Relativistic gases

$E^2 = p^2c^2 + m^2c^4$

Ultrarelativistic limit

$p^2c^2 \gg m^2c^4 \Leftrightarrow p \gg mc^2$ (muons, neutrinos)

$\Rightarrow E \approx pc = \hbar k c$

Classical ideal gas

for ~~$E = pc = \hbar kc$~~ $\boxed{E = \frac{p^2}{2m}} = \frac{\hbar^2 k^2}{2m}$

$Z_1 = \sum_s e^{-\beta E_s}$

$g(k)dk = \frac{Vk^2}{2\pi^2}dk \longleftrightarrow g(p)dp = \frac{4\pi V p^2}{h^3}dp$

$Z_1 = \int_0^\infty g(p)e^{-\frac{\beta p^2}{2m}}dp = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$

Ultrarelativistic ideal gas

$Z_1 = \sum_s e^{-\beta E_s}$ $\quad \boxed{E = pc = \hbar kc}$

$g(k)dk = \frac{Vk^2}{2\pi^2}dk \longleftrightarrow g(p)\,dp = \frac{Vp^2}{2\pi^2\hbar^3}dp \qquad x = \beta pc \rightarrow p = \frac{x}{\beta c}$

$Z_1 = \int_0^\infty g(p)e^{-\beta p^2/2m}dp = \int_0^\infty \frac{Vp^2}{2\pi^2\hbar^3}e^{-\beta pc}dp = \frac{V}{2\pi^2(\beta\hbar c)^3}\int_0^\infty x^2 e^{-x}dx$

$\left[\int_0^\infty x^2 e^{-x}dx = \left(\frac{\partial^2}{\partial\alpha^2}\int_0^\infty e^{-\alpha x}dx\right)_{\alpha=1} = \frac{\partial^2}{\partial\alpha^2}\left(\frac{1}{\alpha}\right)\Big|_{\alpha=1} = \frac{2}{\alpha^3}\Big|_{\alpha=1} = 2 = 2!\right]$

$Z_1 = \frac{V}{2\pi^2(\beta\hbar c)^3}\cdot 2! = \frac{V}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3 = \frac{V}{\Lambda^3}$, $\boxed{\Lambda = \frac{\hbar c}{k_B T}\pi^{2/3}} \propto T^{-1}$

thermal wavelength

$Z_N = \frac{1}{N!}Z_1^N$ $\quad$ vs. $\lambda_{th} = \frac{h}{\sqrt{2\pi m k_B T}} \propto T^{-1/2}$

$Z_N = \frac{V^N}{N!}\left(\frac{k_B T}{\hbar c\,\pi^{2/3}}\right)^{3N} = \frac{V^N}{N!}\left(\frac{1}{\Lambda}\right)^{3N}$

Helmholtz free energy of UR gas

$F = -k_B T\ln(Z_N) = -k_B T\left[N\cdot\ln(V) - N\cdot\ln(N) + N - 3N\ln(\Lambda)\right] =$

$= -k_B T\left[N\cdot\ln\left(\frac{V}{N}\right) + N - 3N\ln(\Lambda)\right] = -Nk_B T\left[-\ln(n) - 3\ln(\Lambda) + 1\right]$

$= Nk_B T\left[\ln(n) + 3\ln(\Lambda) - 1\right] = Nk_B T\left[\ln(n\Lambda^3) - 1\right]$

$\boxed{F = Nk_B T\left[\ln(n\Lambda^3) - 1\right]}$

$\hookrightarrow$ same as classical with λ_{th}

Pressure of UR gas

$p = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(-k_B T N\ln V\right) = \frac{Nk_B T}{V} \Rightarrow pV = Nk_B T$

$$\beta F = N\left[\ln(n) + 3\ln\beta + \ln\Lambda^3 - 1\right]$$

n dep. of β

Energy of UR gas

$$U = \frac{\partial \beta F}{\partial \beta} = \frac{\partial}{\partial\beta}\left(3N\ln\beta\right) = \frac{3N}{\beta}$$

$$\Rightarrow \boxed{U = 3Nk_BT}$$

$$C_V = \frac{\partial U}{\partial T} = 3Nk_B$$

Comparison

UR vs. classical

$p = \frac{Nk_BT}{V}$

$$U = 3Nk_BT \neq U = \frac{3}{2}Nk_BT$$
$$C_V = 3Nk_B \neq C_V = \frac{3}{2}Nk_B$$
} 1/2 x
$$p = \frac{1}{3}\frac{U}{V} = \frac{1}{3}u \neq p = \frac{2}{3}\frac{U}{V} = \frac{2}{3}u$$
} 2x

Entropy

$$S = \frac{U-F}{T} = 3Nk_B - Nk_B\left[\ln(n\Lambda^3) - 1\right] = Nk_B\left[4 - \ln(n\Lambda^3)\right]$$

$$\boxed{S = Nk_B\left[4 - \ln(n\Lambda^3)\right]}$$

adiabatic expansion of UR gas

$dS = 0 \Rightarrow S = \text{const.}$

$n\Lambda^3 = \text{const.} \Rightarrow \frac{N}{V}\left(\frac{\pi^{2/3}\hbar c}{kT}\right)^3 \text{const.} \Rightarrow VT^3$ is const.

Radiation and matter in the universe

$\boxed{\gamma = \frac{c_p}{c_V}}$

↳ CMB γ as UR gas in an adiabatically expanding universe

$pV^{4/3} = \text{const.} \Leftarrow$ relativistic $\Rightarrow VT^3 = \text{const} \Rightarrow T \propto V^{-1/3} \propto \frac{1}{a}$

$pV^{5/3} = \text{const.} \Leftarrow$ non-relativistic $\Rightarrow VT^{3/2}$ const $\Rightarrow T \propto V^{-\frac{2}{3}} \propto \frac{1}{a^2}$

} $\Rightarrow$ non-relativistic gas cools faster than relativistic

relativistic: $\rho \propto \frac{U}{c^2} \propto p \propto V^{-4/3} \propto \frac{1}{a^4}$ — non-relativistic: $\rho \propto \frac{1}{V} \propto \frac{1}{a^3}$

$p = \frac{1}{3}u$

$\boxed{\rho \propto \frac{1}{a^4}}$ photons — $\boxed{\rho \propto \frac{1}{a^3}}$ matter

↳ universe changed from radiation dominated to matter dominated during expansion

after Big Bang

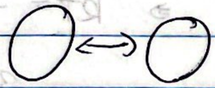
↳ now

Properties of real gases

Ideal gas $pV = nRT$
- dilute gas – negligible interaction between gas particles
- gas particles don't take up space

But irl:

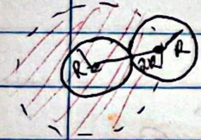
part of volume is excluded by gas particles



attractive forces between gas particles

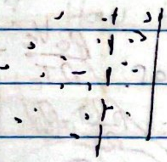
Van der Waals

$$V_{excluded} = \frac{1}{2} n N_a \frac{4}{3}\pi (2R)^3 = n \overbrace{N_a \pi \frac{16}{3} R^3}^{b} = nb$$



pairs

$$p(V - nb) = nRT \Rightarrow p = \frac{nRT}{V - nb}$$



- ~~pressure is redu~~ attractive forces reduce pressure on wall
- # particles is influenced $\propto \frac{nN_a}{V}$ $\quad F_{att} \propto \frac{nN_a}{V}$
- pressure reduction $\propto \left(\frac{nN_a}{V}\right)^2$

$$\Rightarrow p = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \Rightarrow \boxed{\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT}$$

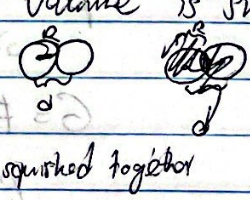
a: parameter for prop to

- define **molar volume** $V_m = \frac{V}{n}$

$$\boxed{\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT}$$

$V_{excluded} = n\, 4 N_a \frac{4}{3}\pi R^3 = nb$ because actual volume is smaller

Van der Waals radius $R = \frac{d}{2}$

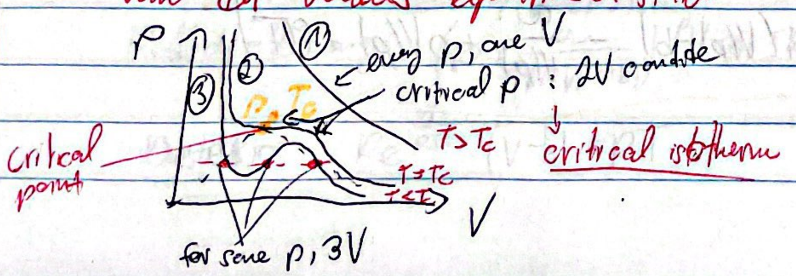


$b_{argon} = 0.03219 \cdot 10^{-3} \Rightarrow R = 1.47 \cdot 10^{-10}\,m$

covalent radius: $R_{argon} = 0.71 \cdot 10^{-10}\,m$ ← squished together

Van der Waals equation of state: $pV^3 - (pb + RT)V^2 + aV - ab = 0$

cubic in V ⇒ 1, 2, 3 sols



Scanned with CamScanner

Critical point

$$\left(p+\frac{a}{V_m^2}\right)(V_m-b)=RT \Rightarrow p=\frac{RT}{V_m-b}-\frac{a}{V_m^2}$$

