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The specific heat of solid

According to the first law of thermodynamics, the amount of heat added to the system (dQ) must be equal to the increase in energy dE of the system plus the amount of work done by the system.

$$dQ = dE + p dv.$$

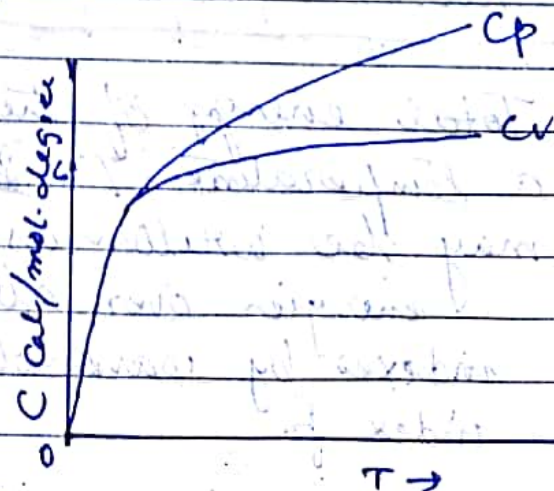
$$dE = \left(\frac{\partial E}{\partial T} \right)_v dT + \left(\frac{\partial E}{\partial v} \right)_T dv.$$

$$dQ = \left(\frac{\partial E}{\partial T} \right)_v dT + \left\{ \left(\frac{\partial E}{\partial v} \right)_T + p \right\} dv.$$

Specific heat in general defined as $\frac{dQ}{dT}$.

Unless one specifies in which way the increase in temperature takes place, the specific heat is undetermined.

By heat capacity we shall usually mean the heat capacity at constant volume, which is more fundamental than heat capacity at constant pressure.



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contribution to the specific heat of solids.

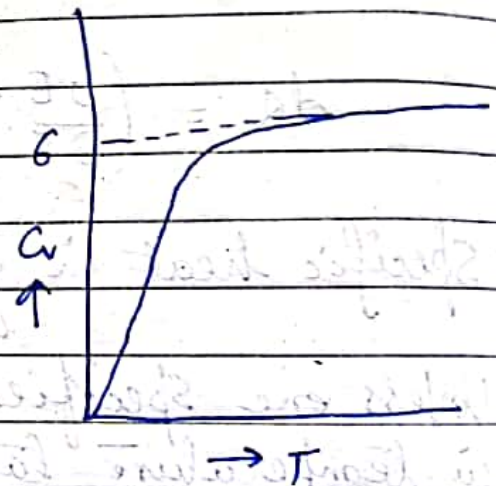
Atomic vibration of the crystal, i.e. the phonon contribution, called lattice heat capacity.

Electronic contribution.

Electronic contribution is small relative to phonon contribution.

$$C_V = AT + BT^3$$

As the temperature is raised from absolute zero, the C_V increases rapidly from zero and finally levels off to a nearly constant value - 6 cal/mol-degree. This is known as Dulong and Petit law.



$$E = 3Nk_B T \Rightarrow C_V = 3Nk_B = 3R = 5.96 \text{ cal/mol-degree}$$

Theory of specific heat

Total energy of the phonons at a temperature T in a crystal may be written as the sum of the energies over all phonon modes, indexed by wavevector k , and polarization index p .

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$$U = \sum_K \sum_P U_{K,P} = \sum_K \sum_P \langle n_{K,P} \rangle \hbar \omega_{K,P}$$

$\langle n_{K,P} \rangle$ is the thermal equilibrium occupancy of phonon of wavevector K and polarization P .

$$\langle n \rangle = \frac{1}{e^{\hbar \omega / k_B T} - 1} \quad (\text{Planck distribution})$$

Einstein's theory of the specific heat

Solid containing N -atoms, could be represented by $3N$ harmonic oscillator of the same frequency ω ($2\pi\nu$). This model implies that atoms vibrate independently of each other.

Average energy of an oscillator was estimated using Planck's theory derived in the context of black body radiation.

The energy of an oscillator

$$E_n = n \hbar \omega \quad n=0, 1, 2, \dots, \infty$$

$$\langle E \rangle = \frac{\sum_{n=0}^{\infty} n \hbar \omega e^{-n \hbar \omega / k_B T}}{\sum_{n=0}^{\infty} e^{-n \hbar \omega / k_B T}}$$

$$S = \sum_{n=0}^{\infty} e^{-n \hbar \omega / k_B T} = \left(1 - e^{-\hbar \omega / k_B T} \right)^{-1}$$

