some time Δt, with prob $p \in [0,1]$. Make Ω_1, Ω_2 small to illustrate.

$\Omega_1 = 5$



$\Omega_2 = 3$

(no merging)

$\Rightarrow$ upper bound on p is

$$p \le \frac{\Omega_2}{\Omega_1}$$

if $\Omega_2 < \Omega_1$, and $p \le 1$ if $\Omega_1 \geq \Omega_2$. But

$$\frac{\Omega_2}{\Omega_1} = e^{-\Delta S} = e^{-(\sim 10^{23})}$$

for macro-decrease. Efficiently, $\Delta S < 0$ impossible.

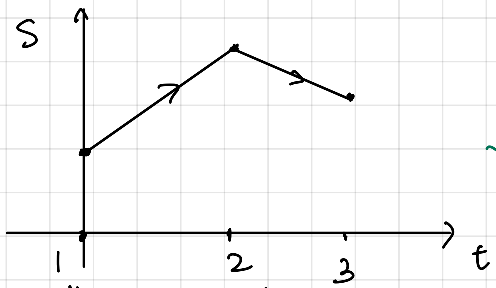
Note In QM, $\Omega = \dim(\mathcal{H})$.

Even this is not totally satisfactory! Consider 3 moments of time.

$$M_1 \longrightarrow M_2 \longrightarrow M_3 .$$

$$S_1 \longrightarrow S_2 \longrightarrow S_3$$

assume random

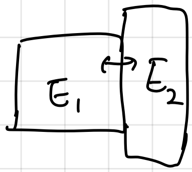


Have to assume info in M_1 is efficiently "lost" and does not affect future predictions. Need to assume this doesn't happen for real boxes of gas.

Def^n Coarse-graining is some process to replace state (e.g. ρ_2 at $M2$) with a higher S random state.

Return to 2 boxes.

$$\Omega_{tot} = \sum_{E_i} \exp\left(\frac{S_1(E_i)}{k} + \frac{S(E_{tot} - E_i)}{k}\right).$$



$$S(E_{tot}) \geq S_1(E_1^{old}) + S_2(E_2^{old}).$$

$$\Delta S \geq 0.$$

Let's maximise.

Set $E_1 = E_i$, $E_2 = E_{tot} - E_i$, is maximal for $E_1 = E_*$ if

$$\frac{d}{dE_1}\left(S_1(E_1) + S_2(E_2)\right) = \left[\frac{dS_1}{dE_1} - \frac{dS_2}{dE_2}\right]_{E_1 = E_*} = 0.$$

in equilibrium. This determines E_*.

Def^n (Temperature) Temperature T is defined by

$$\frac{1}{T} = \frac{\partial S}{\partial E}.$$

Then follows that $T_1 = T_2$ at equilibrium.

If small energy transfer,

$$\delta E_1 = -\delta E_2 \Rightarrow \delta S \approx \left.\frac{dS_1}{dE}\right|_{E_1} \delta E_1 + \left.\frac{dS_2}{dE}\right|_{E_2} \delta E_2$$

$$= \left(\left.\frac{dS_1}{dE}\right|_{E_1} - \left.\frac{dS_2}{dE}\right|_{E_2}\right) \delta E_1$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \delta E_1.$$

$\delta S \geq 0$, so if $T_1 > T_2 \Rightarrow \delta E_1 \leq 0$, $\Rightarrow$ energy flows from hot to cold.

Will evaluate T for ideal gas later, it is usual def^n.

Heat Capacity

Def^n Heat capacity
$$C := \frac{\partial E}{\partial T}.$$

Note: • Should call "energy capacity"

• Can be easily measured.

If we think of $E = E(T)$, then
$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C}{T}.$$
$$\Rightarrow C = T\frac{\partial S}{\partial T}$$

In thermodynamics, looks like
$$C = \frac{\delta Q}{\delta T}$$
heat

Usually important to specify what is held fixed:

C_V — vol V held fixed

C_P — pressure P held fixed.

Can measure entropy differences:
$$\Delta S = \int_{T_1}^{T_2} \frac{C(T)}{T}\, dt$$

easier than counting states

Def^n Specific heat capacity $c := \frac{C}{N}$, where N is no. of particles
$$\frac{\partial S}{\partial E} = \frac{1}{T} \Rightarrow \frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\frac{1}{T} = \frac{\partial T}{\partial E}\left(-\frac{1}{T^2}\right) = -\frac{1}{T^2 C}.$$

Most substances have $C > 0 \Rightarrow \frac{\partial^2 S}{\partial E^2} < 0$

This is called "Thermodynamically systems"

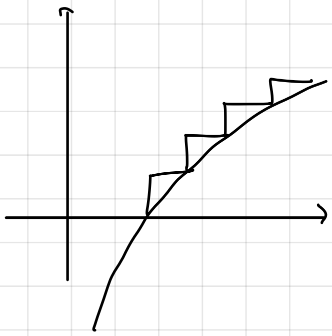
Exceptions: gravitationally bound systems, black holes (Hawking radiation)

Two-State System

Stirling's formula say $\log N! = N\log N - N + \frac{1}{2}\log(2\pi N) + O\left(\frac{1}{N}\right)$

$$\log N! = \sum_{p=1}^{N} \log p \approx \int_1^N \log p \, dp$$
$$= [p\log p - p]_1^N$$
$$= N\log N - (N-1) \approx N\log N - N$$

This is a lower limit



2 state spins: non-interacting, distinguishable 2 states $\uparrow, \downarrow$

let $E_\downarrow = 0$, $E_\uparrow = \varepsilon$, $N_\uparrow$ particles spin up $\Rightarrow N_\downarrow = N - N_\uparrow$.

$$\Rightarrow E = N_\uparrow \varepsilon$$

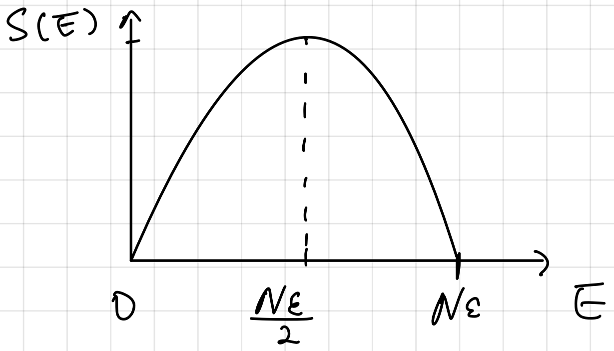
Want to find $\Omega(E)$. Pick $N_\uparrow$ out of N total.

$$\Rightarrow \Omega(E) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

$$\Rightarrow S(E) = k\log\binom{N}{N_\uparrow}$$
$$= k\left[\log(N!) - \log(N_\uparrow!) - \log((N-N_\uparrow)!)\right]$$
$$\approx k\left[N\log N - N - N_\uparrow\log N_\uparrow + N_\uparrow - (N-N_\uparrow)\log(N-N_\uparrow) + N - N_\uparrow\right]$$
$$= k\left[(N-N_\uparrow)\log N + N_\uparrow\log N - N_\uparrow\log N_\uparrow - (N-N_\uparrow)\log(N-N_\uparrow)\right]$$
$$= k\left[(N-N_\uparrow)\log\left(\frac{N-N_\uparrow}{N}\right) + N_\uparrow\log\frac{N_\uparrow}{N}\right]$$
$$= -kN\left[\left(1-\frac{E}{N\varepsilon}\right)\log\left(1-\frac{E}{N\varepsilon}\right) + \frac{E}{N\varepsilon}\log\left(\frac{E}{N\varepsilon}\right)\right]$$

Special cases

- $S(0) = 0.$
- $S(N\varepsilon) = 0.$
- $S(N\varepsilon/2) = kN \log 2$ maximum.



Special case of "Gibbs entropy"

$$S = k \log \Omega$$

assumes such state equally probable.

Gibb's entropy: n-state system with prob $(p_1, \dots, p_n)$

$$S = \sum_{i=1}^{n} (-p_i \log p_i) = tr(\rho \log \rho)$$

in QM. (von Neumann)

Consider $\frac{1}{T} = \frac{\partial S}{\partial E} = \dots = \frac{k}{\varepsilon} \log\left(\frac{N\varepsilon}{E} - 1\right)$

$$\Rightarrow \frac{N_\uparrow}{N} = \frac{E}{N\varepsilon} = \frac{1}{e^{\varepsilon/kT} + 1}$$

As $T \to \infty$,

$$\frac{N_\uparrow}{N} = \frac{1}{2}$$

If $E > N\varepsilon/2$, as E increases, Ω decreases $\Rightarrow T < 0$.

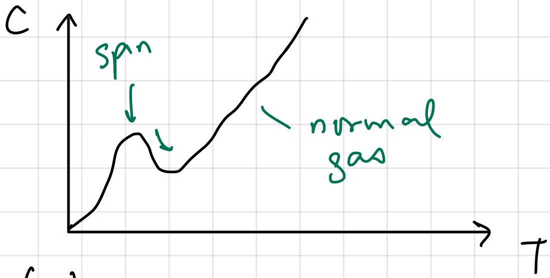
($\frac{1}{T}$ passed through 0!)

Heat capacity is

$$C = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(\frac{N\varepsilon}{e^{\varepsilon/kT}+1}\right) = \frac{N\varepsilon^2}{kT^2} \cdot \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT}+1)^2}$$

- C max. near $kT \sim \varepsilon$
- $T \to 0 \Rightarrow C \sim e^{-\varepsilon/kT} \to 0$ "gap to 1st excited state"
- $T \to \infty \Rightarrow C \sim \frac{1}{T^2} \to 0$ " half the states already ↑ "

Schottky anomaly (for special systems, e.g. paramagnetic salts)



Pressure, Volume, 1st law

Consider volume V of system $\Rightarrow S(E,V) = k \log \Omega(E,V)$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$$ ↖ hold const.

Previously $\frac{1}{T} = \frac{\partial S}{\partial E} \Rightarrow$ 2 sys. keep E_1, E_2 if same T.

Def^n Pressure is

$$p := T\left(\frac{\partial S}{\partial V}\right)_E$$

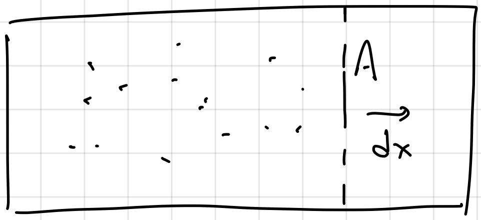
At eqm ($T_1 = T_2$), 2 systems keep V_1, V_2 if same p.

From def^n,

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E V = \frac{1}{T} dE + \frac{p}{T} dV$$

$$\Rightarrow dE = T\,dS - p\,dV$$ [1st law / Clausius relation]

Check : $p = F/A$



$p\,dV = pA\,dx = F\,dx$.

$=$ work done by system.

If $dV < 0 \Rightarrow$ work on sys $\Rightarrow dE > 0$.

$dV > 0 \Rightarrow dE < 0$.

Energy conservation

$T\,dS$ = heat δQ added to the system

$p\,dV$ = work δW done by the system

Heat capacity "$\frac{\delta Q}{\delta T}$".

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\delta Q}{\delta T} = T\left(\frac{\partial S}{\partial T}\right)_V.$$

V fixed $\Rightarrow dV = 0$.

$$C_p = \left(\frac{\delta Q}{\delta T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

Don't use $\frac{\partial E}{\partial T} = C_p$.

Statistical mechanics

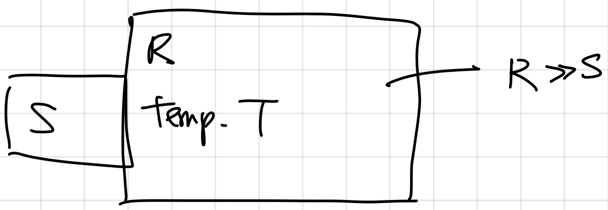
By Boltzmann before we knew about atoms.

$$S = k \log W$$

(Ω)

Canonical Ensemble

Closed system — can we change energy, not matter with outside world.



Changes of T of R is negligible. what is $\Omega(S \& R)$?

$$\Omega(E_{tot}) = \sum_n \Omega_R(E_{tot} - E_n)$$

with $\quad n =$ state of S with energy E_n,

$\quad \Omega_R =$ # states of R

$\quad S_R = k \log \Omega_R$

Energy levels E_n not evenly spaced,

$$\sum_n \to \int dE \; \underbrace{g(E)}_{\text{degeneracy factor}}$$

R large $\Rightarrow \quad E_n \ll E_{tot}$

$$\Rightarrow \Omega(E_{tot}) = \sum_n \exp\left(\frac{S_R(E_{tot} - E_n)}{k}\right)$$

$$\approx \sum_n \exp\left(\frac{S_R(E_{tot})}{k} - \underbrace{\frac{\partial S_R}{\partial E_{tot}}}_{= 1/T} \frac{E_n}{k}\right)$$

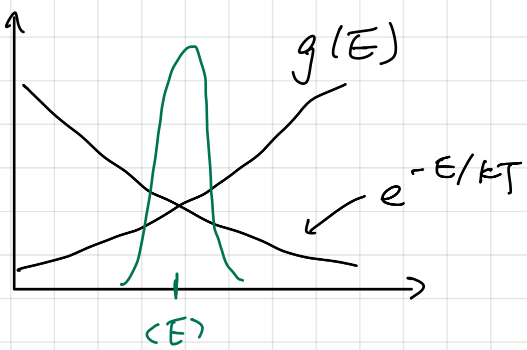
$$\Rightarrow \Omega(E_{tot}) \approx e^{S_R(E_{tot})/k} \sum_n e^{-E_n/kT}$$

$$\Rightarrow \text{\# states with } S \text{ in } |n\rangle = e^{S_R/k} e^{-E_n/kT}$$

prob. of S being in $|n\rangle$ is

$$p(n) = \frac{e^{-E_n/kT}}{\sum_m e^{-E_m/kT}} \qquad \text{(canonical ensemble / Boltzmann distribution)}$$

- R can only play a role fixing T
- $p \sim e^{-E/kT} \Rightarrow$ high E state unlikely
- $T \to 0$, S is in ground state.
- In practice, take as def^n of const. T system.



Def^n Define $\beta := 1/kT$

Def^n Partition function

$$Z := \sum_n e^{-\beta E_n}$$

so Canonical

$$p(n) = \frac{e^{-\beta E_n}}{Z}$$

Z is the most important quantity in statistical physics.

Partition f^n is multiplicative. Consider 2 systems 1 and 2.

$$Z = \sum_{m,n} \exp\left[-\beta\left(E_m^{(1)} + E_n^{(2)}\right)\right] = \sum_m e^{-\beta E_m^{(1)}} \sum_n e^{-\beta E_n^{(2)}} = Z_1 Z_2$$

(QM: $\hat{\rho} = e^{-\beta \hat{H}}/Z$).

Average energy is

$$\langle E \rangle = \sum_n p_n E_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z}$$

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial \beta} \log Z \quad \left(= -Z^{-1} \frac{\partial Z}{\partial \beta} \right)$$

Energy fluctuations ΔE^2 is

$$\Delta E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2.$$

$$= Z^{-1} \frac{\partial^2}{\partial \beta^2} Z - \left(Z^{-1} \frac{\partial}{\partial \beta} Z \right)^2$$

$$= \frac{\partial}{\partial \beta}\left(Z^{-1} \frac{\partial}{\partial \beta} Z \right) = \frac{\partial}{\partial \beta} \frac{\partial}{\partial \beta} \log Z$$

$$\Rightarrow \Delta E^2 = \frac{\partial^2}{\partial \beta^2} \log Z = -\frac{\partial \langle E \rangle}{\partial \beta}$$

Heat capacity

$$C_V = \left.\frac{\partial \langle E \rangle}{\partial T}\right|_V = \frac{\partial \beta}{\partial T} \frac{\partial \langle E \rangle}{\partial \beta} = \frac{1}{kT^2} \Delta E^2$$

$$\rightarrow \Delta E^2 = kT^2 C_V.$$

Comments:

(1) large fluctuation $\longleftrightarrow$ large heat capacity ("fluctuation dissipation thm)

(2) $C_V \sim N$, $E \sim N$ $\Rightarrow$ $\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$. large $N \Rightarrow E$ peaked near $\langle E \rangle$

In thermo limit, microcanonical $\sim$ canonical.

$$E = \langle E \rangle .$$

2 state system revisited:

Single particle

$$Z_1 = \sum_n e^{-\beta E_n} = 1 + e^{-\beta \epsilon} = 2 e^{-\beta\epsilon/2} \cosh(\beta\epsilon/2)$$

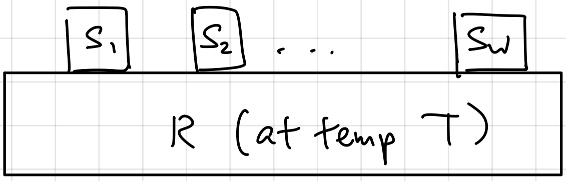
$$\Rightarrow Z = \prod_{k=1}^{N} Z_k = 2^N e^{-N\beta\epsilon/2} \cosh^N(\beta\epsilon/2)$$

$$\Rightarrow \langle E \rangle = -\frac{\partial}{\partial\beta} \log Z = \frac{N\epsilon}{2}\left(1 - \tanh\frac{\beta\epsilon}{2}\right) = \frac{N\epsilon}{1+e^{\beta\epsilon}}$$

Partition f^n automatically handles combinatorics.

