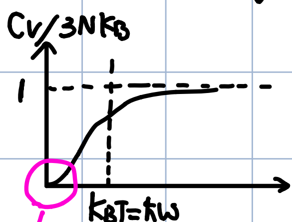
3°. Generally



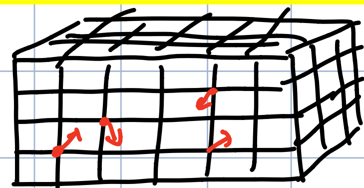
$\frac{k_BT}{\hbar\omega} = \frac{T}{\Theta_E}$ ← system dependant

Quantum Correction

4. Debye's Theory [Solid state]

Assumptions: 1° atoms, N, DOF, 3N
2° Harmonic Oscillation } kept from E's theory

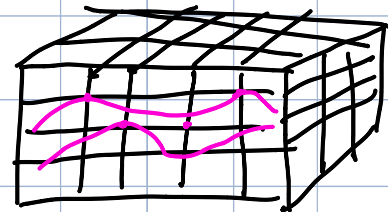
3°



independently

ONE ω (Einstein Frequency)

$Z = Z_1^N$



sound waves (weakly coupled to form a wave)

1° Collective Motion

2° many ω's

3° $0 \le \omega \le \omega_D$, different ω but up to a point

$$Z = \underbrace{\overset{\omega_1}{Z} \cdot \overset{\omega_2}{Z} \cdots\cdots \overset{\omega_{3N}}{Z}}_{3N \text{ independent wave}}$$

each Z is not for one atom but for one wave

same classical limit

Debye: wave eq. $\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{C^2}\frac{\partial^2 u}{\partial t^2}$

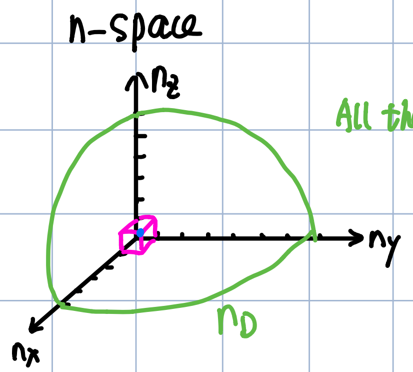
C ← speed of sound

1-D. $\frac{\partial^2 u}{\partial x^2} = \frac{1}{C^2}\frac{\partial^2 u}{\partial t^2}$ $\quad u = A \sin\frac{n_x \pi x}{L} \sin\omega t$, $\omega_{n_x} = \frac{n_x \pi C}{L}$ (Quantization)

A ← amplitude

3-D. n_x, n_y, n_z. $\quad \omega^2 = \frac{\pi^2 c^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$

How many ω's should we use?



All the frequencies inside are adapted

volume $= \frac{1}{8}$ of a ball

$$\# = \frac{\text{Volume}}{\text{volume of a cube}} = \frac{1}{8}\left(\frac{4}{3}\pi n_D^3\right)/1 = 3N$$

$$n_D = \left(\frac{18N}{\pi}\right)^{1/3}$$

$$Z = z^{w(1,1,1)} \, z^{w(1,1,2)} \cdots z^{w_D}$$

$$\ln Z = \sum_{n_1,n_2,n_3} \ln z^{w(n_1,n_2,n_3)} = \sum_{n_1,n_2,n_3} \ln \frac{\exp(-\beta\hbar w_{(n_1,n_2,n_3)}/2)}{1-\exp(-\beta\hbar w_{(n_1,n_2,n_3)}/2)}$$

$= [\text{math}]$

$$\rightarrow E = -\frac{\partial \ln Z}{\partial \beta}, \quad C_V = \frac{\partial \bar{E}}{\partial T}$$

[See Manuals]

Classical Ideal Gas

1. Success before Gibbs

$$Z = (z_1)^N = V^N\left[\frac{2m\pi}{\beta}\right]^{3N/2}, \quad z_1 = V\left[\frac{2m\pi}{\beta}\right]^{3/2}$$

$$P = -k_B T \frac{\partial \ln Z}{\partial V} = \cdots = \frac{Nk_BT}{V} \quad \text{(eq. of state)}$$

$$\bar{E} = \frac{3}{2}Nk_BT \qquad C_V = \frac{3}{2}Nk_B$$

2. Gibbs Paradox

$$S = -\frac{\partial F}{\partial T} = -\frac{\partial}{\partial T}(-k_BT\ln Z)$$

$$= \underline{Nk_B \ln V} + \frac{3Nk}{2}\ln T + \frac{3N}{2}\ln(2\pi mk) + \frac{3}{2}Nk.$$

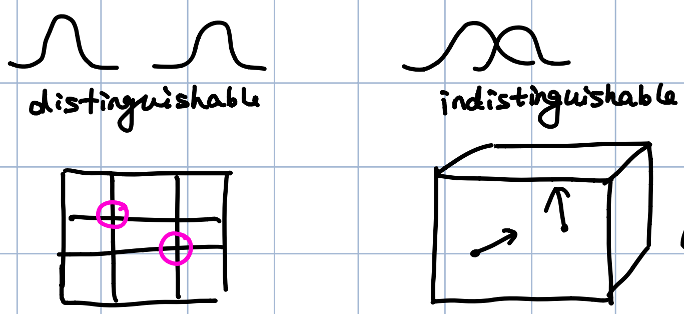
if divided by 2 (N, V),
then where's the extensity?

