Quantum Statistical Mechanics

Breakdown of classical statistical mechanics: we will look at predictions of the heat capacity (an experimentally measurable quantity) for the following three systems:

1. Diatomic ideal gas
2. Vibrations in a solid (phonons)
3. Blackbody radiation (photons)

Historically the last development among the three since the correction prediction requires knowing how to quantize the angular momentum $\hbar^2 \ell(\ell+1)$

Classical SM predicts a finite heat capacity but doesn't take into account the "freezing" of d.o.f.s at low temp.

Classical SM predicts an infinite energy (ultraviolet catastrophe) which led to the development of QM.

Non-interacting diatomic gas

e.g. oxygen

(C.O.M. coordinates)

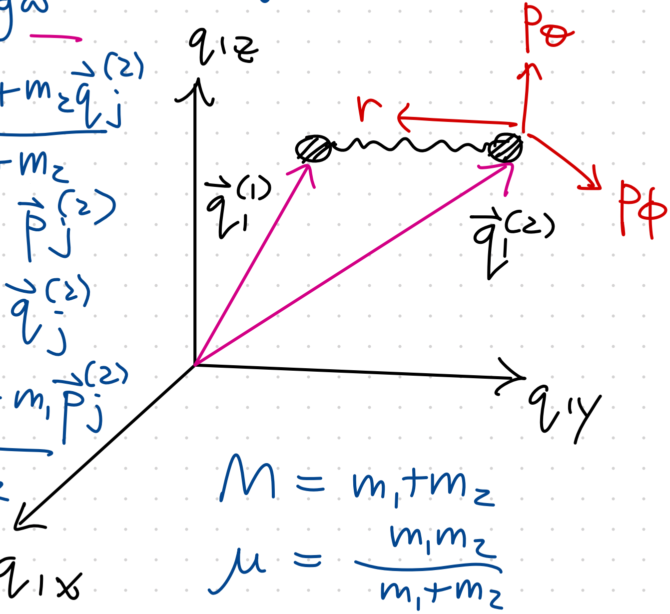
$$\vec{Q}_j = \frac{m_1 \vec{q}_j^{(1)} + m_2 \vec{q}_j^{(2)}}{m_1 + m_2}$$

$$\vec{P}_j = \vec{p}_j^{(1)} + \vec{p}_j^{(2)}$$

(Relative coordinates)

$$\vec{r}_j = \vec{q}_j^{(1)} - \vec{q}_j^{(2)}$$

$$\vec{\pi}_j = \frac{m_2 \vec{p}_j^{(1)} - m_1 \vec{p}_j^{(2)}}{m_1 + m_2}$$



$$M = m_1 + m_2$$

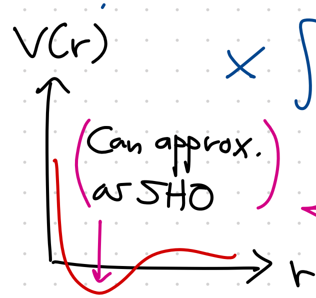
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

Internal d.o.f.

Relative to the second atom in the molecule, the first atom can moves in three directions: along the axis connecting the two atoms, (vibrational modes) or in the other two perpendicular directions denoted θ and ϕ (associated with their own canonical momenta p_θ and p_ϕ.) (rotational modes)

$$Z_N = \frac{Z_1^N}{N!}, \quad Z_1 = \int \frac{d^3Q_j\, d^3P_j}{h^3}\, e^{-\beta P^2/2M}$$

$$\times \int \frac{dr\, dp_r\, d\theta\, dp_\theta\, d\phi\, dp_\phi}{h^3}\, e^{-\beta \pi^2/2\mu}\, e^{-\beta V(r)}$$



Vibrational energy is a function of the distance $\vec{q}_j^{(1)} - \vec{q}_j^{(2)}$