MiCE: $S = k \log \Omega(E)$. What is prob. dist. over states with diff. E?

Take W identical systems



each system states $|n\rangle$, $n = 1, \dots, M$.

no. of systems in $n \approx p(n) W$ as $W \to \infty$. Fix E_{tot} for all S+R.

$$\Rightarrow \Omega_{tot} = \Omega_R \Omega_S$$

what is Ω_S?

(1) List all states $n = 1, \dots, M$

(2) Partition W slots for systems to go into

(3) $\sum$ all slots $= W$

(4) $W!$ is no. of permutations of W systems.

(5) Divide by $[p(n)W]!$ for each n. These permutations don't change the set-up physically.

$$\Rightarrow \Omega_S = \frac{W!}{\prod_n (p(n)W)!}$$

$$\Rightarrow S_{tot} = k(\log \Omega_R + \log \Omega_S) \qquad \text{(ignore } S_R\text{)}$$

$$\Rightarrow S = k \log \Omega_S = (\text{Stirling}) = -kW \sum_n p(n) \log p(n). \quad \leftarrow \text{for } W \text{ systems}$$

1 system: $$\boxed{S = -k \sum_n p(n) \log p(n)} \qquad \text{(Gibb's entropy)}.$$

Note: $\lim_{p \to 0} p \log p = 0.$

S is a f^n of prob. dist.

- MiCE: prob $= f(E) \Rightarrow S = S(E)$. If further $p(n) = \frac{1}{\Omega(n)}$

$$\Rightarrow S = k \log \Omega(E).$$

- CE: prob. $: f(T) \Rightarrow S = S(T)$.

$$p(n) = \frac{e^{-\beta E_n}}{Z} \Rightarrow S = -\frac{k}{Z} \sum_n e^{-\beta E_n} \log\left(\frac{e^{-\beta E_n}}{Z}\right)$$

$$= \frac{k\beta}{Z} \sum_n E_n e^{-\beta E_n} + k \log Z.$$

$$\Rightarrow \boxed{S = k \frac{\partial}{\partial T}(T \log Z)}.$$

As $N \to \infty$, the physical observables should approximately agree.

$$Z = \sum_n e^{-\beta E_n} = \sum_{\{E_i\}} \Omega(E_i) e^{-\beta E_i}. \qquad \text{(strongly peaked)}$$

$\Rightarrow$ Sum dominated by E_* s.t.

$$\frac{\partial}{\partial E}\left(\Omega(E) e^{-\beta E}\right)\Big|_{E=E_*} = 0 \Rightarrow Z \approx \Omega(E_*)\, e^{-\beta E_*}.$$

Use $\frac{1}{T} = \frac{\partial S}{\partial E} = k \frac{\partial \log \Omega}{\partial E} \Rightarrow \beta = \frac{\partial \log \Omega}{\partial E}$

$$\Rightarrow \quad \langle E \rangle = -\frac{\partial}{\partial \beta} \log Z$$

$$= -\frac{\partial}{\partial \beta}\left(\log \Omega - \beta E_*\right)$$

$$= -\frac{\partial E_*}{\partial \beta}\frac{\partial \Omega}{\partial E_*} + E_* + \beta \frac{\partial E_*}{\partial \beta} = E_*$$

$$\Rightarrow \quad \langle E \rangle = E_*$$

Entropy

$$S = k\frac{\partial}{\partial T}\left(T \log Z\right) = k \frac{\partial}{\partial T}\left(T\left(\log \Omega - \beta E_*\right)\right)$$

$$= k \log \Omega - k\beta E_* - kTk\beta^2 \frac{\partial}{\partial \beta}\left(\log \Omega - \beta E_*\right)$$

$$= k \log \Omega$$

Conclude that CE like MiCE at energy E_*.

Maximise entropy subject to some constraint

MiCE : Gibbs $S = -k \sum_n p(n) \log p(n)$ with $p(n) \neq 0$ for states $|n\rangle$ with energy E.

Conditional constraint : $\sum_n p(n) = 1$

Varying $S + \alpha k\left[\left(\sum_n p(n)\right) - 1\right]$. α = Lagrange mult.

$$\Rightarrow \frac{\partial}{\partial p(m)}\left[-\sum_n p(n) \log p(n) + \alpha \sum_n p(n) - \alpha\right] = 0.$$

$$\Rightarrow -\log p(m) - 1 + \alpha = 0$$

$$\Rightarrow p(m) = e^{\alpha - 1} = \text{const.}$$

$$\Rightarrow p = \frac{1}{\Omega}$$

In CE, keep $\langle E \rangle$ fixed $\Rightarrow p \sim e^{-\beta E}$.

Free energy

Def^n (Free energy)

$$F := E - TS$$

This is energy available to do work.

$$dF = dE - d(TS) = TdS - pdV - TdS - SdT.$$
$$= -S\,dT - p\,dV$$
$$\Rightarrow S = -\frac{\partial F}{\partial T}\bigg|_V, \quad p = -\frac{\partial F}{\partial V}\bigg|_T.$$

Recall $E = -\frac{\partial}{\partial \beta}\log Z$, $S = k\frac{\partial}{\partial T}(T\log Z)$

$$\rightarrow F = E - TS = kT^2\frac{\partial}{\partial T}\log Z - kT\log Z - kT^2\frac{\partial}{\partial T}\log Z$$
$$\Rightarrow F = -kT\log Z$$
$$\Rightarrow \beta F = -\log Z$$

Grand canonical ensemble

Consider additional conserved quantity i.e.g. particle no. N, electric charge q.

$$\Rightarrow S = S(E, V, N) = k\log\Omega(E, V, N)$$

Recall $\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N}$. $p = T\frac{\partial S}{\partial V}\bigg|_{E,N}$

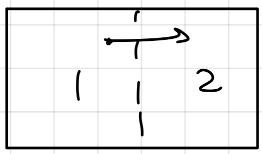
Def^n (Chemical potential)

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

Note $N \sim 10^{23}$.

Repeat T-eqm.

$\Rightarrow$ systems do not exchange particles (on average) if $\mu_1 = \mu_2$ (chem. eqm)



allow particles to move

1^{st} law:
$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN.$$
$$\Rightarrow dE = TdS - pdV + \mu dN$$

Can think $\mu \simeq$ "effective energy cost for adding 1 particle".

Similar remarks apply electric charge q $\Rightarrow$ electrostatic potential ϕ.

Comment: $\mu = -T\frac{\partial S}{\partial N}\Big|_{V,E}$. but 1^{st} law $\mu = \frac{\partial E}{\partial N}\Big|_{S,V}$.

In general, let X, Y, Z be 3 variables with 1 constraint,
$$\frac{\partial X}{\partial Y}\Big|_Z \frac{\partial Y}{\partial Z}\Big|_X \frac{\partial Z}{\partial X}\Big|_Y = -1$$

Const. temp:
$$dF = -SdT - pdV + \mu dN \Rightarrow \mu = \frac{\partial F}{\partial N}\Big|_{T,V}$$

In grand canonical ensemble, fix T, μ.

Def^n let $|n\rangle$ have energy E_n and no. of particles N_n.

Grand canonical partition f^n is
$$\mathcal{Z}(T, \mu, V) = \sum_n e^{-\beta(E_n - \mu N_n)}$$

Same avg as for canonical
$$p(n) = \frac{e^{-\beta(E_n - \mu N_n)}}{\mathcal{Z}}$$
$$S = -k\sum_n p\log p = k\frac{\partial}{\partial T}(T\log \mathcal{Z})$$

Similar arguments.
$$\langle E\rangle - \mu\langle N\rangle = -\frac{\partial}{\partial\beta}\log \mathcal{Z}$$
$$\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\log \mathcal{Z}$$
$$(\Delta N)^2 = \frac{1}{\beta^2}\frac{\partial^2}{\partial\mu^2}\log \mathcal{Z} = \frac{1}{\beta}\frac{\partial\langle N\rangle}{\partial\mu}.$$

Grand canonical potential

$$\Phi = F - \mu N$$

$$\Rightarrow d\Phi = -S\,dT - p\,dV - N\,d\mu.$$

$$\Rightarrow \Phi = -kT \log \mathcal{Z}.$$

Def^n Extensive quantities scales as the system size: E, N, V, S.

Intensive quantities are size indpt: $\frac{1}{T} = \frac{\partial S}{\partial E}$, $p = T\frac{\partial S}{\partial V}$, $\mu = -T\frac{\partial S}{\partial N}$.

$$\underbrace{dE}_{X} = \underbrace{T}_{I}\,\underbrace{dS}_{X} - \underbrace{p}_{I}\,\underbrace{dV}_{X} + \underbrace{\mu}_{I}\,\underbrace{dN}_{X}.$$

$$\underbrace{F}_{X}(T, \lambda V, \lambda N) = \lambda F(T, V, N)$$

$$\Phi(T, \lambda V, \mu) = \lambda \Phi(T, V, \mu)$$

$\Rightarrow \Phi$ must $\sim V$ $\quad \left.\frac{\partial \Phi}{\partial V}\right|_{T,\mu} = -p \Rightarrow \underbrace{\Phi = -p(T,\mu)V}_{\text{eqn of state}}.$

Classical Gases

- gas = particles flying around (in box)

Classical limit, but QM often there in background.

Typically use CE.

1 particle: $H = \underbrace{\frac{p^2}{2m}}_{E_{kin}} + \underbrace{U(q)}_{E_{pot}}$

(micro)state = point in phase space $\{(q_i, p_i)\}$.

$\Sigma \to \int \Rightarrow$ partition f^n for 1 particle is

$$Z_1 = \frac{1}{h^3}\int e^{-\beta H(p,q)}\, d^3p\, d^3q.$$

with $h \approx 6.6 \times 10^{-34}$ Js.

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{q}) \quad , \quad \hat{H}|n\rangle = E_n |n\rangle$$

$\uparrow$ energy eigenstates

$$\mathbb{1} = \int dq \; |q\rangle\langle q| \quad , \quad \mathbb{1} = \int dp \; |p\rangle\langle p|$$

$$\Rightarrow Z_1 = \sum_n e^{-\beta E_n} = \sum_n \langle n| e^{-\beta \hat{H}} |n\rangle$$

$$= \sum_n \langle n| \int dq \; |q\rangle\langle q| e^{-\beta\hat{H}} \int dq' |q'\rangle\langle q'|n\rangle .$$

$$= \int dq \, dq' \left(\langle q| e^{-\beta\hat{H}} |q'\rangle \sum_n \left(\langle q'|n\rangle\langle n|q\rangle \right) \right)$$

Note $\mathbb{1} = \sum_n |n\rangle\langle n|$, $\langle q'|q\rangle = \delta(q-q')$

$$\Rightarrow Z_1 = \int dq \; \langle q| e^{-\beta\hat{H}} |q\rangle = \mathrm{Tr}\left(e^{-\beta\hat{H}}\right) .$$

Note also $\quad e^{\hat{A}} e^{\hat{B}} = e^{\hat{A} + \hat{B} + \frac{1}{2}[\hat{A},\hat{B}] + \dots}$, with $\hat{A} = \hat{q}$, $\hat{B} = \hat{p}$. $[\hat{q},\hat{p}] = i\hbar$,

$$e^{-\beta\hat{H}} = e^{-\beta[\hat{p}^2/2m + U(\hat{q})]} = e^{-\beta \hat{p}^2/2m} \cdot e^{-\beta U(\hat{q})} + O(\hbar) .$$

$\hbar \to 0$ limit

$$\Rightarrow Z_1 = \int dq \;\; \langle q| \; e^{-\beta\hat{p}^2/2m} e^{-\beta U(\hat{q})} \; |q\rangle .$$

Write $U(\hat{q})\,|q\rangle = U(q)\,|q\rangle$,

$$\Rightarrow Z_1 = \int dq \;\; e^{-\beta U(q)} \langle q| e^{-\beta\hat{p}^2/2m} |q\rangle$$

$$= \int dq \, dp \, dp' \left(e^{-\beta U(q)} \langle q|p\rangle \langle p| e^{-\beta\hat{p}^2/2m} |p'\rangle \langle p'|q\rangle \right)$$

Using $\langle q|p\rangle = \langle p|q\rangle^* = \frac{1}{\sqrt{2\pi\hbar}} e^{ipq/\hbar}$, $\langle p|p'\rangle = \delta(p-p')$

$$= \frac{1}{2\pi\hbar} \int dq \, dp \;\; e^{-\beta H(p,q)} \qquad \text{(1D QM)} .$$

In 3D,

$$Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3q \, d^3p \;\; e^{-\beta H(p,q)}$$

Here, # states = phase space vol.

Ideal Gas

"ideal" = particles don't interact, i.e. $U(q) = 0$.

"monatomic" = particles have no structure.

So $Z_1 = Z_1(V, T)$. Note $\int d^3q = V$,

$$Z_1 = \frac{V}{(2\pi\hbar)^3} \int d^3p \; e^{-\beta p^2/2m}$$

$$= \frac{V}{(2\pi\hbar)^3} \int d^3p \; e^{-\beta p_x^2/2m} \, e^{-\beta p_y^2/2m} \, e^{-\beta p_z^2/2m}.$$

$$= V\left(\frac{mkT}{2\pi\hbar^2}\right)^{3/2}$$

using $\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\pi/a}$.

Def^n Thermal de Broglie wavelength is

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}.$$

$$\Rightarrow \quad Z_1 = V/\lambda^3.$$

N indistinguishable particle

$$Z(N, V, T) = \frac{Z_1^N}{N!} = \frac{V^N}{\lambda^{3N} N!}$$

can't distinguish between particles

$$F = -kT \log Z = -kT\left(N \log V - 3N \log \lambda - \log N!\right)$$

$$p = -\left.\frac{\partial F}{\partial V}\right|_T = \frac{NkT}{V} \Rightarrow \boxed{pV = NkT} \quad \text{(ideal gas law)}$$

Note: $\hbar$ has disappeared

- Eqns that link p, T, V are called equations of state (EoS)
- T as defined by $\partial S/\partial E$ actually is temp.
- At higher densities, deviations from ideal gas law ($U \neq 0$).

Equipartition of Energy

$$E = -\frac{\partial}{\partial\beta}\log Z = -\frac{\partial}{\partial\beta}\left(-3N\log\lambda\right) = 3N\frac{\partial}{\partial\beta}\left(\tfrac{1}{2}\log\beta\right) = \tfrac{3}{2}NkT.$$

If gas existed in D spatial dim

$$\Rightarrow Z = \frac{V^N}{\lambda^{DN}N!} \Rightarrow E = \frac{D}{2}NkT$$

Each dof contributes $\frac{NkT}{2}$ to E.

Assume H is quadratic for relavant dof.

Example $\hat{H} = \hat{p}^2/2m + \hat{x}^n$. $n \neq 2 \Rightarrow$ different answer.

Breaks down for QM,

E $\updownarrow \Delta E$ quantised. low E freezes out.

For 1 particle,

$$\langle E\rangle = \frac{\langle p^2\rangle}{2m} \Rightarrow p \sim \sqrt{mE} \sim \sqrt{mkT}$$

de Broglie wave length

$$\sim \frac{h}{p} \sim \lambda.$$

Heat capacity

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{3}{2}Nk$$

Why is k so small in human units?

$k \sim \frac{1}{N} \sim 10^{-23}$

$$E \sim NkT$$

$\mathcal{O}(1)$ $\sim 10^{23}$ $\mathcal{O}(1)$

Def Avogadro's number N_A = # atoms in 12g of C^{12}.

1 mol := N_A atoms.

Ideal gas law: $pV = NkT = nRT$,

where $n = N/N_A$, $R := N_A k \approx 8.3\ \mathrm{J\,K^{-1}mol^{-1}}$ (universal gas const.)

