1. Heat Capacity in solids

$$C = \frac{dU}{dT}$$

U ← internal energy

T ← temperature

- Determines how much energy is required to change the temperature

$$\Delta T = C^{-1} \Delta Q \qquad (\Delta Q = \text{heat transfer})$$

ΔT: change in temp

ΔQ: heat transferred into system

$\rightarrow$ C large $\Rightarrow$ ΔQ must be large

need large ΔQ to get fixed ΔT if C is large

- More carefully

$$C_p = \left.\frac{dU}{dT}\right|_p \neq C_V = \left.\frac{dU}{dT}\right|_V$$

- Mayer's relation

$$C_p - C_v = \frac{TV\alpha^2}{\kappa}$$ v. small → discuss in problems

$$- \alpha = \frac{1}{V}\left.\frac{dV}{dT}\right|_p > 0$$ coefficient of thermal expansion

$$- \beta = -\frac{1}{V}\left.\frac{dV}{dP}\right|_T > 0$$ isothermal compressibility

- in the solid state α is very small (solids do not change volume much due to temperature)

- Specific heat

Q: extensive vs intensive

$$c = \frac{C}{M} \quad \begin{matrix} \leftarrow \text{extensive} \\ \leftarrow \text{extensive} \end{matrix} = [J \cdot K^{-1} \cdot kg^{-1}]$$

$$c_{mol} = \frac{C}{N_{mol}} = \frac{c}{m} = [J \cdot K^{-1} \cdot mol^{-1}]$$

m = molar mass = $\frac{M}{N_{mol}}$

also common to quote per particle

$$\frac{C}{N} \begin{matrix} \leftarrow \text{ext} \\ \leftarrow \text{ext} \end{matrix} = \left[J \cdot K^{-1} \right]$$

- What sets C? Change in # states available at temp T

$$dU = S\,dT - p\,dV \implies C_v = \left.\frac{dU}{dT}\right|_V = T \left.\frac{dS}{dT}\right|_V$$

$S \sim \log W$ W = ways of arranging the system at temperature T

if T increases, expect S increases

$$T \to T + \Delta T$$

$$S \to S + \Delta S \qquad \Delta S = C \frac{\Delta T}{T}$$

Naive

→ S depends on microscopic details

∴ C depends " " "

1-1 Dulong Petit Law

$$\left(\frac{C}{M}\right) m_{atomic} = \text{const.}$$

Universality — applies across many materials with diff microscopics → universality important in physics

→ obviously implicates a role for atoms in determining heat capacity

→ Established decades before atomic theory accepted

→ treated as empirical rule not as evidence for atoms

→ m_X / m_H established from chemical reactions "stoichiometry" work of Dalton + Berzelius (chemists)

→ Dulong + Petit also chemists

→ at the time study of matter, materials + thermal phenomena was considered chemistry

→ Physics concerned mechanics, optics astronomy and electricity

Bottom line

→ Very robust result in era when properties of atomic nuclei were out of reach of direct measurement

→ But why such a simple result ?

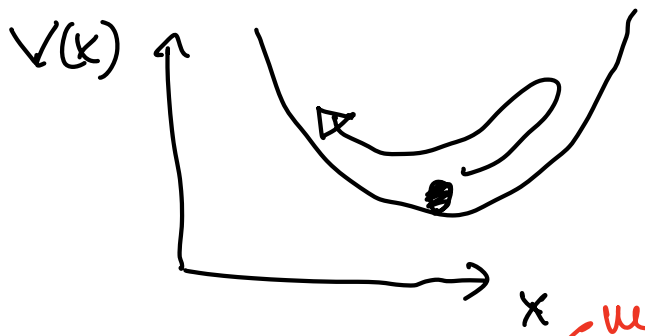
1.2 Boltzmann's theory

— First theory of D-P law

- Main idea: use microscopic theory of classical atoms

→ ideas that microscopic theory of particles could be useful had been floating around and used to great success by Clausius, Maxwell, Joule etc as learned in stat mech

→ Atoms in a solid must be held in place by some potential



Energy $H = \frac{p^2}{2M} + \frac{1}{2}kx^2$

momentum

Energy given by the Hamiltonian

Kinetic

potential

moreover, has energy $\bar{E}$ with probability

$$\text{prob}(\vec{x},\vec{p}) \propto e^{-\beta H(\vec{x},\vec{p})} \qquad \beta = \frac{1}{k_B T}$$