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$$\frac{\partial S}{\partial \left(\frac{1}{k_B T}\right)} = - \sum_{n=0}^{\infty} n \hbar \omega e^{-n \hbar \omega / k_B T}$$

$$= - \frac{\hbar \omega e^{-\hbar \omega / k_B T}}{\left(1 - e^{-\hbar \omega / k_B T}\right)^2}$$

$$\langle E \rangle = \frac{+\hbar \omega e^{-\hbar \omega / k_B T}}{\left(1 - e^{-\hbar \omega / k_B T}\right)^2} \times \left(1 - e^{-\hbar \omega / k_B T}\right)$$

$$= + \frac{\hbar \omega e^{-\hbar \omega / k_B T}}{1 - e^{-\hbar \omega / k_B T}}$$

$$= \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$

$$E = 3N \langle E \rangle = 3N \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$

$$C_V = \frac{\partial E}{\partial T} = 3R \cdot \left(\frac{\hbar \omega}{k_B T}\right)^2 \cdot \frac{e^{\hbar \omega / k_B T}}{\left(e^{\hbar \omega / k_B T} - 1\right)^2}$$

$$\textcircled{D} \quad E_n = \left(n + \frac{1}{2}\right) \hbar \omega$$

$$\langle E \rangle = \frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}$$

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In general total energy can be written as.

$$E = \sum_k \sum_p \frac{\hbar \omega_{k,p}}{e^{\hbar \omega_{k,p}/k_B T} - 1}$$

It is usually convenient to replace the sum over k by an integral.

Suppose that the crystal has $D_p(\omega) d\omega$ modes of a given polarization p in the frequency range ω and $\omega + d\omega$.

$$E = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1}$$

$$C_{lattice} = k_B \sum_p \int d\omega D_p(\omega) \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{-\hbar \omega/k_B T}}{e^{\hbar \omega/k_B T} - 1}$$

Central problem is to find $D(\omega)$, the number of modes per unit frequency range.

In Einstein theory total mode was taken as $3N$.

$$\sum_p \int d\omega D_p(\omega) \equiv 3N$$

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For $kT \gg h\omega$. High temp limit:-

$$E = 3N \frac{h\omega}{e^{\frac{h\omega}{kT}} - 1}$$

$$= 3N k_B T \frac{\frac{h\omega}{k_B T}}{e^{\frac{h\omega}{kT}} - 1} = x \ll 1$$

$$= 3N k_B T \frac{x}{1+x-x}$$

$$= 3N k_B T$$

$C_V = 3N k_B = 3R \Rightarrow$ Reduces to classical result.

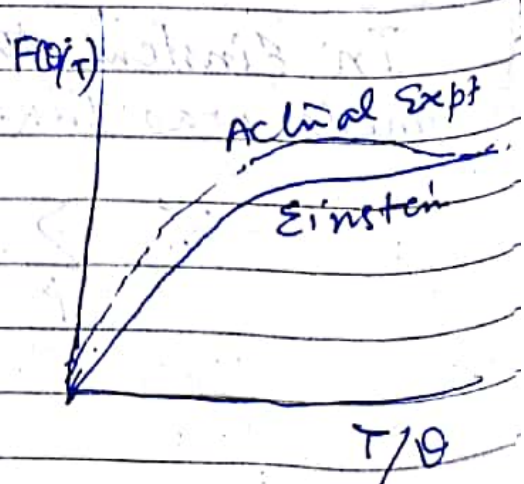
At low temperature

$$\frac{h\omega}{k_B T} = \frac{\theta_E}{T} \quad \theta_E = \frac{h\omega}{k_B T}$$

θ_E is known as Einstein temp.

$$\frac{C_V}{3R} = \left(\frac{\theta_E}{T}\right)^2 \frac{e^{-\theta_E/T}}{(e^{\theta_E/T} - 1)^2} = F_E\left(\frac{\theta_E}{T}\right)$$

Einstein curve deviates from the experimentally observed ones in the region of low temperatures.



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The vibrational modes of a continuous medium & Debye Theory

The discrepancy between Einstein's theory and experimental observation at low temperature was a consequence of oversimplified model. In 1912, Debye tackled the problem from different point of view.

Basic assumption: It is possible to propagate waves through solids covering a wavelength region extending from low frequencies (sound waves) up to short waves (infrared).

In the Debye approximation the velocity of sound is taken as constant for each polarization type, as it would be for a classical continuum. The dispersion relation $\omega = vK$.

Therefore the essential difference between the Debye model and the Einstein model is that Debye considered the vibrational modes of a crystal as a whole whereas Einstein's starting point was to consider the vibration of a single atom, assuming the atomic vibrations to be independent of each other.

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Let us consider for simplicity the vibrational modes of a one dimensional continuous string of length L .

$$\frac{\partial^2 u}{\partial x^2} = \frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2}$$

$$u(x,t) = A \sin \frac{n\pi x}{L} \cos \omega_n t$$

Where n is +ve integer ≥ 1 .

$$k = \frac{n\pi}{L} = \frac{L\pi}{\lambda_n}$$

$$\lambda_n = \frac{2L}{n} \quad \nu_n = \frac{c_s}{\lambda_n} = \frac{c_s n}{2L}$$

The frequency spectrum is discrete, one frequency corresponding to each integer n

$$n = \frac{2L \nu_n}{c_s}$$

No. of possible mode in the frequency range $d\nu$.

$$dn = \frac{2L}{c_s} d\nu$$

In three dimension. $\nabla^2 u = \frac{1}{c_s^2} \frac{\partial^2 u}{\partial t^2}$

$$u(x,y,z) = A \sin \left(\frac{n_x x \pi}{L} \right) \sin \left(\frac{n_y y \pi}{L} \right) \sin \left(\frac{n_z z \pi}{L} \right) \cos 2\pi \nu t$$

Substituting the solution in the differential eqn we get.

$$\left(\frac{\pi^2}{L^2} \right) (n_x^2 + n_y^2 + n_z^2) = \frac{4\pi^2 \nu^2}{c_s^2} = \frac{4\pi^2}{\lambda^2}$$

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The number of possible modes of vibrations $Z(\nu) d\nu$ in the frequency range ν and $\nu + d\nu$ can be obtained.

by counting three positive integers n_x, n_y, n_z within a sphere ~~of~~ of radius of R and $R + dR$.

