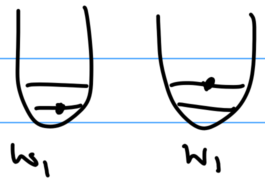
$$E = E_1(\{x_1\}) + E_2(\{x_2\}) + \cdots\cdots$$

quantum #'s of system 1 — quantum #'s of system 2

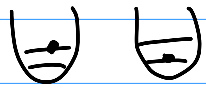
$$e^{-\beta E} = e^{-\beta(E_1+E_2+\cdots\cdots)} = e^{-\beta E_1} e^{-\beta E_2} \cdots$$

$$Q = \sum_{\nu} e^{-\beta E_\nu} = \left(\sum_{\{x_1\}} e^{-\beta E_1}\right)\left(\sum_{\{x_2\}} e^{-\beta E_2}\right) \cdots\cdots$$

If particles are distinguishable:



$|\nu_1 = 0, \nu_2 = 1\rangle$



$|\nu_1 = 1, \nu_2 = 0\rangle$

However with

$$|\psi\rangle = \frac{1}{\sqrt{2}}\left(|\psi_{1s}(1)\rangle|\psi_{2s}(2)\rangle \pm |\psi_{2s}(1)\rangle|\psi_{1s}(2)\rangle\right)$$

$\hat{P}_{12}|\psi\rangle \Rightarrow$ same observable.

interchange 2 identical particles

$$\langle O\rangle = \left(\langle\phi|e^{-i\phi}\,\hat{O}\,e^{i\phi}|\phi\rangle\right)$$

So $\hat{P}_{12}|\psi\rangle = e^{i\phi}|\psi\rangle$

if interchange twice, get same thing.

but $\hat{P}_{12}^{2} |\psi\rangle = |\psi\rangle$

so $\hat{P}_{12} = e^{i2\phi} = 1$

so $\phi = 0, \pi.$

Boson Fermion.

Fermions:

anti-symmetric under change.

$$\Psi(1, 2, 3, \cdots, N) = - \Psi(2, 1 \cdots N)$$

If 2, 1 are the same system, suppose x, x

$$\Psi(x, x \cdots) = - \Psi(x, x \cdots)$$

So $\Psi = 0$

or $\Psi = \frac{1}{\sqrt{2}} \left(|\psi_a(1)\rangle |\psi_b(2)\rangle - |\psi_b(1)\rangle |\psi_a(2)\rangle \right) \overset{\text{if } a=b}{=} 0$

Pauli - Exclusion Principle: No two fermions can be in the same state.

Bosons:

symmetric under change.

$$\Psi(1, 2, 3 \cdots, N) = + \Psi(2, 1, \cdots N)$$

⇒ Occupation number: n_j, # of particles with a corresponding wave function ϕ_j.

⇒ A energy eigenstate ν can be described by a set of occupation #s.

$$\nu = (n_1, n_2 \cdots)$$

Bosons

occupation numbers

orbitals = single particle state.

$$\Psi_N = \sqrt{\frac{n_1!\, n_2! \cdots}{N!}} \sum_{P_{ij}} \hat{P}_{ij}\, \phi_1(1) \cdots\cdots \phi_N(N)$$

all permutations

Fermions

$$\Psi_N = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(N) \\ \vdots & \ddots & & \vdots \\ & & \ddots & \\ \phi_N(1) & \cdots & & \phi_N(N) \end{vmatrix}$$

Slater determinant

$$E_\nu = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \cdots$$

State occupancy (# of particles occupying n_1)

single particle energy

Basis of fock state: $|n_1, n_2, n_3, n_4 \cdots \rangle$

$$Q(N,V,T) = \sum_{\{n_j\}} e^{-\beta \sum_j n_j \varepsilon_j} \quad \text{such that } \sum_j n_j = N$$

Difficult to do so instead:

$$\boxed{\begin{gathered} \Xi(\mu, V, T) = \sum_{n_1} e^{-\beta(n_1 \varepsilon_1 - \mu n_1)} \sum_{n_2} e^{-\beta(n_2 \varepsilon_2 - \mu n_2)} \sum_{n_3} \cdots \\ \text{then find } \langle N \rangle \text{ and dial } \mu \text{ such that} \\ \langle N \rangle = N \qquad \langle N \rangle = z\left(\frac{\partial}{\partial z} \ln \Xi\right)_{\beta, V} \qquad z = e^{\beta\mu} \end{gathered}}$$

fugacity.

If $\hat{H} = \hat{H}_1 + \hat{H}_2 + \cdots$

e.g. $\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \cdots$

This solves TISE:

$$\hat{H}\Psi_N = \left(\hat{H}_1 + \hat{H}_2 \cdots + \hat{H}_N\right)\phi_1(1)\cdots\phi_N(N)$$

$$\stackrel{!}{=} [\phi_2(2)\cdots\phi_N(N)]\underbrace{\hat{H}_1\phi_1(1)}_{\varepsilon_1\phi_1} + [\phi_1(1)\cdots\phi_N(N)]\underbrace{\hat{H}_2\phi_2(2)}_{\varepsilon_2\phi_2}$$

$$\hat{H}\Psi_N = (\varepsilon_1 + \varepsilon_2 + \cdots \varepsilon_N)(\phi_1(1)\phi_2(2)\cdots\phi_N(N))$$

$$\stackrel{!}{=} (\varepsilon_1 + \varepsilon_2 \cdots \varepsilon_N)\Psi_N$$

But it does not satisfy non-commital requirement:

$$[\hat{H}, \hat{P}_{ij}] = 0$$

permutation operator

$$P_{ij}\Psi(\ldots i, \ldots, j \ldots) = \Psi(\ldots, j, \ldots, i \ldots)$$

Last time:

since $P_{ij}^2 \Psi_N = \Psi_N$

$$\hat{P}_{ij}\Psi_N = \lambda\Psi_N$$

$e^{i\theta}$

$\lambda^2 = 1 \implies \theta = 0, \pi$

$\lambda = +1$ bosons $\theta = 0$

$\lambda = -1$ fermions $\theta = \pi$

$$Q = \sum_{|\Psi\rangle} \langle \Psi_N | e^{-\beta \hat{H}} | \Psi_N \rangle = \mathrm{Tr}(e^{-\beta \hat{H}})$$

Fock state: $|\Psi_N\rangle \to |n_1 \cdots n_N\rangle$

$\uparrow$ occupation #:

Fermions: $n_i = 0, 1$

Bosons: $n_i = 0 \cdots N$

Grand Canonical:

\# of particles having energy ε_j

$$\Xi = \sum_{n_1}^{\infty} \sum_{n_2}^{\infty} \sum_{n_3}^{\infty} \cdots e^{-\beta\left(\underbrace{\sum_j n_j \varepsilon_j}_{E_\nu} - \mu \underbrace{\sum_j n_j}_{N_\nu}\right)} = \sum_\nu e^{-\beta(E_\nu - \mu N_\nu)}$$

ν: some configuration of N-particles

$$\overset{!}{=} \sum_{n_1=0}^{\infty} e^{-\beta(n_1\varepsilon_1 - \mu n_1)} \sum_{n_2=0}^{\infty} e^{-\beta(n_2\varepsilon_2 - \mu n_2)} \sum_{n_3=0}^{\infty} \cdots\cdots$$

$$\overset{!}{=} \prod_j \left[\sum_{n_j=0}^{\infty} e^{-\beta(n_j\varepsilon_j - \mu n_j)} \right]$$

$$\ln \Xi = \sum_{\substack{\text{single}\\\text{particle}\\\text{states}, j}} \ln\left(\sum_{n_j} e^{-\beta(\varepsilon - \mu)n_j} \right)$$

$\{n_j\} = 0, 1$ for fermion

$= 0, 1, 2, 3 \cdots$ for boson

sum over all occupation # for a single particle state.

sum over $\{n_j\}$

For Bosons: $n: 0 \to \infty$

$$\sum_{n_j=0}^{\infty} e^{-\beta(\varepsilon - \mu)n_j} = \frac{1}{1 - e^{-\beta(\varepsilon_j - \mu)}}$$

$$\ln \Xi = -\sum_{\substack{j\\\text{single}\\\text{particle}\\\text{states}}} \ln(1 - e^{-\beta(\varepsilon_j - \mu)})$$

$$\sum_{\nu} e^{-\beta(E_\nu - \mu N_0)}$$ $\leftarrow$ ν configuration of N-particle system. specified by a set of $\{n_j\}$

split to

$$\hookrightarrow \sum_{\nu} e^{\sum_j^{\infty}(-\beta(\varepsilon_{j,\nu} n_{j,\nu} - \mu n_{j,\nu}))}$$

$$\hookrightarrow \sum_{\nu} \prod_{j(\nu)}^{\infty} e^{-\beta(\varepsilon_{j,\nu} n_{j,\nu} - \mu n_{j,\nu})}$$

since # of particles is not fixed

$$\hookrightarrow \prod_{j}^{\infty} \sum_{\nu}$$

For Fermions:

$$\sum_{n_j=0}^{1} e^{-\beta(\epsilon_j-\mu)n_j} = 1+e^{-\beta(\epsilon_j-\mu)}$$

$$\ln \Xi = \sum_j \ln\left(1+e^{-\beta(\epsilon_j-\mu)}\right)$$

In the end:

$$\ln \Xi = \mp\underbrace{\sum_j}_{\text{single particle states}} \ln\left(1\mp e^{-\beta(\epsilon_j-\mu)}\right)$$