Entropy : In CE, $S = k\frac{\partial}{\partial T}(T\log Z)$.

$$\frac{\partial}{\partial T}\log\lambda = \frac{\partial}{\partial T}\log\left(\sqrt{\frac{2\pi\hbar^2}{mkT}}\right) = -\frac{1}{2T}.$$

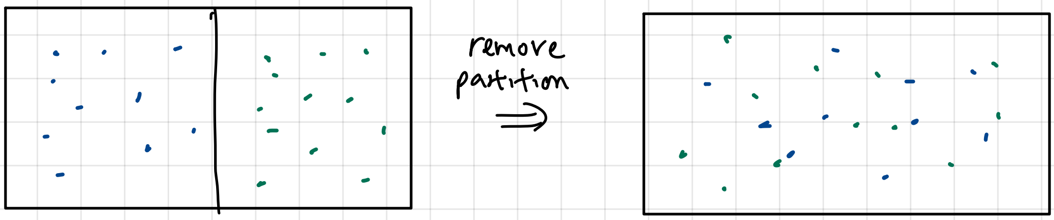
$$\Rightarrow S = k\log Z + kT\frac{\partial}{\partial T}\left(N\log V - 3N\log\lambda - \log N!\right)$$

$$= k\left[\log\frac{V^N}{\lambda^{3N}} - \log N!\right] + kT\cdot\frac{3N}{2T}$$

$$\approx k\left[\log\frac{V^N}{\lambda^{3N}N^N} + N\right] + \frac{3}{2}Nk$$

$$\Rightarrow \boxed{S = Nk\left(\log\frac{V}{\lambda^3 N} + \frac{5}{2}\right)} \quad \text{(Sakur-Tetrode eqn).}$$

- S has $\hbar$ in it. Classically we only measure ΔS, so $\hbar$ drops out.
- S cares about $N!$ in Z. Gibbs noticed before QM.



Irreversible process. S increases!

Not true if gases are identical

<u>Ideal gas in GrCE</u>

View as subvolume in larger gas

$$\mathcal{Z}(\mu, V, T) = \sum_n \left(e^{\beta N_n \mu} e^{-\beta E_n}\right) = \sum_N \left(e^{\beta N\mu}\sum_m e^{-\beta E_m}\right).$$

In GrCE   In CE

$$= \sum_{N=0}^{\infty}\left(e^{\beta\mu N} Z(N, V, T)\right)$$

$$= \sum_{N=0}^{\infty}(e^{\beta\mu})^N\left(\frac{V}{\lambda^3}\right)^N\cdot\frac{1}{N!} = \exp\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)$$

$$\Rightarrow \langle N\rangle = N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\log\mathcal{Z} = \frac{e^{\beta\mu}V}{\lambda^3}.$$

$$\Rightarrow \mu = kT\log\left(\frac{\lambda^3 N}{V}\right)$$

with V/N = vol. per particle. λ de Broglie. $\Rightarrow \lambda^3 \approx \frac{V}{N} \Rightarrow$ QM important

Classical limit : $\lambda \ll V/N \Rightarrow \mu < 0$.

- $\mu > 0$ in special cases, e.g. fermions
- $\mu = \left.\frac{\partial E}{\partial N}\right|_{S,V}$ = energy cost of 1 particle at const. S, V

more dof $\Rightarrow$ S increase unless E decreases $\Rightarrow$ E decreases $\Rightarrow \mu < 0$.

Fluctuations is

$$\Delta N^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \log \mathcal{Z} = N \Rightarrow \frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}} \to 0$$

in thermodynamical limit.

Recall $\quad pV = -\Phi = kT \log \mathcal{Z} = kT \cdot \frac{e^{\beta\mu} V}{\lambda^3} = NkT$ (ideal gas law).

Maxwell distribution

1 particle, ideal gas,

$$\mathcal{Z}_1 = \frac{1}{h^3} \int e^{-\beta p^2/2m} \, d^3q \, d^3p$$

$$= \frac{m^3 V}{h^3} \int e^{-\beta m \underline{v}^2/2} \, d^3\underline{v} \qquad (\underline{v} = p/m)$$

$$= \frac{4\pi m^3 V}{(2\pi\hbar)^3} \int v^2 e^{-\beta m v^2/2} \, dv$$

$\Rightarrow$ prob. that atom is in $[v, v+\delta v]$ is

$$p(v) = \mathcal{N} \, v^2 \exp(-mv^2/2kT),$$

where $\mathcal{N} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2}$. Then

$$\langle v^2 \rangle = \int_0^\infty v^2 p(v) \, dv = \frac{3kT}{m}.$$

$$\Rightarrow \langle \tfrac{1}{2} m v^2 \rangle = \frac{3}{2} kT$$

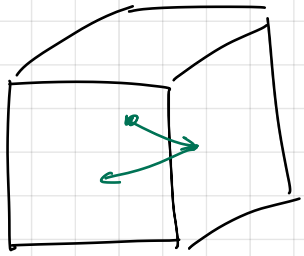
Alternative derivation :

- By rotational invariance, $\tilde{P}(\underline{v}) = \tilde{P}(|\underline{v}|) = \tilde{P}\left(\sqrt{v_x^2 + v_y^2 + v_z^2}\right)$.
- $f(v_x) \cdot f(v_y) \cdot f(v_z)$ — inaccurate, e.g. in relativistic gas : $e^{-\beta m \gamma c^2}$.
- Indpt of direction of $\underline{v}$ $\Rightarrow \tilde{P}\left(\sqrt{v_x^2+v_y^2+v_z^2}\right) \propto f(v_x) f(v_y) f(v_z)$

$$\Rightarrow f(v_x) = e^{-Bv_x^2}.$$

Kinetic Theory

Momentum $\quad p_{i,x} = mv_x \quad p_{f,x} = -mv_x$



$$\Rightarrow \Delta p = 2mv_x, \quad \Delta t = 2L_x/v_x$$

$$\Rightarrow F = \frac{\Delta p}{\Delta t} = \frac{mv_x^2}{L_x}$$

$$p = \frac{F}{L_y L_z} = \frac{mv_x^2}{V}.$$

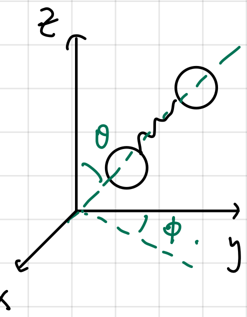
$$\Rightarrow pV = mv_x^2$$

N particles, then $\quad pV = N\langle mv_x^2\rangle = \frac{2}{3}\langle \frac{1}{2}m\underline{v}^2\rangle N$

$$\Rightarrow NkT = \frac{2}{3}\langle \frac{1}{2}m\underline{v}^2\rangle N$$

$$\Rightarrow \langle \frac{1}{2}m\underline{v}^2\rangle = \frac{3}{2}kT.$$

Diatomic Gases



$$H = H_{trans} + H_{rot} + H_{vib}.$$

$$\Rightarrow Z = Z_{trans} Z_{rot} Z_{vib}.$$

For rotation, $\quad H_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}.$

$$\Rightarrow Z_1 = \frac{1}{(2\pi\hbar)^2}\int d\theta\, d\phi\, dp_\theta\, dp_\phi \exp\left[-\beta\left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}\right)\right]$$

$$= \frac{2\pi}{(2\pi\hbar)^2}\left(\int_{-\infty}^{\infty} dp_\theta\, e^{-\beta p_\theta^2/2I}\right)\left(\int_0^\pi d\theta \int_{-\infty}^{\infty} dp_\phi' \sin\theta\, e^{-\beta p_\phi'^2/2I}\right)$$

$p_\phi' = p_\phi/\sin\theta.$

$$= \frac{2\pi}{(2\pi\hbar)^2}\cdot\sqrt{\frac{2\pi I}{\beta}}\cdot 2\cdot\sqrt{\frac{2\pi I}{\beta}} = \frac{2I}{\beta\hbar^2}$$

$$\Rightarrow Z = \frac{Z_1^N}{N!}$$

$$E_1 = -\frac{\partial}{\partial\beta}\log Z_1 = \frac{1}{\beta} = \frac{2}{2}kT$$ dof.

For vibration. $$H_{vib} = \frac{p_\zeta^2}{2m} + \frac{1}{2}m\omega^2\zeta^2.$$

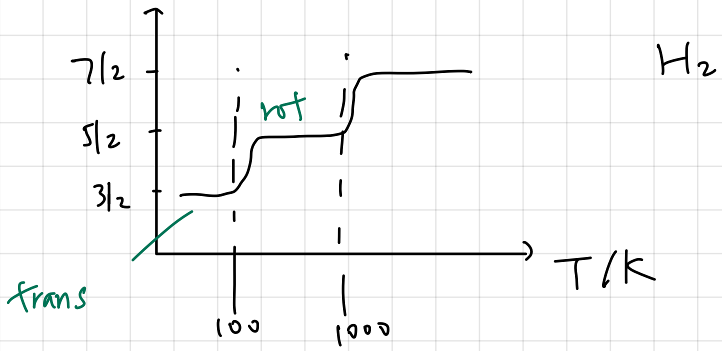
$$Z_1 = \frac{1}{2\pi\hbar}\int d\zeta\, dp_\zeta\, e^{-\beta\left(p_\zeta^2/2m + \frac{1}{2}m\omega^2\zeta^2\right)}$$

$$= \frac{1}{2\pi\hbar}\sqrt{\frac{2\pi m}{\beta}}\cdot\sqrt{\frac{2\pi}{\beta m\omega^2}}$$

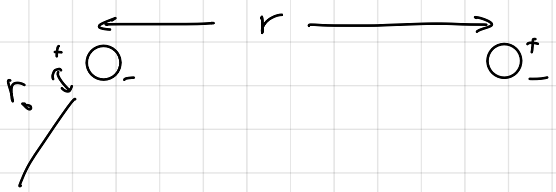
$$= \frac{1}{\beta\hbar\omega} = \frac{kT}{\hbar\omega}.$$

Combining,
$$Z_1 \propto \beta^{3/2}\beta^{-1}\beta^{-1}$$
$$E_1 = -\frac{\partial}{\partial\beta}\log Z = \left(\frac{3}{2}+\frac{2}{2}+\frac{2}{2}\right)kT = \frac{7}{2}kT.$$
$$\Rightarrow C_V = \frac{\partial E}{\partial T} = \frac{7}{2}k$$

In fact, with quantum effect



<u>Interacting Gases</u>



electric moment
$p_1 = q_1 r_0$

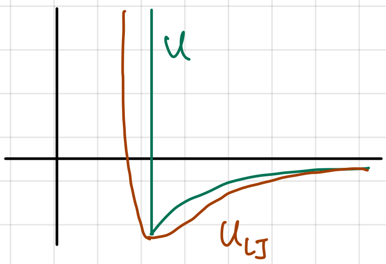
$$\Rightarrow V \sim P_1/r^2 \Rightarrow E \sim P_1/r^3 \Rightarrow p_2 \propto E \propto P_1/r^3$$

$$\Rightarrow V_{\text{dipole}} \sim P_1 P_2 / r^3 \sim 1/r^6 \qquad \text{(van der Waals forces)}$$

So we take

$$U(r) = \begin{cases} -U_0 (r_0/r)^6 & r > r_0 \\ \infty & r < r_0 \end{cases}$$

This is known as the "hard core".



The Lennard-Jones potential

$$U_{LJ}(r) \sim -\left(\frac{r_0}{r}\right)^6 + \left(\frac{r_0}{r}\right)^{12}.$$

Then

$$Z = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int d^{3N}p \, d^{3N}r \; \exp\left[-\beta\left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} U(r_{ij})\right)\right]$$

$$= \frac{1}{N!} \cdot \frac{1}{\lambda^{3N}} \underbrace{\int d^{3N}r \; \exp\left[-\beta \cdot \frac{1}{2} \sum_{i \neq j} U_{ij}\right]}_{I}$$

Mayer $f(r_{ij}) = e^{-\beta U_{ij}} - 1. \Rightarrow e^{-\beta U_{ij}} = 1 + f_{ij}$

$$I = \int d^{3N}r \prod_{i \neq j} (1 + f_{ij})^{1/2}$$

$$\approx \int d^{3N}r \prod_{i \neq j} \left(1 + \tfrac{1}{2} f_{ij}\right).$$

$$= \int d^{3N}r \left(1 + \sum_{i \neq j} \tfrac{1}{2} f_{ij} + \mathcal{O}(f^2)\right)$$

$$= V^N + \sum_{i \neq j} \frac{1}{2} \underbrace{\int d^{3N-6}r}_{V^{N-2}} \underbrace{\int d^3 r_i \int d^3 r_j \, f(r_{ij})}_{\text{Let } \underline{R} = \frac{1}{2}(\underline{r}_i + \underline{r}_j), \ \underline{r} = \underline{r}_i - \underline{r}_j} + \ldots$$

$$= V^N + \sum_{i \neq j} \frac{1}{2} V^{N-2} \underbrace{\int d^3R}_{= V.} \int d^3r \, f(r)$$

$$= V^N \left(1 + \frac{1}{2V} \underbrace{\sum_{i \neq j}}_{\sim N^2} \int d^3r \, f(r) + \ldots\right)$$

$$= V^N \left(1 + \frac{N^2}{2V} \int d^3r\, f(r) + \dots \right)$$

$$\approx V^N \left(1 + \frac{N}{2V} \int d^3r\, f(r) + \dots \right)^N$$

$e^{-\beta U(r)} - 1$.

$$\Rightarrow Z = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \frac{V^N}{\lambda^{3N}} \left(1 + \frac{N}{2V} \int d^3r\, f(r)\right)^N$$

Evaluate integral

$$\int d^3r \left(e^{-\beta U(r)} - 1\right) = 4\pi \int_0^\infty dr\, r^2 \left(e^{-\beta U(r)} - 1\right)$$

$$= 4\pi \left(\int_0^{r_0} r^2(-1)\, dr + \int_{r_0}^\infty r^2 \left(e^{-\beta U_0 (r/r_0)^6} - 1\right) dr \right)$$

$$\approx 4\pi \left[-\frac{1}{3} r_0^3 - \beta U_0 \int_{r_0}^\infty r^2 \left(\frac{r_0}{r}\right)^6 dr \right]$$

$$= -\frac{4\pi}{3} r_0^3 + \frac{4\pi}{3} \beta U_0 r_0^3.$$

$$= -2b + 2a\beta$$

where $b = \frac{2\pi}{3} r_0^3$, $a = \frac{2\pi U_0}{3} r_0^3$.

Then pressure

$$p = \frac{\partial}{\partial V}\left(kT \log Z\right). = \frac{NkT}{V} + NkT \cdot \frac{2}{2V}\left(1 + \frac{N}{V}(a\beta - b)\right)$$

$$= \frac{NkT}{V} + NkT \cdot \frac{N}{V^2}(a\beta - b)$$

$$\Rightarrow \frac{pV}{NkT} = 1 - \frac{N}{V}\left(\frac{a}{kT} - b\right) + O\left(\frac{N^2}{V^2}\right).$$

$$\Rightarrow \boxed{\left(p + \frac{N^2}{V^2} a\right)(V - Nb) = NkT}$$

This is the van der Waals equation.

Quantum Gases

Gas where QM important, e.g. light, phonons

Density of states → often convenient $\sum_n E_n \to \int dE\, g(E)$

density of states

Ideal QM gas: no interactions, model as plane waves

$$\psi = \frac{1}{\sqrt{V}} e^{i\underline{k}\cdot\underline{x}}$$

BC don't matter for large V, so choose periodic BC.

1D : $k_i = \frac{2\pi}{L} n_i,\quad n_i \in \mathbb{Z},$

3D : $E_{\underline{n}} = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2\hbar^2}{2mL^2}(n_1^2 + n_2^2 + n_3^2)\,,\quad k = |\underline{k}|$

Write k_B for Boltzmann const. Note $\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}$.

