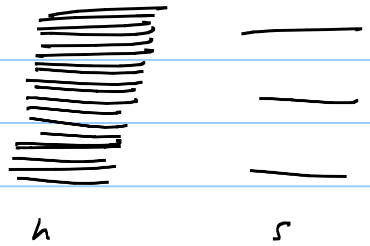
STATISTICAL MECHANICS

Note Title 1/2/2015

Consider a physical system in loose thermal contact with a heat bath. The heat bath is at a temperature T and the combined system has reached thermodynamic equilibrium (all fast processes have happened and slow ones have not).

The total energy of the combined system is $E = E_s + E_h$. The qm energy levels look schematically as



$$E_h >> E_s$$

The basic assumption of eq. stat. mech. is that all microstates of the system, consistent with the overall constraint of const. energy (and perhaps particle no.), are equally probable.

⟹ The probability to find the system in a state with energy E_s is proportional to the number of states in the heat bath at energy $E-E_s$: $\Omega(E-E_s) \propto p(E_s)$

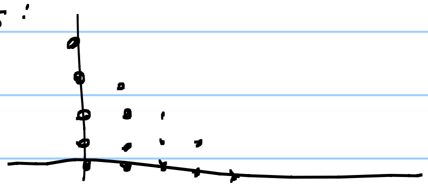
We should really speak of probab. densities and no. of states per energy.

So, $$\frac{p(E_s)}{p(E_s')} = \frac{\Omega(E-E_s)}{\Omega(E-E_s')} = e^{\ln \Omega(E-E_s)} e^{-\ln \Omega(E-E_s')}$$

We would like to expand this in small (ratio) $\frac{E_s}{E}$.

To get a feel for the no. of states as a fxn. of energy let's consider some examples of heat baths.

Collection of N indep. harmonic oscillators:



$$\mathcal{H}_h = \sum_{i=1}^{N} \hbar\omega_i \left(a_i^{\dagger} a_i + \frac{1}{2}\right)$$

A state at energy ε occurs when $n_1, n_2, \dots, n_i, \dots n_N$ satisfy:

$$\hbar\omega_1 (n_1 + \tfrac{1}{2}) + \dots + \hbar\omega_N (n_N + \tfrac{1}{2}) = \varepsilon$$

If $n_1, n_2, .. n_N$ were continuous, this would describe a hypersurface (plane) in N-dimensions.

The number of such states $\propto$ to volume of the hypersurface $\propto \varepsilon^{N-1}$

$$\Rightarrow \quad \Omega(E-E_s) \propto (E-E_s)^{N-1}$$ even if $E_s \ll E$ we cannot accurately expand because N is large.

But,

$$\ln \Omega(E-E_s) \propto (N-1)\ln(E-E_s) = (N-1)\ln\left[E\left(1-\frac{E_s}{E}\right)\right] = (N-1)\left[\ln E - \frac{E_s}{E} + \dots\right]$$

$$\Rightarrow \quad \frac{p(E_s)}{p(E_s')} = e^{\ln \Omega(E-E_s)} \; e^{-\ln \Omega(E-E_s')}$$

$$\propto \quad e^{-\beta E_s} \quad e^{+\beta E_s'}$$

where $\beta \simeq \frac{N-1}{E}$ => for large N, β is $\frac{1}{\text{energy per oscillator}}$

Put differently,

$$\frac{\Omega(E-E_s)}{\Omega(E-E_s')} = \frac{(E-E_s)^{N-1}}{(E-E_s')^{N-1}} = \frac{\left(1-\frac{E_s}{E}\right)^{N-1}}{\left(1-\frac{E_s'}{E}\right)^{N-1}} = \frac{\left(1-\frac{E_s}{(N-1)W}\right)^{N-1}}{\left(1-\frac{E_s'}{(N-1)W}\right)^{N-1}} \longrightarrow e^{-\frac{E_s}{W}} e^{\frac{E_s'}{W}}$$

as $N \to \infty$ where we used

$$\lim_{N\to\infty} \left(1+\frac{x}{N}\right)^N = e^x$$

Second example: particles in the box

$$E = \frac{p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2}{2m} + \dots + \frac{p_{x_N}^2 + p_{y_N}^2 + p_{z_N}^2}{2m} \sim n_{x_1}^2 + n_{y_1}^2 + n_{z_1}^2 + \dots + n_{x_N}^2 + n_{y_N}^2 + n_{z_N}^2$$

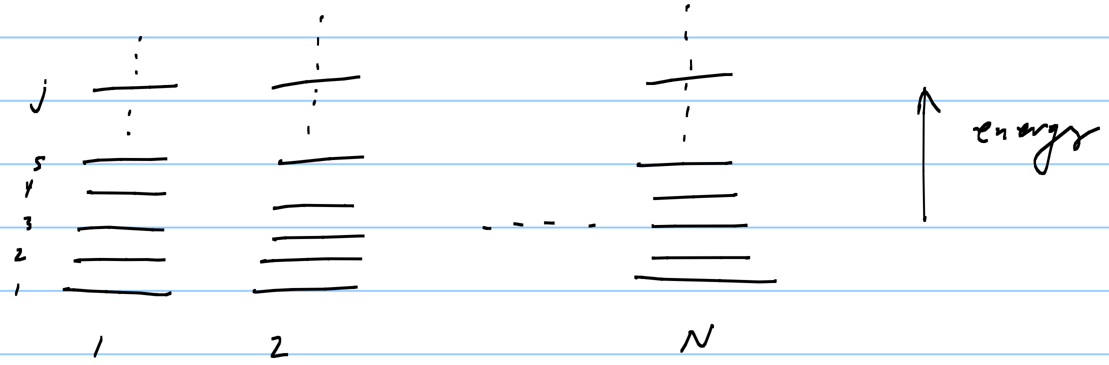
in 3N dim

Total no of states up to $E \propto$ volume of the hypersphere with radius $\propto \sqrt{E}$. Vol $\propto$ radius$^{3N} \propto E^{\frac{3}{2}N}$

$$\Rightarrow \beta \simeq \tfrac{3}{2}N/E \quad \Rightarrow \quad \tfrac{2}{3} \text{ of energy per particle}$$

Third example: (due to Gibbs)

Consider the system in question, loosely thermally coupled to N-1 mental copies of itself. Since the nature of the heatbath does not matter, the N-1 copies of the system can be used for convenience



The total ensemble has energy E.

If a_1 systems out of N are in the state 1,
a_2 ~"~ 2,
⋮
a_j ~"~ j ...

Then, the total energy of the ensemble is

$$\epsilon_1 a_1 + \epsilon_2 a_2 + \dots + \epsilon_j a_j + \dots = E$$ (last eq. is due to constraint)

Moreover, $a_1 + a_2 + \dots + a_j + \dots = N$

How many ways are there to arrange for $a_1, a_2, \dots a_j, \dots$ occupations? Lets say that each mental copy had a different energy. Then, there are N ways to choose the copy with lowest energy, N-1 ways to choose the copy with next lowest energy, N-2 for next etc.
⇒ in this special case, there are N! arrangements.

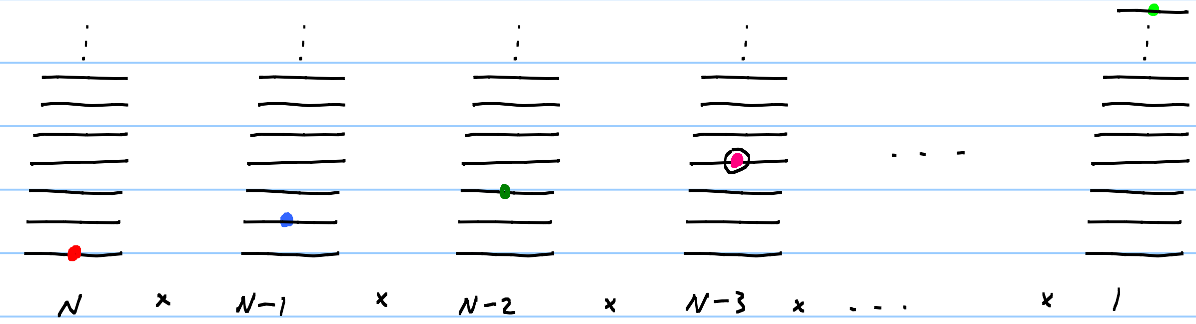
Now, lets say, that there are two copies with lowest energy, everything else being the same. Then, there are N ways to pick the 1st copy for the lowest energy and N-1 for the second, but since the order does not matter we must divide by 2 ⇒

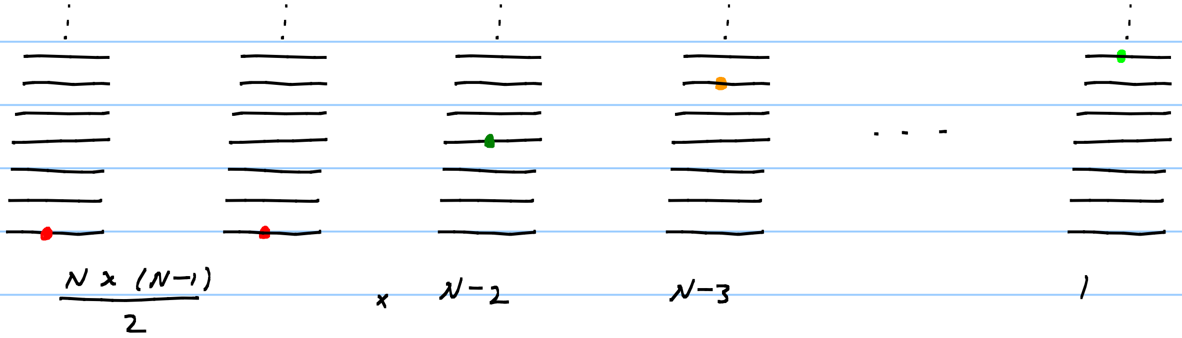
$\frac{N!}{2}$ ways. If 3 copies, then $\frac{N!}{3!}$. If a_1 ways, then $\frac{N!}{a_1!}$. Now, if a_2 copies for the next lowest energy, then $\frac{N!}{a_1!a_2!}$. Therefore, in general there are

$$\boxed{\frac{N!}{a_1!\,a_2!\,a_3!\cdots a_j!\cdots}} \quad \text{ways,}$$

subject to the constraint

$$\sum_j a_j = N \quad , \quad \sum_j \epsilon_j a_j = E .$$





etc.

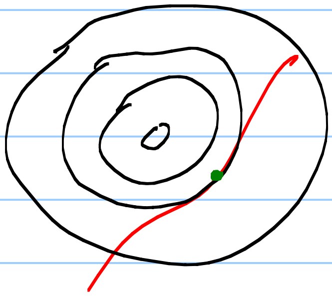
As the number of mental copies $N \to \infty$, the distribution is dominated by the most probable one. We therefore need to find the maximum.

It suffices to find the maximum of the logarithm of $\frac{N!}{a_1!a_2!\cdots a_j!\cdots}$ and to treat the constraints using lagrange multipliers.

Recall:

extremize $g(x,y)$ subject to $f(x,y)=c$

$\nabla g \parallel \nabla f$



achieved by

$$\nabla\Big(g(x,y)-\lambda\left(f(x,y)-c\right)\Big)=0 \qquad \text{and} \qquad f(x,y)-c=0$$

⇒ We need to maximize

$$\ln N! - \sum_j \ln a_j! + \lambda\Big(N-\sum_j a_j\Big) - \beta\Big(E-\sum_j \epsilon_j a_j\Big)$$

N and a_j's are discrete but large, so ignore their discreteness in the optimization.

Let $\Gamma(n) = \int_0^\infty dx\, x^{n-1} e^{-x}$; $du = e^{-x}dx$, $v = x^{n-1}$, $u = -e^{-x}$, $dv = (n-1)x^{n-2}dx$

$$= -e^{-x}x^{n-1}\Big|_0^\infty + (n-1)\int_0^\infty dx\, x^{n-2}e^{-x} = (n-1)\Gamma(n-2)$$

$$= (n-1)(n-2)\Gamma(n-3) = (n-1)(n-2)\cdots\Gamma(1) \quad \text{if } n \text{ is an integer}$$

But $\Gamma(1) = \int_0^\infty dx\, e^{-x} = -e^{-x}\Big|_0^\infty = 1 \Rightarrow \Gamma(n) = (n-1)!$

or $n! = \Gamma(n+1)$

$$\Rightarrow \quad n! = \int_0^\infty dx \; x^n \; e^{-x}$$

$$= \int_0^\infty dx \; e^{n \ln x - x}$$

$$\frac{d}{dx}\left(n \ln x_* - x_* \right) = n \frac{1}{x_*} - 1 = 0 \Rightarrow x_* = n$$

⇒ expand about x_*.

$$\frac{d^2}{dx^2}\left(n \ln x - x \right) = \frac{d}{dx}\left(\frac{n}{x} - 1 \right) = \frac{-n}{x^2}$$

$$\Rightarrow \quad n \ln x - x \simeq n \ln n - n + \frac{1}{2}\left(\frac{-n}{n^2}\right)(x-n)^2 + \ldots$$

⇒ for large n we have:

$$n! \simeq e^{n(\ln n - 1)} \int_0^\infty dx \; e^{-\frac{1}{2n}(x-n)^2}$$

$$\simeq e^{n(\ln n - 1)} \int_{-\infty}^\infty dx \; e^{-\frac{x^2}{2n}} = e^{n(\ln n - 1)} \sqrt{2n} \int_{-\infty}^\infty dx \, e^{-x^2}$$

$$n! \simeq e^{n(\ln n - 1)} \sqrt{2\pi n} = e^{n \ln n - n} \; e^{\frac{1}{2} \ln n} \; e^{\frac{1}{2} \ln 2\pi}$$

$$\Rightarrow \quad \ln n! \simeq n(\ln n - 1)$$ (Stirling's approximation)

$$\ln N! - \sum_j \ln a_j! + \lambda\left(N - \sum_j a_j\right) - \beta\left(E - \sum_j \epsilon_j a_j\right) \simeq$$

$$N(\ln N - 1) - \sum_j a_j(\ln a_j - 1) - \lambda\left(N - \sum_j a_j\right) - \beta\left(E - \sum_j \epsilon_j a_j\right)$$

Extremizing wrt a_j:

$$-(\ln a_j - 1) - \frac{a_j}{a_j} + \lambda + \beta\epsilon_j = 0 \qquad \forall j$$

$$\Rightarrow \ln a_j = -\lambda - \beta\epsilon_j \Rightarrow a_j = e^{-\lambda - \beta\epsilon_j}$$

Taking the derivative wrt Lagrange multipliers, we have

$$N = \sum_j a_j \quad \text{and} \quad E = \sum_j \epsilon_j a_j$$

$$\Rightarrow \frac{E}{N} = U = \frac{\sum_j \epsilon_j e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}}$$ is the internal energy of a system of interest

or

$$U = -\frac{\partial}{\partial\beta}\ln\left(\sum_j e^{-\beta\epsilon_j}\right)$$

and

$$\frac{a_j}{N} = \frac{e^{-\beta\epsilon_j}}{\sum_k e^{-\beta\epsilon_k}} = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_j}\ln\left(\sum_k e^{-\beta\epsilon_k}\right)$$

is the probability to find our system in the state j.

β is a Lagrange multiplier whose value, in principle, depends on U. However, its physical meaning is not clear at the moment.

Assume now, that we have 2 systems A and B, loosely coupled (thermally), and are coupled to a heat bath.

Then the probability to find A in energy ϵ_A and B in energy ϵ_B is

$$\frac{e^{-\beta(\epsilon_A+\epsilon_B)}}{\sum_{\{\varepsilon\}} e^{-\beta\varepsilon}} = \frac{e^{-\beta\epsilon_A}\, e^{-\beta\epsilon_B}}{\sum_j e^{-\beta\epsilon_{Aj}} \sum_k e^{-\beta\epsilon_{B_k}}}$$

The probability that the total system is such that the A system is at energy ϵ_A is

$$\sum_{\epsilon_B} \frac{e^{-\beta\epsilon_A}\, e^{-\beta\epsilon_B}}{\left(\sum_j e^{-\beta\epsilon_{A_j}}\right)\left(\sum_k e^{-\beta\epsilon_{B_k}}\right)} = \frac{e^{-\beta\epsilon_A}}{\sum_j e^{-\beta\epsilon_{A_j}}}$$

i.e. the same as if B was not present.
Similarly for B to be at ϵ_B is $\dfrac{e^{-\beta\epsilon_B}}{\sum_j e^{-\beta\epsilon_{B_j}}}$

We see that when two systems are placed in loose contact with each other, they have the same β. Temperature has similar property.

Moreover, recall that $U = \dfrac{\sum_j \epsilon_j e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}}$, so

$$\frac{\partial U}{\partial \beta} = \frac{\sum_j \left(-\epsilon_j^2 e^{-\beta \epsilon_j}\right)}{\sum_j e^{-\beta \epsilon_j}} + \sum_j \epsilon_j e^{-\beta \epsilon_j} \frac{\sum_k \epsilon_k e^{-\beta \epsilon_k}}{\left(\sum_j e^{-\beta \epsilon_j}\right)^2}$$

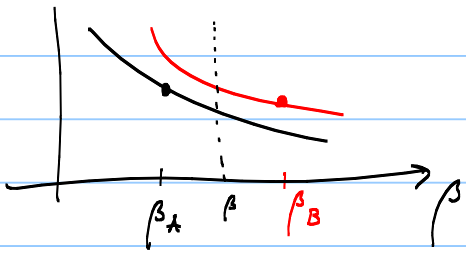
$$= \frac{1}{\left(\sum_j e^{-\beta \epsilon_j}\right)^2} \sum_{j,k} \left(-\epsilon_j^2 + \epsilon_j \epsilon_k\right) e^{-\beta(\epsilon_j + \epsilon_k)}$$

$$= \frac{-1}{2\left(\sum_j e^{-\beta \epsilon_j}\right)^2} \sum_{jk} (\epsilon_j - \epsilon_k)^2 e^{-\beta(\epsilon_j + \epsilon_k)} \quad < 0$$

⇒ the internal energy is a monotonically decreasing function of β.

Therefore, if we start with two systems A and B at β_A and β_B then by conservation of energy, after mixing,

$$U_A(\beta_A) + U_B(\beta_B) = U_A(\beta) + U_B(\beta)$$



$$\Rightarrow \quad \beta_A < \beta < \beta_B$$

and the system with smaller β looses energy while the system with larger β gains energy.

⇒ equal β's must mean equal temperature, and high temperature must mean small β.

To figure out what function of temperature β is we need to make a connection to thermodynamics.

Review of thermodynamics:

definitions: adiabatic walls completely isolate a system of interest from all outside influences

walls separating two systems that are not adiabatic put the two systems in thermal contact (thin sheet of metal)

isolated system, left alone for a suitably long time will relax to a state where no further changes are noticable, calld equilibrium.

Zeroth law of thermodynamics:
if two systems A and B are each in equilibrium with a third body C, then they are also in equilibrium with each other.

This allows us to define a concept of temperature.
Consider a gas, definied by pressure & volume (need not be ideal)
(if homog., we only need p & V to specify thermod. state)

A is in state (p_1, V_1) & C in (p_3, V_3)

To test if in th. eq., place them in thermal contact, and see in the state changes.

For generic values of (p_1, V_1) & (p_3, V_3) they will not be in eq. e.g. suppose that we choose p_1, V_1, p_3 then there will be a special value of V_3 for which nothing happens when they are placed in thermal contact.

$$\Rightarrow \quad F_{AC}(p_1, V_1; p_3, V_3) = 0 \quad \text{or} \quad V_3 = f_{AC}(p_1, V_1; p_3)$$

When B & C are in eq., we also have a constraint

$$\Rightarrow F_{BC}(p_2, V_2; p_3, V_3) = 0 \quad \text{or} \quad V_3 = f_{BC}(p_2, V_2; p_3)$$

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

According to zeroth law systems A and B must also be in equilibrium. This means that $(\star)$ must be equivalent to a constraint

$$F_{AB}(p_1, V_1; p_2, V_2) = 0$$

does not depend on p_3!

This means that p_3 dependence in $(\star)$ is such that it can be canceled on both sides. When this cancellation is performed, there is a relationship between the states of system A and system B:

$$\theta_A(p_1, V_1) = \theta_B(p_2, V_2)$$

The value of $\theta(p, V)$ is called temperature of the system. The function $T = \theta(p, V)$ is called equation of state.

Nothing tels us yet why we should pick $\theta(p,V)$ rather than $\sqrt{\theta}$, say. In the mean time pick a reference system, ideal gas equation of state,

$$T = \frac{pV}{Nk_B} = \frac{pV}{nR}$$

n is the amount of the substance in mols
R is a universal constant $8.314\ldots \frac{J}{mol \cdot K}$
(measured in the limit of vanishing density)

1^{st} law of thermodynamics:

The amount of work required to change an isolated system from state 1 to state 2 is independent of how the work is performed
(conservation of energy)

$U(P,V)$ must be a function of state

However, for systems that are not isolated, the change of energy is not equal to the amount of work done.
For example, take two systems at different temperature and place them in thermal contact. We need not do any work, but the energy of each system will change.
Therefore there are other ways to change the energy of the system than by doing work. $\Delta U = Q + W$
Q is the amount of energy that was transfered to sys. that can't be accounted by work

quasistatic process: add and subtract energy very slowly so that at every stage of the process the system is effectively in equilibrium (p, V) describe it

$$dU = \text{đ}Q - \text{đ}W = \left(TdS - PdV \right)$$

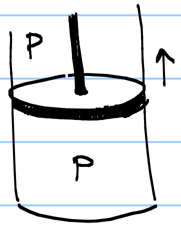
exact differential

integral indep. of path in p, V

not exact differentials

(assuming a one component uniform system which can only do work by expanding against pressure)

The second term on the right states that the system looses internal energy by doing work.



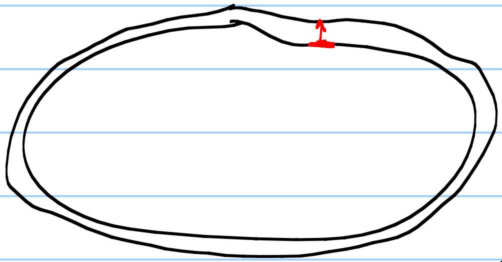
$F_z = PA \Rightarrow F_z\, dz = P\, A dz = PdV$

is the work done by the gas/fluid

$\Rightarrow$ it must loose PdV worth

of internal energy

in general



$$\iint d\vec{A} \cdot \delta h\, \hat{n} = dV$$

$$\iint P d\vec{A} \cdot \delta h\, \hat{n} = PdV$$

$$\iint d\vec{F} \cdot \delta h\, \hat{n} = dW$$

reversible processes: happy to work in both directions of time (special case of quasi-static processes)

must lie in equilibrium at each point along the path and there must be no friction involved.

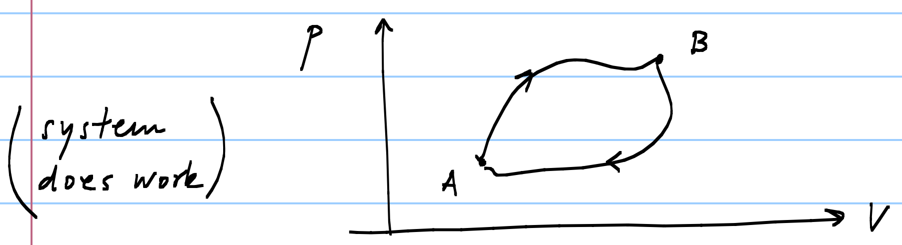
Second Law à la Kelvin: No process is possible whose sole effect is to extract heat from a hot reservoir and convert this entirely into work

Second Law à la Clausius: No process is possible whose sole effect is the transfer of heat from a colder to hotter body

(they are equivalent)

THIS WILL ALLOW US TO DEFINE ENTROPY!

Consider a reversible process on the p-V diagram:



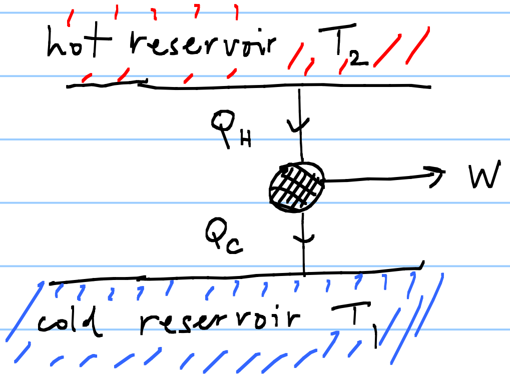
$\oint dE = 0$ because we return to the original state, but

$\oint p\,dV \neq 0 \Rightarrow \oint dW \neq 0$

by conservation of energy

If this is reversible, then take this route counter clockwise. Heat will be absorbed, work will be done. Why does it not violate 2^{nd} law of thermodynamics?

Reversible process does more than just extract heat, it also deposits some elsewhere.



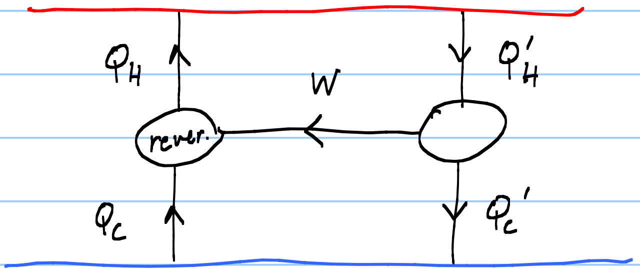
efficiency defined as

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

Carnot's theorem: of all engines operating between two reservoirs, a reversible engine is the most efficient.

Corollary: all reversible engines have the same efficiency which depends only on the temperature of the reservoirs.

Connect an engine which is not reversible to a reversible engine running backwards, and construct them in such way that they give same work.



$$\eta' = \frac{W}{Q_H'} = \frac{Q_H' - Q_c'}{Q_H'}$$

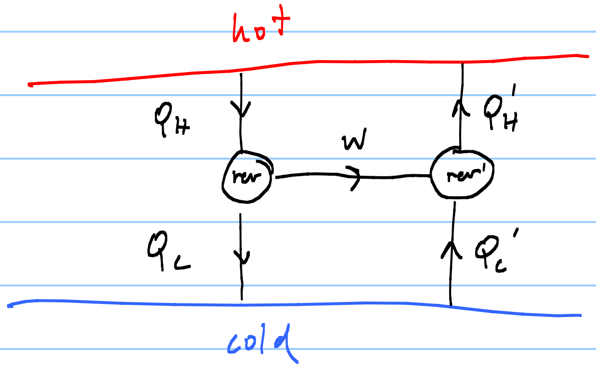
1^{st} law $\quad Q_H' - Q_H = Q_c' - Q_c$

$$\Rightarrow Q_H' - Q_c' = Q_H - Q_c \quad \Rightarrow \quad \eta' = \frac{Q_H - Q_c}{Q_H'}$$

2^{nd} law (heat must flow from hot to cold)

$$Q_H' > Q_H \; \left(\text{and } Q_c' > Q_c \right) \Rightarrow \eta' = \frac{Q_H}{Q_H'} \frac{Q_H - Q_c}{Q_H} < \frac{Q_H - Q_c}{Q_H} = \eta$$

Now assume that the primed engine is reversible afterall,



$$\eta' = \frac{W}{Q_H'} = \frac{Q_H' - Q_C'}{Q_H'}$$

$$= \frac{Q_H - Q_C}{Q_H'}$$

by 2nd law $Q_H > Q_H'$ $\Rightarrow \eta' = \frac{Q_H}{Q_H'}\left(\frac{Q_H - Q_C}{Q_H}\right) \geq \eta$

$\Rightarrow$ if the primed engine is reversible its efficiency is the same as the unprimed engine.

this is all independent of the details of the reversible engine $\Rightarrow$

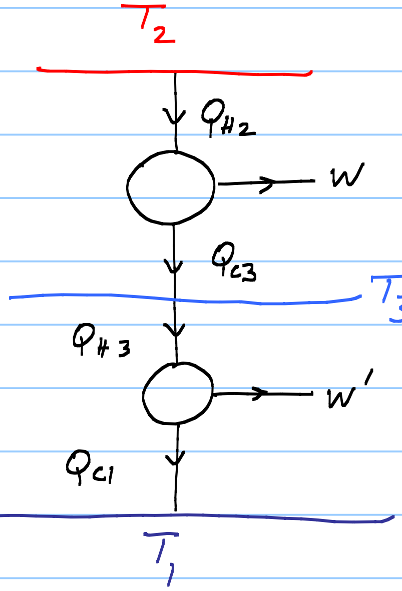
for a reversible engine $\eta = \eta(T_1, T_2)$

$$\eta(T_2, T_1) = 1 - \frac{Q_{C1}}{Q_{H2}}$$

$$Q_{H2} - Q_{C1} = W + W'$$

$$\eta(T_2, T_3) = 1 - \frac{Q_{C3}}{Q_{H2}}$$

$$\eta(T_3, T_1) = 1 - \frac{Q_{H3}}{Q_{C1}} = 1 - \frac{Q_{C3}}{Q_{C1}}$$



$\frac{q_{c3}}{q_{H2}} = 1-\eta(T_2, T_3)$; $\frac{q_{c3}}{q_{c1}} = 1-\eta(T_3, T_1)$

$$\Rightarrow \frac{\left(\frac{q_{c3}}{q_{H2}}\right)}{\left(\frac{q_{c3}}{q_{c1}}\right)} = \frac{q_{c1}}{q_{H2}} = \frac{1-\eta(T_2, T_3)}{1-\eta(T_3, T_1)} = 1-\eta(T_2, T_1)$$

⇒ RHS does not depend on T_3 ⇒ it must cancel on the LHS

the only way this will happen for all $T_1 < T_3 < T_2$ is if

$$1-\eta(T, T') = \frac{\theta(T')}{\theta(T)}$$

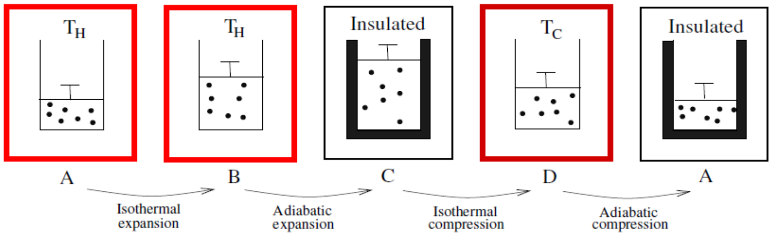
[*check

$$\frac{\frac{\theta(\cancel{T_3})}{\theta(T_2)}}{\frac{\theta(\cancel{T_3})}{\theta(T_1)}} \overset{?}{=} \frac{\theta(T_1)}{\theta(T_2)}$$ ✓]

where $\theta(t)$ is some unknown, but universal fxn because it must be the same for every reversible engine.

