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# EINSTEIN THEORY OF SPECIFIC HEAT

## SOLVED PROBLEMS

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# EINSTEIN'S THEORY OF SPECIFIC HEAT

- Einstein explained the specific heat of solid with the concept of quantum mechanics.
- A solid contains N number of atoms.
- N atoms represents 3N 1-D quantum HARMONIC OSCILLATORS .
- These oscillators have discrete energy values.
- The atoms vibrate independently of each other.
- But the atoms have the same angular frequency of vibration.
- The oscillators are distinguishable Located at different lattice points.
- Although the atoms are QUANTUM OSCILLATORS, their energy distribution is given by the MAXWELL-BOLTZMANN statistics.

# EXPRESSION OF ENERGY OF ATOMS ACCORDING TO QUANTUM MECHANICS

Planck ( $E_n = n\hbar\omega \quad n = 0, 1, 2, \ldots$tors (atoms) in a solid have quantized energies

$$E_n = n\hbar\omega \qquad n = 0, 1, 2, \ldots$$

[later QM showed $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$ s actually correct]

Einstein (1907): model a solid as a collection of 3N independent 1-D oscillators, all with constant ω, and use Planck's equation for energy levels

https://youtu.be/St2rEAnUYAg

# THE EXPRESSION OF AVERAGE ENERGY OF AN OSCILLATOR ACCORDING TO EINSTEIN

According to Einstein, the probability f(v) that an oscillator have the frequency v is given by, $f(v) = 1/(e^{hv/kT} - 1)$. Hence the average energy for an oscillator whose frequency of vibration is v is

Average energy per oscillator $$\overline{E} = h\nu f(\nu) = \frac{h\nu}{e^{h\nu/k_BT} - 1}$$

and not $\bar{E} = kT$.

# THEORY OF EINSTEIN THEORY OF SPECIFIC HEAT

The quantised energies of the oscillators are

$$\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu \simeq nh\nu, \quad n = 0, 1, 2, \cdots \tag{5.6.1}$$

neglecting $\frac{1}{2}h\nu$, the temperature-independent '*zero point energy*' whose inclusion in the energy does not affect the specific heat.

The number of oscillators $N_n$ of each energy state is determined from the Boltzmann function as

$$N_n = N_0 e^{-\varepsilon_n/kT} = N_0 e^{-nh\nu/kT}, \tag{5.6.2}$$

$N_0$ being the number of oscillators in the zero energy state.

And, the average vibrational energy of an oscillator is given by

$$\bar{\varepsilon} = \frac{\varepsilon}{N} = \frac{\sum_n N_n \varepsilon_n}{\sum_n N_n} = \frac{h\nu}{e^{h\nu/kT} - 1} \tag{5.6.3}$$

For one mole of solids, the total energy of the crystal is, taking into account three independent directions,

$$E_{\text{mol}} = 3N_A \bar{\varepsilon} = \frac{3N_A h\nu}{e^{h\nu/kT} - 1}, \quad N = N_A = \text{Avogadro number}.$$

$$\therefore \text{ Molar specific heat, } C_V = \left(\frac{dE}{dT}\right)_V = 3N_A k \left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} \tag{5.6.4}$$

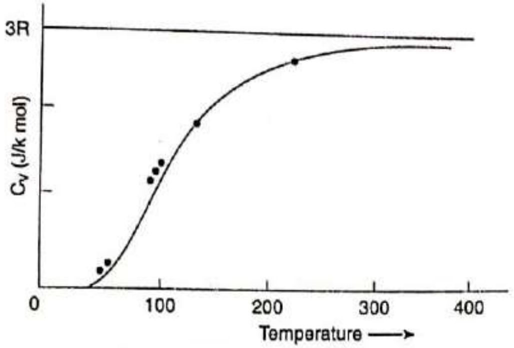


**Fig. 5.9** Einstein specific heat curve

The Einstein specific heat curve is fairly close to the experimental curve except at very low temperatures (Fig. 5.9). In the low temperature range, the Einstein's specific heat approaches zero more rapidly then the observed values. But, at high temperatures, it approaches the classical value. We shall now consider the following *two* limiting cases: (i) ***high temperature range*** and (ii) ***low temperature range*** separately. Before we do so, we give an alternative form to (5.6.4).