<u>1 particle</u> : $Z_1 = \sum_n e^{-\beta E_n}$,

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \Rightarrow \frac{E_n}{k_B T} = \beta \frac{\hbar^2 k^2}{2m} \sim \frac{\lambda^2 \underline{n}^2}{L^2}$$

Box is large $\lambda \ll L \Rightarrow$ many $\underline{n}$ with $E_n \leq k_B T$.

$$\Rightarrow \sum_{\underline{n}} \approx \int d^3 n = \frac{L^3}{(2\pi)^3}\int d^3 k = \frac{4\pi V}{(2\pi)^3}\int k^2\, dk$$

Note $E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk$

$$\Rightarrow \sum_{\underline{n}} \approx \frac{V}{2\pi^2}\int \sqrt{\frac{2mE}{\hbar^2}}\,\frac{m}{\hbar^2}\, dE =: \int g(E)\, dE$$

$$\Rightarrow g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

power depend on dimension

$g(E)\,dE$ = # states in $[E, E+dE)$

Relativistic Systems

All that changes is $E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4} \Rightarrow dE = \frac{\hbar^2 k c^2}{E} dk$

$$\Rightarrow k^2 dk = \frac{E\,dE}{\hbar^2 c^2} \frac{\sqrt{E^2 - m^2c^4}}{\hbar c}$$

$$\Rightarrow g(E) = \begin{cases} \frac{VE}{2\pi^2 \hbar^3 c^3}\sqrt{E^2 - m^2c^4} & \text{massive} \\ \frac{VE^2}{2\pi^2 \hbar^3 c^3} & \text{massless} \end{cases}$$

↑ e.g. gas of photons

Photons : Blackbody radiation

Def^n A blackbody is an idealised object that absorbs 100% of incident radiation. Colour of glow at Temp T is blackbody radiation.

2nd law relates absorption to emission. In particular, ignore atomic makeup (absorption lines / emission lines). Blackbody rad. is gas of photons at temp. T.

Photons: Wavelength λ, freq $\omega = \frac{2\pi c}{\lambda} = kc$. Energy $E = \hbar\omega$ $(m=0)$

2 transverse polarisations $\Rightarrow g(E)$ picks up extra factor of 2.

$$\Rightarrow g(E)\,dE = \frac{VE^2}{\pi^2\hbar^3c^3} dE = \underbrace{\frac{V\omega^2}{\pi^2 c^3}}_{=\tilde{g}(\omega)} d\omega$$

$= \tilde{g}(\omega)$ = # States in $[\omega, \omega + d\omega)$

Photons not conserved. Could work w/ GrCE with $\mu = 0 \Rightarrow \Phi = F$.

Here we stick to CE. Partition f^n for photons at ω_n

$$Z_{\omega_n} = 1 + e^{-\beta\hbar\omega_n} + e^{-2\beta\hbar\omega_n} + \dots = \frac{1}{1 - e^{-\beta\hbar\omega_n}}$$

ignoring zero point energy.

Take all freq. $\Rightarrow$ Z's multiply $\Rightarrow$ $\log Z$ adds

$$\Rightarrow \log Z = \int_0^\infty \tilde{g}(\omega) \log Z_\omega \, d\omega$$

$$= -\frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 \log(1 - e^{-\beta\hbar\omega}) \, d\omega$$

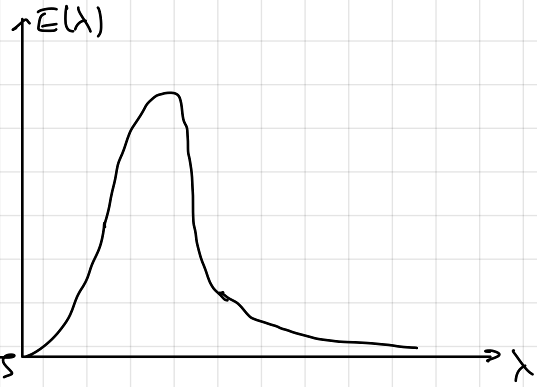
This gives Planck distribution.

$$E_{tot} = -\frac{\partial}{\partial\beta} \log Z = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \, d\omega = \int_0^\infty E(\omega) \, d\omega.$$

$$\Rightarrow E(\omega) = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$ = photon energy density over freq.

- As T decreases, ω_{max} decreases

  $\Rightarrow$ λ_{max} increases



$$\omega_{max} = \zeta \frac{k_B T}{\hbar}.$$

$$\left.\frac{dE(\omega)}{d\omega}\right|_{\omega_{max}} = 0 \Rightarrow \zeta \text{ satisfies } 3 - \zeta = 3e^{-\zeta}.$$

$$\Rightarrow \zeta \approx 2.822$$

Roughly gives "colour" blackbody glow.

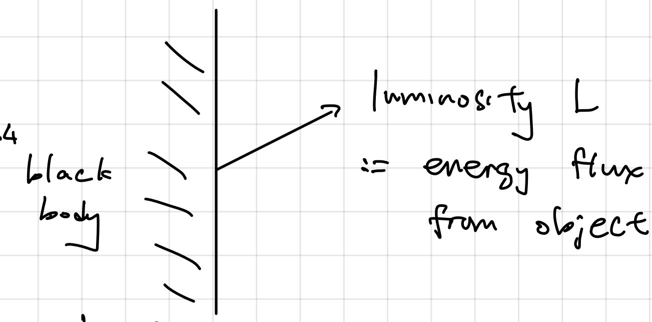
We then have

$$E = \int_0^\infty E(\omega) \, d\omega = \frac{V}{\pi^2 c^3} \frac{(k_B T)^4}{\hbar^3} \overbrace{\int_0^\infty \frac{x^3}{e^x - 1} \, dx}^{\pi^4/15}$$

$$\Rightarrow \frac{E}{V} = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} T^{4}$$ ← spacetime dim.

$$L = \frac{E}{V} \cdot \frac{c}{4} = \sigma T^4,$$

where $\sigma = \dfrac{\pi^2 k_B^4}{60\hbar^3 c^2} \approx 5.67 \times 10^{-8} \, J m^{-2} s^{-1} K^{-4}$



- factor of c to get flux.
- factor of $\frac{1}{4}$ ∵ flux goes away from object

• Angular integral : $\frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \, \sin\theta \, (c \cos\theta) = \frac{c}{4}$

normal dir.

This is <u>Stefan-Boltzmann law.</u>

Calculate pressure from free energy F.

$$F = -k_B \log Z$$

$$= \frac{V k_B T}{\pi^2 c^3} \int_0^\infty \omega^2 \log(1 - e^{-\beta\hbar\omega}) \, d\omega$$

$$= -\frac{V\hbar}{3\pi^2 c^3} \int_0^\infty \frac{\omega^3 e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \, d\omega$$

IBP

$$= -\frac{V\hbar}{3\pi^2 c^3} \frac{1}{\beta^4 \hbar^4} \int_0^\infty \frac{x^3}{e^x - 1} dx = -\frac{V\pi^2}{45\hbar^3 c^3} (k_B T)^4$$

$$P = -\frac{\partial F}{\partial V}\bigg|_T = -\frac{\pi^2}{45\hbar^3 c^3} (k_B T)^4 = \boxed{\frac{1}{3}} \frac{E}{V} = \frac{4}{3} \frac{\sigma}{c} T^4$$

important in cosmology

Entropy

$$S = -\frac{\partial F}{\partial T}\bigg|_V = \frac{16 V \sigma}{3c} T^3$$

$$C_V = \frac{\partial E}{\partial T}\bigg|_V = \frac{16 V \sigma}{c} T^3 .$$

<u>Cosmic Microwave Background</u>

Photons left after big bang — universe become transparent.

Measured by COBE, WMAP, Planck,

$$\text{CMB} \approx 2.725 \, K,$$

within 10^{-5} fraction.

Classical limit $\hbar \to 0$ of Planck.

$$E(\omega) \xrightarrow{\hbar \to 0} \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{\beta \hbar \omega} = \frac{V \omega^2 k_B T}{\pi^2 c^3} = E_{RJ}(\omega)$$

The "Rayleigh – Jeans" answer.

Problem:

$$\int_0^\infty E_{RJ}(\omega)\, d\omega = \infty \Rightarrow \text{"ultraviolet catastrophe".}$$

This is resolved by QM: for $\hbar\omega \gg k_B T$, can't even excite 1 photon.

Phonons

Vibrations of crystal = sound waves.

QM: EM waves → photons

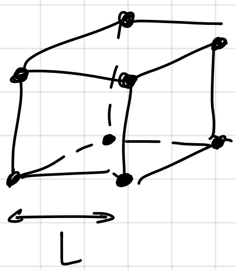
Sound waves → phonons.

Phonon energy: $E = \hbar\omega = \hbar k c_s$ ← speed of sound

- Use c_s
- 3 polarisation states, not 2
- Upper freq. limit:

$$\lambda = \frac{2\pi c_s}{\omega} > L.$$

$$\Rightarrow \omega < \omega_D$$



3N dof, includes longitudinal modes

where ω_D: Debye frequency.

Expect that $\omega_D \sim \left(\frac{N}{V}\right)^{1/3} \cdot c_s$. What is the prop. const.?

Debye: # atoms $= N$, each has 3 directions $\Rightarrow 3N$ dof

$$3N = \int_0^{\omega_D} \tilde{g}(\omega)\, d\omega$$

ω_D — some max. freq.

$\tilde{g}(\omega)$ — # states for one phonon at ω.

$$\Rightarrow 3N = \int_0^{\omega_D} \frac{3}{2} \frac{V\omega^2}{\pi c_s^3} \, d\omega = \frac{V\omega_D^3}{2\pi^2 c_s^3}$$

$$\Rightarrow \omega_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3} c_s . \qquad \text{(max. freq.)}$$

Def^n Debye temp. $T_D = \frac{\hbar\omega_D}{k_B}$ ~ temp. at which max. freq. excited.

$T_D \approx 100\,K$ (lead), $2000\,K$ (diamond). typically $200-400\,K$.

Phonons not conserved, upper bound on ω

$$Z_\omega = \frac{1}{1-e^{-\beta\hbar\omega}}, \quad \log Z = \int_0^\infty \tilde{g}(\omega) \log Z_\omega \, d\omega$$

$$\Rightarrow E = \int_0^{\omega_D} \hbar\omega \frac{\tilde{g}(\omega)}{e^{\beta\hbar\omega}-1} \, d\omega$$

$$= \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\beta\hbar\omega}-1} \, d\omega$$

$$= \frac{3V(kT)^4}{2\pi^2(\hbar c_s)^3} \int_0^{T_D/T} \frac{x^3}{e^x-1} \, dx$$

no analytic sol^n.

(1) $T \ll T_D \Rightarrow$ upper bound is ∞.

$$\int_0^\infty \frac{x^3}{e^x-1} \, dx = \frac{\pi^4}{15} \qquad \text{like photon}$$

$$\Rightarrow C_V = \frac{\partial E}{\partial T}\Big|_V = \frac{2\pi^2}{5} \frac{Vk^4}{(\hbar c_s)^3} T^3 = Nk \frac{12\pi^4}{5} \left(\frac{T}{T_D}\right)^3$$

(2) $T \gg T_D \Rightarrow$ Taylor expand $e^x - 1 \approx x$

$$\Rightarrow \int_0^{T_D/T} \frac{x^3}{x} \, dx = \frac{1}{3}\left(\frac{T_D}{T}\right)^3 + \dots$$

$$\Rightarrow E \sim T, \quad C_V \sim \frac{Vk^4 T_D^3}{2\pi^2\hbar^3 c_s^3} = 3Nk$$

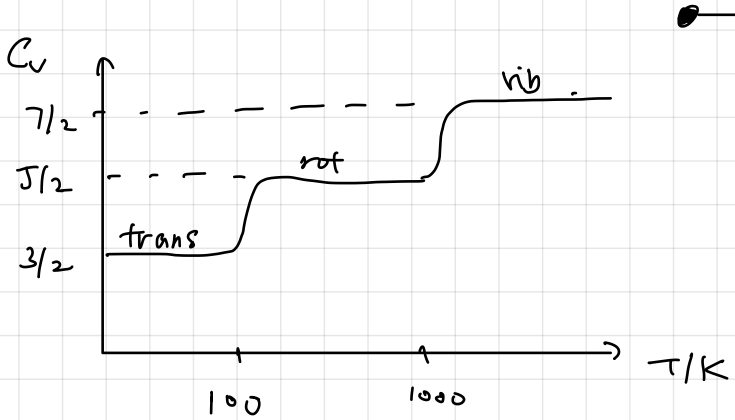
For more accurate answers, corrections to dispersion relation.

$\omega(k)$ for $\omega \sim \omega_D$.

- high T known since 1800's "Dulong - Petit law".
- Debye's new contribution was limit (1).

Diatomic gas

Classical: trans, rotations, vibrations.



Rotations

$$H = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin\theta}$$

QM $\Rightarrow$ E levels: $E = \frac{\hbar^2}{2I} j(j+1)$, j spin $= 0, 1, 2, \ldots$

with degeneracy $2j+1$ (c.f. $|j,m\rangle$).

$$Z_{rot} = \sum_{j=0}^{\infty} (2j+1)\, e^{-\beta\hbar^2 j(j+1)/2I}$$

For $T \gg \frac{\hbar^2}{2Ik_B} \Rightarrow \frac{\beta\hbar^2}{2I} \ll 1$. (high T)

$$Z_{rot} \approx \int_0^\infty (2x+1)\, e^{-\beta\hbar^2 x(x+1)/2I}\, dx$$

$$\approx \frac{2I}{\beta\hbar^2} = Z_{rot,\,classical}$$

neglect 1's

For $T \ll \frac{\hbar^2}{2Ik_B}$ (low T),

$$Z_{rot} = 1$$

T doesn't suffice to excite even $j=1$ states.

Vibrations

Harmonic oscillator

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right) \quad \text{(including zero point energy)}$$

vibration freq. of molecule

$$\Rightarrow Z_{vib} = \sum_n e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= e^{-\beta\hbar\omega/2} \sum_n e^{-\beta\hbar\omega n}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

For high T, $T \gg \frac{\hbar\omega}{k_B} \rightarrow Z_{vib} \approx \frac{1}{\beta\hbar\omega}$

low T, $T \ll \frac{\hbar\omega}{k_B} \rightarrow Z_{vib} \approx e^{-\beta\hbar\omega/2}$ (ZPE).

Bosons

In QM, 2 types of particles.

- Bosons : integer spin, $\psi(\underline{r_1}, \underline{r_2}) = \psi(\underline{r_2}, \underline{r_1})$
- Fermions : $\frac{1}{2}$ + integer spin, $\psi(\underline{r_1}, \underline{r_2}) = -\psi(\underline{r_2}, \underline{r_1})$.

p, n, e fermions. $\Rightarrow$ Atoms made of even # p, n, e $\rightarrow$ boson (e.g. He^4)
odd $\rightarrow$ fermion (e.g. He^3).

Thermal de Broglie wavelength is

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

T small $\Rightarrow \lambda$ large $\sim$ particle separation $\left(\frac{V}{N}\right)^{1/3} \Rightarrow$ QM important.

<u>Bose - Einstein Gas</u> (monoatomic, non-interacting)

Notation : State $|r\rangle$, # particle in $|r\rangle$: n_r

Bosons indistinguishable, described by $n_0, n_1, n_2, \ldots$

In CE :

$$Z = \sum_{\{n_r\}} e^{-\beta \sum_r n_r E_r}$$

sum over $\{n_r\}$ with $\sum_r n_r = N$.

tricky

Use GrCE instead with chem. pot. $\mu \Rightarrow N$ can fluctuate.

In GrCE : any state can have any # particles

$$Z_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = \frac{1}{1 - e^{-\beta(E_r - \mu)}}.$$

Converges only if $E_r - \mu > 0$. Fix $E_0 = 0$, then need $\mu < 0$.

$$\Rightarrow \quad Z = \prod_r \frac{1}{1 - e^{-\beta(E_r - \mu)}}$$

$$\Rightarrow N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \log Z = \sum_r \frac{1}{e^{-\beta(E_r - \mu)} - 1} =: \sum_r \langle n_r \rangle$$

where

$$\langle n_r \rangle = \frac{1}{e^{-\beta(E_r - \mu)} - 1}$$

This is the BE dist. Thermal limit $\Rightarrow$, $n_r \approx \langle n_r \rangle$.

Def^n Fugacity is $z := e^{\beta\mu}$

In BE gas, $\mu < 0 \Rightarrow 0 < z < 1$.

Ideal BE gas.