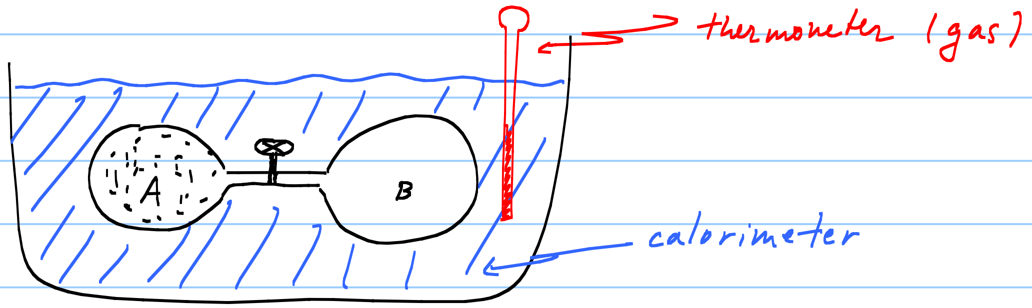
$\theta(t)$ is independent of the physical substance
can use it as a thermometer.

Carnot's engine:



Let's connect $\theta(T)$ to T for the ideal gas using Carnot's engine. In order to do that, however, we will need the internal energy of an ideal gas. This we will argue based on experiment:

Joule experiment: take as independent state variables T, V



A filled w/ gas, B evacuated

- let it equilibrate i.e. fixed T
- open the valve; gas moves into B until the pressure is equal
- the reading on the thermometer hardly changed
  $\Rightarrow$ no heat escaped from the bath/calorimeter
  $\Rightarrow$ no heat to/from gas chamber either

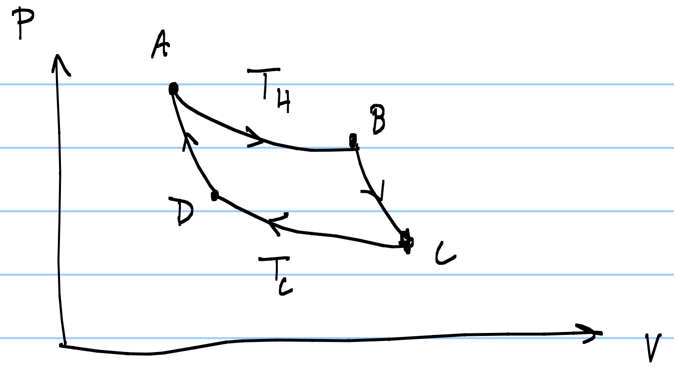
1st law: $\Delta U = Q - W = -W$

the volumes of the two chambers have not changed

$\Rightarrow W = 0 \quad \Rightarrow \Delta U = 0$

but volume of the gas increased $\Rightarrow U$ is indep. of V

$$\Rightarrow U = U(T)$$



A→B : $dU = 0$ b/c T is fixed T_H and $U = U(T)$

$$dU = \bar{d}Q - \bar{d}W \Rightarrow PdV = \bar{d}Q$$

$$PV = nRT_H \Rightarrow nRT_H \frac{dV}{V} = \bar{d}Q$$

$$\Rightarrow Q_H = nRT_H \ln \frac{V_B}{V_A}$$

B→C : adiabatic $\Rightarrow \bar{d}Q = 0 \Rightarrow dU = -PdV$

$$\left(\frac{dU}{dT}\right) dT = -nRT \frac{dV}{V} \Rightarrow \left(\frac{dU}{dT}\right)\frac{dT}{T} = -nR\frac{dV}{V}$$

$$\Rightarrow \int_{T_H}^{T_c} \left(\frac{dU}{dT}\right)\frac{dT}{T} = -nR \ln \frac{V_c}{V_B}$$

C→D : heat dumped $Q_c = nRT_c \ln \frac{V_c}{V_D}$

D→A : $$\int_{T_c}^{T_H} \left(\frac{dU}{dT}\right)\frac{dT}{T} = -nR \ln \frac{V_A}{V_D}$$

Add B→C and D→A. The LHS's cancel and so

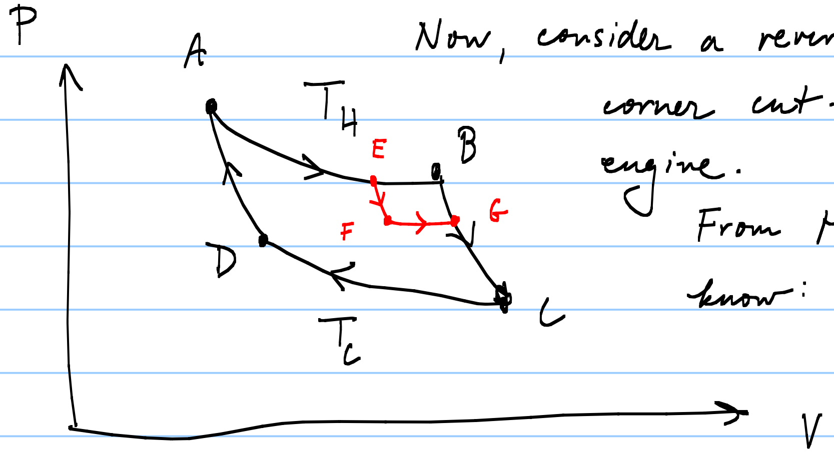
$$0 = -nR \ln \frac{V_c}{V_B} - nR \ln \frac{V_A}{V_D} \Rightarrow \ln\left(\frac{V_A}{V_D}\frac{V_c}{V_B}\right) = 0 \Rightarrow \frac{V_c}{V_D} = \frac{V_A}{V_B}$$

$$\eta = \frac{Q_H - Q_c}{Q_H} = 1 - \frac{nRT_c \ln \frac{V_c}{V_D}}{nRT_H \ln \frac{V_B}{V_A}} = 1 - \frac{T_c}{T_H}$$

$$\Rightarrow \boxed{\theta(T) = T}$$

Also note that $1 - \frac{Q_c}{Q_H} = 1 - \frac{T_c}{T_H} \Rightarrow \frac{Q_H}{T_H} - \frac{Q_c}{T_c} = 0$

$\Rightarrow \sum_{i=1}^{2} \frac{Q_i}{T_i} = 0$ provided that heat absorbed is positive and heat dumped is negative



Now, consider a reversible cycle, but with a corner cut-off due to a mini-Carnot engine.

From the original C. engine we know: $\frac{Q_{AB}}{T_H} + \frac{Q_{CD}}{T_c} = 0$

for the mini-C. engine: $\frac{Q_{EB}}{T_H} + \frac{Q_{GF}}{T_{FG}} = 0$

So, for the upper process.

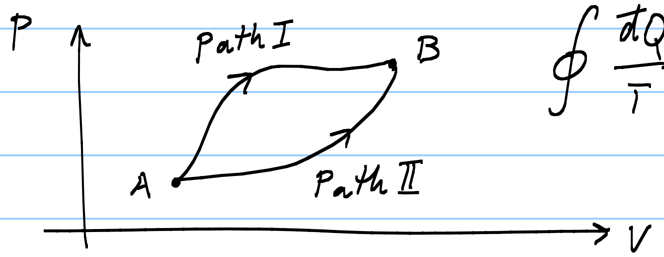
$$\frac{Q_{AE}}{T_H} + \frac{Q_{FG}}{T_{FG}} + \frac{Q_{CD}}{T_c} = \frac{Q_{AB} - Q_{EB}}{T_H} + \frac{Q_{FG}}{T_{FG}} + \frac{Q_{CD}}{T_c} =$$

$$= \boxed{\frac{Q_{AB}}{T_H}} - \frac{Q_{EB}}{T_H} + \frac{Q_{FG}}{T_{FG}} + \boxed{\frac{Q_{CD}}{T_c}} = -\frac{Q_{EB}}{T_H} + \frac{Q_{FG}}{T_{FG}} = -\frac{Q_{EB}}{T_H} - \frac{Q_{GF}}{T_{FG}} = 0$$

$$\Rightarrow \sum_{i=1}^{3} \frac{Q_i}{T_i} = 0.$$

We can continue to subdivide any reversible cycle into a large amount of Carnot subcycles, and summing up all contributions Q/T along the path, we find that to total heat absorbed in any reversible cycle must obey:

$$\oint \frac{\text{đ}Q}{T} = 0$$



$$\oint \frac{\text{đ}Q}{T} = \int_{A\to B,\ \text{path I}} \frac{\text{đ}Q}{T} + \int_{B\to A,\ \text{path II}} \frac{\text{đ}Q}{T} = 0$$

$$\Rightarrow \int_{A\to B,\ \text{path I}} \frac{\text{đ}Q}{T} = -\int_{B\to A,\ \text{path II}} \frac{\text{đ}Q}{T} = \int_{A\to B,\ \text{path II}} \frac{\text{đ}Q}{T}$$

⇒ it does not matter how we get from A to B, as long as it is in a reversible way, the integral over $\text{đ}Q/T$ is the same.

⇒ $\frac{\text{đ}Q}{T}$ is an exact differential. Call it dS.

S, just like the internal energy, is a state fxn of the system: it depends only on the state variables p, V.

⇒ As long as the system is in equilibrium, it has a well defined entropy.

⇒ 1st law of t.d.: $dU = TdS - PdV$

irreversibility: consider paths which are not reversible

By Carnot's theorem, we know that the efficiency of an irreversible engine is smaller than that of a reversible engine.

$$\Rightarrow \quad 1-\frac{Q_c'}{Q_H'} \leq 1-\frac{Q_c}{Q_H} \quad ; \quad Q_H'-Q_c' = Q_H-Q_c$$

* they do the same work

$$^{*}\left(\Rightarrow \quad Q_H'-Q_c' \leq \frac{Q_H'}{Q_H}\left(Q_H-Q_c\right) \quad \Rightarrow \quad 1 \leq \frac{Q_H'}{Q_H} \Rightarrow \quad Q_H' \geq Q_H \right)$$

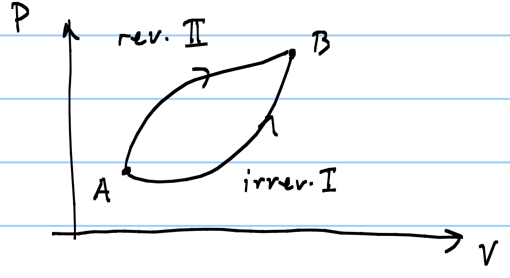
so
$$\frac{Q_H'}{T_H}-\frac{Q_c'}{T_c} = \frac{Q_H'}{T_H}-\frac{Q_H'-Q_H+Q_c}{T_c} = Q_H'\left(\frac{1}{T_H}-\frac{1}{T_c}\right)+\frac{Q_H-Q_c}{T_c}$$

$$= Q_H'\left(\frac{1}{T_H}-\frac{1}{T_c}\right)+\overset{\downarrow}{\frac{Q_H}{T_H}}-\frac{Q_H}{T_H}+\frac{Q_H}{T_c}-\overset{\downarrow}{\frac{Q_c}{T_c}}$$

$$= Q_H'\left(\frac{1}{T_H}-\frac{1}{T_c}\right)-Q_H\left(\frac{1}{T_H}-\frac{1}{T_c}\right) = \left(Q_H'-Q_H\right)\left(\frac{1}{T_H}-\frac{1}{T_c}\right) \leq 0$$

⇒ same process of subdivision of an arbitrary irreversible path gives

$$\boxed{\oint_{\text{irrev.}} \frac{\bar{d}Q}{T} \leq 0} \qquad \text{(Clausius inequality)}$$



$$\int_{I}\frac{\bar{d}Q}{T}-\int_{II}\frac{\bar{d}Q}{T} \leq 0 \Rightarrow \int_{I}\frac{\bar{d}Q}{T} \leq S(B)-S(A)$$

take I to be adiabatic. Then $\bar{d}Q\big| = 0$ along I

⇒ $S(B) \geq S(A)$ entropy of an isolated system never decreases

Note that the increase of entropy is a consequence of the second law of t.d., the 2^{nd} law itself is either the Kelvin's or Claussius' statement about heat flow.

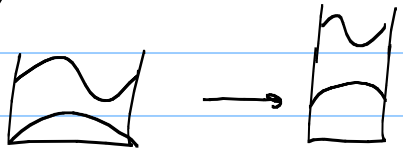
Now, let's go back to the statistical description of a system.

when:

$$U = \frac{\sum_j \epsilon_j \cdot e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}} = -\frac{\partial}{\partial\beta}\ln\Big(\overbrace{\sum_j e^{-\beta\epsilon_j}}^{Z}\Big)$$

Consider a process in which we do some infinitesimal work on our subsystem while it is connected to the heat bath and when we are done, we change the temperature of the heat bath infinitesimally.

When we do work on the system, we change the energy levels.
E.g. particle in the box



because $\left[\frac{p^2}{2m}\right] = \frac{1}{L^2}$

Now, $$d\ln Z = \frac{\partial \ln Z}{\partial\beta}d\beta + \sum_j \frac{\partial \ln Z}{\partial \varepsilon_j} d\varepsilon_j$$

Recall that the probability to find the subsystem in the state j w/ energy ϵ_j is:

$$\frac{e^{-\beta\epsilon_j}}{\sum_k e^{-\beta\epsilon_k}} = -\frac{1}{\beta}\frac{\partial}{\partial\epsilon_j}\ln\Big(\sum_k e^{-\beta\epsilon_k}\Big)$$

$\Rightarrow$ $p(\varepsilon_j) = -\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_j}\ln Z$. Therefore:

$$d\ln Z = \frac{\partial \ln Z}{\partial \beta}\,d\beta + \sum_j \frac{\partial \ln Z}{\partial \varepsilon_j}\,d\varepsilon_j$$

$$= -U\,d\beta - \beta\sum_j p(\varepsilon_j)\,d\varepsilon_j$$

$\Rightarrow$ $\sum_j p(\varepsilon_j)\,d\varepsilon_j$ must be the work done on the system

and so $-\sum_j p(\varepsilon_j)\,d\varepsilon_j$ is the work done by the system

$$d\ln Z = -U\,d\beta + \beta\,\text{đ}W = -d(U\beta) + dU\,\beta + \beta\,\text{đ}W$$

$$\Rightarrow \quad d(\beta U + \ln Z) = \beta\,(dU + \text{đ}W)$$

$$\Rightarrow \quad dU = \frac{1}{\beta}\,d(\beta U + \ln Z) - \text{đ}W$$

$$\Rightarrow \quad \text{đ}Q = \frac{1}{\beta}\,d(\beta U + \ln Z) = T\,dS$$

$$\Rightarrow \quad \big(\beta U + \ln Z + \overset{\text{set to zero by Nernst theorem}}{\text{const}}\big) \propto S \quad \text{and} \quad \beta \propto \frac{1}{T}$$

with the same (universal) proportionality constant

$\Rightarrow$ so let $\boxed{\beta = \frac{1}{k_B T}}$ then

$$\boxed{S = k_B(\beta U + \ln Z) = \frac{U}{T} + k_B \ln Z}$$

Alternative, but equivalent expression for entropy:

$$S = k_B \left(\beta \frac{\sum_j \epsilon_j e^{-\beta\epsilon_j}}{\sum_{j'} e^{-\beta\epsilon_{j'}}} + \ln \sum_{j'} e^{-\beta\epsilon_{j'}} \right)$$

$$= k_B\left(\sum_j \beta\epsilon_j \, p(\epsilon_j)\right) + k_B \ln \sum_{j'} e^{-\beta\epsilon_{j'}}$$

$$= -k_B \sum_j p(\epsilon_j) \ln e^{-\beta\epsilon_j} + k_B \overset{=1}{\left(\sum_j p(\epsilon_j)\right)} \ln \sum_{j'} e^{-\beta\epsilon_{j'}}$$

$$= -k_B \sum_j p(\epsilon_j) \ln \frac{e^{-\beta\epsilon_j}}{\sum_{j'} e^{-\beta\epsilon_{j'}}} = -k_B \sum_j p(\epsilon_j) \ln p(\epsilon_j)$$

Partition fxn $Z = \sum_j e^{-\beta\epsilon_j}$ (* Z is sometimes denoted by Q, your book does that)

Let us define the Helmholtz free energy F as

$$Z = e^{-\beta F} = e^{-\frac{F}{k_B T}}$$

(* F is sometimes denoted by A)

Let's understand how F and S are related.

$$S = \frac{U}{T} + k_B \ln Z = \frac{1}{T}\left(-\frac{\partial}{\partial\beta} \ln Z\right) + k_B \ln Z$$

$$\frac{\partial}{\partial\beta} = \frac{\partial}{\partial \frac{1}{k_B T}} = k_B \frac{\partial T}{\partial \frac{1}{T}} \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T} \Rightarrow$$

$$S = k_B T \frac{\partial \ln Z}{\partial T} + k_B \ln Z = \frac{\partial}{\partial T}\left(k_B T \ln Z\right) = -\frac{\partial F}{\partial T}$$

$$S = \frac{U}{T} + k_B \ln Z = \frac{U}{T} - \frac{F}{T} \Rightarrow F = U - TS$$

$$dF = dU - dT\,S - T\,dS = -S\,dT - P\,dV$$

This makes sense, because $F = F(T, V) \Rightarrow$

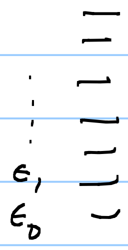
$$dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV \Rightarrow$$

$$\frac{\partial F}{\partial T} = -S \quad \text{and} \quad \frac{\partial F}{\partial V} = -P$$

Ideal gas of indistinguishable particles: bosons or fermions:

Case I. particle number is not conserved
Case II. particle number is conserved

Case I:



The state of the system of non-interacting bosons (ideal gas) is determined by the no. of bosons occupying each level.

$\Rightarrow$ the total energy of a state with n_0 bosons in ϵ_0, n_1 in ϵ_1, ..., n_r in ϵ_r, ... is

$$E = n_0 \epsilon_0 + n_1 \epsilon_1 + \dots + n_r \epsilon_r + \dots$$

For bosons there is no restriction on how many can be in a given level $\Rightarrow$ $n_0 = 0, 1, 2, \dots$, $n_1 = 0, 1, 2, \dots$ because the total no. of bosons is not conserved.

After decay from an exited state, there is an extra photon which was not there before.

$$Z = \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \cdots \sum_{n_r=0}^{\infty} \cdots e^{-\beta(n_0\epsilon_0 + n_1\epsilon_1 + \dots + n_r\epsilon_r + \dots)}$$

$$= \left(\frac{1}{1-e^{-\beta\epsilon_0}}\right)\left(\frac{1}{1-e^{-\beta\epsilon_1}}\right)\cdots\left(\frac{1}{1-e^{-\beta\epsilon_r}}\right)\cdots$$

$$\Rightarrow \quad Z = \prod_{j=0}^{\infty} \frac{1}{1-e^{-\beta\epsilon_j}}$$

$$U = -\frac{\partial \ln Z}{\partial \beta} = +\frac{\partial}{\partial \beta} \sum_{j=0}^{\infty} \ln\left(1-e^{-\beta\epsilon_j}\right) = \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta\epsilon_j}-1}$$

Consider photons: $\epsilon = c|\vec{p}| = \hbar c|\vec{k}|$; $k_x = \frac{2\pi}{L_x} m_x, \; m_x = 0, \pm 1, ..$

$$\sum_j (\dots) \longrightarrow \sum_{k_x} \sum_{k_y} \sum_{k_z} \sum_{\text{polariz.}} (\dots)$$

$$\frac{1}{\Delta k_x} \sum_{k_x} \Delta k_x \longrightarrow \frac{L_x}{2\pi} \int_{-\infty}^{\infty} dk_x \quad \Rightarrow$$

$$U = 2 \frac{L_x L_y L_z}{(2\pi)^3} \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z \, \frac{\hbar c|\vec{k}|}{e^{\hbar c|\vec{k}|/k_B T} - 1}$$

change to spherical polar coordinates

$$U = 2 \frac{V}{(2\pi)^3} \int_0^\infty dk\, k^2 \int_0^{2\pi} d\phi \int_{-1}^{1} d\cos\theta \frac{\hbar c k}{e^{\beta \hbar c k} - 1}$$

$$= \frac{2}{(2\pi)^3} 4\pi V \int_0^\infty dk\, k^2 \frac{\hbar c k}{e^{\beta \hbar c k} - 1} .$$

Let $\beta \hbar c k = x$ then $k = \frac{x}{\beta \hbar c}$ $\Rightarrow$

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

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

$$6.49 \simeq \frac{\pi^4}{15} = I_3$$

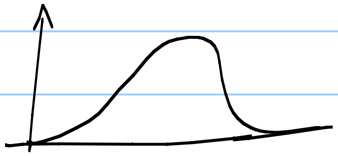
expect it to be a positive no. of order 1 (come back to it later)

What is the energy density of the radiation in a given (angular) frequency interval?

$$du = \frac{1}{\pi^2} dk\, k^2 \frac{\hbar c k}{e^{\beta \hbar c k} - 1} ; \quad ck = \omega \Rightarrow k = \frac{\omega}{c}$$

$$du = \frac{1}{\pi^2} \frac{d\omega}{c} \frac{\omega^2}{c^2} \frac{\hbar \omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} = \frac{\hbar \omega^3}{\pi^2 c^3} \frac{d\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1}$$

This is Planck's formula.



$$-\left.\frac{\partial F}{\partial V}\right)_T = P$$

$$-\beta F = \ln Z \Rightarrow F = -\frac{1}{\beta}\ln Z = \frac{1}{\beta}\sum_j \ln\left(1-e^{-\beta\epsilon_j}\right)$$

But, $U = \frac{\partial}{\partial\beta}\sum_j \ln\left(1-e^{-\beta\epsilon_j}\right)$

$$\int_\infty^\beta d\beta'\, U(\beta') = \sum_j \ln\left(1-e^{-\beta\epsilon_j}\right) = \beta F$$

and

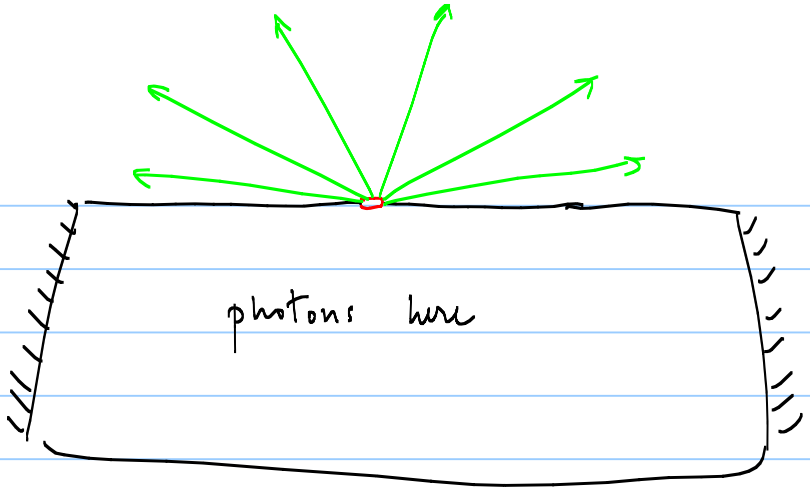
$$U(\beta') = V\,\frac{I_3}{\pi^2}\,\frac{1}{\hbar^3 c^3}\left(\frac{1}{\beta'}\right)^4$$

$$\int_\infty^\beta d\beta'\, U(\beta') = -\frac{1}{3}\beta\, U(\beta) = \beta F$$

$$\Rightarrow F = -\frac{1}{3}U \quad \text{and} \quad P = -\left.\frac{\partial F}{\partial V}\right)_T = \frac{1}{3V}U$$

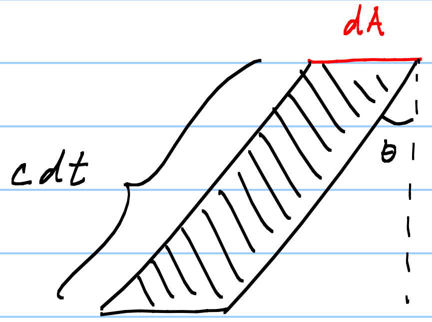
$$\boxed{PV = \frac{1}{3}U}$$

Now, consider a container whose inner walls are perfectly reflecting. There is a tiny hole in such container and some of the photons escape through it. (This is an example of a black body radiation) (Any radiation that goes through the hole bounces around, being reflected many times, but eventually gets absorbed before escaping. Any light coming out of the hole must have been emitted from the walls, representative of a perfect black body)



How much energy is emitted per unit time?

in a time interval dt only photons which are $c\,dt$ away from the hole, and have the momentum in the right direction escape:



$$dV = (c\,dt\cos\theta)\,dA$$

photons must have

$$\vec{k} = (k_x, k_y, k_z) = k(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

$\Rightarrow$ in the sum (integral) over $\vec{k}$ we must restrict ourselves only to k's satisfying the above constraint $\Rightarrow$

$$d^3k = k^2 dk \;\; d(\cos\theta)\, d\phi$$

For each θ, ϕ we can sum over $|\vec{k}|$. The emitted energy will come from those regions of real space where $0 \le \phi \le 2\pi$ and $0 \le \theta \le \frac{\pi}{2}$.

$\Rightarrow$ the energy emitted is:

$$2\int_0^\infty \frac{dk\,k^2}{(2\pi)^3}\int_0^1 d(\cos\theta)\int_0^{2\pi} d\phi \;\frac{\hbar c k}{e^{\beta\hbar c k}-1}\;\; c\,dt\,dA\,\cos\theta$$

this is just like $\frac{U}{V}$, but with an extra $c\,dt\,dA$

and with a factor $2\pi \int_0^1 dx\, x = \pi$ instead of

$$2\pi \int_{-1}^{1} dx = 4\pi \quad \Rightarrow$$

energy emitted $= \frac{1}{4}\, c\, dt\, dA\, \frac{U}{V}$

$$= \frac{\pi^2}{60} \frac{(k_B T)^4}{\hbar^3 c^2}\, dt\, dA$$

$$\boxed{\frac{E_{em.}}{dt\, dA} \qquad \sigma T^4}$$

where σ Stefan constant

$$\sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2} = 5.670 \times 10^{-8} \frac{W}{m^2 K^4}$$

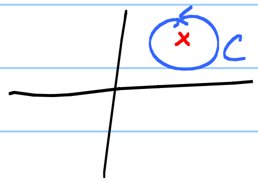
$\hookrightarrow$ Stefan-Boltzmann law of black body radiation

---

How do we know that $\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$?

I should stress that this is not particularly important. However, evaluating this integral proceeds by using an important technique, which we will use for other important results, so it is good to use it in practice.

