Lattice Specific Heat: A New Generalized Approach

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Abstract: - Peter Debye developed method for estimating the phonon contribution to the specific heat (heat capacity) in a solid, known as the Debye model in thermodynamics and solid-state physics. This model correctly explains the low temperature dependence of the heat capacity, which is proportional to T^3. It also recovers the Dulong-Petit law at high temperatures. But due to simplifying assumptions, its accuracy suffers at intermediate temperatures. He assumed that $v = \omega/k$ as a general case, but in fact it is not, since v is constant of ω and k only for small k values but he used this assumption for the whole volume of K space Brillouin zone. In this paper we make a generalized approach by choosing the real values of v which are not a constant of ω and k to generalize Debye model. The phonon vibrational energy and heat capacity results of this approach are the same as those presented in the ordinary Debye model for low and high temperatures and give proper results for other temperature values.

Key-Words: - Debye model, Thermal properties, Statistical method, Brillouin zone, Γ function, Heat capacity.

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1 Introduction

Valuable information about the various energetic contributions of a material are provided from heat capacity measurements. Many theories are presented to express these contributions by simple models depending on the mean energy of the system through statistical methods and then transforming the mean energy into a heat capacity functions. Fitting these theoretical heat capacity functions with heat capacity data are very useful to extract valuable information about many energetic contribution inside the system. Vibrational, electronic, magnetic, superconducting, and lattice vacancies are the mean contributions to the heat capacity of the crystal of the solid [1–5]. The vibrational contribution dominates the heat capacity at all but low temperatures (below about 10 or 15 K) where the other contributions become observable. These contributions can be determined by fitting the low-temperature heat capacity data to different combinations of these theoretical functions and selecting the best fit but determining the fit that most correctly models the data and underlying energy contributions is not trivial [6]. In this work, the authors are seeking to we introduce a generalized approach by choosing the real values of v which are not a constant of ω and k to generalize Debye model.

2 The Debye Model

The thermal properties, in the Debye model, are determined by the solid lattice vibrations. The vibrational frequencies form a continuous spectrum with a cutoff at an upper limit ω_D such that the total number of normal modes of vibration is $3N$ of which N are the number of the solid atoms which can harmonically displaced from lattices. Debye Main Postulates are [1–5]:

a- A solid of N atoms would have 3N vibration modes.

b-The angular frequency ω of mode must depend on it is wave vector K.

c-There must be same maximum angular frequency ω_m , such that 3N which is the total number of distinguishable modes.

$$3N = \int_0^{\omega_m} g(\omega).d\omega \qquad (1)$$

d-ω_m should be the upper limit for the integral describing the total vibrational energy

$$U = \int_0^{\omega_D} \frac{\hbar\omega.g(\omega)}{\exp(\frac{\hbar\omega}{KT})-1} d\omega \qquad (2)$$

e- It should be possible to obtain useful results by expressing $g(\omega)$ as though the phase velocity $v = \omega/k$; v_o is a suitably chosen speed of sound for all modes of vibration.

f-It is convenient to express the operation of Debye model in terms of the parameter $\theta_D = \hbar\omega_D/k_B$ with dimension of temperature, rather than in terms of the limiting frequency $\omega_D = k_B\theta_D/\hbar$ or a maximum radius $k_D = \omega_D/r_o$ in reciprocal space. Since a sphere of radius k_D occupies the same volume of K-space as a true Brillouin zone. Thus, a phonon with a wave vector comparable with k_D(frequency compare with ω_D, energy compare with $k_B\theta_D$) is a phonon near boundaries.

$$g(\omega) = \frac{\omega^2}{2\pi^2}\left[\frac{1}{v_L^3} + \frac{2}{v_T^3}\right] \qquad (3)$$

Where v_L, v_T represents the speeds of transmission of longitudinal and transverse waves but since they are different, then Debye approximation consists as:

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_o^3} \quad \text{where } 0 < \omega < \omega_D \qquad (4)$$

3 Material and method

3.1 Notes on Debye Postulates

Debye assumed that $v = \omega/k$ as a general case, but in fact it is not, since v is constant of ω and k only for small k values but he used this assumption for the whole volume of K space Brillouin zone.