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \frac{4L^2\nu^2}{c_s^2}$$

No. of points in a shell between R and $R + dR$.

$$\frac{1}{8} \left\{ \frac{4}{3} \pi (R + dR)^3 - \frac{4}{3} \pi R^3 \right\}$$

$$= \frac{4}{3} \pi (R^3 + 3R^2 dR + 3R(dR)^2)$$

$$- \frac{4}{3} \pi R^3$$

$$= \frac{1}{8} 4\pi R^2 dR = \frac{\pi}{2} R^2 dR$$

$$= \frac{\pi}{2} \times \frac{4L^2\nu^2}{c_s^2} \cdot \frac{2L d\nu}{c_s} = \frac{4\pi L^3}{c_s^3} \nu^2 d\nu$$

$$Z(\nu) d\nu = \frac{4\pi L^3 \nu^2 d\nu}{c_s^3}$$

$$dR = \frac{4L^2 \nu}{c_s^2} \cdot \frac{2L d\nu}{2L\nu} = \frac{2L d\nu}{c_s}$$

$$= \frac{2L d\nu}{c_s}$$

$$Z(\nu) d\nu = \frac{4\pi V}{c_s^3} \nu^2 d\nu$$

Consider two transverse modes and one longitudinal mode.

$$Z(\nu) d\nu = 4\pi V \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \nu^2 d\nu$$

Crystal consisting of N atoms is limited by total number of vibrational modes to 3N.

Therefore, frequency spectrum corresponding to a perfect continuum is cut off so as to comply with total of 3N modes.

Therefore, Debye cut off procedure leads to a maximum frequency ν_D .

$$\int_0^{\nu_D} Z(\nu) d\nu = 4\pi V \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N$$

$$\nu_D^3 = \frac{3N}{4\pi V} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right)^{-1}$$

In an actual crystal $\frac{N}{V} \sim 10^{23} / \text{cm}^3$

Velocity of sound 10^5 cm/sec .

this gives $\nu_D \sim 10^{13}$ per sec

$$\lambda_{\text{min}} \equiv \sim 1 \text{ \AA}$$

radiating continuum theory may be at fault, especially at high frequency region.

$$E = \int_0^{\nu_D} Z(\nu) \frac{h\nu^3}{e^{K_B T} - 1} d\nu$$

$$= g_N \cdot \nu_D^3 = \frac{g_N}{4\pi V} \left(\frac{2}{c^3} + \frac{1}{c^3} \right)$$

$$= \left(\frac{2}{c^3} + \frac{1}{c^3} \right) = \frac{g_N}{4\pi V \nu_D^3}$$

$$\int_0^{\nu_D} Z(\nu) d\nu = 4\pi V \cdot \frac{g_N}{4\pi V \nu_D^3} \int_0^{\nu_D} \nu^2 d\nu$$

$$= \frac{g_N}{\nu_D^3} \int_0^{\nu_D} \nu^2 d\nu$$

$$E = \int_0^{\nu_D} \frac{g_N}{\nu_D^3} \cdot \frac{h\nu^3 d\nu}{e^{h\nu/K_B T} - 1}$$

$$= g_N \left(\frac{K_B T}{h\nu_D} \right)^3 \cdot \frac{h\nu_D^3 \cdot h^3}{(K_B T)^3} \int_0^{\nu_D} \frac{\nu^3 d\nu}{e^{h\nu/K_B T} - 1}$$

$$\text{Let } x = \frac{h\nu}{K_B T} \quad x_m = \frac{h\nu_D}{K_B T}$$

$$E = g_N \cdot \left(\frac{K_B T}{h\nu_D} \right)^3 \int_0^{x_m} \frac{x^3 dx}{(e^x - 1)}$$

introduce

$$\theta_D = \frac{h\nu_D}{K_B} \quad x_m = \frac{\theta_D}{T}$$

For $T \gg \theta_D$. $C_V = 3N K_B$.

For $T \ll \theta_D$. at low temperature

$$\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$E = \frac{3}{5} \pi^4 N K_B T \left(\frac{T}{\theta_D} \right)^3 \text{ for } T \leq \theta_D$$

$E \propto T^4$ at low temperatures

$$C_V = \frac{12}{5} \pi^4 N K_B \left(\frac{T}{\theta_D} \right)^3$$

This is famous Debye T^3 law.

In general

$$C_V = 3R \cdot 3 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{e^{-x^4}}{(e^x - 1)^2} dx$$

$$= 3R F_D \left(\frac{\theta_D}{T} \right)$$

F_D is the Debye function.