↳ critical point is inflection point

$$\left(\frac{\partial p}{\partial V_m}\right)_T=0,\quad \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T=0,\quad p=\frac{RT}{V_m-b}-\frac{a}{V_m^2}$$

$$\left.\begin{aligned}\left(\frac{\partial p}{\partial V_m}\right)_T &= -\frac{RT}{(V_m-b)^2}+\frac{2a}{V_m^3}=0 \Rightarrow RT=\frac{2a(V_m-b)^2}{V_m^3}\\ \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T &= \frac{2RT}{(V_m-b)^3}-\frac{6a}{V_m^4}=0 \Rightarrow RT=\frac{3a(V_m-b)^3}{V_m^4}\end{aligned}\right\} \rightarrow 3\,\frac{V_m-b}{V_m}=2$$

$$\Downarrow$$

$$\boxed{V_c^m=3b}$$

$$RT=\frac{2a(3b-b)^2}{27b^3}=\frac{2a\,4b^2}{27b^3}=\frac{8a}{27b}$$

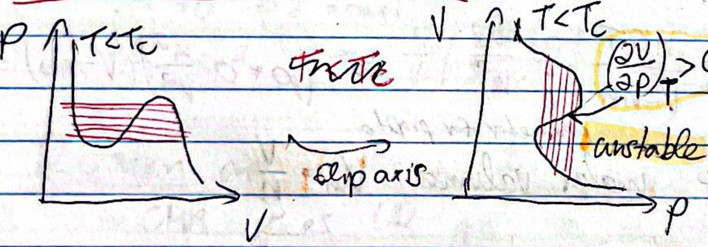
$$\Rightarrow \boxed{T_c=\frac{8a}{27Rb}}$$

$$\boxed{p_c=\frac{a}{27b^2}}$$

- compression factor Van der Waals gas $\boxed{\frac{p_cV_c}{RT_c}=\frac{3}{8}n}$

(vs. ideal gas: $\frac{pV}{RT}=1n$)

Van der Waals isotherm $T<T_c$



$$\left(\frac{\partial V}{\partial p}\right)_T>0$$

$$\left.\begin{aligned}U&=\frac{3}{2}Nk_BT\\ pV&=Nk_BT\end{aligned}\right\} U\propto pV$$

$\Rightarrow p\uparrow \Rightarrow V\uparrow$

$U\uparrow \Rightarrow p\uparrow$

Gibbs function of VdW gas

$$p=-\left(\frac{\partial F}{\partial V_m}\right)_T \Rightarrow F=-\int p\,dV_m+f(T)=-\int\left(\frac{RT}{V_m-b}-\frac{a}{V_m^2}\right)dV_m+f(T)$$

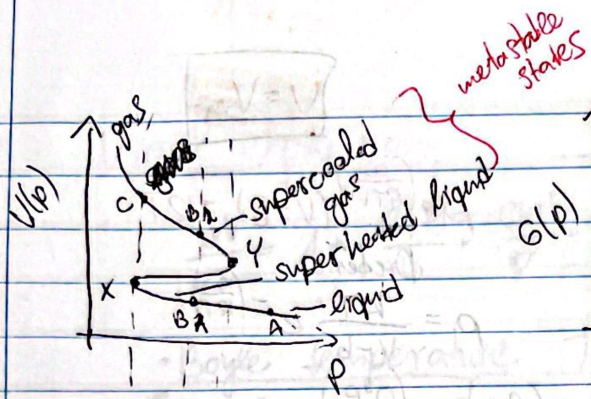
at const. T

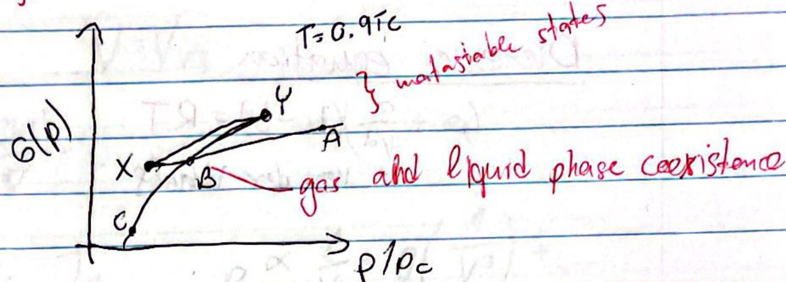
$$F=-RT\ln(V_m-b)-\frac{a}{V_m}+f(T)$$

$$G=F+pV_m=-RT\ln(V_m-b)-\frac{a}{V_m}+pV_m+f(T)$$

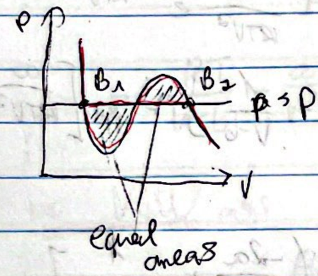
$$\underbrace{pV_m^3-(pb+RT)V_m^2+aV_m-ab=0}_{V(p)\ \rightarrow \text{not always single valued}}$$

$$\boxed{G(p)=-RT\ln(V(p)-b)-\frac{a}{V(p)}+pV(p)+f(T)}$$





Maxwell construction



$$G(p_{B_2}) - G(p_{B_1}) = \int_{p_{B_1}}^{p_{B_2}} \left(\frac{\partial G}{\partial p}\right)_T dp = 0 \text{ along isotherm}$$

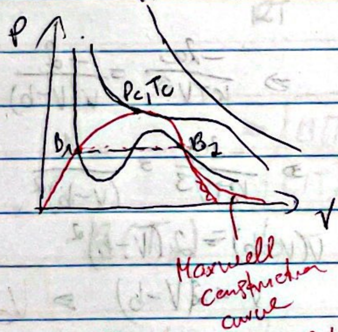
$$G = U - TS + pV$$

$$dG = dU - TdS - SdT + pdV + Vdp$$

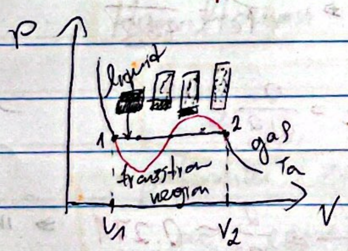
$$dG = -SdT + Vdp \Rightarrow \boxed{V = \left(\frac{\partial G}{\partial p}\right)_T}$$

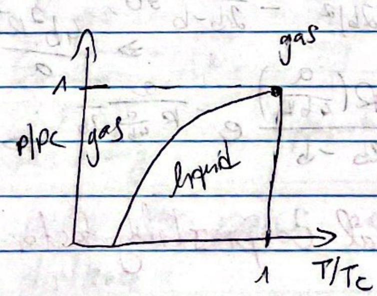
$$G(p_{B_2}) - G(p_{B_1}) = \int_{p_{B_1}}^{p_{B_2}} V\, dp = 0 \text{ along isotherm}$$

? How to find B_1 & B_2



Phase equilibrium





Equations of state

for 1 mole

Van der Waals $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

Berthelot $\left(p + \frac{a}{TV^2}\right)(V - b) = RT$

Clausius $\left(p + \frac{a}{T(V-c)^2}\right)(V - b) = RT$

Redlich-Kwong $\left(p + \frac{a}{\sqrt{T}V(V+b)}\right)(V - b) = RT$

Dieterici $p e^{\frac{a}{RTV}}(V - b) = RT$

$n = 1$

$\boxed{V = V_m}$

Dieterici equation

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT$$

von der Waals

$$p e^{\left(\frac{a}{RTV}\right)}(V-b) = RT$$

Dieterici

$$p = \frac{RT}{V-b} e^{-\left(\frac{a}{RTV}\right)}$$

· find critical point $\left(\frac{\partial p}{\partial V}\right)_T = \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$

↳ inflection

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} e^{-\frac{a}{RTV}} + \frac{RT}{V-b}\frac{a}{RTV^2} e^{-\frac{a}{RTV}}$$

$$= \underbrace{\frac{RT}{V-b} e^{-\frac{a}{RTV}}}_{=p}\left[\frac{a}{RTV^2} - \frac{1}{V-b}\right] = p\left[\frac{a}{RTV^2} - \frac{1}{V-b}\right] = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \underbrace{\left(\frac{\partial p}{\partial V}\right)_T}_{=0 \text{ at inflection}}\left[\frac{a}{RTV^2} - \frac{1}{V-b}\right] + p\left(\frac{-2a}{RTV^3} + \frac{1}{(V-b)^2}\right] = 0$$

$\Rightarrow \frac{a}{RTV^2} - \frac{1}{V-b} = 0 \quad (\vee\ p = 0)$

$\frac{-2a}{RTV^3} + \frac{1}{(V-b)^2} = 0$

$\Rightarrow \frac{-2a}{RTV^3} = \frac{-2}{V(V-b)}$

$\Rightarrow \frac{-2a}{RTV^3} = \frac{-1}{(V-b)^2}$

$=$

$\Rightarrow V(V-b) = 2(V-b)^2$

$V = 2(V-b) \Rightarrow \boxed{V_c = 2b}$

$\frac{a}{RT(2b)^2} - \frac{1}{2b-b} = 0 \Rightarrow \frac{4b^2RT}{a} = b \Rightarrow \boxed{T_c = \frac{a}{4bR}}$

$P_c = \frac{R\left(\frac{a}{4bR}\right)}{2b-b} e^{-\frac{a}{R\frac{a}{4bR}2b}} \Rightarrow \boxed{P_c = \frac{a}{4b^2}e^{-2}}$

a, b differs per gas
⇒ differs per gas

critical compressibility factor: $\boxed{\frac{p_cV_c}{RT_c} = \frac{2}{e^2} = 0.271}$ ⇒ indep. of type of gas

← better

vs. Van der Waals $\frac{p_cV_c}{RT_c} = \frac{3}{8} = 0.375$

Virial expansion $V = V_m$

$$\boxed{\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots}$$

- Boyle temperature T_B
  $\hookrightarrow B(T_B) \equiv 0 \Rightarrow \boxed{T = T_B}$ $p \propto \frac{1}{V} + O\left(\frac{1}{V^3}\right) + \dots$
  small
- Boyle's law
  $p \propto \frac{1}{V}$ for const. V