$-$ Bosons

$+$ Fermions

$$\langle n_j\rangle = \sum_\nu n_j \frac{e^{-\beta(E_\nu-\mu N_\nu)}}{\Xi}$$

$$= \sum_{n_j} n_j\, e^{-\beta(\epsilon_j-\mu)n_j}\, \frac{1}{\Xi} \sum_{\substack{\text{all}\\ \text{other}\\ \text{states}}}$$

$$\langle n_j\rangle = -\frac{\partial}{\partial(\beta\epsilon_j)} \ln \Xi$$

$$\langle n_j\rangle = \frac{1}{e^{\beta(\epsilon_j-\mu)}\mp 1}$$

$-$ for bosons

$+$ for fermions

$N \to \langle N\rangle = \sum_j \langle n_j\rangle$ dial μ

Bosons:

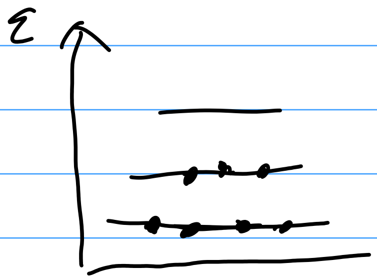
$$\Xi = \prod_j \sum_{n_j=0}^{\infty} \left(\underbrace{e^{-\beta(\varepsilon_j-\mu)}}\right)^{n_j}$$

$r < 1$ for geometric series to converge.

↳ $\varepsilon - \mu > 0$

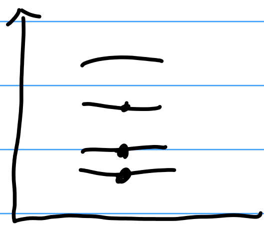
So $\mu < \varepsilon_j$ for all ε.

So for $\varepsilon_{min} = 0$, μ must be negative.



Bosons

in low T, high ρ



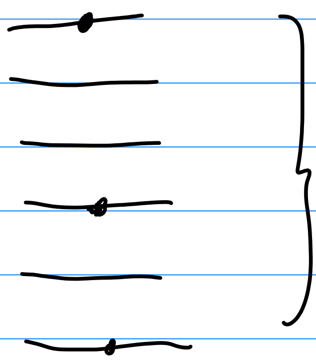
Fermions

in low T, high ρ

Classical limit: → $\langle n_j \rangle \ll 1$

or when $\mu \ll 0$

$\mu = \frac{H}{N} - \frac{TS}{N}$



sparse.

$\Rightarrow$ At classical limit $\mu << \varepsilon_j$ (0)

$$\langle n \rangle = \frac{1}{e^{-\beta\mu} e^{\beta\varepsilon_j} \mp 1} \longrightarrow e^{\beta\mu} \underbrace{e^{-\beta\varepsilon_j}}_{\propto \text{ Boltzmann factor.}}$$

Dial μ:

$$N = \langle N \rangle = \sum_j \langle n_j \rangle$$

$$\stackrel{!}{=} e^{\beta\mu} \underbrace{\sum_j e^{-\beta\varepsilon_j}}_{q_1 \text{ : \# of thermally accessible states}}$$

$$e^{\beta\mu} = \frac{N}{q_1}$$

$$\boxed{\begin{aligned} &\hookrightarrow \mu = k_B T \ln\left(\frac{N}{q_1}\right) \\ &\qquad = -k_B T \ln\left(\frac{q_1}{N}\right) \end{aligned}}$$

$\hookrightarrow$ require $\frac{N}{q_1} << 1$

so that μ is very negative

μ : large negative #.

or $\rho << \lambda_{th}^3$

classical limit: $q_1 \gg N \Rightarrow \mu$ large and negative.

Find the partition function: Q:

$$G = \mu\langle N\rangle = A + pV$$

$$k_BT\ln\frac{N}{q_1} \qquad -k_BT\ln Q \qquad k_BT\ln\Xi:$$

$$\ln\Xi \doteq \mp\sum_j \ln\left(1 \mp e^{-\beta(\varepsilon_j-\mu)}\right)$$

$$= \mp\sum_j \ln\left(1 \mp e^{-\beta\varepsilon_j}e^{\beta\mu}\right)$$

Taylor expand

$$\simeq \sum_j e^{-\beta\varepsilon_j}e^{\beta\mu}$$

$$\simeq \langle N\rangle$$

$$\hookrightarrow \quad Nk_BT(\ln N - \ln q_1) = -k_BT\ln Q + k_BTN$$

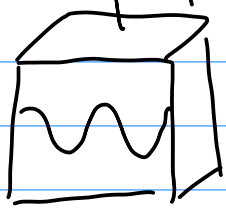
$$\hookrightarrow \quad \ln Q = \ln q_1^N - (N\ln N - N)$$

$$\boxed{Q = \frac{1}{N!}q_1^N}$$ classical limit

identical particles.

$$Q \overset{?}{=} \sum_{\substack{\text{state}\\\text{of particle 1}}} \sum \sum e^{-\beta(\varepsilon_1+\varepsilon_2+\cdots)}$$ ← gets overcount by N!

Density of States:



Use peridic BC:

or $\psi(x) = \psi(x+L)$

$\psi(y) = \psi(y+L)$

$\psi(z) = \psi(z+L)$

$$\psi = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}} \qquad \varepsilon = \frac{\hbar^2}{2m}\vec{k}^2$$

$$\vec{k} = n_x \frac{2\pi}{L}\hat{x} + n_y \frac{2\pi}{L}\hat{y} + n_z \frac{2\pi}{L}\hat{z}$$

$$n_x, n_y, n_z : (-\infty, \infty)$$

So we have $g(k) = \dfrac{1 \text{ state}}{\left(\frac{2\pi}{L}\right)^3}$ value of the k-space.

$$q_1 = \sum_k e^{-\beta\varepsilon(\vec{k})} = \int d^3\vec{k}\, g(k)\, e^{-\beta\varepsilon(\vec{k})}$$

$$= \int d\varepsilon\, \underbrace{g(\varepsilon)}_{\frac{dN}{d\varepsilon}}\, e^{-\beta\varepsilon}$$

$$q_1 = \int_{-\infty}^{\infty} dk_x \int_{-\infty}^{\infty} dk_y \int_{-\infty}^{\infty} dk_z\, \underbrace{\frac{V}{(2\pi)^3}}_{g(k)} \exp\left\{-\beta\frac{\hbar^2}{2m}(k_x^2+k_y^2+k_z^2)^2\right\}$$

can also work in spherical coordinate:

$$g(k)\,d^3k = g(k)\,k^2 \sin\theta\, dk\, d\theta\, d\phi$$

Note: $$\int_{k_1}^{k_2} g(k)\,dk = \int_{\varepsilon(k_1)}^{\varepsilon(k_2)} g(\varepsilon)\,d\varepsilon$$

$$g(\varepsilon)\,d\varepsilon = g(k)\,dk$$

$$\boxed{g(\varepsilon) = g(k)\frac{dk}{d\varepsilon}}$$

$$g(\varepsilon)d\varepsilon = \frac{V}{2\pi^2}\frac{dk}{d\varepsilon} = \frac{V}{2\pi^2}\left[\frac{d}{dk}\left(\frac{\hbar^2 k^2}{2m}\right)\right]^{-1}$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)\varepsilon^{1/2}\,d\varepsilon$$

Back to solving q_1:

$$q_1 = \frac{V}{(2\pi)^3}\left(\int_{-\infty}^{\infty} dk_x\, e^{\frac{-\beta\hbar^2}{2m}k_x^2}\right)\left(\int_{-\infty}^{\infty} dk_y\, e^{\frac{-\beta\hbar^2}{2m}k_y^2}\right)\left(\int_{-\infty}^{\infty} dk_z\, e^{\frac{-\beta\hbar^2}{2m}k_z^2}\right)$$

$$= \frac{V}{(2\pi)^3}\left[\left(\frac{2m}{\beta\hbar^2}\right)^{1/2}\sqrt{\pi}\right]^3$$

$$\boxed{q_1 = \frac{V}{\lambda_{th}^3} \quad \text{where} \quad \lambda_{th} = \left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2}}$$

classical indistinguishable

$$\boxed{Q = \frac{q_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N}$$

With $p \sim \frac{h}{\lambda} \sim \sqrt{2m\langle E\rangle}$ or $\lambda \sim \frac{h}{\sqrt{2m\langle E\rangle}}$

and since $\langle E\rangle \sim k_B T$

$$\lambda \sim \frac{h}{\sqrt{2mk_BT}}$$

Ex: Ar at 300K:

$$\lambda_{th} = 1.5\times10^{-11}\ m$$

$$\mu = k_BT\ln\left(\frac{N}{q_1}\right) = k_BT\ln\left(\frac{N}{V/\lambda_{th}^3}\right)$$

$$\stackrel{!}{=} k_BT\ln\left(\rho\lambda_{th}^3\right) \qquad ; \rho = \frac{N}{V}$$

with $\rho \sim 10^{19}\ cm^{-3}$

$$\mu \sim -18\,k_BT \quad \text{with } \langle \varepsilon\rangle \sim \tfrac{3}{2}k_BT$$

free energy to add particles

$$\mu = \frac{G}{N} = \frac{H}{N} - \frac{TS}{N}$$: μ is negative since TS term is dominating

$$\langle E\rangle = \left(-\frac{\partial}{\partial\beta}\ln Q\right)_{N,V} \qquad \text{where } \ln Q = \ln\left(\frac{1}{N!}q_1^N\right)$$

$$\stackrel{!}{=} -\frac{\partial}{\partial\beta}\left[-\ln(N!) + N\ln V - N\ln\lambda_{th}^3\right]$$

$$\stackrel{!}{=} \frac{3N}{\lambda_{th}}\frac{\partial}{\partial\beta}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{1/2}$$

$$\stackrel{!}{=} \frac{3N}{\lambda_{th}}\,\frac{1}{2}\,\frac{\lambda_{th}}{\beta} = \frac{3}{2}Nk_BT$$