3.2 Result and Discussion

For small k values:

$$sin\left(\frac{ka}{z}\right) = \left(\frac{ka}{z}\right);\ sin^3\left(\frac{ka}{z}\right) = \left(\frac{ka}{z}\right)^3$$

$$U = \frac{3\hbar}{2\pi^2 v_o^3}\int_0^{\omega_{max}} \frac{\omega^3(\frac{ka}{z})^3}{(\frac{ka}{z})^3[\exp(\frac{\hbar\omega}{k_B T})-1]} d\omega \qquad (5)$$

$$v_\circ = \omega_D^3 V/6H^2 N_A$$

$$U = \frac{9N_A}{\omega_D^3}\int_0^{\omega_{max}} \frac{\hbar\omega^3}{\exp(\frac{\hbar\omega}{k_B T})-1} d\omega \qquad (6)$$

Which is the result Debye had obtained. At low temperature:

$$U = \frac{9N_A}{\omega_D^3}\int_0^{\omega_{max}} \frac{\hbar\omega^3}{\exp(\frac{\hbar\omega}{k_B T})-1} d\omega \qquad (7)$$

The heat capacity is:

$$C_v = \left(\frac{dU}{dT}\right)_v$$

$$= \frac{9N_A}{\omega_D^3}\int_0^{\omega_{max}} \frac{\hbar\omega^3(-1)e^{\frac{\hbar\omega}{k_B T}}(-1)\frac{\hbar\omega}{k_B T^2}}{\left(e^{\frac{\hbar\omega}{k_B T}}\right)^2} d\omega$$

$$= \frac{9N_A k_B}{\omega_D^3}\left(\frac{\hbar}{k_B T}\right)\int_0^{\omega_{max}} \omega^4 e^{-\frac{\hbar\omega}{k_B T}} d\omega \qquad (8)$$

Using Γ function

Let $y = \hbar\omega/kT$, $dy = \left(\frac{\hbar}{kT}\right)d\omega$ and use them in the last equation

$$C_v = \frac{9R}{\omega_D^3}\left(\frac{kT}{\hbar}\right)^3 \Gamma(5) = \frac{9R}{\left(\frac{k\theta_D}{\hbar}\right)^3}\left(\frac{kT}{\hbar}\right)^3 \times 24$$

$$= 1796\left(\frac{T}{\hbar\theta_D}\right)^3 \qquad (9)$$

$$C_v \propto T^3$$

At high temperature, we use the expansion:

$$e^{\frac{\hbar\omega}{kT}} = 1 + \frac{\hbar\omega}{kT} + \frac{1}{2!}\frac{\hbar\omega}{kT} + \cdots \qquad (10)$$

$$U = \frac{9N_A}{\omega_D^3}\int_0^{\omega_{max}} \frac{\hbar\omega^3}{1 + \frac{\hbar\omega}{kT} + \cdots - 1} d\omega$$

$$= \frac{9N_A KT}{\omega_D^3}\int_0^{\omega_{max}} \omega^2 d\omega$$

$$= \frac{9N_A kT}{3} = 3RT \qquad (11)$$

$$C_v = \left(\frac{dU}{dT}\right)_v = 3R \qquad (12)$$

For k value near to Brillouin zone boundaries

$$U = \int_0^{\omega_{max}} \frac{3\hbar\omega^3 (\frac{ka}{z})^3}{2\pi^2 v_0^3 \sin^3(\frac{ka}{z})[\exp(\frac{\hbar\omega}{k_B t}) - 1]} d\omega \qquad (13)$$