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\frac{1}{1-\frac{b}{V}} - \frac{a}{V^2}$$

geometric series

for VdW gas

$$\frac{pV}{RT} = \left(1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \dots\right) - \frac{a}{RTV}$$

$$\frac{pV}{RT} = 1 + \underbrace{\frac{b - \frac{a}{RT}}{V}}_{B(T)} + \underbrace{\left(\frac{b}{V}\right)^2}_{C(T)} + \dots$$

compare with: $\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots$

$$\Rightarrow \boxed{\begin{aligned} B(T) &= b - \frac{a}{RT} \\ C(T) &= b^2 \end{aligned}}$$

VdW similar to ideal gas

$\cdot\ B(T_B) = b - \frac{a}{RT_B} = 0 \Rightarrow \boxed{T_B = \frac{a}{bR} = \frac{27}{8} T_C}$

$T_C = \frac{8}{27}\frac{a}{bR}$

for N particle gas

Hamiltonian: $\boxed{H = \underbrace{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}}_{\text{kinetic energy}} + \underbrace{U(\vec{x}_1, \dots, \vec{x}_n)}_{\text{potential energy}}}$

- potential energy only for pairs and only depends on separation distance:

$$U(\vec{x}_1, \dots, \vec{x}_n) = \sum_{i<j} V(|\vec{x}_i - \vec{x}_j|)$$

Partition function $Z = \int \dots \int e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} - \beta U(\vec{x}_1, \dots, \vec{x}_n)} d\vec{x}_1 \dots d\vec{x}_N\, d\vec{p}_1 \dots d\vec{p}_N$

$$Z = \underbrace{\int e^{-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}} d\vec{p}_1 \dots d\vec{p}_N}_{Z_{kin}} \underbrace{\int e^{-\beta U} d\vec{x}_1 \dots d\vec{x}_N}_{Z_{pot}}$$

$Z = \underbrace{Z_{kin}}_{\text{ideal gas law}} \cdot Z_{pot} = e \int e^{-\beta U} d\vec{x}_1 \dots d\vec{x}_N$

ideal gas

$$Z = Z_{kin} \cdot Z_{pot} \xrightarrow[U=0]{} Z_{kin}$$

$$Z_{pot}(U=0) = 1 = C \int d\vec{x}_1 \dots d\vec{x}_N = C \cdot V^N \Rightarrow C = \frac{1}{V^N}$$

$$\Rightarrow Z_{pot} = \frac{1}{V^N} \int e^{-\beta U} d\vec{x}_1 \dots d\vec{x}_N$$

$$U = \sum_{i<j} \nu(|\vec{x}_i - \vec{x}_j|)$$

to prepare to approx. $\ln(1+x) \approx x$ for $x \ll 1$ $\Rightarrow$

$$Z_{pot} = \frac{1}{V_N} \int e^{-\beta U} + 1 - 1 \, d\vec{x}_1 \dots d\vec{x}_N$$

$$Z_{pot} = 1 + \frac{1}{V_N} \int \underbrace{\left(e^{-\beta \sum_{i<j} \nu(|x_i - x_j|)} - 1\right)}_{\text{only important when particles close together } (|x_i - x_j| \text{ small})} dx_1 \dots dx_N$$

↳ suppose gas is dilute and close to ideal

$\Rightarrow$ only two particles close together $\Rightarrow$

$\Rightarrow$ only 1 pair at a time interacting

$$\frac{N(N-1)}{2} \approx \frac{N^2}{2} \text{ different pairs}$$

$$Z_{pot} = 1 + \frac{N^2}{2V^N} \int e^{-\beta\nu|\vec{x}_1 - \vec{x}_2|} - 1 \, d\vec{x}_1 \dots d\vec{x}_N$$

we can integrate over $\int d\vec{x}_3 \dots d\vec{x}_N = V^{N-2}$

$$Z_{pot} = 1 + \frac{N^2}{2V^N} V^{N-2} \int \left(e^{-\beta\nu|\vec{x}_1 - \vec{x}_2|} - 1\right) dx_1 dx_2$$

only relative distance matters $\Rightarrow$ integrate one more coord.

$$Z_{pot} = 1 + \frac{N^2}{2V^2} V \int \left(e^{-\beta\nu|\vec{x}|} - 1\right) d\vec{x}$$

$d\vec{x}$: vector pointing from one particle to the other

$$Z_{pot} = 1 + \frac{N}{V2} \underbrace{\int \left(e^{-\beta\nu|\vec{x}|} - 1\right) d\vec{x}}_{= -B'(T)}$$

$$\boxed{Z_{pot} = 1 - \frac{N}{V} B'(T)}$$

Thermodynamics

$$F = -k_B T \ln Z = -k_B T \ln(Z_{kin} Z_{pot}) =$$

$$= -k_B T \ln(Z_{kin}) - k_B T \ln(Z_{pot}) =$$

$$= F_{kin} - k_B T \ln\Big(1 - \underbrace{\frac{N}{V} B'(T)}_{\text{deviations from ideal gas}}\Big)$$

$\Rightarrow$ assume small $\Rightarrow B'(T)$ small $\Rightarrow \ln(1+x) \approx x$

$$\approx F_{kin} + \frac{N k_B T}{V} B'(T)$$

$$-\left(\frac{\partial F}{\partial V}\right)_T = p = \frac{N k_B T}{V} + \frac{N k_B T}{V^2} B'(T) \Rightarrow \frac{pV}{N k_B T} = 1 + \frac{B'(T)}{V}$$

$$\frac{pV}{Nk_BT} = 1 + \frac{B'(T)}{V} \Rightarrow \frac{pV}{nN_Ak_BT} = 1 + \frac{B'(T)}{V}$$

$$\Rightarrow \frac{pV_m}{RT} = 1 + \frac{B'(T)/n}{V_m} = \underbrace{1 + \frac{B(T)}{V}}_{\text{first order viral expansion}}$$

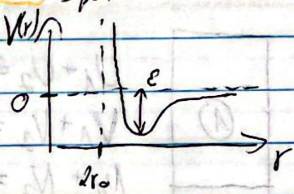
→ other terms if more particle interaction

Second viral coefficient

$$B'(T) = \frac{N}{2}\int\left(1 - e^{-\beta V(|\vec{x}|)}\right) d\vec{x} = \frac{N}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(1 - e^{-\beta V(|\vec{x}|)}\right) dx\,dy\,dz =$$

$$= \frac{N}{2}\int_0^{\infty}\int_0^{2\pi}\int_0^{\pi}\left(1 - e^{-\beta V(r)}\right) r^2 \sin\theta \, d\theta\, d\phi\, dr = \frac{N}{2}\int_0^{\infty} 4\pi r^2\left(1 - e^{-\beta V(r)}\right) dr$$

$$\Rightarrow \boxed{B'(T) = \frac{N}{2}\int_0^{\infty} 4\pi r^2\left(1 - e^{-\beta V(r)}\right) dr}$$



$$\begin{cases} V(r) = \infty & \text{for } r < 2r_0 \\ \beta V(r) = \frac{V(r)}{k_BT} \ll 1 & \text{for } r > 2r_0 \end{cases}$$

$$B'(T) = \frac{N}{2}\int_0^{2r_0} 4\pi r^2\Big(1 - \overbrace{e^{-\beta V(r)}}^{\simeq 0}\Big) dr + \frac{N}{2}\int_{2r_0}^{\infty} 4\pi r^2 \underbrace{\left(1 - e^{-\beta V}\right)}_{\simeq \beta V \text{ because } \beta V \ll 1} dr =$$

$$= \frac{N}{2}\int_0^{2r_0} 4\pi r^2 dr + \frac{N}{2}\int_{2r_0}^{\infty} \beta V(r) 4\pi r^2 dr$$

$$= \frac{N}{2} 4\pi \frac{1}{3}(2r_0)^3 + \frac{N}{k_BT} 2\pi \int_{2r_0}^{\infty} r^2 V(r)\, dr =$$

$$= \underbrace{nN_a\left(\frac{16}{3}\pi r_0^3\right)}_{b} + \frac{n}{k_BT}\underbrace{2\pi N_a \int_{2r_0}^{\infty} r^2 V(r)\, dr}_{-a} = nb - \frac{an}{k_BT}$$

from: $V_{excluded} = n 4 N_a \frac{4}{3}\pi R^3 = nb$

$$B'(T) = n\left(b - \frac{a}{k_BT}\right) \Rightarrow \boxed{B(T) = \frac{B'(T)}{n}} = b - \frac{a}{k_BT}$$

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V}$$

Second viral coeff. of van der Waals eq.