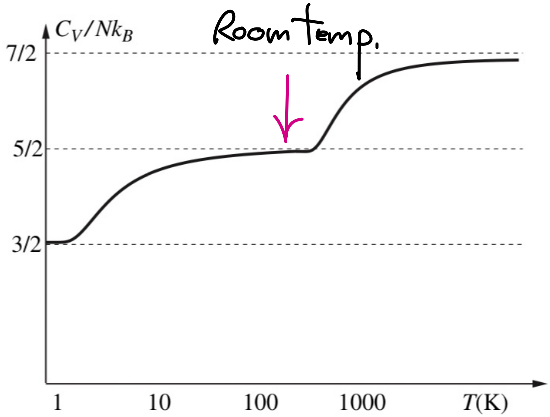
$$\int \underbrace{\frac{d^3Q_j\, d^3P_j}{h^3}\, e^{-\beta P^2/2M}}_{\substack{\text{translational} \\ 3}} \times \int \underbrace{\frac{d\theta\, dp_\theta\, d\phi\, dp_\phi}{h^2}\, e^{-\beta(p_\theta^2+p_\phi^2)/2\mu}}_{\substack{\text{rotational} \\ 2}}$$

$$\times \int \frac{dr\, dp_r}{h}\, \underbrace{e^{-\beta p_r^2/2\mu}\, e^{-\beta V(r)}}_{\substack{2 \\ \text{vibrational}}}$$

According to the equipartition thm, each harmonic d.o.f. should give $\frac{1}{2}kT$ of energy.

$$U = NkT\left(\frac{3}{2}+1+1\right) = \frac{7}{2}NkT \Rightarrow C_v = \left.\frac{\partial U}{\partial T}\right|_V = \frac{7}{2}Nk$$

Room Temp.



Log plot →

Doesn't agree with experiments!

Vibrational modes

Quantum analysis

$$H_{vib} = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$\boxed{\sum_{n=0}^{\infty} a r^n = \frac{a}{1-r}}$$

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= \underbrace{e^{-\beta\hbar\omega/2}}_{\text{zero-point energy}} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n = \boxed{\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}}$$

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

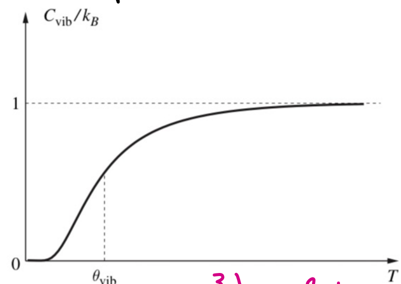
$$\langle E_{vib}\rangle = -\frac{\partial \ln Z_{vib}}{\partial\beta} = \frac{\hbar\omega}{2} + \hbar\omega\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$C_v = \frac{\partial\langle E_{vib}\rangle}{\partial T} = \boxed{k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{-\beta\hbar\omega}}{\left(1-e^{-\beta\hbar\omega}\right)^2}}$$

Characteristic temperature $\Theta = \hbar\omega/k_B$

$$\Rightarrow C_v = k_B\left(\frac{\Theta}{T}\right)^2 \frac{e^{-\Theta/T}}{\left(1-e^{-\Theta/T}\right)^2}$$

High Temp: $k_B e^{-\Theta/T} \sim k_B$



$\Theta \sim 10^3$ to 10^4 K

(To ensure that quantum stat. mech. is consistent with classical stat. mech., we assert that the Planck constant "h" here is the same as the "h" in $\int \frac{dx\,dp}{h}$)

Rotational modes

Classical analysis $H_{rot} = \frac{1}{2I}\left(p_\theta^2 + \frac{p_\phi^2}{\sin^2\theta}\right) = \frac{L^2}{2I}$

$$Z_{rot} = \frac{\int d\theta\, dp_\theta\, d\phi\, dp_\phi}{h^2}\; e^{-\beta\left(p_\theta^2 + p_\phi^2/\sin^2\theta\right)/2I}$$

$$= \underbrace{\frac{2\pi}{h^2}}_{\phi\text{ integral}} \cdot \underbrace{\sqrt{2\pi I kT}}_{p_\theta\text{ integral}} \cdot \int_0^\pi d\theta\, \underbrace{\sqrt{2\pi I \sin^2\theta\, kT}}_{p_\phi\text{ integral}}$$

$$= \frac{4\pi}{h^2}\cdot 2\pi I k_B T = \frac{2Ik_BT}{\hbar^2} \longleftarrow \hbar = \frac{h}{2\pi}$$