Let $\Theta_E = h\nu/k$ where $\Theta_E$, having the unit of temperature, is the ***characteristic temperature*** known as the ***Einstein temperature***. Introducing $\Theta_E$ we get from (5.5.4)

$$C_V = 3N_A k \left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2} \qquad (5.6.5)$$

**(i) For high temperatues:** For temperatures such that $kT \gg h\nu$ or $T \gg \Theta_E$,

$$e^{h\nu/kT} - 1 = 1 + h\nu/kT + \cdots - 1 = h\nu/kT$$

$\therefore$ From (5.6.3)

$$\bar{\varepsilon} = \frac{h\nu}{h\nu/kT} = kT$$

$$\therefore \; E = 3N_A kT = 3RT$$

$$\therefore \; C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R, \qquad (5.6.6)$$

the same as the classical result—the familiar ***Dulong-Petit's law***.

**(ii) For low temperatures:** For temperatures such that $h\nu \gg kT$ or $\Theta_E \gg T$, we have $e^{h\nu/kT} \gg 1$. Thus,

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT}}$$

$$\therefore \; E_{\text{mol}} = 3N_A\bar{\varepsilon} = 3N_A h\nu e^{-h\nu/kT}$$

$$\text{and} \quad C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N_A h\nu \left[e^{-h\nu/kT} \cdot \frac{h\nu}{kT^2}\right]$$

$$= 3N_A k \left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT} \qquad (5.6.7)$$

$$= 3N_A k \left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}, \text{ in terms of } \Theta_E. \qquad (5.6.8)$$

Thus, for $T \ll \Theta_E$, the heat capacity is proportional to $e^{-\Theta_E/T}$ which is more important than the term $(\Theta_E/T)$. Thus, with decreasing temperature in the low temperature range, $C_V$ falls off almost exponentially. However, experiments show, $C_V \propto T^3$ for most of the solids, i.e., much more slowly.

While the Einstein's model provides a much better explanation for the temperature variation of specific heat than the classical theory, it cannot account for, as already stated, the values of specific heat at very low temperatures. The discrepancy is due to the oversimplified assumption that the atomic oscillators vibrate *independently* at the *same frequency*. In fact, the oscillators are coupled together and a number vibrational frequencies, rather than a single one, is possible. This is accounted for in Debye's model which we shall now describe and discuss.

**https://youtu.be/bmrt6T-R62s**

**https://youtu.be/HYgSSLSMPeM**

# COMPARISON STUDY BETWEEN DULONG PETIT LAW AND EINSTEIN'S SPECIFIC HEAT OF SOLIDS

| Dulong-Petit model (1819) | Einstein model (1907) |
|---|---|
| • Atoms on lattice vibrate independently of each other | • Atoms on lattice vibrate independently of each other |
| • Completely classical | • Quantum mechanical (vibrations are quantised) |
| • Heat capacity independent of temperature ($3Nk_B$) | • Agreement with experiment good at very high ($\sim 3Nk_B$) and very low ($\sim 0$) temperatures, but not inbetween |
| • Poor agreement with experiment, except at high temperatures | |

# SOLVED PROBLEM

3. If the Einstein temperature for a material is 157 K, find the value of $C_v$, for that material at 100 K in caloric per mole per K using Einstein's formula. Also, calculate Einstein's frequency.

**Ans.** Einstein's formula is

$$C_v = 3R \frac{x^2 e^x}{(e^x - 1)^2}$$

where $x = \Theta_E / T$. Here $\Theta_E = 157$ K and $T = 100$K. Therefore, $x = 157/100 = 1.57$. Since $R = 1.99$ cal. per mole per K, we have

$$C_v = \frac{3 \times 1.99 \times (1.57)^2 e^{1.57}}{(e^{1.57} - 1)^2} = 4.88 \text{ cal. mol}^{-1}.\text{K}^{-1}$$

Einstein's frequency is

$$\nu = \frac{k_B \Theta_E}{h} = \frac{1.38 \times 10^{-23} \times 157}{6.6 \times 10^{-34}} = 3.28 \times 10^{12} \text{ Hz}$$

▶ **Example 6.** *Calculate the Einstein's frequency for $C_V$ for which the Einstein's temperature is 230 K.*

**Solution:** Einstein's temperature $\Theta_E$ is given by

$$\Theta_E = \frac{h\nu}{k} \Rightarrow \nu = \frac{k}{h}\Theta_E = \frac{1.38 \times 10^{-23}}{6.6 \times 10^{-34}} \times 230$$

$$= 4.81 \times 10^{12} \text{ Hz}$$