Law of corresponding ~~terms~~ states

• using reduced coordinates: $\tilde{p} = \frac{p}{p_c}$, $\tilde{V} = \frac{V}{V_c}$, $\tilde{T} = \frac{T}{T_c}$

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(\tilde{p}p_c + \frac{a}{(\tilde{V}V_c)^2}\right)(\tilde{V}V_c - b) = R\tilde{T}T_c$$

$$\tilde{p} + \frac{1}{\tilde{V}^2}\frac{a}{p_cV_c^2} = \frac{\tilde{T}}{\tilde{V}V_c - b}\,\frac{RT_c}{p_c}$$

$$\tilde{p} + \frac{1}{\tilde{V}^2}\underbrace{\frac{a}{p_c V_c^2}}_{= \frac{a \cdot 27b^2}{a \cdot 9b^2} = 3} = \frac{\tilde{T}}{\tilde{V}V_c - b}\underbrace{\frac{RT_c}{p_c}}_{= R\frac{8a}{27Rb}\frac{27b^2}{a} = 8b}$$

$$\boxed{\begin{aligned} V_c &= 3b \\ T_c &= \frac{8a}{27Rb} \\ p_c &= \frac{a}{27b^2} \end{aligned}}$$

$$\Rightarrow \left(\tilde{p} + \frac{3}{\tilde{V}^2}\right) = \frac{8b\tilde{T}}{3b\tilde{V} - b} \Rightarrow \boxed{\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right) = \frac{8\tilde{T}}{3\tilde{V} - 1}}$$

↳ indep. of a and b

$\Rightarrow$ in reduced coord., the eq. of state is same for every gas

compressibility

$$\Rightarrow z = \frac{pV}{RT} = \frac{\tilde{p}\tilde{V}}{\tilde{T}}\underbrace{\frac{p_c V_c}{RT_c}}_{= \frac{3}{8} \text{ for VdW}}$$

↳ 1 for ideal gas

$$\boxed{z = \frac{3}{8}\frac{\tilde{p}\tilde{V}}{\tilde{T}}}$$

Phase Transitions

$$U_1 + U_2 = U$$
$$V_1 + V_2 = V$$
$$N_1 + N_2 = N$$
$$S_1 + S_2 = S$$

frame earlier: ① ②

in equilibrium : $dS = 0$

$$\boxed{\left(\frac{\partial S}{\partial U_1}\right)_{V_1, N_1} dU_1 + \left(\frac{\partial S}{\partial N_1}\right)_{V_1, E_1} dN_1 + \left(\frac{\partial S}{\partial V_1}\right)_{E_1, N_1} dV_1 = 0}$$

$$T_1 = T_2 \qquad p_1 = p_2 \qquad \mu_1 = \mu_2$$

$$p = T\frac{\partial S}{\partial V} \qquad \frac{1}{T} = \frac{\partial S}{\partial U} \qquad \mu = -T\frac{\partial S}{\partial N}$$

Equilibrium of two phases

$$dS = \underbrace{\left(\frac{\partial S}{\partial U}\right)}_{= \frac{1}{T}} dU + \underbrace{\left(\frac{\partial S}{\partial V}\right)}_{= \frac{p}{T}} dV + \underbrace{\left(\frac{\partial S}{\partial N}\right)}_{-\frac{\mu}{T}} dN$$

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{\mu}{T}dN$$

$$dU = TdS - pdV + \mu dN$$

Gibbs free energy $\quad G = U + pV - TS$

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

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} \qquad \boxed{dG = \sum_i \mu_i dN_i}$$

↳ extensive : $G = N \cdot g$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} = g(T,p) \quad \text{Gibbs free energy per particle}$$

alternative way:

↳ equilibrium: $\mu_1 = \mu_2 \Rightarrow g_1(T,p) = g_2(T,p)$

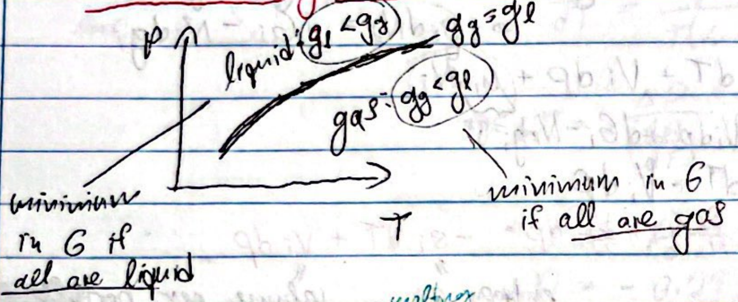
G at minimum $\Rightarrow dG = 0$

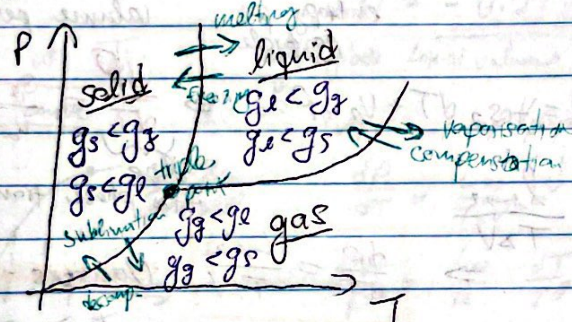
and $G = N_1 g_1 + N_2 g_2$

$$dG = \left(N_1 \frac{\partial g_1}{\partial T} + N_2 \frac{\partial g_2}{\partial T}\right)\underbrace{dT}_{=0 \text{ at equilibrium}} + \left(N_1 \frac{\partial g_1}{\partial p} + N_2 \frac{\partial g_2}{\partial p}\right)\underbrace{dp}_{=0 \text{ at equilibrium}} + g_1 dN_1 + g_2 \underbrace{dN_2}_{=-dN_1} = 0$$

$$\Rightarrow (g_1 - g_2)\, dN_1 = 0 \quad \Rightarrow \quad g_1 = g_2$$

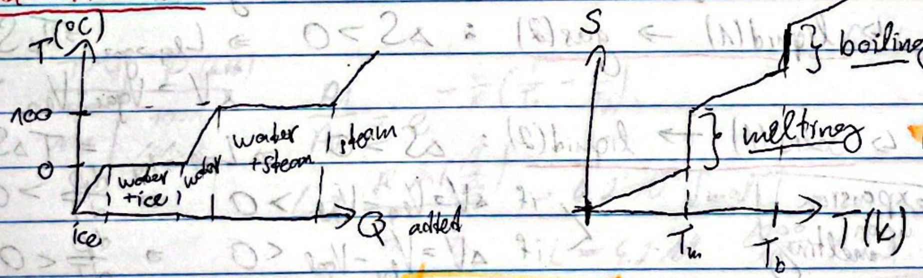
Phase diagrams





Latent heat

$dQ = TdS \Rightarrow Q = L = T\Delta S$ (latent heat)



latent heat of vaporisation: $L_V = T_b (S_f - S_i)$

... fusion: $L_f = T_m (S_f - S_i)$

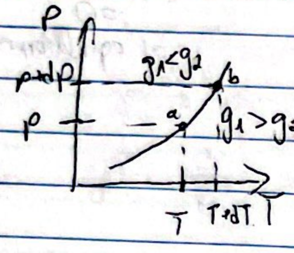
- Trouton's rule $\boxed{\frac{L_V}{T_b} \approx 10R} \approx 83 \text{ kJ/mol}$, $\frac{L_V}{T_b} = \Delta S$

$$\Delta S = \Delta(k \ln(\Omega)) = k \ln \Omega_V - k \cdot \ln \Omega_l = k \ln\left(\frac{\Omega_V}{\Omega_l}\right)$$

$$\frac{\Omega_V}{\Omega_l} \approx \left(\frac{V_V}{V_l}\right)^{N_A} \approx \left(\frac{\rho_l}{\rho_V}\right)^{N_A} \approx \underbrace{(10^3)^{N_A}}_{\text{water for example}}$$

$$\Rightarrow \Delta S = k \cdot \ln\left((10^3)^{N_A}\right) = \underbrace{k N_A}_{R} \underbrace{\ln(10^3)}_{\approx 7} \approx 7R$$

Clausius – Clapeyron equation



$g_1(b) = g_2(b)$

$g_1(a) = g_2(a)$ $\Rightarrow$ $dg_1 = dg_2$ along the phase eq. curve

$G_i = N_i g_i \Rightarrow dG_i = N_i dg_i + g_i dN_i$

$\Rightarrow g_i dN_i = dG_i - N_i dg_i$

$\Rightarrow dG_i = -S_i dT + V_i dp + \mu_i dN_i$

$dG_i = -S_i dT + V_i dp + dG_i - N_i dg_i$; $\mu_i = g_i$

$N_i dg_i = -S_i dT + V_i dp$

$\Rightarrow dg_i = -\frac{S_i}{N_i} dT + \frac{V_i}{N_i} dp = -s_i\, dT + v_i\, dp$

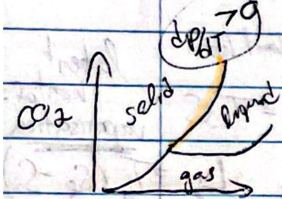
s_i = entropy per particle, v_i = volume per particle

$dg_1 = dg_2$

$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP \Rightarrow \underbrace{\frac{dP}{dT}}_{\text{slope of the phase transition curve}} = \frac{s_2 - s_1}{v_2 - v_1}$ } per particle, mole, kg, ...

$\Rightarrow \frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{l_{1\to 2}}{T\Delta V}$

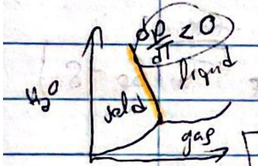
$\Rightarrow \boxed{\frac{dp}{dT} = \frac{L_{1\to 2}}{T\Delta V}}$ Clausius - Clapeyron eq



! latent heat and volume change should be calculated on same basis (mole / kg / ...)

