

Acoustic Waves and Debye Temperature – A Study

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Abstract: *In this paper how the specific heat of a substance (Crystalline Solids/metal Alloys/crystals etc) varies with the temperature particularly at very Low Temperatures (close to 4 K) is analysed briefly using the Einstein’s and Debye Models apart from the Classical Theory of lattice specific heat and also how the ultrasonic velocity comes into the picture in the derivation / calculation of Debye Temperature as per his model.. The specific heat of a substance is the quantity of heat that is required to raise one gram molecule of the substance through one degree centigrade. Normally we determine the specific heat of a substance at Room Temperature (RT). The value of the specific heat either increases or more or less remains constant at higher Temperatures. But at very Low Temperatures (close to ~4K) the specific heat of a substance approaches close to Zero . According to the Classical Theory the lattice specific of a solid crystalline materials remains constant and is independent of temperature. Einstein’s Model shows that the sp.ht do vary with the temperature to which the solid is subjected and approaches ~ Zero exponentially. But this is not in agreement with the experimental observations which varies as T^3 as a function of temperatures may be ~ 4K.Finally Debye’s Model was successful (T^3) and all are discussed in this communication.*

PAC Nos. 61.82 F,62.40,63.20,43.35

1. Basic theory of Lattice Specific Heat

It is well known that in a crystalline solids the atoms are arranged in a periodic manner (say linear chain of molecules) connected by a mass less spring and the same is extended to three dimensional containing ‘N’ number of atoms. As the temperature of the system is varied that is heat energy is supplied to the substance and as the atoms are coupled together , they start vibrating and hence there is a frequency of vibration /elastic waves etc. In short it is the case of three dimensional harmonic oscillator. Normally in such conditions the velocities of the elastic waves are in the region $10^3 - 10^4$ m/sec which are very close to the velocity of sound waves in metallic crystalline solids (~4000 m/sec). It is known that the energy of electro-magnetic waves are quantized and the quantum of energy is called ‘photon’. Similarly the energy of lattice vibrations or elastic waves (Acoustic Waves)is also quantized and the quantum of this energy is known as ‘phonon’ and the energy is again by $\epsilon = h\nu$ and for ‘n’ number of atoms $\epsilon = n h\nu$.

2. Classical Theory

In continuation of the basic theory on lattice sp.ht of a substance , as the temperature of the substance is raised /changed there is an excitation of the waves (elastic waves) the average energy of each harmonic oscillator can be derived as

$$\epsilon_{av} = \left[\int \epsilon \exp[-\epsilon/k_B T] d\epsilon \right] / \left[\int \exp[-\epsilon/k_B T] d\epsilon \right] \dots\dots 1$$

and further in can be shown that

$$\epsilon_{av} = k_B T \dots\dots\dots 2$$

so the total energy of 3N one dimensional harmonic oscillator becomes

$$E = 3 N \epsilon_{av} = 3 N k_B T \dots\dots\dots 3$$

As the lattice sp.ht at constant volume

$$C_v = [\partial E/\partial T] \dots\dots\dots 4$$

If

ω is the angular frequency of the wave

β is the spring constant

c is the longitudinal stiffness

ρ is the mass per unit length of the line ‘a’ contains mass less spring and an atom of mass ‘m’ and v_s ($\sqrt{c/\rho}$) is the velocity of sound waves of the medium (material) (*Pl note that the velocity of sound waves in the substance plays a role*) then it can be shown that as per classical theory that the average energy

ϵ of each harmonic oscillator is given by

$\epsilon = k_B T$ and the total energy E of a crystal containing 3N harmonic Oscillator is given by (or can be shown to be)

$$E = 3N \epsilon = 3N k_B T \dots\dots\dots 5$$

and as the lattice sp.ht at constant volume C_v

$$C_v = [\partial E/\partial T] = 3N k_B = \sim 3R = 6 \text{ cal/mole-K} \dots\dots\dots 6$$

which is independent of temperature..

