The Quantum Harmonic Crystal

The energy of a vibrational mode is related to its amplitude:

$$u_\ell = \frac{\epsilon}{\sqrt{M_\ell}} \, e^{i(\vec{k}\cdot\vec{R}_\ell^0 - \omega t)}$$

$$\underbrace{\frac{\epsilon}{\sqrt{M_\ell}}}_{} \rightsquigarrow \text{amplitude}$$

Classically, this is a continuous function, i.e. the atom can oscillate $\bar{w}$ any amplitude/energy.

→ The energy of the mode, found by taking the time avg.) of the oscillation, is

$$E = \frac{1}{2} M_\ell \omega^2 \left(\frac{\epsilon}{\sqrt{M_\ell}}\right)^2 = \frac{1}{2}\omega^2 \epsilon^2$$

For the corresponding quantum system, the energy, and therefore, amplitude of oscillation, is quantized.

Just like the quantum harmonic oscillator, the result is:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \Rightarrow \text{Appendix L for derivation}$$

Recall there are $3N$ normal modes, divided amonst 3 phonon branches ⟹ monatomic only

In general, $3 \cdot N_b \cdot N$ modes

$3 \cdot N_b$ branches

$x,y,z \overset{\llcorner}{} \quad \hookrightarrow$ # atoms in basis ⟹ $3 \cdot N_b = DOF$

Each mode will have a distinct "n":

$$E_{s,k} = (n_{s,k} + \tfrac{1}{2}) \hbar \omega_s(k)$$

Energy in mode s,k

s labels branch

$\rightarrow$ k gives frequency ω.

Total energy of the system:

$$U = \sum_{s,k} (n_{s,k} + \tfrac{1}{2}) \hbar \omega_s(k)$$

$n_{s,k} \rightarrow$ phonon occupancy, # of phonons in state s,k.

The energy diff. of adding/removing a phonon from the system is a constant, regardless of n_{sk}:

$$\Delta E = \hbar \omega_s(k)$$

Analagous to photons, think of phonons as a (quasi) particle w energy $\hbar \omega_s(k)$ which exist in the lattice & can interact: Absorption/emission of a phonon

Phonons are bosons, ∴

$$n_s(k) = \frac{1}{e^{\beta \hbar \omega_s(k)} - 1}$$

$\Rightarrow \beta = \frac{1}{k_B T}$

Aside: Longitudinal $\rightarrow$ spin 0

Transverse $\rightarrow$ spin 1

like photons

– The occupancy of phonon mode s, k, given by $n_s(k)$, obeys Bose-Einstein stats.

The photon analogue:

Photon	Phonon	
$\hbar \omega$	$\hbar \omega_s(k)$	Energy
2 for each k (polarizations)	$3 \cdot N_b = $ DOF per k	# modes
$\omega = kc$ ↓ speed of light	$\omega = kc_s$ ↓ speed of sound (low k)	Speed
$\rho(\omega) d\omega = \dfrac{V \omega^2}{\pi^2 c^3} d\omega$ ↳ 2 polarizations	$\dfrac{3}{2} \dfrac{V \omega^2}{\pi^2 c_s^3} d\omega$ ↳ 3 polarizations (low temp → $\omega \propto k$)	Density of states

Lattice specific heat

$$U = \sum_{s,k} \left(n_s(k) + \tfrac{1}{2} \right) \hbar \omega_s(k) \quad \underline{\text{OR}} \quad U = \int_0^\infty n(\omega) \, \hbar \omega \, \rho(\omega) \, d\omega$$

occupancy   phonons energy   density of states

$$C_v = \left. \frac{dU}{dT} \right|_v$$

recall: $u = \int f(\epsilon) \, D(\epsilon) \, \epsilon \, d\epsilon$

for e^-'s.