↳ liquid (1) → gas (2) : $\Delta S > 0 \Rightarrow L_{liq\to gas} = T\Delta S > 0$

$\Delta V = V_{gas} - V_{liq} > 0$ } $\frac{dp}{dT} > 0$



↳ solid (1) → liquid (2) : $\Delta S > 0 \Rightarrow L_{sol\to liq} = T\Delta S > 0$

* expansion upon melting

if $\Delta V = V_{liq} - V_{sol} > 0 \Rightarrow \frac{dp}{dT} > 0$ most substances*

if $\Delta V = V_{liq} - V_{sol} < 0 \Rightarrow \frac{dp}{dT} < 0$ water, Si, Bi

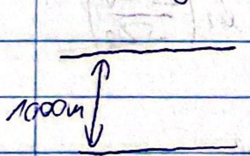
☆ $L_{ice\to water} = 3.35 \cdot 10^5\ J kg^{-1}$ at 273.15 K, 1 bar

Glacier

$\rho^{-1} = V_{ice} = 1091\ cm^3/kg$

$\rho^{-1} = V_{water} = 1000\ cm^3/kg$

$\frac{dP}{dT} = \frac{L_{ice\to water}}{T(V_{water} - V_{ice})} = \frac{3.35 \cdot 10^5}{273.15 \cdot (-91 \cdot 10^{-6})} = -135\ bar \cdot K^{-1}$



$P_{top} = 1 bar$, $T_{top} = 0°C$

$P_{bot} = 100 bar$, $T_{bot} = ?$ } melting temperature

1 bar ≈ 10 m water

$\frac{\Delta p}{\Delta T} = \frac{P_{bot} - P_{top}}{T_{bot} - T_{top}} = -135\ bar\ K^{-1} \Rightarrow \Delta T = \frac{\Delta p}{-135} = -\frac{99}{135} = -0.73 K$

$T_{bot} = T_{top} + \Delta T = -0.73°C$

melting T ↳ less than 0 °C

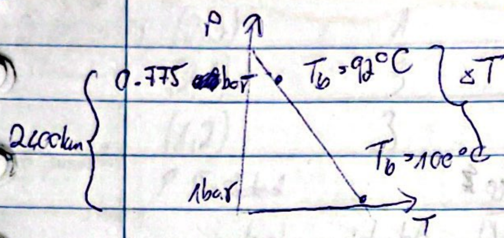
when heating up, bottom melts first ⇒ glacier slides

at lower temp

88

☆ boiling & pressure

- $L_{liquid \to vapor} = 2.26 \cdot 10^6 \ J kg^{-1}$
- $V_v = 1.67 \cdot 10^6 \ cm^3 kg^{-1}$



$\Delta T = 8K$, $\Delta p = -225 \ mbar$

$$\frac{dp}{dT} = \frac{L_{l \to v}}{T(V_v - V_l)} = \frac{2.26 \cdot 10^6}{373.15 \cdot 1.67} = 3.6 \ kPa K^{-1}$$

$$= 36 \ mbar K^{-1}$$

$$\Rightarrow \Delta T = \frac{\Delta p}{\left(\frac{dp}{dT}\right)} = \frac{-225}{36} = -6.25K$$

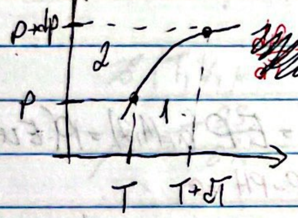
but above: $-8K$

$$p = p_0 e^{-h/7km} = p_0 e^{-2.4/7} = 0.71 p_0 \ ✓$$

$$\Delta p = -0.29 \ bar \Rightarrow \Delta T = -8K$$

p vs. T

Vapor pressure curve



negligible liquid volume

$$\Delta V \approx V_{vapor} \ , \ pV_{vapor} = RT$$

$$\frac{dp}{dT} = \frac{L_{12}}{T \Delta V} = \frac{L_{12}}{T} \frac{p}{RT} = \frac{L_{12}}{T^2 R} p$$

$$\frac{dp}{p} = \frac{L_{12}}{R} \frac{dT}{T^2}$$

$$\ln p = -\frac{L_{12}}{RT} + C \Rightarrow \boxed{p = Ce^{-\frac{L_{12}}{RT}}}$$

for L_{12} temp. indep.

☆

$T(°C)$	$p \ (kPa)$
90	70.1
100	101.3

$$\frac{p_1}{p_2} = e^{-\frac{L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$L = \frac{R \ln\left(\frac{p_2}{p_1}\right)}{\frac{1}{T_1} - \frac{1}{T_2}} = 4.2 \cdot 10^4 \ J mol^{-1}$$

$$L = 4.2 \cdot 10^4 \cdot \frac{1000}{18} = 2.3 \cdot 10^6 \ J kg^{-1}$$

L dependent on T

$$dH = TdS + Vdp \Big|_{const. \ p} = TdS = dQ$$

$$c_p = \left(\frac{\partial Q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$C_{p,vap} - C_{p,liq} = \left(\frac{\partial H_{vap}}{\partial T}\right)_p - \left(\frac{\partial H_{liq}}{\partial T}\right)_p = \left(\frac{\partial (H_{vap} - H_{liq})}{\partial T}\right)_p = \left(\frac{\partial \Delta H}{\partial T}\right)_p$$

$$\Delta G = \Delta H - T\Delta S = \Delta H - L(T) \underset{\text{on phase boundary}}{=} 0 \Rightarrow \left(\frac{\partial L(T)}{\partial T}\right)_p = C_{p,vap} - C_{p,liq}$$

$$\Rightarrow L(T) = L_0 + (C_{p,vap} - C_{p,liq}) T$$

$$\frac{dp}{dT} = \frac{pL_0(T)}{RT^2} = \frac{p\cdot(L_0 + \Delta C T)}{RT^2}$$

$$\ln p = -\frac{L_0}{RT} + \frac{\Delta C}{R}\ln(T) \Rightarrow \boxed{p = p_0 e^{\left(-\frac{L}{RT} + \frac{\Delta C}{R}\ln(T)\right)}}$$

Quantum gases

Hamiltonian of 2 identical particles:

$$H(1,2) = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + V(x_1, x_2)$$

$$H(1,2) = H(2,1) = H \Rightarrow V(x_1,x_2) = V(x_2,x_1)$$

$$\begin{cases} H(1,2)\, u_E(1,2) = E u_E(1,2) \\ H(2,1)\, u_E(2,1) = E\, u_E(2,1) \end{cases}$$ identical so we can relabel

$$\Rightarrow \boxed{H(1,2)\, u_E(2,1) = E u_E(2,1)}$$

↳ define exchange operator for 2 particle wavefunction:

$$P\,\Psi(1,2) = \Psi(2,1)$$

$$H(P u_E(1,2)) = H u_E(2,1) = E\, u_E(2,1) = E P\, u_E(1,2) = P(E u_E(1,2)) =$$

$$= P(H u_E(1,2)) \Rightarrow [H,P] = HP - PH = 0$$

⇒ H and P are commuting operators, thus P is a constant of motion

- eigenvalues of P

$$P^2\Psi(1,2) = P\Psi(2,1) = \Psi(1,2)$$

$$\Leftrightarrow P^2 = 1 \Leftrightarrow \boxed{P = \pm 1}$$

- eigenstates of P

$$P = 1 : \quad \Psi^S(1,2) = \frac{1}{\sqrt{2}}\left(\Psi(1,2) + \Psi(2,1)\right)$$

$$P = -1 : \quad \Psi^A(1,2) = \frac{1}{\sqrt{2}}\left(\Psi(1,2) - \Psi(2,1)\right)$$

symmetric – bosons or antisymmetric – fermions under particle exchange

fermions	× bosons
↳ antisymmetric	↳ symmetric
↳ half-integer spin	↳ integer spin
$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$	0, 1, 2, 3
also for compound particles: ^3He (spin ½)	^4He (spin 0)

- suppose 2 fermions in states s and r: $\Psi^A(1,2) = \frac{1}{\sqrt{2}}\left(\phi_s(1)\phi_r(2) - \phi_s(2)\phi_r(1)\right)$

  – if $s = r$: $\Psi^A(1,2) = 0$

  ⇒ two fermions cannot be in the same state

Particles and states

1 particle, 2 states, 3 particles

# particles (state 1, state 2)	distinguishable classical	indistinguishable classical & indist. bosons
(3,0)	1	1
(0,3)	1	1
(2,1)	3	1
(1,2)	3	1

degeneracies

indistinguishable fermions – 2 single particle states, 3 particles

3,0; 0,3; 2,1; 1,2 } 0

⇒ not possible – there cannot be more than one identical fermions in same state

Grand partition function – Gibbs distribution

$$P_j = \frac{1}{\mathcal{Z}} e^{\beta(\mu N_j - E_j)}$$

$$\mathcal{Z}(T,V,\mu) = \sum_j e^{\beta(\mu N_j - E_j)}$$

$$\mu = -T\frac{\partial S}{\partial N}$$

small system

$\boxed{\{n_1, n_2, n_3, \dots\} \text{ defines a state } j \text{ of the small system}}$

ε_3, ε_2, ε_1 ↑ i

$$N_j = \sum_i n_i, \quad E_j = \sum_i n_i \varepsilon_i$$

$$\mathcal{Z} = \sum_{n_1}\sum_{n_2}\dots e^{\beta(\mu \sum_i n_i - \sum_i n_i \varepsilon_i)} = \sum_{n_1}\sum_{n_2}\dots e^{\beta n_1(\mu-\varepsilon_1)} e^{\beta n_2(\mu-\varepsilon_2)}\dots$$

$$= \underbrace{\left(\sum_{n_1} e^{\beta n_1(\mu-\varepsilon_1)}\right)}_{\mathcal{Z}_1}\underbrace{\left(\sum_{n_2} e^{\beta n_2(\mu-\varepsilon_2)}\right)}_{\mathcal{Z}_2}\dots$$ – one particle states

$$\Rightarrow \boxed{\mathcal{Z} = \prod_{i=1}^{\infty}\mathcal{Z}_i, \quad \mathcal{Z}_i = \sum_{n_i} e^{\beta n_i(\mu-\varepsilon_i)}}$$

probability that the gas is in a state: $\{n_1, n_2, n_3, \dots\}$

$$P(n_1, n_2, \dots) = \frac{e^{\beta(\mu(n_1+n_2+\dots) - (n_1\varepsilon_1 + n_2\varepsilon_2 + \dots))}}{\mathcal{Z}} = \frac{e^{\beta n_1(\mu-\varepsilon_1)}}{\mathcal{Z}_1}\frac{e^{\beta n_2(\mu-\varepsilon_2)}}{\mathcal{Z}_2}\dots$$

$P_1(n_1)$ $P_2(n_2)$

normalised

$$\Rightarrow \boxed{P(n_1, n_2, \dots) = \prod_{i=1}^{\infty} P_i(n_i), \quad P_i(n_i) = \frac{e^{\beta n_i(\mu-\varepsilon_i)}}{\mathcal{Z}_i}}$$

probability of finding n_i particles in single particle state i is indep. of #particles in other states