$A = -k_B T \ln Q$ ← potential for canonical ensemble.

use $p = \left(\frac{-\partial A}{\partial V}\right)_{T,N}$

$$P = \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Q)_{T,N} = \frac{N k_B T}{V}$$

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = \frac{3}{2} N k_B$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{N,P} = \frac{\partial}{\partial T}\left(\langle E \rangle + pV\right) = \frac{5}{2} k_B N$$

$$S = \left(\frac{-\partial A}{\partial T}\right)_{V,N} = -\left(\frac{\partial}{\partial T} - k_B T \ln Q\right)$$

$$= k_B \ln Q + k_B T \frac{\partial}{\partial T} \ln Q$$

$$= k_B \ln Q - \frac{1}{T}\underbrace{\left(\frac{\partial}{\partial \beta} \ln Q\right)_{N,V}}_{\langle E \rangle}$$

$$= k_B \ln Q + \frac{3}{2} N k_B$$

$$= k_B \left[-\ln N! + N \ln \left(\frac{V}{\lambda_{th}^3}\right)\right] + \frac{3}{2} N k_B$$

$$\lambda_{th} = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$= k_B \left[-N \ln N + N + N \ln \left(\frac{V}{\lambda_{th}^3}\right)\right] + \frac{3}{2} N k_B$$

For classical gas →

$$\boxed{S = N k_B \ln \left(\frac{V}{N \lambda_{th}^3}\right) + \frac{3}{2} N k_B}$$

Sackor-Tetrode Equation.

If there is no $N!$

$$Q' = q_1^N = \left(\frac{V}{\lambda_{th}^3}\right)^N \rightarrow S' = N k_B \ln \left(\frac{V}{\lambda_{th}^3}\right) + \frac{3}{2} k_B N$$

↖ Not extensive.

$$Q = (?) \underbrace{\int dq_1 \cdots \int dq_N \int dp_1 \cdots \int dp_N \; e^{-\beta H(q_1 \cdots q_N, p_1 \cdots p_N)}}_{\text{Integral over all phase space.}}$$

$q \cdot p \sim$ action $\sim$ $J \cdot S$ $[h]$

so $(?)$ must $\propto \dfrac{1}{(ah)^{3N}}$ to make unit right

a: dimensionless

$(?)$ also $\propto \dfrac{1}{N!}$ to avoid over counting

With experiment, find $a = 1$ with $dS = \dfrac{C_p dT}{T}$

so $(?) = \dfrac{1}{N!(h)^{3N}}$.

$\dfrac{dP}{dT} = \dfrac{\Delta S}{\Delta V}$ during phase transitions.

and $\dfrac{dq\,dp}{h}$

Harmonic Oscillator: $\mathcal{H}(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$

Classical: $Q = \frac{1}{h}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dp \, e^{-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2\right)}$

$$\stackrel{!}{=} \frac{1}{h}\left(\frac{2\pi m}{\beta}\right)^{1/2}\left(\frac{2\pi}{m\omega^2}\right)^{1/2}$$

$$\stackrel{!}{=} \frac{1}{\beta\hbar\omega}$$

$$\stackrel{!}{=} \frac{k_B T}{\hbar\omega}$$

<u>Quantum:</u>

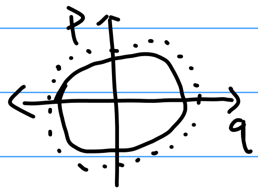
$$Q = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

$$\stackrel{!}{=} e^{-\frac{\beta\hbar\omega}{2}} \frac{1}{1-e^{-\beta\hbar\omega}}$$

high temperature limit: $\beta \to \infty$

$$Q = \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{1-(1-\beta\hbar\omega)} = \frac{k_B T}{\hbar\omega}$$

Phase space: $\frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2 = E$



$$\left(\frac{q}{\sqrt{\frac{2E}{m\omega^2}}}\right)^2 + \left(\frac{p}{\sqrt{2mE}}\right)^2 = 1$$

$$A = \pi\left(\sqrt{\frac{2E}{m\omega^2}}\right)\left(\sqrt{2mE}\right) = \frac{2\pi E}{\omega}$$

Know from QM: $\Delta E = \hbar\omega$.

$$\Delta A = \frac{2\pi}{\omega}\Delta E = 2\pi\hbar = h$$

$$\boxed{Q = \sum_{\text{states}} e^{-\beta\varepsilon} \rightarrow \underbrace{\int \frac{dq^M\, dp^M}{h^M (N_A!\, N_B! \cdots)}}_{\sum_{\text{states}}} e^{-\beta\mathcal{H}} \quad \text{and} \quad M = \#\text{ of DoF}}$$

With $\mu = k_B T \ln(\rho \lambda_{th}^3)$

for μ : large negative

$$\rho \lambda_{th}^3 \ll 1 \qquad \text{where} \quad \rho = \frac{N}{V}$$

with $\Delta x \Delta p \sim h$

with $\Delta p \sim \sqrt{k_B T M}$

$$\Delta x \sim \frac{h}{\sqrt{k_B T M}} \sim \lambda_{th}$$

We do not worry about QM if:

$$\lambda_{th}^3 \ll \rho = \frac{V}{N} \leftarrow \text{Volume occupied by each particle.}$$

If $\lambda_{th} >$ or $\sim \sqrt[3]{\frac{V}{N}}$, then wave functions of particles overlap with each other

Reduced Distribution Function:

with $n(\vec{r},\vec{p})$: distribution function

$$N = \iint d^3r\, d^3p\; n(\vec{r},\vec{p})$$

with $N = \sum_i \langle n_i \rangle$

occupation #

$$\sum \langle n_i \rangle \rightarrow \sum_i n(\vec{r}_i,\vec{p}_i)\, h^3 = N$$

$$d^3\vec{r}\, d^3\vec{p}\; n(\vec{r}_i,\vec{p}_i) = \frac{\langle n_i \rangle}{h^3} \longrightarrow \frac{e^{-\beta H}}{q_1} \rightarrow q_1 = \frac{V}{\lambda_{th}^3}$$

$$n(\vec{r}_i,\vec{p}_i)\, d^3\vec{r}\, d^3\vec{p} = \frac{N e^{-\frac{\beta p^2}{2m}}}{h^3\, V/\lambda_{th}^3}\, d^3\vec{r}\, d^3\vec{p}$$

$$n(\vec{p})\, d^3\vec{p} = \underbrace{\int_{\text{space}} d^3\vec{r}}_{V}\; n(\vec{r},\vec{p})\, d^3\vec{p}$$

$$n(\vec{p})\, d^3\vec{p} = N \frac{\lambda_{th}^3}{h^3}\, e^{-\frac{\beta p^2}{2m}}\, d^3p$$

$$\stackrel{!}{=} N \frac{1}{(2\pi m k_B T)^{3/2}}\, e^{-\frac{\beta \vec{p}^2}{2m}}$$

$$f(r_1, r_2, \cdots p_1, p_2 \cdots) \propto e^{-\beta H(r^N, p^N)}$$

$$1 = \frac{\int d^3\vec{r}_1\, d^3\vec{r}_2\, d^3\vec{r}_3 \cdots \int d^3\vec{p}_1 \cdots\; e^{-\beta H(r^N,p^N)}}{\int d^3\vec{r}_1\, d^3\vec{r}_2 \cdots \int d^3p_1 \cdots \int d^3p_N\; e^{-\beta H(r^N,p^N)}}$$

$$n(\vec{p}) = N \frac{\int d^3\vec{r}_1 \cdots \int d^3\vec{r}_N \int d^3\vec{p}_2 \cdots \int d^3\vec{p}_N \, e^{-\beta H}}{\int dr^N \int dp^N \, e^{-\beta H}}$$

Pair Correlation Function:

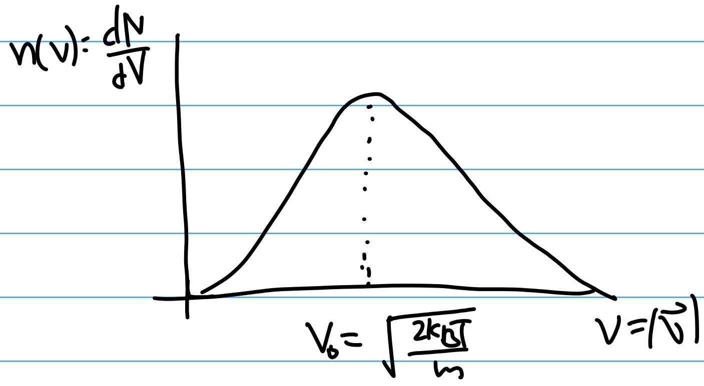
$$g(\vec{r}_1, \vec{r}_2) = N(N-1) \frac{\overbrace{\int d^3\vec{r}_3 \cdots \int d^3\vec{r}_N}^{V^{N-2} \text{ for ideal gas}} \int d^3\vec{p}_1 \cdots \int d^3\vec{p}_N \, e^{-\beta H}}{\underbrace{\int dr^N}_{V^N \text{ ideal gas}} \int dp^N \, e^{-\beta H}}$$

$$n(\vec{v})\,d^3\vec{v} = N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{\beta m |v|^2}{2}} \, d^3\vec{v}$$

Maxwell distribution for velocities

with $d^3\vec{v} = v^2 4\pi \, dv$

$$n(\vec{v})\,dv = N 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\beta \frac{1}{2} m |v|^2} \, dv$$



$$\langle v \rangle = \frac{1}{N}\int dv \, n(v) \, v = \sqrt{\frac{8k_BT}{\pi m}}$$

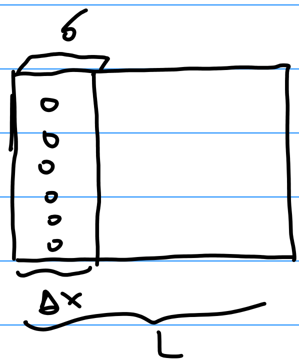
$$v_{rms} = \sqrt{\frac{3k_BT}{m}}$$

Mean - free - Path:

$$\lambda = \frac{1}{\rho \sigma}$$

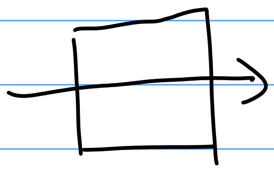
cross-section

density $= \frac{N}{V}$



$P_{trans} = 1 - \rho \sigma \Delta x$

$\stackrel{!}{=} e^{-\rho \sigma x} = e^{-\frac{x}{\lambda}}$



$P = \chi E$

polarization

susceptibility

absorption $\propto \operatorname{Im}(\chi)$

$$\chi(t) = -\beta \frac{d}{dt} \langle \underbrace{\delta A(0)\, \delta A(t)}_{\text{Fluctuations}} \rangle$$

time-correlation function

$$\chi(\omega) = -i\omega\beta \int_0^\infty dt\, e^{-i\omega t} \langle \delta A(0)\, \delta A(t) \rangle$$

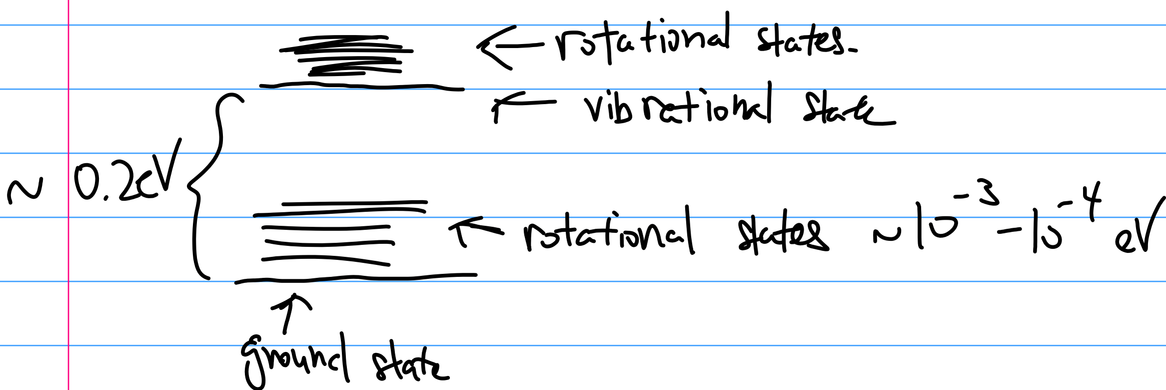
$$C_v = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = \frac{3}{2}Nk_B = \frac{3}{2}nR = 12.47\ \text{J/mol K}\ N$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\langle E\rangle + PV\right) = \frac{\partial}{\partial T}\left(\frac{3}{2}Nk_BT + Nk_BT\right)$$

$$\overset{!}{=} \frac{5}{2}Nk_B$$

$$\overset{!}{=} 20.78\ \text{J/mol K}\ N$$

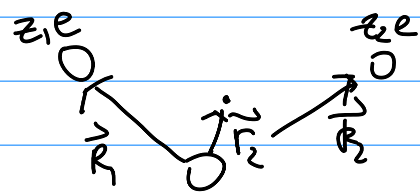
Diatomic Molecules:



$$\hat{H} = \sum_{i=1}^{N}\frac{\hat{p}_i^2}{2m} + \sum_{\substack{(ij)\\ \text{pairs}}}\frac{1}{4\pi\epsilon_0}\frac{e^2}{|\vec{r}_1-\vec{r}_2|} - \sum_{i\alpha}\frac{1}{4\pi\epsilon_0}\frac{e^2 Z_\alpha}{|\vec{r}_i-\vec{R}_\alpha|}$$

$$+ T_N + V_{NN}$$

↳ repulsion



Born - Oppenheimer Approximation:

Wave function of molecule:

$$\underset{\substack{\uparrow \\ \text{electron} \\ \text{position}}}{\Psi(r_i}, \underset{\substack{\uparrow \\ \text{nucleus} \\ \text{position}}}{R_\alpha)} = \underset{\substack{\uparrow \\ \text{electron} \\ \text{wavefunction}}}{\psi_{elec}(r_i | R_\alpha)} \underset{\substack{\uparrow \\ \text{nuclear wavefunction}}}{\chi(R_\alpha)}$$

$$\chi = \underset{\substack{\uparrow \\ \text{Vibrational} \\ \text{(SHO)}}}{\psi_{vib}(R)} \underset{\substack{\uparrow \\ \text{Rotational} \\ \text{(Rigid Motor)}}}{\psi_{rot}(\theta, \phi)}$$

$\psi_{vib}(R) = \psi_{SHO}(R)$ for $E_v = (v + \frac{1}{2})\hbar w$

$Q = \frac{1}{N!} q_1^N$ where $q_1 = q_{trans}\, q_{int}$

$q_{vib} = \sum e^{-\beta \varepsilon_{trans}} + e^{-\beta \varepsilon_{int}}$

$$\boxed{q_{vib} = \left(e^{\theta_{vib}/2T} - e^{-\theta_{vib}/2T} \right)^{-1} \quad \text{where } \theta_{vib} = \frac{\hbar w}{k_B}}$$

For $\hat{H}_{rot} = \frac{\hat{L}^2}{2I}$

$\hookrightarrow \psi_{rot} = \underset{\substack{\uparrow \\ \text{it can be symmetric or anti-symmetric.}}}{Y_J^m(\theta, \phi)}$ spherical Harmonics

where $m = +J, J-1 \cdots 0 \cdots -J+1, -J$

So we have degeneracy of $g_J = 2J+1$

$$\hat{H} Y_J^m = \frac{\hat{L}^2}{2I} Y_j^m$$

$$= \underbrace{\frac{J(J+1)\hbar^2}{2I}}_{J(J+1)B} Y_j^m$$

then $$\boxed{q_{rot} = \sum_{J=0}^{\infty} (2J+1) \exp\{-\beta J(J+1)B\}}$$

Operations that keep electrons fixed with nuclear interchange.

$$\underbrace{(\underset{\substack{\uparrow \\ \text{reflection} \\ \text{of electron}}}{\sigma_{v,e}} \times \underset{\substack{\uparrow \\ \text{Inversion}}}{i_e})}_{\text{For electrons}} \times \underset{\substack{\uparrow \\ \text{rotation by} \\ 180°}}{C_2}$$

Since

$$|\psi_{\substack{nuc \\ spin}}\rangle = \begin{cases} \left.\begin{array}{l} |1\ 1\rangle = |\uparrow\uparrow\rangle \\ |1\ 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |1\ {-1}\rangle = |\downarrow\downarrow\rangle \end{array}\right\} (+) \\ \\ |0\ 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)\} (-) \end{cases}$$

Since both $|\psi_{\substack{nuc\\spin}}\rangle$ and ψ_{rot} can be symmetric or anti-symmetric, should consider them together.

$$q_{\substack{rot/\\nuc\\spin}} = \sum_{J=0}^{\infty} g_{IJ} \exp\{-\beta J(J+1)B\}$$