1 particle : $E = \frac{\hbar^2 k^2}{2m}$ $\Rightarrow$ # states in $[E, E+dE)$ is

$$g(E)\,dE = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}\,dE$$

$$\Rightarrow N = \sum_r \langle n_r\rangle = \int dE\; g(E)\langle n_r\rangle dE$$
$$= \int \frac{g(E)}{z^{-1}e^{\beta E}-1}\,dE = N(\mu, T).$$

N usually fixed experimentally $\Rightarrow$ need to invert $N(\mu,T) \to \mu(T,N)$

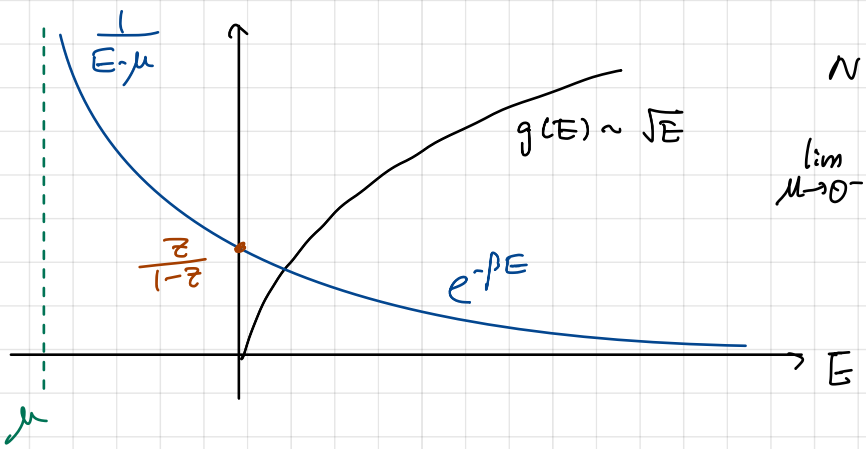
$$E_{tot} = \int \frac{g(E)\,E}{z^{-1}e^{\beta E}-1}\,dE$$

Pressure :

$$p = -\Phi/V \quad (\Phi \text{ scales like } V)$$

$$\Rightarrow pV = \frac{1}{\beta}\log \mathcal{Z} = -\frac{1}{\beta}\sum_r \log\left(1 - ze^{-\beta E_r}\right)$$
$$= -\frac{1}{\beta}\int g(E)\,\log\left(1 - ze^{-\beta E}\right) dE$$
$$\overset{IBP}{=} \frac{2}{3}\int \frac{E\,g(E)}{z^{-1}e^{-\beta E}-1}\,dE = \frac{2}{3}E_{tot}.$$

because $g(E) \sim E^{1/2}$.



$$N = \int_0^\infty g(E)\langle n_r\rangle dE$$

$$\lim_{\mu\to 0^-} N(\mu,\beta) = \text{finite}$$

Increase μ until correct N is reached.

At high T, $z = e^{\beta\mu} \ll 1$.

$$\Rightarrow \frac{N}{V} = \frac{1}{V}\int \frac{g(E)}{z^{-1}e^{\beta E}-1}\,dE$$

$$= \frac{1}{4\pi}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{E^{1/2}}{z^{-1}e^{\beta E}-1}\,dE$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \sqrt{x}\,e^{-x}(1-ze^{-x}+\dots)\,dx \qquad (x=\beta E)$$

$$= \dots \qquad (x=u^2)$$

$$= \frac{z}{\lambda^3}\left(1+\frac{z}{2\sqrt{2}}+\dots\right), \qquad (*)$$

For $z \ll 1 \Rightarrow \frac{\lambda^3 N}{V} \ll 1 \Rightarrow \lambda \ll$ distance

Const. $N \Rightarrow \mu$ changes as $\beta \to 0$,

$$\frac{N}{V} = \text{const.} \approx \frac{z}{\lambda^3} \Rightarrow z \sim T^{-3/2}, \quad \mu \to -\infty.$$

High T EoS of BE:

$$\frac{E}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \frac{E^{3/2}}{z^{-1}e^{\beta E}-1}\,dE$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{z}{\beta^{5/2}}\int_0^\infty x^{3/2}e^{-x}(1-ze^{-x}+\dots)\,dx \qquad (x=\beta E,\ z\ll 1)$$

$$= \frac{3z}{2\lambda^3\beta}\left(1+\frac{z}{4\sqrt{2}}+\dots\right)$$

Eliminate z by inverting $(*)$ for $z \ll 1$:

$$z \approx \frac{\lambda^3 N}{V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}+\dots\right)$$

$$\Rightarrow \frac{E}{V} = \frac{3}{2}\frac{N}{\beta V}\left(1-\frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V}+\dots\right)\left(1+\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}+\dots\right)$$

$$\Rightarrow pV = \frac{2}{3}E = Nk_BT\left(1-\underbrace{\frac{\lambda^3 N}{4\sqrt{2}\,V}}_{=B_2(T)\ 2^{\text{nd}}\text{ virial term}}+\dots\right)$$

"$-$" means bosons have lower p at high T limit

BE condensation

Def^n $\quad \Gamma(n) = \int_0^\infty u^{n-1} e^{u}\, du \quad , \quad \Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$

Def^n (polylog) $\quad g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1}e^{x} - 1}\, dx .$

$$\Rightarrow g_n(z) = \frac{z}{\Gamma(n)} \int_0^\infty \left(x^{n-1} e^{-x} \sum_{m=0}^{\infty} z^m e^{-mx} \right) dx$$

$$= \frac{1}{\Gamma(n)} \sum_{m=1}^{\infty} z^m \int_0^\infty n^{-1} e^{-mx}\, dx$$

$$\Rightarrow g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n} \quad \text{monotonically increasing with } z.$$

Def^n $\quad \zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s} \quad \left[g_n(1) = \zeta(n) \right] \quad . \quad \zeta(\frac{3}{2}) \approx 2.612 .$

$$\frac{N}{V} = \frac{1}{4\pi} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{E^{1/2}}{z^{-1} e^{\beta E} - 1}\, dE = \frac{1}{\lambda^3} g_{3/2}(z) \qquad (*)$$

Fix N/V, decrease $T \Rightarrow \lambda$ increases $\Rightarrow g_{3/2}(z)$ inc. $\Rightarrow z$ inc.

Def^n $\quad T_c :=$ temp. s.t. $(*)$ gives $z = 1$

$$T_c = \left(\frac{2\pi\hbar^2}{km} \right) \left(\frac{1}{g_{3/2}(1)} \frac{N}{V} \right)^{2/3} , \quad \lambda_c = \sqrt{\frac{2\pi\hbar^2}{k T_c m}} = \left(g_{3/2}(1) \frac{V}{N} \right)^{1/3}$$

Actually not $z = 1$ at $T = T_c$. What if $T < T_c$?

Problem: $\lim_{\mu \to 0} N(\mu, T) =$ finite, decreases with T.

Mistake: We used

$$\sum_k \approx \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0 \sqrt{E}\, dE$$

Ground State $E = 0$ doesn't contribute. Missing particle in ground state.

$$\langle n_0 \rangle = \frac{1}{e^{\beta(E_0 - \mu)} - 1} = \frac{1}{z^{-1} - 1} = \frac{z}{1 - z}$$

$E_0 = 0$

- $z \neq 1$, $\langle n_0 \rangle$ small.
- $z \simeq 1 - \frac{1}{N}$, $\langle n_0 \rangle \approx N$.

Correct (*):

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z}$$

For $T < T_c$, z close to 1

$$\Rightarrow N \approx \frac{V}{\lambda^3} g_{3/2}(1) + \langle n_0 \rangle$$

$$\Rightarrow \frac{n_0}{N} = 1 - \frac{V}{N\lambda^3} g_{3/2}(1) = 1 - \left(\frac{\lambda_c}{\lambda}\right)^3 = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

So $T < T_c$, a macroscopic fraction of paticle are in ground state. This is called BE condensation.

1st expt: 1995. Rb. Na. Li. $N \sim 10^4 \ldots 10^7$ atoms. $T_c \sim 10^{-7}$ K.

EoS:

$$pV = \frac{2}{3} E_{tot} = \frac{2}{3} \int \frac{E g(E)}{z^{-1} e^{-\beta E} - 1} dE = \frac{kTV}{\lambda^3} g_{5/2}(z)$$

Ground state atoms negligible

$$T < T_c \Rightarrow z \approx 1 \Rightarrow p = \frac{kT}{\lambda^3} g_{5/2}(1)$$

$$\Rightarrow p \sim T^{5/2}, \quad p \text{ indpt. of } N/V.$$

<u>Heat capacity (phase transitions)</u> (C_V near T_c)

$$\frac{E_{tot}}{V} = \frac{3}{2} p = \frac{3}{2} \frac{kT}{\lambda^3} g_{5/2}(z) \sim T^{5/2}$$

$$\Rightarrow \frac{C_V}{V} = \frac{1}{V} \frac{\partial E_{tot}}{\partial T} = \frac{15}{4} \frac{k}{\lambda^3} g_{5/2}(z) + \frac{3}{2} \frac{kT}{\lambda^3} \frac{d g_{5/2}}{dz} \cdot \frac{dz}{dT}$$

Case 1 : $T < T_c$.

$$z \approx 1 \Rightarrow \frac{dz}{dT} = 0 \Rightarrow C_V \approx \frac{15}{4} \frac{Vk}{\lambda^3} g_{5/2}(1)$$

Case 2 : $T \gtrsim T_c$

$$g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n} \Rightarrow \frac{dg_n}{dz} = \frac{1}{z} g_{n-1}(z)$$

$$\Rightarrow \frac{dg_{5/2}}{dz} = z^{-1} g_{3/2}(z)$$

As $T \to T_c$,

$$\frac{dg_{5/2}}{dz} \to g_{3/2}(1).$$

Need $\frac{dz}{dT}$. (*) valid, so

$$\frac{N\lambda^3}{V} = g_{3/2}(z)$$

e.g. $z = 1 - 10^{-3} \Rightarrow n_0 = 10^3 \Rightarrow z \approx 1$ and yet $n_0/N \approx 0$

$$\frac{dg_{3/2}}{dz} = \frac{1}{z} g_{1/2} = \frac{1}{z} \cdot \frac{1}{\Gamma(1/2)} \int_0^\infty \frac{x^{-1/2}}{z^{-1}e^x - 1} dx$$

diverges as $z \to 1$.

$$= \frac{1}{z} \cdot \frac{1}{\Gamma(1/2)} \int_0 \frac{x^{-1/2}}{z^{-1}(1+x) - 1} dx + \text{finite term}$$

$$= \frac{1}{\Gamma(1/2)} \int_0 \frac{x}{(1-z)+x} dx + \text{finite}$$

$$= \frac{2}{\sqrt{1-z}} \cdot \frac{1}{\Gamma(1/2)} \int_0 \frac{1}{1+u^2} du + \ldots \qquad u = \sqrt{x/1-z}$$

So series exp

$$g_{3/2}(z) \approx g_{3/2}(1) + A\sqrt{1-z}$$

$$\Rightarrow \frac{N\lambda^3}{V} = g_{3/2}(z) \approx g_{3/2}(1) + A\sqrt{1-z}.$$

$$\Rightarrow z \approx 1 - \frac{1}{A^2}\left[g_{3/2}(1) - \frac{N\lambda^3}{V}\right]^2$$

Critical temp. is

$$T_c = \cdots \quad \Rightarrow \quad \left(\frac{T_c}{T}\right)^{3/2} = \frac{\lambda^3 N}{V} \cdot \frac{1}{g_{3/2}(1)}$$

$$\Rightarrow z \approx 1 - \frac{(g_{3/2}(1))^2}{A^2}\left(1 - \left(\frac{T_c}{T}\right)^{3/2}\right)^2 \approx 1 - B\left(\frac{T - T_c}{T_c}\right)^2$$

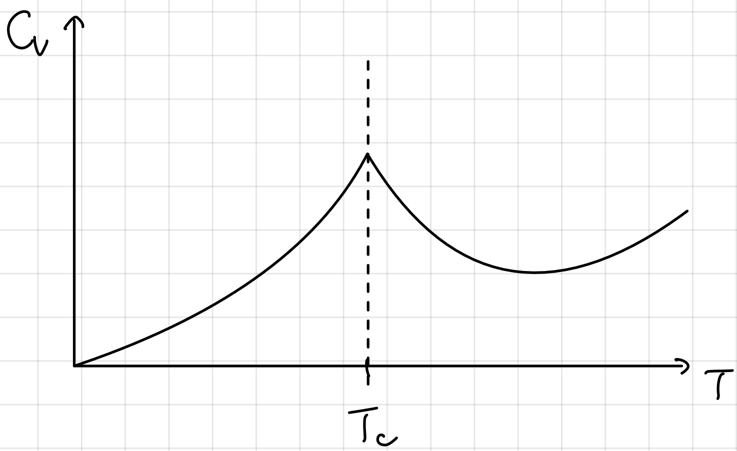
$T = T_c(1+\varepsilon)$

If $T \gtrsim T_c$, then

$$C_V = \frac{15}{4}\frac{kV}{\lambda^3} g_{5/2}(z) + b\frac{dz}{dT} = \frac{15}{4}\frac{kV}{\lambda^3} g_{5/2}(z) - b\,\frac{T-T_c}{T}$$

for some $b > 0$.

2^{nd} term goes to 0 as $T \to T_c$, but finite slope, so 1^{st} deriv. of C_V discontinuous



Not smooth in thermodynamical limit $(N \gg 1)$

Ideal Fermion Gas

Non-interacting fermions, e.g. He^3, e^- in metals or white dwarfs, n in neutron stars.

Spin : $\mathbb{Z} + \frac{1}{2}$. $\quad \psi(\underline{r}_1, \underline{r}_2) = -\psi(\underline{r}_1, \underline{r}_2) \Rightarrow$ Pauli exclusion

In GrCE:

$$Z_r = \sum_{n=0,1} e^{-\beta n(E_r-\mu)} = 1 + e^{-\beta(E_r-\mu)}$$

(In boson, $\frac{1}{1-x}$. in fermion. $1+x$)

$$Z = \prod_r Z_r$$

$$\Rightarrow \quad N = \langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu}\log Z = \sum_r \frac{1}{e^{\beta(E_r-\mu)}+1} =: \sum_r \langle n_r \rangle$$

$$\Rightarrow \quad \boxed{\langle n_r \rangle = \frac{1}{e^{\beta(E_r-\mu)}+1}} \qquad \text{(Fermi-Dirac dist}^{n}\text{)}$$

Here, μ can be either positive or negative, unlike bosons ($\mu<0$)

<u>Non-relativistic case</u>

1 particle: $E = \frac{\hbar^2 k^2}{2m}$.

Degeneracy for spin s: $g_s = 2s+1$, e.g. e^-: $g_s = 2$

$$\Rightarrow \quad g(E) = \frac{g_s V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

$$\Rightarrow N = \int_0^\infty \frac{g(E)}{z^{-1}e^{\beta E}+1}\,dE, \quad E_{tot} = \int_0^\infty \frac{E\,g(E)}{z^{-1}e^{\beta E}+1}\,dE$$

$$pV = -\Phi = \frac{1}{\beta}\log Z = \frac{1}{\beta}\int g(E)\log\left(1+ze^{-\beta E}\right) = \frac{2}{3}E_{tot}$$

At high T. (analogous to Bosons),

$$pV = Nk_B T\left(1 + \underbrace{\frac{\lambda^3 N}{4\sqrt{2}\,g_s V}}_{=B_2(T)} + \cdots\right)$$

2nd virial

fermion $\Rightarrow$ increase pressure p.

For low T ($T \to 0$), then FD dist.

$$\frac{1}{e^{\beta(E-\mu)}+1} \to \begin{cases} 1 & E<\mu \\ 0 & E>\mu \end{cases}$$

ie. each fermion falls down to lowest unoccupied state.

Def^n Fermi energy $E_F := \mu(T=0)$ at fixed N.

$= $ energy max of the occupied states (at $T=0$)

Def^n Fermi temp. $T_F := E_F / k_B$

Note $T_F \sim 10^4\,K$ e^- in metals

$10^7\,K$ e^- in white dwarfs.

In momentum space, $\hbar k_F = \sqrt{2mE_F}$. States with $|k| < k_F$ filled.

Find $E_F(N)$: $T \to 0$

$$\Rightarrow N = \int_0^\infty \frac{g(E)}{z^{-1}e^{\beta E}+1}\,dE = \int_0^{E_F} g(E)\,dE = \frac{g_s V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$\Rightarrow E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g_s}\frac{N}{V}\right)^{2/3}$$

$$E = \langle E\rangle = \int_0^{E_F} E g(E)\,dE = \frac{3}{5} N E_F$$

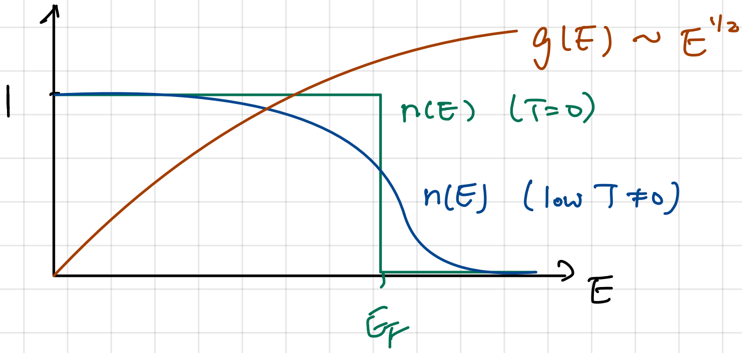
$$\Rightarrow pV = \frac{2}{5} N E_F.$$

This is called degeneracy pressure ($\neq 0$ at $T=0$). This holds white dwarfs and neutron stars.