Mean occupation numbers

$$\langle n_i \rangle = \sum_{n_1, n_2 \dots} n_i P(n_1, n_2, \dots) = \sum_{n_1, n_2 \dots} n_i P_1(n_1) P_2(n_2) \dots P_i(n_i) \dots$$

$$= \underbrace{\left(\sum_{n_1} P_1(n_1)\right)}_{=1} \underbrace{\left(\sum_{n_2} P_2(n_2)\right)}_{=1} \dots \left(\sum_{n_i} n_i P_i(n_i)\right)$$

$$\langle n_i \rangle = \sum_{n_i} n_i P_i(n_i) = \sum_{n_i} n_i \frac{e^{\beta n_i(\mu - \varepsilon_i)}}{\mathcal{Z}_i} = \frac{1}{\beta} \frac{\partial \ln(\mathcal{Z}_i)}{\partial \mu}$$

$$\mathcal{Z}_i = \sum_{n_i} e^{\beta n_i(\mu - \varepsilon_i)}$$

$$\Rightarrow \boxed{\langle n_i \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}_i}{\partial \mu}}$$

Fermions

$$\mathcal{Z}_i = \sum_{n_i = 0,1} e^{\beta n_i(\mu - \varepsilon_i)} = 1 + e^{\beta(\mu - \varepsilon_i)}$$

together

$$\Rightarrow \boxed{\mathcal{Z}_i = \left(1 \pm e^{\beta(\mu - \varepsilon_i)}\right)^{\pm 1}}$$

+ fermions

− bosons

$$\langle n_i \rangle = \frac{1}{\beta} \frac{\partial \ln(\mathcal{Z}_i)}{\partial \mu} = $$

$$= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln\left(1 + e^{\beta(\mu - \varepsilon_i)}\right) =$$

$$= \frac{1}{\beta} \frac{1}{1 + e^{\beta(\mu - \varepsilon_i)}} \beta e^{\beta(\mu - \varepsilon_i)} \Rightarrow$$

$$\boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}} \leq 1$$

$$= f(E)$$

Fermi - Dirac

Bosons

$$\mathcal{Z}_i = \sum_{n_i = 0}^{\infty} e^{\beta n_i(\mu - \varepsilon_i)} \overset{\text{geo series}}{=} \frac{1}{1 - e^{\beta(\mu - \varepsilon_i)}}$$

converges if $\boxed{\mu < \varepsilon_i}$ for $\forall i$

$\Rightarrow$ $\mu < \varepsilon_1$ = single particle ground state, taken as 0 by convention

$\Rightarrow$ $\mu < 0$ for bosons

chemical potential of a gas of bosons is always negative

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial}{\partial \mu} \ln\left(1 - e^{\beta(\mu - \varepsilon_i)}\right) =$$

$$= -\frac{1}{\beta} \frac{1}{1 - e^{\beta(\mu - \varepsilon_i)}} \left(-\beta e^{\beta(\mu - \varepsilon_i)}\right)$$

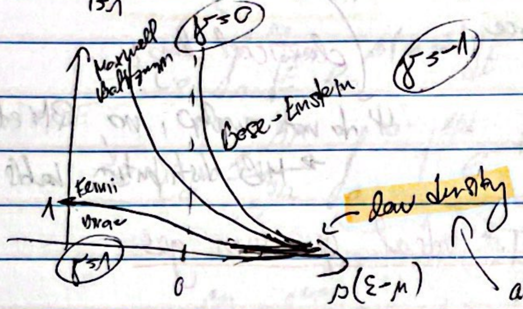
$$\Rightarrow \boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}} = f(E)$$

Bose - Einstein

- distributions of fixed μ and T $\Rightarrow$ $\varepsilon_i \to E$
  - $\rightarrow$ system in equilibrium w/ heat bath & particle reservoir

$$N = \sum_{i=1}^{\infty} \langle n_i \rangle = \int_0^\infty f(E)\, g(E)\, dE \longrightarrow \text{density of states}$$

$$U = \sum_{i=1}^{\infty} \langle n_i \rangle \varepsilon_i = \int_0^\infty E\, f(E)\, g(E)\, dE$$



all similar result

$$f(\varepsilon, \beta, \mu) = \frac{1}{e^{\beta(\varepsilon-\mu)} + \gamma}$$

The classical limit $\boxed{\langle n_i \rangle \ll 1, \ \forall i}$

· single particle energies:

$$\underset{\overset{|||}{0}}{\varepsilon_1} \le \varepsilon_2 \le \dots \le \varepsilon_i \le \dots$$

$$e^{\beta(\varepsilon_1-\mu)} = e^{-\beta\mu} \le e^{\beta(\varepsilon_i-\mu)} = e^{\beta\varepsilon_i} e^{-\beta\mu}$$

$$\varepsilon_i \ge 0 \Rightarrow e^{\beta\varepsilon_i} \ge 1, \ \forall i$$

$$\Rightarrow \boxed{e^{-\beta\mu} \le e^{\beta(\varepsilon_i-\mu)} \quad \forall i}$$

$$\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} \ll 1 \Leftrightarrow e^{\beta(\varepsilon_i-\mu)} \gg 1 \Leftrightarrow \boxed{e^{-\beta\mu} \gg 1}$$

classical limit

$$\Rightarrow \boxed{\langle n_i \rangle = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \pm 1} \longrightarrow e^{\beta(\mu-\varepsilon_i)}}$$

$$\langle N \rangle = \sum_i \langle n_i \rangle = \sum_i e^{\beta(\mu-\varepsilon_i)} = \sum_i e^{\beta\mu} e^{-\beta\varepsilon_i} = e^{\beta\mu} \underbrace{\sum_i e^{-\beta\varepsilon_i}}_{Z_1(T,V)}$$

? When will we have $\boxed{e^{-\beta\mu} \gg 1}$

$$\Rightarrow e^{-\beta\mu} = \frac{Z_1(T,V)}{\langle N \rangle} = \frac{Z_1^{trans} Z_1^{int}}{\langle N \rangle}$$

$$\bullet\ Z_1^{trans} (\oplus) = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} = V n_Q$$

$$\lambda_{th} = \left(\frac{1}{n_Q} \right)^{1/3} = \frac{h}{\sqrt{2\pi m k_B T}} = \left(\frac{3}{2\pi} \right)^{1/2} \lambda_{dB}$$

$$\boxed{\lambda_{th} \approx \lambda_{dB}}$$

$$\bullet\ Z_1^{int} = \sum_{\alpha=1} e^{-\beta\varepsilon_\alpha^{int}} = 1 + \sum_{\alpha=2} e^{-\beta\varepsilon_\alpha^{int}} \ge 1$$

$$\varepsilon_1 = 0 \Rightarrow \varepsilon_1^{int} = 0$$

$$\Rightarrow e^{-\beta\mu} = \frac{V}{\langle N \rangle} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \underbrace{Z_1^{int}}_{\ge 1} \ge \frac{V}{\langle N \rangle} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} = \frac{V}{\langle N \rangle} \lambda_{th}^{-3}$$

$$\boxed{e^{-\beta\mu} \gg 1 \text{ if } \frac{V}{\langle N \rangle} \frac{1}{\lambda_{th}^3} \gg 1}$$

$$\frac{V}{\langle N\rangle}\frac{1}{\lambda_{th}^3} \gg 1 \Rightarrow \left(\frac{l}{\lambda_{th}}\right)^3 \approx \left(\frac{l}{\lambda_{MB}}\right)^3 \gg 1$$

$l = \left(\frac{V}{\langle N\rangle}\right)^{1/3}$ interparticle distance

$\Rightarrow \boxed{l \gg \lambda_{th} \approx \lambda_{MB}}$ classical limit

ψ do not overlap, no QM effects, → MB distribution holds

Number of particles - ideal quantum gas

$$N = \sum_i \langle n_i\rangle = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}\pm 1}$$

integral

$$N = \int_0^\infty g(E)\frac{1}{e^{\beta(E-\mu)}\pm 1}\,dE$$

$E = \frac{p^2}{2m}$

$g(p)\,dp = \delta\frac{V}{h^3}4\pi p^2\,dp$

$g(E)\,dE = \delta\frac{V}{h^3}2\pi(2m)^{3/2}\sqrt{E}\,dE$

$$\boxed{N = \underbrace{\delta\frac{V}{h^3}2\pi(2m)^{3/2}}_{\equiv C_0}\int_0^\infty \frac{\sqrt{E}\,dE}{e^{\beta(E-\mu)}\pm 1}}$$

$\boxed{\delta = 2S+1 = \text{\# possible spin states}}$

Internal energy - ideal quantum gas

$$U = \sum_i \langle n_i\rangle\varepsilon_i = \sum_i \frac{\varepsilon_i}{e^{\beta(\varepsilon_i-\mu)}\pm 1}$$

sum → integral

$$U = \int g(E)\frac{E}{e^{\beta(E-\mu)}\pm 1}\,dE \Rightarrow$$

$$\Rightarrow \boxed{U = \underbrace{\delta\frac{V}{h^3}2\pi(2m)^{3/2}}_{\equiv C_0}\int_0^\infty \frac{E^{3/2}}{e^{\beta(E-\mu)}\pm 1}\,dE}$$

Grand potential - ideal quantum gas

$\boxed{\Phi_G = -\frac{2}{3}U \qquad \Phi_G = -pV}$

$$\Phi_G = -\frac{1}{\beta}\ln\mathcal{Z} = -\frac{1}{\beta}\ln\left(\prod_{i=1}^\infty \mathcal{Z}_i\right) = -\frac{1}{\beta}\sum_{i=1}^\infty \ln\mathcal{Z}_i$$

$$\Rightarrow \boxed{\Phi_G = \mp\frac{1}{\beta}\sum_{i=1}^\infty \ln\left(1\pm e^{\beta(\mu-\varepsilon_i)}\right)}$$