At the Brillouin zone boundaries: $k = k_D, \omega = \omega_D$ and Brillouin zone volume= $(\frac{k_D}{2})^3 = (\frac{\pi}{2})^3$

$$U = \frac{3(\frac{\pi}{2})^3\hbar}{2\pi^2 v_0^3}\int_0^{\omega_D} \frac{\omega^3}{[\exp(\frac{\hbar\omega}{k_B t}) - 1]} d\omega \qquad (14)$$

$$\frac{3N_A}{V} = \frac{\omega_D^3}{2\pi^2 v_0^3}, V = (\frac{\pi}{2})^3$$

$$U = \frac{9N_A}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\,\omega^3}{[\exp(\frac{\hbar\omega}{k_B t}) - 1]} d\omega \qquad (15)$$

Since we are at Brillouin zone boundaries, we are dealing with high temperature.

Using $\exp(\frac{\hbar\omega}{k_B t})$ expansion we will get

$$U = \frac{9N_A k}{\omega_D^3}\int_0^{\omega_D} \omega^2 T d\omega = \frac{9}{3} R \frac{\omega_D^3}{\omega_D^3} = 3R \qquad (16)$$

Choosing mid points between $k = 0$ and k_{max};

$$\frac{ka}{z} = \frac{\pi}{6}, \frac{\pi}{4}, \frac{\pi}{3}, \ldots.$$

For $\frac{ka}{z} = \frac{\pi}{6}$:

$$(\frac{\pi}{6})^3 = \frac{1}{27}(\frac{\pi}{2})^3 = \frac{1}{27}V, \sin^3\left(\frac{\pi}{6}\right) = 0.125$$

$$\frac{(\frac{\pi}{6})^3}{\sin^3\left(\frac{\pi}{6}\right)} = 0.3V$$

$$\frac{(\frac{\pi}{4})^3}{\sin^3\left(\frac{\pi}{4}\right)} = 0.35V$$

$$\frac{(\frac{\pi}{3})^3}{\sin^3\left(\frac{\pi}{3}\right)} = 0.45V$$

Where $V = (\frac{\pi}{2})^3$

If we use any one of the above values

$$U = \frac{0.3\,V\,.3\hbar}{2\pi^2 v_0^3}\int_0^{\omega_D} \frac{\omega^3}{[\exp(\frac{\hbar\omega}{k_B t}) - 1]} d\omega \qquad (17)$$

$$U = \frac{2.7N_A}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\,\omega^3}{[\exp(\frac{\hbar\omega}{k_B t}) - 1]} d\omega \qquad (18)$$

$$C_v = \left(\frac{dU}{dT}\right)_v$$

$$= \frac{2.7N_A}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3(-1)e^{\frac{\hbar\omega}{k_B T}}(-1)\frac{\hbar\omega}{k_B T^2}}{\left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} d\omega \qquad (19)$$

Let $y = \frac{\hbar\omega}{k_B T}$, $dy = \frac{\hbar}{kT} d\omega$

$$C_v = \frac{2.7N_A k}{\omega_D^3}(\frac{\hbar}{kT})^2 \int_0^{\omega_D} \frac{e^{-y}\left(\frac{kT}{\hbar}\right)^5 y^4}{(e^y - 1)^2} dy$$

$$= \frac{2.7N_A k}{\left(\frac{k\theta_D}{\hbar}\right)^3}(\frac{kT}{\hbar})^3 \int_0^{\omega_D} \frac{y^4\, e^{-y}}{(e^y - 1)^2} dy \qquad (24)$$

$$C_v = 2.7R(\frac{T}{\theta_D})^3.\mathrm{const.} = \mathrm{const.}\,T^3 \qquad (20)$$

4 Conclusion

We have introduced a generalized approach by choosing the real values of v which are not a constant of ω and k to generalize Debye model. The phonon vibrational energy and heat capacity results of this approach are the same as those presented in the ordinary Debye model for low and high temperatures and give proper results for other temperature values.

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