For low nonzero T, tricky since $n(E)$ discts at $T=0$. Assume

(1) at small T, only expect FD to change near $E = E_F$

(2) Assume $\left.\frac{d\mu}{dT}\right|_{T=0} = 0$



<u>Claim</u> : $\frac{dN}{dT} = 0$ at $T=0$. if $\frac{d\mu}{dT} = 0$ at $T=0$.

Pf:
$$\frac{dN}{dT} = \frac{d}{dT} \int_0^\infty \frac{g(E)}{e^{\beta(E-\mu)}+1} dE$$

$$= \int_0^\infty g(E) \frac{d}{dT} \left(\frac{1}{e^{\beta(E-\mu)}+1} \right) dE$$

since $\frac{d}{dT}(FD) = 0$ except near E_F

$\mu = E_F$, no $\mu(T)$.

$$\approx g(E_F) \int_0^\infty \frac{\partial}{\partial T} \left(\frac{1}{e^{\beta(E-\mu)}+1} \right) dE$$

odd in $E-E_F$

$$\Rightarrow \frac{dN}{dT} \approx g(E_F) \int_0^\infty \frac{E-E_F}{(k_B T)^2} \cdot \frac{1}{4\cosh^2(\beta(E-E_F/2))} dE \approx 0$$

even in $E-E_F$

$\square$

$$C_V = \left.\frac{\partial E}{\partial T}\right|_{N,V} = \int_0^\infty E g(E) \frac{\partial}{\partial T} \left(\frac{1}{e^{\beta(E-\mu)}+1} \right) dE$$

Taylor expand $Eg(E) \sim E^{3/2} \Rightarrow Eg(E) \approx E_F g(E_F) + \frac{3}{2} g(E_F)(E-E_F)$

$$\Rightarrow C_V = \int_0^\infty dE \left[\underbrace{E_F g(E_F)}_{\text{even}} + \underbrace{\tfrac{3}{2} g(E_F)(E-E_F)}_{\text{odd}} \right] \underbrace{\frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-E_F)}+1} \right)}_{\text{odd in } (E-E_F)}$$

contributions far from E_F negligible ($\mu > 0$)
$$\approx \int_{-\infty}^\infty dE \left[E_F g(E_F) + \tfrac{3}{2} g(E_F)(E-E_F) \right] \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-E_F)}+1} \right)$$

$$\approx \frac{3}{2} g(E_F) T \int_{-\infty}^\infty \frac{x^2}{4\cosh^2\frac{x}{2}} dx, \quad x = \beta(E-E_F).$$

$$\Rightarrow C_V \sim T g(E_F).$$

Interpretation: at low T, only particles within $\Delta E \approx kT$ of E_F matter.
Each particle pick up energy $\sim kT$, but $\sim g(E_F)\, kT$ such particles

$$\Rightarrow E \approx \text{const.} + g(E_F)\,(kT)^2$$

$$\Rightarrow C_V \sim Nk \frac{T}{T_F}$$

Actual factors (Sommerfeld expansion)

$$\Rightarrow C_V = Nk \frac{\pi^2}{2} \frac{T}{T_F}.$$

Metal at low temp: $C_V = \gamma T + \alpha T^3$

e^-. phonons

White Dwarfs and the Chandrasekhar limit

Star exhausts fuel (H, He, ...), $T \to 0$, held by degeneracy pressure
(if deg. pressure of $e^- \Rightarrow$ white dwarf)

Const. density

$$\Rightarrow E_{grav} = -\frac{3}{5}\frac{GM^2}{R}, \qquad G = \text{Newton's const.}$$

Minimise $E_{grav.} + E_{kin} \Rightarrow R \sim M^{-1/3}$.
Shrinks as we add mass

$$\Rightarrow E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{g_s}\frac{N}{V}\right)^{2/3} \text{ increase}$$

$\Rightarrow$ gas becomes relativistic

Ultrarelativistic regime ($g_s = 2$)

$$g(E) = \frac{V}{\pi^2 \hbar^3 c^3}\left(E^2 - \frac{m^2c^4}{2} + \dots\right) \qquad (\text{assume } E \gg m)$$

$$E_{kin} = \int_0^{E_F} E\, g(E)\, dE = \frac{V}{\pi^2 \hbar^3 c^3}\left(\frac{1}{4}E_F^4 - \frac{m^2c^4}{4}E_F^2 + \dots\right)$$

$$N = \int_0^{E_F} g(E)\, dE = \frac{V}{\pi^2 \hbar^3 c^3}\left(\frac{1}{3}E_F^3 - \frac{m^2c^4}{2}E_F + \dots\right)$$

In WD, $M \sim N m_p$ ← proton mass, $V = \frac{4}{3}\pi R^3$. Eliminate E_F in E_{kin}, N to leading order.

$$\Rightarrow E_{grav} + E_{kin} = \left[\frac{3\hbar c}{4}\left(\frac{9\pi M^4}{4 m_p^4}\right)^{1/3} - \frac{3}{5}GM^2\right]\frac{1}{R} + O(R).$$

Case 1: if $\frac{1}{R}$ term > 0 $\Rightarrow$ $\frac{dE_{tot}}{dR} = 0$ has sol^n $\Rightarrow$ $\exists$ eqm

Case 2: < 0 $\Rightarrow$ no eqm $\Rightarrow$ neutron stars or BH.

This happens if $M > M_c \sim \left(\frac{\hbar c}{G}\right)^{3/2} \cdot \frac{1}{m_p^2}$. in reality, $M_c \simeq 1.5 M_\odot$.

Classical Thermodynamics

Macro description with no reference to microphysics. Broadly applicable.

Temperature and zeroth law of thermodynamics

Def^n Insulated system : no influence from outside, adiabatic walls

Diathermal system: non-moving walls, but heat flow possible.

Equilibrium : no change with time.

For now, assume system has p, V.

0th law: If 2 systems A, B are in eqm with third sys. C, then A, B are in eqm with each other (transitivity property)

If A in state (p_1, V_1), C in (p_3, V_3). A and C eqm, then p_1, p_3, V_1 fix V_3, $= f_{AC}(p_1, V_1, p_3)$

If B, C eqm, then $V_3 = f_{BC}(p_2, V_2, p_3)$.

$$\Rightarrow f_{AC}(p_1, V_1, p_3) = f_{BC}(p_2, V_2, p_3)$$

must be indpt of p_3, so $\exists f^n$ $\Theta_A(p_1, V_1) = \Theta_B(p_2, V_2)$ in eqm.

Define $T = \Theta(p, V)$ up to reparameterisation ("eqn of state)

Any monotonic $f(\Theta)$ would work equally well for this arg.

$\exists$ canonical choice from Carnot cycles or ideal gas law

$$T = \frac{Nk}{pV}$$

0th law $\Rightarrow$ 2 sys in eqm have same T.

1st law: the amount of work req'd to change an otherwise isolated sys from state 1 to state 2 is indpt of path (how work is done)

$\Rightarrow \exists f^n$ $E(p, V)$ (energy) s.t. $\Delta E = W$. If heat, $\Delta E \neq W$, a change resulting from T differences alone is called heat Q.

$$\Rightarrow \Delta E = Q + W$$

Note NOT $E = Q + W$.

$$dE = \frac{\partial E}{\partial p} dp + \frac{\partial E}{\partial V} dV$$

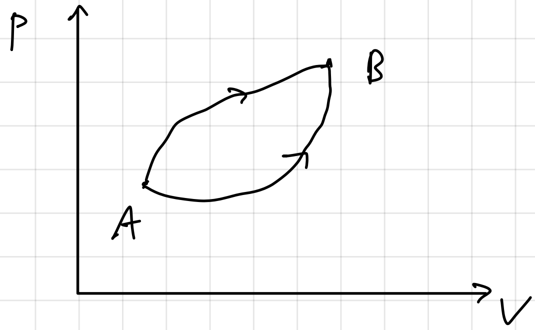
but not so for W.

$$dE = đQ + đW.$$

$đ$: $\nexists$ f^n $W(p,V)$ s.t. $dW = -p\,dV$.

Def^n Quasi-static process : energy transfer where sys always effectively in eqm. ("slow" change)

Vary sys. in QS way



$$\Delta E = \int dE = E(p_2, V_2) - E(p_1, V_1)$$

indpt. on path. but

$$W = -\int p\,dV \text{ depends on path.}$$

2nd law :

Def^n Reversible process is a quasi-static process that can also be run backwards.

For cycle process. $\oint dE = 0$. but general $\oint p\,dV \neq 0$. So 1st law

$$\Rightarrow \oint dQ = \oint p\,dV$$

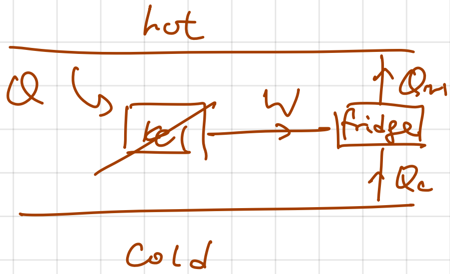
Useful to transform heat into work. 2nd law limits the ability to do so.

2nd law (Kelvin) : No process is possible w/ sole effect extracts heat and converts back to work.

(Clausius) : No process is pos. with sole effect of transforming heat from colder to hotter body.

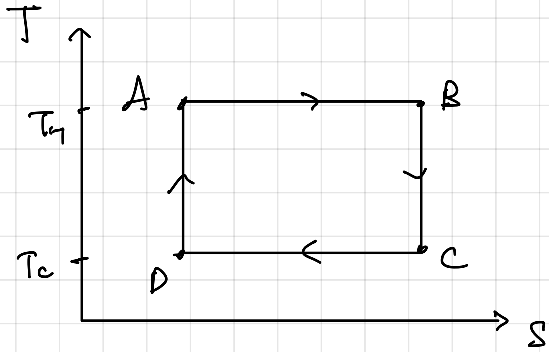
Note : Kelvin $\Leftrightarrow$ Clausius

Example (Cl $\Rightarrow$ Kel)



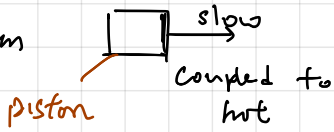
The Carnot Cycle

For a reversible cycle, $\int dQ = -\int dW$

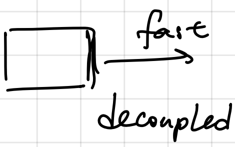


$A \rightarrow B$: isothermal expansion (T_H = const.)

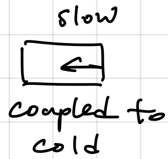
Q_H into system



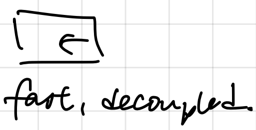
$B \rightarrow C$: adiabatic expansion $Q = 0$, T, p decrease



$C \rightarrow D$: isothermal contraction, T_c = const., Q_c out

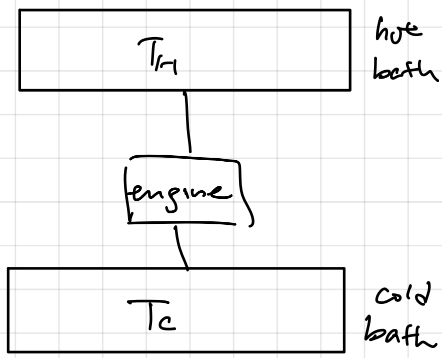


$D \rightarrow A$: adiabatic contraction. $Q = 0$, T, p increase



Adiabatic : $v_{piston} \ll v_{mol} \sim c_s$. (velocity)

Net heat absorbed : $Q_H - Q_c = W$



Def^n efficiency of engines

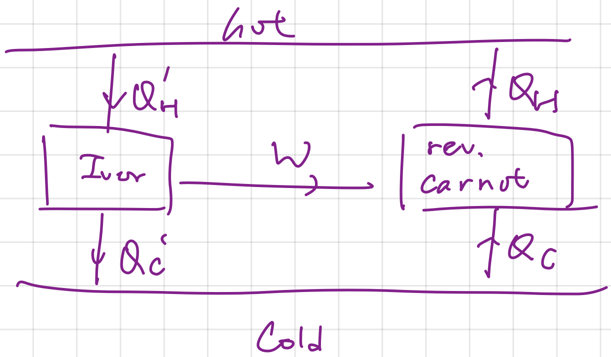
$$\eta := \frac{W}{Q_H} = 1 - \frac{Q_c}{Q_H}$$

Kelvin's 2nd law forbids $\eta = 1 \Leftrightarrow Q_C = 0$

Thm (Carnot's thm) Of all engines operating between hot bath H and cold bath C, a reversible one is most efficient

$\Rightarrow$ All rev. engines have same $\eta(T_H, T_C)$

Pf: Consider irreversible engine "Irvr", use to drive reversed carnot.



$\Rightarrow Q_H' - Q_H$ extracted from H.

$Q_C' - Q_C = Q_H' - Q_H$ deposited to C.

Clausius 2nd $\Rightarrow Q_H' \geq Q_H$

$$\Rightarrow \eta_{Irvr} = 1 - \frac{Q_C'}{Q_H'} = \frac{Q_H' - Q_C'}{Q_H'}$$

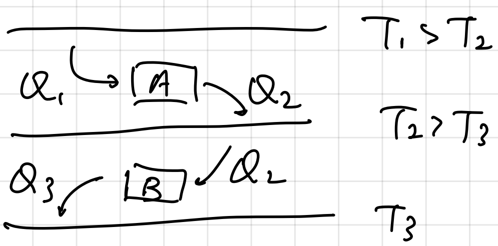
$$= \frac{Q_H - Q_C}{Q_H'} \leq \frac{Q_H - Q_C}{Q_H} = \eta_{carnot}.$$

So if both reversible ($\geq$ and $\leq$) $\Rightarrow \eta_{rev} = \eta(T_H, T_C)$

Thermodynamic temp scale and ideal gas

0th law $\Rightarrow \exists f^n\ \Theta(p, V)$ whose equality $\Rightarrow$ thermal eq.

Consider 2 Carnot engines A, B



Then
$$Q_2 = Q_1 [1-\eta(T_1, T_2)]$$
$$Q_3 = Q_2 [1-\eta(T_2, T_3)] = Q_1 (1-\eta(T_1, T_2))(1-\eta(T_2, T_3))$$

Regard A, B as compound carnot engine,

$$Q_3 = Q_1 [1-\eta(T_1, T_3)]$$

$$\Rightarrow 1-\eta(T_1, T_3) = (1-\eta(T_1, T_2))(1-\eta(T_2, T_3)).$$

$$\Rightarrow 1-\eta(T_1, T_2) = \frac{f(T_2)}{f(T_1)}.$$

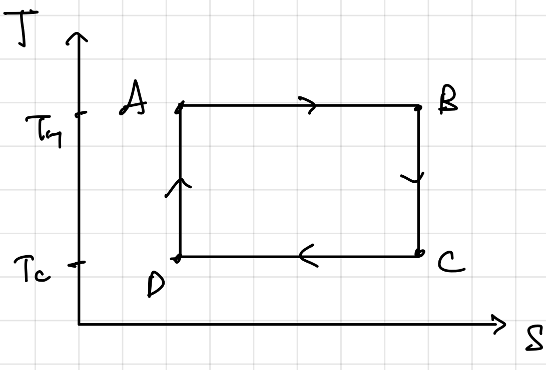
Def^n Thermodynamic temp : choose T s.t. $\eta = 1 - T_2/T_1$, agrees with ideal gas

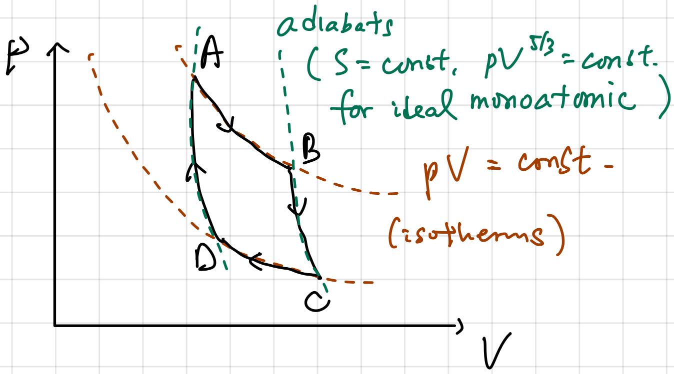
Carnot for ideal gas

$$pV = NkT \Rightarrow T = \frac{pV}{Nk}$$

Energy:

$$E = \frac{3}{2} NkT \qquad (C_V \text{ measurable}).$$





$A \to B$: isothermal exp. $dT = 0 \Rightarrow dE = 0 \Rightarrow đQ = -đW$.

$$\Rightarrow Q_H = \int_A^B đQ = -\int_A^B -đW$$
$$= \int_A^B p\,dV$$
$$= \int_A^B \frac{NkT_H}{V} dV = NkT_H \log(V_B/V_A)$$

$C \to D$: isothermal contraction:

$$Q_c = -NkT_c \log(V_D/V_c) = NkT_c \log(V_c/V_D) > 0$$

$Q_c > 0 \Rightarrow$ heat given away.