Following usual framework of stat mech

$$Z \propto \int d^3\vec{x} \int d^3\vec{p}\, e^{-\beta H(\vec{x},\vec{p})}$$

Avg Energy $\quad u = -\dfrac{d \log Z}{d\beta} = 3 k_B T \quad$ per atom

will do this in the homework problems

$$\therefore \quad C = N_{\text{atoms}} \frac{du}{dT} = 3 k_B N_{\text{atoms}}$$

$$C_{\text{mol}} = \frac{C}{N_{\text{mol}}} = 3 k_B N_A = 3R$$

→ modern statement of DP law

- Successes
  - Explains Dulong-Petit law

1.3 Einsteins correction

- Failures of Boltzmanns result

  - $C_{diamond} \approx 0.24\ C_{DP}$ $(T = 300K)$

→ strong tension with Boltzmann result

→ hard to explain why it would be lower

  - $C_{diamond} \approx 0.15\ C_{DP}$ $(T = 243K)$ $= -30C$

→ by 1875 measurements performed as low as -30, and it was found the tension just gets worse

↪ this is the story of science progress is made when technology allows us to access regimes beyond old theories

- Main idea: treat atoms as quantum oscillators

→ followed planck who had recently had success in deriving the black-body spectrum by quantising light.

$$\mathcal{Z} = \mathrm{tr}\left[e^{-\beta H}\right]$$ ← quantum mechanical partition function

Hamiltonian $H_{1D} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2$ $\quad [x, p] = i\hbar$

recalling results from your quantum courses

$$H_{1D}|n\rangle = E_n|n\rangle, \quad E_n = (n+\tfrac{1}{2})\hbar\omega \quad \omega = \sqrt{\frac{k}{m}}$$

$$\therefore \mathcal{Z}_{1D} = \sum_{n=0}^{\infty} \langle n|e^{-\beta H}|n\rangle$$

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

evaluate in the usual way

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

$$\rightarrow Z_{1D} = \frac{e^{\beta\hbar\omega/2}}{e^{\beta\hbar\omega} - 1}$$

however we want to study an oscillator in 3D space $\vec{x} = (x_1, x_2, x_3)$ $\vec{p} = (p_1, p_2, p_3)$

$$\hat{\vec{x}} = (x_1, x_2, x_3) \quad \hat{\vec{p}} = (p_1, p_2, p_3) \quad [x_a, p_b] = i\hbar\delta_{ab}$$

$$H_{3D}|\vec{n}\rangle = E_{\vec{n}}|\vec{n}\rangle \quad E_{\vec{n}} = (n_1 + n_2 + n_3 + \frac{3}{2})\hbar\omega$$

$$Z_{3D} = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \langle \vec{n}| e^{-\beta H} |\vec{n}\rangle$$

$$Z_{3D} = Z_{1D}^3$$

follows because the three coordinate pairs (x_i, p_i) don't interact

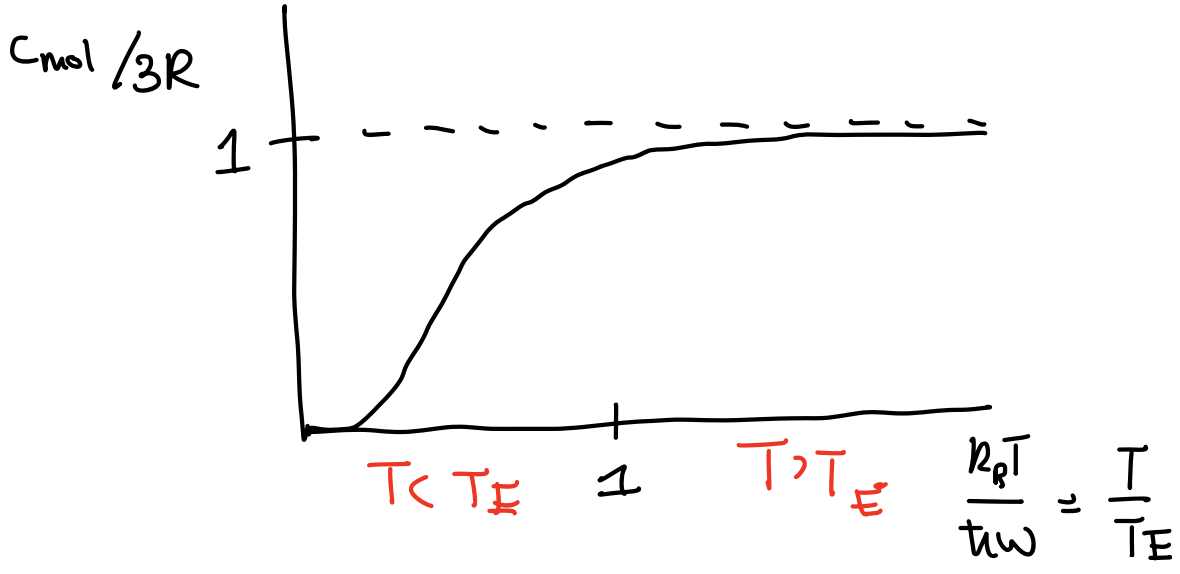
$$u_{atom} = -\frac{d\log Z}{d\beta} = -3\frac{d\log Z_{1D}}{d\beta} = 3\hbar\omega\left[n_B(\beta\hbar\omega) + \frac{1}{2}\right]$$