Thus according to classical theory the value of the lattice specific heat is 3 R (= 5.96 Cal/mole-K) and is constant for all the solids and also is independent of temperature (RT/HT LT). But the experimental observations for very LT (~ 4 k)the sp.ht approaches Zero value . The Classical Theory is not able to explain the reason behind it as it assumed that the energy of harmonic oscillators is *continuous*.

3. Einstein’s Model

Einstein tried to solve this problem and tried to give the reason for the variation of Sp.ht at various temperatures including very LT by using Quantum Mechanical Model where the energy of the elastic waves /harmonic oscillators varies in ‘discrete’ energy spectrum and are quantized.. Einstein proceeded with his theory assuming that the vibrations of the harmonic oscillators have only single/fixed frequency and obtained an expression for the variation of Sp.ht with temperature including RT ,HT and LT (~4K) temperatures .

Einstein using Planck's quantum theory and also wave mechanical model showed that the 'discrete' energy levels of harmonic oscillator as

$$E_n = [n+1/2]h\omega_o .$$

He further derived an expression for the average energy levels of the harmonic oscillator as

$$E = \sum_{n=0}^{\infty} E_n \exp[-E_n/k_B T] / \sum_{n=0}^{\infty} \exp[-E_n/k_B T] \dots 7$$

replacing the integration (continuum model) by Summation (Discrete)

After rigorous mathematical derivations the expression for the average energy becomes

$$E = h\omega_o / \exp[h\omega_o /k_B T] - 1 \dots \dots \dots 8$$

As $C_v = [\partial E/\partial T]_v$ hence $E = 3N E$

$$C_v = 3N k_B [\theta_E/T]^2 \exp \theta_E/T / \{[\exp \theta_E/T] - 1\}^2 \dots \dots \dots 9$$

Where θ_E is called as Einstein's Temperature and ($\theta_E = h\omega_o$)

He split the temperatures into two parts one $T \gg \theta_E$ and the other $T \ll \theta_E$.

For larger values of T , $[h\omega_o /k_B T] \rightarrow 0$ from which we get As $C_v = [\partial E/\partial T]_v$ hence $E = 3N E = 3N k_B T = \sim 3R T = 6 \text{ cal/mole-K}$ which is independent of temperature.

So, even/again according to Einstein's Model the Sp.ht is $3R$ at $T \gg \theta_E$ and does not vary much with HT falling in line with the Classical Theory.

at, $T \ll \theta_E$, $[k_B T] \ll [h\omega_o]$
 $C_v = [\partial E/\partial T]_v = 3N k_B [\theta_E/T]^2 \{ \exp -\theta_E/T \} \dots \dots 10$

Thus, at very LT ($T \ll \theta_E$) the Sp.ht of Solids/Crystals of course approaches close to Zero at very LT ($\sim 4K$) exponentially. But according to experimentalist/experimental observations the Sp.ht though approaches \sim Zero at very LT but it varies as T^3 with temperature and not Exponentially.

4. Debye Model

Einstein assumed a over simplified model (single/fixed frequency for the harmonic oscillators) but in actual case the atoms are bound together three dimensionally in a crystal and form a coupled oscillations not with a fixed frequency (of course discrete energy) but with a range of frequencies and Debye also invoked Stefan's Law of Black Body Radiation of T^4 the difference being photons obey Stefan's Law at all temperatures where as 'phonons' obey generally at Low temperatures which is shown at the later part of this section (3). According to Debye, the crystals on heating/cooling can propagate elastic waves of wave-lengths/frequencies ranging from low frequencies (velocity of sound waves in solids is $\sim 4000\text{m/sec}$ as given earlier) to high frequencies corresponding to IR absorption i.e., crystals can have a number of modes of vibrations. The density of modes $Z(\nu)$ is a number of vibrational modes per unit frequency range.