B-E stats: $n(\omega) = \dfrac{1}{e^{\hbar\omega/k_B T} - 1}$

and $\rho(\omega) \propto \omega^2$ (low temp limit, Debye model)

$\therefore u \propto \displaystyle\int \dfrac{\omega^3}{e^{\hbar\omega/k_B T} - 1} \, d\omega$

let $x = \dfrac{\hbar\omega}{k_B T}$ $\Rightarrow$ $dx = \dfrac{\hbar}{k_B T} \, d\omega$

$\therefore u \propto \left(\dfrac{k_B T}{\hbar}\right)^4 \underbrace{\displaystyle\int \dfrac{x^3}{e^x - 1} \, dx}_{= \text{constant}}$
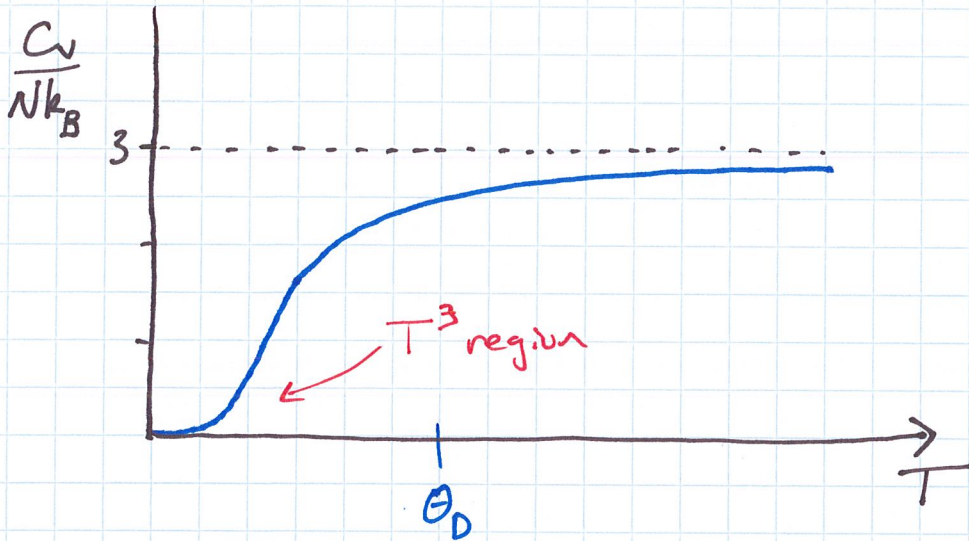
$\therefore u \propto T^4$

$\therefore C_v = \left.\dfrac{du}{dT}\right|_v \propto T^3$

Note, this result is in the low temp limit, such that

$\omega \propto k \Rightarrow$ Debye model $\Rightarrow \theta_D \gg T$

Debye temp. $\approx 100's \ K$.

@ high temp. C_v trends to the classical value of $C_v = 3Nk_B$

Combine w̄ electronic (semiclassical) result:

$$C_v = \gamma T + \beta T^3$$

↑ electronic

↑ lattice

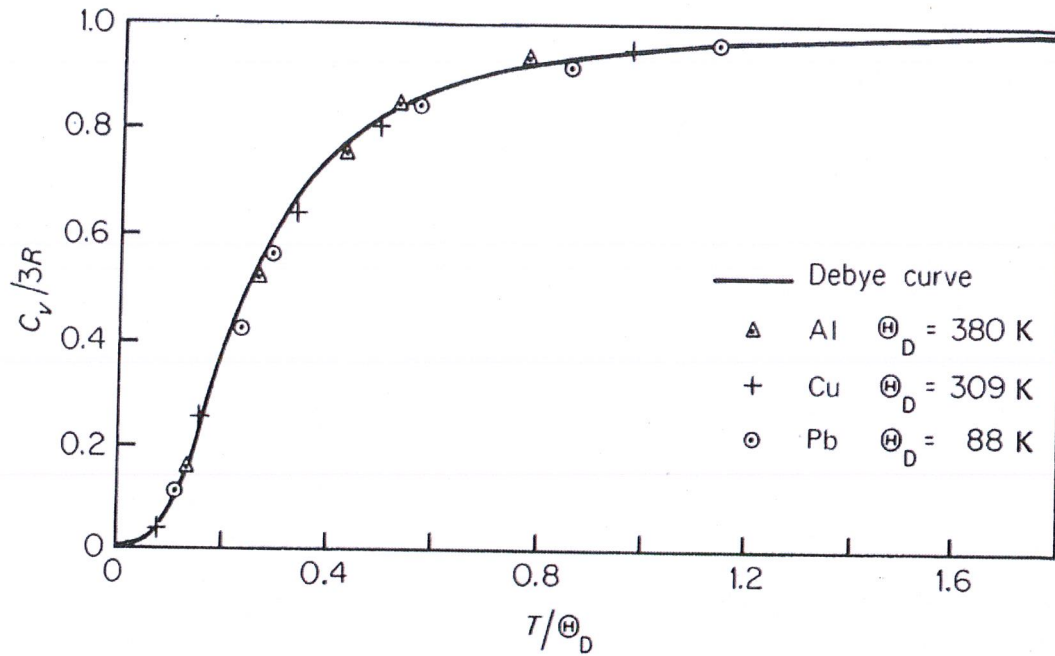- Excellent agreement w̄ experiment!

Fig. 6.7. Comparison of Debye's heat capacity curve, Eq. (6.27), with observations. Full line: Debye's curve. Experimental points for aluminium, copper and lead are plotted for the Debye temperatures shown. (Data from : *A Compendium of the Properties of Materials at Low Temperature, Part II: Properties of Solids.* Wadd Technical Report 60–56, Part II, 1960.)
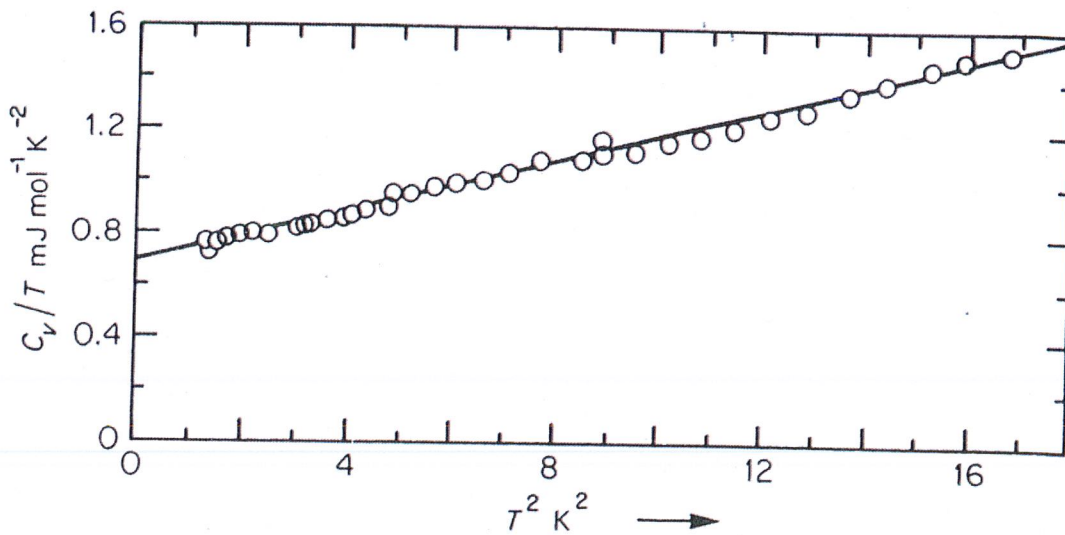

Fig. 6.2. Atomic heat capacity of copper. (W. S. Corak, M. P. Garfunkel, C. B. Satterthwaite and Aaron Wexler, *Phys. Rev.,* **98**, 1699 (1955).)