where $n_B(x) = \frac{1}{e^x - 1}$ is the Bose factor

$$c_{mol} = N_A \frac{du_{atom}}{dT} = 3R(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

$T \to \infty$, $\beta \to 0$, $c_{mol} \to 3R$

$T \to 0$, $\beta \to \infty$ $c_{mol} \sim 3R(\beta\hbar\omega)^2 e^{-\beta\hbar\omega} \to 0$



$T_E \approx 1300K$ (diamond) $>> T_{Room}$

Einstein's success:

- Expained $C_{mol} \to 0$ behaviour of solids at low temp

→ However notable disagreement at low T

→ point out $C_{mol} \sim T^3$ behaviour

1.4 Debye's low T-calculation

- Failure of Einsteins calculation
  - Notable deviation at low T
  - Einsteins result decays much faster than empirical observations

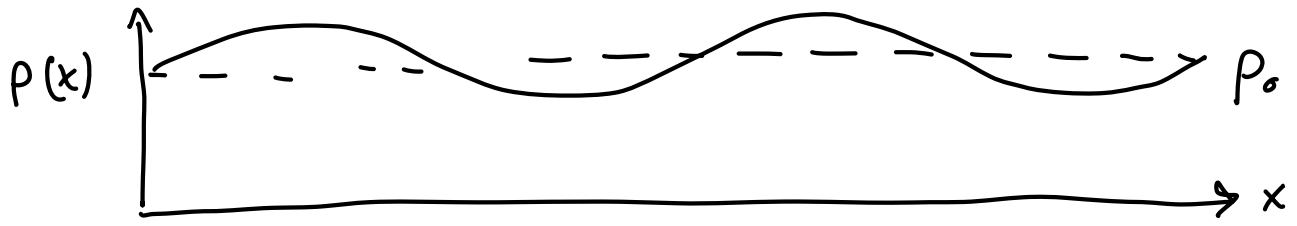
- Main Idea: Assume low energy excitations are waves $\omega_k = v|k|$

  ↖ velocity → here $v_g = v_p$

$$U = 3\sum_{\vec{k}} \hbar\omega_{\vec{k}} \left[n_B(\beta\hbar\omega_k) + \frac{1}{2} \right] \qquad (*)$$

↑ what values of k are we summing over here

these correspond to displacements like density waves



assume p satisfies a wave equation

$$\frac{d^2p}{dt^2} = v^2 \frac{d^2p}{dx^2}$$

solutions look like $p(x,t) = p_0 + \delta p(\omega_k t - kx)$

with $\omega_k = v|k|$

→ these vibrations are pressure waves p-waves

→ also 2x polarisations of shear waves → factor 3

– Assume periodic boundary conditions on a 3D system of linear size L (ie $L \times L \times L$)

$$\vec{r} = \vec{r} + L\vec{m} \qquad m_a \in \mathbb{Z}$$

= integer

$$\therefore \vec{k} \cdot (m_1 L, m_2 L, m_3 L) = 2\pi p \qquad p \in \mathbb{Z}$$

$$\Longrightarrow k_b = \frac{2\pi n_b}{L}$$

approximate the sum with an integral

$$\sum_{\vec{k}} f(\omega_{\vec{k}}) = \sum_{\vec{k}} f(v|k|) = \sum_{\vec{n}} f\left(\frac{2\pi v}{L}|\vec{n}|\right)$$

