$$U(T) = \sum_{j_x = -\infty}^{+\infty} \sum_{j_y} \sum_{j_z} \sum_{\epsilon=1}^{2} \hbar\omega\left[\frac{1}{2} + \left(\frac{1}{e^{\beta\hbar\omega} - 1}\right)\right]$$

periodic B.C.

polarizations

Planck distribution

Dispersion relation $\omega = ck$ (no dispersion)

$$\sum_{j_x} \rightarrow \int_{j_x} d_{j_x} \quad \text{continuum limit}$$

$$j_x = \frac{k_x L}{2\pi} \quad \text{(periodic Boundary Conditions)}$$

$$d_{j_x} = dk_x\left(\frac{L}{2\pi}\right)$$

$$\int_{j_x} d_{j_x} \int_{j_y} d_{j_y} \int_{j_z} d_{j_z}$$

polarizations

V

$$U(T) = \left[\cancel{u_0} + 2\iiint_{k_x k_y k_z} \left(\frac{(\hbar c k \beta) k_B T}{e^{\beta\hbar c k} - 1}\right) \frac{dk_x\, dk_y\, dk_z\, L^3}{2\pi \cdot 2\pi \cdot 2\pi}\right]$$

∞

Cartesian k_x, k_y, k_z $\longrightarrow$ Spherical Polar

k_r, θ_k, φ_k

$$U(T) = k_B T V \frac{2}{8\pi^3} \underbrace{\int_{\theta_k=0}^{\pi} \sin\theta_k \, d\theta_k \int_{\varphi_k=0}^{2\pi} d\varphi_k}_{4\pi} \int_{k_r=0}^{\infty} k_r^2 \frac{\hbar c k_r \beta}{e^{\hbar c k_r \beta} - 1} dk_r$$

Define $x = \beta \hbar c k_r$, $dx = \beta \hbar c \, dk_r$

dimensionless $\qquad k = |\vec{k}| = k_r$

$$U(T) = V \frac{k_B T}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \underbrace{\int_{x=0}^{\infty} \frac{x^3 \, dx}{e^x - 1}}_{\frac{\pi^4}{15}}$$

Energy Density

$$u = \frac{U(T)}{V} = \underbrace{\left(\frac{8\pi^5 k_B^4}{15 h^3 c^3}\right)}_{a} T^4 = a T^4$$

Radiation Constant

$a = \frac{4}{c}\sigma$ Stefan-Boltzmann constant

Heat Capacity

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

$$\lim_{T\to 0} C_V = 0 \quad \text{third law}$$

Entropy $\quad dQ = T\,dS \Rightarrow dS = \frac{dQ}{T} = \frac{C_V\,dT}{T}$

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

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

$$F = U - TS$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_{VN} dT + \left(\frac{\partial F}{\partial V}\right)_{TN} dV + \left(\frac{\partial F}{\partial N}\right)_{TV} dN$$

$$F = -k_B T \ln(Z)$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{TN}$$

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

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

$$p = \frac{1}{3}aT^4 = \frac{1}{3}\frac{U}{V} = \frac{1}{3}u$$

characteristic of relativistic

Avg. Number of Photons

$$N(T) = \sum_{j_x\, j_y\, j_z = -\infty}^{+\infty} \sum_{\epsilon=1}^{2} \frac{1}{e^{\beta\hbar\omega} - 1}$$

$$= 16\pi V \frac{T^3 k_B^3}{h^3 c^3} \underbrace{\frac{1}{2}\int_{x=0}^{\infty} \frac{x^2}{e^x - 1}\, dx}_{\zeta(3)}$$

$\zeta(3)$ Riemann Zeta function

$\simeq 1.20$

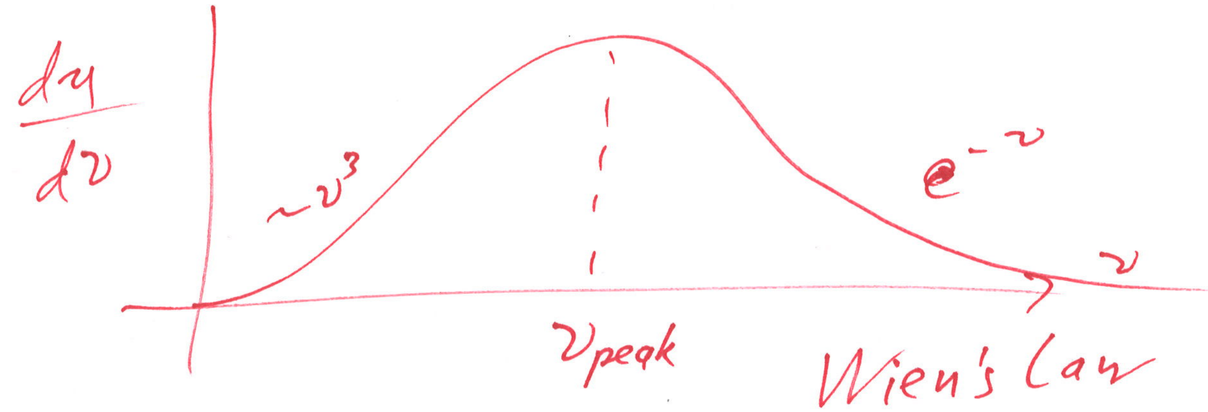
$$u = \frac{U}{V} = \frac{1}{\pi^2}\int_{k=0}^{\infty} dk \boxed{\frac{k^2 \hbar c k}{e^{\beta\hbar c k} - 1}} \quad \frac{du}{dk}$$