Recall Cauchy's theorem:

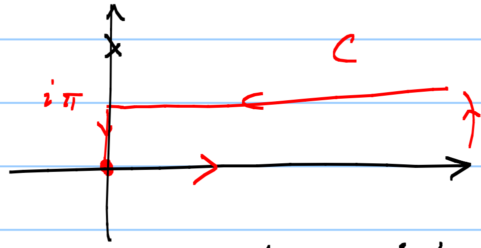


$$\frac{1}{2\pi i} \oint_C \frac{dz}{z - z_0} f(z) = f(z_0)$$

$\uparrow$ analytic (near z_0)

Take $I_n = \int_0^\infty dx \, \frac{x^n}{e^x - 1}$; $n = 1, 3, 5, \ldots$

Consider $\oint_C dz \, \frac{z^n}{e^z - 1}$ where



Because the integrand is analytic, the result must be 0 ⇒

$$\oint_C dz \, \frac{z^n}{e^z - 1} = 0.$$

So,

$$0 = \int_0^\infty dx \, \frac{x^n}{e^x - 1} + \int_\infty^0 d(x + i\pi) \, \frac{(x + i\pi)^n}{e^{i\pi} e^x - 1} + \int_1^0 d(i\pi y) \frac{(i\pi y)^n}{e^{i\pi y} - 1}$$

Start w/ the last term

$$-(i\pi)^{n+1} \int_0^1 dy \, \frac{y^n \left(e^{-i\pi y} - 1\right)}{\left(e^{i\pi y} - 1\right)\left(e^{-i\pi y} - 1\right)} =$$

$$-(i\pi)^{n+1} \int_0^1 dy \, \frac{y^n (\cos \pi y - 1 - i \sin \pi y)}{2 - 2\cos(\pi y)}$$

For n odd, the real part is

$$= (i\pi)^{n+1} \, \frac{1}{2} \int_0^1 dy \, y^n = (-1)^{\frac{n+1}{2}} \, \pi^{n+1} \, \frac{1}{2(n+1)}$$

So,

$$0 = \int_0^\infty dx \frac{x^n}{e^x - 1} + Re \int_0^\infty dx \frac{(x+i\pi)^n}{e^x+1} + (-1)^{\frac{n+1}{2}} \frac{\pi^{n+1}}{2(n+1)}$$

Recall the binomial theorem: $(a+b)^n = \sum_{j=0}^{n} a^{n-j} b^j \binom{n}{j}$

So,

$$0 = \int_0^\infty dx \frac{x^n}{e^x-1} + Re \sum_{j=0}^{n} \binom{n}{j} (i\pi)^j \int_0^\infty dx \frac{x^{n-j}}{e^x+1} + \frac{(-1)^{\frac{n+1}{2}} \pi^{n+1}}{2(n+1)}$$

For $n=3$ of interest to us, we have $j=0$ and $j=2$ give contribution to the real part. That requires us to know

$$\int_0^\infty dx \frac{x}{e^x+1} \quad \text{and} \quad \int_0^\infty dx \frac{x^3}{e^x+1} .$$

This we can relate to the integral of interest:

$$\int_0^\infty dx \frac{x^m}{e^x-1} - \int_0^\infty dx \frac{x^m}{e^x+1} = \int_0^\infty dx\, x^m \frac{e^x+1-(e^x-1)}{(e^x+1)(e^x-1)}$$

$$= \int_0^\infty dx\, x^m \frac{2}{e^{2x}-1} = \frac{1}{2^m} \int_0^\infty dx \frac{x^m}{e^x-1}$$

$$\Rightarrow \quad \left(1 - \frac{1}{2^m}\right) \int_0^\infty dx \frac{x^m}{e^x-1} = \int_0^\infty dx \frac{x^m}{e^x+1}$$

$n = 1$:

$$0 = \int_0^\infty dx \, \frac{x}{e^x - 1} + \int_0^\infty dx \, \frac{x}{e^x + 1} - \frac{\pi^2}{4}$$

$$0 = \int_0^\infty dx \, \frac{x}{e^x - 1} \left(1 + \frac{1}{2} \right) - \frac{\pi^2}{4} \qquad / \cdot \frac{2}{3}$$

$$\int_0^\infty dx \, \frac{x}{e^x - 1} = \frac{\pi^2}{6}$$

$n = 3$:

$$0 = \int_0^\infty dx \, \frac{x^3}{e^x - 1} + Re \sum_{j=0}^{3} \binom{n}{j} (i\pi)^j \int_0^\infty dx \, \frac{x^{n-j}}{e^x + 1} + \frac{\pi^4}{8}$$

$$= \int_0^\infty dx \, \frac{x^3}{e^x - 1} + \int_0^\infty dx \, \frac{x^3}{e^x + 1} + \binom{3}{2} (-\pi^2) \int_0^\infty dx \, \frac{x}{e^x + 1} + \frac{\pi^4}{8}$$

$$= \int_0^\infty dx \, \frac{x^3}{e^x - 1} \left(1 + 1 - \frac{1}{2^3} \right) - 3\pi^2 \frac{1}{2} \int_0^\infty dx \, \frac{x}{e^x - 1} + \frac{\pi^4}{8}$$

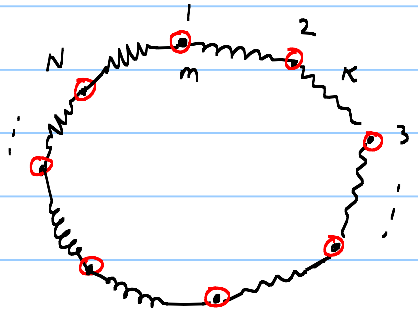
$$0 = \frac{15}{8} \int_0^\infty dx \, \frac{x^3}{e^x - 1} - \frac{3\pi^2}{2} \frac{\pi^2}{6} + \frac{\pi^4}{8}$$

$$\int_0^\infty dx \, \frac{x^3}{e^x - 1} = \frac{8}{15} \left(\frac{3\pi^4}{12} - \frac{\pi^4}{8} \right) = \frac{8\pi^4}{15} \left(\frac{1}{4} - \frac{1}{8} \right) = \frac{\pi^4}{15}$$

Quantum mechanics of lattice vibrations:

We will consider an idealized model of a 1D chain with particles connected by harmonic springs. Treatment of 3D is easily generalizable and connection to a real solid is treated in your book (Ch 7, sec 4). For your hwk you need to think about a 2D solid in Debye appx. which I will explain on 1D example.

So,



$$\Rightarrow \mathcal{H} = \frac{-\hbar^2}{2m}\sum_{j=1}^{N} \frac{d^2}{dx_j^2} + \frac{1}{2}K\sum_{j=1}^{N} (x_{j+1}-x_j)^2$$

and $x_{N+1} = x_1$

How do we solve this q.m. problem?

Let

$$x_j = \frac{1}{\sqrt{N}}\sum_{k=1}^{N} e^{i\frac{2\pi}{N}kj}\, x(k) \qquad (1)$$

then

$$\frac{d}{dx_j} = \sum_{k=1}^{N} \frac{dx(k)}{dx_j}\frac{d}{dx(k)}$$

⇒ we need to know $x(k)$ as a function of x_j.

⇒ invert (1)

$$x_j = \frac{1}{\sqrt{N}}\sum_{k=1}^{N} e^{i\frac{2\pi}{N}kj}\, x(k) \qquad \Big/ \cdot\, e^{-i\frac{2\pi}{N}pj}$$

$$\sum_{j=1}^{N} e^{-i\frac{2\pi}{N}pj}\, x_j = \frac{1}{\sqrt{N}}\sum_{k=1}^{N}\left[\sum_{j=1}^{N} e^{i\frac{2\pi}{N}(k-p)j}\right] x(k)$$

Now, the series in question is geometric, so

$$s_N = \sum_{j=1}^{N} \alpha^j \quad ; \quad s_N - \alpha s_N = \alpha - \alpha^{N+1} \Rightarrow s_N = \frac{\alpha(1-\alpha^N)}{1-\alpha}$$

but for us, $\alpha = e^{i\frac{2\pi}{N}(k-p)}$ so $\alpha^N = e^{i2\pi(k-p)}$
and since $k-p$ is an integer $\alpha^N = 1$.

⇒ the numerator in s_N vanishes. Therefore if the denominator is finite, then $s_N = 0$.
This happens when $\alpha \neq 1$ or $k \neq p$, $(k \neq p \pm N, \ldots)$
When $k = p$, we need to go back to the sum: $\sum_{j=1}^{N} 1 = N$

$$\Rightarrow \quad \sum_{j=1}^{N} e^{i\frac{2\pi}{N}(k-p)j} = N\,\delta_{k,p} \longleftarrow$$

Kronecker delta function

$$\sum_{j=1}^{N} e^{-i\frac{2\pi}{N}pj}\, x_j = \frac{1}{\sqrt{N}} \sum_{k=1}^{N} \left[\underbrace{\sum_{j=1}^{N} e^{i\frac{2\pi}{N}(k-p)j}}_{N\,\delta_{k,p}} \right] x(k) = \sqrt{N}\; x(p)$$

$$\Rightarrow \quad x(k) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} e^{-i\frac{2\pi}{N}kj}\, x_j$$

$$\frac{d}{dx_j} = \sum_{k=1}^{N} \frac{dx(k)}{dx_j} \frac{d}{dx(k)} = \sum_{k=1}^{N} \frac{1}{\sqrt{N}} \sum_{j'=1}^{N} e^{-i\frac{2\pi}{N}kj'} \overbrace{\frac{dx_{j'}}{dx_j}}^{\delta_{jj'}} \frac{d}{dx(k)}$$

$$= \frac{1}{\sqrt{N}} \sum_{k=1}^{N} e^{-i\frac{2\pi}{N}kj} \frac{d}{dx(k)}$$

$$\sum_{j=1}^{N} \frac{d}{dx_j}\frac{d}{dx_j} = \frac{1}{N}\sum_{k=1}^{N}\sum_{k'=1}^{N}\sum_{j=1}^{N} e^{-i\frac{2\pi}{N}kj}\, e^{-i\frac{2\pi}{N}k'j}\frac{d}{dx(k)}\frac{d}{dx(k')}$$

$k+k' = 0, N, 2N, \ldots$ but $k=1,\ldots,N$ and $k'=1,\ldots,N$

$\Rightarrow$ unless $k=N$, $k'=N-k$. When $k=N$, $k'=N$.

$$\Rightarrow \sum_{j=1}^{N} \frac{d}{dx_j}\frac{d}{dx_j} = \left(\sum_{k=1}^{N-1}\frac{d}{dx(k)}\frac{d}{dx(N-k)}\right) + \frac{d}{dx(N)}\frac{d}{dx(N)}$$

$$\frac{1}{2}K\sum_{j=1}^{N}(x_{j+1}-x_j)^2 =$$

$$\frac{1}{2}K\sum_{j=1}^{N}\frac{1}{N}\sum_{k=1}^{N}\sum_{k'=1}^{N}\left(e^{i\frac{2\pi}{N}k(j+1)} - e^{i\frac{2\pi}{N}kj}\right)x(k)\left(e^{i\frac{2\pi}{N}k'(j+1)} - e^{i\frac{2\pi}{N}k'j}\right)x(k')$$

$$= \frac{K}{2}\sum_{k=1}^{N}\sum_{k'=1}^{N}\left(\frac{1}{N}\sum_{j=1}^{N}e^{i\frac{2\pi}{N}(k+k')j}\right)\left(e^{i\frac{2\pi}{N}k}-1\right)\left(e^{i\frac{2\pi}{N}k'}-1\right)x(k)\,x(k')$$

$k'=N-k$ if $k\neq N$, if $k=N$ then $k'=N$

$$= \frac{K}{2}\sum_{k=1}^{N-1}\left(e^{i\frac{2\pi}{N}k}-1\right)\left(e^{-i\frac{2\pi}{N}k}-1\right)x(k)\,x(N-k) +$$

$$\frac{K}{2}\left(e^{i\frac{2\pi}{N}N}-1\right)\left(e^{-i\frac{2\pi}{N}N}-1\right)x(N)\,x(N) = \frac{K}{2}\sum_{k=1}^{N-1}4\sin^2\left(\frac{\pi}{N}k\right)x(k)\,x(N-k)$$

So, we have

$$\mathcal{H} = \frac{-\hbar^2}{2m}\left(\sum_{k=1}^{N-1}\frac{d}{dx(k)}\frac{d}{dx(N-k)}\right) - \frac{\hbar^2}{2m}\frac{d}{dx(N)}\frac{d}{dx(N)} + \frac{K}{2}\sum_{k=1}^{N-1}4\sin^2\left(\frac{\pi}{N}k\right)x(k)\,x(N-k)$$

This decouples the problem.

Obviously, $k = N$ is solved by plane waves, but that is just

$$x(N) = \frac{1}{\sqrt{N}} \sum_{j=1}^{N} x_j \quad \Rightarrow \text{prop. to CM coordinate} \quad \text{(Not excited)}$$

For $k \neq N$,

$$\mathcal{H} = \frac{-\hbar^2}{2m} \sum_{k=1}^{N-1} \frac{d}{dx(k)} \frac{d}{dx(N-k)} + \frac{1}{2} m \sum_{k=1}^{N-1} \omega_k^2 \, x(k) x(N-k)$$

where $\omega_k = 2\sqrt{\frac{K}{m}} \left| \sin\left(\frac{\pi}{N} k\right) \right|$ and we introduce

$$\sqrt{\frac{\hbar}{2m} \frac{1}{\omega_k}} \frac{\partial}{\partial x(N-k)} + \sqrt{\frac{m\omega_k}{2\hbar}} \, x(k) = a_k$$

$$-\sqrt{\frac{\hbar}{2m\,\omega_k}} \frac{\partial}{\partial x(k)} + \sqrt{\frac{m\omega_k}{2\hbar}} \, x(N-k) = a_k^{+}$$

$$[a_k, a_p^{+}] = \delta_{k,p}$$

$$a_k^{+} a_k = \frac{-1}{\omega_k} \frac{\hbar}{2m} \frac{\partial}{\partial x(N-k)} \frac{\partial}{\partial x(k)} + \frac{m\omega_k}{2\hbar} x(N-k) x(k) - \frac{1}{2}$$

$$\Rightarrow \quad \mathcal{H} = \sum_{k=1}^{N-1} \omega_k \left(a_k^{+} a_k + \frac{1}{2} \right) + \overset{\swarrow \text{ ignore}}{H_{CM}}$$

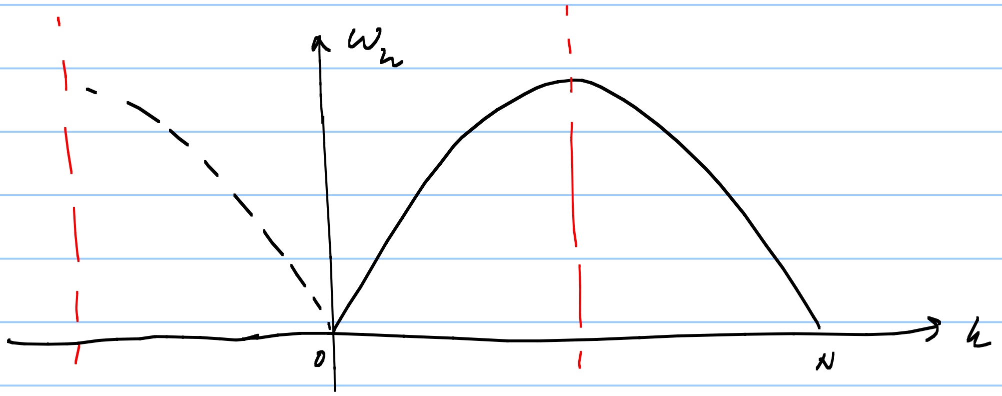
$$E = \sum_{k=1}^{N-1} \omega_k \left(n_k + \frac{1}{2} \right)$$

$$Z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum_{n_{N-1}=0}^{\infty} e^{-\beta \left[\omega_1 \left(n_1 + \frac{1}{2} \right) + \omega_2 \left(n_2 + \frac{1}{2} \right) + \dots + \omega_{N-1} \left(n_{N-1} + \frac{1}{2} \right) \right]}$$

$$= \text{const} \cdot \sum_{n_1=0}^{\infty} \cdots \sum_{n_{N-1}=0}^{\infty} e^{-\beta \omega_1 n_1} \cdots e^{-\beta \omega_{N-1} n_{N-1}}$$

⇒ ignoring the overall constant we get

$$Z = \prod_{k=1}^{N-1} \frac{1}{1 - e^{-\beta \omega_k}}$$



These modes are called phonons. Note that at low k, the energy of the mode is linear in k ⇒

$\omega_k = cp$ where $p = \pi \frac{k}{N}$ and c is speed of sound

$$U = \sum_{k=1}^{N-1} \frac{\omega_k}{e^{\beta \omega_k} - 1} = \sum_{k=1}^{N-1} \frac{2 \sqrt{\frac{K}{m}} \left| \sin\left(\frac{\pi}{N} k \right) \right|}{e^{\beta \, 2 \sqrt{\frac{K}{m}} \left| \sin\left(\frac{\pi}{N} k \right) \right|} - 1}$$

Let $\frac{2\pi}{N}k = p$, then $\Delta p = \frac{2\pi}{N}$ $\Rightarrow$

$$U = \frac{1}{\Delta p}\sum_{k=1}^{N-1} \Delta p \frac{2\sqrt{\frac{k}{m}}\left|\sin\frac{p}{2}\right|}{e^{\beta 2\sqrt{\frac{k}{m}}\left|\sin\frac{p}{2}\right|}-1} = N\int_{0\to-\pi}^{2\pi\to\pi}\frac{dp}{2\pi}\frac{2\sqrt{\frac{k}{m}}\left|\sin\frac{p}{2}\right|}{e^{\beta 2\sqrt{\frac{k}{m}}\left|\sin\frac{p}{2}\right|}-1}$$

because periodic integrant

in the limit of $T\to 0$, we can expand $\sin\frac{p}{2}\simeq\frac{p}{2}$

in the limit of $T\to\infty$, we have $\frac{U}{N} = k_B T$

Debye approximation: take just the linear dispersion and cut off the integral by k_D. k_D is chosen in such a way that the total no. of modes is fixed to the correct value from the exact expression, N in this case.
Similarly ω_{k_D} is ω_D the Debye freq.
and
$\Theta_D = \frac{\hbar\omega_D}{k_B}$ is the Debye temp.

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digression on peculiarity of Bose (Einstein) statistics for ideal gas:

if we have two particles and two states ϵ_1 & ϵ_2 for each
(think two coins, head or tail)
Then classically we would say that
1st particle in ϵ_1 and 2nd in ϵ_2
is a distinct state from 2nd in ϵ_1 and 1st in ϵ_2.
we would count twice a state in which ϵ_1 singly occ. & ϵ_2 singly occ.

Q.m. we do not consider this to be a distinct state. We count it only once:

i.e. in $\sum_{n_0=1}^{\infty} \sum_{n_1=1}^{\infty} \cdots \sum_{n_j=1}^{\infty} \cdots e^{-n_0\beta\epsilon_0} e^{-n_1\beta\epsilon_1} \cdots e^{-n_j\beta\epsilon_j} \cdots$

we only care about how many times the ϵ_1 &' ϵ_2 are occupied, not allowing for any additional specification

$\Rightarrow$ $n_1 = 1$ &' $n_2 = 1$ is counted just once.

$\Rightarrow$ when drawn at random from a box with two bosons each in either one of two states. $\frac{1}{3}$ of the time we would find "head" and "tail" result, not $\frac{1}{2}$ of the time.

Fixed particle number: (ideal Bose gas)

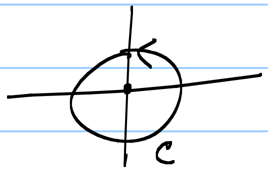
$$Z = \sum_{n_0=0}^{\infty} \sum_{n_1=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \left(e^{-\beta\epsilon_0}\right)^{n_0} \left(e^{-\beta\epsilon_1}\right)^{n_1} \cdots \left(e^{-\beta\epsilon_j}\right)^{n_j} \cdots \delta_{n,\, n_0+n_1+\cdots+n_j+\cdots}$$

Kronecker δ-function

How should we implement this constraint?

Use Cauchy's theorem:

$$\delta_{n,m} = \oint_c \frac{d\xi}{2\pi i} \frac{1}{\xi^{n+1}} \xi^m$$



clearly, for $n = m$ we get 1. For $m > n$, the integrant is analytic ⇒ int. trivially vanishes

For $n > m$, $\oint_C \frac{d\xi}{2\pi i} \frac{1}{\xi^{1+n-m}}$, but $F(a) = \oint_C \frac{d\xi}{2\pi i(\xi - a)} = 1$

and $\frac{\partial F}{\partial a} = \oint_C \frac{d\xi}{2\pi i (\xi - a)^2} = \frac{\partial 1}{\partial a} = 0$

this works for any integer power larger than 1.

$$\Rightarrow \quad \delta_{n, \sum_{j=0} n_j} = \oint_C \frac{d\xi}{2\pi i} \frac{1}{\xi^{n+1}} \left(\xi^{n_0} \xi^{n_1} \cdots \xi^{n_j} \cdots \right)$$

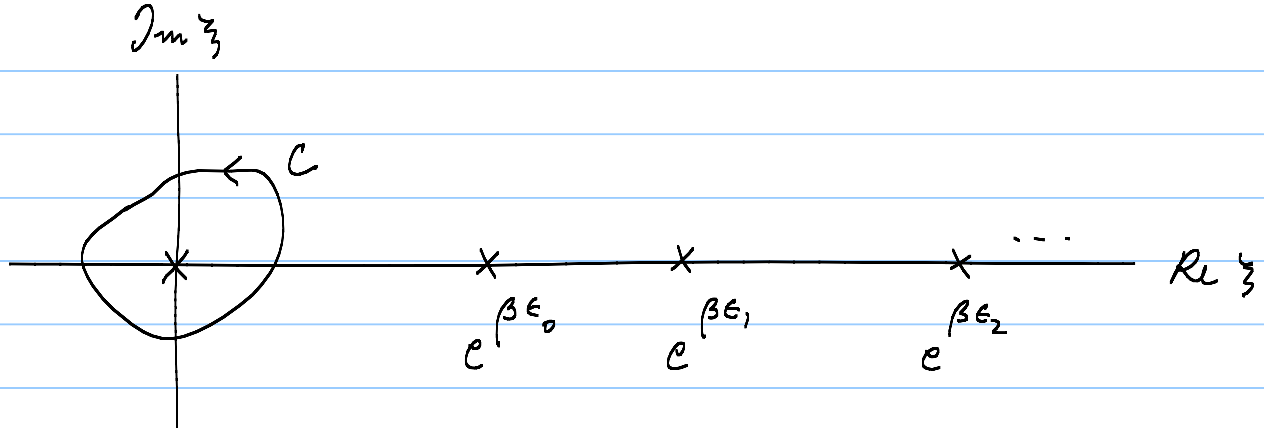
⇒ interchanging the order of summation & contour integr. we find:

$$Z = \oint_C \frac{d\xi}{2\pi i} \frac{1}{\xi^{n+1}} \sum_{n_0=0}^{\infty} \cdots \sum_{n_j=0}^{\infty} \cdots \left(\xi e^{-\beta\epsilon_0} \right)^{n_0} \cdots \left(\xi e^{-\beta\epsilon_j} \right)^{n_j} \cdots$$

$$Z = \oint_C \frac{d\xi}{2\pi i} \frac{1}{\xi^{n+1}} \prod_{j=0}^{\infty} \frac{1}{1 - \xi e^{-\beta\epsilon_j}}$$

we are interested in evaluating this integral in the thermodynamic limit $n \to \infty$.

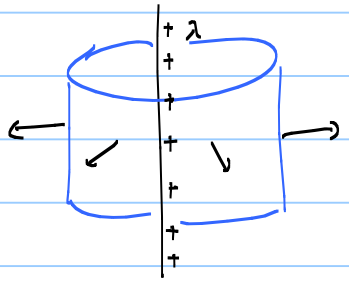
What is the analytic structure of the integrant?



$$Z = \oint_C \frac{dz}{2\pi i}\, e^{-(n+1)\ln z}\, e^{-\sum_{j=0}^{\infty} \ln(1 - z e^{-\beta\epsilon_j})} = \oint \frac{dz}{2\pi i}\, e^{\Phi(z)}$$

The real part of $\Phi(z)$ can be thought of as a fictitious electrostatic potential associated with a lines of charge perpendic to the x-y plane, going through $x=0$ and $x = e^{\beta\epsilon_j}$ for $j = 0, 1, 2, \ldots$

Indeed :



$$\oiint \vec{E}\cdot d\vec{A} = \frac{Q_{enc}}{\varepsilon_0} \; ; \; E_r\, 2\pi r L = \frac{Q_{enc}}{\varepsilon_0}$$

$$\Rightarrow E_r = \frac{\lambda}{2\pi\varepsilon_0}\frac{1}{r}$$

$$-\vec{\nabla} V = \vec{E} \Rightarrow -\left(\hat{r}\frac{\partial}{\partial r} + \frac{\hat{\phi}}{r}\frac{\partial}{\partial \phi} + \hat{z}\frac{\partial}{\partial z}\right) V = \vec{E} = \frac{\lambda}{2\pi\varepsilon_0}\frac{\hat{r}}{r}$$

$$\Rightarrow -\frac{dV}{dr} = \frac{\lambda}{2\pi\varepsilon_0}\frac{1}{r} \Rightarrow V = -\frac{\lambda}{2\pi\varepsilon_0}\ln r + \underbrace{\text{const.}}_{\text{can ignore}}$$

Now, $\ln z = \ln\left(|z| e^{i\phi}\right) = \ln|z| + i\phi \Rightarrow \mathrm{Re}\,\ln z = \ln|z|$

So, $\mathrm{Re}\,\Phi(z)$ is proportional to electrical potential due to the mentioned distribution of charges.

In the integral $\oint_c \frac{dz}{2\pi i} e^{\Phi(z)}$; $\Phi(z) \propto n$

$\Rightarrow$ the imaginary part gives rise to very rapid oscillations which suppress the value of the integral. The contribution to the integral (when $n \to \infty$) comes from regions with constant phase; there the cancelations are avoided.

Is there a physical picture that would help us think about $\Im m\, \Phi(z)$? Yes! Cauchy-Riemann conditions.

Start by noticing that $\frac{\partial \Phi(z)}{\partial z^*} = \frac{\partial \Phi}{\partial x}\frac{\partial x}{\partial z^*} + \frac{\partial \Phi}{\partial y}\frac{\partial y}{\partial z^*} =$

$$= \frac{\partial \Phi}{\partial x}\frac{\partial}{\partial z^*}\left(\frac{z+z^*}{2}\right) + \frac{\partial \Phi}{\partial y}\frac{\partial}{\partial z^*}\left(\frac{z-z^*}{2i}\right) = \frac{1}{2}\left(\frac{\partial \Phi}{\partial x} + i\frac{\partial \Phi}{\partial y}\right)$$

but $\Phi = \Phi(x+iy) \Rightarrow \frac{\partial \Phi}{\partial x} = \Phi'$ and $\frac{\partial \Phi}{\partial y} = i\Phi'$

$$\Rightarrow \frac{\partial \Phi}{\partial z^*} = \frac{1}{2}\left(\Phi' + i \cdot i\,\Phi'\right) = 0$$

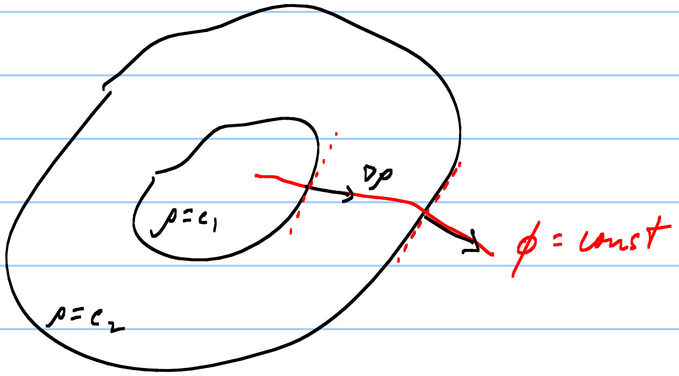
Now, let $\Phi(z) = \underbrace{\rho(x,y)}_{Re\,\Phi} + i\underbrace{\phi(x,y)}_{\Im m\,\Phi}$ where ρ & ϕ are real

$$\Rightarrow \frac{\partial \Phi}{\partial z^*} = \frac{1}{2}\left(\frac{\partial \rho}{\partial x} + i\frac{\partial \phi}{\partial x} + i\left(\frac{\partial \rho}{\partial y} + i\frac{\partial \phi}{\partial y}\right)\right) = 0$$

$\Rightarrow \boxed{\frac{\partial \rho}{\partial x} = \frac{\partial \phi}{\partial y}}$ and $\boxed{\frac{\partial \phi}{\partial x} = -\frac{\partial \rho}{\partial y}}$ Cauchy-Riem. conditions

$$\frac{\partial \rho}{\partial x}\frac{\partial \phi}{\partial x} + \frac{\partial \rho}{\partial y}\frac{\partial \phi}{\partial y} = 0 \Rightarrow \left(\frac{\partial \rho}{\partial x}, \frac{\partial \rho}{\partial y}\right)\cdot\left(\frac{\partial \phi}{\partial x}, \frac{\partial \phi}{\partial y}\right) = 0$$

$\Rightarrow \boxed{\nabla\rho \cdot \nabla\phi = 0}$ $\Rightarrow$ contours of constant ϕ are perpendicular to contours of constant ρ



If Re Φ is like electrical potential associated w/ the given charge distribution, then Im Φ is like the electrical field.