$$\approx \int d^3\vec{n}\, f\left(\frac{2\pi v|\vec{n}|}{L}\right)$$

$$= \left(\frac{L}{2\pi}\right)^3 \int d^3k\, f(v|\vec{k}|)$$

assume isotropic

$$\int d^3k = \int dk\, k^2 \int d^2\Omega$$

$$\int d^2\Omega = 4\pi$$

$$= \frac{L^3}{2\pi^2} \int dk\, k^2 f(vk)$$

$$= \frac{L^3}{2\pi^2 v^3} \int d\omega\, \omega^2 f(\omega)$$

$$= \int d\omega\, g(\omega) f(\omega)$$

$$g(\omega) = \frac{L^3\omega^2}{2\pi^2 v^3} = \text{density of states}$$

$$\boxed{\sum_{\vec{k}} \to \left(\frac{L}{2\pi}\right)^3 \int d^3\vec{k} \longrightarrow \int d\omega\, g(\omega)}$$

this is a frequently used simplifying replacement

– Debye frequency and Temp

$$\#\text{ atoms} = N = \rho L^3$$

turns out to be useful to write this as

$$g(\omega) = \frac{3N\omega^2}{\omega_D^3} \quad \text{where} \quad \omega_D = (6\pi^2\rho)^{1/3} v$$

Debye frequency

similarly $T_D = \frac{\hbar\omega_D}{k_B}$

using this result on (*) then we have

$$U = \int_0^\infty d\omega\, g(\omega) \cdot 3\hbar\omega \left[n_B(\beta\hbar\omega) + \frac{1}{2} \right]$$

$$= \int_0^\infty d\omega\, g(\omega) \cdot 3\hbar\omega\, n_B(\beta\hbar\omega) + (T \text{ indep. cons.})$$

Let $x = \beta\hbar\omega$

$$= \frac{9Nk_BT^4}{T_D^3} \int_0^\infty dx\, x^3 n_B(x) + \left(\frac{\pi^4}{15} \right) \quad \text{''} \quad)$$

$$= \frac{3\pi^4 N k_B T^4}{5\, T_D^3} + (\ \ll\ )$$

$$c_{mol} = \frac{1}{N_{mol}} \frac{dU}{dT} = \frac{12}{5}\pi^4 \cdot R \cdot \left(\frac{T}{T_D}\right)^3$$

Success: gets the $\sim T^3$ low-T scaling

Failure: lost the $c_{mol} = 3R$ high T limit

Debye's interpolation

Main-idea: introduce a cutoff ω_c

$$U = \int_0^{\omega_c} d\omega\, g(\omega) \cdot 3\hbar\omega \left[n_B(\beta\hbar\omega) + \frac{1}{2} \right]$$

here Debye introduced a cutoff as he knew "really" the system was N_{atoms} coupled oscillators

$$N = \int_0^{\omega_c} d\omega\, g(\omega) = \int_0^{\omega_c} d\omega\, \frac{3N\omega^2}{\omega_D^3} = N\frac{\omega_c^3}{\omega_D^3}$$

atoms = # oscillators

$$\therefore \quad \underline{\omega_c = \omega_D}$$

Set $x = \beta\hbar\omega$ again $\therefore \quad x_D = \beta\hbar\omega_D = \frac{T_D}{T}$

$$U = \frac{9NK_BT^4}{T_D^3}\int_0^{T_D/T} dx\, x^3 n_B(x) + (T \text{ indep const})$$

for $T \ll T_D$
- T_D/T large
- integral converges
- recover $U \sim T^4$ and hence $C \sim T^3$

for $T \gg T_D$
- Use $x \ll 1$ expansion $n_B \approx \frac{1}{x}$
- $U = \frac{9NK_BT^4}{T_D^3}\int_0^{T_D/T} dx\, x^2 = 3NK_BT$

$$- C_{mol} = \frac{1}{N_{mol}} \frac{dU}{dT} = \frac{3Nk_B}{N_{mol}} = 3N_A k_B = 3R$$

Debye's successes: – good agreement with data at high and low T

failures: – Seems ad hoc

– we assumed $\omega_n = vk$

– it is known that this breakdown for $k \sim \frac{2\pi}{a}$ ← lattice spacing

– Still some disagreement at intermediate T

– Metals $C \sim \gamma T + \alpha T^3$

Summary of part 1

	Success	Failure
Boltzmann → Kinetic theory of solids	DP law	no T dep
Einstein + Q Mechanics	T dependence $C \xrightarrow{T \to 0} 0$	no $\sim T^3$
Debye + collective modes	$C \sim T^3$	ad hoc + not $\sim T$ behavior