If the inter atomic distance is small compared to the wave length of elastic waves, the crystal can be assumed to be 'continuum' from the point of view of the wave and there is an upper limit to the frequency to the elastic wave which Debye called it as ν_D and $\theta_D = h \nu_D \dots$

Though the velocity of sound waves in a solid materials have both longitudinal and transverse waves for simplicity we will take the average and call it as v_s . with ν_D as upper limit in his continuum model he showed that

$$\nu_D^3 = 9N/4\pi V [3/v_s^3]^{-1} \dots \dots 11$$

In his derivations for the variation of sp.ht with temperatures he also split the temperatures into two parts

one at $T \gg \theta_D$ and the other $T \ll \theta_D$. where θ_D is called as Debye Temperature.

Debye's derivations :

$$\theta_D/T \quad E = 9N k_B T [T/\theta_D]^3 \int [x^3 dx / \exp^x - 1] \dots \dots \dots 12$$

i) **at high temperatures** $T \gg \theta_D$ $\exp^x - 1 \sim x$ and E reduces to

$$E = 3 N k_B T \text{ and as } C_v = [\partial E/\partial T]_v = 3 N k_B = 3R = 6\text{cal/mole-K}$$

Again even according to Debye's derivations the Sp.ht is $\sim 3R$ at $T \gg \theta_D$ and does not vary much with HT falling in line with the Classical Theory.

ii) **at Low temperatures** $T \ll \theta_D$

the derivation for E leads to

$$E = 9N k_B T [T/\theta_D]^3 [\pi^4/15] \dots \dots \dots 13$$

$$= [3/5][\pi^4] N k_B [T^4/\theta_D^3] \dots \dots \dots 14$$

$$C_v = [\partial E/\partial T]_v = [12/5] N \pi^4 N k_B [T^3/\theta_D] \dots \dots \dots 15$$

(Pl refer T^4 law mentioned earlier in the same section 3)
 Thus Debye successfully showed that the the sp.ht does not fall of 'exponentially' as per Einstein's Model but varies as T^3 agreeing with the experimentalists observations. Thus at low temperatures the Sp.ht is proportional to T^3 and generally holds good for $T < \theta_D/10$
 From Debye 's theory one can calculate the expression for Debye Temperature for Solids is as follows :

$$\theta_D = h \nu_D/k \text{ and } \nu_D^3 = [9N/4\pi V] \{ [1/v_l^3 + 2/v_t^3] \}^{-1} \dots 15$$

where the symbols are the usual physical constants.

And ν_l and ν_t can be replaced by v_s the mean sound velocity, thus paving the way for θ_D calculation. As there is a cap on the frequency limit it also means the velocity of elastic waves is also maximum depending on the material(s) and to some extent it can be said that the Debye

Temperature is the temperature at which the Acoustic Waves (Elastic waves) is maximum . Debye temperature is NOT the Melting Point or Boiling Point of a substance.

5. Summing up

To sum up , the variation of lattice sp.ht of solid crystals/metallic alloys etc with temperature particularly at very low temperature $\sim 4\text{K}$ has been explained starting from the Classical Theory, Einstein's Model and finally Debye Model who has shown successfully the sp.ht varies as T^3 agreeing very well with the experimentally observed values done by the experimentalists . Debye Temperature can be easily done in any Post –graduate labs with XRD facilities for their own grown crystalline solid materials/alloys or for standard samples like Copper, Aluminum, Iron etc . A brief Mathematical derivations of Debye Temperature including Einstein' s θ_E will be presented at the time of the Lecture and how the Acoustic Waves (Sound velocity) comes into picture for the calculation of θ_D has also been explained.

As an analysis , one can take it up as some sort of Desk Work is there any correlation (Not formula wise) between Debye Temperature and say velocity of sound waves, At.Wt , density , Stiffness constant, elasticity etc. On an rough analysis it has been found that Diamond has a very high Debye Temperature (2200K)and its Velocity of sound waves is abnormally high (12,200 m/sec) where as for most of the solids v is $\sim 4000\text{-}5000$ m/sec. For Ferro-magnetic materials like Fe, CO, and Ni the Debye temperatures are more or less 180 -200 K . Like that one can do some sort of analysis even as a project work at M.Sc level.

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