Also note that $\frac{\partial}{\partial x}\left(\frac{\partial \rho}{\partial x} - \frac{\partial \phi}{\partial y}\right) = 0$ AND $\frac{\partial}{\partial y}\left(\frac{\partial \phi}{\partial x} + \frac{\partial \rho}{\partial y}\right) = 0$

$\Rightarrow$ adding the two equations gives $\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} = 0.$

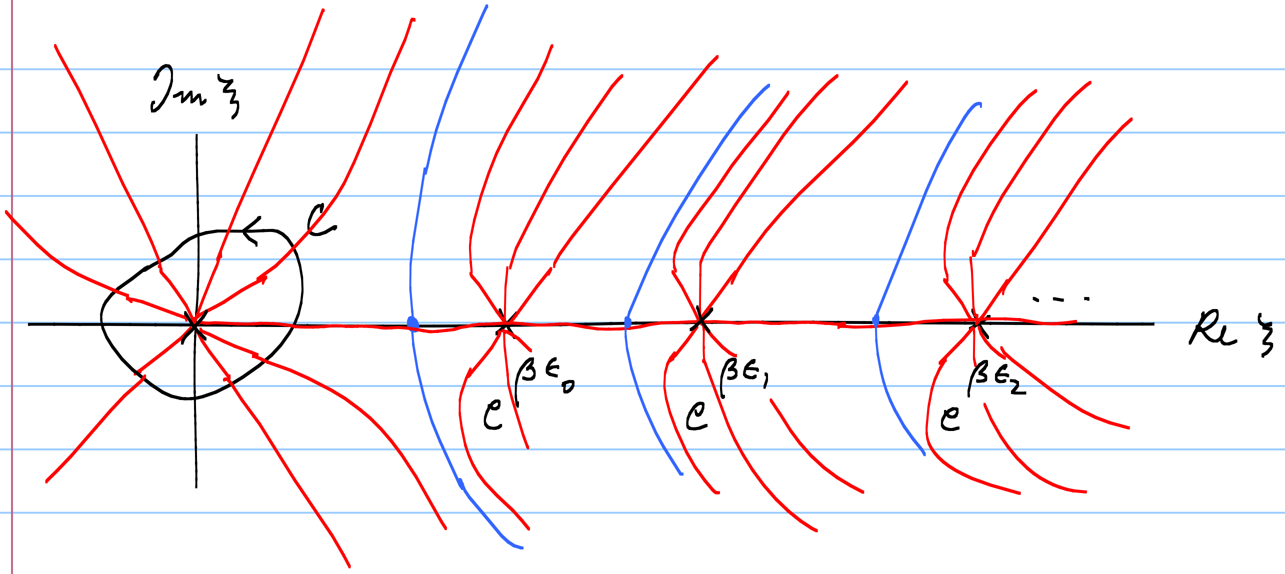
Also, $\frac{\partial}{\partial y}\left(\frac{\partial \rho}{\partial x} - \frac{\partial \phi}{\partial y}\right) = 0$ AND $\frac{\partial}{\partial x}\left(\frac{\partial \phi}{\partial x} + \frac{\partial \rho}{\partial \sigma}\right) = 0$

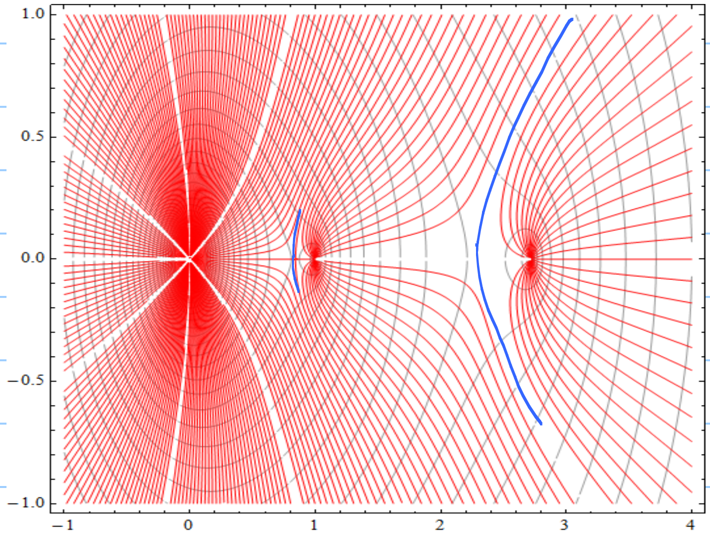
$$\Rightarrow \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0$$

So, if ρ has a minimum along, say, x-axis at say x_0, then clearly $\left.\frac{\partial^2 \rho}{\partial x^2}\right|_{x_0} > 0$ (b.c. its a minimum)

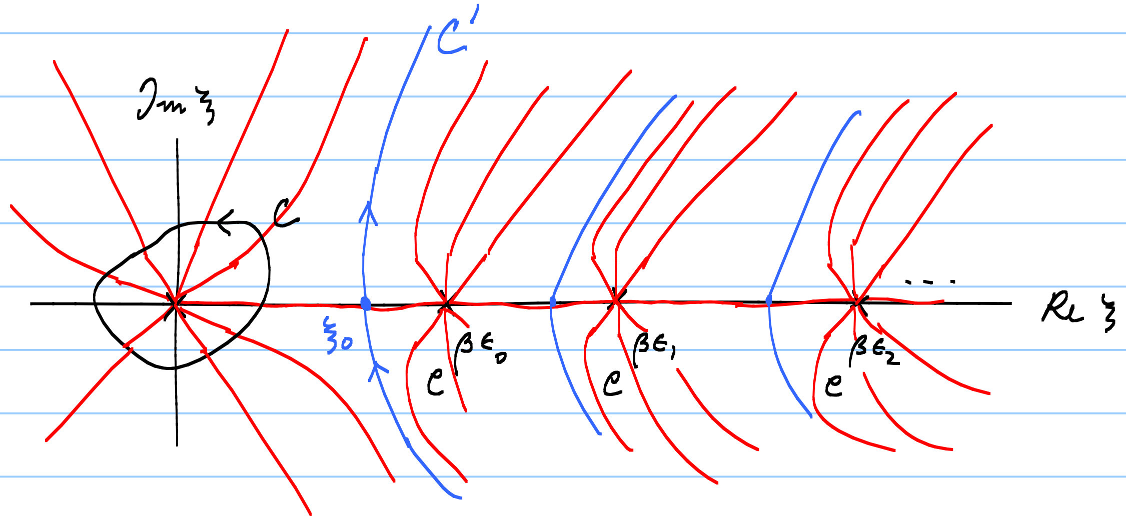
and $\left.\frac{\partial^2 \rho}{\partial y^2}\right|_{x_0} < 0$ otherwise we could not satisfy $\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} = 0.$

* same goes for ϕ.





So, deform the contour C to go to infinity and come back through the 1st blue line



What is the value of the $\Im \Phi(z)$ along the blue line?

At ξ_0, $\frac{\partial \rho}{\partial x} = 0 \Rightarrow$ by C.-R. $\frac{\partial \rho}{\partial x} = \frac{\partial \phi}{\partial y} = 0$

$\Rightarrow$ as we move vertically up from ξ_0, the phase does not change. But along the real axis, between 0 and $e^{\beta \epsilon_0}$ the phase is zero $\Rightarrow$ the $\Im \Phi(z)$ along the 1st blue line is zero.

As we move from 0 to $e^{\beta \epsilon_0}$ along the real axis, the integrand is dominated by $\frac{1}{x^{n+1}}$ $\Rightarrow$ it starts large and positive and decreases. But near $x = e^{\beta \epsilon_0}$, the term $\frac{1}{1 - x e^{-\beta \epsilon_0}}$ dominates and becomes large and positive

$\Rightarrow$ ρ has a minimum at $\xi = \xi_0 = x_0$.

Therefore $\left.\frac{\partial^2 \rho}{\partial x^2}\right|_{\xi_0} > 0$ and $\left.\frac{\partial^2 \rho}{\partial y^2}\right|_{\xi_0} < 0$ $\Rightarrow$ the integrand decreases as we move away from the real axis (think of equipotential lines, i.e. $\Re \Phi(z)$)

Now, let's find out what is the value of ξ_0, the value of the integrant @ ξ_0 and how fast it decreases along the blue line.

$$\frac{\partial \Phi}{\partial z} = 0 \Rightarrow \frac{\partial}{\partial z}\left[-(n+1)\ln z - \sum_{j=0}^{\infty} \ln\left(1 - z e^{-\beta \epsilon_j}\right)\right]_{\xi_0} = 0$$

$$\frac{-(n+1)}{\xi_0} + \sum_{j=0}^{\infty} \frac{e^{-\beta\epsilon_j}}{1-\xi_0 e^{-\beta\epsilon_j}} = 0$$

$$n+1 = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{\xi_0}e^{\beta\epsilon_j}-1} \longrightarrow \boxed{n = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{\xi_0}e^{\beta\epsilon_j}-1}}$$

$$\Phi(\xi_0) = -(n+1)\ln\xi_0 - \sum_{j=0} \ln\left(1-\xi_0 e^{-\beta\epsilon_j}\right)$$

And

$$\left.\frac{\partial^2\Phi}{\partial x^2}\right|_{\xi_0} = \left.\frac{\partial^2\rho}{\partial x^2}\right|_{\xi_0} = \frac{n+1}{\xi_0^2} + \sum_{j=0}^{\infty} \frac{1}{\left(e^{\beta\epsilon_j}-\xi_0\right)^2} > 0$$

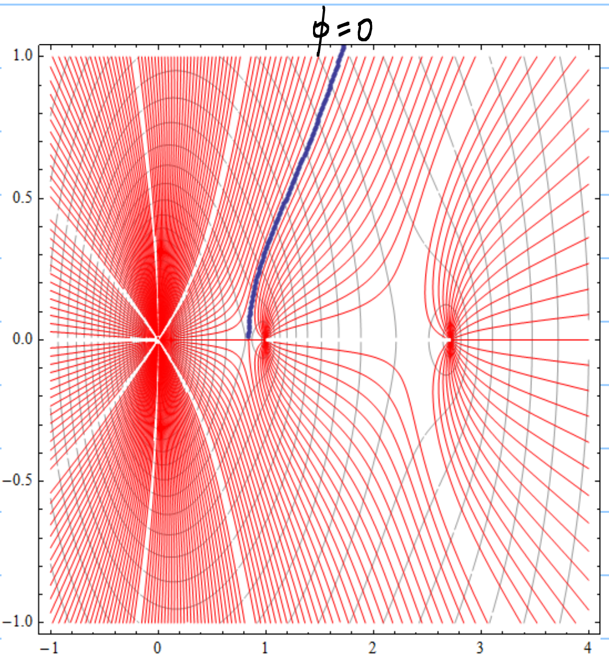
But, C.-R. gives $\frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} = 0 \Rightarrow \frac{\partial^2\rho}{\partial y^2} < 0$

Also note that $\left.\frac{\partial^2\rho}{\partial x^2}\right|_{\xi_0} \propto n$ which is very large

$\Rightarrow$ the minimum is very deep along the real axis, and by C.-R. the maximum is very steep along the blue line.

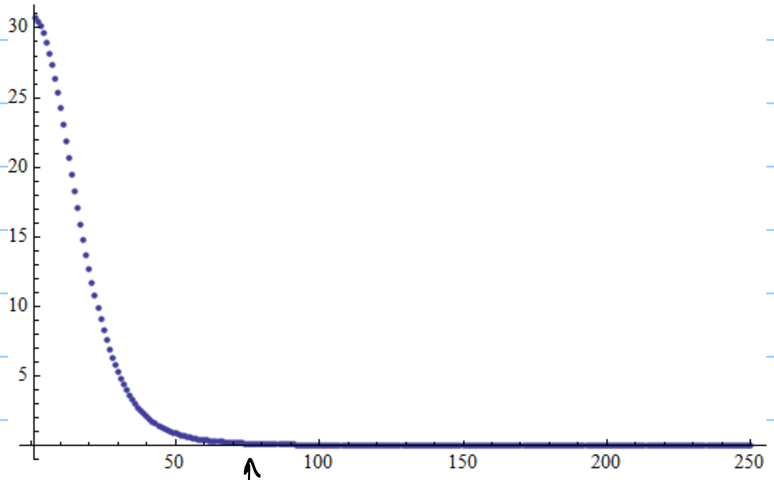
Therefore, only the immediate vicinity of the ξ_0 contributes significantly to the integral.

$n = 5, \quad \beta\epsilon_0 = 0, \quad \beta\epsilon_1 = 1, \quad \beta\epsilon_2 = 2, \quad \beta\epsilon_3 = 3, \quad \beta\epsilon_4 = 4$



$e^{\Phi(z)}$

along the $\phi = 0$ contour



discrete index along the contour

$$Z = \int_{c'} \frac{dz}{2\pi i} e^{\Phi(z)} = \int_{c'} \frac{dz}{2\pi i} e^{\rho(x,y) + i\phi(x,y)}$$

$$= \int_{c'} \frac{dz}{2\pi i} e^{\rho(x,y)} \simeq \int_{-\delta}^{\delta} \frac{d(iy)}{2\pi i} e^{\rho(x_0,0)} e^{\frac{1}{2}\frac{\partial^2 \rho}{\partial y^2}\Big|_{x_0,y=0} y^2}$$

$$= e^{\rho(x_0,0)} \int_{-\delta}^{\delta} \frac{dy}{2\pi} e^{\frac{y^2}{2}\left(\frac{\partial^2 \rho}{\partial y^2}\Big|_{x_0,y=0}\right)}$$

But $\frac{\partial^2 \rho}{\partial y^2}\Big|_{x_0,y=0}$ is very large $(\mathcal{O}(n))$ and negative

$\Rightarrow$ we have a very steep Gaussian $\Rightarrow$ we can send $\delta \to \infty$.

$$Z = e^{\rho(x_0,0)} \frac{1}{\sqrt{2\pi}\sqrt{\frac{\partial^2 \rho}{\partial y^2}\Big|_{\xi_0}}}$$

$$\rho(x_0,0) = \Phi(\xi_0) = -(n+1)\ln \xi_0 - \sum_{j=0}^{\infty} \ln(1-\xi_0 e^{-\beta\epsilon_j})$$

$$\ln Z = \underbrace{-(n+1)\ln\xi_0}_{\mathcal{O}(n)} - \underbrace{\sum_{j=0}^{\infty}\ln\left(1-\xi_0 e^{-\beta\epsilon_j}\right)}_{\mathcal{O}(n)} - \underbrace{\ln\sqrt{2\pi\rho_{yy}}}_{\mathcal{O}(\ln n)}$$

↳ neglect

if we define $\overset{\text{chemical potential}}{\mu}$ as $\xi_0 = e^{\beta\mu} = e^{\mu/k_BT}$, then

$$\boxed{\begin{aligned} \ln Z &= -\frac{n}{k_BT}\mu - \sum_{j=0}^{\infty} \ln\left(1 - e^{-(\epsilon_j-\mu)/k_BT}\right) \\ \text{where} \quad n &= \sum_{j=0}^{\infty} \frac{1}{e^{(\epsilon_j-\mu)/k_BT} - 1} \end{aligned}}$$

Let's compute the internal energy of such ideal Bose gas.

$$U = -\frac{\partial \ln Z}{\partial\beta} = n\frac{\partial}{\partial\beta}(\beta\mu) + \sum_{j=0}^{\infty} \frac{1}{1 - e^{-\beta\epsilon_j}e^{\beta\mu}} \frac{\partial}{\partial\beta}\left(-e^{-\beta\epsilon_j}e^{\beta\mu}\right)$$

$$= n\frac{\partial}{\partial\beta}(\beta\mu) + \sum_{j=0}^{\infty} \frac{e^{-\beta(\epsilon_j-\mu)}}{1 - e^{-\beta(\epsilon_j-\mu)}} \frac{\partial}{\partial\beta}\left(\beta\epsilon_j - \beta\mu\right)$$

$$= n\frac{\partial}{\partial\beta}(\beta\mu) + \sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j-\mu)} - 1} \left(\epsilon_j - \frac{\partial}{\partial\beta}(\beta\mu)\right)$$

$$= n\frac{\partial}{\partial\beta}(\beta\mu) + \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta(\epsilon_j-\mu)} - 1} - n\frac{\partial}{\partial\beta}(\beta\mu)$$

$$\Rightarrow \quad \boxed{U = \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta(\epsilon_j-\mu)} - 1}}$$

Under what conditions can we replace the discrete sum over the (single particle) energy states with the integral the way we did for photons?

Let's study particles in a box : $\epsilon_j = \frac{\hbar^2}{2m} \vec{k}_j^{\,2}$

$$k_x = \frac{2\pi}{L_x} n_x \; ; \quad n_x = 0, \pm 1, \pm 2, \ldots$$

$$\Rightarrow \Delta k_x = \frac{2\pi}{L_x} \Rightarrow \Delta k_x \, \Delta k_y \, \Delta k_z = \frac{(2\pi)^3}{V}$$ which is small when V is large

total particle number

p. fraction occupying ϵ_j

$$n = \sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$$

$$= V \frac{1}{(2\pi)^3} \sum_{n_x} \sum_{n_y} \sum_{n_z} \Delta k_x \, \Delta k_y \, \Delta k_z \, \frac{1}{e^{\beta\left(\frac{\hbar^2 \vec{k}^2}{2m} - \mu\right)} - 1}$$

if the fxn. to be summed is small compared to V, then we can safely replace the sum by an integral because the contribution from each n_x, n_y, n_z is small as $V \to \infty$.

However, if $\mu = -\frac{1}{\beta}\frac{\lambda}{V}$ where λ is some no. of $O(1)$

then for $\vec{k} = 0$, $$\frac{1}{e^{\cancel{\beta} \frac{1}{\cancel{\beta}} \frac{\lambda}{V}} - 1} \simeq \frac{1}{1 + \frac{\lambda}{V} - 1} = \frac{V}{\lambda}$$ ⇒ macroscopic occupation of the single part. ground st.

which is as large as $\frac{1}{\Delta k_x \Delta k_y \Delta k_z}$ ⇒ when μ is so close to zero, the contribution from $\vec{k} = 0$ is <u>not</u> infinitesimal

We will keep this in mind. For now, let's assume that μ is not this close to zero.

Then,

$$\frac{n}{V} = \int \frac{d^3k}{(2\pi)^2} \frac{1}{e^{\beta\left(\frac{\hbar^2k^2}{2m} - \mu\right)} - 1} = \frac{4\pi}{8\pi^3} \int_0^\infty dk\, k^2 \frac{1}{e^{\beta\frac{\hbar^2k^2}{2m}} e^{-\beta\mu} - 1}$$

Let $\beta \frac{\hbar^2k^2}{2m} = x^2 \Rightarrow \frac{\beta\hbar^2}{2m} k\, dk = x\, dx, \quad k = \sqrt{\frac{2m}{\beta\hbar^2}}\, x$

$$\frac{n}{V} = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2\beta}\right)^{\frac{3}{2}} \int_0^\infty dx \frac{x^2}{e^{x^2 - \beta\mu} - 1}$$

$$\frac{n}{V} = \frac{1}{2\pi^2} \left(2k_BTm\right)^{3/2} \frac{1}{\hbar^3} F_2\left(\frac{\mu}{k_BT}\right)$$

we see that because $\mu \leq 0$, F_2 is monot. increasing. It reaches its maximum at $\mu = 0$. What is its value there?

$$\int_0^\infty dx \frac{x^2}{e^{x^2} - 1} = \frac{\sqrt{\pi}}{4} \zeta\left(\tfrac{3}{2}\right) \simeq 1.15758$$

$\Rightarrow$ we arrive at a peculiar situation: For a fixed temperature, we can't seem to be able to increase the density past a maximal value. This is strange because $\sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}$ can be increased without any bound by adjusting $\mu \to \epsilon_0^-$

It must be, that as we increase the density for fixed T, (or decrease T with fixed density), μ gets so close to 0^- that the $\vec{k}=0$ state is macroscopically occupied. This is called Bose-Einstein condensation.

What about the next excited state?
its energy is $\frac{\hbar^2}{2m}\frac{1}{L^2} = \frac{\hbar^2}{2m} V^{-\frac{2}{3}}$

$\Rightarrow$ its occupation is
$$\frac{1}{1+\beta\frac{\hbar^2}{2m}V^{-\frac{2}{3}}-1} \simeq V^{\frac{2}{3}}$$

which is large, but $\Delta k_x \Delta k_y \Delta k_z \sim \frac{1}{V}$ $\Rightarrow$ still infinites. when $V\to\infty$.

So, for all the other levels, we can replace the sum with the integral and keep $\mu=0$.

So, we either adjust $\mu<0$ such that

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(2k_BTm\right)^{3/2}\frac{1}{\hbar^3}F_2\left(\frac{\mu}{k_BT}\right)$$

is satisfied or we have $\mu=0$ and

$$\swarrow \frac{\sqrt{\pi}}{4}\zeta\left(\frac{3}{2}\right)$$

$$\frac{n}{V} = \frac{n_0}{V} + \frac{1}{2\pi^2}\left(2k_BTm\right)^{3/2}\frac{1}{\hbar^3}F_2(0)$$

This is analogous to having saturated (quantum) vapor.

$$\frac{\cancel{2}\sqrt{2}}{\cancel{2}\cancel{\pi^2}} \frac{\overset{2}{\cancel{8}}\pi^{\cancel{3}}}{h^3} (k_B T m)^{3/2} \frac{\sqrt{\pi}}{\cancel{4}} \zeta(\tfrac{3}{2})$$

$$= (2\pi\, k_B T m)^{3/2} \frac{1}{h^3} \underbrace{\zeta(\tfrac{3}{2})}_{2.612}$$

$$U = \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta(\epsilon_j-\mu)}-1} = V\int \frac{d^3k}{(2\pi)^3} \frac{\frac{\hbar^2k^2}{2m}}{e^{\beta\frac{\hbar^2k^2}{2m}}e^{-\beta\mu}-1} =$$

$$= V\frac{4\pi}{8\pi^3}\int_0^\infty dk\,k^2\, \frac{\hbar^2k^2}{2m}\,\frac{1}{e^{\beta\frac{\hbar^2k^2}{2m}}e^{-\beta\mu}-1} \quad ; \quad x^2 = \beta\frac{\hbar^2k^2}{2m}$$

$$x\,dx = \frac{\beta\hbar^2}{2m}k\,dk$$

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

⇒ above the B.E. condensation $\mu<0$ and

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\int_0^\infty dx\, \frac{x^2}{e^{x^2-\beta\mu}-1}$$

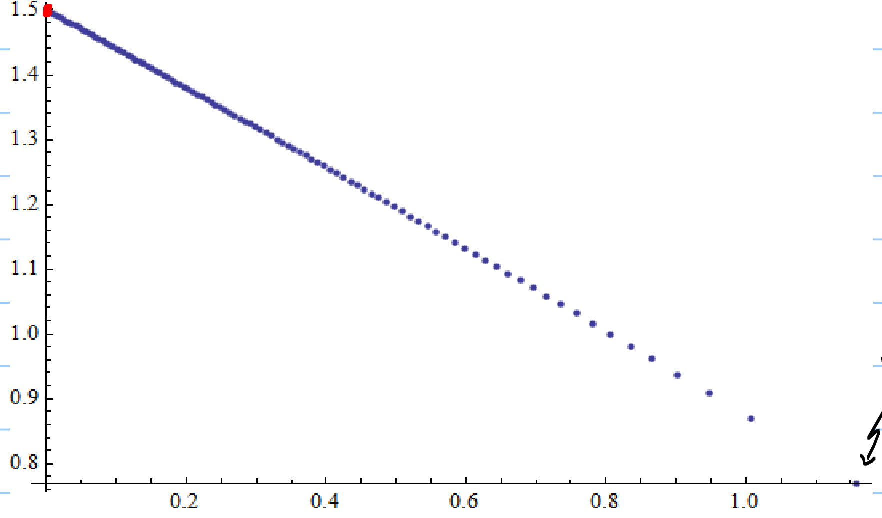
$$\frac{U}{n} = k_BT\, \frac{\int_0^\infty dx\, \frac{x^4}{e^{x^2}e^{-\beta\mu}-1}}{\int_0^\infty dx\, \frac{x^2}{e^{x^2}e^{-\beta\mu}-1}} = k_BT\,\frac{F_4\left(\frac{\mu}{k_BT}\right)}{F_2\left(\frac{\mu}{k_BT}\right)} = k_BT\,\Phi\left(\frac{2\pi^2 n}{V}\left[\frac{\hbar^2}{2m k_BT}\right]^{3/2}\right)$$

- for μ large and negative, expand to get $\dfrac{\int_0^\infty dx\, x^4 e^{-x^2}\cancel{e^{\beta\mu}}}{\int_0^\infty dx\, x^2 e^{-x^2}\cancel{e^{\beta\mu}}} = \dfrac{3}{2}$

$U = \frac{3}{2} n k_BT$: THIS IS IDEAL GAS !

ideal gas (small density, large Temp)

$$\frac{U}{n k_B T}$$



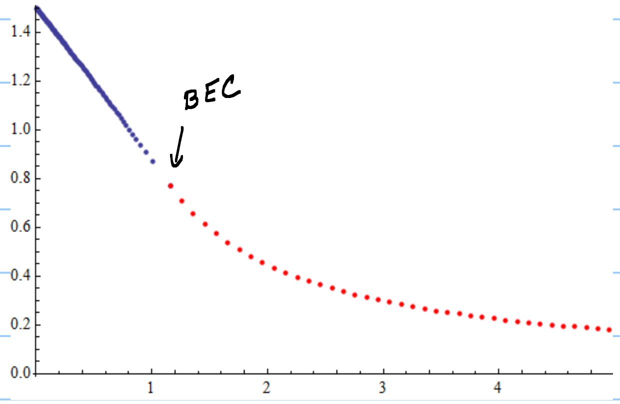
$$\frac{2\pi^2 n}{V}\left(\frac{\hbar^2}{2m}\frac{1}{k_B T}\right)^{3/2}$$

After BEC starts,

$$\frac{U}{n k_B T} = \frac{V}{n}\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\overbrace{\int_0^\infty dx\,\frac{x^4}{e^x-1}}^{\frac{3\sqrt{\pi}}{8}\zeta(\frac{5}{2})\ \simeq\ 0.892}$$

$$= \frac{V}{n}\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}k_B T\right)^{3/2}\frac{3\sqrt{\pi}}{8}\zeta(\tfrac{5}{2})$$

$$\frac{U}{n k_B T}$$



$$\frac{2\pi^2 n}{V}\left(\frac{\hbar^2}{2m}\frac{1}{k_B T}\right)^{3/2}$$

For $\xi < 1$ (before BEC) *recall $\xi = e^{\frac{\mu}{k_BT}}$

we have

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}k_BT\right)^{3/2}\int_0^\infty dx\,\frac{x^2}{\frac{1}{\xi}e^{x^2}-1}$$

Now,

$$\ln Z = -n\ln\xi - V\int\frac{d^3k}{(2\pi)^3}\ln\left(1-\xi e^{-\beta\frac{\hbar^2k^2}{2m}}\right)$$

$$Z = e^{-\beta F} \Rightarrow \ln Z = -\beta F \quad \text{and} \quad \frac{-\partial F}{\partial V} = P$$

$$\frac{\partial \ln Z}{\partial V} = -\frac{n}{\xi}\frac{\partial\xi}{\partial V} - \int\frac{d^3k}{(2\pi)^3}\ln\left(1-\xi e^{-\beta\frac{\hbar^2k^2}{2m}}\right)$$

$$-V\int\frac{d^3k}{(2\pi)^3}\frac{1}{1-\xi e^{-\beta\frac{\hbar^2k^2}{2m}}}\left(-\frac{\partial\xi}{\partial V}e^{-\beta\frac{\hbar^2k^2}{2m}}\right)$$

$$= -\frac{n}{\xi}\frac{\partial\xi}{\partial V} - \int\frac{d^3k}{(2\pi)^3}\ln\left(1-\xi e^{-\beta\frac{\hbar^2k^2}{2m}}\right)$$

$$+\frac{\partial\xi}{\partial V}\frac{1}{\xi}\boxed{V\int\frac{d^3k}{(2\pi)^3}\frac{1}{\frac{1}{\xi}e^{\beta\frac{\hbar^2k^2}{2m}}-1}} \leftarrow n$$

$$\boxed{PV = \frac{2}{3}U}$$

$$\frac{\partial\ln Z}{\partial V} = -\int\frac{d^3k}{(2\pi)^3}\ln\left(1-\xi e^{-\beta\frac{\hbar^2k^2}{2m}}\right) = \frac{-1}{2\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\int_0^\infty dx\,x^2\ln\left(1-\xi e^{-x^2}\right)$$

integrate by parts: $$\frac{\partial\ln Z}{\partial V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2}\frac{2}{3}\int_0^\infty dx\,\frac{x^4}{\frac{1}{\xi}e^{x^2}-1} = \frac{2}{3}\frac{U}{V}\frac{1}{k_BT} = \frac{P}{k_BT}$$

Fixed particle number: (ideal Fermi gas)

we will use the same method to perform the restricted sum

$$Z = \oint_c \frac{d\xi}{2\pi i} \frac{1}{\xi^{n+1}} \prod_{j=0}^{\infty} \left(1 + \xi e^{-\beta \epsilon_j}\right)$$

$$= \oint_c \frac{dz}{2\pi i} e^{\Phi(z)}$$

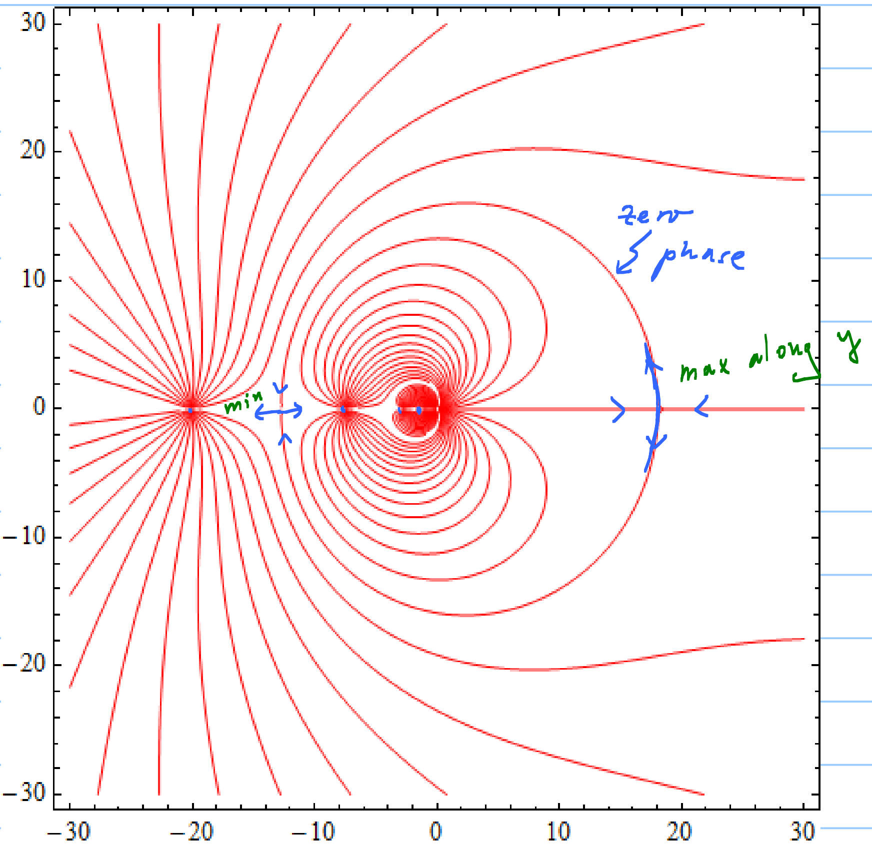
where $\Phi(z) = -(n+1)\ln z + \sum_{j=0}^{\infty} \ln\left(1 + z e^{-\beta\epsilon_j}\right)$

We can still think of this as a distribution of line charges, but the one at origin has an opposite charge from the ones at $z_j = -e^{\beta \epsilon_j}$.