$$\hbar c k = \hbar\omega = h\nu \leftarrow$$ ν is frequency

$$\hbar c\, dk = h\, d\nu$$

$$\frac{du}{d\nu} = \frac{1}{\pi^2 c^2} \frac{h\nu^3}{e^{\beta h\nu} - 1}$$

$$\frac{du}{d\lambda} = ?$$



Wien's Law

$\nu \propto T$

$$\lambda_{peak} \neq \frac{c}{\nu_{peak}}$$

What if we don't throw out the zero point energy?

$$Z = e^{-\frac{\beta\hbar\omega}{2}} \frac{1}{1-e^{-\beta\hbar\omega}} \cdot \left(\frac{e^{+\frac{\beta\hbar\omega}{2}}}{e^{+\frac{\beta\hbar\omega}{2}}}\right)$$

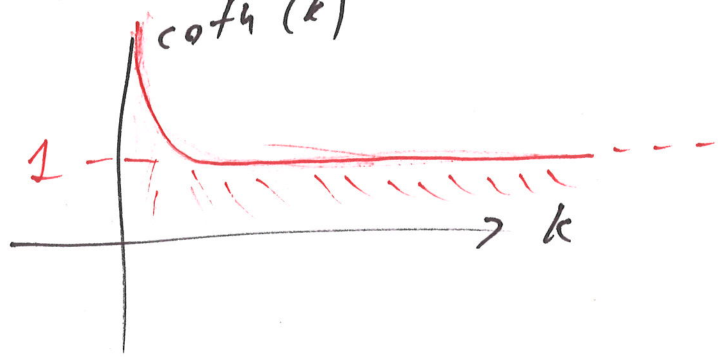
$$= \frac{1}{e^{+\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}} = \frac{1}{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$= \frac{1}{2}\operatorname{csch}\left(\frac{\beta\hbar\omega}{2}\right)$$

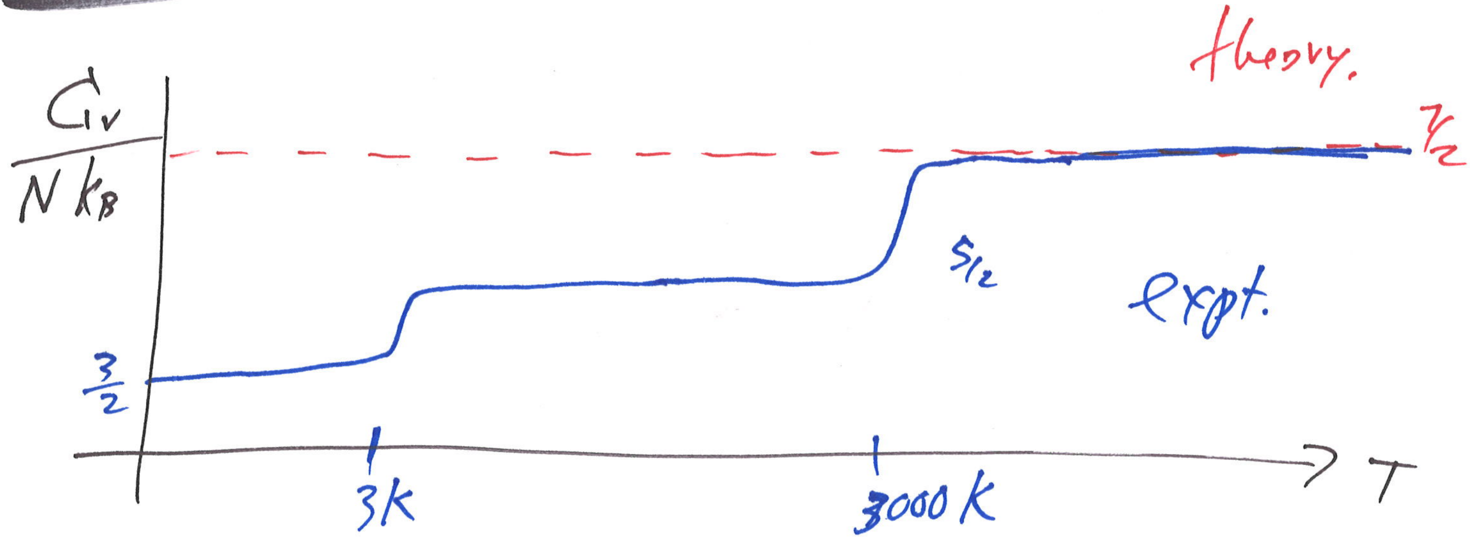
$$U = -\frac{\partial \ln(Z)}{\partial\beta} = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$$

