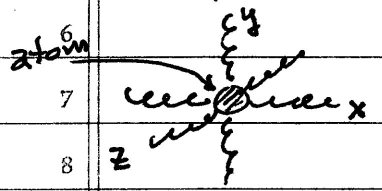
Phonons - Application to Bose-Einstein Statistics

Specific Heat - from Stat. Mechanics & Thermodynamics

$$\text{Heat Capacity} \equiv C \equiv \frac{dU}{dT} \qquad \frac{\text{increase in thermal energy}}{\text{change in temperature}} \quad \left[\frac{J/mol}{K}\right]$$

Find an expression for U ⇒ model the solid as a collection of atoms vibrating independently on springs with equal force constants in the x, y, and z direction.



The internal energy of each atom → classical equipartition theorem.

In one dimension → 2 degrees of freedom ① KE ② PE

$$\text{Internal energy of each atom} \rightarrow \overset{\text{oscillators/atom}}{3} \times \overset{\text{degrees of freedom}}{2} \left(\frac{k_B T}{2}\right)$$

For one mole, we have:

$$U = {}^{3}\,\underline{N_A 2k_B T} = \underline{N_A k_B T} = 3RT$$

where $R = 8.31 \dfrac{J}{mol \cdot K}$

$$C = \frac{dU}{dT} = 3R \approx 25 \frac{J}{mol \cdot K}$$

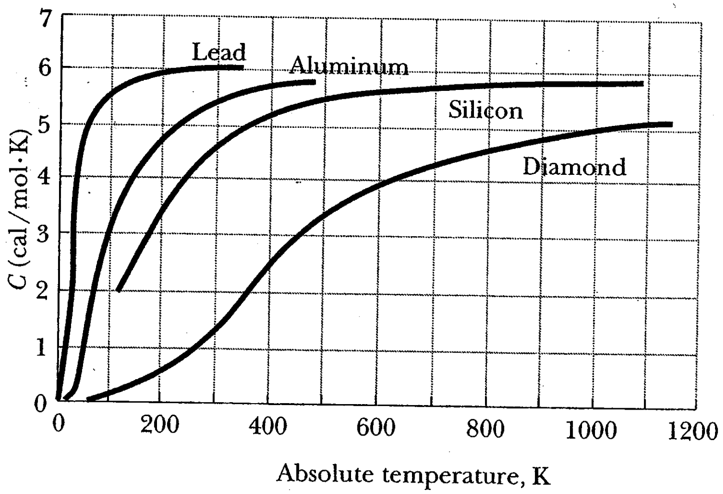


Figure 9.9 The dependence of specific heat on temperature for several solid elements.

Phonons – Heat Capacity

The Heat Capacity approaches 3R at high temperatures.
What about lower temperatures?

Einstein (1907) – Assumed that sound, or lattice waves, in the solid had quantized energies and could be considered as particles → phonons.

⇒ Assumed that each one-dimensional atomic oscillator in the solid has the same frequency, ω, and

⇒ Assumed that each atomic oscillator can be modeled as a quantum-mechanical harmonic oscillator with energy levels $\hbar\omega(n + 1/2)$

⇒ We find that varying number of phonons of energy $\hbar\omega$ are constantly emitted and absorbed by the quantum oscillators.

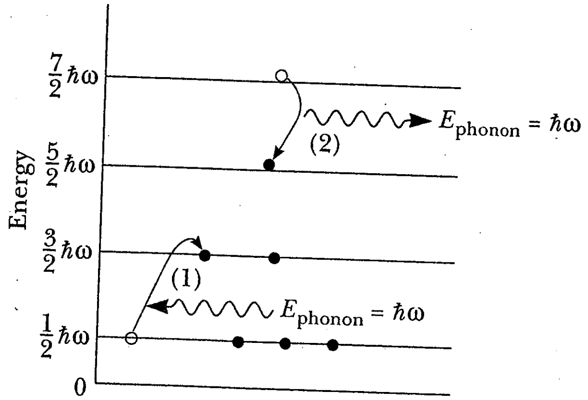


Figure 9.10 Quantum oscillator energy levels. Dots indicate the number of oscillators occupying each level. Process (1) is an upward transition produced by the absorption of a phonon with energy $\hbar\omega$. Process (2) is a downward transition accompanied by the emission of a phonon with energy $\hbar\omega$.

① Assume oscillator transitions are only allowed between adjacent states (levels)
② All phonons have the same energy, $\hbar\omega$,
③ Phonons are bosons and the number of phonons is not fixed;
Their # increases with temperature T.

Phonons – Heat Capacity

$U \Rightarrow$ the internal energy per mole of solid is primarily the energy carried by the phonons. The contribution due to "free" electrons → small.

Let $f_{\text{phonon}}(\hbar\omega) = \dfrac{1}{e^{\hbar\omega/kT}-1}$ ⇐ The probability that a phonon with quantized energy $(\hbar\omega)$ exists in a solid at temperature T.

The energy of 1 mole of solid can be expressed by:

$$U = \overset{\substack{\text{Bose-Einstein}\\ \text{probability}}}{f_{\text{phonon}}}\;\underset{\text{energy/phonon}}{(\hbar\omega)}\;(\underbrace{g}_{\text{statistical wt. for 1 mole of solid.}} = \overset{\text{\# of dimensions = 3}}{3}N_A)$$

$$U = 3N_A \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$$

Heat Capacity

$$\boxed{C \equiv \frac{dU}{dT} = 3R\left(\frac{\hbar\omega}{kT}\right)^2 \frac{e^{\hbar\omega/kT}}{\left(e^{\hbar\omega/kT}-1\right)^2}}$$

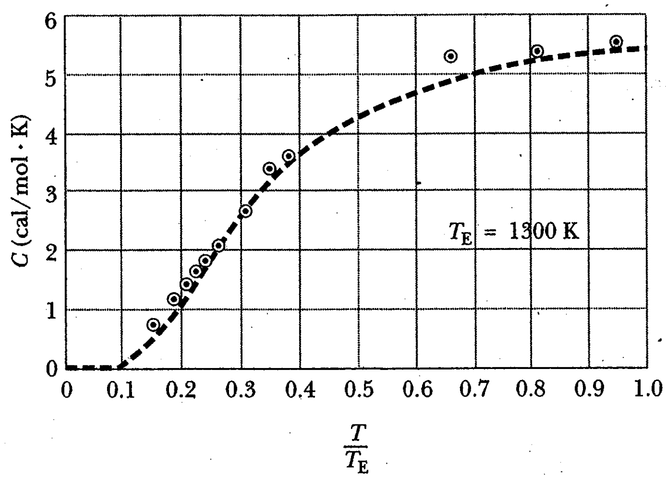


Figure 9.11 Einstein's specific heat formula fitted to Weber's experimental data for diamond. This figure is adapted from A. Einstein, *Ann. Physik.* 4(22):180, 1907.

Observations:

① $C(T) \to 0$ as $T \to 0$

② $C(T) \to 3R$ for large T

③ $C(T) \to T^3$ as $T \to 0$ } Not from the above expression for C(T). Peter Debye took into account the collective motion of neighboring atoms as well as transverse & longitudinal vibrations.