For Fermi-Dirac

negative charges on negative axis

contour of zero phase after n+1 negative line charges



We now deform our contour c to coincide with the zero phase contour. The remaining real part has a maximum at the positive value of x.

$$\left.\frac{\partial \Phi}{\partial z}\right|_{z_0} = 0 = -\frac{n+1}{z_0} + \sum_{j=0}^{\infty} \frac{1}{1 + z_0 e^{-\beta \epsilon_j}} e^{-\beta \epsilon_j} \quad ; \quad z_0 = e^{\beta\mu}$$

$$n+1 = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{z_0} e^{\beta \epsilon_j} + 1} \quad \text{or} \quad n = \sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}$$

$$\boxed{\begin{aligned} \ln Z &= -\beta n \mu + \sum_{j=0}^{\infty} \ln\left(1 + e^{-\beta(\epsilon_j - \mu)}\right) \\ n &= \sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} \end{aligned}}$$

internal energy:

$$U = -\frac{\partial \ln Z}{\partial \beta} = -\left(-n\mu - \beta n \frac{\partial \mu}{\partial \beta} + \sum_{j=0}^{\infty} \frac{e^{-\beta(\epsilon_j - \mu)}}{1 + e^{-\beta(\epsilon_j - \mu)}} \left(-\epsilon_j + \mu + \beta \frac{\partial \mu}{\partial \beta}\right)\right)$$

$$= n\mu + \beta n \frac{\partial \mu}{\partial \beta} + \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta(\epsilon_j - \mu)} + 1} - \left(\mu + \beta \frac{\partial \mu}{\partial \beta}\right) \sum_{j=0}^{\infty} \underbrace{\frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}}_{n}$$

$$\boxed{U = \sum_{j=0}^{\infty} \frac{\epsilon_j}{e^{\beta(\epsilon_j - \mu)} + 1}}$$

Pressure: recall that $dF = -SdT - PdV$

therefore $-\frac{\partial F}{\partial V}\Big)_T = P$. Moreover, $Z = e^{-\beta F} \Rightarrow$

$$-\frac{1}{\beta}\ln Z = F$$

$$\Rightarrow P = k_B T \frac{\partial \ln Z}{\partial V}\Big)_T$$

$$= k_B T \frac{\partial}{\partial V}\left(-\beta n\mu + \sum_{j=0}^{\infty} \ln\left(1+e^{-\beta(\epsilon_j-\mu)}\right)\right)$$

$$= k_B T\left(-\frac{n}{k_B T}\frac{\partial \mu}{\partial V} + \sum_{j=0}^{\infty}\frac{e^{-\beta(\epsilon_j-\mu)}}{1+e^{-\beta(\epsilon_j-\mu)}}(-\beta)\left(\frac{\partial \epsilon_j}{\partial V} - \frac{\partial \mu}{\partial V}\right)\right)$$

$$= -n\frac{\partial \mu}{\partial V} - \sum_{j=0}^{\infty}\frac{\partial \epsilon_j}{\partial V}\frac{1}{e^{\beta(\epsilon_j-\mu)}+1} + \frac{\partial \mu}{\partial V}\underbrace{\sum_{j=0}^{\infty}\frac{1}{e^{\beta(\epsilon_j-\mu)}+1}}_{n}$$

$$\Rightarrow \boxed{P = -\sum_{j=0}^{\infty}\frac{\partial \epsilon_j}{\partial V}\frac{1}{e^{\beta(\epsilon_j-\mu)}+1}}$$

For a non-relativistic particle

$$\epsilon = \frac{\hbar^2}{2m}\vec{k}^2 = \frac{\hbar^2}{2m}\left(\left(\frac{2\pi}{L_x}n_x\right)^2 + \left(\frac{2\pi}{L_y}n_y\right)^2 + \left(\frac{2\pi}{L_z}n_z\right)^2\right)$$

$$V = L_x L_y L_z \Rightarrow \epsilon = \text{const.}\ V^{-\frac{2}{3}} \Rightarrow \frac{\partial \epsilon}{\partial V} = -\frac{2}{3}\,\text{const}\ V^{-\frac{5}{3}}$$

$$\Rightarrow P = \frac{2}{3}\frac{1}{V}U \Rightarrow \boxed{PV = \frac{2}{3}U}$$

$$\ln Z = -n \ln \xi + \sum_{j=0}^{\infty} \ln\left(1 + \frac{1}{\xi} e^{-\beta \epsilon_j}\right) \quad ; \quad \xi = e^{\beta\mu}$$

For $\epsilon_j = \frac{\hbar^2 k^2}{2m}$ we have (in 3D)

$$\ln Z = -n \ln \xi + V \int \frac{d^3k}{(2\pi)^3} \ln\left(1 + \frac{1}{\xi} e^{-\beta \frac{\hbar^2 k^2}{2m}}\right)$$

Now,

$$\int \frac{d^3k}{(2\pi)^3} \ln\left(1 + \frac{1}{\xi} e^{-\beta \frac{\hbar^2 k^2}{2m}}\right) = \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} \int_0^{\infty} dx\, x^2 \ln\left(1 + \frac{1}{\xi} e^{-x^2}\right)$$

$$= \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} \left(\frac{1}{3} x^3 \ln\left(1 + \frac{1}{\xi} e^{-x^2}\right)\Bigg|_0^{\infty} - \int_0^{\infty} dx\, \frac{x^3}{3} \frac{\frac{1}{\xi}(-2x) e^{-x^2}}{1 + \frac{1}{\xi} e^{-x^2}} \right)$$

$$= \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} \cdot \frac{2}{3} \int_0^{\infty} dx\, \frac{x^4}{\xi e^{x^2} + 1}$$

$$= \frac{2}{3} \frac{1}{k_B T} \int \frac{d^3k}{(2\pi)^3} \frac{\epsilon_k}{\xi e^{\beta \epsilon_k} + 1} = \frac{2}{3} \frac{1}{k_B T} \frac{U}{V} = \frac{P}{k_B T}$$

$$\ln Z = -n \ln \xi + V \int \frac{d^3k}{(2\pi)^3} \ln\left(1 + \frac{1}{\xi} e^{-\beta \frac{\hbar^2 k^2}{2m}}\right)$$

$$\boxed{\ln Z = -n \ln \xi + \frac{PV}{k_B T}}$$

classical limit: $\xi \to 0$ or $\mu \to -\infty$

$$U \simeq V \int \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \xi e^{-\beta \frac{\hbar^2 k^2}{2m}}$$

$$n \simeq V \int \frac{d^3k}{(2\pi)^3} \xi e^{-\beta \frac{\hbar^2 k^2}{2m}}$$

$$\frac{U}{V} \simeq \xi \, k_B T \frac{1}{2\pi^2} \left(\frac{2m k_B T}{\hbar^2} \right)^{3/2} \int_0^\infty dx \, x^4 e^{-x^2}$$

$$\frac{n}{V} \simeq \xi \frac{1}{2\pi^2} \left(\frac{2m k_B T}{\hbar^2} \right)^{3/2} \int_0^\infty dx \, x^2 e^{-x^2}$$

$$\frac{U}{n} = k_B T \frac{\int_0^\infty dx \, x^4 e^{-x^2}}{\int_0^\infty dx \, x^2 e^{-x^2}}$$

$$I(\alpha) = \int_0^\infty dx \, e^{-\alpha x^2} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \; ; \quad -\frac{\partial I(\alpha)}{\partial \alpha} = I_2 \; ; \quad + \frac{\partial^2 I(\alpha)}{\partial \alpha^2} = I_4$$

$$\sqrt{\frac{\pi}{4}} \frac{1}{2\alpha^{3/2}} \leftarrow I_2 \; ; \quad -\frac{3}{2}\sqrt{\frac{\pi}{4}} \frac{1}{2\alpha^{5/2}} \longleftarrow I_4 \; ; \quad \frac{I_4}{I_2} = \frac{3}{2}$$

$$U = n k_B T \frac{\int_0^\infty dx \, x^4 e^{-x^2}}{\int_0^\infty dx \, x^2 e^{-x^2}} = \frac{3}{2} n k_B T = \frac{3}{2} PV \Rightarrow \boxed{PV = n k_B T}$$

In the degenerate (quantum limit): $\xi = e^{\frac{\mu}{k_B T}} \to \infty$

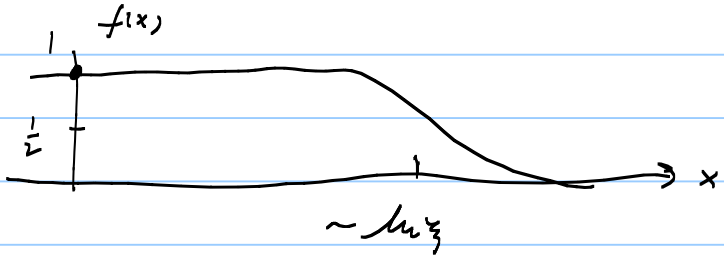
consider $$n = \sum_{j=0}^{\infty} \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{\xi} e^{\beta \epsilon_j} + 1}$$

and the x-dependence of the occupation factor:

$$f(x) = \frac{1}{\frac{1}{\xi} e^{x} + 1} = \frac{1}{e^{x - \ln \xi} + 1}$$

for $x << \ln \xi$; $f(x) \simeq 1$

$x >> \ln \xi$; $f(x) \simeq 0$



Consider non-relativistic gas : $\epsilon = \frac{\hbar^2 k^2}{2m}$

$$n = V \int \frac{d^3 k}{(2\pi)^3} \frac{1}{\frac{1}{\xi} e^{\beta \frac{\hbar^2 k^2}{2m}} + 1}$$

$$= V \frac{1}{2\pi^2} \left(\frac{2 m k_B T}{\hbar^2} \right)^{3/2} \int_0^{\infty} dx \, x^2 \frac{1}{\frac{1}{\xi} e^{x^2} + 1}$$

$$\Rightarrow \frac{n}{V} = \frac{1}{2\pi^2} \left(\frac{2 m k_B T}{\hbar^2} \right)^{3/2} \int_0^{\infty} dx \frac{x^2}{e^{x^2 - \ln \xi} + 1}$$

$$= \frac{1}{2\pi^2} \left(\frac{2 m k_B T}{\hbar^2} \right)^{3/2} \left[\int_0^{\sqrt{\ln \xi}} dx \frac{x^2}{e^{x^2 - \ln \xi} + 1} + \int_{\sqrt{\ln \xi}}^{\infty} dx \frac{x^2}{e^{x^2 - \ln \xi} + 1} \right]$$

$$\frac{1}{e^{+a}+1} = \frac{e^{-a}}{1+e^{-a}} = \frac{e^{-a}+1-1}{e^{-a}+1} = 1-\frac{1}{e^{-a}+1}$$

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\left[\int_0^{\sqrt{\ln\xi}} dx\left(x^2-\frac{x^2}{e^{-x^2+\ln\xi}+1}\right)+\right.$$

$$\left.+\int_{\sqrt{\ln\xi}}^{\infty} dx\,\frac{x^2}{e^{x^2-\ln\xi}+1}\right)$$

$$= \frac{1}{2\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi-\int_0^{\sqrt{\ln\xi}} dx\,\frac{x^2}{e^{\ln\xi-x^2}+1}+\int_{\sqrt{\ln\xi}}^{\infty} dx\,\frac{x^2}{e^{x^2-\ln\xi}+1}\right]$$

in the first integral, let $y=\ln\xi-x^2$, then $dy=-2x\,dx$

$x=\sqrt{\ln\xi-y}$

$$\int_0^{\sqrt{\ln\xi}} dx\,\frac{x^2}{e^{\ln\xi-x^2}+1} = \int_{\ln\xi}^{0} dy\,\frac{-1}{2\sqrt{\ln\xi-y}}\;\frac{\ln\xi-y}{e^{y}+1} =$$

$$\frac{1}{2}\int_0^{\ln\xi} dy\;\frac{(\ln\xi-y)^{\frac{1}{2}}}{e^{y}+1}$$

in the second integral let $y=x^2-\ln\xi$; $dx=\dfrac{dy}{2\sqrt{y+\ln\xi}}$

$$\int_{\sqrt{\ln\xi}}^{\infty} dx\,\frac{x^2}{e^{x^2-\ln\xi}+1} = \frac{1}{2}\int_0^{\infty} dy\;\frac{(y+\ln\xi)^{\frac{1}{2}}}{e^{y}+1}$$

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi - \frac{1}{2}\int_0^{\ln\xi} dy \, \frac{(\ln\xi - y)^{\frac{1}{2}}}{e^y+1} + \frac{1}{2}\int_0^{\infty} dy \, \frac{(y+\ln\xi)^{\frac{1}{2}}}{e^y+1}\right]$$

$$= \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi - \frac{\sqrt{\ln\xi}}{2}\int_0^{\ln\xi} dy \, \frac{\left(1-\frac{y}{\ln\xi}\right)^{\frac{1}{2}}}{e^y+1} + \frac{\sqrt{\ln\xi}}{2}\int_0^{\infty} dy \, \frac{\left(1+\frac{y}{\ln\xi}\right)^{\frac{1}{2}}}{e^y+1}\right]$$

$$= \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi - \frac{\sqrt{\ln\xi}}{2}\int_0^{\ln\xi}\frac{dy}{e^y+1}\left(1-\frac{y}{2\ln\xi}+\dots\right) + \frac{\sqrt{\ln\xi}}{2}\int_0^{\infty}\frac{dy}{e^y+1}\left(1+\frac{y}{2\ln\xi}+\dots\right)\right]$$

$$= \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi + \frac{\sqrt{\ln\xi}}{2}\int_{\ln\xi}^{\infty}\frac{dy}{e^y+1} + \frac{1}{2\sqrt{\ln\xi}}\int_0^{\infty}\frac{dy\, y}{e^y+1} - \frac{1}{4\sqrt{\ln\xi}}\int_{\ln\xi}^{\infty}\frac{dy\, y}{e^y+1} + \dots\right]$$

How big is the second term for large ξ? Note that

$$\int_{\ln\xi}^{\infty}\frac{dy}{e^y+1} < \int_{\ln\xi}^{\infty}\frac{dy}{e^y} = e^{-\ln\xi} \Rightarrow \text{exponentially small}$$

similarly the 4th term

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{\frac{3}{2}}\left[\frac{1}{3}\ln^{3/2}\xi + \frac{1}{2\sqrt{\ln\xi}}\overbrace{\int_0^\infty \frac{dy\, y}{e^y+1}}^{\pi^2/12} + \dots\right]$$

$$= \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{\frac{3}{2}}\left(k_B T \ln\xi\right)^{\frac{3}{2}}\left[1 + \frac{\pi^2}{8}\frac{1}{\ln^2\xi} + \dots\right]$$

since $\xi \equiv e^{\frac{\mu}{k_B T}}$ we can write:

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(k_B T\right)^{\frac{3}{2}}\left(\frac{1}{3}\left(\frac{\mu}{k_B T}\right)^{\frac{3}{2}} + \frac{\pi^2}{24}\sqrt{\frac{k_B T}{\mu}} + \dots\right)$$

$$\boxed{\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{\mu^{3/2}}{3} + \frac{\pi^2}{24}\frac{(k_B T)^2}{\sqrt{\mu}} + \dots\right)}$$

<u>internal energy</u>:

$$U = V\int\frac{d^3k}{(2\pi)^3}\,\frac{\frac{\hbar^2 k^2}{2m}}{\frac{1}{\xi}e^{\beta\frac{\hbar^2 k^2}{2m}} + 1}$$

$$\frac{U}{V} = \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{3/2}\cdot k_B T\cdot\int_0^\infty dx\,\frac{x^4}{e^{x^2-\ln\xi}+1}$$

now,

$$\int_0^{\sqrt{\ln\xi}} dx\, x^4\left(1 - \frac{1}{e^{\ln\xi - x^2}+1}\right) + \int_{\sqrt{\ln\xi}}^\infty dx\, x^4\,\frac{1}{e^{x^2-\ln\xi}+1} =$$

$$= \frac{1}{5}\ln^{5/2}\xi - \int_0^{\sqrt{\ln\xi}} dx \, \frac{x^4}{e^{\ln\xi - x^2}+1} + \int_{\sqrt{\ln\xi}}^{\infty} dx \, \frac{x^4}{e^{x^2-\ln\xi}+1} = (\ldots)$$

in the 1st integral, let $y = \ln\xi - x^2 \Rightarrow dy = -2x\,dx$

$$\Rightarrow dx = -\frac{dy}{2x} = -\frac{dy}{2\sqrt{\ln\xi - y}}$$

in the 2nd, let $y = x^2 - \ln\xi \Rightarrow dy = 2x\,dx$

$$\Rightarrow dx = \frac{dy}{2x} = \frac{dy}{2\sqrt{\ln\xi + y}}$$

$$(\ldots) = \frac{1}{5}\ln^{5/2}\xi - \frac{1}{2}\int_0^{\ln\xi} dy \, \frac{(\ln\xi - y)^{3/2}}{e^y+1} + \frac{1}{2}\int_0^{\infty} dy \, \frac{(\ln\xi + y)^{3/2}}{e^y+1}$$

$$\simeq \frac{1}{5}\ln^{5/2}\xi - \frac{1}{2}\ln^{3/2}\xi \int_0^{\infty} \frac{dy}{e^y+1}\left(1 - \frac{3}{2}\frac{y}{\ln\xi} + \ldots\right)$$

$$+ \frac{1}{2}\ln^{3/2}\xi \int_0^{\infty} \frac{dy}{e^y+1}\left(1 + \frac{3}{2}\frac{y}{\ln\xi} + \ldots\right)$$

$$= \frac{1}{5}\ln^{5/2}\xi + \frac{3}{2}\ln^{1/2}\xi \int_0^{\infty} \frac{dy\, y}{e^y+1} + \ldots$$

$$= \frac{1}{5}\ln^{5/2}\xi + \frac{3}{2}\ln^{1/2}\xi \cdot \frac{\pi^2}{12} + \ldots$$

$$\frac{U}{V} \simeq \frac{1}{2\pi^2}\left(\frac{2m k_B T}{\hbar^2}\right)^{3/2} \cdot k_B T \cdot \left(\frac{1}{5}\ln^{5/2}\xi + \frac{3}{2}\ln^{\frac{1}{2}}\xi \cdot \frac{\pi^2}{12} + \dots\right)$$

$$= \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(k_B T)^{5/2}\left(\frac{1}{5}\left(\frac{\mu}{k_B T}\right)^{\frac{5}{2}} + \frac{3\pi^2}{24}\left(\frac{\mu}{k_B T}\right)^{\frac{1}{2}} + \dots\right)$$

$$\boxed{\frac{U}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{1}{5}\mu^{\frac{5}{2}} + \frac{3\pi^2}{24}\mu^{\frac{1}{2}}(k_B T)^2 + \dots\right)}$$

What is the heat capacity at fixed V in this limit?

$$dU = dQ - PdV \Rightarrow \text{fixed } V \Rightarrow dU = dQ$$

$$C_V = \frac{dQ}{dT} = \frac{dU}{dT} \ ; \quad c_v = \frac{C_v}{V}.$$

So, we need the T-dependence of μ at small T (large ξ)

We first solve for μ at $T=0$ $\Rightarrow$ the leading order term in

$$\frac{n}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{\mu^{3/2}}{3} + \frac{\pi^2}{24}\frac{(k_B T)^2}{\sqrt{\mu}} + \dots\right)$$

$$\frac{n}{V} = \frac{1}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{3/2}$$

Then, we expand $\mu = \mu_0 + \delta\mu$ is small $\delta\mu$.

We get:

$$-\frac{1}{3}\mu_0^{3/2} + \frac{1}{3}\mu_0^{\frac{3}{2}}\left(1 + \frac{\delta\mu}{\mu_0}\right)^{3/2} + \frac{\pi^2}{24}\frac{(k_B T)^2}{\sqrt{\mu_0}} = 0$$

$$\frac{1}{3}\sqrt{\mu_0}\;\frac{3}{2}\,\delta\mu + \frac{\pi^2}{24}\frac{(k_BT)^2}{\sqrt{\mu_0}} = 0 \;\Rightarrow\; \delta\mu = -\frac{\pi^2}{12}\frac{(k_BT)^2}{\mu_0}$$

Now, we go back to the expression for the internal energy, and expand in small T.

$$\frac{U}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{1}{5}\mu^{\frac{5}{2}} + \frac{3\pi^2}{24}\mu^{\frac{1}{2}}(k_BT)^2 + \cdots\right)$$

$$\simeq \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(\frac{1}{5}(\mu_0+\delta\mu)^{\frac{5}{2}} + \frac{3\pi^2}{24}(\mu_0+\delta\mu)^{\frac{1}{2}}(k_BT)^2 + \cdots\right)$$

$$\simeq \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{1}{5}\mu_0^{\frac{5}{2}}\left(1+\frac{5}{2}\frac{\delta\mu}{\mu_0}\right) + \frac{3\pi^2}{24}\sqrt{\mu_0}\,(k_BT)^2 + \cdots\right)$$

$$\simeq \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{1}{5}\mu_0^{\frac{5}{2}} + \frac{1}{2}\mu_0^{\frac{3}{2}}\left(-\frac{\pi^2}{12}\frac{(k_BT)^2}{\mu_0}\right) + \frac{3\pi^2}{24}\sqrt{\mu_0}\,(k_BT)^2 + \cdots\right)$$

$$\simeq \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{1}{5}\mu_0^{\frac{5}{2}} - \frac{\pi^2}{24}\sqrt{\mu_0}\,(k_BT)^2 + \frac{3\pi^2}{24}\sqrt{\mu_0}\,(k_BT)^2 + \cdots\right)$$

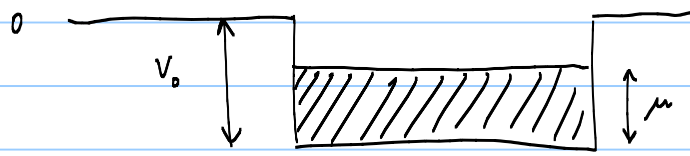
$$\frac{U}{V} \simeq \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{1}{5}\mu_0^{\frac{5}{2}} + \frac{\pi^2}{12}\sqrt{\mu_0}\,(k_BT)^2 + \cdots\right)$$

$$C_V = \frac{\partial U}{\partial T} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\frac{\pi^2}{6}\sqrt{\mu_0}\;k_B^2\,T$$

$$\frac{n}{V} = \frac{1}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{3/2} \;\Rightarrow\; \boxed{C_V = \frac{\pi^2}{2}V\frac{k_B^2T}{\mu_0}\frac{n}{V} = \frac{\pi^2}{2}Nk_B\left(\frac{k_BT}{\mu_0}\right)}$$

Thermionic emission:

electrons in a metal act like particles in a (self-consistently determined) potential well.



work function of a metal

$V_0 - \mu = \phi$

As we increase temperature, some of the scattering states above V_0 get populated. This means that some electrons "evaporate". If we place another piece (anode) of metal with a large potential difference wrt to the "hot" metal, then the evaporated electrons will fly off and collect on the anode. Our goal is to calculate this current as a fxn. of temperature.

Consider lanar interface. This means the axis above is, z (say). Then, let's use $\vec{k}$ to label the wavevector of the electrons at the energies above 0. Then the current density is:

$$2\int_{-\infty}^{\infty}\frac{dk_x}{2\pi}\int_{-\infty}^{\infty}\frac{dk_y}{2\pi}\int_{0}^{\infty}\frac{dk_z}{2\pi}\,\frac{e\hbar k_z}{m}\,\frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m}+\phi\right)}+1} \simeq$$

$$2\frac{e\hbar}{m}\int_0^\infty\frac{dk_{\parallel}\,k_{\parallel}}{2\pi}\int_0^\infty\frac{dk_z\,k_z}{2\pi}\,e^{-\frac{1}{k_BT}\frac{\hbar^2k_{\parallel}^2}{2m}}\,e^{-\frac{1}{k_BT}\frac{\hbar^2k_z^2}{2m}}\,e^{-\frac{\phi}{k_BT}} =$$

$$2\frac{e\hbar}{m}\left(\frac{2m\,k_BT}{\hbar^2}\right)^2\frac{1}{4\pi^2}\int_0^\infty dx\,x\,e^{-x^2}\int_0^\infty dy\,y\,e^{-y^2}\,e^{-\frac{\phi}{k_BT}} =$$

$$2\,\frac{e\hbar}{m}\left(\frac{m\,k_B T}{\hbar^2}\right)^2\frac{1}{\pi^2}\,\frac{1}{4}\,e^{-\phi/k_BT} =$$

$$2\,\frac{e\,m\,k_B^2T^2}{h^3}\,\frac{8\pi^3}{4\pi^2}\,e^{-\frac{\phi}{k_BT}} = \boxed{\frac{4\pi e m k_B^2}{h^3}\cdot T^2\cdot e^{-\frac{\phi}{k_BT}} = j}$$

Richardson – Dushman "law"

$$\frac{4\pi e m k_B^2}{h^3} = 1.202\,\frac{A}{m^2K^2}$$

Coupling of external magnetic field to spin:

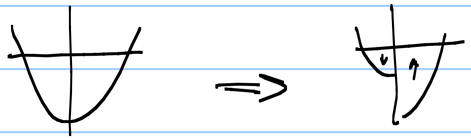
$$E_\sigma = \frac{\hbar^2k^2}{2m} + \sigma\,\mu_B B \quad ; \quad \sigma = \pm$$

$$\ln Z = -\beta n\mu + \sum_{j=0}^{\infty}\ln\left(1+e^{-\beta(\epsilon_j-\mu)}\right)$$

$$n = \sum_{j=0}^{\infty}\frac{1}{e^{\beta(\epsilon_j-\mu)}+1}$$

Start w/ n in the limit of T→0.

$$n = V\int\frac{d^3k}{(2\pi)^3}\left[\Theta\left(\frac{\hbar^2k^2}{2m}+\mu_B B-\mu\right)+\Theta\left(\frac{\hbar^2k^2}{2m}-\mu_B B-\mu\right)\right]$$



$$n = V \frac{1}{2\pi^2} \int_0^{\sqrt{2m(\mu-\mu_B B)/\hbar^2}} dk\, k^2 \quad + \quad V \frac{1}{2\pi^2} \int_0^{\sqrt{2m \frac{\mu+\mu_B B}{\hbar^2}}} dk\, k^2$$

$$= \frac{V}{2\pi^2} \left(\frac{1}{3} \left(\frac{2m}{\hbar^2}(\mu-\mu_B B)\right)^{3/2} + \frac{1}{3} \left(\frac{2m}{\hbar^2}(\mu+\mu_B B)\right)^{3/2} \right)$$

if $B = 0$ then $\mu = \mu_0 = \left(3\pi^2 \frac{n}{V}\right)^{\frac{2}{3}} \frac{\hbar^2}{2m}$

if $B \neq 0$ then $\mu = \mu_0 + \delta\mu$. For small B, $\delta\mu$ is small.

$$2\mu_0^{3/2} = (\mu - \mu_B B)^{3/2} + (\mu + \mu_B B)^{3/2}$$

the solution to this equation for μ is the same if $B \to -B$. so we see that μ is an even function of B.

$$\Rightarrow \delta\mu \sim \mathcal{O}(B^2)$$

magnetization is

$$M = \mu_B V \int \frac{d^3k}{(2\pi)^3} \left[\Theta\left(\frac{\hbar^2 k^2}{2m} - \mu_B B - \mu \right) - \Theta\left(\frac{\hbar^2 k^2}{2m} + \mu_B B - \mu \right) \right]$$

$$= \mu_B \frac{V}{2\pi^2} \left(\frac{1}{3} \left(\frac{2m}{\hbar^2}(\mu+\mu_B B)\right)^{3/2} - \frac{1}{3} \left(\frac{2m}{\hbar^2}(\mu-\mu_B B)\right)^{3/2} \right)$$

This is an odd function of B. Expand it to leading order in small B:

$$M = \mu_B \frac{V}{6\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \mu^{3/2} \left(\left(1 + \frac{\mu_B B}{\mu}\right)^{3/2} - \left(1 - \frac{\mu_B B}{\mu}\right)^{3/2} \right)$$

$$\mu_0 = \left(3\pi^2 \frac{n}{V}\right)^{\frac{2}{3}} \frac{\hbar^2}{2m} = \epsilon_F$$

$$M = \mu_B \frac{V}{6\pi^2} \left(\frac{2m\mu_0}{\hbar^2}\right)^{3/2} \cdot 3 \frac{\mu_B B}{\mu_0} + \dots$$

$$\frac{M}{V} = \mu_B \frac{3}{2} \frac{n}{V} \frac{\mu_B B}{\mu_0} \Rightarrow M = \frac{3}{2} n \frac{\mu_B^2 B}{\epsilon_F}$$

$$\boxed{\chi = \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{3}{2} n \frac{\mu_B^2}{\varepsilon_F}}$$ Pauli paramagnetic susceptibility

in the limit of high temperature $\mu \to -\infty$:

$$n = V \int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}} e^{\beta\mu} \left(e^{-\beta\mu_B B} + e^{\beta\mu_B B}\right)$$

$$\frac{n}{V} = e^{\beta\mu} \, 2\cosh\left(\frac{\mu_B B}{k_B T}\right) \int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}}$$

$$\frac{M}{V} = \mu_B \int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}} e^{\beta\mu} \left(e^{\beta\mu_B B} - e^{-\beta\mu_B B}\right)$$

$$\frac{M}{n} = \mu_B \frac{2\sinh\left(\frac{\mu_B B}{k_B T}\right)}{2\cosh\left(\frac{\mu_B B}{k_B T}\right)} = \mu_B \tanh \frac{\mu_B B}{k_B T}$$

$$M \simeq \mu_B n \frac{\mu_B B}{k_B T} \Rightarrow \boxed{\chi = n \frac{\mu_B^2}{k_B T}}$$ Currie-Weiss

coupling of the magnetic field to the orbital motion of el's.

