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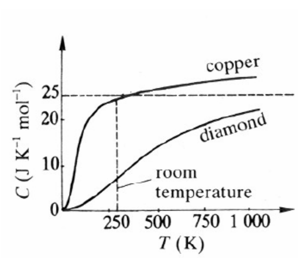
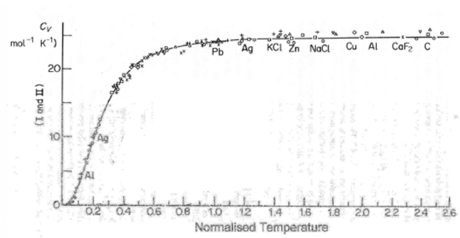
PHYS432
Materials Physics

Heat Capacity

What is heat capacity?

$$C = \frac{\partial U}{\partial T}$$ where U is the total energy (C is normally measured at constant pressure).





When scaled for temperature, $C(T)$ has common features for most solids:

- $C \approx 3R$ per mole for high temperatures
- $C \to 0$ as $T \to 0$
- $C \propto T^3$ for $T \approx 0$

Heat Capacity

Classically:

$$C = \frac{\partial U}{\partial T} = 3R$$

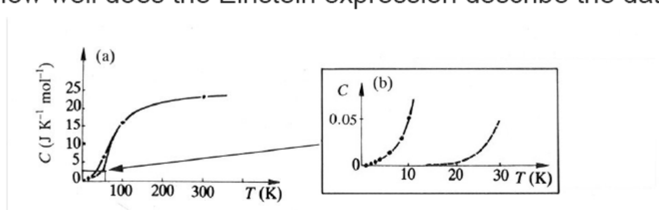
Bad at low T

	273K (J/K)	77K (J/K)
Cu	24.3	12.5
Al	23.8	9.1
Au	25.2	19.1
Rb	26.7	23.6
Fe	24.8	8.1
Na	27.6	20.4
NaCl	24.6	14.0
Diamond	5.0	0.1
Glass	15.0	4.0

Not bad for RT (for many solids)

Heat Capacity

How well does the Einstein expression describe the data?



The Einstein model gives good agreement with experimental data for high T but not for very low T.

Do atoms on a lattice really behave as independent oscillators?

Bonded together $\Rightarrow$ vibrations of an atom affects its neighbours.

How can this be included? Dealing with waves not just oscillations.

Heat Capacity

- Debye model:

Now, include strong interactions between atoms.

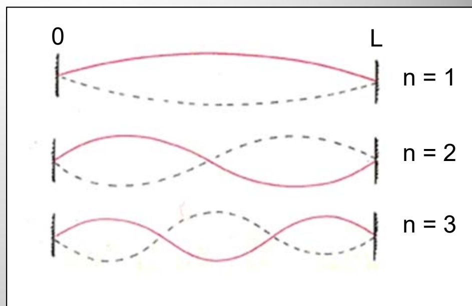
Consider a cubic solid of dimension, L ($V = L^3$)

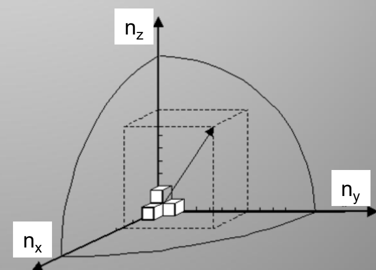
Need number of states below some maximum value of *n*, n_{max}.

$$N = \frac{1}{8}\left(\frac{4}{3}\pi n_{\max}^3\right) = \frac{kV}{6\pi^2}$$

$$N \rightarrow \frac{\omega^3 V}{6\pi^2 v} \quad \text{in limit of small } k$$

(model: monatomic, so ∃ only acoustic modes)





Heat Capacity

- Debye model:

Combine Einstein's result for <E> of quantum oscillators with concept of density of states, *g(ω)*, to get (with introduction of factor of three to allow for longitudinal & transverse modes of oscillation):

$$U = 3\int_0^{\omega_{\max}} \frac{g(\omega)\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega$$

Compute heat capacity from this

$$C = \frac{\partial U}{\partial T}$$

Heat Capacity

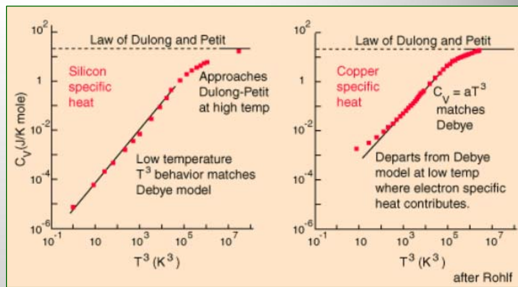
- Debye model:

Now, include strong interactions between atoms.

At low T Debye gives

$$C = \frac{12R\pi}{5}\left(\frac{T}{\theta_D}\right)^3$$

$$\text{where } \theta_D \equiv \frac{\hbar\omega_{\max}}{k_B} = \text{ the Debye temperature}$$



- But, for conductors, it's not quite right at really low T (several K)! Need electronic contribution:

A relatively simple model gives

$$C = C_{electronic} + C_{vibrational}$$

$$C_{metal} = \underbrace{\frac{\pi^2 N_A k^2}{2E_F} T}_{\text{Electronic specific heat proportional to temperature } T} + \underbrace{\frac{12\pi^4 N_A k}{5T_D^3} T^3}_{\text{Vibrational specific heat proportional to cube of temperature } T}$$