In classical limit:

$$q_{\substack{rot/\\nuc\\spin}} \simeq \frac{\overbrace{(2I_A+1)(2I_B+1)}^{\text{nuclear spin state degeneracy.}}}{\sigma_{AB}} \underbrace{\sum_{J=0}^{\infty}(2J+1)\exp\{-\beta J(J+1)B\}}_{q_{rot}}$$

$$\sigma_{AB}\begin{cases}2 & \text{if } A=B\\ 1 & \text{if } A\neq B\end{cases}$$

$$\left(\sim \int_0^{\infty} dJ\, J(J+1)\exp\{-\beta J(J+1)B\}\right)$$

$$\stackrel{!}{=} \frac{T}{\theta_{rot}} = \frac{2I_0 T k_B}{\hbar^2}$$

$$\psi_{tot} = \underset{\substack{\text{symmetric}\\ \text{for } H_2}}{\psi_{elec}}\ \underset{\text{symmetric}}{\psi_{vib}}\ \psi_{rot}\,|\psi_{\substack{nuc\\spin}}\rangle$$

$$q_{int} = q_{ele}\ \underset{(SHO)}{q_{vib}}\ q_{\substack{rot/\\nuc\\spin}} \qquad \theta_{vib} = \frac{\hbar\omega}{k_B} \qquad \theta_{rot} = \frac{\hbar^2}{2I_0 k_B}$$

nuc spin. for proton, $I=\frac{1}{2}$

$$\stackrel{!}{=} g_0\exp\{-\beta\varepsilon_{ele}\}\left[\exp\left\{\frac{\theta_{vib}}{2T}\right\} - \exp\left\{\frac{-\theta_{vib}}{2T}\right\}\right]^{-1}\left(\frac{(2I_A+1)(2I_B+1)}{\sigma_{AB}}\frac{T}{\theta_{rot}}\right)$$

$$\sigma_{AB} = \begin{cases}1 & A\neq B\\ 2 & A=B\end{cases}$$

For diatomic.

In classical limit high T.

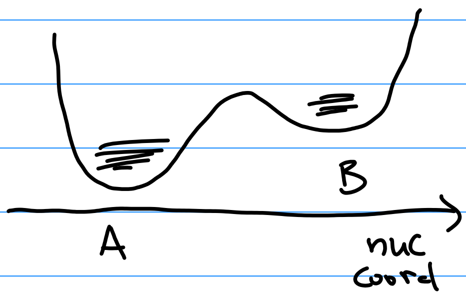
Finally $$q_1 = q_{trans}\, q_{int} = \frac{V}{\lambda_{th}^3} q_{int}$$

$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{P}_i^2}{2m} + \sum_{(ij)} \frac{1}{4\pi\varepsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \leftarrow \text{e-e interaction}$$

$$- \frac{1}{4\pi\varepsilon_0} \sum_{i\alpha} \frac{e^2 Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} + \sum_{\alpha\beta} \frac{(Z_\alpha e)(Z_\beta e)}{|\vec{R}_\alpha - \vec{R}_\beta|} + \sum_{\alpha=1}^{M} \frac{1}{2M_\alpha} \hat{P}_\alpha^2$$

e-N interaction N-N interaction T_N

Chemical Equilibrium:



$$\frac{N_A}{N_B} = \frac{\sum_i e^{-\beta A_i}}{\sum_i e^{-\beta B_i}} = \frac{q_A}{q_B}$$

$$\hookrightarrow \frac{N_A}{q_A} = \frac{N_B}{q_B}$$

For classical limit $\langle n \rangle \ll 1$:

$$\mu = k_B T \ln \frac{N}{q_1}$$

since $\dfrac{N_A}{q_A} = \dfrac{N_B}{q_B}$

$$\hookrightarrow \boxed{\mu_A = \mu_B}$$

Ex: $A \rightleftharpoons B$

For equilibrium: minimize Helmholtz free energy.

$$dA = \sum_i u_i \, dN_i = 0$$

$$= u_A dN_A + u_B dN_B = 0$$

To conserve particles: $dN_A + dN_B = 0$

$dN_A = -dN_B$

$$dN_A (u_A - u_B) = 0$$

With: $aA + bB \rightleftharpoons cC + dD$

then $a u_A + b u_B = c u_C + d u_D$

$$a u_A + b u_B - c u_C - d u_D = 0$$

So chemical equilibrium:

$$\sum \nu_i u_i = 0$$

↳ product has negative
↳ reactant has positive.

← always true

For classical limit:

$$\mu_i = k_B T \ln\left(\frac{N_i}{q_i}\right)$$

$$\overset{!}{=} k_B T \ln\left(\frac{\rho_i V}{q_i}\right)$$

then $$\sum_i \nu_i \mu_i = \cancel{k_B T} \sum_i \nu_i \ln\left(\frac{\rho_i V}{q_i}\right) = 0$$

$$\overset{!}{=} \sum_i \ln\left(\frac{\rho_i V}{q_i}\right)^{\nu_i} = 0$$

$$\overset{!}{=} \ln\left(\underbrace{\prod_i \left(\frac{\rho_i V}{q_i}\right)^{\nu_i}}_{=1}\right) = 0$$

Law of mass action

$$\boxed{\prod_i \rho_i^{\nu_i} = \prod_i \left(\frac{q_i}{V}\right)^{\nu_i} = K_c(T)}$$

ratio of concentration

For classical and non-interacting

Ex: $A + B \rightleftharpoons AB$

$$\frac{\rho_A \rho_B}{\rho_B} = \left(\frac{q_A}{V}\right)\left(\frac{q_B}{V}\right)\left(\frac{q_{AB}}{V}\right)^{-1} = K_c(T)$$

Ex: $H^+ + e^- \rightleftharpoons H$

$$\frac{\rho_{H^+}\,\rho_{e^-}}{\rho_H} = \frac{\left(q_{H^+}/V\right)\left(q_{e^-}/V\right)}{\left(q_H/V\right)}$$

$$q_{e^-} = \underset{\substack{\uparrow \\ \text{account} \\ \text{for spin}}}{2}\frac{V}{\lambda_{th}^3} \qquad q_{H^+} = \underset{\substack{\uparrow \\ \text{spin}}}{2}\frac{V}{\lambda_{th}^3}$$

$$q_H = \underset{\substack{\uparrow \\ \text{spin.}}}{4}\frac{V}{\lambda_{th}^3}\,e^{-\beta\varepsilon_{elec}}$$

$$\boxed{\frac{\rho_{H^+}\,\rho_e}{\rho_H} = \frac{1}{\lambda_e^3}\,e^{-\beta(13.6eV)}}$$

$$\rho_e = \rho_{H^+} = \underset{\substack{\uparrow \\ \text{ionized fraction}}}{X}\,\rho_0 \qquad \text{and} \qquad \rho_H = (1-X)\,\rho_0$$

Fermion

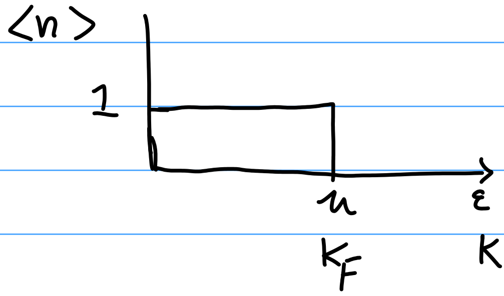
$$\langle n(\varepsilon)\rangle = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$ ← no restriction on μ.

Bosons:

$$\langle n(\varepsilon)\rangle = \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$ ← $\mu < \varepsilon$.

For fermion : $T \to 0$

$$\langle n\rangle = \frac{1}{e^{\infty(\varepsilon-\mu)}+1} \quad \begin{cases} \text{for } \varepsilon > \mu, & \langle n\rangle = 0 \\ \text{for } \varepsilon < \mu, & \langle n\rangle = 1 \end{cases}$$



Dial μ so:

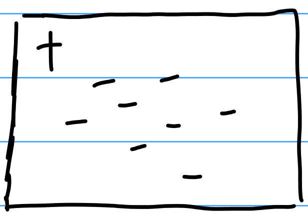
$$\sum_{i,\ \text{all states}} \langle n_i\rangle = N$$

$$\int d^3\vec{k}\, g(\vec{k}) \langle n(\varepsilon(\vec{k}))\rangle = N$$

$$\hookrightarrow = \int_0^\infty 4\pi k^2 dk\, g(k) \langle n(\varepsilon(\vec{k}))\rangle$$

Electron in 3D:

Jellium (Sommerfield) model.



$$g(\vec{k})d^3k = \overset{\text{spin}}{2} \frac{V}{(2\pi)^3} d^3\vec{k}$$

$$g(k)dk = \frac{V}{\pi^2} k^2 dk$$

$$N = \sum \langle n_i\rangle \to \int_0^{k_F} dk \left(\frac{V}{\pi^2}k^2\right) 1 + \int_{k_F}^{\infty} dk \left(\frac{V}{\pi^2}k^2\right) 0$$

$$N = \frac{V}{\pi^2}\frac{k_F^3}{3}$$

$$\hookrightarrow \quad N = \frac{V}{\pi^2}\,\frac{k_F^3}{3}$$

$$\hookrightarrow \boxed{k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} = \left(3\pi^2 \rho\right)^{1/3}}$$

$$\varepsilon_{\vec{k}} = \frac{\hbar^2 |k|^2}{2m}$$

Fermi-Level

$$\boxed{\mu = \varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3}}$$

Do it via $\int \varepsilon(k) g(\varepsilon)$:

$$N = \int_0^{\varepsilon_F} d\varepsilon \, g(\varepsilon) \, 1$$

$$= \int_0^{\varepsilon_F} d\varepsilon \; g(k) \left(\frac{\partial \varepsilon}{\partial k}\right)^{-1}$$

$$= \int_0^{\varepsilon_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2} \, d\varepsilon$$

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

$$\hookrightarrow \varepsilon_F = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3}$$ ← same answer.