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = +\frac{\partial \ln\beta}{\partial\beta} = k_BT \Rightarrow C_V = k_B$$

Quantum analysis

$$Z_{rot} = \sum_{\ell=0}^{\infty} \exp\left[-\frac{\beta}{2I}\hbar^2\ell(\ell+1)\right]\underbrace{(2\ell+1)}^{\text{degeneracy}}$$

Let $\Theta = \hbar^2/2Ik_B$. $\Rightarrow$ $Z_{rot} = \sum_{\ell=0}^{\infty} e^{-\Theta\ell(\ell+1)/T}(2\ell+1)$

$T \gg \Theta$

$$\sum_{\ell=0}^{\infty} \to \int_0^\infty d\ell,\quad x = \ell(\ell+1),\; dx = (2\ell+1)\,d\ell$$

$$Z_{rot} = \int_0^\infty dx\; e^{-(\Theta/T)x} = \boxed{\frac{T}{\Theta}} \quad \text{(Classical limit)}$$

$T \ll \Theta$ First few terms dominate

$$Z_{rot} = 1 + 3e^{-2\Theta/T} + \mathcal{O}(e^{-6\Theta/T})$$

Using $\ln(1+x) = x - \frac{x^2}{2} + \mathcal{O}(x^3)$

$$\ln Z_{rot} \approx 3e^{-2\Theta/T} = 3e^{-2\Theta k_B \beta}$$

$$\therefore \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} \approx 6 k_B \Theta e^{-2\Theta/T}$$

$$\Rightarrow C_V = \frac{\partial \langle E \rangle}{\partial T} \approx 3k_B \underbrace{\left(\frac{2\Theta}{T}\right)^2 e^{-2\Theta/T}}$$

$\Theta \sim 1$ to 10 K

vanishes at lower T due to quantum statistics

$x^2 e^{-x} \to \infty \cdot 0$ as $T \to 0$

But by L'Hospital rule

$$\lim_{x\to 0} x^2 e^{-x} = \lim_{x \to 0} \frac{d^2 x^2}{dx^2} \frac{d^2 e^{-x}}{dx^2} = 0$$

Solids

Classically, atoms that form a solid can have small vibrations around there equilibrium in all three directions, except very long wavelenght modes (small wave numbers k) that correspond to the translations of the whole solid. So in the thermodynamic limit, $\langle E \rangle \approx 3Nk_BT \Rightarrow c_V \approx 3k_B$

Kinetic + potential

No restoring force

Quantum analysis

$$Z_1 = \frac{e^{-\beta\hbar\omega(k)/2}}{1-e^{-\beta\hbar\omega(k)}}$$

(Same as the vibrational modes)

$$Z_N = e^{-\beta E_0} \prod_{j,\vec{k}} \frac{1}{1-e^{-\beta\hbar\omega_j(\vec{k})}}$$

Include the zero-point energies of all oscillators

No $N!$ factor because the atoms are distinguishable by their locations.

$(j,\vec{k})$ enumerates the quantum microstates
j labels modes and $\vec{k}$ the wave vectors

$$\langle E\rangle = E_0 + \sum_{j,\vec{k}} \hbar\omega_j(\vec{k}) \langle n_j(\vec{k})\rangle$$

$$\langle n_j(\vec{k})\rangle = \frac{\sum_{n=0}^{\infty} n e^{-\beta\hbar\omega n}}{\sum e^{-\beta\hbar\omega n}} = -\frac{1}{\hbar\omega}\frac{\partial \ln}{\partial\beta}\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$= + \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

The Einstein model

All vibrations are quantized and have the same universal frequency ω.

