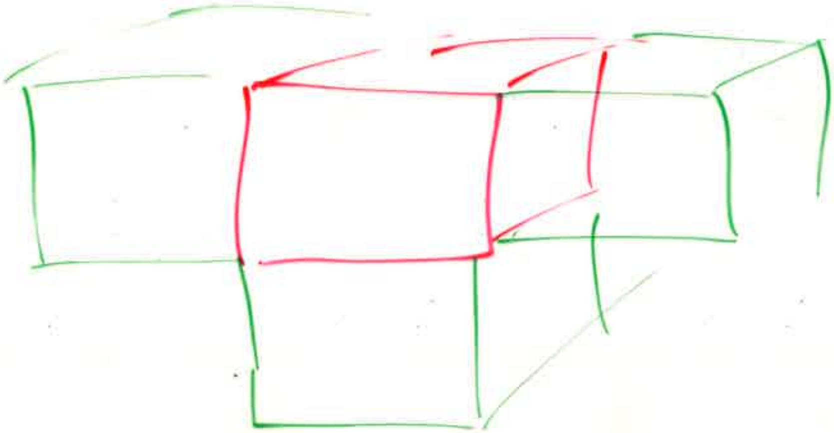
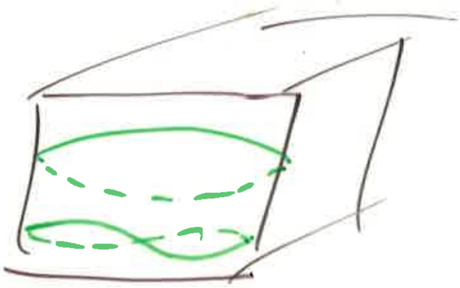
Periodic Boundary Conditions



$$\int \frac{d^3k}{(2\pi)^3}$$

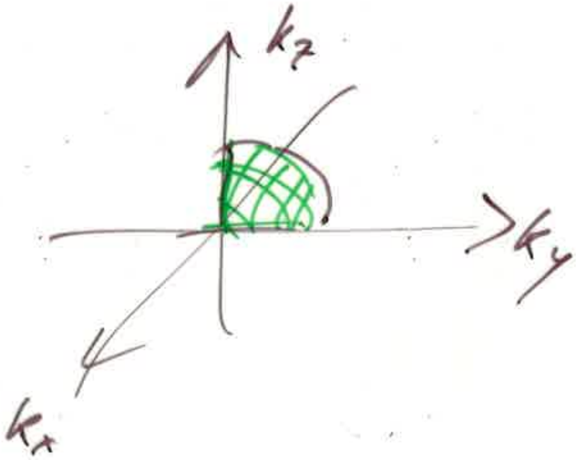
integrate over all k

Hard wall B.C.



$$\frac{1}{8}\int \frac{d^3k}{(\pi)^3}$$

integrate over first octant



Heat capacity

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v = \frac{32\pi^5 k_B^4 T^3 V}{15 h^3 c^3}$$

$$\lim_{T\to 0} C_v = 0 \qquad \text{(third Law)}$$

Entropy

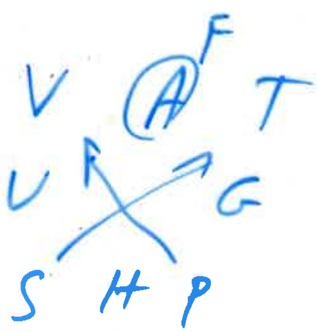
$$S \quad \int_0^T \frac{C_v(T')}{T'}\,dT' = \frac{32}{45}\frac{\pi^5 k_B^4 T^3}{h^3 c^3} V$$

Pressure

1st Law $dU = T\,dS - P\,dV + \mu\,dN$

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

$$p = T\left(\frac{\partial S}{\partial V}\right)_{UN} = \frac{\frac{32}{45}\pi^5 k_B^4 T^4}{h^3 c^3}$$ wrong



Pressure $\qquad dF = -S\,dT - p\,dV + \mu\,dN$

$$F = U - TS \leftarrow$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{TN} \qquad F = -k_B T \ln(Z)$$

$$F = U - TS = aVT^4 - \frac{4}{3}aVT^4 = -\frac{1}{3}aVT^4$$

$$-\left(\frac{\partial F}{\partial V}\right)_{TN} = +\frac{1}{3}aT^4 = \frac{1}{3}\frac{U}{V} = \frac{1}{3}u \quad \checkmark$$

Number of Photons

1.20... Riemann zeta function

$$N = 16\pi\,\zeta(3)\,\frac{V T^3 k_B^3}{h^3 c^3}$$

$$\int_{x=0}^{\infty} \frac{x^2}{e^x - 1}\,dx = 2\zeta(3)$$

Planck distribution solves the UV catastrophe.

$$\text{Energy Density} = u = \frac{U}{V} = \frac{1}{\pi^2}\int_{k_r=0}^{\infty} dk_r \, \frac{k_r^2 \, \hbar c k_r}{e^{\beta \hbar c k_r} - 1}$$