$$= \frac{\hbar c k}{2}\coth\left(\frac{\beta\hbar c k}{2}\right)$$

$$\int dV\, u \propto \int_{k=0}^{\infty} k^3 \coth(\cdots k) \rightarrow \infty$$



Heat Capacity for a diatomic gas



for C-O

Classical Canonical Partition Function ~~for~~ a diatomic gas

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

correct entropy to avoid the Gibbs paradox

$dx_1 dy_1 dz_1$

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

$d^3p_1 = dp_{1x}\, dp_{1y}\, dp_{1z}$

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

Define:

Define Center of Mass coordinates

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

$$M = m_1 + m_2$$

Relative coordinates

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

$$\mu = \frac{m_1 m_2}{m_1+m_2} < m_1 \text{ or } m_2$$

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

$$\frac{V}{v_Q} \qquad z_{\substack{vib\\rot}}$$

$$z_{\substack{vib\\rot}} = \underbrace{\int \frac{dp'\,dr'}{h}\, e^{-\beta\frac{p'^2}{2\mu}}\, e^{-\beta\frac{1}{2}\mu\omega^2 r'^2}}_{\text{vibrations}} \cdot \underbrace{\int \frac{d^2\Omega\, d^2L}{h^2}\, e^{-\beta\frac{L^2}{2I}}}_{\text{rotations}}$$

$$z^{\text{classical}}_{tot} = \underbrace{\frac{V}{v_Q}}_{\text{translation}} \cdot \underbrace{\frac{1}{h}\sqrt{\frac{2\pi\mu}{\beta}}\cdot\sqrt{\frac{2\pi}{\mu\beta a^2}}}_{\text{vibration}} \cdot \underbrace{\frac{4\pi}{h^2}\left(\sqrt{\frac{2\pi I}{\beta}}\right)^2}_{\text{rotations}}$$

$$\epsilon = -\frac{\partial \ln(z)}{\partial\beta} = \underbrace{\frac{3}{2}\frac{1}{\beta}}_{\text{translations}} + \underbrace{\frac{1}{2}\frac{1}{\beta} + \frac{1}{2}\frac{1}{\beta}}_{\text{vibrations}} + \underbrace{1\,\frac{1}{\beta}}_{\text{rotation}}$$

$$\boxed{\ln\left(z^{\text{class}}_{tot}\right) = \ln\left(\frac{V}{v_Q}\right) + \ln\sqrt{\frac{1}{\beta}} + \ln\sqrt{\frac{1}{\beta}} + \ln\left(\frac{1}{\beta}\right) + \ln(\cdots)}$$

$$-\frac{1}{2}\ln\beta$$

$$\epsilon = \frac{3}{2}k_BT + 1\,k_BT + 1\,k_BT = \frac{7}{2}k_BT$$

↑ Equipartition theorem

$$c_V = \frac{\partial\epsilon}{\partial T} = \frac{7}{2}k_B$$

$\frac{1}{2}k_BT$ for every quadratic degree of freedom

Quantum Mechanics for vibrations (1905) Einstein Debye

$$E_j^{vib} = (j + \tfrac{1}{2})\hbar\omega \qquad \text{Quantum Harmonic Oscillator}$$

$$z_{QM}^{vib} = \sum_{j=0}^{\infty} e^{-\beta E_j} = \sum_{j=0}^{\infty} e^{-\beta(j+\frac{1}{2})\hbar\omega}$$

$$= e^{-\beta\frac{\hbar\omega}{2}} \sum_{j=0}^{\infty} e^{-\beta j\hbar\omega} = \left(e^{-\beta\frac{\hbar\omega}{2}}\right)\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)$$

$$\epsilon_{QM}^{vib} = -\frac{\partial \ln(z_{QM}^{vib})}{\partial\beta} = \frac{\hbar\omega}{2} + \left(\frac{\hbar\omega e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) \cdot \frac{e^{+\beta\hbar\omega}}{e^{+\beta\hbar\omega}}$$

$$= \frac{\hbar\omega}{2} + \left(\frac{\hbar\omega}{e^{+\beta\hbar\omega}-1}\right)$$

heat capacity

$$c_{QM}^{vib} = \frac{\partial \epsilon_{QM}^{vib}}{\partial T} = \emptyset + k_B\left(\frac{\hbar\omega}{k_B T}\right)^2\left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}}-1}\right)$$