Working out pressure:

$$p = -\frac{\partial A}{\partial V}\Big)_{T,N} \rightarrow \frac{\partial\langle E\rangle}{\partial V}\Big)_{S,N}$$

$$\langle E\rangle = \sum \varepsilon_i \langle n(\varepsilon_i)\rangle$$
$$\overset{!}{=} \int d\varepsilon\, g(\varepsilon)\, \langle n(\varepsilon)\rangle\, \varepsilon_i$$
$$\overset{!}{=} \int_0^{\varepsilon_F} d\varepsilon\, g(\varepsilon)(1)\, \varepsilon_i$$

$$\langle E\rangle = \int_0^{\varepsilon_F} d\varepsilon \left(\frac{3}{2}\frac{N}{\varepsilon_F}\left(\frac{\varepsilon}{\varepsilon_F}\right)^{1/2}(1)\,\varepsilon\right)$$

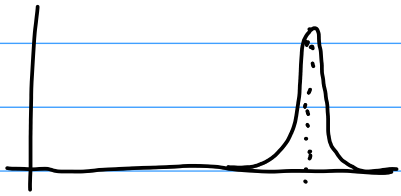
$$\boxed{\begin{aligned}\langle E\rangle &= \frac{3}{5} N \varepsilon_F \\ &\downarrow \\ \langle \varepsilon\rangle &= \frac{3}{5}\varepsilon_F\end{aligned}} \Rightarrow \boxed{\begin{aligned} p &= -\frac{\partial\langle E\rangle}{\partial V}\Big)_{S,N} \\ p &= \frac{2}{3}\frac{\langle E\rangle}{V} \leftarrow \text{general for non-relativistic 3D gas}\end{aligned}}$$

$$K_T = -V\left(\frac{\partial p}{\partial V}\right)_T = \frac{2}{3}\varepsilon_F \rho$$

isothermal compressibility

$$I(T) = \int_0^\infty d\varepsilon\, \underbrace{\overset{\substack{\text{DoS}\\ \downarrow}}{g(\varepsilon)}\;\overset{\substack{\text{what}\\ \text{you want}\\ \downarrow}}{h(\varepsilon)}}_{\phi(\varepsilon)}\;\underbrace{\overset{\substack{\text{F.D.}\\ \downarrow}}{\langle n(\varepsilon)\rangle}}_{f}$$

$-\dfrac{\partial\langle n(\varepsilon)\rangle}{\partial\varepsilon}$



$$\int_0^\infty d\varepsilon\; \phi(\varepsilon)\, f(\varepsilon)$$

taylor expansion.

$$\overset{!}{=} \cancel{\Phi(\varepsilon)\, f\Big|_0^\infty} - \int_0^\infty d\varepsilon\; \Phi(\varepsilon)\, \frac{\partial f}{\partial \varepsilon}$$

$\Phi(0)=0 \quad f(\infty)=0$

where $\Phi(\varepsilon) = \int_0^\varepsilon d\varepsilon'\, \phi(\varepsilon') = \int_0^\varepsilon d\varepsilon'\, g(\varepsilon')\, h(\varepsilon')$

$$\int_0^\infty d\varepsilon\, \phi f = \int_0^\infty d\varepsilon \underbrace{\left(\frac{-\partial f}{\partial\varepsilon}\right)}_{\text{even}} \left(\Phi(\mu) + \underbrace{\cancel{\frac{\partial\Phi}{\partial\varepsilon}\Big|_\mu (\varepsilon-\mu)}}_{\text{odd}} + \frac{1}{2}\frac{\partial^2\Phi}{\partial\varepsilon^2}\Big|_\mu (\varepsilon-\mu)^2 + \cdots\right)$$

$$\overset{!}{\approx} \Phi(\mu) \underbrace{\int_0^\infty d\varepsilon \left(\frac{-\partial f}{\partial\varepsilon}\right)}_{1} + \frac{1}{2}\frac{\partial^2\Phi}{\partial\varepsilon^2}\Big|_\mu \frac{\pi^2}{6}(k_B T)^2$$

$$\boxed{\int_0^\infty d\varepsilon\; \phi(\varepsilon)\, \langle n(\varepsilon)\rangle = \underbrace{\int_0^\mu d\varepsilon\; \phi(\varepsilon)}_{\Phi(\mu)} + \frac{\pi^2}{6}(k_B T)^2 \underbrace{\frac{\partial\phi}{\partial\varepsilon}}_{\frac{\partial^2\Phi}{\partial\varepsilon^2}}\Big|_\mu}$$

Find μ first with $\phi = g(\varepsilon)\ 1$

for 3D electron gas?

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{1}{g(\varepsilon_F)} \frac{\partial g}{\partial \varepsilon}\bigg|_{\varepsilon_F}$$

$$\frac{\langle E \rangle}{N} = \frac{3}{5}\varepsilon_F + \frac{\pi^2}{6}(k_B T)\big(g(\varepsilon_F) k_B T\big)$$

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \left(\frac{\pi^2}{2} N k_B\right)\left(\frac{k_B T}{\varepsilon_F}\right)$$

For Fermion: $\langle n_j \rangle = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$

$N = \sum_j \langle n_j \rangle$: defines μ

If $\langle n_j \rangle \ll 1$: (classical)

$$\langle n_j \rangle = e^{-\beta(\varepsilon - \mu)} = e^{\beta\mu} e^{-\beta\varepsilon}$$

$$N = e^{\beta\mu} \sum e^{-\beta\varepsilon} = e^{\beta\mu} q_1$$

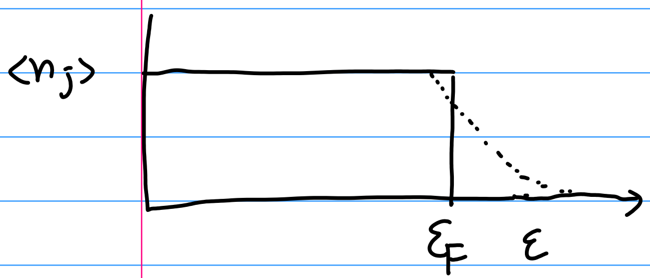
$$\mu = kT \ln\left(\frac{N}{q_1}\right)$$

with $q_1 = \frac{V}{\lambda_{th}^3} q_{int.}$ $\quad \lambda_{th} = \sqrt{\frac{\hbar^3}{2mk_BT}}$

Then $\mu = k_BT \ln(\rho \lambda_{th}^3) - k_BT \ln(q_{int})$

Classical limit when $\rho\lambda_{th}^3 \ll 1$

Now consider quantum, $k_BT \ll \varepsilon_F$



$$N = \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon = \int_0^{k_F} g(k) 4\pi k^2 \frac{2V}{(2\pi)^3} dk$$

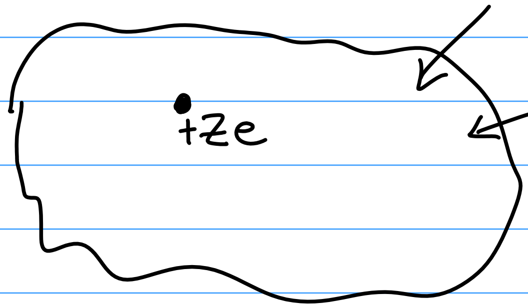
$$\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3} = \frac{\hbar^2}{2m} k_F$$

define $v_F = \frac{\hbar k_F}{m}$

Thomas - Fermi Model:

cloud of electron

Fundamental approx:
$\varepsilon_F \gg$ non-mean field interaction.