ν = linear frequency

$$\hbar c k = \hbar \omega = h\nu$$

$[\omega] = \frac{\text{rad}}{\text{sec}}$

$[\nu] = \frac{1}{\text{sec}} = \text{Hz}$

$\omega = 2\pi\nu$

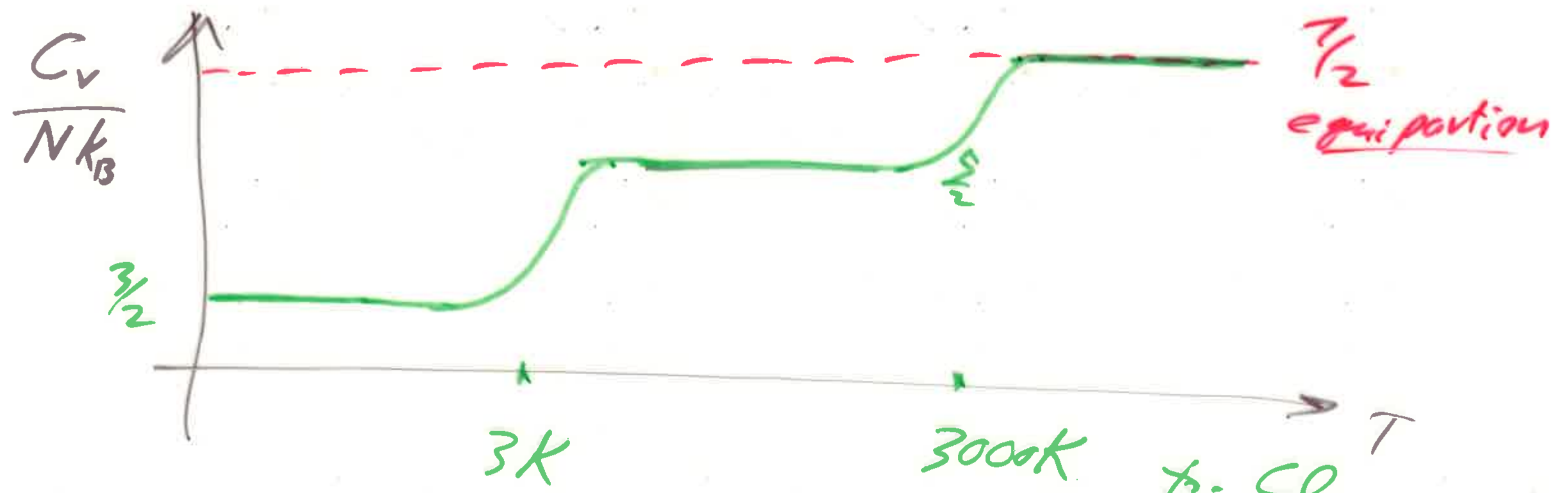
$$u(\nu) = \frac{1}{\pi^2 c^2} \frac{h\nu^3}{e^{\beta h\nu} - 1}$$

$u(\nu) \rightarrow$ small $\nu \ll 1$: $e^{\beta h \nu} \simeq 1 + \beta h\nu + \cdots$

$u(\nu) \sim \nu^2$

$u(\nu) \rightarrow$ large $\nu \gg 1$: $u(\nu) \sim e^{-\nu}$

(2) Heat capacity for diatomic gas



Classical Canonical Partition function

$$Z(T,V,N) = \frac{1}{N!}\, z^N \leftarrow \text{one molecule}$$

$\frac{1}{N!}$ to avoid Gibbs paradox

$$z = \int \frac{d^3p_1\, d^3r_1\, d^3p_2\, d^3r_2}{h^6} \exp\left[-\beta\left\{\frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(\vec{r}_1 - \vec{r}_2)\right\}\right]$$

$V(\vec{r}_1 - \vec{r}_2)$: potential energy

$$\vec{p}_1^{\,2} \equiv \vec{p}_1 \cdot \vec{p}_1 = p_{1x}^2 + p_{1y}^2 + p_{1z}^2$$

Define $\vec{R}_{cm} = \dfrac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$ $\qquad \vec{P}_{cm} = \vec{p}_1 + \vec{p}_2$

Center of Mass Coord's $\qquad M = m_1 + m_2$

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relative coordinates

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \qquad \vec{p} = \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1+m_2}$$

$$\mu = \frac{m_1 m_2}{m_1+m_2} \quad \text{reduced mass}$$

$$z = \underbrace{\int \frac{d^3P_{cm}\, d^3R_{cm}}{h^3}\, e^{-\beta\frac{\vec{P}_{cm}^{\,2}}{2M}}}_{\text{translation}} \cdot \underbrace{\int \frac{d^3p\, d^3r}{h^3}\, e^{-\frac{\beta\vec{p}^{\,2}}{2\mu} - \beta V(\vec{r})}}_{\text{vibrations + rotations}}$$