$\oplus$ fermions

$\ominus$ bosons

integral

$$\Phi_G = \mp\frac{1}{\beta}C_0\int_0^\infty \ln\left(1\pm e^{\beta(\mu-E)}\right)\sqrt{E}\,dE$$

by parts

$$= \mp\frac{2}{3}\frac{C_0}{\beta}E^{3/2}\ln\left(1\pm e^{\beta(\mu-E)}\right)\Big|_0^\infty$$

$E = \infty : e^{-\beta E}\to 0$

$E = 0 : E \to 0$

$$\pm\frac{2}{3}\frac{C_0}{\beta}\int_0^\infty E^{3/2}\,d\left(\ln\left(1\pm e^{\beta(\mu-E)}\right)\right)$$

$$= \pm\frac{2}{3}\frac{C_0}{\beta}\int_0^\infty E^{3/2}\frac{\pm e^{\beta(\mu-E)}(-\beta)}{1\pm e^{\beta(\mu-E)}}dE = \boxed{-\frac{2}{3}C_0\int_0^\infty \frac{E^{3/2}}{e^{\beta(E-\mu)}\pm 1}dE} = \Phi_G$$

Using classical limit $e^{-\beta\mu} \gg 1$

$$e^{\beta E} \geq 1 \Rightarrow e^{\beta(E-\mu)} \gg 1$$

$$N = C_0 \int_0^\infty \frac{\sqrt{E}}{e^{\beta(E-\mu)} \pm 1} dE$$

$$\Rightarrow C_0 \int_0^\infty \sqrt{E}\, e^{\beta(\mu-E)} dE = C_0 e^{\beta\mu} \int_0^\infty \sqrt{E}\, e^{-\beta E} dE$$

$t = \beta E$

$$= C_0 \frac{e^{\beta\mu}}{\beta^{3/2}} \underbrace{\int_0^\infty t^{1/2} e^{-t} dt}_{\Gamma(3/2)} = C_0 \frac{e^{\beta\mu}}{\beta^{3/2}} \Gamma\left(\frac{3}{2}\right)$$

$$U = C_0 \frac{e^{\beta\mu}}{\beta^{5/2}} \underbrace{\int_0^\infty t^{3/2} e^{-t} dt}_{\Gamma} = C_0 \frac{e^{\beta\mu}}{\beta^{3/2}} \Gamma\left(\frac{5}{2}\right) = C_0 \frac{e^{\beta\mu}}{\beta^{5/2}} \frac{3}{2} \Gamma\left(\frac{3}{2}\right)$$

$$\boxed{\Gamma(n) = \int_0^\infty t^{n-1} e^{-t} dt \qquad \Gamma(n+1) = n\Gamma(n)}$$

$$\Rightarrow \left.\begin{aligned} U &= \frac{3}{2}\frac{N}{\beta} = \frac{3}{2} N k_B T \\ \Phi_G &= -\frac{2}{3} U = -PV \end{aligned}\right\} PV = Nk_BT \checkmark$$

Fermions & Bosons

$$N = C_0 \int_0^\infty \frac{E^{1/2}}{e^{\beta(E-\mu)} \pm 1} dE = C_0 \int_0^\infty \frac{E^{1/2}}{z^{-1} e^{\beta E} \pm 1} dE =$$

$z = e^{\beta\mu}$ fugacity

$\boxed{x = \frac{E}{k_BT}}$

$$= C_0 (k_BT)^{3/2} \int_0^\infty \frac{x^{1/2}}{z^{-1} e^{x} \pm 1} dx \quad \begin{cases} FD \oplus \\ BE \ominus \end{cases}$$

$\Rightarrow$ Fermi-Dirac integral $\quad f_n(z) = \int_0^\infty \frac{x^n}{z^{-1}e^x + 1} dx$

Bose-Einstein integral $\quad g_n(z) = \int_0^\infty \frac{x^n}{z^{-1}e^x - 1} dx$

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

$$= \sum_{m=0}^\infty z^{m+1} \int_0^\infty x^n e^{-(m+1)x} dx \underset{y = (m+1)x}{\overset{geo}{=}} \sum_{m=0}^\infty \frac{z^{m+1}}{(m+1)^{n+1}} \underbrace{\int_0^\infty y^n e^{-y} dy}_{\Gamma}$$

$$= \Gamma(n+1) \sum_{m=0} \frac{z^{m+1}}{(m+1)^{n+1}} \underset{k=m+1}{=} \Gamma(n+1) \underbrace{\sum_{k=1}^\infty \frac{z^k}{k^{n+1}}}_{= Li_{n+1}(z)} = \Gamma(n+1)\, Li_{n+1}(z)$$

= polylogarithm

similarly for $f_n(z)$:

$$\boxed{\begin{aligned} f_n(z) &= -\Gamma(n+1)\, Li_{(n+1)}(-z) \\ g_n(z) &= \Gamma(n+1)\, Li_{(n+1)}(z) \end{aligned}}$$

$$N = C_0 (k_B T)^{3/2} \int_0^\infty \frac{x^{1/2}}{z^{-1}e^x \pm 1}\,dx \Rightarrow \mp \Gamma\left(\tfrac{3}{2}\right) Li_{\frac{3}{2}}(\mp z) \qquad \begin{matrix} FD \\ BE \end{matrix}$$

$n = \frac{1}{2}$

$$U = C_0 (k_B T)^{5/2} \int_0^\infty \frac{x^{3/2}}{z^{-1}e^x \pm 1}\,dx = \mp \Gamma\left(\tfrac{5}{2}\right) Li_{\frac{5}{2}}(\mp z)$$

$$\Rightarrow \boxed{U = \frac{\Gamma(\frac{5}{2})}{\Gamma(\frac{3}{2})} N k_B T \frac{Li_{5/2}(\mp z)}{Li_{3/2}(\mp z)} = \underbrace{\frac{3}{2} N k_B T}_{\text{classic}} \underbrace{\frac{Li_{5/2}(\mp z)}{Li_{3/2}(\mp z)}}_{\text{quantum effects}}}$$

Fermi gas

metal

free electrons in metal $\approx$ Fermi gas

$$N = C_0 \int_0^\infty \frac{\sqrt{E}}{e^{\beta(E-\mu)} + 1}\,dE$$

$$C_0 = g \frac{2\pi V}{h^3}(2m)^{3/2} = g \frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} = \frac{4\pi V}{h^3}(2m)^{3/2}$$

$2s+1 = 2$ for electrons

$$\Rightarrow N = \frac{4\pi V}{h^3}(2m)^{3/2} \int_0^\infty \frac{E^{1/2}\,dE}{e^{\beta(E-\mu)} + 1}$$

↳ if N, V are known $\Rightarrow$ $\mu = \mu(T)$ by solving eq.

↳ define Fermi energy $\boxed{E_F = \mu(T=0)}$

· claim: $E_F > 0$

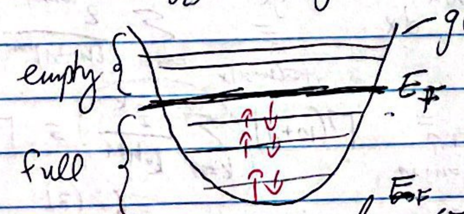
↳ skip proof – see lecture 15

$$f(E) = \frac{1}{e^{\beta(E-\mu)} + 1} \xrightarrow[T \to 0]{} \frac{1}{e^{\beta(E-E_F)} + 1} = \frac{1}{e^{\frac{E-E_F}{k_B T}} + 1}$$

$$\boxed{\begin{aligned} &\text{If } E > E_F \Rightarrow e^{\frac{E-E_F}{k_B T}} \xrightarrow[T \to 0]{} e^{\infty} \Rightarrow f(E) = 0 \\ &\text{If } E < E_F \Rightarrow e^{\frac{E-E_F}{k_B T}} \longrightarrow e^{-\infty} \Rightarrow f(E) = 1 \end{aligned}}$$

Electrons (spin-$\frac{1}{2}$ fermions) at $T=0$

$$N = \int_0^\infty f(E)\, g(E)\, dE$$



for $E > E_F$: $f(E) = 0$

for $E < E_F$: $f(E) = 1$

$$\Rightarrow N = \int_0^{E_F} g(E)\,dE = \frac{4\pi V}{h^3}(2m)^{3/2} \int_0^{E_F} E^{1/2}\,dE =$$

$$= \frac{4\pi V}{h^3}(2m)^{3/2} \frac{2}{3} E^{3/2} \Rightarrow \boxed{E_F = \frac{h^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{2/3} = k_B T_F}$$

T_F: Fermi temperature

$$U = \int_0^\infty E\, f(E)\, g(E)\, dE \underset{\text{at } T=0}{=} \int_0^{E_F} E\, g(E)\, dE = \frac{4\pi V}{h^3}(2m)^{3/2}\int_0^{E_F} E^{3/2} dE$$

$$U = \frac{4\pi V}{h^3}(2m)^{3/2}\frac{2}{5}E_F^{5/2} = \frac{3}{5}NE_F = \frac{3}{5}Nk_BT_F$$

$$E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{2S+1}\frac{N}{V}\right)^{2/3} = k_BT_F = \frac{h^2}{2m}\left(\frac{3}{4\pi(2S+1)}\frac{N}{V}\right)^{2/3}$$

$$E_F = \frac{h^2}{2m}\left(\frac{3}{8\pi}\frac{N}{V}\right)^{2/3} = k_B T_F \quad \text{for electrons } S=1/2$$