$k_BT \ll \varepsilon_F$

charge density: $$\varsigma(r) = -e\underbrace{\rho(\vec{r})}_{\text{electron gas}} + \underbrace{Ze\,\delta(\vec{r})}_{\text{ion}}$$

$$\mu = \varepsilon_F[\rho(r)] - e\phi(r) = \text{const} = 0$$

$$e\phi(r) = \frac{\hbar^2}{2m}\left(3\pi^2\rho\right)^{2/3}$$

or $$\rho = \left(\frac{2me}{\hbar^2}\phi(r)\right)^{3/2}\frac{1}{3\pi^2}$$

With Poisson Equation:

$$\nabla^2\phi = \frac{-\varsigma(r)}{\varepsilon_0}$$

$$= \frac{e(2me)^{3/2}}{3\pi^2\hbar^2\varepsilon_0}\left[\phi(r)\right]^{3/2} - \frac{1}{\varepsilon_0}Ze\,\delta^3(r)$$

Solving the Poisson Eq:

Thomas Fermi Model.

$$\begin{cases} \phi(r) = \dfrac{1}{4\pi\epsilon_0} \dfrac{Ze}{r} \Phi\left(\dfrac{r Z^{1/3}}{0.885 a_0}\right) & a_0 = \dfrac{4\pi\epsilon_0 \hbar^2}{m_e e^2} \\ \Phi(r) = \left[1 + \left(\dfrac{r^3}{144}\right)^{\lambda}\right]^{-1/\lambda} & \lambda = 0.257 \end{cases}$$

$$\rho(r) = \frac{1}{3\pi^2}\left(\frac{2m_e}{\hbar^2}\phi(r)\right)^{3/2}$$

$$D(r) = 4\pi r^2 \rho(r)$$

radial # density

$$E_{TF}(r) = \int dr\, 4\pi r^2 \rho(r) \frac{3}{5} \varepsilon_F \rho(r)$$

$$-\frac{1}{4\pi\epsilon_0}\int_0^\infty 4\pi r^2 dr \frac{\rho Z e}{r}$$

$$+\frac{1}{2}\frac{1}{4\pi\epsilon_0}\int_0^\infty d\vec{r}_1 \int_0^\infty d\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

$$\Rightarrow E_{TF} = -1.538 \underbrace{\left(\frac{1}{2}\frac{e^2}{4\pi\epsilon_0 a_0}\right)}_{13.6\,\mathrm{eV}} Z^{7/3}$$

Quantum Picture:

$$\hat{H}\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3 \cdots\cdots) = E_0 \psi(\cdots\cdots)$$

electron 1

Later (1964) showed $E_0 = E[\rho(r)]$

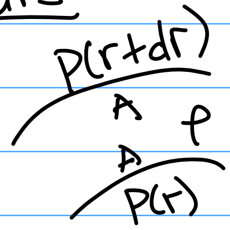
energy is a functional of density

$$K = \frac{k_B T}{\varepsilon_F} \ll 1$$ cold atoms, Fermi-Dirac Relevant

interaction energy includes gravity

$$\tau = \frac{U_{ij}}{k_B T} \gg 1$$ hot atoms, Fermi-Dirac irrelevant

Stars:



$$F_g = \frac{-G\rho A M(r)\,dr}{r^2}$$

$$P(r)A - P(r+dr)A = F_g$$

Hydrostatic Equilibrium

$$\frac{\partial P}{\partial r} = \frac{-G M(r)\,\rho(r)}{r^2}$$

Consider:

$$\frac{\cancelto{0}{P(\text{surface})} - P(0)}{R} = \frac{-GM\left(\frac{M}{R^3}\right)}{R^2}$$

then

$$P(0) \cong \frac{GM^2}{R^4}$$

$$E = N\left[\frac{3}{5}\varepsilon_F - \frac{3}{4\pi}\frac{1}{4\pi\epsilon_0}e^2 k_F\right]$$

↑ Fermi-Energy ← electrostatic repulsion

$$= \frac{e^2}{4\pi\epsilon_0}\left[2.88\,\alpha_0 N^{5/3} V^{-5/3} - 3.05 N^{-4/3} V^{-1/3}\right]$$

$$P = \frac{\partial E}{\partial V}\bigg|_{S,N} = \frac{e^2}{4\pi\epsilon_0}\left[1.92\,\alpha_0 \rho^{5/3} - 1.01\,\rho^{4/3}\right] = \frac{GM^2}{R^4}$$

Solving R:

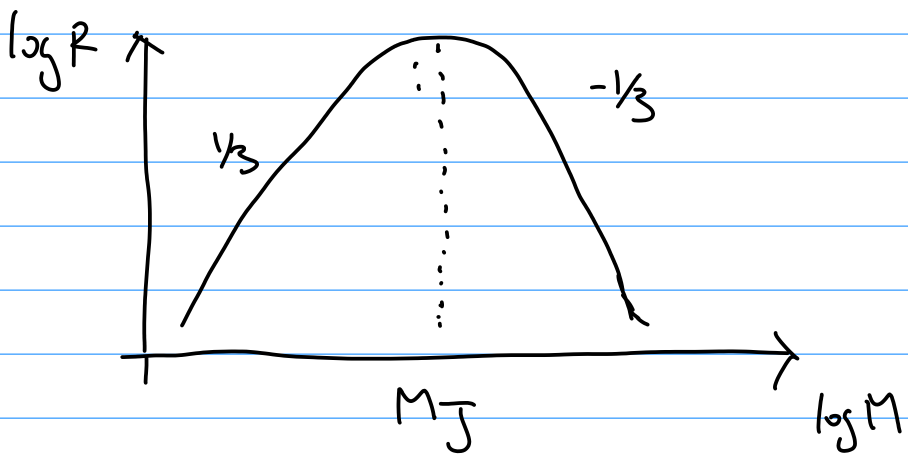
$$R = \frac{e^2}{4\pi\epsilon_0} \frac{\alpha_0}{\epsilon M^{1/3}} \frac{1}{M_r^{5/3}} \left[\frac{1}{1 + \frac{e^2/4\pi\epsilon_0}{\epsilon M^{2/3} M_p^{1/3}}} \right]$$

For small mass: $M << \left(\frac{e^2}{4\pi\epsilon_0\epsilon}\right)^{3/2} \frac{1}{m_p^2} \cong 10^{27} kg \sim M_J)$

$$R \sim M^{1/3}$$

For large mass: $M \gg M_J$

$$R \sim M^{-1/3}$$



$$M_{chandrasehkar} = \left(\frac{\hbar c}{G}\right)^{3/2} \frac{1}{M_p^2} \cong 2M_\odot$$

$= 1.4 M_\odot$ (with real calculation)

Bosons : (Quantum Degenerate Gas)

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

Why photons have $\mu=0$? Since N varies with photon, e.g. put N photons in a box, N can change.

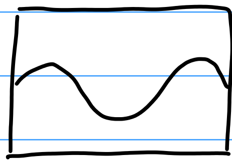
To minimize $\left.\frac{\partial A}{\partial N}\right)_{T,V} = 0 = \mu$

Normally find μ by

$$\sum_i \langle n_i \rangle = N$$

but for photon N changes, so it doesn't work.

Consider black box:



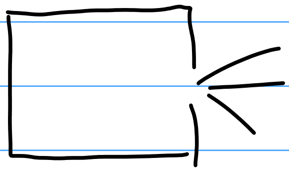
$$g(\vec{k}) = 2\frac{V}{(2\pi)^3}\, d^3\vec{k}$$

2 for polarization.

$$g(k)dk = 2\frac{V}{(2\pi)^3} 4\pi k^2 dk = \frac{V}{\pi^2} k^2 dk$$

then $$\langle E \rangle = \int_0^\infty \frac{V}{\pi^2} k^2 \hbar c k \frac{1}{e^{\beta\hbar c k}-1} dk$$

$$\frac{\langle E \rangle}{V} = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} T^4$$



energy flux per area:

$$J = \frac{c}{4}\frac{\langle E \rangle}{V}$$

$$J \overset{!}{=} \sigma T^4$$

radiates photon away $\propto T^4$

Stefan Boltzmann const

$$\sigma = \frac{\pi^2 k_B{}^4}{60 \hbar^3 c^2}$$

$$A = -\frac{1}{\beta}\ln Q \qquad p = \left(-\frac{\partial A}{\partial V}\right)_T$$

$$\Xi = \sum_{\text{states}} e^{-\beta(\varepsilon - \cancel{\mu})N} = e^{-\beta \varepsilon N} = Q$$

$$\ln Q = \ln \Xi = -\sum_j \ln\left(1 - e^{-\beta \hbar c k_j}\right)$$

convert $\sum_j$ to $\int dk\, g(k)$

$$A = \frac{-1}{\beta}\ln Q$$

$$\overset{!}{=} \frac{-1}{\beta}\int_0^\infty dk\, \frac{V}{\pi^2}k^2 \ln\left(1 - e^{\beta \hbar c k_j}\right)$$

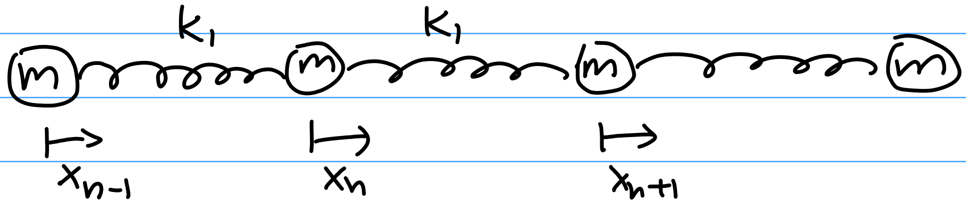
$$\overset{!}{=} -V\frac{\pi^2 k_B{}^4}{45 \hbar^3 c^3} = -\frac{\langle E \rangle}{3}$$

then $\quad p = \left(-\frac{\partial A}{\partial V}\right)_T = \frac{1}{3}\frac{\langle E \rangle}{V}$

Now consider: spectrum: $\frac{dN}{d\nu\, dt}$ frequency

$$\frac{\langle E\rangle}{V} = \int d\omega\, \underbrace{g(\omega)}_{k^2 \sim \omega^2} \langle n(\omega)\rangle\, \hbar\omega = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{e^{\beta\hbar\omega}-1}$$

Phonon: quasi-particles, excitation of HO



$$F_n = k_1(x_{n+1}-x_n) - k_1(x_n - x_{n-1})$$
$$\overset{!}{=} k_1 x_{n+1} - 2k_1 x_n + k_1 x_{n-1}$$

let $X_n = \tilde{A}_n e^{-i\omega(k)t}$ wave vector

Since atoms are the same:

$$|\tilde{A}_n| = |\tilde{A}_{n-1}|$$

$$\tilde{A}_{n+1} = e^{i\theta}\tilde{A}_n$$
$$\tilde{A}_n = e^{i\theta}\tilde{A}_{n-1} \quad \text{or} \quad \tilde{A}_{n-1} = e^{-i\theta}\tilde{A}_n$$

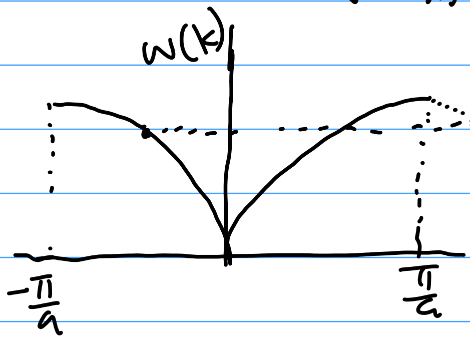
Since $\quad x \sim e^{ikx}$

$$\theta = \underbrace{\frac{2\pi}{\lambda}}_{k} a$$

$$m\ddot{x}_n = -m|w(k)|^2 \tilde{A} = k_1 \tilde{A}_n e^{-ika} - 2k_1\tilde{A}_n + k_1\tilde{A}_n e^{ika}$$

$$w(k) = \sqrt{\frac{2k_1}{m}} \left(1-\cos(ka)\right)^{1/2}$$

$$\stackrel{!}{=} \sqrt{\frac{2k_1}{m}}\, 2\left|\sin\left(\frac{ka}{2}\right)\right|$$



$$\langle E\rangle = \sum_{\text{modes}} \langle n\rangle_k \hbar w(\vec{k})$$

$$= \int_{-\pi/a}^{\pi/a} dk \left(\frac{L}{2\pi}\right) \hbar w(k) \frac{1}{e^{\beta\hbar w(k)}-1}$$

$$\Xi = \sum_{\substack{\nu \\ \text{all states}}} e^{-\beta(E_\nu - \mu N_\nu)}$$

$$= \sum_{\substack{n_1, n_2 \cdots \\ \text{occupation \#}}} e^{-\beta(\sum n_j \varepsilon_j - \mu \sum n_j)}$$

$$= \sum e^{-\beta \sum_j (\varepsilon_j - \mu) n_j}$$

$$= \sum e^{-\beta(\varepsilon_1 - \mu) n_1} e^{-\beta(\varepsilon_2 - \mu) n_2} \cdots$$

$$= \prod_{\text{modes } j} \left(\sum_{n_j} e^{-\beta(\varepsilon_j - \mu) n_j} \right)$$

$$= \prod_{\substack{\text{modes} \\ j}} \frac{1}{1 - e^{-\beta(\varepsilon_j - \mu)}}$$

$\mu = 0$
$\varepsilon_j = \hbar \omega_j$

$$= \prod \frac{1}{1 - e^{-\beta \hbar \omega_j}}$$

Now consider mass bosons:

$$N \to \langle N \rangle = \sum_j \langle n(\varepsilon_j) \rangle$$

$$= \int_0^\infty d\varepsilon \underbrace{g(\varepsilon)}_{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \varepsilon^{1/2}} \frac{1}{e^{\beta(\varepsilon-\mu)}-1}$$

$z = \beta\mu$ and let $x = \beta\varepsilon$

$$\frac{N}{V} = \rho = \frac{2\pi(2mk_BT)^{3/2}}{h^3} \underbrace{\int_0^\infty dx\, x^{1/2} \frac{1}{z^{-1}e^x - 1}}_{\propto g_{3/2}}$$

$$\rho = \frac{1}{\lambda_{th}^3} g_{3/2}(z)$$

\# density of bosons in a black box

Where $g_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dx\, x^{\nu-1} \frac{1}{z^{-1}e^x - 1}$

$$= \sum_{n=1}^\infty \frac{z^N}{n^\nu} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \dots$$

Since ρ has a maximum, when $z=1$

$\max\{g_{3/2}\} = 2.612$,

$$\rho_{max} = T^{3/2} \frac{h^3}{(2\pi m k_B)^{3/2}} 2.612$$

This is because we didn't include ground state during the integral.

Can also workout:

$$\beta P V = \ln \Xi = \frac{V}{\lambda_{th}^{3/2}} g_{3/2}(z)$$

Fix max ρ problem:

$$N = \underbrace{\langle n(\varepsilon=0)\rangle}_{\frac{1}{e^{\beta(0-\mu)}-1}} + \int_0^\infty d\varepsilon\, g(\varepsilon) \langle n(\varepsilon)\rangle$$

$$\frac{1}{e^{\beta(0-\mu)}-1} = \frac{1}{z^{-1}-1} = \frac{z}{1-z}$$

$$\boxed{N = \underbrace{\frac{z}{1-z}}_{N_0} + \underbrace{\frac{V}{\lambda_{th}^3} g_{3/2}(z)}_{N'}}$$

as $z \to 1$, all particles go to ground state.

When $T < T_c$, $N \sim N_0$

Define T_c when $N \sim N'$

$$T_c = \frac{2\pi\hbar^2}{m k_B (2.612)^{3/2}} \left(\frac{N}{V}\right)^{2/3}$$

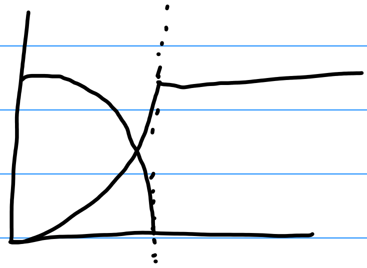
For Ar, for $\rho = \frac{N}{V} = 2.7\times10^{19}\ \mathrm{cm}^{-3}$, $T_c = 3\mathrm{mK}$

$$N = N_0 + N'$$

$$\overset{!}{=} N_0 + N'_{max} \leftarrow \text{for } T < T_c$$

$$\overset{!}{=} N_0 + N\left(\frac{T}{T_c}\right)^{3/2}$$

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



$$\langle E \rangle = -\left(\frac{\partial}{\partial \beta} \ln \Xi\right)_{z,V}$$

$$\overset{!}{=} -\left(\frac{\partial}{\partial \beta} \beta p V\right)_{z,V}$$

$$\overset{!}{=} -\left(\frac{\partial}{\partial \beta} \frac{V}{\lambda_{th}^3} g_{3/2}(z)\right)_{z,V} \qquad z \to 1$$

$$\langle E \rangle \overset{|}{=} \frac{3}{2} g_{3/2}(z) \frac{1}{\beta} \frac{V}{\lambda_{th}^3}$$

$$p = \frac{2}{3} \frac{\langle E \rangle}{V}$$

$$\frac{C_V}{Nk_B} = \frac{1}{Nk_B}\left(\frac{\partial\langle E\rangle}{\partial T}\right)_V$$

$$\stackrel{!}{=} \frac{1}{Nk_B}\frac{\partial}{\partial T}\left(\frac{3}{2}pV\right)$$

$$\stackrel{!}{=} \frac{1}{Nk_B}\frac{\partial}{\partial T}\left(\frac{3}{2}k_BT\, g_{3/2}(z)\frac{V}{\lambda_{th}^3}\right)$$ for $T<T_c$, $z=1$
ignore dependence on z.

$$\stackrel{!}{=} \frac{3}{2}\,\frac{5}{2}\,\frac{V}{N\lambda_{th}^3}\, g_{3/2}(1)$$

$$\frac{C_V}{Nk_B} \stackrel{!}{=} 5.0306\,\frac{1}{\rho\lambda_{th}^3}$$

at T_c $\quad \rho\lambda_{th}^3 = 2.613$

$$\frac{C_V}{Nk_B} = 1.925$$ while ideal gas: $\frac{C_V}{Nk_B} = 3/2$

For $T>T_c$:

$$z\frac{\partial}{\partial z}g_\nu(z) = g_{\nu-1}(z)$$

$$\hookrightarrow \frac{C_V}{Nk_B} = \frac{15}{4}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{9}{4}\frac{g_{3/2}(z)}{g_{1/2}(z)}$$

with $\quad \mu, z \Rightarrow \sum\langle n\rangle = N$

$$\hookrightarrow \rho = \frac{1}{\lambda_{th}^3}\, g_{3/2}(z)$$