1 $\vec{B} = B\hat{z}$; $\vec{A} = ?$; $\vec{\nabla}\times\vec{A} = \vec{B}$

$$\begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \partial_x & \partial_y & \partial_z \\ A_x & A_y & A_z \end{vmatrix} = B\hat{z} \Rightarrow \partial_x A_y - \partial_y A_x = B$$

Let $A_y = Bx$ and $A_x = 0$. This is called Landau gauge

$$\hat{H} = \frac{p_x^2}{2m} + \frac{(p_y - \frac{e}{c}A_y)^2}{2m} + \frac{p_z^2}{2m}$$

$$= \frac{p_x^2}{2m} + \frac{\left(p_y - \frac{eB}{c}x\right)^2}{2m} + \frac{p_z^2}{2m}$$

$$\hat{H}\psi(x,y,z) = E\,\psi(x,y,z) \quad ; \quad \psi(x,y,z) = e^{ik_z z} e^{iky}\phi(x)$$

$$\Rightarrow \left(\frac{p_x^2}{2m} + \frac{(\hbar k - \frac{eB}{c}x)^2}{2m} + \frac{\hbar^2 k_z^2}{2m}\right)\phi(x) = E\,\phi(x)$$

$$\left(\frac{p_x^2}{2m} + \frac{1}{2}m\left(\frac{eB}{mc}\right)^2\left(x - \frac{\hbar c}{eB}k\right)^2 + \frac{\hbar^2 k_z^2}{2m}\right)\phi(x) = E\,\phi(x)$$

$\frac{eB}{mc} = \omega_c \longleftarrow$ cyclotron frequency

Let $X = x - \frac{\hbar c}{eB}k$, then $p_x = \frac{\hbar}{i}\frac{\partial}{\partial x} = \frac{\hbar}{i}\frac{\partial}{\partial X}$

$$\left[\frac{p_x^2}{2m} + \frac{1}{2} m \omega_c^2 X^2\right] \phi(x) = \left(E - \frac{\hbar^2 k_z^2}{2m}\right) \phi(x)$$

this is the Schrödinger equation for harmonic oscillator =>

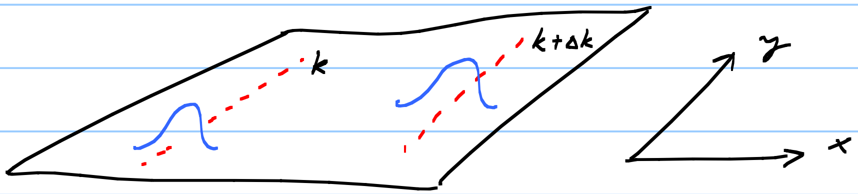
$$E = \hbar \omega_c \left(n + \frac{1}{2}\right) + \frac{\hbar^2 k_z^2}{2m}$$

$\Rightarrow \quad \phi = \phi\left(x - \frac{\hbar c}{eB} k\right)$ which have the form of a polynomial times a gaussian

$$\psi = e^{ik_z z} e^{iky} \phi\left(x - \frac{\hbar c}{eB} k\right)$$

What is the degeneracy of the Landau levels ?
Fix n, k_z , then how many k's ?

Assume that the system has dimensions $L_x L_y L_z$.
Then, as we change k, we move the center of the gaussian:



$$k = 0, \pm \frac{2\pi}{L_y}, \pm \frac{4\pi}{L_y}, \cdots, \pm (j_{max} - 1) \frac{2\pi}{L_y}, j_{max} \frac{2\pi}{L_y}$$

Now, the right most position of the gaussians can be $\frac{L_x}{2}$.
Therefore :

$$\frac{L_x}{2} = \frac{\hbar c}{eB} k_{max} = \frac{\hbar c}{eB} j_{max} \frac{2\pi}{L_y} \Rightarrow j_{max} = \frac{1}{2} \frac{L_x L_y}{2\pi} \frac{eB}{\hbar c}$$

degeneracy $= 2j_{max} = L_x L_y \frac{eB}{hc}$

$\frac{hc}{e}$ is the (elementary) flux quantum $4.136 \times 10^{-15}\ T\,m^2$

So, each Landau level contains $L_x L_y \frac{eB}{hc}$ states.

Recall,

$$\ln Z = -n \ln \xi + \sum_{j=0}^{\infty} \ln\left(1 + \xi e^{-(\beta\epsilon_j}\right)$$

$$n = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{\xi} e^{\beta\epsilon_j} + 1}$$

$$\sum_{j=0}^{\infty} (\dots) = \sum_{k_z} \sum_{n=0}^{\infty} L_x L_y \frac{eB}{hc} (\dots)$$

$$\boxed{\begin{aligned} \ln Z &= -n \ln \xi + V \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \ln\left[1 + \xi e^{-\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c (n + \frac{1}{2})\right)}\right] \\ n &= V \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c (n + \frac{1}{2})\right)} + 1} \end{aligned}}$$

if $k_B T \gg \hbar\omega_c$ then each term in the sum changes little as $n \longrightarrow n+1$ $\Rightarrow$ use Euler-MacLaurin formula the final result of the derivation is

$$\sum_{n=0}^{\infty} F(n+\tfrac{1}{2}) \simeq \int_{0}^{\infty} dy\, F(y) + \frac{1}{24} F'(0)$$

Euler-Maclaurin formula

$$\int_{k}^{k+1} f(x)\,dx \doteq \int_{k}^{k+1} v\,du = uv\Big|_{k}^{k+1} - \int_{k}^{k+1} u\,dv$$

Let $du = dx$; $v = f(x)$

$u = x-a$; $dv = f'(x)\,dx$

$$\int_{k}^{k+1} f(x)\,dx = f(k+1)(k+1-a) - f(k)(k-a) - \int_{k}^{k+1} dx\, f'(x)\,(x-a)$$

Now, make a depend on k. If we make $a = k + \frac{1}{2}$

then $1-a = \frac{1}{2} - k$ and

$$f(k+1)\,\tfrac{1}{2} - f(k)\,(-\tfrac{1}{2}) - \int_{k}^{k+1} dx\, f'(x)\,(x-k-\tfrac{1}{2}) =$$

$$\tfrac{1}{2}\Big(f(k+1) + f(k)\Big) - \int_{k}^{k+1} dx\, f'(x)\,\Big(x - \text{Floor}(x) - \tfrac{1}{2}\Big)$$

where $\text{Floor}(7.1) = 7$, $\text{Floor}(7.8) = 7$ is the integer part of the real number.

$$\int_k^{k+1} f(x)\,dx = \frac{1}{2}\left(f(k+1) + f(k)\right) - \int_k^{k+1} dx\, f'(x)\, P_1(x)$$

where $P_1(x) := x - \text{Floor}(x) - \frac{1}{2}$

$$\sum_{k=0}^{n} \int_k^{k+1} f(x)\,dx = \sum_{k=0}^{n} \frac{1}{2}\left(f(k+1) + f(k)\right) - \int_0^{n+1} dx\, f'(x)\, P_1(x)$$

$$= \frac{1}{2} f(0) + \frac{1}{2} f(n+1) + \left(f(1) + f(2) + \dots + f(n)\right) - \int_0^{n+1} dx\, f'(x)\, P_1(x)$$

Next consider $\int_k^{k+1} dx\, f'(x) P_1(x)$ and integrate it by parts in order to increase the degree of derivative on f (*recall, that we are assuming that f is a slowly varying fcn)

$du = P_1(x)\,dx \qquad v = f'(x)$

$u = \frac{1}{2} P_2(x) \qquad dv = f''(x)\,dx$

on the interval $k \leq x < k+1$, $P_1(x) = x - k - \frac{1}{2}$

$$\Rightarrow \quad u = \frac{1}{2}x^2 - kx - \frac{1}{2}x + b = \frac{1}{2}(x-k)^2 - \frac{1}{2}(x-k) + \tilde{b}$$

Now, choose $\tilde{b}$ so that the area under $P_2(x)$ vanishes:

$$\int_k^{k+1} P_2(x)\,dx = \int_0^1 dy \left(\frac{1}{2}y^2 - \frac{1}{2}y + \tilde{b}\right) = \frac{1}{2}\left(\frac{1}{3} - \frac{1}{2}\right) + \tilde{b} = \frac{-1}{12} + \tilde{b}$$

$\Rightarrow \tilde{b} = \frac{1}{12}$ and

$$P_2(x) = \left(x - \text{Floor}(x)\right)^2 - \left(x - \text{Floor}(x)\right) + \frac{1}{6}$$

$$\int_k^{k+1} dx \; f'(x) P_1(x) = \frac{1}{2} P_2(x) f'(x) \Big|_k^{k+1} - \int_k^{k+1} \frac{1}{2} P_2(x) f''(x)\, dx$$

$$= \frac{1}{2}\Big(P_2(k+1) f'(k+1) - P_2(k) f'(k) \Big) - \frac{1}{2} \int_k^{k+1} f''(x) P_2(x) dx$$

$$\left.\begin{aligned} \frac{1}{2} P_2(k+1) &= \frac{1}{2}\cdot 1^2 - \frac{1}{2}\cdot 1 + \frac{1}{12} = \frac{1}{12} \\ \frac{1}{2} P_2(k) &= \frac{1}{2}\cdot 0^2 - \frac{1}{2}\cdot 0 + \frac{1}{12} \end{aligned}\right\} \Rightarrow P_2(k+1) = P_2(k) = \frac{1}{6}$$

$$\Rightarrow \int_k^{k+1} dx \; f'(x) P_1(x) = \frac{1}{12}\Big(f'(k+1) - f'(k) \Big) - \frac{1}{2} \int_k^{k+1} f''(x) P_2(x) dx$$

$$\sum_{k=0}^{n} \int_k^{k+1} dx \; f'(x) P_1(x) = \int_0^{n+1} dx \; f'(x) P_1(x)$$

$$= \frac{-1}{12} f'(0) + \frac{1}{12} f'(0) - \frac{1}{2} \int_0^{n+1} dx \; f''(x) P_2(x)$$

Finally:

$$\int_0^{n+1} f(x) dx = \frac{1}{2} f(0) + \frac{1}{2} f(n+1) + \sum_{k=1}^{n} f(k) + \frac{1}{12} f'(0) - \frac{1}{12} f'(n+1) + \underset{\substack{\downarrow \\ \text{ignore}}}{\frac{1}{2}\int_0^{n+1} dx \; f''(x) P_2(x)}$$

as $n \to \infty$ we have (assuming $f(\infty) = 0$)

$$\int_0^{\infty} f(x) dx \simeq \frac{1}{2} f(0) + \sum_{k=1}^{\infty} f(k) + \frac{1}{12} f'(0) \quad \text{or}$$

$$\sum_{n=0}^{\infty} f(n) \cong \int_0^{\infty} f(x) dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0)$$

Now, we need

$$\sum_{n=0}^{\infty} F\left(n+\tfrac{1}{2}\right) = \int_0^{\infty} dx\, F\left(x+\tfrac{1}{2}\right) + \tfrac{1}{2} F\left(\tfrac{1}{2}\right) - \tfrac{1}{12} F'\left(\tfrac{1}{2}\right)$$

$$= \int_{\frac{1}{2}}^{\infty} dy\, F(y) + \tfrac{1}{2} F\left(\tfrac{1}{2}\right) - \tfrac{1}{12} F'\left(\tfrac{1}{2}\right)$$

$$= \int_0^{\infty} dy\, F(y) - \int_0^{\frac{1}{2}} dy\, F(y) + \tfrac{1}{2} F\left(\tfrac{1}{2}\right) - \tfrac{1}{12} F'\left(\tfrac{1}{2}\right)$$

on this (short) interval
$F(y) \simeq F(0) + y\, F'(0)$
$F\left(\tfrac{1}{2}\right) \simeq F(0) + \tfrac{1}{2} F'(0)$
$F'(y) \simeq F'(0)$

so,

$$\int_0^{\frac{1}{2}} dy \left(F(0) + y\, F'(0)\right) = \tfrac{1}{2} F(0) + \tfrac{1}{2} y^2 \Big|_0^{\frac{1}{2}} \cdot F'(0)$$

$$= \tfrac{1}{2} F(0) + \tfrac{1}{8} F'(0)$$

$$\int_0^{\infty} dy\, F(y) - \int_0^{\frac{1}{2}} dy\, F(y) + \tfrac{1}{2} F\left(\tfrac{1}{2}\right) - \tfrac{1}{12} F'\left(\tfrac{1}{2}\right) \simeq$$

$$\int_0^{\infty} dy\, F(y) - \cancel{\tfrac{1}{2} F(0)} - \tfrac{1}{8} F'(0) + \cancel{\tfrac{1}{2} F(0)} + \tfrac{1}{4} F'(0) - \tfrac{1}{12} F'(0) =$$

$$\boxed{\int_0^{\infty} dy\, F(y) + \tfrac{1}{24} F'(0) \simeq \sum_{n=0} F\left(n+\tfrac{1}{2}\right)}$$

$$\ln Z = -N\ln\xi + V\frac{eB}{hc}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\sum_{n=0}^{\infty}\ln\left[1+\xi e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+\hbar\omega_c(n+\frac{1}{2})\right)}\right]$$

$$\simeq -N\ln\xi + V\frac{eB}{hc}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_{0}^{\infty}dy\,\ln\left[1+\xi e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+\hbar\omega_c y\right)}\right]$$

$$+\frac{V}{24}\frac{eB}{hc}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{1}{\frac{1}{\xi}e^{\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+\hbar\omega_c y\right)}+1}\cdot\left(\frac{-\hbar\omega_c}{k_BT}\right)$$

$$\hbar\omega_c = \hbar\frac{eB}{mc}: \qquad V\frac{eB}{hc}\frac{1}{\hbar\omega_c} = \frac{V}{h\cdot\hbar}m = V\frac{m}{\hbar^2}\frac{1}{2\pi}$$

$$\ln Z \simeq -N\ln\xi + V\frac{m}{\hbar^2}\overbrace{\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_{0}^{\infty}\frac{dy}{2\pi}\ln\left(1+\xi e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)}^{\text{B doesn't appear explicitly, but may appear in } \xi}$$

$$-\frac{V}{24}\frac{eB}{hc}\frac{\hbar eB}{mc}\frac{1}{k_BT}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{1}{\frac{1}{\xi}e^{\frac{1}{k_BT}\frac{\hbar^2k_z^2}{2m}}+1}$$

for $\xi \gg 1$ we have for the last term:

$$-\frac{V}{24}\frac{e^2B^2}{hc^2}\frac{1}{\sqrt{mk_BT}}\frac{2\sqrt{2}}{2\pi}\sqrt{\ln\xi}$$

$$= -V\frac{\sqrt{2}}{24\pi}\frac{e^2B^2}{hc^2}\frac{1}{\sqrt{mk_BT}}\frac{\sqrt{\mu}}{\sqrt{k_BT}}$$

This last term depends on B^2. In order to determine whether $\ln Z$ contains any other contribution to this order in B, we need to analyse the correction to the chemical potential due to B.

So,

$$n = V \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c\left(n+\frac{1}{2}\right)\right)} + 1}$$

$$n \simeq V \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} dy \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c y\right)} + 1}$$

$$+ \frac{1}{24} V \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \left(\frac{d}{dy} \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c y\right)} + 1} \right) \Bigg|_{y=0}$$

$$n \simeq V \frac{\cancel{eB}}{h\cancel{c}} \frac{m\cancel{c}}{\hbar \cancel{e}\cancel{B}} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} dy \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + y\right)} + 1}$$

$$- \frac{V}{24} \frac{eB}{hc} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \frac{\hbar\omega_c}{k_B T} \frac{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c y\right)}}{\left(\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + \hbar\omega_c y\right)} + 1\right)^2} \Bigg|_{y=0}$$

$$n = V \frac{m}{\hbar^2} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} \frac{dy}{2\pi} \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + y\right)} + 1}$$

$$- \frac{V}{24} \frac{eB}{hc} \frac{\hbar eB}{mc} \frac{1}{k_B T} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \frac{1}{4 \cosh^2\left(\frac{1}{2k_B T} \frac{\hbar^2 k_z^2}{2m} - \frac{1}{2} \ln \xi\right)}$$

we see that the first term corresponds to the expression for the particle number in terms of the chemical potential in the absence of the magnetic field. The second term corresponds to the correction of order B^2.

For concreteness, assume the degenerate limit i.e. $\xi \to \infty$.

$$V \frac{m}{\hbar^2} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} \frac{dy}{2\pi} \frac{1}{\frac{1}{\xi} e^{\frac{1}{k_B T}\left(\frac{\hbar^2 k_z^2}{2m} + y\right)} + 1} \longrightarrow V \frac{m}{\hbar^2} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} \frac{dy}{2\pi} \, \theta\left(\frac{\hbar^2 k_z^2}{2m} + y - k_B T \ln \xi\right)$$

$$= V \frac{2m}{\hbar^2} \int_0^{k_z^{max}} \frac{dk_z}{2\pi} \int_0^{y^{max}} \frac{dy}{2\pi} \quad \text{where } y^{max} = k_B T \ln \xi - \frac{\hbar^2 k_z^2}{2m}, \; k_z^{max} = \sqrt{\frac{2m}{\hbar^2}} \sqrt{k_B T \ln \xi}$$

$$= V \frac{2m}{\hbar^2} \frac{1}{2\pi} \int_0^{k_z^{max}} \frac{dk_z}{2\pi} \left(k_B T \ln \xi - \frac{\hbar^2 k_z^2}{2m}\right) =$$

$$= V \frac{2m}{\hbar^2} \frac{1}{(2\pi)^2} \left((k_B T \ln \xi)^{3/2} \sqrt{\frac{2m}{\hbar^2}} - \frac{\hbar^2}{2m} \frac{1}{3} \left(\frac{2m}{\hbar^2}\right)^{3/2} (k_B T \ln \xi)^{3/2} \right)$$

$$V\,\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\,\frac{1}{\frac{1}{\xi}e^{\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}+1}\longrightarrow\frac{2V}{3}\,\frac{1}{(2\pi)^2}\left(\frac{k_BT}{\hbar^2/2m}\ln\xi\right)^{3/2}$$

This is exactly the expressin for n spinless fermions with $\xi = e^{-\mu/k_BT}$ in the degenerate limit for $B=0$.

So, our expression for n looks as follows:

$$n(B,\xi) = n(0,\xi) + B^2\,\delta n(\xi)$$

Our task is to solve for ξ such that we obtain n predetermined by, say, its $B=0$ value.
Therefore, let $\xi = \xi_0 + \delta\xi$. Then, to order we are working, we have

$$n(B,\xi) = n(0,\xi_0) + \left.\frac{\partial n(0,\xi)}{\partial\xi}\right|_{\xi_0}\delta\xi + B^2\,\delta n(\xi_0)$$

since the $n(0,\xi_0)$ is the desired particle number, we must have

$$\left.\frac{\partial n(0,\xi)}{\partial\xi}\right|_{\xi_0}\delta\xi = -B^2\,\delta n(\xi_0) \qquad \text{or}$$

$$\delta\xi = -B^2\,\frac{\delta n(\xi_0)}{\left(\left.\frac{\partial n(0,\xi)}{\partial\xi}\right|_{\xi_0}\right)}$$

We could proceed by explicitly computing $\delta\xi$, but we do not have to use more than the fact that $\delta\xi \sim \mathcal{O}(B^2)$ to show that the result for magnetization in grand canonical ensemble and canonical ensemble is the same.

To this end we have:

$$\ln Z \simeq -n\ln\xi + V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\ln\left(1+\xi e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)$$

$$-\frac{V}{24}\frac{eB}{hc}\frac{\hbar eB}{mc}\frac{1}{k_BT}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{1}{\frac{1}{\xi}e^{\frac{1}{k_BT}\frac{\hbar^2k_z^2}{2m}}+1}$$

where the last term, in the limit $\xi\to\infty$, is

$$-\frac{V}{24}\frac{e^2B^2}{hc^2}\frac{1}{\sqrt{mk_BT}}\frac{\sqrt{2}}{\pi}\sqrt{\ln\xi}$$

For the first two terms:

$$-n\ln(\xi_0+\delta\xi)+V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\ln\left(1+(\xi_0+\delta\xi)e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)$$

$$\simeq -n\ln\xi_0 - n\frac{\delta\xi}{\xi_0}+V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\ln\left(1+\xi_0 e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)$$

$$+V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\frac{1}{1+\xi_0e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}}\,\delta\xi\, e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}$$

$$= -n \ln \xi_0 + V \frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\ln\left(1+\xi_0 e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)$$

$$-n\frac{\delta\xi}{\xi_0}+\frac{\delta\xi}{\xi_0}V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\frac{1}{\frac{1}{\xi_0}e^{\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}+1}$$

But, as we have just seen,

$$n = n(B=0,\xi_0) = V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\frac{1}{\frac{1}{\xi_0}e^{\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}+1}$$

Therefore,

$$-n\frac{\delta\xi}{\xi_0}+\frac{\delta\xi}{\xi_0}V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\frac{1}{\frac{1}{\xi_0}e^{\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}+1}=0$$

And, to $O(B^2)$:

$$\ln Z \simeq -n\ln \overset{\downarrow}{\xi_0} + V\frac{m}{\hbar^2}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\int_0^{\infty}\frac{dy}{2\pi}\ln\left(1+\overset{\downarrow}{\xi_0} e^{-\frac{1}{k_BT}\left(\frac{\hbar^2k_z^2}{2m}+y\right)}\right)$$

$$-\frac{V}{24}\frac{eB}{hc}\frac{\hbar eB}{mc}\frac{1}{k_BT}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\frac{1}{\frac{1}{\xi_0}e^{\frac{1}{k_BT}\frac{\hbar^2k_z^2}{2m}}+1}$$

So, in the limit $\xi \to \infty$:

$$-\frac{F(B,n)}{k_BT} = -\frac{F(0,n)}{k_BT} - V\,\frac{\sqrt{2}}{24\pi}\,\frac{e^2B^2}{hc^2}\,\frac{1}{\sqrt{mk_BT}}\sqrt{\ln\xi_0}$$

$$\boxed{F(B,n) = F(0,n) + V\,\frac{\sqrt{2}}{24\pi}\,\frac{e^2B^2}{hc^2}\sqrt{\frac{\mu_0}{m}} + \mathcal{O}(B^4)}$$

where $$\frac{2V}{3}\,\frac{1}{(2\pi)^2}\left(\frac{\mu_0}{\hbar^2/2m}\right)^{3/2} = n$$

We see that the free energy increases with increasing B,
$\Rightarrow$ diamagnetism

$$M = -\frac{\partial F}{\partial B} = -\frac{\sqrt{2}}{12\pi}\,\frac{e^2B}{hc^2}\sqrt{\frac{\mu_0}{m}} = \chi_{\text{Landau}}\,B$$

adding factor of 2 for spin we get $\chi^{\text{spin }\frac{1}{2}}_{\text{Landau}} = -\frac{1}{3}\chi_{\text{Pauli}}$

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for $k_BT \gtrsim \hbar\omega_c$, but $k_BT \ll \mu$, we need a different procedure.

So far, we were mainly focused on the canonical ensemble (fixed particle number). For free fermions we have

$$\ln\mathcal{Z} = -N\ln\xi + \sum_{j=0}^{\infty}\ln\left(1+\xi e^{-\beta\epsilon_j}\right);\quad \mathcal{Z} = e^{-\frac{F}{k_BT}};\quad \xi = e^{\frac{\mu}{k_BT}}$$

So, $$F = k_B T N \ln e^{\frac{\mu}{k_B T}} - k_B T \sum_{j=0}^{\infty} \ln\left(1 + \xi e^{-\beta \epsilon_j}\right)$$

$$F = N\mu - k_B T \sum_{j=0}^{\infty} \ln\left(1 + \xi e^{-\beta \epsilon_j}\right)$$

let

$\Omega = F - N\mu$. This is called the grand canonical potential

We would have gotten Ω if we did not restrict the sum over all states to have a fixed (large) particle number:

$$\mathcal{Z} = \sum_{n_0=0}^{1} \sum_{n_1=0}^{1} \cdots \sum_{n_j=0}^{1} \cdots e^{-\sum_{j=0}^{\infty}\left(\frac{\epsilon_j n_j}{k_B T} - \frac{\mu n_j}{k_B T}\right)} = \prod_{j=0}^{\infty}\left(1 + e^{-\frac{\epsilon_j - \mu}{k_B T}}\right)$$

$$= e^{-\frac{\Omega}{k_B T}}$$

In the grand canonical ensemble, the chemical potential is set externally, rather than the particle number.
(For example, contact with a large particle reservoir is established by grounding a sample)

We will now compute Ω for the Landau level problem.

$$\Omega = -k_B T \cdot V \cdot \frac{eB}{hc} \sum_{\sigma=\pm} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \ln\left(1 + e^{-\beta(\epsilon_{n,\sigma} - \mu)}\right)$$

where $\epsilon_{n,\sigma} = \frac{\hbar^2 k_z^2}{2m^*} + \hbar\omega_c^*\left(n + \frac{1}{2}\right) + \sigma \mu_B B$; $\sigma = +(-)$ is ↑ (↓)

We will find this identity useful:

$$\sum_{n=-\infty}^{\infty} e^{2\pi i n x} = \sum_{k=-\infty}^{\infty} \delta(x-k) \longleftarrow$$

sometimes called the Dirac comb

So,

$$\Omega = -k_B T \cdot V \cdot \frac{eB}{hc} \sum_{\sigma=\pm} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} d\epsilon \sum_{n=-\infty}^{\infty} \delta(\epsilon_n - \epsilon) \ln\left(1+e^{-\beta(\epsilon-\tilde{\mu}_\sigma)}\right)$$

where

$$\tilde{\mu}_\pm = \mu - \frac{\hbar^2 k_z^2}{2m^*} \mp \frac{1}{2}\hbar\omega_c \quad \text{and} \quad \epsilon_n = \hbar\omega_c^*(n+\tfrac{1}{2}) > 0$$

Now,

$$\sum_{n=-\infty}^{\infty} \delta(\epsilon_n - \epsilon) = \sum_{n=-\infty}^{\infty} \delta\left(\hbar\omega_c^*(n+\tfrac{1}{2}) - \epsilon\right) = \frac{1}{\hbar\omega_c^*} \sum_{n=-\infty}^{\infty} \delta\left(n+\tfrac{1}{2} - \frac{\epsilon}{\hbar\omega_c^*}\right)$$

$$= \frac{1}{\hbar\omega_c^*} \sum_{k=-\infty}^{\infty} e^{2\pi i k\left(\frac{1}{2} - \frac{\epsilon}{\hbar\omega_c^*}\right)} = \frac{1}{\hbar\omega_c^*} \sum_{k=-\infty}^{\infty} (-1)^k e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}}$$

⇒

$$\Omega = -k_B T \cdot V \cdot \frac{eB}{hc} \sum_{\sigma=\pm} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} d\epsilon \sum_{k=-\infty}^{\infty} \frac{(-1)^k}{\hbar\omega_c^*} e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}} \ln\left(1+e^{-\beta(\epsilon-\tilde{\mu}_\sigma)}\right)$$

Next, separate $k=0$ term from $k \neq 0$.

$$\frac{\Omega}{V} = -k_B T \frac{eB}{hc} \sum_{\sigma=\pm} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \int_0^{\infty} \frac{d\epsilon}{\hbar\omega_c^*} \ln\left(1+e^{-\frac{\epsilon-\tilde{\mu}_\sigma}{k_B T}}\right)$$

$$-k_B T \frac{eB}{hc} \sum_{\sigma=\pm} \int_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{k=1}^{\infty} 2 \frac{(-1)^k}{\hbar\omega_c^*} \operatorname{Re} \int_0^{\infty} d\epsilon \, e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}} \ln\left(1+e^{-\frac{\epsilon-\tilde{\mu}_\sigma}{k_B T}}\right)$$

In the above expression, it is the second term that contains the oscillatory contribution.

