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

quantum #'s
of system 1

quantum #'s
of system 2

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

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

If particles are distinguishable:

$$|v_1 = 0, v_2 = 1\rangle$$

w_1 w_1

$$|v_1 = 1, v_2 = 0\rangle$$
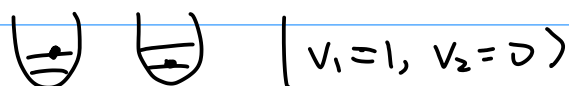
However   with

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

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

interchange 2 identical particles

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

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

$\swarrow$ if interchange twice, get same thing.

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

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

so $\quad \phi = 0, \pi$.

$\qquad\qquad\qquad \nearrow \qquad \uparrow$

$\qquad$ Boson $\qquad\qquad$ Fermion.

Fermions :

$\qquad$ anti-symmetric under change.

$$\Psi(1,2,3,\cdots,N) = \overset{\swarrow}{-} \Psi(2,1\cdots N)$$

If $\quad 2, 1$ are the same system, suppose x, x

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

So $\quad \Psi = 0$

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

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

Bosons :

$\qquad\qquad\qquad$ symmetric under change.

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

$\Rightarrow$ occupation number: n_j, # of particles with a corresponding wave function ϕ_j.

$\Rightarrow$ 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.

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

Fermions

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

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: $\;|n_1, n_2, n_3, n_4 \cdots \rangle$

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

Difficult to do so instead:

$$\Xi(u, V, T) = \sum_{n_1} e^{-\beta(n_1 \varepsilon_1 - u n_1)} \sum_{n_2} e^{-\beta(n_2 \varepsilon_2 - u n_2)} \sum_{n_3} \cdots$$

then find $\langle N \rangle$ and dial u such that
$$\langle N \rangle = N \qquad \langle N \rangle = z\left(\frac{\partial}{\partial z} \ln \Xi\right)_{\beta, V} \qquad z = e^{\beta u}$$

fugacity.

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

e.g., $\dfrac{P_1^2}{2m} + \dfrac{P_2^2}{2m} + \cdots$

This solves TISE:

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

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

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

$$\stackrel{1}{=} \left(\varepsilon_1 + \varepsilon_2 \cdots \varepsilon_N \right) \Psi_N$$

But it does not satisfy non-commital requirements

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

$\uparrow$ permutation operator

$$P_{ij} \, \Psi \left(\cdots i, \cdots, j \cdots \right) = \Psi \left(\cdots, j, \cdots, i \cdots \right)$$

Last time:
  since $\qquad P_{ij}^2 \, \Psi_N = \Psi_N$

$$\hat{P}_{ij} \, \Psi_N = \lambda \, \Psi_N$$
$\qquad \qquad \uparrow e^{i\theta}$

$$\lambda^2 = 1 \qquad \Longrightarrow \qquad \theta = 0, \pi$$

$\qquad \qquad \qquad \qquad \lambda = +1 \quad$ bosons $\quad \theta = 0$
$\qquad \qquad \qquad \qquad \lambda = -1 \quad$ fermions $\quad \theta = \pi$

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

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

occupation #:

Fermions: $n_i = 0, 1$

Bosons: $n_i = 0 \cdots N$

Grand Canonical:

#of particles having energy ε_j

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

$\nu \leftarrow$ some configuration of N- particles

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

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

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

$\{n_j\} = 0, 1$ for fermion
$= 0, 1, 2, 3 \cdots$ for boson

$\leftarrow$ Sum over all occupation # for a single particle state.

$\leftarrow$ sum over $\{n_j\}$

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

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

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

split to

$$\sum_\nu e^{-\beta(E_L - u N_\sigma)}$$

← ν configuration of N-particle system. specified b/ a set of $\{n_j\}$

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

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

since # of particles is not fixed

$$\hookrightarrow \prod_j^\infty \sum_\nu$$

For Fermions:

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

$$\ln \boxminus = \sum_j \ln\left(1 + e^{-\beta(\varepsilon_j - u)}\right)$$

In the end:

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

single particle states

$$\begin{array}{cc} - & \text{Bosons} \\ + & \text{Fermions} \end{array}$$

$$\langle n_j \rangle = \sum n_j \frac{e^{-\beta(E_v - u N_v)}}{\boxminus}$$

$$= \frac{1}{\boxminus} \sum_{n_j} n_j \, e^{-\beta(\varepsilon_j - u)n_j} \frac{1}{\boxminus} \sum_{\substack{\text{all} \\ \text{other} \\ \text{states}}}$$

$$\langle n_j \rangle = -\frac{\partial}{\partial(\beta\varepsilon_j)} \ln \boxminus$$

$$\boxed{\langle n_j \rangle = \frac{1}{e^{\beta(\varepsilon_j - u)} \mp 1} \qquad \begin{array}{l} - \text{ for bosons} \\ + \text{ for fermions} \end{array}}$$

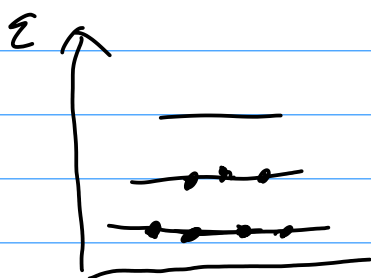$$N \to \langle N \rangle = \sum_j \langle n_j \rangle \qquad \text{dial } u$$

Bosons :

$$\boxminus = \prod_j \sum_{n_i=0}^{\infty} \left(\underbrace{e^{-\beta(\varepsilon_j - u)}}_{} \right)^{n_j}$$

$r < 1$ for geometic series to converge.
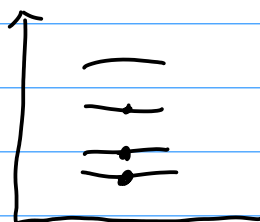
$\hookrightarrow \varepsilon - u > 0$

So $u < \varepsilon_j$ for all ε.

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

Bosons

in low T, high ρ

Fermions

in low T, high ρ

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

or when $u \ll 0$

$$\overset{\check{}}{u} = \frac{H}{N} - \frac{TS}{N}$$

sparse.
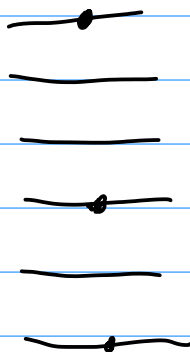
$\Rightarrow$ At classical limit $\quad \mu \ll \varepsilon_j (o)$

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

Dial μ:

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

$$\underline{1} \quad e^{\beta \mu} \underbrace{\sum_j e^{-\beta \varepsilon_j}}_{q_1 : \text{ \# of thermally accessible states}}$$

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

$\hookrightarrow \quad \mu = k_B T \ln\left(\frac{N}{q_1}\right)$

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

so that μ is very negative

μ: large negative #.

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

$$| = -k_B T \ln\left(\frac{q_1}{N}\right)$$

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

Find the partition function: Q:

$$E = u \langle N \rangle = A + pV$$

$$\nearrow \qquad \nearrow \qquad \rightleftharpoons k_B T \ln \Xi :$$

$$k_B T \ln \frac{N}{q_1} \qquad -k_B T \ln Q$$

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

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

Taylor expand

$$\doteq \sum_j e^{-\beta \varepsilon_j} e^{\beta u}$$

$$\doteq \langle N \rangle$$

$$\hookrightarrow N k_B T \left(\ln N - \ln q_1 \right) = -k_B T \ln Q + k_B T N$$

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

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

$$\underset{\text{identical particles.}}{\uparrow}$$

$$Q \overset{o}{\doteq} \underset{\substack{\text{state} \\ \text{of particle 1}}}{\sum} \sum \sum e^{-\beta(\varepsilon_1 + \varepsilon_2 + \cdots)} \quad \leftarrow \text{gets overcount.}$$
$$\text{by } N!$$

Density of States:
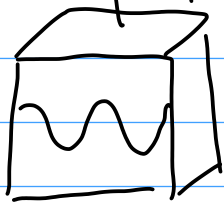
use periodic BC:

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

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

$$= \int d\varepsilon \; g(\varepsilon) \; e^{-\beta \varepsilon}$$

$$\searrow \frac{dN}{d\varepsilon}$$

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

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:

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

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

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

$$\boxed{\underset{\substack{\text{classical}\\ \text{indistinguishable}}}{\longrightarrow}\; Q = \frac{q_1^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N}$$

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

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

$$\lambda \sim \frac{h}{\sqrt{2m k_B T}}$$

Ex: Ar at 300k:

$$\lambda_{th} = 1.5 \times 10^{-11} \, m$$

$$u = k_B T \ln \left(\frac{N}{q_1} \right) = k_B T \ln \left(\frac{N}{V/\lambda_{th}^3} \right)$$
$$= k_B T \ln \left(\rho \lambda_{th}^3 \right) \qquad \bigg\} \, \rho = \frac{N}{V}$$

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

$$\longrightarrow u \sim -18 \, k_B T \qquad \text{with} \quad \langle \varepsilon \rangle \sim \frac{3}{2} k_B T$$

free energy to add particles

$$u = \frac{G}{N} = \frac{H}{N} - \frac{TS}{N} \quad : \quad u \text{ is negative since } TS \text{ term is dominating}$$

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

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

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

$$= \frac{3N}{\lambda_{th}} \frac{1}{2} \frac{\lambda_{th}}{\beta} = \frac{3}{2} N k_B T$$

$$A = -k_B T \ln Q \quad \leftarrow \text{ potential for canonical ensemble.}$$

use $\quad P = \left(\dfrac{-\partial A}{\partial V}\right)_{T,N}$

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

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

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

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

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

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

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

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

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

For classical gas $\rightarrow$

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

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

Sackor-Tetrode Equation.

If there is no $N!$

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

$\nwarrow$ Not extensive.

$$Q = (?) \int dq_1 \cdots \int dq_N \int dp_1 \cdots \int dp_N \, e^{-\beta H (q_1 \cdots q_N, \, p_1 \cdots p_N)}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

Integral over all phase space.

$$q \cdot p \sim \text{action} \sim J \cdot s \; [h]$$

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

$\underbrace{}$ 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: $\mathcal{H}(x,p) = \dfrac{p^2}{2m} + \dfrac{1}{2}mw^2x^2$

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

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

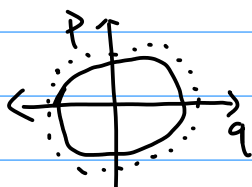$$= \frac{1}{\beta \hbar w}$$

$$= \frac{k_B T}{\hbar w}$$

Quantum:
$$Q = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar w}$$

$$= e^{-\beta\frac{\hbar w}{2}}\; \frac{1}{1 - e^{-\beta\hbar w}}$$

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

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

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

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

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

Know from QM!
$\Delta E = \hbar w$.

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

$$Q = \sum_{states} e^{-\beta \varepsilon} \rightarrow \int \frac{dq^M \, dp^M}{\underbrace{h^M (N_A! \, N_B! \cdots)}_{\substack{\sum \\ states}}} e^{-\beta H}$$

$$\underbrace{\qquad}_{\substack{\sum \\ states}} \quad \text{and} \quad M = \# \text{ of DoF}$$

With $\quad u = k_B T \ln \left(\rho \, \lambda_{th}^3 \right)$

for u : large negative

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

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

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

We do not worry about QM if:

$$\lambda_{th}^3 \ll \rho = \frac{V}{N} \quad \leftarrow \quad \begin{array}{l} \text{volume occupied} \\ \text{by each particle.} \end{array}$$

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

Reduced Distribution Function:

with $\quad h(\vec{r}, \vec{p})$: distribution function.

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

with $\quad N = \sum \langle n_i \rangle$

$\qquad\qquad\qquad \hookleftarrow$ occupation #

$$\sum \langle n_i \rangle \to \sum_i n(\vec{r_i}, \vec{p_i}) \, h^3 = N$$

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

$$\Big\downarrow\hookrightarrow \quad n(\vec{r_i}, \vec{p_i}) \, d^3\vec{r} \, d^3\vec{p} = \frac{N e^{-\frac{\beta p^2}{2m}}}{h^3 \, V/\lambda_{th}^3} \, d^3\vec{r} \, d^3\vec{p}$$

$$h(\vec{p}) \, d^3\vec{p} = \int_{\underset{\underset{V}{\smile}}{space}} d^3\vec{r} \; n(\vec{r}, \vec{p}) d^3\vec{p}$$

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

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

$$f(r_1, r_2, \dots P_1, P_2 \dots) \propto e^{-\beta H(r^N, p^N)}$$

$$1 = \frac{\int d^3\vec{r_1} \, d^3\vec{r_2} \, d^3\vec{r_3} \cdots \int d^3\vec{p_1} \cdots \quad e^{-\beta H(r^N, p^N)}}{\int d^3\vec{r_1} \, d^3\vec{r_2} \cdots \int d^3\vec{p_1} \cdots \int d^3 p_N \; e^{-\beta H(r^N, p^N)}}$$

$$n(\vec{p}) = N \frac{\int d^3\vec{r_1} \cdots \int d^3\vec{r_N} \int d^3\vec{p_2} \cdots \int d^3\vec{p_N} \; e^{-\beta H}}{\int dr^N \int dp^N \; e^{-\beta H}}$$
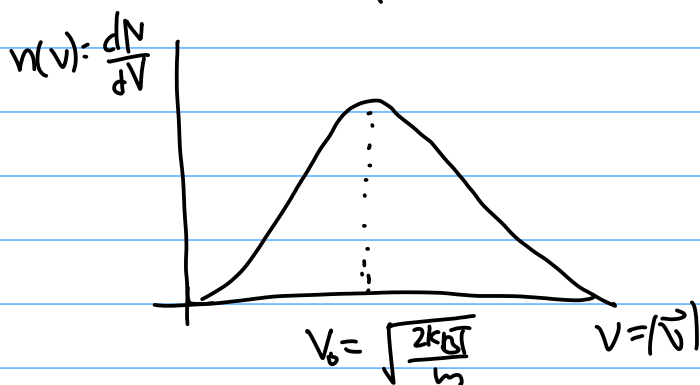
Pair Correlation Function:

$$g(\vec{r_1}, \vec{r_2}) = N(N-1) \frac{\overbrace{\int d^3\vec{r_3} \cdots \int d^3\vec{r_N}}^{V^{N-2} \text{ for ideal gas}} \int d\vec{p_1} \cdots \int d\vec{p_N} \; e^{-\beta H}}{\underbrace{\int dr^N \int dp^N \; e^{-\beta H}}_{V^N \text{ ideal gas}}}$$

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

↑ Maxwell distribution for velocities

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

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

$n(v) = \frac{dN}{dV}$

$$V_0 = \sqrt{\frac{2k_B T}{m}} \qquad v = |\vec{v}|$$

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

$$V_{rms} = \sqrt{\frac{3 k_B T}{m}}$$

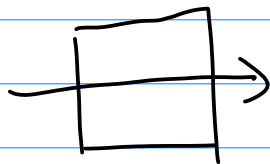Mean - free - Path: $\qquad \lambda = \dfrac{1}{\rho \sigma}$

$\uparrow$ cross-section

\# density $= \dfrac{N}{V}$
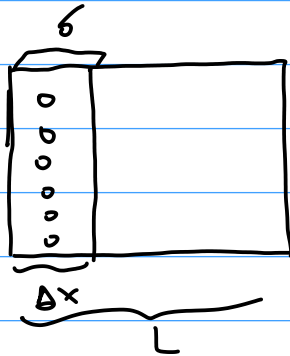
$$P_{trans} = 1 - \rho \sigma \Delta x$$

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

$$\underset{\text{polarization}}{\overset{\longrightarrow}{P}} = \underset{\text{susceptability}}{X} E$$

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

$$\chi(t) = -\beta \dfrac{d}{dt} \underbrace{\langle \delta A(0) \, \delta A(t) \rangle}_{\text{Fluctuations}} \xleftarrow{\text{time-correlation function}}$$

$$\chi(w) = -iw\beta \int_0^\infty dt \; e^{-iwt} \langle \delta A(0) \, \delta A(t) \rangle$$

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T} \right)_V = \frac{3}{2} N k_B = \frac{3}{2} n R = 12.47 \, \tfrac{J}{mol \, k} \, N$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \frac{\partial}{\partial T} \left(\langle E \rangle + PV \right) = \frac{\partial}{\partial T} \left(\frac{3}{2} M k_B T + N k_B T \right)$$

$$\overset{!}{=} \frac{5}{2} N k_B$$

$$\overset{!}{=} 20.78 \, \tfrac{J}{mol \, k} \, N$$

Diatomic Molecules:

$\longleftarrow$ rotational states.

$\longleftarrow$ vibrational state

$\sim 0.2 eV$

$\longleftarrow$ rotational states $\sim 10^{-3} - 10^{-4} eV$

$\uparrow$ ground state
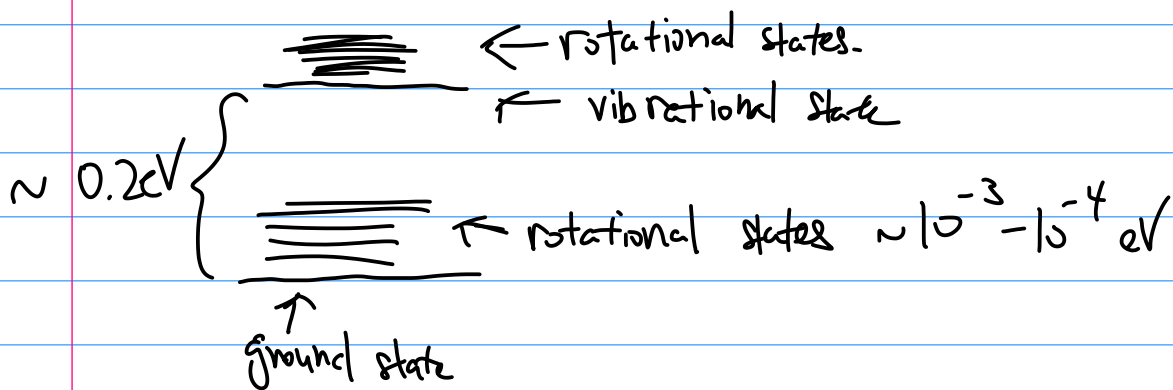
$$\hat{H} = \sum_{i=1}^{N} \frac{\hat{P}_i^2}{2m} + \sum_{(i,j) \atop pairs} \frac{1}{4 \pi \epsilon_0} \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} - \sum_{i \alpha} \frac{1}{4 \pi \epsilon_0} \frac{e^2 Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|}$$

$$+ T_N + V_{NN}$$

$\hookrightarrow$ repulsion
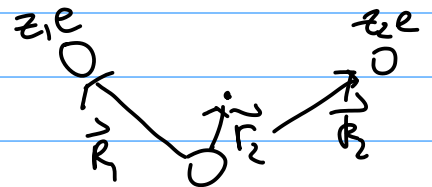
Born - Oppenheimer Approximation:

Wave function of molecule:

$$\bar{\Psi}(r_i, R_2) = \psi_{elec}(r_i | R_2) \, \chi(R_2)$$

electron position   nucleus position   electron wavefunction   nuclear wavefunction

$$\chi = \psi_{vib}(R) \, \psi_{rot}(\theta, \phi)$$

Vibrational (SHO)   Rotational (Rigid Motor)

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

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

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

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

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

$$\hookrightarrow \psi_{rot} = Y_J^m(\theta, \phi) \qquad \text{spherical Harmonics}$$
$$\text{where} \quad m = +J, J-1 \cdots 0 \cdots -J+1, -J$$

it can be symmetric or anti-symmetric.

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.

$$\left(\sigma_{v,e} \times i_e \right) \times C_2$$

$\uparrow$ reflection of electron — $\uparrow$ Inversion — $\uparrow$ rotation by $180°$

$\underbrace{\hspace{4cm}}_{\text{For electrons}}$

Since

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

Since both $|\psi_{nuc\,spin}\rangle$ and ψ_{rot} can be

symmetric or anti-symmetric, should consider them together.

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

In classical limit:

nuclear spin state degeneracy.

$$q_{rot/\,nuc\,spin} \cong \underbrace{\frac{(2I_A+1)(2I_B+1)}{\sigma_{AB}}}\;\underbrace{\sum_{J=0}^{\infty} (2J+1)\,\exp\{-\beta\,J(J+1)B\}}_{q_{rot}}$$

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

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

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

symmetric for H_2 ↓   symmetric ↑

$$\psi_{tot} = \psi_{elec}\,\psi_{vib}\,\psi_{rot}\,|\psi_{nuc\,spin}\rangle$$

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

$$q_{int} = q_{ele}\;q_{vib}\;\underset{(SHO)}{}\;q_{rot/\,nuc\,spin}$$

$$\theta_{vib} = \frac{\hbar w}{k_B}$$ nuc spin. $$\theta_{rot} = \frac{\hbar^2}{2I_0 k_B}$$

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

For diatomic.

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

↑ In classical limit high T.

Finally

$$q_1 = q_{trans}\;q_{int}$$

$$= \frac{V}{\lambda_{th}^3}\;q_{int}$$

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

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

$$\underrightarrow{\text{e-N interaction}} \qquad\qquad \underset{\uparrow}{\text{N-N interaction}} \qquad\qquad \underset{\uparrow}{T_N}$$

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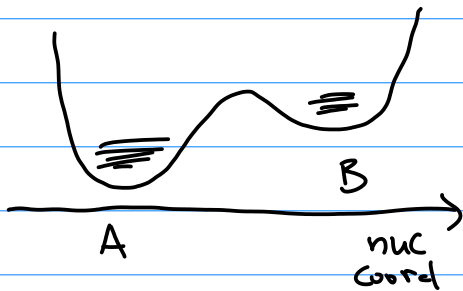
$$\frac{N_A}{N_B} = \frac{\sum_i e^{-\beta A_i}}{\sum_i e^{-\beta B_i}} = \frac{q_A}{q_B}$$

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

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

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

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

$$\hookrightarrow \boxed{u_A = u_B}$$

Ex: $A \rightleftharpoons B$

For equilibrium: minimize Helmholtz free energy.

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

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

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: ← always true

$$\sum v_i u_i = 0$$

↳ product has negative
↳ reactant has positive.

For classical limit:

$$u_i = K_B T \ln\left(\frac{N_i}{q_i}\right)$$

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

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

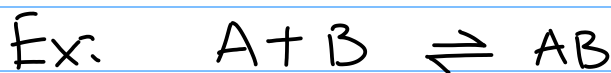$$\overset{!}{=} \sum_i \ln\left(\frac{\rho_i V}{q_i}\right)^{\nu_i} = 0$$

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

Law of mass action

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

↑ 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: $H^+ + e^- \rightleftharpoons H$

$$\frac{P_{H^+} P_{e^-}}{P_H} = \frac{\left(q_{H^+}/N\right)\left(q_{e^-}/N\right)}{\left(q_H/N\right)}$$
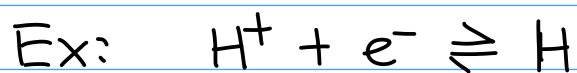
$$q_{e^-} = 2\frac{V}{\lambda_{th}^3}$$
$\uparrow$
account
for spin

$$q_{H^+} = 2\frac{V}{\lambda_{th}^3}$$
$\uparrow$
spin

$$q_H = 4\frac{V}{\lambda_{th}^3}e^{-\beta\mathcal{E}_{elec}}$$
$\uparrow$
spin.

$$\boxed{\frac{P_{H^+} P_e}{P_H} = \frac{1}{\lambda_e^3}e^{-\beta(13.6eV)}}$$

$$P_e = P_{H^+} = X P_0 \qquad \text{and} \qquad P_H = (1-X)P_0$$
$\uparrow$
ionized fraction

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: $T \to 0$

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

Dial μ so:
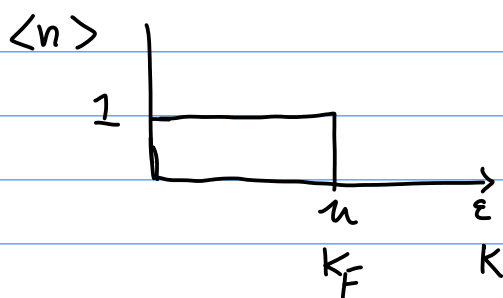
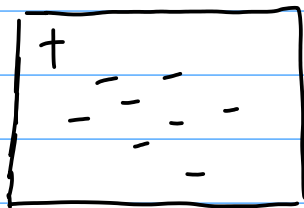$$\sum_{\substack{i \\ \text{all states}}} \langle n_i \rangle = N$$

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

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

Electron in 3D:

Jellium
(Sommerfield)
model.

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

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

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

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

$\rightarrow \quad N = \dfrac{V}{\pi^2} \dfrac{k_F^3}{3}$

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

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

← Fermi-level

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

Do it via $\oint \varepsilon(k) \, g(\varepsilon)$:

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

$= \displaystyle\int_0^{\varepsilon_F} d\varepsilon \, g(k) \left(\dfrac{\partial \varepsilon}{\partial k} \right)^{-1}$

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

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

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

Working out pressure:

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

$$\langle E \rangle = \sum \varepsilon_i \langle n(\varepsilon_i) \rangle$$

$$= \int d\varepsilon \, g(\varepsilon) \langle n(\varepsilon) \rangle \varepsilon_i$$

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

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

$$\boxed{\langle E \rangle = \frac{3}{5} N \varepsilon_F \\ \downarrow \\ \langle e \rangle = \frac{3}{5} \varepsilon_F}$$

$$\Rightarrow$$

$$\boxed{P = -\frac{\partial \langle E \rangle}{\partial V}\Big)_{S,N} \\ P = \frac{2}{3} \frac{\langle E \rangle}{V}} \leftarrow \text{general for non-relativistic 3D gas}$$

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

$\nearrow$
isothermal
compressibility

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

$$\underbrace{\qquad}_{\phi(\varepsilon)} \quad \underbrace{\qquad}_{f}$$

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

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

$$= \cancel{\Phi(\varepsilon) f \Big|_0^\infty} - \int_0^\infty d\varepsilon \, \Phi(\varepsilon) \frac{\partial f}{\partial \varepsilon} \quad \nearrow \text{taylor expansion.}$$

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

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

$$\int_0^\infty d\varepsilon \, \phi f = \int_0^\infty d\varepsilon \left(\frac{-\partial f}{\partial \varepsilon} \right) \left(\Phi(u) + \frac{\partial \Phi}{\partial \varepsilon}\Big|_u (\varepsilon - u) + \frac{1}{2} \frac{\partial^2 \Phi}{\partial \varepsilon^2}\Big|_u (\varepsilon - u)^2 + \cdots \right)$$

$$\underset{\text{even}}{\uparrow} \qquad\qquad \underset{\text{odd}}{\uparrow}$$

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

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

$$\frac{\partial^2 \Phi}{\partial \varepsilon^2}$$

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

for 3D electron gas?

$$u = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{1}{g(\varepsilon_F)} \left.\frac{\partial g}{\partial \varepsilon}\right|_{\varepsilon_F}$$

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

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

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

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

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

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

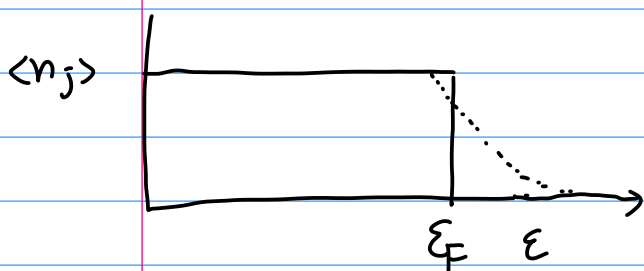$\qquad N = e^{\beta\mu} \sum e^{-\beta\varepsilon} = e^{\beta\mu} q_1$

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

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

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

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

Now consider quantum, $\qquad k_BT \ll \varepsilon_F$

$\langle n_j \rangle$

$N = \displaystyle\int_0^{\varepsilon_F} g(\varepsilon)\, d\varepsilon = \int_0^{k_F} g(k)\, 4\pi k^2 \dfrac{2V}{(2\pi)^3}\, dk$
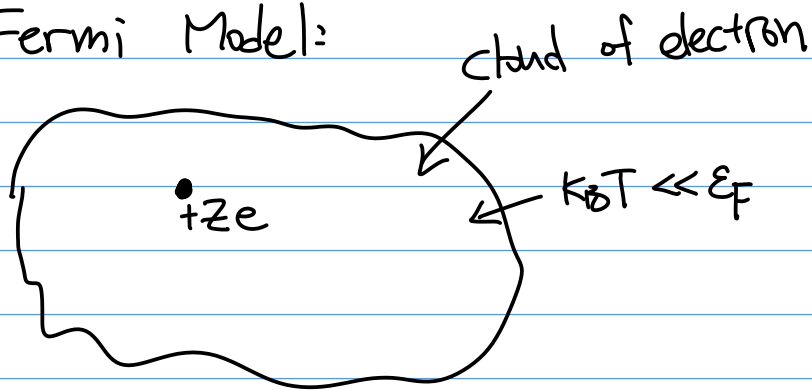
$\varepsilon_F = \dfrac{\hbar^2}{2m}(3\pi^2 \rho)^{2/3} = \dfrac{\hbar^2}{2m} k_F$

define $\qquad V_F = \dfrac{\hbar k_F}{m}$

Thomas - Fermi Model:

Cloud of electron

+ze

$K_B T \ll \varepsilon_F$

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

charge density: $\zeta(r) = -e \, \rho(\vec{r}) + ze \, \delta(\vec{r})$

electron gas   ion

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

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

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

With   Poisson   Equation:

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

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

Solving the Poisson Eq:

Thomas Fermi Model.
$$\phi(r) = \frac{1}{4\pi\epsilon_o} \frac{Ze}{r} \Phi\left(\frac{r\,z^{1/3}}{0.885\,\alpha_o}\right) \qquad \alpha_o = \frac{4\pi\epsilon_o \hbar^2}{m_e e^2}$$

$$\Phi(r) = \left[1 + \left(\frac{r^3}{144}\right)^\lambda\right]^{-1/\lambda} \qquad \lambda = 0.257$$

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

radial →
density

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

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

$$-\frac{1}{4\pi\epsilon_o}\int_o^\infty 4\pi r^2 dr\, \frac{\rho\, Ze}{r}$$

$$+\frac{1}{2}\frac{1}{4\pi\epsilon_o}\int_o^\infty d\vec{r_1}\int_o^\infty d\vec{r_2}\, \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{|\vec{r_1}-\vec{r_2}|}$$

$$\Rightarrow E_{TF} = -1.538 \underbrace{\left(\frac{1}{2}\frac{e^2}{4\pi\epsilon_o\alpha_o}\right)}_{13.6eV} z^{7/3}$$

Quantum Picture:

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

electron 1

Later (1964) showed

$$E_0 = E[\rho(r)]$$

energy is a functional of density

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

← interaction energy includes gravity

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

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:

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

(with $P(\text{surface}) = 0$ noted above)

then

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

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

$\uparrow$ Fermi-Energy. $\nwarrow$ electrostatic repulsion

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

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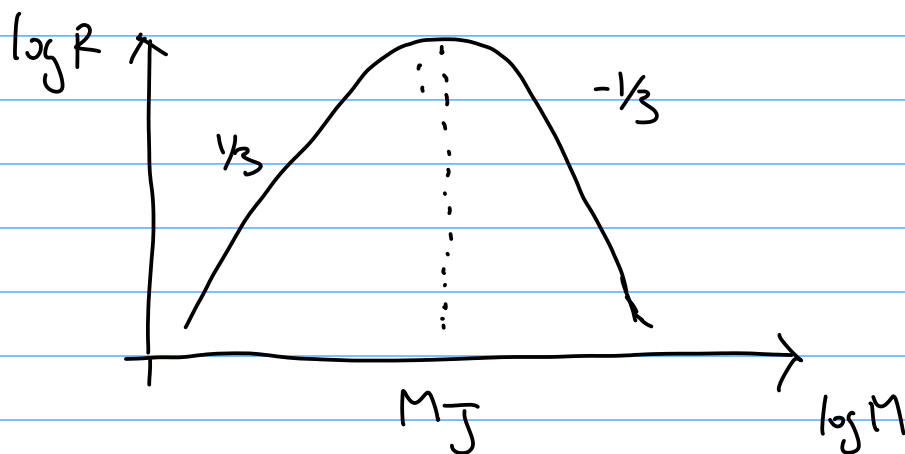
Solving R:

$$R = \frac{e^2}{4\pi\epsilon_0} \frac{a_0}{\epsilon M^{1/3}} \frac{1}{M_r^{5/3}} \left[\frac{1}{1 + \frac{e^2/4\pi\epsilon_0}{\epsilon M^{2/3} M_p^{1/3}}} \right]$$

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

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

For large mass: $M \gg M_J$

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

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

$$= 1.4 M_\odot \text{ (with real calculation)}$$

Bosons : (Quantum Degenerate Gas)

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

Why photons have $u = 0$? Since N varies with photon, e.g. put N photons in a box, N can change.
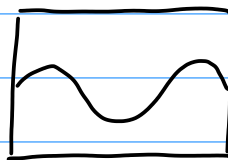
To minimize $\left. \dfrac{\partial A}{\partial N} \right)_{T,V} = 0 = u$

Normally find u by

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

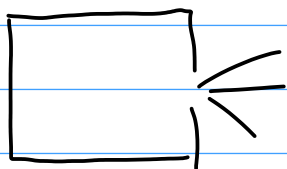but for photon N changes, so it doesn't work.

Consider black box:

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

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:

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

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

radiates photon
away $\propto T^4$

Stefan Boltzmann const

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

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

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

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

$$\downarrow \text{ convert } \sum_j \text{ to } \int dk \, g(k)$$

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

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

$$\stackrel{!}{=} -V \frac{\pi^2 k_B{}^4}{45 \, \hbar^3 c^3} = -\frac{\langle E \rangle}{3}$$
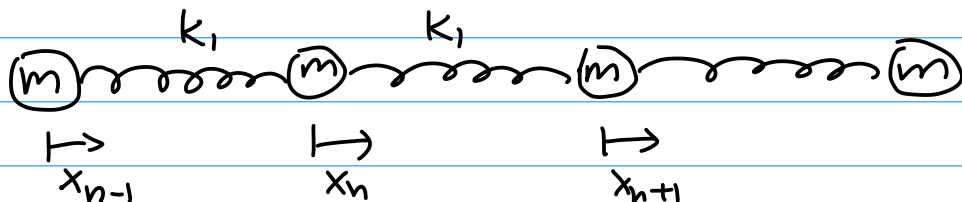
then $$p = \left(-\frac{\partial A}{\partial V}\right)_T = \frac{1}{3} \frac{\langle E \rangle}{V}$$

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

$$\frac{\langle E \rangle}{V} = \int d\omega\, g(\omega)\, \langle n(\omega) \rangle\, \hbar W = \frac{\hbar \omega^3}{\Pi^2 c^3}\, \frac{1}{e^{\beta \hbar W} - 1}$$

$$\underbrace{}_{k^2 \sim \omega^2}$$

Phonon: quasi-particles ,   excitation of photon

$$F_n = k_1 (x_{n+1} - x_n) - k_1 (x_n - x_{n-1})$$

$$= k_1 x_{n+1} - 2k_1 x_n + k_1 x_{n-1}$$

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

Since atoms are the same:

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

$$\tilde{A}_{n+1} = e^{i\theta}\, \tilde{A}_n$$
$$\tilde{A}_n = e^{i\theta}\, \tilde{A}_{n-1} \qquad \text{or} \quad \tilde{A}_{n-1} = e^{-i\theta}\, \tilde{A}_n$$
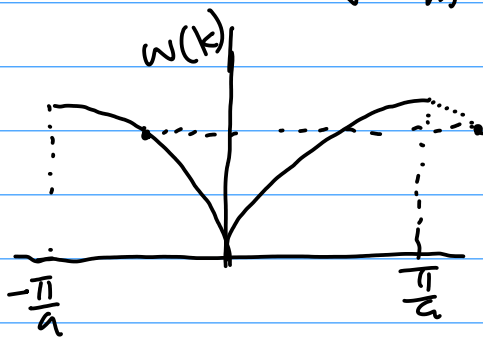
Since $x \sim e^{ikx}$

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

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

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

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

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

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