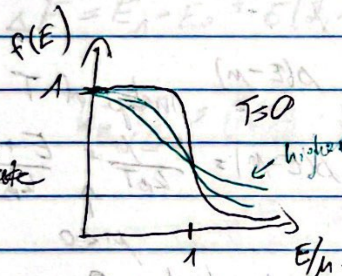
For metals: $\frac{N}{V} = 10^{22} - 10^{23}$ electrons/cm^3

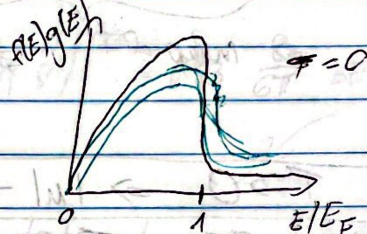
$\Rightarrow E_F \approx 5\,eV$

$\Rightarrow T_F \approx 5\cdot 10^4 K$ - much higher than room T

$\Rightarrow$ for room $T \ll T_F$: extremely deg. Fermi gas

completely degenerate





$$\mu(T) \approx E_F\left(1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2\right)$$

Electronic heat capacity

$$\boxed{C_V = \underbrace{\frac{\pi^2}{2}R\frac{T}{T_F}}_{\text{electrons}} + \underbrace{\frac{12}{5}\pi^4 R\left(\frac{T}{\Theta_D}\right)^3}_{\text{lattice vibrations}}} \quad \text{per mole}$$

- start with degenerate Fermi gas
- raise temp. to $T \ll T_F$ $\Rightarrow e^-$ gain energy $\sim k_BT$.
- only electrons close to Fermi energy can make the jump to higher levels

\# electrons promoted to higher level: $\Delta N \approx \underbrace{f(E_F)}_{\approx 1} g(E_F) k_B T$

$$g(E_F) = \frac{4\pi V}{h^3}(2m)^{3/2}\sqrt{E_F}$$
$$N = \frac{4\pi V}{h^3}(2m)^{3/2}\frac{2}{3}E_F^{3/2}$$

$$\Delta N \approx \frac{3}{2}\frac{N}{E_F}k_BT = \frac{3}{2}N\frac{T}{T_F}$$
$$\Delta E \approx \Delta N k_B T = \frac{3}{2}Nk_B\frac{T^2}{T_F}$$

$$\boxed{T_F = \frac{E_F}{k_B} = \frac{\hbar^2}{2mk_B}\left(\frac{3\pi^2 N}{V}\right)^{2/3}}$$
$$\boxed{\Theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar}{k}\left(\frac{6\pi^2 N}{V}\right)^{1/3} v_s}$$

$$C_V = \frac{\partial E}{\partial T} \approx 3Nk_B\frac{T}{T_F} \Rightarrow 3nR\frac{T}{T_F}$$

more sophisticated treatment: $C_V = \frac{\pi^2}{2}nR\frac{T}{T_F}$

- at room temp. $\frac{T}{T_F}$ = small $\Rightarrow$ electron contribution very small compared to 3R of lattice

Bose - Einstein condensation

- ideal gas of bosons of spin 0
- BE occupation number

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

- total # bosons: $N = \sum \langle n_i \rangle$

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

$$N = \frac{2\pi V (2m)^{3/2}}{h^3} \int_0^\infty \frac{E^{1/2}}{e^{\beta(E-\mu)}-1} dE$$

$\boxed{\mu < 0}$

$$\underbrace{\frac{N}{V}}_{\text{const. density: indep. of } T} = \frac{2\pi(2m)^{3/2}}{h^3} \underbrace{\int_0^\infty \frac{E^{1/2}}{e^{\beta(E-\mu)}-1} dE}_{\Rightarrow \text{ indep of } T}$$

$\Rightarrow e^{\beta(E-\mu)}$ indep. of T

$\Rightarrow \beta(E-\mu) = \frac{E-\mu}{k_B T} = \frac{E+|\mu|}{k_B T}$ is indep. of T ($\mu < 0$)

$\Rightarrow \boxed{\text{If } T \to 0 \Rightarrow |\mu| \to 0}$

$\Rightarrow$ There $\exists T = T_c$ for which $|\mu| = 0$

condensation temperature

$\Rightarrow$ thus it seems that the gas cannot be cooled below T_c

at T_c: $$\frac{N}{V} = \frac{2\pi(2m)^{3/2}}{h^3} (k_B T_c)^{3/2} \underbrace{\int_0^\infty \frac{\sqrt{x}}{e^x - 1} dx}_{2.612 \cdot \frac{\sqrt{\pi}}{2}} \qquad \boxed{x = \frac{E}{k_B T_c}}$$

$$\Rightarrow \boxed{\frac{N}{V} = 2.612 \cdot \left(\frac{2\pi m k_B T_c}{h^2}\right)^{3/2}}$$ defines T_c

When moving from ~~grounds~~ sum $\Rightarrow$ integral,

we assumed $E_0 = 0$ $\Rightarrow$ no contribution to integral

$\Rightarrow$ causing trouble now because

there's many particles in ground state at low T

$$N = \sum_i \frac{1}{e^{\beta(E_i-\mu)}-1}$$

$$= N_0 + N(E>0) = \frac{1}{e^{-\beta\mu}-1} + \underbrace{\frac{2\pi V(2m)^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{E}}{e^{\beta(E-\mu)}-1} dE}_{\text{as earlier}}$$

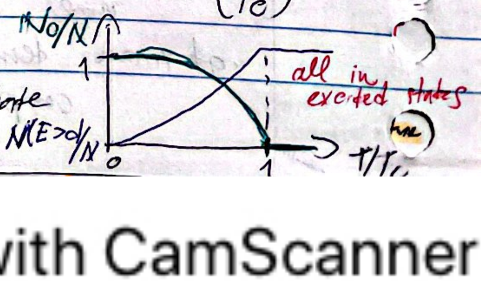
particles in ground state with $E = 0$

$$N_0 = N - N(E>0)$$

$$N(E>0) = N\left(\frac{T}{T_c}\right)^{3/2}$$

$$\frac{N_0}{N} = 1 - \frac{N(E>0)}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

fraction of particles in zero-energy ground state



BEC in rubidium vapor

10 000 Rb atoms in a box of ~ 10 μm

$$\frac{N}{V} \sim \frac{10^4}{(10^{-5})^3} \to 10^{19} m^{-3}$$

interparticle spacing: $\ell \approx \frac{1}{(10^{19})^{1/3}} \approx 5 \cdot 10^{-7} m$ } extremely dilute gas

atomic radius Rb: $r_b \approx 2.4 \cdot 10^{-10} m$

$$\frac{N}{V} = 2.61 \left(\frac{2\pi m k_B T_c}{h^2}\right)^{3/2} \qquad m \approx 1.4 \cdot 10^{-25} kg$$

$$\Rightarrow \underline{T_c = 8.2 \cdot 10^{-8} K}$$

- particles in a box:

$$E = \frac{\pi^2 \hbar^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$$

$$\Delta E = E_1 - E_0 = E(2,1,1) - E(1,1,1) = \ldots = \frac{3h^2}{8mL^2}$$

$$k_B T_c = 0.53 \cdot \left(\frac{h^2}{2\pi m}\right)\left(\frac{N}{V}\right)^{2/3} = 0.53 \frac{8}{6\pi} \Delta E \cdot N^{2/3}$$

large ← # particles in system ← large

$$\boxed{k_B T_c >> \Delta E}$$

⇒ condensation to ground state occurs at thermal energies much larger than the distance between the ground state and first excited state

$$V_Q = (\lambda_{th})^3 = \frac{h^3}{(2\pi m k T)^{3/2}} \approx 2.7 \cdot 10^{-19} m^3$$

Physical volume: $V_{phys} \approx \frac{(10^{-5})^3}{10\,000} \approx 10^{-19} m^3$

$$\Rightarrow \boxed{V_Q \approx V_{phys}}$$

↳ although the gas is very dilute, quantum aspects become important because wavelengths of particles overlap

For $T < T_c$ only consider particles not in ground state because $E_0 = 0$:

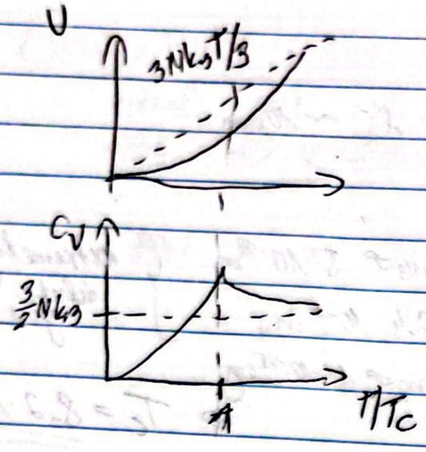
$$U = \frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \frac{E^{3/2}}{e^{\beta(E-\mu)}-1}\,dE \approx \frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \frac{E^{3/2}}{e^{\beta E}-1}\,dE \qquad \boxed{\begin{array}{c} T < T_c \\ \Rightarrow \mu \approx 0 \end{array}}$$

$$= \frac{2\pi V}{h^3}(2m)^{3/2}(k_B T)^{5/2}\underbrace{\int_0^\infty \frac{x^{3/2}}{e^x - 1}\,dx}_{\approx 1.341 \cdot \frac{3\sqrt{\pi}}{4}} \approx 2.01 \cdot V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} k_B T$$

$\frac{N}{V} = ?$ ... as above

$$\Rightarrow U = 0.77 N k_B \left(\frac{T}{T_c}\right)^{3/2}$$

$$C_V = \frac{\partial U}{\partial T} = \frac{5}{2}\, 0.77 N k_B \left(\frac{T}{T_c}\right)^{3/2} = 1.92 N k_B \left(\frac{T}{T_c}\right)^{3/2}$$



Why ground state problem matters for bosons but not fermions?

- only 1 or 2 fermions in ground state ⇒ negligible
- but at low T, <u>many</u> bosons in ground state