So we need:

$$\int_0^\infty d\epsilon\, e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}} \ln\left(1+e^{-\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}\right) =$$

$$\frac{\hbar\omega_c^*}{2\pi i k}\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}} \ln\left(1+e^{-\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}\right)\Bigg|_0^\infty - \frac{\hbar\omega_c^*}{2\pi i k}\int_0^\infty d\epsilon\, e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}} \frac{\left(-\frac{1}{k_BT}\right)}{e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}+1} =$$

$$\underset{\substack{\Big\downarrow \\ \text{not oscillatory}}}{\frac{\hbar\omega_c^*}{2\pi i k}\ln\left(1+e^{\frac{\tilde{\mu}_\sigma}{k_BT}}\right)} + \underbrace{\frac{1}{2\pi i k}\frac{\hbar\omega_c^*}{k_BT}\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{1}{e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}+1}}_{\text{contains the oscillatory contribution}}$$

$$\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}} \frac{1}{e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}+1} = \frac{\hbar\omega_c^*}{2\pi i k}\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{1}{e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}+1}\Bigg|_0^\infty$$

$$-\frac{\hbar\omega_c^*}{2\pi i k}\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{-1}{\left(e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}+1\right)^2}\frac{1}{k_BT}\, e^{\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}} =$$

$$\frac{-\hbar\omega_c^*}{2\pi i k}\frac{1}{e^{-\beta\tilde{\mu}_\sigma}+1} + \frac{1}{2\pi i k}\frac{\hbar\omega_c^*}{k_BT}\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{1}{4\cosh^2\left(\frac{\epsilon-\tilde{\mu}_\sigma}{2k_BT}\right)}$$

$$\int_0^\infty d\epsilon\, e^{2\pi i k \frac{\epsilon}{\hbar\omega_c^*}} \ln\left(1+e^{-\frac{\epsilon-\tilde{\mu}_\sigma}{k_BT}}\right) = \frac{\hbar\omega_c^*}{2\pi i k}\ln\left(1+e^{\frac{\tilde{\mu}_\sigma}{k_BT}}\right) +$$

$$\frac{1}{2\pi i k}\frac{\hbar\omega_c^*}{k_BT}\left(\frac{-\hbar\omega_c^*}{2\pi i k}\frac{1}{e^{-\beta\tilde{\mu}_\sigma}+1} + \frac{1}{2\pi i k}\frac{\hbar\omega_c^*}{k_BT}\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{1}{4\cosh^2\left(\frac{\epsilon-\tilde{\mu}_\sigma}{2k_BT}\right)}\right)$$

It is the last term that's responsible for oscillations.

$$\int_0^\infty d\epsilon\, e^{2\pi i k\frac{\epsilon}{\hbar\omega_c^*}}\frac{1}{4\cosh^2\left(\frac{\epsilon-\tilde{\mu}_\sigma}{2k_BT}\right)} =$$

$$k_BT\int_{-\frac{\tilde{\mu}_\sigma}{k_BT}}^{\infty} d\xi\, e^{2\pi i k\left(\frac{k_BT\xi+\tilde{\mu}_\sigma}{\hbar\omega_c^*}\right)}\frac{1}{4\cosh^2\left(\frac{1}{2}\xi\right)} =$$

$$k_BT\, e^{2\pi i k\frac{\tilde{\mu}_\sigma}{\hbar\omega_c^*}}\int_{-\frac{\tilde{\mu}_\sigma}{k_BT}}^{\infty} d\xi\, e^{2\pi i k\left(\frac{k_BT}{\hbar\omega_c^*}\right)\xi}\frac{1}{4\cosh^2\left(\frac{1}{2}\xi\right)}$$

Now, $\tilde{\mu}_\sigma = \mu - \frac{\hbar^2 k_z^2}{2m^*} - \sigma\frac{1}{2}\hbar\omega_c$. We see that for $\mu \gg \hbar\omega_c \sim \hbar\omega_c^*$,

$\tilde{\mu}_\sigma \sim \mu$ unless $\frac{\hbar^2 k_z^2}{2m^*} \sim \mu$. But the oscillatory term in front of the integral restricts $\frac{\hbar^2 k_z^2}{2m^*}$ to $\sim \frac{\hbar\omega_c^*}{k} \ll \mu$.

Therefore, we can replace the lower limit by $-\infty$.

The error can be bounded by replacing the oscillatory factor by 1 ⇒ the error is exponentially small in μ/k_BT.

$$\Rightarrow \quad k_BT\, e^{2\pi i k \frac{\tilde{\mu}_\sigma}{\hbar\omega_c^*}} \int_{-\infty}^{\infty} d\xi\, e^{2\pi i k \frac{k_BT}{\hbar\omega_c^*}\xi} \frac{1}{4\cosh^2\left(\frac{1}{2}\xi\right)}$$

The last integral can be done:

$$\int_{-\infty}^{\infty} d\xi\, e^{i\alpha\xi} \frac{1}{4\cosh^2\left(\frac{1}{2}\xi\right)} = \frac{\pi\alpha}{\sinh(\pi\alpha)}$$

$$\Rightarrow \quad k_BT\, e^{2\pi i k\frac{\mu}{\hbar\omega_c^*}}\, e^{-2\pi i k \frac{\left(\frac{\hbar^2k_z^2}{2m^*}\right)}{\hbar\omega_c^*}}\, e^{-i\pi k \frac{m^*}{m}\sigma} \frac{2\pi^2 k\cdot\left(\frac{k_BT}{\hbar\omega_c}\right)}{\sinh\left(2\pi^2 k\left(\frac{k_BT}{\hbar\omega_c}\right)\right)}$$

Note that: $\displaystyle\int_{-\infty}^{\infty} dx\, e^{i\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}\, e^{i\frac{\pi}{4}}$

$$\Omega_{osc} = -\cancel{k_BT}\frac{eB}{hc}\sum_{\sigma=\pm}\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\sum_{k=1}^{\infty} 2\,\frac{(-1)^k}{\hbar\omega_c^*}\, Re\Bigg[\frac{-1}{(2\pi k)^2}\cdot\left(\frac{\hbar\omega_c^*}{\cancel{k_BT}}\right)^2\cdot$$

$$\cancel{k_BT}\, e^{2\pi i k\frac{\mu}{\hbar\omega_c^*}}\, e^{-2\pi i k\frac{\left(\frac{\hbar^2k_z^2}{2m^*}\right)}{\hbar\omega_c^*}}\, e^{-i\pi k\frac{m^*}{m}\sigma}\frac{2\pi^2 k\cdot\left(\frac{k_BT}{\hbar\omega_c}\right)}{\sinh\left(2\pi^2 k\left(\frac{k_BT}{\hbar\omega_c}\right)\right)}\Bigg]$$

$$\Omega_{osc} = 4\,\frac{eB}{hc}\cdot\hbar\omega_c^*\cdot\int_{-\infty}^{\infty}\frac{dk_z}{2\pi}\sum_{k=1}^{\infty}\frac{(-1)^k}{4\pi^2k^2}\cos\left(\pi k\frac{m^*}{m}\right)\cdot$$

$$\cdot\, Re\left[e^{2\pi i k\frac{\mu}{\hbar\omega_c^*}}\,e^{-2\pi i k\frac{\left(\frac{\hbar^2k_z^2}{2m^*}\right)}{\hbar\omega_c^*}}\;\frac{2\pi^2k\cdot\left(\frac{k_BT}{\hbar\omega_c}\right)}{\sinh\left(2\pi^2k\left(\frac{k_BT}{\hbar\omega_c}\right)\right)}\right]$$

$$\frac{\sqrt{\cancel{\pi}}}{\sqrt{\cancel{2}\cancel{\pi}k\,\frac{\hbar^{\cancel{2}}}{\cancel{2}m^*}\,\frac{1}{\cancel{\hbar}\omega_c^*}}}\,e^{-i\frac{\pi}{4}} = \frac{e^{-i\frac{\pi}{4}}}{\sqrt{k\,\frac{\hbar\cancel{m^*}c}{\cancel{m^*}eB}}} = \sqrt{\frac{2\pi}{k}}\sqrt{\frac{eB}{hc}}\,e^{-i\frac{\pi}{4}}$$

$$\Omega_{osc} = \frac{1}{\sqrt{2\pi}}\left(\frac{eB}{hc}\right)^{\frac{3}{2}}\cdot\cancel{\hbar\omega_c^*}\cdot\sum_{k=1}^{\infty}\frac{(-1)^k}{\cancel{\pi^2}k^{5/2}}\cos\left(\pi k\frac{m^*}{m}\right)\cdot\cos\left(2\pi k\frac{\mu}{\hbar\omega_c^*}-\frac{\pi}{4}\right)\cdot$$

$$\cdot\,\frac{2\cancel{\pi}^2k\cdot\left(\frac{k_BT}{\cancel{\hbar\omega_c^*}}\right)}{\sinh\left(2\pi^2k\left(\frac{k_BT}{\hbar\omega_c^*}\right)\right)}$$

$$= \frac{eB}{hc}\sqrt{\frac{eB}{\hbar c}}\,\frac{\cancel{2}k_BT}{\cancel{2}\pi}\sum_{k=1}^{\infty}\frac{(-1)^k}{k^{3/2}}\cos\left(\pi k\frac{m^*}{m}\right)\frac{\cos\left(2\pi k\frac{\mu}{\hbar\omega_c^*}-\frac{\pi}{4}\right)}{\sinh\left(2\pi^2k\,\frac{k_BT}{\hbar\omega_c^*}\right)}$$

$$= k_BT\,\frac{1}{2\pi^2}\left(\frac{\hbar eB}{\hbar^2c}\right)^{3/2}\sum_{k=1}^{\infty}\frac{(-1)^k}{k^{3/2}}\cos\left(\pi k\frac{m^*}{m}\right)\frac{\cos\left(2\pi k\frac{\mu}{\hbar\omega_c^*}-\frac{\pi}{4}\right)}{\sinh\left(2\pi^2k\,\frac{k_BT}{\hbar\omega_c^*}\right)}$$

$$= \frac{k_BT}{2\pi^2\hbar^3}\left(m^*\hbar\omega_c^*\right)^{3/2}\sum_{k=1}^{\infty}\frac{(-1)^k}{k^{3/2}}\cos\left(\pi k\frac{m^*}{m}\right)\frac{\cos\left(2\pi k\frac{\mu}{\hbar\omega_c^*}-\frac{\pi}{4}\right)}{\sinh\left(2\pi^2k\,\frac{k_BT}{\hbar\omega_c^*}\right)}$$

$$\boxed{\Omega_{osc} = \frac{\sqrt{2}}{\pi^2} \frac{k_B T}{\hbar^3} \left(m^* \frac{\hbar \omega_c^*}{2} \right)^{3/2} \sum_{k=1}^{\infty} \frac{(-1)^k}{k^{3/2}} \cos\left(\pi k \frac{m^*}{m}\right) \frac{\cos\left(2\pi k \frac{\mu}{\hbar\omega_c^*} - \frac{\pi}{4}\right)}{\sinh\left(2\pi^2 k \frac{k_B T}{\hbar \omega_c^*}\right)}}$$

*For comprehensive treatise see

D. Shoenberg "Magnetic oscillations in metals"

Free energy of an ideal gas in the classical limit ($\xi \to 0$):

(fermions)

$$\ln \mathcal{Z} = -N \ln \xi + \sum_{j=0}^{\infty} \ln\left(1 + \xi e^{-\beta \epsilon_j}\right) \simeq -N \ln \xi + \xi \sum_{j=0}^{\infty} e^{-\beta\epsilon_j}$$

$$N = \sum_{j=0}^{\infty} \frac{1}{\frac{1}{\xi} e^{\beta \epsilon_j} + 1} \simeq \xi \sum_{j=0}^{\infty} e^{-\beta \epsilon_j}$$

$$\Rightarrow \ln \mathcal{Z} \simeq -N \ln\left(\frac{N}{\sum\limits_{j=0}^{\infty} e^{-\beta\epsilon_j}}\right) + N = -\frac{F}{k_B T}$$

Let $\sum\limits_{j=0}^{\infty} e^{-\beta\epsilon_j} \equiv \zeta \hookleftarrow$ zeta

$$\boxed{F = k_B T \cdot N \left(\ln \frac{N}{\zeta} - 1\right)}$$

If we have mixed ideal gas, made out of R "species," then

$$F = \sum_{r=1}^{R} k_B T N_r \left(\ln\left(\frac{N_r}{\zeta_r}\right) - 1 \right) ; \quad \sum_r N_r = N$$

For example, $R=2$: $N_2 = N - N_1$ and

$$F = k_B T \left(N_1 \ln \frac{N_1}{\xi_1} - N_1 + N_2 \ln \frac{N_2}{\xi_2} - N_2 \right)$$

$$F = k_B T \left(N_1 \ln \frac{N_1}{\xi_1} + (N - N_1) \ln \frac{N - N_1}{\xi_2} - N \right)$$

$$\frac{\partial F}{\partial N_1} = k_B T \left(\ln \frac{N_1}{\xi_1} + 1 - \ln \frac{N - N_1}{\xi_2} - 1 \right) = k_B T \left(\ln \frac{N_1}{\xi_1} - \ln \frac{N_2}{\xi_2} \right) = 0$$

By setting $\frac{\partial F}{\partial N_1}$ to zero we are seeking such values of F that extremize the free energy; in such combined system, "N_2" species can "transmute" to "N_1" species.

$$\Rightarrow \quad k_B T \ln \frac{N_1}{\xi_1} = k_B T \ln \frac{N_2}{\xi_2} \quad , \text{ but } \quad \frac{N_{1,2}}{\xi_{1,2}} = e^{\frac{\mu_{1,2}}{k_B T}}$$

Therefore: $\mu_1 = \mu_2$.

So, if we allow the particles to "transmute" into each other, then the condition for thermal equilibrium is that the chemical potentials must be the same.

For chemical reactions occuring in a gas phase, such as

$$2 H_2 + O_2 \rightleftarrows 2 H_2O$$

we can use the same principle. Clearly, we have 3 "species" in this example

If, due to the above chemical reaction, the number of O_2 molecules increases by λ, then the number of H_2 molecules increases by 2λ and the number of H_2O molecules decreases by 2λ.

$$\left.\begin{array}{llll} (1) & O_2 & \Rightarrow & b_1 = 1 \\ (2) & H_2 & \Rightarrow & b_2 = 2 \\ (3) & H_2O & \Rightarrow & b_3 = -2 \end{array}\right\} \quad \delta N_r = b_r \lambda$$

In this notation, the chemical reaction is $\sum_{r=1}^{R} b_r B_r = 0.$

Let λ be infinitesimal. Then,

$$\delta F = \sum_{r=1}^{R} k_B T \left[\lambda b_r \left(\ln\left(\frac{N_r}{\xi_r}\right) - 1 \right) + \cancel{N_r} \frac{\lambda b_r}{\cancel{N_r}} \right]$$

$$= \lambda \cdot k_B T \cdot \sum_{r=1}^{R} b_r \ln \frac{N_r}{\xi_r} = \lambda \sum_{r=1}^{R} b_r \mu_r = 0$$

$$\Rightarrow \quad \boxed{b_1 \mu_1 + b_2 \mu_2 + \dots + b_R \mu_R = 0}$$

Note that quite generally, $\frac{\partial \ln Z}{\partial N} = -\ln \xi = -\ln e^{\frac{\mu}{k_B T}} = -\frac{\mu}{k_B T}$

$$Z = e^{-F/k_B T} \quad \Rightarrow \quad \frac{\partial F}{\partial N} = \mu .$$

Moreover, for multiple species, which cannot react (transmute) among each other:

$$\ln Z = \sum_{m=1}^{M} \left(-N_m \ln \xi_m + \sum_{j=0}^{\infty} \ln\left(1 + \xi_m e^{-\beta \epsilon_j^{(m)}}\right) \right)$$

$$\frac{\partial F}{\partial N_m} = \mu_m \Rightarrow \text{for } F(T, V, N_1, N_2, \dots, N_R) \text{ consider}$$

$$\Delta F = \sum_{r=1}^{R} \frac{\partial F}{\partial N_r} b_r = \sum_{r=1}^{R} \mu_r b_r$$

In a thermodynamic equilibrium of a chemical reaction then

$$\Delta F = 0 = \sum_{r=1}^{R} k_B T \left(b_r \ln N_r - b_r \ln \xi_r \right)$$

So, let

$$\Delta F_0 = - k_B T \sum_{r=1}^{R} b_r \ln \xi_r$$

then

$$0 = \Delta F_0 + k_B T \ln \left[\prod_{r=1}^{R} N_r^{b_r} \right]$$

$$\Rightarrow \boxed{N_1^{b_1} \cdot N_2^{b_2} \cdots N_R^{b_R} = e^{-\frac{\Delta F_0}{k_B T}}}$$

Law of mass action

for $2H_2 + O_2 \rightleftarrows 2H_2O$

$$\frac{N_{H_2O}^2}{N_{H_2}^2 \; N_{O_2}} = K_N(T, V)$$

equilibrium reaction constant

Crude model for rotational modes of a diatomic molecule:

$$\Rightarrow \quad \underset{\substack{\uparrow \\ \text{moment of inertia}}}{I} = (2m)\, b^2 \quad \text{and} \quad \hat{\mathcal{H}}_{rot} = \frac{\hat{\vec{L}}^2}{2I}$$

$$E_{rot} = \frac{\hbar^2}{2I}\, l(l+1)$$ for $l = 0, 1, 2, \ldots$

each l is $2l+1$ fold degenerate due to the azimuthal q. #.

$(-l, -l+1, \ldots, 0, \ldots l-1, l)$

For a dilute concentration of such molecules:

$$F = k_B T \left(N \ln \left[\frac{N}{\sum\limits_{j=0}^{\infty} e^{-\beta \epsilon_j}} \right] - N \right)$$

Now,

$$\sum_{j=0}^{\infty} e^{-\beta \epsilon_j} = V \int \frac{d^3k}{(2\pi)^3} \sum_{l=0}^{\infty} (2l+1)\, e^{-\beta \frac{\hbar^2 k^2}{2m}}\, e^{-\beta \frac{\hbar^2 l(l+1)}{2I}}$$

Let $\Theta_{rot} = \frac{\hbar^2}{2I} = \frac{\hbar^2}{4mb^2}$. This sets the energy scale to which we can compare $k_B T$.

For $\Theta_{rot} >> k_B T$, the rotational degree of freedom is frozen out and:

$$F \simeq k_B T \left(N \ln \left(\frac{N}{V \int \frac{d^3k}{(2\pi)^3}\, e^{-\beta \frac{\hbar^2 k^2}{2m}}} \right) - N \right)$$

For $\Theta_{rot} << k_B T$, the rot. degrees of freedom are excited and we can approximate the sum by an integral.

$$F \tilde{=} k_B T \left(N \ln \left[\frac{N}{V \int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}} \int_0^\infty dx (2x+1) e^{-\beta \Theta_{rot} x(x+1)}} \right] - N \right)$$

Let $y = x(x+1)$ then $dy = (2x+1)dx \Rightarrow$

$$F \tilde{=} k_B T \left(N \ln \left[\frac{N}{V \int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}} \int_0^\infty dy\, e^{-\beta \Theta_{rot} y}} \right] - N \right)$$

Recall, $$\int \frac{d^3k}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}} = \frac{\sqrt{\pi}}{4\pi^2} \left(\frac{2m}{\hbar^2} k_B T \right)^{3/2}$$

and $$\int_0^\infty dy\, e^{-\beta \Theta_{rot} y} = \frac{k_B T}{\Theta_{rot}}$$

The internal energy is $\mathcal{U} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\left(-\frac{F}{k_B T} \right)$

$$\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T} = \frac{1}{k_B} \frac{\partial \frac{1}{\beta}}{\partial \beta} \frac{\partial}{\partial T} = -\frac{1}{k_B \beta^2} \frac{\partial}{\partial T} = -k_B T^2 \frac{\partial}{\partial T}$$

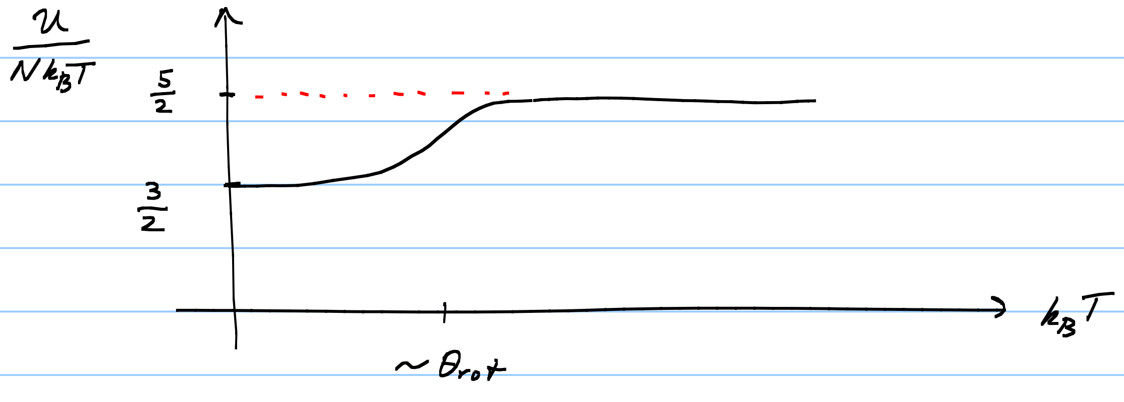
$$\frac{F}{k_BT} \simeq N \ln\left[\frac{\frac{N}{V}}{\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}k_BT\right)^{3/2}\frac{\sqrt{\pi}}{2}}\right] - N \qquad \text{if} \quad k_BT \ll \Theta_{rot}$$

$\Rightarrow$

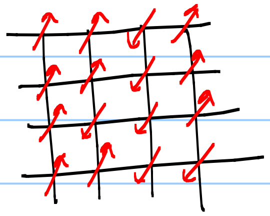
$$\mathcal{U} = -k_BT^2\frac{\partial}{\partial T}\left(\frac{F}{k_BT}\right) \simeq -k_BT^2\left(-N\frac{\partial}{\partial T}\ln T^{3/2}\right) = \frac{3}{2}Nk_BT$$

$$\frac{F}{k_BT} \simeq N \ln\left[\frac{\frac{N}{V}}{\frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}k_BT\right)^{3/2}\frac{\sqrt{\pi}}{2}\quad\frac{k_BT}{\Theta_{rot}}}\right] - N \qquad \text{if} \quad k_BT \gg \Theta_{rot}$$

$\Rightarrow \quad \mathcal{U} \simeq \frac{5}{2}Nk_BT$ $\qquad$ * equipartition (classical ↔ dilute)



Ising model of a ferromagnet:



$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_i s_i$$

$$s_i s_j = \left(s_i - \langle s_i \rangle + \langle s_i \rangle \right)\left(s_j - \langle s_j \rangle + \langle s_j \rangle \right)$$

$$= \langle s_i \rangle \langle s_j \rangle + \left(s_i - \langle s_i \rangle \right) \langle s_j \rangle + \langle s_i \rangle \left(s_j - \langle s_j \rangle \right) + \left(s_i - \langle s_i \rangle \right)\left(s_j - \langle s_j \rangle \right)$$

if the deviation from average is small, then we may be justified in neglecting the last term.

So, $s_i s_j \simeq - \langle s_i \rangle \langle s_j \rangle + s_i \langle s_j \rangle + \langle s_i \rangle s_j$

Assume the system remains translationally invariant.
Then $\langle s_i \rangle = \langle s \rangle$. There are DN bonds in D-dim. cubic lattice.

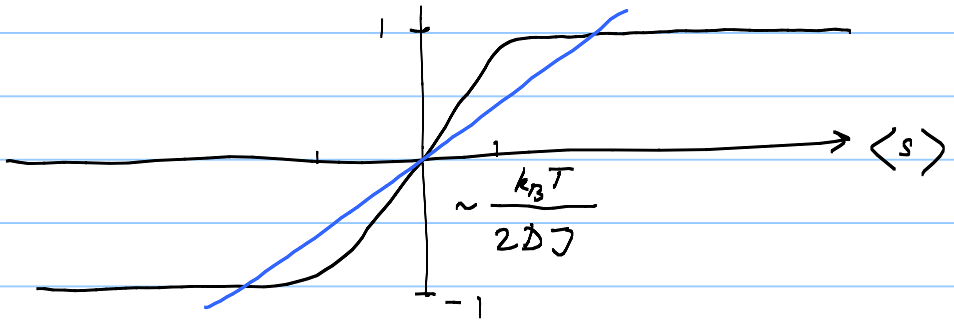
$$\mathcal{Z} = \sum_{s_1 = \pm} \sum_{s_2 = \pm} \cdots \sum_{s_N = \pm} e^{-\beta \mathcal{H}} \simeq e^{-\frac{JD}{k_B T} N \langle s \rangle^2} \cdot \left(\sum_{s = \pm} e^{\frac{2JD}{k_B T} \langle s \rangle s} \right)^N$$

$$= e^{-\frac{DNJ}{k_B T} \langle s \rangle^2} e^{N \ln \left[2 \cosh \left(\frac{2DJ \langle s \rangle + B}{k_B T} \right) \right]}$$

self-consistency: $\frac{1}{N}\frac{1}{Z}\frac{\partial Z}{\partial(\beta B)}\Big|_{B=0} = \langle s\rangle$

coordination number

$$\boxed{\tanh\left(\frac{2DJ\langle s\rangle}{k_B T}\right) = \langle s\rangle}$$



At low T, there are three solutions, $\langle s\rangle = 0$ is free energy maximum ⇒ two nontrivial solutions ⇒ spontan. magnetization

At high T, only $\langle s\rangle = 0$ remains.

⇒ there is a phase transition (when the slopes match)

$$\frac{2DJ}{k_B T_c}\langle\cancel{s}\rangle = \langle\cancel{s}\rangle \Rightarrow k_B T_c = 2DJ$$

Now, $\tanh x \simeq x - \frac{1}{3}x^2 + \ldots$

Assume that we deviate a little bit away from T_c.

Then, $$\tanh\left(\frac{2DJ\langle s\rangle}{k_B T}\right) = \langle s\rangle$$

$$\Rightarrow \quad \frac{2DJ\langle s\rangle}{k_B(T_c+\delta T)} - \frac{1}{3}\left(\frac{2DJ\langle s\rangle}{k_B(T_c+\delta T)}\right)^3 \simeq \langle s\rangle$$

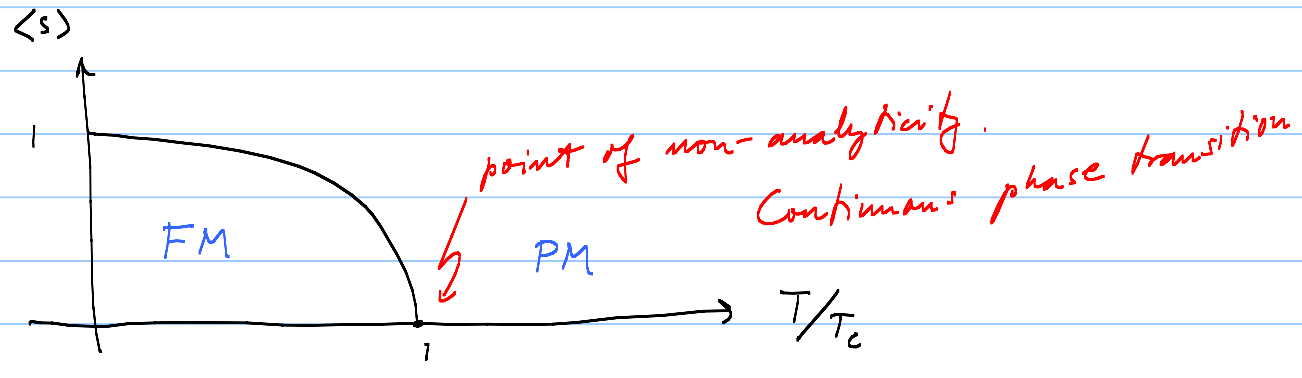
$$\frac{T_c}{T_c+\delta T} - \frac{\langle s\rangle^2}{3}\left(\frac{T_c}{T_c+\delta T}\right)^3 = 1$$

$$1 - \frac{\langle s\rangle^2}{3}\left(\frac{1}{1+\frac{\delta T}{T_c}}\right)^2 = \frac{T_c+\delta T}{T_c} = 1 + \frac{\delta T}{T_c}$$

mean-field exponent

$$\langle s\rangle^2 \simeq -3\,\frac{\delta T}{T_c} \quad \Rightarrow \quad \langle s\rangle = \sqrt{3}\left(\frac{T_c-T}{T_c}\right)^{\frac{1}{2}} \quad \text{for } T<T_c$$

$$\langle s\rangle = 0 \qquad \text{for } T \geq T_c$$



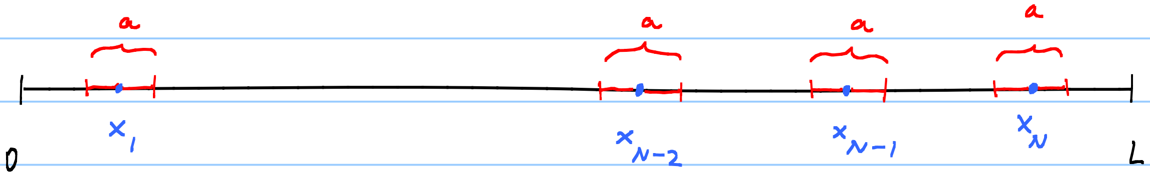
Classical hard sphere gas in 1D (Tonks gas) + Mayer expansion

Note Title 4/7/2015

$$u(x_i - x_j) = \begin{cases} \infty & \text{if } |x_i - x_j| < a \\ 0 & \text{if } |x_i - x_j| \geq a \end{cases}$$

$$Z = \frac{1}{N!}\frac{1}{h^N}\left[\int_{-\infty}^{\infty} dp \; e^{-\frac{p^2}{2m}\frac{1}{k_BT}}\right]^N \int dx_1 \int dx_2 \cdots \int dx_N \; e^{-\frac{1}{k_BT}\sum_{i<j} u(x_i - x_j)}$$

$$= \frac{1}{N!}\left(\frac{\sqrt{2m\,k_BT}}{h}\sqrt{\pi}\right)^N Q_N = \frac{1}{N!}\left(\frac{k_BT \;\; m}{2\pi \cdot \hbar^2}\right)^{\frac{N}{2}} Q_N(T,L) \; .$$



clearly $\quad x_{N-1} + a \leq x_N \leq L - \frac{a}{2} = Y_N$

$$x_{N-2} + a \leq x_{N-1} \leq L - \frac{3a}{2} = Y_{N-1}$$

$$x_{N-3} + a \leq x_{N-2} \leq L - \frac{5a}{2} = Y_{N-2}$$

$$\vdots$$

$$x_{j-1} + a \leq x_j \leq L - \frac{a}{2} - (N-j)a = Y_j$$

$$\vdots$$

$$\frac{a}{2} \leq x_1 \leq L + \frac{a}{2} - Na = Y_1$$

There are $N!$ possible permutations among the labels. This cancels the $1/N!$ pre-factor.