$$\langle E\rangle = E_0 + 3N\hbar\omega \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$\Theta = \hbar\omega/k_B$

$$C_V = 3Nk_B\left(\frac{\Theta}{T}\right)^2 \frac{e^{-\Theta/T}}{(1-e^{-\Theta/T})^2}$$

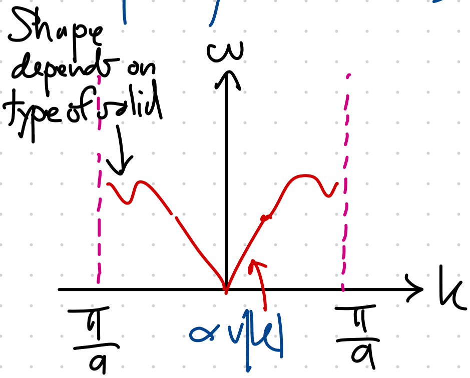
However, experimentally C_V decays much more slowly as T^3 (without the exponial factor). A more sophisticated model solves this problem

The Debye model

Wavelength λ

wave number $k = \frac{2\pi}{\lambda}$

frequency $\omega = \omega(k)$ (Dispersion relation)



Brillouin zone

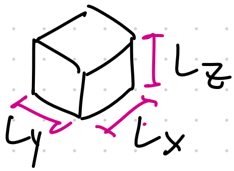
At low T, thermal energy only excites long wavelenght modes. These modes are phonons (acoustic modes = sound) that can propagate through the solid without much distortion with

$$\omega = vk$$

Speed of sound in the solid

(In general, $v = \frac{\partial \omega}{\partial k}$)

In a box



$$\vec{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z}\right)$$

$$\Rightarrow dN = \prod_{j=1}^{3} \frac{dk_j}{2\pi/L_j} = \frac{V}{(2\pi)^3} d^3k$$

$$\langle E \rangle \to E_0 + 3\int dN \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Integral: $\omega = vk \Rightarrow 3\frac{V}{(2\pi)^3}\int d^3k \frac{\hbar v k}{e^{\beta\hbar v k} - 1}$

$T \ll \Theta$ Small $\vec{k}$'s dominate and can take the integration lim to ∞

$x = \beta\hbar v k$

$$\text{Integral} = 3\frac{V}{(2\pi)^3}\int d^3k \frac{\hbar v k}{e^{\beta\hbar v k}-1}$$

$$\approx \frac{3V}{8\pi^3}\int\left(\frac{k_BT}{\hbar v}\right)^3 d^3x \frac{k_BT x}{e^x-1}$$

$$= \frac{3V}{8\pi^3}\left(\frac{k_BT}{\hbar v}\right)^3 k_BT \int \overset{4\pi}{\cancel{d\Omega}} \underbrace{\int_0^\infty dx \frac{x^3}{e^x-1}}$$

$$\sigma_v(z) = \frac{1}{\Gamma(v)}\int_0^\infty dx \frac{x^{v-1}}{\frac{e^x}{z}-1} \qquad 3! \cdot \underbrace{\frac{1}{\Gamma(4)}\int_0^\infty dx \frac{x^{4-1}}{e^x-1}}$$

$$\lim_{z\to 1}\sigma_v(z) = \zeta(v) \qquad \zeta(4) = \frac{\pi^4}{90}$$

$$\Gamma(n) = (n-1)!$$

$$= \frac{3V}{8\pi^3}\frac{(k_BT)^4}{(\hbar v)^3} 4\pi \cdot \frac{\pi^4}{15} = \boxed{\frac{\pi^2}{10} V \frac{(k_BT)^4}{(\hbar v)^3}}$$

Black-body radiations

2 polarization states

$$\frac{2V}{(2\pi)^3}\int d^3k \, \frac{\hbar c k}{e^{\beta c k}-1} \qquad \text{Same integral}$$

$$E = V\frac{\pi^2}{15}\frac{(k_B T)^4}{(\hbar c)^3}$$