Another: freeze of DOF

3. Particle inDinstinguishibility (Semi-Classical Version of QM)

Go back to the model: $H=\frac{1}{2m}\sum p_i^2+V$

We labeled the particle!



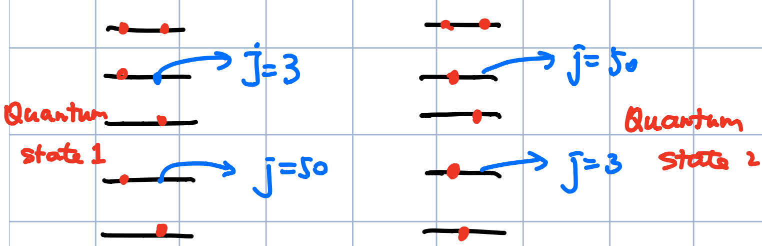
size of wave packet $\propto \delta p$.

cannot be labeled!

$Z=\sum e^{-\beta H}$, $H=\frac{1}{2m}\sum p_j^2$ $\qquad z=\int d\vec{r}_1 d\vec{p}_1\, e^{-\frac{p_1^2}{2m}} \int d\vec{r}_2 d\vec{p}_2\, e^{-\frac{p_2^2}{2m}} \cdots = z_1^N$

CORRECTION

4. Indistinguishable ideal gas



In Distinguishable situation: QS 1 & 2 Different

In inDistinguishable situation: QS 1 & 2 The SAME

Dist. version: How many "different" states are they? (in fact the same) $N!$

We have overestimate $N!$ times.

To semiclassically fix the problem.

$$\underset{\text{indist.}}{Z} = \frac{1}{N!}\underset{\text{dist.}}{Z} = \frac{1}{N!} z_1^N$$

$\boxed{\text{Stirling Formula } N! \sim N^N/e^N \ldots}$

$$\Rightarrow \underset{\text{indist.}}{Z} = \left(\frac{e}{N}\right)^N z_1^N = \left(\frac{e}{N}\right)^N V^N\left(\frac{2\pi m}{\beta}\right)^{3N/2} = \left(\frac{V}{N}\right)^N\left(\frac{2\pi m}{\beta}\right)^{3N/2} e^N$$

$$\underset{\text{indist.}}{\ln Z} = \underset{\text{dist.}}{\ln Z} - N\ln N$$

$$\underset{\text{indist.}}{F} = -k_BT \underset{\text{indist.}}{\ln Z}$$

$$p = -k_BT\left(\frac{\partial \ln Z}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V} \quad \text{(NO CHANGES)}$$

$$\bar{E} = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N,V} = \frac{3}{2}Nk_BT$$

unaffected

$$S = -\frac{\partial F}{\partial T} = Nk_B \ln\frac{V}{N} + \frac{3Nk_B}{2}\ln T + \frac{3N}{2}\ln(2\pi m k) + \frac{5Nk_B}{2}$$

cut the system by half → $S_{half} = \frac{1}{2}S$ Gibbs Paradox is resolved

How big is our wave packet?

Size → de Broglie wavelength.

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

$E = p^2/2m$ single particle energy.

Estimate from thermal (stat-Mech)

$E \simeq \frac{3}{2}k_BT \quad p^2 \simeq 2m\cdot\frac{3}{2}k_BT = 3mk_BT$

$$\lambda_{dB} \simeq \frac{h}{\sqrt{3mk_BT}} = \frac{6.626\times10^{-34}}{\sqrt{3\times300\cdot4\times10^{-3}\div6\div10^{23}\cdot k_B}} = 2\,\text{Å}$$

$\lambda \ll l$ distinguishable or $\lambda \sim l$ indistinguishable

Also Note: $l = \left(\frac{V}{N}\right)^{1/3}$ the distance between molecules.

1 liter $\left(\frac{10^{-3}}{6\times10^{23}}\right)^{1/3}$ m $= 10^{-9}$ m $= 10\,\text{Å}$

⇒ λ_{dB} is smaller but similar than the atomic/modecular distance. So we need N!

The above is semiclassical "fix"