$B \to C$: adiabatic exp. $\quad đQ = 0 \Rightarrow dE = -p\,dV = \frac{3}{2}Nk\,dT$

$$pV = NkT \Rightarrow -\frac{NkT}{V}dV = \frac{3}{2}Nk\,dT$$

$$\Rightarrow -\frac{dV}{V} = \frac{3}{2}\frac{dT}{T}$$

$$\Rightarrow -\log V = \frac{3}{2}\log T + \text{const.}$$

$$\Rightarrow p \sim V^{-5/3}.$$

$$\Rightarrow TV^{2/3} = \text{const.}$$

$$\Rightarrow T_H V_B^{2/3} = T_c V_c^{2/3} \Rightarrow \frac{T_c}{T_H} = \frac{V_B^{2/3}}{V_c^{2/3}}$$

$D \to A$: $\quad T_c V_D^{2/3} = T_H V_A^{2/3} \Rightarrow \frac{T_c}{T_H} = \frac{V_A^{2/3}}{V_D^{2/3}} = \frac{V_B^{2/3}}{V_c^{2/3}}.$

Balance: $\quad \eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H}\frac{\log(V_c/V_D)}{\log(V_B/V_A)} = 1 - \frac{T_c}{T_H}.$

$\Rightarrow$ Thermal T (Carnot) = ideal gas law T.

Entropy (Classical thermo)

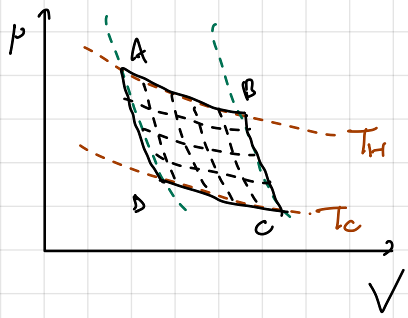
Notation: count Q as heat absorbed by engine $\Rightarrow Q < 0$ releases heat

Set $T_1 = T_H$, $T_2 = T_c \Rightarrow Q_1 = Q_H$, $Q_2 = -Q_c$.

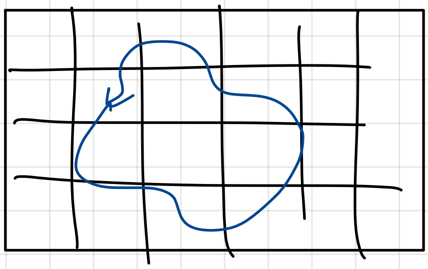
In Carnot cycle, $\frac{Q_c}{Q_H} = \frac{T_c}{T_H} \Rightarrow \sum_{i=1}^{2}\frac{Q_i}{T_i} = 0.$

true for each cycle

Subdivide into infinitesimal reversible cycles.



Can approximate any reversible cycle through some path on grid



$\Rightarrow$ any rev. cycle has $\oint \frac{đQ}{T} = 0$.

$\Rightarrow$ between any 2 states A, B, $\int_A^B \frac{đQ}{T}$

is path ind. if rev.

Def^n Fix some reference state θ, for any state A with p, V, define

entropy

$$S(p,V) := \int_\theta^A \frac{đQ}{T} \quad (+\text{ const.})$$

as given by rev. path. $\frac{đQ}{T} = dS$.

$\Rightarrow$ 1st law: $dE = -đQ + dW = TdS - pdV$

Irreversibility

$$\eta_{irr} = 1 - \frac{Q_c'}{Q_H'} < \eta_{carnot} = 1 - \frac{Q_c}{Q_H}$$

$$\Rightarrow \frac{Q_H' - Q_c'}{Q_H} < \frac{Q_H - Q_c}{Q_H}$$

Compare irrev. and rev. engines doing same work W.

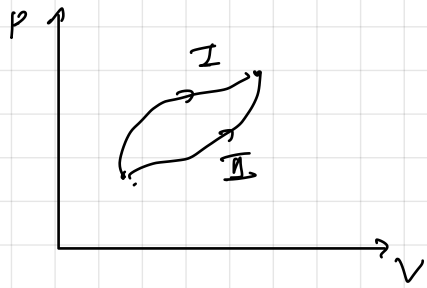
$$W = Q_H' - Q_c' = Q_H - Q_c \Rightarrow \frac{1}{Q_H'} < \frac{1}{Q_H}$$

$$\Rightarrow \frac{Q_H'}{T_H} - \frac{Q_c'}{T_c} = \underbrace{\frac{Q_H}{T_H} - \frac{Q_c}{T_c}}_{=0} + \underbrace{(Q_H' - Q_H)}_{>0}\underbrace{\left(\frac{1}{T_H} - \frac{1}{T_c}\right)}_{<0} < 0.$$

$$\Rightarrow \frac{Q_1'}{T_1} + \frac{Q_2'}{T_2} \leq 0 \quad \text{in general}$$

$$\Rightarrow \boxed{\oint \frac{đQ}{T} \leq 0} \quad \text{for any cycle (Clausius ineq.)}$$

Let I (possibly) irrev., II rev.,



$$\oint \frac{đQ}{T} = \int_I \frac{đQ}{T} - \int_{II} \frac{đQ}{T} \leq 0$$

$$\Rightarrow \int_I \frac{đQ}{T} \leq S(B) - T(A).$$

If path I also adiabatic, $đQ = 0 \Rightarrow S(B) \geq S(A)$. $\Rightarrow$ entropy increases for an isolated sys = 2nd law.

If I rev, then $\Delta S = 0$.

Thermodynamic Potentials

Many variables : $p, V, T, E, S, \ldots$

Can choose any 2 to describe system. Best choice depends.

E.g. $E(S,V)$: $dE = TdS - pdV$.

Free energy (good when T const.)

$$F = E - TS \quad \Rightarrow \quad dF = -SdT - pdV. \quad \text{("Legendre transform")}$$

$$\Rightarrow \left.\frac{\partial F}{\partial T}\right|_V = -S, \quad \left.\frac{\partial F}{\partial V}\right|_T = -p.$$

Why "free"? Consider isothermal process

$$\Rightarrow dF = -pdV \Rightarrow F(B) - F(A) = \int_A^B -pdV = -\text{WD by sys}$$

ΔF = work "free" to be used at const. T.

Gibbs Free energy

Def^n $G := E + pV - TS$

Then $dG = -SdT + Vdp$. Good if fixed p, T.

e.g. sys. S with fixed T, reservoir R with vol. s.t. $V_{tot} = V_R + V_S$.

$$\Rightarrow S_{tot}(E_{tot}, V_{tot}) = S_R(E_{tot} - E_S, V_{tot} - V_S) + S_S(E_S, V_S)$$

$$\approx S_R(E_{tot}, V_{tot}) - \frac{\partial S_R}{\partial E_{tot}} E_S - \frac{\partial S_R}{\partial V_{tot}} V_S + S(E_S, V_S)$$

$$= S_R - \frac{1}{T}(E_S + pV_S - TS_S) \qquad \left.\frac{\partial S}{\partial V}\right|_E = \frac{p}{T}.$$

So S_{tot} max. when G min.

With N, then $dF = -SdT - pdV + \mu dN$

$$dG = -SdT + Vdp + \mu dN$$

$$G(\underbrace{T, p}_{int}, \underbrace{N}_{ext.}) \Rightarrow G(p, T, N) = \mu(p, T) N, \quad \text{with } \mu = \frac{\partial G}{\partial N} = \frac{G}{N}.$$

Enthalpy

Def^n $\quad H = E + pV.$

$$\Rightarrow dH = TdS + Vdp.$$

Maxwell Relations

$$E(S, V) \Rightarrow \left.\frac{\partial E}{\partial S}\right|_V = T, \quad \left.\frac{\partial E}{\partial V}\right|_S = -p.$$

2nd derivatives commute, so

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \Rightarrow \boxed{-\left.\frac{\partial p}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S}$$

Can do the same for F, G, H

$$F(T, V): \quad \boxed{\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V}$$

$$G(T, p): \quad \boxed{\left.\frac{\partial S}{\partial p}\right|_T = -\left.\frac{\partial V}{\partial T}\right|_p.}$$

$$H(S, p): \quad \boxed{\left.\frac{\partial T}{\partial p}\right|_S = \left.\frac{\partial V}{\partial S}\right|_p.}$$

Further ∂'s to get relations for C_V, C_p.

<u>3rd law</u>? "Nernst's Postulate" $\lim_{T\to 0} S(T) = 0$ for many but not all Q sys.

(can be false if ground state is degenerate).

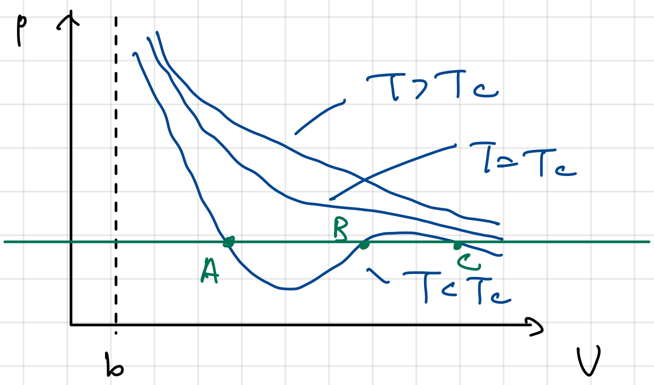
<u>Phase Transitions</u>

Abrupt discts changes as we change some param.

Liquid-gas transition: Recall vdW EoS:

$$p = \frac{kT}{v-b} - \frac{a}{v^2}, \quad v = \frac{V}{N} = (\text{density})^{-1}.$$

Plot isotherms.



3 Shapes:

$T > T_c$: $\approx$ ideal gas. can ignore b/v^2 term

$T = T_c$, $kT_c = \frac{8a}{27b} \Rightarrow$ inflection pt.

$T < T_c$, $kT \approx \frac{a}{v}$ for both local min and max.

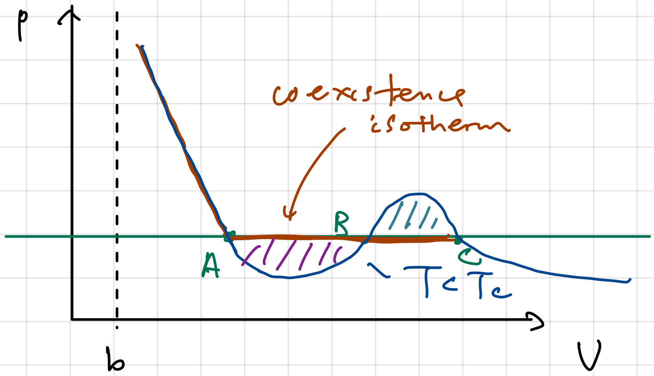
for some values of p, more than 1 V possible.

At V_B: $\left.\frac{dp}{dV}\right|_T > 0 \Rightarrow$ unstable.

- If expand sys $\Rightarrow$ p inc.
- If contract $\Rightarrow$ p dec.

At V_A : $v \gtrsim b \Rightarrow$ atoms are almost as close as they could be $\Rightarrow$ liquid
vdW EoS not strictly valid, but run with it.

At V_C : $v \gg b \Rightarrow$ gas phase.



Between A, C, coexistence of both liquid, gas

Use Gibbs

$$G = \mu(p, T) N ,$$

$\mu = G/N$. since $\partial G / \partial N = \mu$.

At A, $\mu = \mu_{liq.}$. At C, $\mu = \mu_{gas}$

At eqm, $\mu_{liq} = \mu_{gas}$, $p_{liq.} = p_{gas}$.

Along the isotherm of vdW :

$$d\mu = \frac{\partial \mu}{\partial p}\Big|_T dp \Rightarrow \frac{\partial \mu}{\partial p}\Big|_T dp = \frac{1}{N} \frac{\partial G}{\partial p}\Big|_{M,T} = \frac{V}{N}.$$

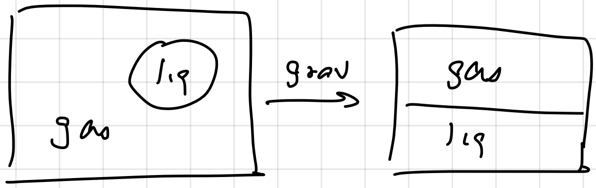
Integrate $\Rightarrow$ $\mu(p, T) = \mu_{liq} + \int_{p_{liq}}^{p} \frac{V(\tilde{p}, T)}{N} d\tilde{p}$.

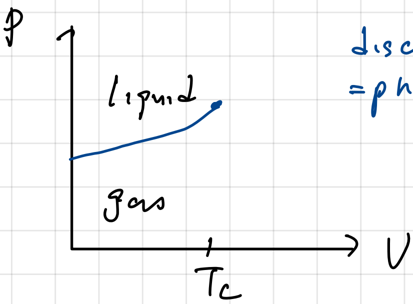
but $p_{liq} = p_{gas} \Rightarrow$ horizontal line between A and C.

Then $\mu_{gas} = \mu_{liq.} + 0 \Rightarrow$ integral must vanish, so

$$0 = \int_A^C V \, dp = \int_A^B V \, dp + \int_B^C V \, dp$$

$\rightarrow$ shaded area equal





discts across line = phase transition

We have $\mu_{liq} = \mu_{gas} \Rightarrow G_{liq} = G_{gas}$.

Change of G along line

$$dG_{liq} = -S_{liq}\, dT + V_{liq}\, dp = dG_{gas} = -S_{gas}\, dT + V_{gas}\, dp.$$

Combine dp, dT term,

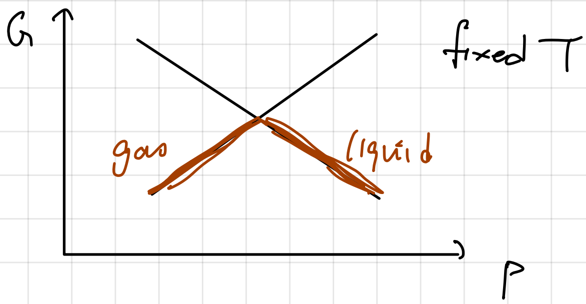
$$\Rightarrow \frac{dp}{dT} = \frac{S_{gas} - S_{liq}}{V_{gas} - V_{liq}}$$

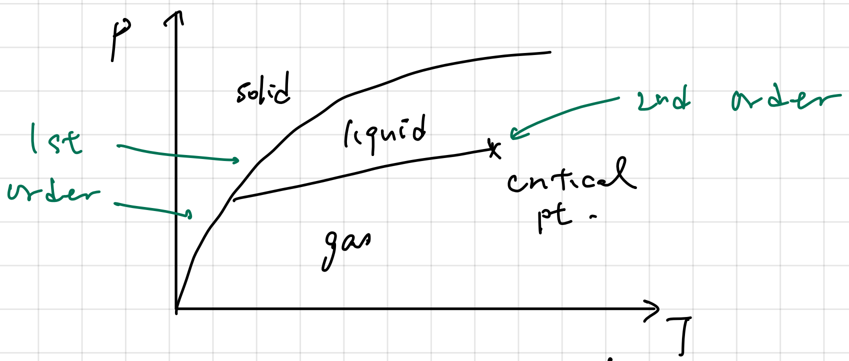
<u>Def^n</u> latent heat $L := (S_{gas} - S_{liq})T$ = amount of $đQ$ add to turn liq. to gas

$$\Rightarrow \frac{dp}{dT} = \frac{L}{T(V_{gas} - V_{liq})} \qquad \text{(Clausius - Clapeyron eqn)}$$

<u>Def^n</u> For an <u>n-th</u> order phase transition, the <u>n-th</u> derivative of appropriate thermo pot. is discts.
minimising

For liquid-gas in p-T plane G: $V = \frac{\partial G}{\partial p}$, $S = -\frac{\partial G}{\partial T}$ $\left(= -\frac{\partial F}{\partial T}\right)$.