So,

$$Z = \left(\frac{k_B T \quad m}{2\pi \cdot \hbar^2}\right)^{\frac{N}{2}} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-2}+a}^{Y_{N-1}} dx_{N-1} \int_{x_{N-1}+a}^{Y_N} dx_N$$

$$= \left(\frac{m \cdot k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-2}+a}^{Y_{N-1}} dx_{N-1} \overset{Y_{N-1}}{\left(Y_N - x_{N-1} - a\right)}$$

$$= \left(\frac{m \ k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2} \left[\frac{-1}{2}\left(Y_{N-1} - x_{N-1}\right)^2\right]_{x_{N-2}+a}^{Y_{N-1}}$$

$$= \left(\frac{m \ k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2} \ \frac{1}{2}\left(Y_{N-1} - x_{N-2} - a\right)^2$$

$$= \left(\frac{m \ k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2} \ \frac{1}{2}\left(Y_{N-2} - x_{N-2}\right)^2$$

$$= \left(\frac{m \ k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-4}+a}^{Y_{N-3}} dx_{N-3} \ \left(\frac{-1}{2 \cdot 3}\right)\left(Y_{N-2} - x_{N-2}\right)^3 \Bigg|_{x_{N-3}+a}^{Y_{N-2}}$$

$$= \left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \int_{x_1+a}^{Y_2} dx_2 \int_{x_2+a}^{Y_3} dx_3 \cdots \int_{x_{N-4}+a}^{Y_{N-3}} dx_{N-3}\, \frac{1}{2\cdot 3} \left(Y_{N-3} - x_{N-3}\right)^3$$

for $j = N-\ell$ it is

$$\left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{\frac{a}{2}}^{Y_1} dx_1 \cdots\cdot \int_{x_{N-\ell-1}+a}^{Y_{N-\ell}} dx_{N-\ell} \qquad \frac{1}{1\cdot 2\cdot 3\cdots \ell} \left(Y_{N-\ell} - x_{N-\ell} \right)^{\ell}$$

let $\ell = N-1$ then

$$\left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \int_{a/2}^{Y_1} dx_1 \quad \frac{1}{(N-1)!} \left(Y_1 - x_1 \right)^{N-1} =$$

$$\left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \frac{1}{N!} \quad (-1) \left(Y_1 - x_1 \right)^{N} \Bigg|_{\frac{a}{2}}^{Y_1} =$$

$$\left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \frac{1}{N!} \left(Y_1 - \frac{a}{2} \right)^{N} = \left(\frac{m\, k_B T}{2\pi \hbar^2}\right)^{N/2} \frac{1}{N!} \left(L - Na \right)^{N} = Z$$

$$\ln Z = -\frac{F}{k_B T} \; ; \qquad dF = -S\,dT - P\,dL \Rightarrow -\frac{\partial F}{\partial L} = P$$

$$P = \frac{\partial}{\partial L}\left(k_B T \ln Z \right) = k_B T \frac{\partial}{\partial L}\left(N \ln (L - Na) \right) = \boxed{\frac{N\, k_B T}{L - Na} = P}$$

excluded vol. ↗

Attempt to build systematic expansion in powers of $\frac{N}{V}$. If the gas is dilute, then we expect analytic expansion in N/V.

$$Z_N = \frac{1}{N!}\int \prod_{j=1}^{N} \frac{d^3p_j \, d^3r_j}{h^3} \, e^{-\sum_{j=1}^{N} \frac{p_j^2}{2m}\frac{1}{k_BT}} \, e^{-\sum_{i>j} u(r_i-r_j)/k_BT}$$

Planck's constant

$$= \frac{1}{N!}\frac{1}{h^{3N}}\left[\int_0^\infty dp\,p^2\, 4\pi\, e^{-\frac{p^2}{2mk_BT}}\right]^N \int \prod_{j=1}^{N} d^3r_j \, e^{-\frac{1}{k_BT}\sum_{i>j} u(r_i-r_j)}$$

$$= \frac{1}{N!}\left(\frac{2\pi m k_BT}{h^2}\right)^{\frac{3N}{2}} \int \prod_{j=1}^{N} d^3r_j \, e^{-\frac{1}{k_BT}\sum_{i>j} u(r_i-r_j)}$$

$u(r)$ need not be small for some values of r. Think about the hard-core repulsion of two ^{4}He atoms. Therefore, expansion in powers of u is not justified. We should attempt expanding in powers of density, starting from the dilute limit (i.e. ideal gas).

On the other hand, consider $f_{ij} = e^{-\beta u(r_i-r_j)} - 1$. This is -1 when u is large and 0 when u is small $\Rightarrow$ it is bounded. Moreover, if u is short ranged, then so is f.

$$\int \prod_{j=1}^{N} d^3r_j \, e^{-\frac{1}{k_BT}\sum_{i>j} u(r_i-r_j)} = \int \prod_{j=1}^{N} d^3r_j \, (1+f_{ij})$$

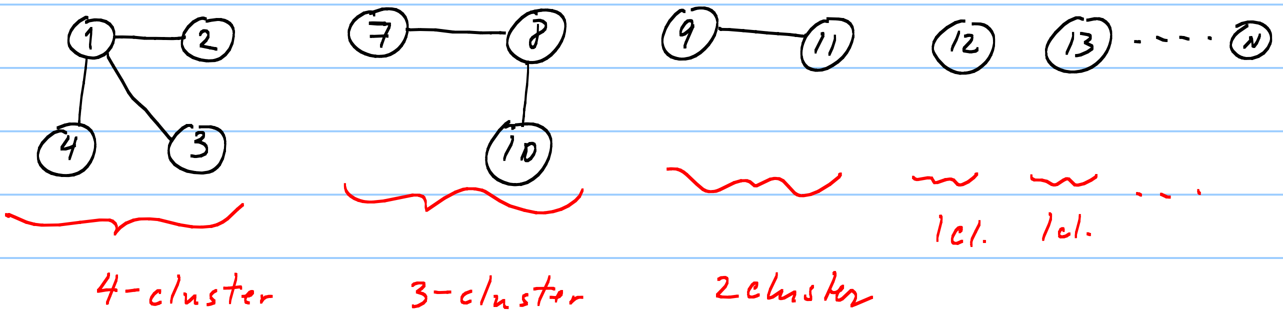
Now, $\int \prod_{j=1}^{N} d^3r_j \, (1+f_{ij}) =$

$$\int \left(\prod_{j=1}^{N} d^3r_j\right)(1+f_{12})(1+f_{13})(1+f_{14})\cdots(1+f_{1j})\cdots(1+f_{1N})$$
$$(1+f_{23})(1+f_{24})\cdots(1+f_{2j})\cdots(1+f_{2N})$$
$$(1+f_{34})\cdots(1+f_{3j})\cdots(1+f_{3N})$$
$$\ddots \qquad \vdots$$
$$(1+f_{N-1,N})$$

Every term can be represented by a labeled graph.
For example, the term

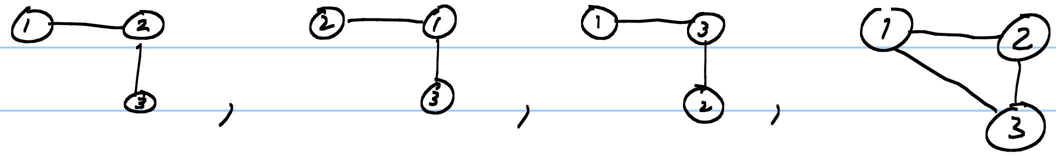
$$\int d^3r_1\, d^3r_2 \cdots d^3r_N \quad f_{12}\, f_{13}\, f_{14} \quad f_{78}\, f_{8\,10} \quad f_{9\,11}$$

$$\Updownarrow$$



Considering an arbitrary term in the expansion $\prod_{i<j}(1+f_{ij})$, we can ask how many 1-clusters does it contain. Denote this by m_1. Then, how many 2-clusters; m_2. How many 3-clusters; m_3. etc.

Note that although 1-and 2-clusters are unique ① & ②—③, starting from 3-clusters, there are several ones:

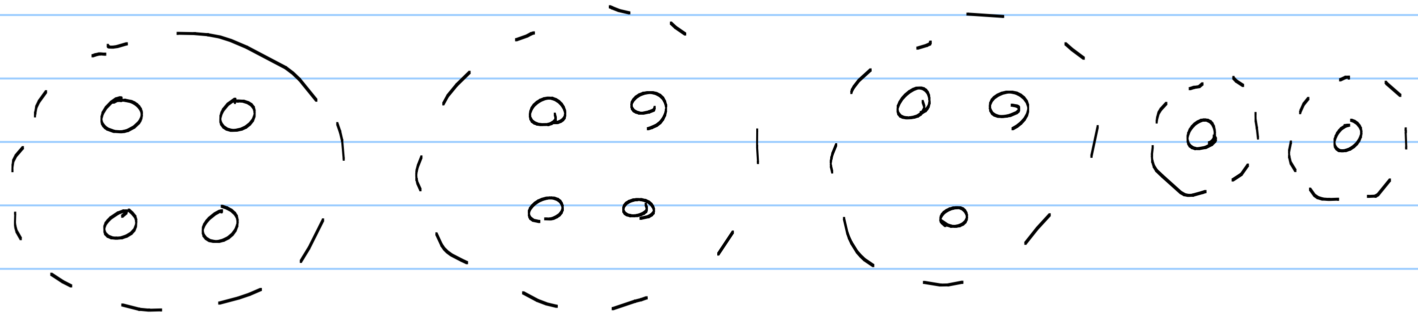


Clearly, for every term, we must have

$$1 \cdot m_1 + 2 \cdot m_2 + 3 m_3 + \dots + N m_N = N$$

$$\Rightarrow \quad \sum_{l=1}^{N} l \, m_l = N$$

Consider now, erasing labels on the vertices and the bonds on the clusters. E.g.:

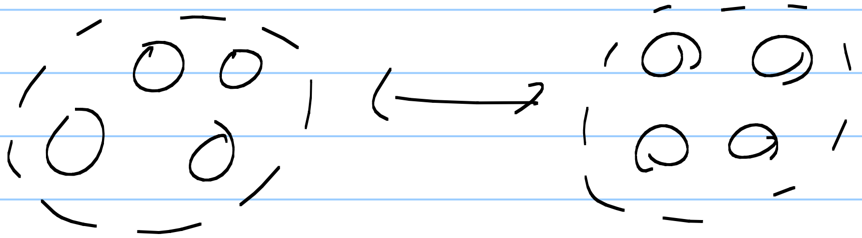


Here we have $m_1 = N-11$, $m_2 = 0$, $m_3 = 1$, $m_4 = 2$, $m_5 = 0 \dots$

How many different ways are there to label the dots? $N!$

If we do not want to count permuted labels WITHIN the cluster as distinct, then there are $\dfrac{N!}{(1!)^{m_1}(2!)^{m_2}\cdots(l!)^{m_l}\cdots}$ ways to label the dots.

Also, we do not want to count as separate graphs obtained by exchanging all labels within one l-cluster and another l-cluster :



$$\frac{N!}{(1!)^{m_1}(2!)^{m_2}(3!)^{m_3}\cdots(l!)^{m_l}\cdots(N!)^{m_N}} \qquad \frac{1}{m_1!\,m_2!\cdots m_l!\cdots m_N!}$$

So, this is the no. of ways to label $\{m_l\}$ clusters, ignoring label order within a cluster and among equal l-clusters.

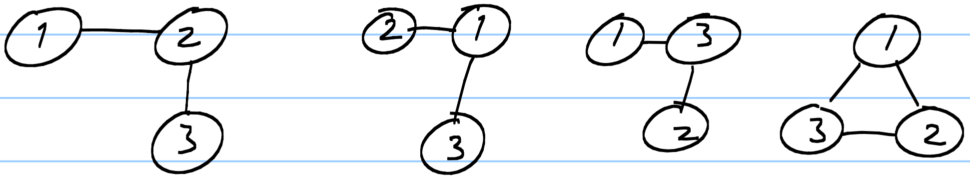
Now we ask how many distinct ways are there to assign bonds, such that they correspond to distinct terms in

$$\int\left(\prod_{i=1}^{N} d^D r_i\right) \prod_{i>j}(1+f_{ij}).$$

1-cluster : ① unique way

2-cluster : ② unique way

3-cluster :



etc. i.e. 4-ways

Let $b_1 = \int d^3r = V$

$$b_2 = \int d^3r_1\, d^3r_2\, f_{12} = \int d^3R \int d^3r \left(e^{-\beta u(r)} - 1\right)$$

$$= V \int d^3r \left(e^{-\beta u(r)} - 1\right)$$

$$b_3 = \int d^3r_1\, d^3r_2\, d^3r_3 \left(f_{12} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{13} f_{23}\right)$$

$$= 3V \left[\int d^3r \left(e^{-\beta u(r)} - 1\right)\right]^2 +$$

$$V \int d^3r_1\, d^3r_2 \left(e^{-\beta u(r_1)} - 1\right)\left(e^{-\beta u(r_1 - r_2)} - 1\right)\left(e^{-\beta u(r_2)} - 1\right)$$

$\vdots$

Then $\int \left(\prod_{j=1}^{N} d^3r_j\right) \prod_{i<j} \left(1 + f_{ij}\right) =$

$$\sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \cdots \sum_{m_\ell=0}^{\infty} \cdots \frac{N!}{(1!)^{m_1}(2!)^{m_2}\cdots(\ell!)^{m_\ell}} \frac{1}{m_1!\, m_2! \cdots m_\ell! \cdots}$$

$$\cdot \left(b_1^{m_1} b_2^{m_2} \cdots b_\ell^{m_\ell} \cdots\right) \delta_{N, \sum_{j=1}^{\infty} j m_j}$$

we set $N \to \infty$ here because once j exceeds N, the δ-fcn kills its contribution

So,

$$\oint_C \frac{d\xi}{2\pi i} \frac{1}{\xi^{N+1}} \; N! \prod_{\ell=1}^{\substack{\infty \\ \downarrow \\ N}} \left[\sum_{m_\ell=0}^{\infty} \left(\frac{\xi^\ell b_\ell}{\ell!} \right)^{m_\ell} \frac{1}{m_\ell!} \right] =$$

$$\oint_C \frac{d\xi}{2\pi i} \frac{N!}{\xi^{N+1}} \, e^{\sum_{\ell=1}^{N} \frac{\xi^\ell b_\ell}{\ell!}} \quad ; \quad b_\ell = V \bar{b}_\ell$$

where $\bar{b}_\ell$ is intrinsic (indep. of V as $V \to \infty$)

Seek saddle point :

$$\frac{(N+1)}{\xi_0} = \sum_{\ell=1}^{N} \frac{V \bar{b}_\ell}{(\ell-1)!} \xi_0^{\ell-1}$$

$$\boxed{\frac{N}{V} \simeq \sum_{\ell=1}^{N} \frac{\bar{b}_\ell}{(\ell-1)!} \xi_0^{\ell}}$$

$$\ln \mathcal{Z}_N \simeq \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} e^{-(N+1)\ln \xi_0} \, e^{V \sum_{\ell=1}^{N} \bar{b}_\ell \frac{\xi_0^\ell}{\ell!}} \right]$$

$$= \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) - (N+1) \ln \xi_0 + V \sum_{\ell=1}^{N} \bar{b}_\ell \frac{\xi_0^\ell}{\ell!} = -\frac{F}{k_B T}$$

$$dF = -S\,dT - P\,dV \Rightarrow -\frac{\partial F}{\partial V} = P$$

So, $P = k_B T \dfrac{\partial \ln Z}{\partial V} =$

$$k_B T \frac{\partial}{\partial V}\left(-N \ln \xi_0 + V \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{l!} \right) =$$

$$k_B T \left(-N \frac{1}{\xi_0} \frac{\partial \xi_0}{\partial V} + \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{l!} + V \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l-1}}{(l-1)!} \frac{\partial \xi_0}{\partial V} \right)$$

But $\dfrac{N}{V} = \displaystyle\sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{(l-1)!} \Rightarrow \frac{N}{\xi_0} = V \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l-1}}{(l-1)!}$

So,

$$P = k_B T \left(-V \sum_{l=1}^{N} \cancel{b_l \frac{\xi_0^{\,l-1}}{(l-1)!}} \frac{\partial \xi_0}{\partial V} + \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{l!} + V \sum_{l=1}^{N} \cancel{b_l \frac{\xi_0^{\,l-1}}{(l-1)!}} \frac{\partial \xi_0}{\partial V} \right)$$

$$\Rightarrow \frac{P}{k_B T} = \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{l!}$$

So, $$\boxed{P = k_B T \sum_{l=1}^{N} b_l \frac{\xi_0^{\,l}}{l!}}$$

$$\boxed{\frac{N}{V} \simeq \sum_{l=1}^{N} \frac{b_l}{(l-1)!} \xi_0^{\,l}}$$

$b_1 = 1 \Rightarrow$ to this order

$$\frac{N}{V} = \xi_0 \quad \text{and} \quad \frac{P}{k_B T} = b_1 \xi_0 = \frac{N}{V} \quad \swarrow \text{ ideal gas eq. of state}$$

$$b_2 = \int d^3r \left(e^{-\beta u(r)} - 1 \right) \quad \text{so}$$

0th order solution

$$\frac{N}{V} = \xi_0 + b_2 \xi_0^2 \; ; \quad \text{Let} \quad \xi_0 = \frac{N}{V} + \delta\xi$$

$\Rightarrow$

$$\frac{N}{V} = \frac{N}{V} + \delta\xi + b_2 \left(\frac{N}{V} + \delta\xi \right)^2 \simeq \frac{N}{V} + \delta\xi + b_2 \left(\frac{N}{V} \right)^2 + \ldots$$

$$0 = \delta\xi + b_2 \left(\frac{N}{V} \right)^2 \Rightarrow \delta\xi = - b_2 \left(\frac{N}{V} \right)^2$$

So, to this order $\xi_0 = \frac{N}{V} - b_2 \left(\frac{N}{V} \right)^2$

Substituting to the equation for pressure we have:

$$\frac{P}{k_B T} = \frac{N}{V} - b_2 \left(\frac{N}{V}\right)^2 + \frac{1}{2} b_2 \left(\frac{N}{V}\right)^2 + \ldots$$

$$= \frac{N}{V} - \frac{b_2}{2} \left(\frac{N}{V}\right)^2 + \ldots$$

3rd order: Let $\xi_0 = \frac{N}{V} - b_2 \left(\frac{N}{V}\right)^2 + B \left(\frac{N}{V}\right)^3$

so, substitute to

$$\frac{N}{V} \simeq \sum_{l=1}^{N} \frac{b_l}{(l-1)!} \xi_0^l$$

$$\simeq \frac{N}{V} - b_2 \left(\frac{N}{V}\right)^2 + B \left(\frac{N}{V}\right)^3 + b_2 \left(\left(\frac{N}{V}\right)^2 - 2 b_2 \left(\frac{N}{V}\right)^3\right) + \frac{b_3}{2} \left(\frac{N}{V}\right)^3$$

$$0 = \left(B - 2 b_2^2 + \frac{b_3}{2}\right) \left(\frac{N}{V}\right)^3 \Rightarrow B = 2 b_2^2 - \frac{1}{2} b_3$$

$$\frac{P}{k_B T} = \sum_{l=1}^{N} b_l \frac{\xi_0^l}{l!} \simeq \frac{N}{V} - \frac{1}{2} b_2 \left(\frac{N}{V}\right)^2 + \left(2 b_2^2 - \frac{1}{2} b_3\right) \left(\frac{N}{V}\right)^3$$

$$+ \frac{1}{2} b_2 \left(\left(\frac{N}{V}\right)^2 - 2 b_3 \left(\frac{N}{V}\right)^3\right) + \frac{1}{6} b_3 \left(\frac{N}{V}\right)^3$$

$$\frac{P}{k_B T} \simeq \frac{N}{V} - \frac{1}{2} b_2 \left(\frac{N}{V}\right)^2 + \left(b_2^2 - \frac{1}{3} b_3\right) \left(\frac{N}{V}\right)^3 + \mathcal{O}\left(\left(\frac{N}{V}\right)^4\right)$$

$$b_2 = \int d^3 r \left(e^{-\beta u(r)} - 1\right) ; \quad b_3 = 3 b_2^2 + \frac{1}{V} \int d^3 r_1 \, d^3 r_2 \, d^3 r_3 \, f_{12} f_{13} f_{23}$$

So,

$$\frac{P}{k_B T} = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \dots$$

$$B_2(T) = -\frac{1}{2} b_2$$

$$B_3(T) = -\frac{1}{3V}\int d^3r_1\, d^3r_2\, d^3r_3\; f_{12} f_{13} f_{23}$$

$$b_2 = \int d^3r \left(e^{-\beta u(r)} - 1\right) = 4\pi \int_0^\infty dr\, r^2 \left(e^{-\beta u(r)} - 1\right)$$

$$\simeq 4\pi \int_0^a dr\, r^2 (-1) - 4\pi \int_a^\infty dr\, r^2 \frac{u_0}{r^6}\frac{1}{k_B T}$$

$$= -\frac{4}{3}\pi a^3 - 4\pi \frac{u_0}{k_B T}\int_a^\infty dr \frac{1}{r^4} = -\frac{4\pi}{3}a^3 - \frac{4\pi}{3}a^3\left(\frac{u_0}{a^6}\frac{1}{k_B T}\right)$$

$$b_2 = -\frac{4}{3}\pi a^3\left(1 + \frac{1}{k_B T}\frac{u_0}{a^6}\right)$$

$$\frac{P}{k_B T} = \frac{N}{V} + \frac{1}{2}\frac{4\pi a^3}{3}\left(1 + \frac{1}{k_B T}\frac{u_0}{a^6}\right)\left(\frac{N}{V}\right)^2$$

Now, $u_0 < 0$ so

$$P = k_B T \frac{N}{V} + \frac{2\pi a^3}{3}\left(\frac{N}{V}\right)^2 k_B T - \frac{2\pi a^3}{3}\frac{|u_0|}{a^6}\left(\frac{N}{V}\right)^2$$

this came from "excluded" volume

$$P + \frac{2\pi a^3}{3} \frac{|u_0|}{a^6} \left(\frac{N}{V}\right)^2 = k_B T \left(\frac{N}{V}\right)\left[1 + \underbrace{\frac{2\pi a^3}{3}}\left(\frac{N}{V}\right)\right]$$

$$P + \frac{2\pi a^3}{3} \frac{|u_0|}{a^6} \left(\frac{N}{V}\right)^2 \cong k_B T \left(\frac{N}{V}\right)\left[\frac{1}{1 - \frac{2\pi a^3}{3}\left(\frac{N}{V}\right)}\right]$$

or

$$\boxed{P + \alpha\left(\frac{N}{V}\right)^2 = \frac{N k_B T}{V - \beta N}}$$

van der Waals equation of state

treat α & β as phenomenological parameters

Recall that at the beginning of this course we proved that the entropy of an isolated system never decreases:

$$\Delta S \geq 0$$

Consider the total system composed of the (sub) system and the heat bath. Then,

$$\Delta S_{tot} = \Delta S_0 + \Delta S \geq 0$$

; but the temp. of heat bath does not change because we assume h.b. to be much larger than our (sub) system

$$\Rightarrow \Delta S_0 = \frac{\overset{\text{heat absorbed by heat bath}}{\Delta Q_0}}{T_0} \Rightarrow \underset{\text{heat absorbed by (sub) system}}{\Delta Q} = -\Delta Q_0$$

$$\Delta S \geq \frac{\Delta Q}{T_0} = \frac{1}{T_0}\left(\Delta E + \Delta W\right)$$

$$0 \geq \underbrace{\left(\Delta E - T_0 \Delta S\right)}_{\Delta F} + \Delta W$$

$$\boxed{-\Delta F \geq \Delta W}$$

the maximum amount of work a (sub) system can do when connected to a heat bath is equal to Helmholtz free energy.

if V is held constant, then $\Delta V = 0$ and

$$0 \geq \Delta E - T_0 \Delta S = \Delta(E - TS) \equiv \Delta F$$

⇒ the Helmholtz free energy decreases until it reaches minimum.

What if pressure is controlled externally, instead of volume? If the pressure of the reservoir is p_0 then the pressure of the (sub) system is also p_0 (by mechanical equilibrium).

Then, $\Delta S_{tot} = \Delta S_0 + \Delta S \geq 0$

other form of work (magnetic, electr. but not mechanical)

$$\Delta S \geq -\Delta S_0 = \frac{\Delta Q}{T_0} = \frac{1}{T_0}\left(\Delta E + p_0 \Delta V + \Delta W^*\right)$$

$$T_0 \Delta S \geq \Delta E + p_0 \Delta V + \Delta W^*$$

$$-\left(\Delta E - T_0 \Delta S + p_0 \Delta V\right) \geq \Delta W^*$$

Let $G = E - TS + pV$ then because of eq. w/ reservoir $T = T_0$ & $p = p_0$ and

$-\Delta G \geq \Delta W^*$ ⇒ maximum amount of work that can be done is given by the Gibbs free energy G.

If all external parameters except the volume of the (sub) system are kept fixed, then $\Delta W^* = 0$ and $\Delta G \leq 0$ ⇒

stable equilibrium situation corresponds to minimum G.

Equilibrium between phases:

Consider phase 1 and 2 coexisting (e.g. ice + liquid H_2O)

Assume that p and T are externally controlled.

Then:

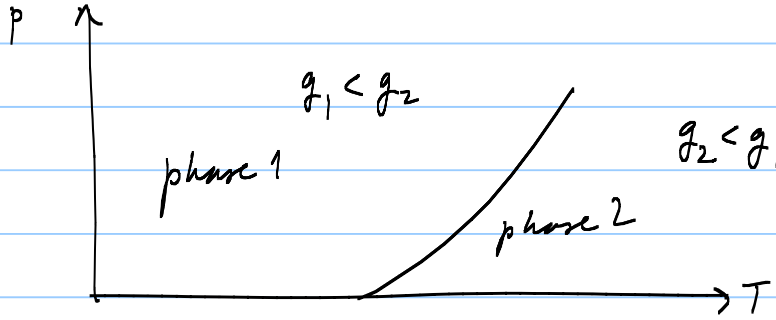
$$G(T,p) = N_1 g_1(T,p) + N_2 g_2(T,p) \quad \& \quad N = N_1 + N_2.$$

where $g_{1,2}$ is the Gibbs free energy of the phase 1, 2 per particle.

Assume WLOG that $g_1(T,p) < g_2(T,p)$.
Then we can minimize $G(T,p)$ by letting $N_1 = N$ and $N_2 = 0$
$\Rightarrow$ one phase only.

Therefore, if there is to be a coexistence between 1 & 2 we must have $g_1(T,p) = g_2(T,p)$.

Geometrically, this corresponds to intersection of surfaces above p-T plane and therefore to curves in p-T plane:



We'd like to figure out an equation for the shape of the coexistence curve.

To this end,

$$g_1(T+dT, p+dp) = g_2(T+dT, p+dp)$$

$$\cancel{g_1(T,p)} + \left.\frac{\partial g_1}{\partial T}\right)_p dT + \left.\frac{\partial g_1}{\partial p}\right)_T dp = \cancel{g_2(T,p)} + \left.\frac{\partial g_2}{\partial T}\right)_p dT + \left.\frac{\partial g_2}{\partial p}\right)_T dp$$

But, $G = E - TS + pV$; $dE = \text{đ}Q - \text{đ}W = TdS - pdV$

$$dG = dE - dT\,S - TdS + dp\,V + p\,dV$$

$$= \cancel{TdS} - \cancel{pdV} - SdT - \cancel{TdS} + dp\,V + \cancel{p\,dV}$$

$$\Rightarrow \left.\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left.\frac{\partial G}{\partial p}\right)_T = V$$

$$-\frac{S_1}{N_1}\,dT + \frac{V_1}{N_1}\,dp = -\frac{S_2}{N_2}\,dT + \frac{V_2}{N_2}\,dp$$

$$\boxed{\frac{dp}{dT} = \frac{\left(\frac{S_1}{N_1} - \frac{S_2}{N_2}\right)}{\left(\frac{V_1}{N_1} - \frac{V_2}{N_2}\right)}}$$

← Clausius– Clapeyron equation

The numerator is the difference of specific entropies of the two phases and the denominator the difference of specific volumes.

But, in a 1st order phase transition, we need to supply LATENT HEAT in order to transfer the low T phase to high T phase at T_c:

$$L_{12} = T(S_2 - S_1)$$

at the begining there are N particles in phase 1 and none in phase 2
$\Rightarrow$ specific entropy is $\frac{S_2}{N}$.

at the end there are N particles in phase 2 and none in phase 1.
$\Rightarrow$ specific entropy is $\frac{S_1}{N}$.

Similarly with specific volumes $\Rightarrow$

$$\frac{dp}{dT} = \frac{L_{12}}{T(V_2 - V_1)}$$

E.g. liquid to gas transition $V_2 = V_{gas} > V_1 = V_{liquid}$

$L_{12} > 0$ (latent heat of vaporization)

$\Rightarrow$ $\frac{dp}{dT} > 0$, the phase boundary curves up.

Since often $V_{gas} \gg V_{liquid}$, $V_2 - V_1 \simeq V_2 \simeq \frac{Nk_BT}{p}$

$$\frac{dp}{dT} = \frac{L_{12}}{N k_B T^2} p \Rightarrow \frac{dp}{p} = \frac{L_{12}}{k_B N} \frac{dT}{T^2}$$

$$\ln p = \frac{L_{12}}{k_B N}\left(\frac{-1}{T}\right) + \text{const} : \quad p = p_0 e^{-\frac{(L_{12}/N)}{k_B T}} = p_0 e^{-\frac{\ell_{12}}{k_B T}}$$

vapor pressure (a very rapidly increasing fxn of T)

e.g. What about solid to liquid phase boundary?

Usually the volume of the liquid phase of N particles is higher than the volume of the crystal phase of N particles. (Thermal motion requires more space)

Therefore $V_2 - V_1 > 0$.

Also, the specific entropy of the solid is typically lower than the entropy of the liquid. Therefore,

$$S_2 - S_1 > 0 \Rightarrow \frac{dp}{dT} > 0.$$

But, for water near freezing, the specific volume of ice is actually larger than of liquid $\Rightarrow$ $V_2 - V_1 < 0$ and $\frac{dp}{dT} < 0$: