

Anharmonic Crystal Interactions:

The harmonic theory used in the lattice vibrations of solids assumes that the anharmonic terms in the lattice potential energy expansion are neglected while the quadratic term is retained. This assumption may have several consequences:

1. There is no thermal expansion.
2. Interaction between lattice waves do not exist and single elastic wave does not decay or change its form with time.
3. Elastic constants are equal in both adiabatic and isothermal processes.
4. Elastic constants do not depend on pressure and temperature.
5. The heat capacity becomes constant at high temperature when $T > \Theta$.

In real crystals non of the above mentioned consequences is satisfied accurately. Deviations in interatomic distances of solid may be attributed to the neglect of anharmonic terms. Some experiments show that the phonon-phonon interaction is important at high temperatures at which the atomic displacements become large. The interaction of two phonons produces a third phonon at a frequency equal the sum of the frequencies of the two phonons. The existence of one phonon causes a periodic elastic strain which (through the anharmonic interaction) modulates in space and time the elastic constant. A second phonon perceives the modulation of the elastic constant and thereupon is scattered to produce a third phonon. This shows that mean free path (the mean distance between successive collisions of phonon) is inversely proportional to the temperature. For larger temperatures, the number of phonons involved in the collision becomes larger. In this case the

inclusion of anharmonic terms in the lattice potential energy is very important.

Thermal Expansion:

The thermal expansion can be understood when the anharmonic terms in the expansion of lattice potential energy are considered.

$$U(x) = U(x_0) - \frac{(x-x_0)}{1!} \left. \frac{dU(x)}{dx} \right|_{x=x_0} + \frac{(x-x_0)^2}{2!} \left. \frac{d^2U(x)}{dx^2} \right|_{x=x_0} - \frac{(x-x_0)^3}{3!} \left. \frac{d^3U(x)}{dx^3} \right|_{x=x_0} + \dots O(x^3)$$

When the first (constant) and second terms (net force at equilibrium) are neglected and considering higher terms, one may get:

$$U(x) = cx^2 - gx^3 - fx^4$$

Here x_0 is taken equal zero such that x will represent the displacement of atoms from their equilibrium positions at absolute zero temperature. The constant c , g and f are obtained from the above expansion as cofactors of x^2 , x^3 and x^4 . The term x^3 represents the asymmetry of the mutual repulsion of atoms (first anharmonic term). The term x^4 represents the softening of the vibration at large amplitudes (second anharmonic term).

Now, we will calculate the mean separation of a pair of atoms at temperature T . The possible values of x due to their thermodynamic probability will be weighted by the Boltzmann distribution function, such that the average of x is expressed as:

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} e^{-\beta U(x)} x dx}{\int_{-\infty}^{\infty} e^{-\beta U(x)} dx}$$

Where $\beta = \frac{1}{k_B T}$. For displacements that have anharmonic terms with energies which are small as compared to $k_B T$, one can expand the exponentials as follows:

$$\int_{-\infty}^{\infty} e^{-\beta U(x)} x dx \approx \int_{-\infty}^{\infty} dx e^{-\beta c x^2} (x + \beta g x^4 + \beta f x^5) \approx \frac{3\pi^{1/2} g \beta^{-3/2}}{4c^{3/2}}$$

The expansion of the exponential can be written as

$$\int_{-\infty}^{\infty} e^{-\beta U(x)} dx \approx \int_{-\infty}^{\infty} dx e^{-\beta c x^2} (1 + \beta g x^3 + \beta f x^4).$$

Here it must be noted that the exponential $e^{-\beta c x^2}$ is not included in the expansions conducted in both denominator and numerator. However, the integral

$$\int_{-\infty}^{\infty} dx e^{-\beta c x^2} = \sqrt{\frac{\pi}{\beta c}}.$$

Thus the mean separation of a pair of atoms at temperature T has the expression:

$$\langle x \rangle = \frac{3g}{4c^2} k_B T$$

This result $\langle x \rangle$ of is proportional to $k_B T$, which indicates that it lies in the classical region.

Transmission of Heat in Dielectrics and Thermal Conductivity:

Heat in dielectrics is transmitted entirely by phonons because there are no mobile electrons in insulators. The transmission of heat by phonons can be explained using the phonon gas model. Here, the phonons are traveling randomly in space in all directions. This motion corresponds to that of phonons in all k 's in the Brillouin zone. The using of gas model allows us to use the concepts adopted by the kinetic theory of gases. Kinetic theory of gases provides a definition to the average distance between two successive collisions called the mean free path. Thus the mean free path of a phonon $\langle \ell_x \rangle$ can be related to the

mean speed $\langle v_x \rangle$ when the phonon travels in the solid by an average time t_c , simply as, $\langle \ell_x \rangle = \langle v_x \rangle t_c$.

The flux of thermal energy (or heat current density) is found proportional to the temperature gradient as follows:

$$j_U \propto \frac{dT}{dx}.$$

When the two ends of a sample have two different temperatures such that $T_1 > T_2$, the heat flows from the hotter to the cooler end.

$$\Delta T = T_2 - T_1$$

When the phonon travels between successive collisions a distance $\Delta x = \ell_x$, the difference in temperature can be written as:

$$\Delta T = \frac{dT}{dx} \ell_x$$

If the phonon travels the average distance of $\langle \ell_x \rangle$ with an average speed of $\langle v_x \rangle = v_x$ in an average time t_c between successive collisions, then $\langle \ell_x \rangle = \langle v_x \rangle t_c$. This implies that

$\Delta T = \frac{dT}{dx} \langle v_x \rangle t_c$ and the phonon gives up the heat energy $c_v \Delta T$. In a

solid, when the number of phonons per unit volume is n , the heat energy released by phonons is $c_v n \Delta T$. Thus the net flux of energy released by a solid is

$$j_U = -nc_v v_x \Delta T$$

Inserting $\Delta T = \frac{dT}{dx} v_x t_c$ into the last relation and using $\ell_x = v_x t_c$, one can get

$$j_U = -nc_v v_x \frac{dT}{dx} v_x t_c$$

From the kinetic theory of gases one has $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \langle v^2 \rangle$.

Considering $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = v_x^2$, we can get $\langle v_x^2 \rangle = \frac{\langle v^2 \rangle}{3}$. Thus,

$$j_U = -nc_v \langle v_x^2 \rangle \frac{dT}{dx} t_c = -\frac{nc_v}{3} \langle v^2 \rangle \frac{dT}{dx} t_c$$

But $\langle v^2 \rangle = v^2$, $C_v = nc_v$ and $\ell = vt_c$, may give

$$j_U = -\frac{C_v}{3} v \ell \frac{dT}{dx}.$$

This allows us to define the thermal conductivity $K = \frac{1}{3} C_v v \ell$ of the solid material which represents the constant of proportionality.

Notes:

The dependence of K on temperature allows us to look into the dependence of C_v , v and ℓ on temperature. The dependence of C_v on temperature has been already studied. The speed v is found to be essentially insensitive to temperature. However, the mean free path ℓ depends strongly on temperature. This means that ℓ is determined by the collision process in solid. However, the collision process may have different mechanisms in solid such as (a) phonon-phonon collisions, (b) Phonon collision with imperfections and (c) phonon collision with external boundaries of the sample. The phonon-phonon collision is the most important at high temperatures at which the atomic displacements become large. Here, it is important to include the anharmonic term in the lattice potential energy, especially when ℓ is larger than the interatomic distance. In this case, ℓ is found inversely proportional to temperature. Here, for higher temperatures the number of phonons involved in the collision becomes bigger.