Solid breaks translations and rotations down to smaller subgroup. (crystal), e.g. "order parameter".

vdW EoS: $$p = \frac{kT}{v-b} - \frac{a}{v^2} \qquad (v = V/N)$$

$$\Rightarrow \quad pv^3 - (pb + kT)v^2 + av - ab = 0$$

Crit pt. $kT_c = 8a/27b$, $T = T_c$, all 3 roots of cubic coincide

$$p_c (v - v_c)^3 = 0$$

$$\Rightarrow v_c = 3b, \quad p_c = \frac{a}{27b^2}.$$

Def^n Compressibility $\kappa = -\frac{1}{v}\left.\frac{dv}{dp}\right|_T$ not $1/k_B T$

__Critical Exponents__ (approach critical pt.)

- Approach T_c along coexistence curve, $v_{gas} - v_{liq} \sim (T_c - T)^\beta$
- Approach along isotherm: $p - p_c \sim (v - v_c)^\delta$
- Approach from above $(T - T_c) \to 0^+$: $\kappa \sim (T - T_c)^{-\gamma}$.

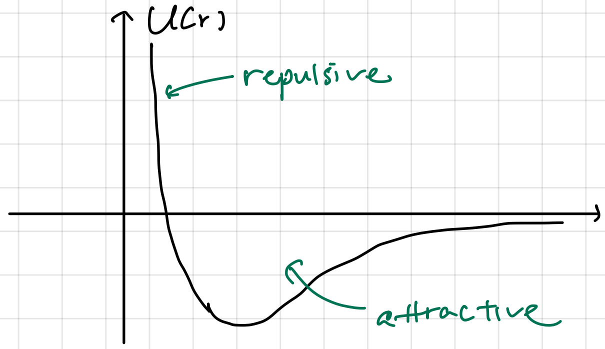
where

	vdW EoS	experiment	
β	$\frac{1}{2}$	≈ 0.32	Theory
δ	3	≈ 4.8	$\neq$
γ	1	≈ 1.2	expt.

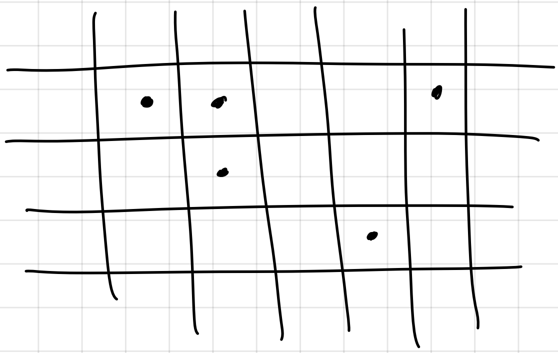
Universality: same for Ne, Ar, Kr, Xe, N_2, O_2, CO, CH_4, ...

$$Z = \underbrace{\frac{1}{(2\pi\hbar)^d} \int d^d p \, e^{-\beta p^2/2m}}_{\text{depends only on } \beta, N} \underbrace{d^d q \, e^{-\beta U(q_1, q_2, \dots)}}_{\text{Study this}}$$

The potential is



Break d-dim space into d-dim cubes



• atoms

Assume each cube contains $n = 0$ or 1 atoms ($\approx$ short distance repulsion)

Assume atoms "like" being in adjacent cubes ($\approx$ vdW attraction)

$$E = -\underset{u>0}{u} \sum_{\langle i,j \rangle} n_i n_j - \tilde{\mu} \sum_i n_i$$

$u > 0$; $\langle i,j \rangle$: nearest neighbours ; $\tilde{\mu}$: chemical potential-like term (also has β depend. piece from KE).

Equivalent to <u>Ising model</u> of spins in magnet.

Ising model: N lattice sites in d-dim, each spin up $\uparrow$ or down $\downarrow$.

$$\begin{array}{lccc}
\uparrow : S_i = +1 \ — & \uparrow & \downarrow & \downarrow \\
 & \uparrow & \uparrow & \downarrow \\
\downarrow : S_i = -1 \ — & \downarrow & \uparrow & \downarrow
\end{array}$$

(Classical bits, not qubits)

$$E = -\underset{\text{interaction}}{J} \sum_{\langle i,j \rangle} S_i S_j - \underset{\text{magnetic field}}{B} \sum_{i=1}^{N} S_i .$$

(to relate to Ising model, set $S_i = 2n_i - 1$, shift const. into B term).

- \# of nearest neighbour $q = 2d$.
- Consider $J > 0$. (preferred to be aligned).

CE :

$$Z = \sum_{\{S_i\}} e^{-\beta E[S_i]}$$

Def^n Magnetisation $\quad m := \frac{1}{N} \sum_i \langle S_i \rangle = \frac{1}{N\beta} \frac{\partial}{\partial B} \log Z$

(Similar to $v = V/N$ in fluid), but at $B=0$, $\uparrow$ vs $\downarrow$ sym

How to solve ?

- Do Σ explicitly, hard ! exact sol^n in $d=1$ ✓

  $d=2$, $B=0$ complicated

- Mean field theory : approximate S_i using some const. m in order to neglect fluctuations in the $\langle ij \rangle$ term

- Statistical field theory : use tools from QFT like renormalisation.

  Critical pts described by CFT

  conformal : scale invariant.

  Correlation lengths get long at 2nd order.

Mean Field theory

m is avg spin

$$S_i S_j = [(S_i - m) + m]\,[(S_j - m) + m]$$

$$= (S_i - m)(S_j - m) + m(S_i - m) + m(S_j - m) + m^2$$

Assume fluctuations are small. summed over $\langle ij \rangle$, but $\langle (S_i - m)^2 \rangle$ can still be large.

$$\Rightarrow E = -J \sum_{\langle ij \rangle} \left[m(S_i + S_j) - m^2 \right] - B \sum_i S_i$$

$$= \underbrace{\tfrac{1}{2} J N q}_{\text{Overall factor}} m^2 - (Jqm + B) \sum_i S_i \,.$$

$\frac{1}{2}JNqm^2$ const. $\rightarrow$ no effect on physics.

In non-interacting sys.

$$B_{eff} = B + Jqm$$

$$Z = \sum_{\text{states}} e^{-\beta E} = e^{-\frac{1}{2}\beta JNqm^2}\left(e^{-\beta B_{eff}} + e^{\beta B_{eff}}\right)^N$$

$$= e^{-\frac{1}{2}\beta JNqm^2}\, 2^N \cosh^n(\beta B_{eff})$$

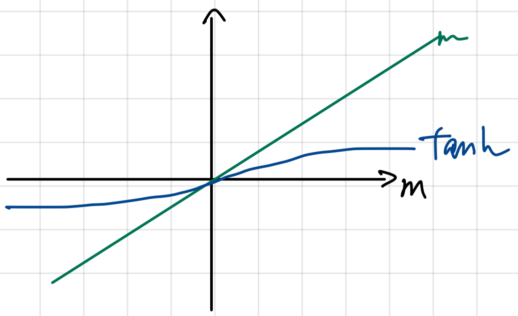
$$\Rightarrow m = \frac{1}{N\beta}\frac{\partial}{\partial B}\log Z = \tanh(\beta B + \beta Jqm).$$

Implicit eqn for m.

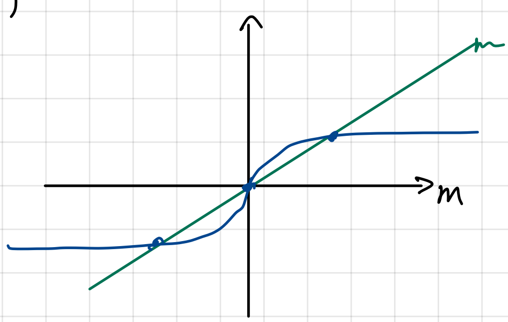
Case 1 : $B = 0$ $\Rightarrow$ $m = \tanh(\beta Jqm)$. Using $\tanh x \approx x - \frac{1}{3}x^3$

slope at $m=0$: βJq.

(a)



(b)



unbroken at high T

critical temp.

$\beta Jq < 1 \Rightarrow 1$ sol : $m = 0$.

high T : spin randomise

broken $m \mapsto -m$ symmetry at low T.

$\beta Jq > 1 \Rightarrow 3$ sol : $m = 0, \pm m_0$.

low T : spins align,

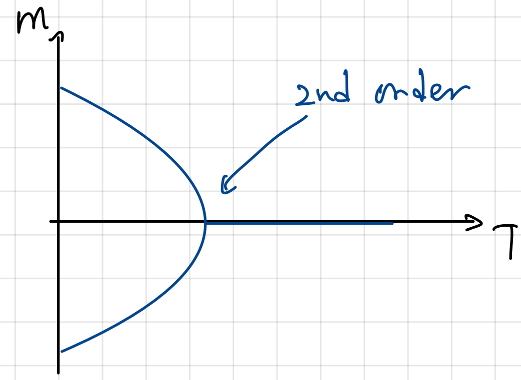
$T \to 0 \Rightarrow \tanh \to \text{sgn} \Rightarrow m_0 = \pm 1$.

Case 2 : $B \neq 0$

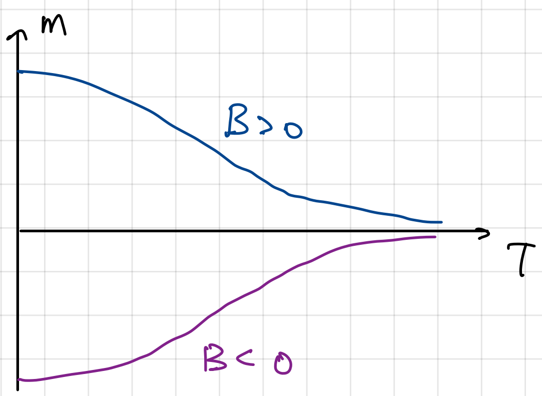
(a) $\beta \to 0$: $m = \tanh(\beta(B + Jqm)) \approx \beta(B + Jqm) \Rightarrow m \approx B/kT$.

(b) $T \to 0$: m asymptote to ± 1 as before but now B determines sign (other sol^n is metastable)

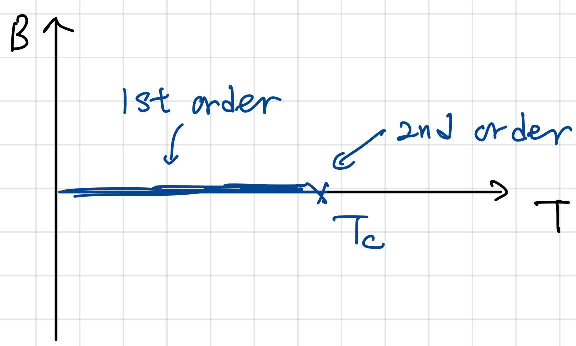
$\underline{B = 0}$



$\underline{B \neq 0}$



below T_c 1st order transition



Critical exponents

(i). m at $B = 0$ as $T \to T_c$ from below.

$$m = \tanh(\beta B + \beta J q m) = \tanh(\beta J q m)$$

At $T = T_c \Rightarrow \beta J q = 1$

$T \lesssim T_c \Rightarrow \beta J q = 1 + \varepsilon$

$$\Rightarrow m = \tanh\left[(1+\varepsilon) m\right]$$

$$\approx (1+\varepsilon) m - \frac{(1+\varepsilon)^3}{3} m^3 \approx (1+\varepsilon) m - \frac{1+3\varepsilon}{3} m^3$$

$$\Rightarrow 1 \approx 1 + \varepsilon - \frac{1+3\varepsilon}{3} m^2$$

$$\Rightarrow m \approx \pm\sqrt{3\varepsilon}.$$

And $\varepsilon = \dfrac{Jq}{kT} - \dfrac{Jq}{kT_c} \approx \dfrac{Jq}{kT^2}(T_c - T)$

$$\Rightarrow m \sim \pm (T_c - T)^{1/2}$$

(c.f. $V_{gas} - V_{liq} \sim (T_c - T)^{1/2}$).

(2) $T = T_c$, how does m vary as $B \to 0$?

$$\beta J q = 1 \Rightarrow m = \tanh\left(\frac{B}{Jq} + m\right)$$

Expand tanh at small B, m

$$\Rightarrow m \approx \frac{B}{Jq} + m - \frac{1}{3}\left(\frac{B}{Jq} + m\right)^3 \approx \frac{B}{Jq} + m - \frac{1}{3}m^3 + \dots$$

$$\Rightarrow \frac{1}{3}m^3 \approx \frac{B}{Jq}$$

$$\Rightarrow m \sim B^{1/3}$$

(c.f. $V_{gas} - V_{liq} \sim (p - p_c)^{1/3}$ along isotherm)

Def^n Magnetic susceptability $\chi := N \left.\frac{\partial m}{\partial B}\right|_T$ (analogous to κ).

(3) Fix $B = 0$. Study χ as $T \to T_c$ for $T \geq T_c$

$$m = \tanh(\beta B + \beta J q m)$$

$$\Rightarrow \chi = \frac{N\beta}{\underbrace{\cosh^2(\beta J q m)}_{=1 \text{ as } T \to T_c}}\left(1 + \frac{Jq}{N}\chi\right) \approx N\beta\left(1 + \frac{Jq}{N}\chi\right)$$

$$\Rightarrow N\beta \approx \chi(1 - \beta J q) \sim \chi\left(\frac{1}{T_c} - \frac{1}{T}\right)$$

$$\Rightarrow \chi \sim (T - T_c)^{-1}$$

(c.f. $\kappa \sim (T - T_c)^{-1}$ for gas)

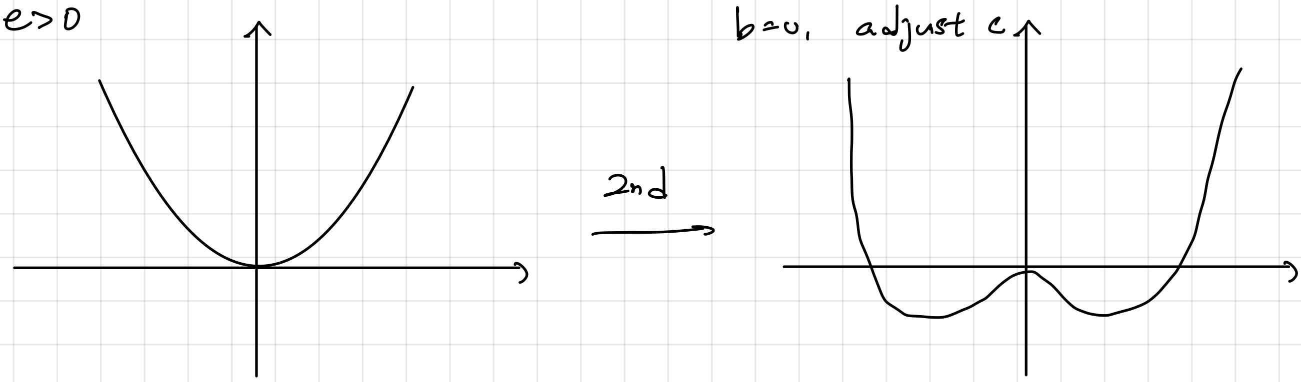
Landau theory

Free energy $\quad F = F(m) = a + bm + cm^2 + dm^3 + em^4 + \cdots$

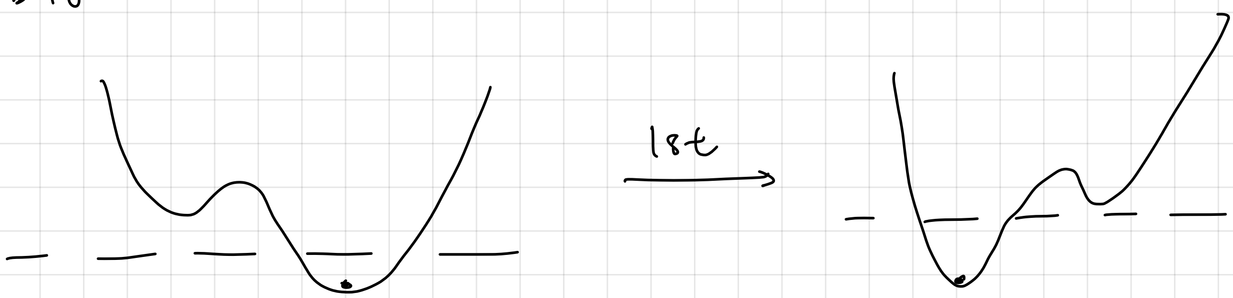
Can shift horizontal / vertical, so

$$F = bm + cm^2 + em^4 \qquad (e > 0, \text{ fix } e)$$

$e > 0$ $\qquad$ $b = 0$, adjust c



$b \neq 0$



m = order parameter. $\quad m = 0 \Rightarrow$ unbroken. $\quad m \neq 0 \Rightarrow$ broke.