Quantum statistical Mechanics

Microcanonical; E, V, N, $p = \frac{1}{\Gamma(E)}$ all equal.

$$S = -k_B \ln \Gamma(E)$$

canonical

$$Z = \sum_n e^{-\beta E_n} = e^{-\beta A(T,V,N)}$$

grand canonical

$$\mathcal{G} = \sum_n e^{-\beta E_n + \mu\beta N_n} = e^{-\beta A + \beta\mu N}$$
$$= e^{\frac{PV}{k_B T}}$$

Density matrix.

If we have a classical probability. (ensemble)

e.g. $|\psi_n\rangle$ basis. P_n of being in $|\psi_n\rangle$ $\sum P_n = 1$

$$\underbrace{\langle\langle \mathcal{O} \rangle\rangle}_{\text{hermitian operator}} = \underbrace{\sum_n P_n \underbrace{\langle \psi_n | \mathcal{O} | \psi_n \rangle}_{\text{Quantum average}}}_{\text{classical average}}$$

$\langle\langle O \rangle\rangle = \mathrm{Tr}(\rho O)$

ρ operator : density matrix.

$$\rho = \sum_n p_n \underbrace{|\psi_n\rangle\langle\psi_n|}_{\text{Projector}}$$

$$\mathrm{Tr}(\rho O) = \sum_m \langle\psi_m| \sum_n p_n |\psi_n\rangle\langle\psi_n| O \underset{\text{basis}}{|\psi_m\rangle} =$$

$$= \sum_{nm} p_n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{nm}} \langle\psi_n|O|\psi_m\rangle$$

$$= \sum_n p_n \langle\psi_n|O|\psi_n\rangle \quad \checkmark.$$

$$\mathrm{Tr}\rho = \mathrm{Tr}(\rho \cdot \mathbb{1}) = \sum_n p_n = 1.$$

$$\rho|\psi_n\rangle = \sum_m p_m |\psi_m\rangle\langle\psi_m|\psi_n\rangle = p_n|\psi_n\rangle$$

$|\psi_n\rangle$ eigenvectors of ρ. all real

$$\rho = \begin{pmatrix} p_1 & & \\ & \ddots & \\ & & p_n \end{pmatrix}$$ in that basis.

After change of basis

ρ is operator such that.

$\rho = \rho^{+}$

$\mathrm{Tr}\,\rho = 1$ $\Rightarrow$ eigenvalues $0 \leq p_n \leq 1$.

$\rho \geq 0$ all eigenvalues ≥ 0. (p_n can be zero)

in the basis where ρ is diagonal we get back

$$\rho = \sum_n p_n |\psi_n\rangle\langle\psi_n|$$

Time evolution

$$\partial_t |\psi(t)\rangle = -i\frac{H}{\hbar}|\psi(t)\rangle$$

$$\rho(t) = \sum_n p_n \; |\psi_n(t)\rangle\langle\psi_n(t)|$$

$$\partial_t \rho = \sum_n p_n \left(-i\frac{H}{\hbar}|\psi_n\rangle\langle\psi_n|\right) + \sum_n p_n \left(|\psi_n\rangle\langle\psi_n|\frac{iH}{\hbar}\right)$$

$$= -\frac{i}{\hbar}\left(H\rho - \rho H\right) = \frac{i}{\hbar}[\rho, H]$$

We can think of canonical ensemble as

$$\rho = \frac{e^{-\beta H}}{Z}$$

and grand canonical

$$\rho = \frac{e^{-\beta H + \beta\mu N}}{\mathcal{Z}}$$

energy eigenstates.

$$\langle\langle \mathcal{O} \rangle\rangle = \mathrm{Tr}(\rho\,\mathcal{O}) = \sum_n \langle \psi_n | \rho\, \mathcal{O} | \psi_n \rangle =$$

$$= \underbrace{\frac{1}{Z} \sum_n e^{-\beta E_n} \underbrace{\langle \psi_n | \mathcal{O} | \psi_n \rangle}_{\text{quantum average}}}_{\text{thermal average.}} \quad ;$$

Ideal gases.

~~Boltzmann~~, Bose, Fermi.

$\{n_p\}$; ~~$n_p = 0 - \infty$ Boltzmann~~

ϵ_p

$n_p = 0 - - \infty$ Bose

$n_p = 0, 1$ Fermi

$$E = \sum_p n_p \epsilon_p \qquad N = \sum_p \epsilon_p$$

$$\Xi = \sum_{\{n_p\}} e^{-\beta E_{\{n_p\}} + \beta\mu N_{\{n_p\}}}$$

$$= \sum_{\{n_p\}} e^{-\beta \sum_p \epsilon_p n_p + \beta\mu \sum_n n_p}$$

$$= \sum_{\{n_p\}} \prod_p e^{(-\beta\epsilon_p + \beta\mu) n_p} = \prod_p \sum_{n_p} e^{(-\beta\epsilon_p + \beta\mu) n_p}$$

$$\sum_{\{n_p\}} \cancel{\prod_p} z_1^{n_1} z_2^{n_2} - - z_M^{n_M}$$

$$\left(\sum_{n_1} z_1^{n_1}\right)\left(\sum_{n_2} z_2^{n_2}\right) - - \left(\sum_{n_M} z_M^{n_M}\right)$$

Bose

$$\sum_{n_p=0}^{\infty} e^{\overbrace{(-\beta\varepsilon_p+\beta\mu)}^{<0} n_p} = \frac{1}{1-e^{-\beta\varepsilon_p+\beta\mu}}$$

Fermi

$$\sum_{n_p=0}^{\infty} e^{(-\beta\varepsilon_p+\beta\mu) n_p} = 1 + e^{-\beta\varepsilon_p+\beta\mu}.$$

$$\mathcal{Z}_B = \prod_p \frac{1}{1-e^{-\beta\varepsilon_p+\beta\mu}}$$

$$\frac{pV}{k_B T} = \ln \mathcal{Z}_B = -\sum_p \ln\left(1-e^{-\beta\varepsilon_p+\beta\mu}\right)$$

$$\mathcal{Z}_F = \prod_p \left(1+e^{-\beta\varepsilon_p+\beta\mu}\right)$$

$$\frac{pV}{k_B T} = \ln \mathcal{Z}_F = \sum_p \ln\left(1+e^{-\beta\varepsilon_p+\beta\mu}\right)$$

~~if $e^{-\beta\varepsilon_p+\beta\mu} \ll 1$ $\ln(1\pm\varepsilon) \simeq \pm\varepsilon$~~

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial \ln \Sigma}{\partial \mu} \quad ; \quad E = -\frac{\partial \ln \Sigma}{\partial \beta}$$

$$N_B = +\frac{1}{\cancel{\beta}} \sum_p \frac{+e^{-\beta\varepsilon_p + \beta\mu}\cancel{\beta}}{1 - e^{-\beta\varepsilon_p + \beta\mu}} = \sum_p \frac{1}{e^{\beta\varepsilon_p - \beta\mu} - 1}$$

$$N_F = +\frac{1}{\cancel{\beta}} \sum_p \frac{e^{-\beta\varepsilon_p + \beta\mu}\cancel{\beta}}{1 + e^{-\beta\varepsilon_p + \beta\mu}} = \sum_p \frac{1}{e^{\beta\varepsilon_p - \beta\mu} + 1}$$

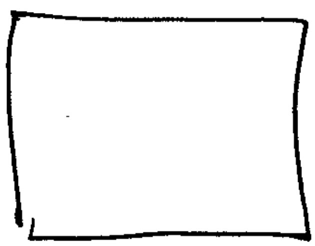
$$E_B = \sum_p \frac{\varepsilon_p e^{-\beta\varepsilon_p + \beta\mu}}{1 - e^{-\beta\varepsilon_p + \beta\mu}} = \sum_p n_p \epsilon_p$$

$$E_F = \sum_p \frac{\varepsilon_p e^{-\beta\varepsilon_p + \beta\mu}}{1 + e^{-\beta\varepsilon_p + \beta\mu}} = \sum_n n_p \varepsilon_p .$$

$$n_p^{(B)} = \frac{1}{e^{\beta\varepsilon_p - \beta\mu} - 1} \quad ; \quad n_p^{(F)} = \frac{1}{e^{\beta\varepsilon_p - \beta\mu} + 1}$$

$$0 \leq n_p^{(F)} \leq 1 .$$

Ideal gas



$$e^{i\frac{px}{\hbar}}$$

$x \to x+L$ periodic

$$e^{\hbar\frac{2\pi i}{L}\frac{p}{\hbar}x}$$

$$p = \frac{2\pi\hbar}{L}n$$

$$d^3n = \frac{V}{(2\pi)^3\hbar^3}\,d^3p$$

$$\frac{p\cancel{V}}{k_BT} = \ln \Xi_B = -\frac{\cancel{V}}{(2\pi)^3\hbar^3}\int d^3p\,\ln\left(1-e^{-\beta\epsilon_p+\beta\mu}\right)$$

spin 1/2.

$$\frac{P}{k_BT} = \ell\,\Xi_F = \frac{2}{(2\pi)^3\hbar^3}\int d^3p\,\ln\left(1+e^{-\beta\epsilon_p+\beta\mu}\right)$$

$$N_B = \frac{V}{h^3}\int d^3p\,\frac{1}{e^{\beta\epsilon_p-\beta\mu}-1}$$

1/2

$$N_F = \frac{2V}{h^3}\int d^3p\,\frac{1}{e^{\beta\epsilon_p-\beta\mu}+1}$$

if $e^{\beta\varepsilon_p - \beta\mu} >> 1.$

$e^{-\beta\varepsilon_p + \beta\mu} << 1.$

Both give (classical or Boltzmann gas) — except spin

$$\frac{p}{k_B T} = \frac{1}{h^3}\int d^3p \; e^{-\beta\varepsilon_p + \beta\mu}$$

$$= \frac{e^{\beta\mu}}{h^3}\int d^3p \; e^{-\frac{\beta p^2}{2m}} = \frac{e^{\beta\mu}}{h^3}\left(\sqrt{\frac{2m\pi}{\beta}}\right)^3$$

$$N = \frac{V}{h^3}\int d^3p \; e^{-\beta\varepsilon_p + \beta\mu} = \frac{V}{h^3}e^{\beta\mu}\left(\sqrt{\frac{2m\pi}{\beta}}\right)^3$$

$$\frac{p}{k_B T} = \frac{N}{V} \qquad pV = Nk_B T \checkmark$$

Also $\frac{N}{V}\left(\frac{h^2\beta}{2m\pi}\right)^{3/2} = e^{\beta\mu}$

$$\boxed{\frac{\mu}{k_B T} = \ln\frac{N}{V} + \frac{3}{2}\ln\left(\frac{\beta h^2}{2m\pi}\right)} \checkmark$$

Fermi gas

$$p = \frac{(2s+1) k_B T}{h^3} 4\pi \int_0^\infty p^2 dp \ln\left(1 + e^{-\beta \frac{p^2}{2m} + \beta\mu}\right)$$

$$\frac{1}{v} = \frac{4\pi}{h^3}(2s+1)\int_0^\infty p^2 dp \frac{1}{e^{\beta p^2/2m - \beta\mu} + 1}$$

$$x = \sqrt{\frac{\beta}{2m}}\, p$$

pressure

$$p = \frac{(2s+1) k_B T}{h^3} 4\pi \left(\frac{2m}{\beta}\right)^{3/2} \int_0^\infty x^2 dx \ln\left(1 + e^{\beta\mu} e^{-x^2}\right)$$

$$= (2s+1) \frac{4\pi k_B T}{h^3} (2m k_B T)^{3/2} \sum_{n=0}^{\infty} \int_0^\infty x^2 \frac{(-)^{n+1}}{n} e^{\beta\mu n} e^{-nx^2}$$

$$\int_0^\infty x^2 e^{-nx^2} = -\frac{1}{2}\frac{\partial}{\partial n}\sqrt{\frac{\pi}{n}} = \frac{1}{4}\frac{\sqrt{\pi}}{n^{3/2}}$$

$$= (2s+1) \frac{4\pi k_B T}{h^3} (2m k_B T)^{3/2} \sum_{n=0}^{\infty} \frac{(-)^{n+1} e^{\beta\mu n}}{n^{5/2}} \frac{\sqrt{\pi}}{4}$$

$$= (2s+1) \frac{\cancel{4}\pi k_B T}{h^3} (2m k_B T)^{3/2} \frac{\sqrt{\pi}}{\cancel{4}} f_{5/2}(e^{\beta\mu})$$

$$\frac{P}{k_B T} = (2s+1)\left(\frac{2m\pi k_B T}{h^2}\right)^{3/2} f_{5/2}(e^{\beta\mu})$$

$$= \frac{(2s+1)}{\lambda^3} f_{5/2}(e^{\beta\mu}) \qquad \lambda = \sqrt{\frac{h^2}{2m\pi k_B T}}$$

$$\frac{1}{v} = \frac{4\pi}{h^3}\left(\frac{2m}{\beta}\right)^{3/2}(2s+1)\int_0^\infty x^2 dx \;\frac{e^{-x^2+\beta\mu}}{1+e^{-x^2+\beta\mu}}$$

$$= \frac{4\pi}{h^3}\left(\frac{2m}{\beta}\right)^{3/2}\int_0^\infty x^2 dx \; e^{-x^2+\beta\mu}\sum_{n=0}^\infty (-)^n e^{-nx^2+\beta\mu n}$$

$$= \frac{4\pi}{h^3}(2m k_B T)^{3/2}\int_0^\infty x^2 dx \sum_{n=1}^\infty (-)^{n+1} e^{-nx^2+\beta\mu n}$$

$$= \frac{4\pi}{h^3}(2m k_B T)^{3/2}\cancel{\int_0^\infty x^2 dx}\sum_{n=1}^\infty (-)^{n+1}\frac{e^{\beta\mu n}}{n^{3/2}}\frac{\sqrt{\pi}}{4}$$

$$= \left(\frac{2m\pi k_B T}{h^2}\right)^{3/2}(2s+1)\, f_{3/2}\big(\underbrace{e^{\beta\mu}}_{z}\big)$$

$$\boxed{\begin{aligned}\frac{P}{k_B T} &= \frac{(2s+1)}{\lambda^3} f_{5/2}(z)\\ \frac{1}{v} &= \frac{(2s+1)}{\lambda^3} f_{3/2}(z)\end{aligned}}$$

$z \geq 0$

Fermi

(12)

Bose gas

$$\frac{P}{kT} = \frac{1}{\lambda^3} g_{5/2}(z)$$

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

$$g_a = \sum_{l=1}^{\infty} \frac{z^l}{l^a}$$

$$N_B = \frac{V}{h^3} 4\pi \int_0^\infty p^2 dp \frac{1}{e^{\frac{\beta p^2}{2m} - \beta\mu} - 1}$$

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

$e^{\beta\mu} = z \geq 0$

$$\frac{N_B}{V} = \frac{4\pi}{h^3} (2mk_BT)^{3/2} \underbrace{\int_0^\infty x^2 dx \frac{z e^{-x^2}}{1-z e^{-x^2}}}_{X\to\infty \quad \int \text{finite}}$$

$X \to 0$

$$X \to 0 \quad \frac{z e^{-x^2}}{1-z e^{-x^2}} \to \frac{z}{1-z}$$

$0 \leq z \leq 1$ Bose

Can have a problem if $z = 1$.

We need $0 \leq z \leq 1$ $\mu \leq 0$.

But if $z = 1$

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

$\int_0 \frac{x^2 dx}{x^2}$ finite

$1-e^{-x^2} = 1-(1-x^2+\ldots) = x^2$

as $T \to 0$ N is lower than actual N??

$\mu \to 0 \qquad z \to 1.$

$$\frac{N_B}{V} = \frac{4\pi}{h^3}(2mk_BT_c)^{3/2} \int_0^\infty x^2 dx \frac{e^{-x^2}}{1-e^{-x^2}}$$

Notice in 2d $\displaystyle\int_0^\infty \frac{x\,dx\, e^{-x^2}}{1-e^{-x^2}}$ diverges at 0!

$\Rightarrow$ no Bose-einstein Condensate.

For $T<T_c$ μ stays at 0.

$$N_B = N_{\text{condensate}} + N_{\text{gas}}.$$

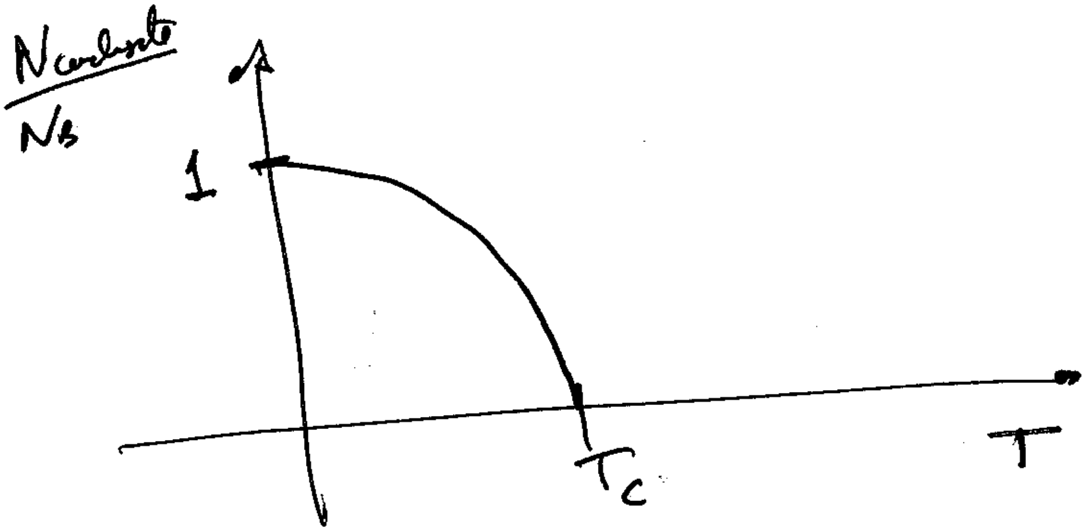
$$N_{\text{gas}} = V\frac{4\pi}{h^3}(2mk_BT)^{3/2} \int_0^\infty \frac{x^2 dx}{e^{x^2}-1}.$$

$$N_{\text{condensate}} = N_B - N_{\text{gas}}.$$

$\Downarrow$ lowest energy state $\vec{p}=0$

$$N_{\text{condensate}} = \frac{4\pi V}{h^3}\int_0^\infty \frac{x^2 dx}{e^{x^2}-1}(2mk_B)^{3/2}\left(T_c^{3/2} - T^{3/2}\right)$$

$$\frac{N_{condensate}}{V} = \frac{\cancel{N}N_B}{V}\left(1 - \left(T/T_c\right)^{3/2}\right).$$ ← critical exponent



Other Bose gases

Gas of photons

$\varepsilon = \hbar\omega \qquad k = \omega/c = \frac{2\pi}{\lambda}$

$p = \hbar k$

$\boxed{\varepsilon_p = pc}$

2 polarizations

Canonical ensemble, N not conserved, equiv. to $\mu = 0$

$$\ln Z = -\beta A = -\frac{2V}{(2\pi\hbar)^3}\int d^3p \, \ln\left(1 - e^{-\beta pc}\right)$$

$$= -\frac{8\pi V}{(2\pi\hbar)^3}\int_0^\infty p^2 dp \, \ln\left(1 - e^{-\beta pc}\right) \qquad x = \beta pc$$

$$= -\frac{8\pi V}{(2\pi\hbar)^3}\frac{1}{(\beta c)^3}\underbrace{\int_0^\infty x^2 dx \, \ln\left(1 - e^{-x}\right)}_{-\pi^4/45}$$

$$= -2\sum_{n=1}^\infty \frac{1}{n^4}$$

$$A = \frac{-8\pi V}{(2\pi\hbar c)^3}(k_B T)^4 \frac{\pi^4}{45}$$

$$A = -\frac{\pi^2}{45}\frac{V(k_B T)^4}{(\hbar c)^3}$$

grand-can./ can.

$$\frac{pV}{k_B T} = -\beta A.$$

$$p = -\frac{\partial A}{\partial V} = \frac{\pi^2}{45}\frac{(k_B T)^4}{(\hbar c)^3} \Rightarrow \boxed{A = -pV}$$

$$S = -\frac{\partial A}{\partial T} = \frac{4\pi^2}{45}\frac{V k_B^4 T^3}{(\hbar c)^3}$$

$$U = A + TS = \frac{\pi^2}{45}\frac{V(k_B T)^4}{(\hbar c)^3}\left(-1+4\right) = \frac{\pi^2}{15}\frac{V(k_B T)^4}{(\hbar c)^3}$$

E

$$U = -3A = 3pV \qquad \boxed{pV = \frac{1}{3}U}$$

Summary

$$U = \frac{\pi^2}{15}\frac{V(k_B T)^4}{(\hbar c)^3} \quad \text{energy}$$

$$p = \frac{\pi^2}{45}\frac{(k_B T)^4}{(\hbar c)^3}$$

$$S = \frac{4}{45}\pi^2\frac{V k_B^4 T^3}{(\hbar c)^3}$$

$$S \sim VT^3 \sim V(E/V)^{3/4} \sim V^{1/4} E^{3/4}$$

$$\boxed{C_V = T \left.\frac{\partial S}{\partial T}\right)_V = \frac{4\pi^2}{15} \frac{V k_B^4 T^3}{(\hbar c)^3}} \qquad \left(= -\left.\frac{\partial \sigma}{\partial T}\right)_V \right)$$

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polarization

$$N = \frac{2 \times 4\pi V}{(2\pi\hbar)^3} \int_0^\infty p^2 dp \underbrace{\frac{1}{e^{\beta pc} - 1}}_{\to n_p}$$

$\varepsilon = pc$

$$N = \frac{8\pi V}{(2\pi\hbar c)^3} \int_0^\infty \frac{\varepsilon^2 d\varepsilon}{e^{\beta\varepsilon} - 1}$$

$$E = \frac{8\pi V}{(2\pi\hbar c)^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\beta\varepsilon} - 1}$$

$\varepsilon = \hbar\omega$

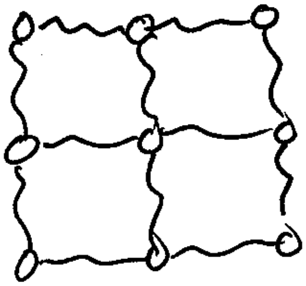
$$u = \frac{E}{V} = \frac{\hbar^4}{\pi^2 (\hbar c)^3} \int_0^\infty \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}$$

$$\boxed{u(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1}}$$

energy in $\omega, \omega + d\omega$ is $u(\omega, T) d\omega$

Planck's law

Phonons



N atoms

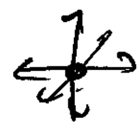
3N modes.

$\omega_1 - - \omega_{3N}$ harmonic oscillators.

Sound waves

$$e^{i\vec{k}\cdot\vec{x}}, \quad k_x = \frac{2\pi}{L_x} n_x, \quad k_y = \frac{2\pi}{L_y} n_y, \quad k_z = \frac{2\pi}{L_z} n_z$$

$$d^3 n = \underbrace{\frac{V}{(2\pi)^3}}_{\text{density of states in } \vec{k} \text{ variables.}} d^3 k$$

3 polarizations: 

# of phonons states in $d^3k \rightarrow \frac{3V}{(2\pi)^3} d^3k$

$k = \omega / c_s$; c_s speed of sound.

$\hbar\omega$: energy. $\rightarrow$ n phonons $\varepsilon = n\hbar\omega$

$$\frac{3V}{(2\pi)^3} 4\pi k^2 dk = \underbrace{\frac{3V}{(2\pi c_s)^3} 4\pi \omega^2 d\omega}_{f(\omega) \text{ density of states on } \omega}$$

$$3N = \int_0^{\omega_m} f(\omega)\, d\omega = \frac{V}{(2\pi^2 c_s^3)}\, \omega_m^3$$

$$\omega_m = \left(\frac{6\pi^2 N c_s^3}{V} \right)^{1/3} = \left(\frac{6\pi^2 N}{V} \right)^{1/3} c_s$$

$$k_m = \left(\frac{6\pi^2 N}{V} \right)^{1/3} \Rightarrow \lambda_m = \frac{2\pi}{k_m} = 2\pi \left(\frac{V}{6\pi^2 N} \right)^{1/3}$$

$$= \left(\frac{8\pi^3 v}{6\pi^2} \right)^{1/3} = \left(\frac{4}{3}\pi v \right)^{1/3}$$

$\sim$ atomic distance ✓

$$\ln Z = -\beta A = - \int_0^{\omega_m} f(\omega)\, d\omega \ \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= - \frac{3V}{2\pi^2 c_s^3} \int_0^{\omega_m} \omega^2\, d\omega \ \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= - \frac{3V}{2\pi^2 c_s^3} \frac{(k_B T)^3}{\hbar^3} \int_0^{\beta\hbar\omega_m} x^2\, dx \ \ln\left(1 - e^{-x}\right)$$

$\boxed{\omega_m \text{ depends on } V}$

$$A = \frac{3V}{2\pi^2 c_s^3} \frac{(k_B T)^4}{\hbar^3} \int_0^{\hbar\omega_m/k_B T} x^2 dx \ln(1-e^{-x})$$

Define T_D (Debye)

$$k_B T_D = \hbar\omega_m = \left(\frac{6\pi^2 N}{V}\right)^{1/3} \hbar c_s$$

$$(k_B T_D)^3 = 6\pi^2 \frac{N}{V} (\hbar c_s)^3$$

$$\frac{V}{N} = v = 6\pi^2 \left(\frac{\hbar c_s}{k_B T_D}\right)^3$$

$$A = \frac{3}{2\cancel{\pi^2}\cancel{c_s^3}} \frac{(k_B T)^4}{\cancel{\hbar^3}} 6\cancel{\pi^2} N \frac{\cancel{(\hbar c_s)^3}}{(k_B T_D)^3} \int_0^{T_D/T} x^2 dx \ln(1-e^{-x})$$

$$A = 9 k_B N \frac{T^4}{T_D^3} \int_0^{T_D/T} x^2 dx \ln(1-e^{-x})$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \int_0^{\omega_m} f(\omega) d\omega \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial E}{\partial \beta} = \frac{1}{k_B T^2} \int_0^{\omega_m} f(\omega) d\omega \frac{(\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

$$C_V = \frac{\hbar^2}{k_B T^2} \frac{12\pi V}{(2\pi c_s)^3} \int_0^{\omega_m} \frac{\omega^4 e^{\beta\hbar\omega} d\omega}{(e^{\beta\hbar\omega}-1)^2}$$

$$= \frac{\hbar^2}{k_B T^2} \frac{\cancelto{3}{12}\pi V}{\cancelto{2}{8}\pi^3 c_s^3} \frac{1}{(\beta\hbar)^5} \int_0^{\beta\hbar\omega_m} \frac{x^4 e^x dx}{(e^x-1)^2}$$

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

$$= \frac{3}{2\cancel{\pi^2}} \frac{k_B^{\cancel{4}} T^3}{\cancel{\hbar^3} \cancel{c_s^3}} 6\cancel{\pi^2} N \frac{\cancel{\hbar^3} \cancel{c_s^3}}{\cancel{k_B^3} T_D^3} \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x-1)^2}$$

$$= 9 k_B N \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x-1)^2}$$

$$\boxed{\frac{C_V}{k_B N} = 9 \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x dx}{(e^x-1)^2}}$$

Suppose $\lambda \sim 10^{-10}$ m

$k = \frac{2\pi}{\lambda} \sim 10^{10}$ 1/m

$c_s \sim 10^3$ m/s $\qquad \omega = 10^{13}$ 1/s

$$\hbar c_s = \hbar c \frac{c_s}{c} = 200 \text{ MeV fm} \times \frac{10^3 \cancel{m/s}}{3\times10^8 \cancel{m/s}} \approx 1\times10^{-3} \text{ MeV fm}$$

$$\hbar\omega = \hbar c_s \frac{\omega}{c_s} = 10^{-3} \text{ MeV} \times 10^{-15} \text{m} \; 10^{10} \text{ 1/m}$$

$$= 10^{-8} \text{ MeV} = 10^{-2} \text{ eV}$$

$300°K \quad 0.025$ eV

$T_0 \sim 100°K$.

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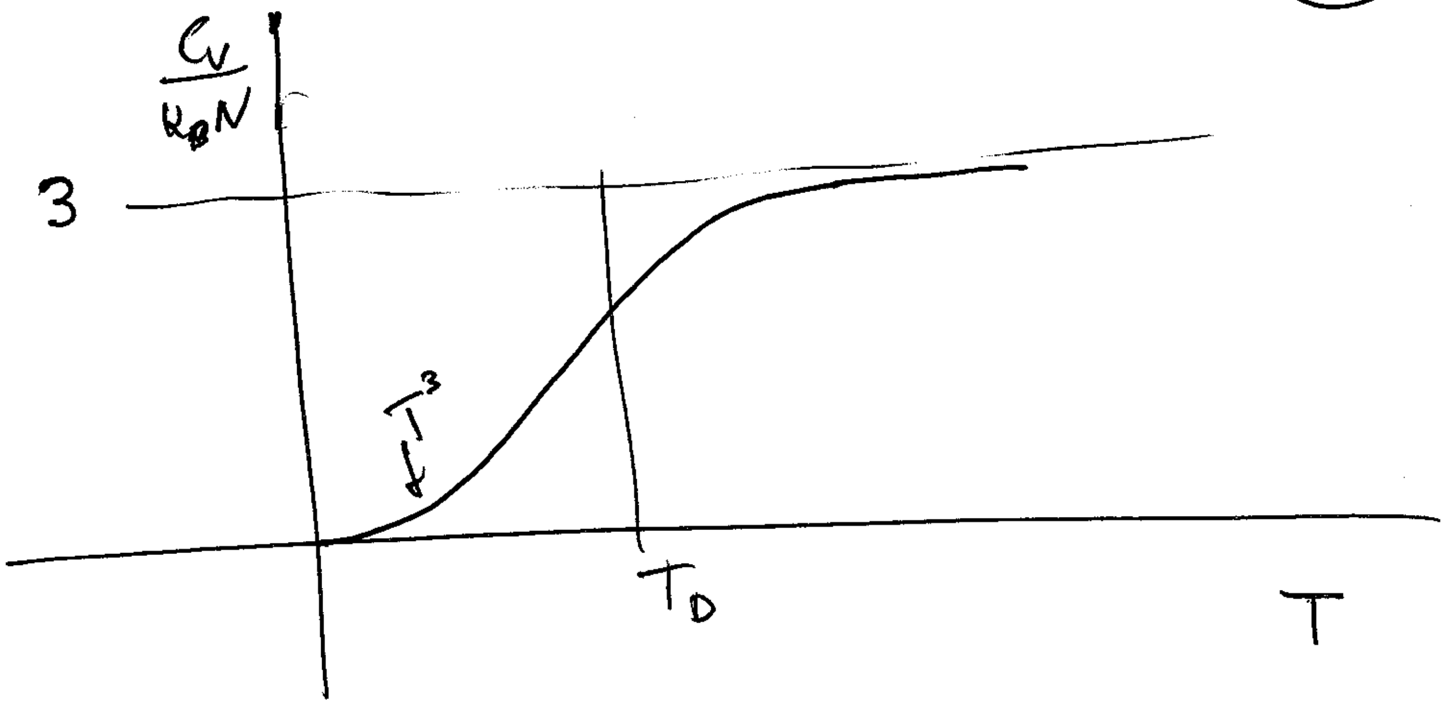
i) $T \ll T_D$

$$\frac{C_V}{K_B N} = 9\left(\frac{T}{T_D}\right)^3 \int_0^\infty \frac{x^4 e^x dx}{(e^x-1)^2}$$

ii) $T \gg T_D$

$$\frac{C_V}{K_B N} \simeq 9\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 dx}{x^2} = 3$$


$\frac{C_V}{k_B N}$
3
T^3
T_D
T