Section 6: Thermal properties

Heat Capacity

There are two contributions to thermal properties of solids: one comes from *phonons* (or lattice vibrations) and another from *electrons*. This section is devoted to the thermal properties of solids due to lattice vibrations (the contribution from electrons in metals will be considered separately). First, we consider the *heat capacity* of the *specific heat*. The heat capacity C is defined as the heat ΔQ which is required to raise the temperature by ΔT, i.e.

$$C = \frac{\Delta Q}{\Delta T}. \tag{6.1}$$

If the process is carried out at constant volume V, then $\Delta Q = \Delta E$, where ΔE is the increase in internal energy of the system. The heat capacity at constant volume C_V is therefore given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V. \tag{6.2}$$

The contribution of the phonons to the heat capacity of the crystal is called the *lattice heat capacity*.

The total energy of the phonons at temperature T in a crystal can be written as the sum of the energies over all phonon modes, so that

$$E = \sum_{\mathbf{q}p} \langle n_{\mathbf{q}p} \rangle \hbar \omega_p(\mathbf{q}), \tag{6.3}$$

where $\langle n_{\mathbf{q}p} \rangle$ is the thermal equilibrium occupancy of phonons of wavevector $\mathbf{q}$ and mode p ($p = 1\ldots3s$, where s is the number of atoms in a unit cell). The angular brackets denote the average in thermal equilibrium. Note that we assumed here that the zero-point energy is chosen as the origin of the energy, so that the ground energy lies at zero. Now we calculate this average.

Consider a harmonic oscillator in a thermal bath. The probability to find this oscillator in an excited state, which is characterized by a particular energy E_n is given by the Boltzmann distribution:

$$P_n = P_0 e^{-n\hbar\omega/k_B T}, \tag{6.4}$$

where the constant P_0 is determined from the normalization condition

$$\sum_{n=0}^{\infty} P_n = 1, \tag{6.5}$$

so that

$$P_0 = \left(\sum_{n=0}^{\infty} e^{-n\hbar\omega/k_B T}\right)^{-1}. \tag{6.6}$$

The average excitation number of the oscillator is given by

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n = \frac{\sum_{n=0}^{\infty} n e^{-n\hbar\omega/k_B T}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega/k_B T}} \ . \tag{6.7}$$

The summation in the enumerator can be performed using the known property of geometrical progression:

$$\sum_{n=0}^{\infty} x^n = 1 \ . \tag{6.8}$$

Using this property we find:

$$\sum_{n=0}^{\infty} n x^n = x \frac{d}{dx} \sum_{n=0}^{\infty} x^n = x \frac{d}{dx} \frac{1}{1-x} = \frac{x}{(1-x)^2} \ , \tag{6.9}$$

where $x = e^{-\hbar\omega/kT}$. Thus we obtain

$$\langle n \rangle = \frac{x}{(1-x)} = \frac{1}{x^{-1}-1} = \frac{1}{e^{\hbar\omega/k_B T}-1} \ . \tag{6.10}$$

The distribution given by Eq. (6.10) is known as the Planck distribution. Coming back to the expression for the total energy of the phonons, we find that

$$E = \sum_{\mathbf{q}p} \frac{\hbar\omega_p(\mathbf{q})}{e^{\hbar\omega_p(\mathbf{q})/k_B T}-1} \ . \tag{6.11}$$

Usually it is convenient to replace the summation over $\mathbf{q}$ by an integral over frequency. In order to do this we need to introduce the *density of modes* or the *density of states* $D_p(\omega)$. $D_p(\omega)d\omega$ represents the number of modes of a given number s in the frequency range $(\omega, \omega + d\omega)$. Then the energy is

$$E = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{e^{\hbar\omega/k_B T}-1} \tag{6.12}$$

The lattice heat capacity can be found by differentiation of this equation with respect to temperature, so that

$$C_V = \frac{\partial E}{\partial T} = k_B \sum_p \int d\omega D_p(\omega) \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T}-1)^2} \ . \tag{6.13}$$

We see that the central problem is to find the density of states $D_p(\omega)$, the number of modes per unit frequency range.

Density of states. Consider the longitudinal waves in a long bar. The solution for the displacement of atoms is given by

$$u(x) = A e^{iqx} \ , \tag{6.14}$$

where we omitted a time-dependent factor as irrelevant for the present discussion. We shall now consider the effects of the boundary conditions on this solution. These boundary conditions are determined by the external constraints applied to the ends of the bar. The most convenient type of boundary condition is known as the *periodic boundary condition.* By this we mean that the right end of the bar is constrained in such a way that it is always in the same state of oscillation as the left end. It is as if the bar were deformed into a circular shape so that the right end joined the left. Given that the length of the bar is L, if we take the origin as being at the left end, the periodic condition means that

$$u(x = 0) = u(x = L),$$ (6.15)

where u is the solution given by Eq.(6.14). If we substitute (6.14) into (6.15), we find that

$$e^{iqL} = 1.$$ (6.16)

This equation imposes a condition on the admissible values of q:

$$q = n\frac{2\pi}{L},$$ (6.17)

where $n = 0, +1, \pm 2$, etc. When these values are plotted along a *q-axis,* they form a one-dimensional mesh of regularly spaced points. The spacing between the points is $2\pi/L$. When the bar length is large, the spacing becomes small and the points form a quasi-continuous mesh.

Each q-value of (6.17) represents a *mode* of vibration. Suppose we choose an arbitrary interval dq in q-space, and look for the number of modes whose q's lie in this interval. We assume here that L is large, so that the points are quasi-continuous, which is true for the macroscopic objects. Since the spacing between the points is $2\pi/L$, the number of modes is

$$\frac{L}{2\pi} dq.$$ (6.18)

We are interested in the number of modes in the frequency range $d\omega$ lying between $(\omega, \omega + d\omega)$. The *density of states $D(\omega)$* is defined such that $D(\omega)d\omega$ gives this number. Comparing this definition with (6.18), one may write $D(\omega)d\omega = (L/2\pi) dq$, or $D(\omega) = (L/2\pi)/(d\omega/dq)$. We note from Fig. 1, however, that in calculating $D(\omega)$ we must include the modes lying in the negative q-region as well as in the positive region. The effect is to multiply the above expression for $D(\omega)$ by a factor of two. That is,

$$D(\omega) = \frac{L}{\pi} \frac{1}{d\omega/dq}$$ (6.19)

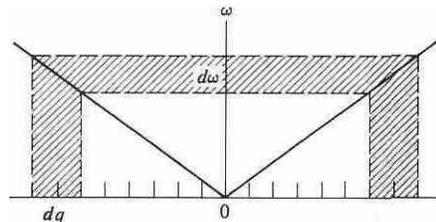We see that the density of states $D(\omega)$ is determined by the dispersion relation $\omega = \omega(q)$.

Fig.1

Now we extend these results to the 3D case. The wave solution analogous to (6.14) is

$$\mathbf{u} = \mathbf{A}e^{i\left(q_x x + q_y y + q_z z\right)},$$
(6.20)

where the propagation is described by the wave vector $\mathbf{q} = (q_x, q_y, q_z)$, whose direction specifies the direction of wave propagation. Here again we need to take into account the boundary conditions. For simplicity, we assume a cubic sample whose edge is L. By imposing the periodic boundary conditions, one finds that the allowed values of q must satisfy the condition

$$e^{iq_x L} = e^{iq_y L} = e^{iq_z L} = 1.$$
(6.21)

Therefore, the values are given by

$$\left(q_x, q_y, q_z\right) = \left(l\frac{2\pi}{L}, m\frac{2\pi}{L}, n\frac{2\pi}{L}\right),$$
(6.22)

where l, m, n are some integers.

If we plot these values in a q-space, as in Fig. 2, we obtain a three-dimensional cubic mesh. The volume assigned to each point in this q-space is $(2\pi/L)^3$.
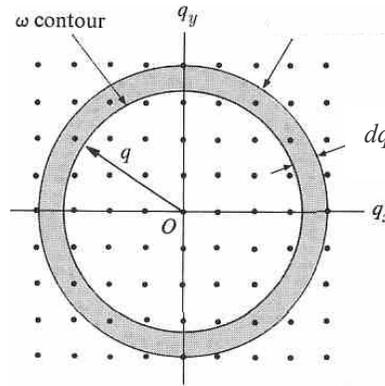

Fig. 2 Allowed values of **q** for a wave traveling in 3 dimensions. Only the cross section in the (q_x, q_y) plane is shown. The shaded circular shell is used for counting the modes.

Each point in Fig. 2 determines one mode. We now wish to find the number of modes lying in the spherical shell between the radii q and $q + dq$, as shown in Fig.2. The volume of this shell is $4\pi q^2 dq$, and since the volume per point is $(2\pi/L)^3$, it follows that the number we seek is

$$\left(\frac{L}{2\pi}\right)^3 4\pi q^2 dq = \frac{V}{(2\pi)^3} 4\pi q^2 dq$$
(6.23)

where $V = L^3$ is the volume of the sample. By definition of the density of modes, this quantity is equal to $D(\omega)d\omega$. Thus, we arrive at

$$D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq}.$$
(6.24)

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We note that Eq.(6.24) is valid only for an *isotropic solid*, in which the vibrational frequency, ω, does not depend on the direction of **q**. Also we note that in the above discussion we have associated a single mode with each value of *q*. This is not quite true for the 3D case, because for each *q* there are actually three different modes, one longitudinal and two transverse, associated with the same value of *q*. In addition, in the case of non-Bravais lattice we have a few sites, so that the number of modes is 3*s*, where *s* is the number of non-equivalent atoms. This should be taken into account by index *p*=1…3*s* in the density of states as was done before because the dispersion relations for the longitudinal and transverse waves are different, and acoustic and optical modes are different.

Debye model

The Debye model assumes that the acoustic modes give the dominant contribution to the heat capacity. Within the Debye approximation the velocity of sound is taken a constant independent of polarization as it would be in a classical elastic continuum. The dispersion relation is written as

$$\omega = \text{v} q ,\tag{6.25}$$

where v is the velocity of sound.

In this approximation the density of states is given by

$$D(\omega) = \frac{V\omega^2}{2\pi^2 \text{v}^3} ,\tag{6.26}$$

i.e. the density of states increases quadratically with the frequency.

The normalization condition for the density of states determines the limits of integration over ω. The lower limit is obviously ω=0. The upper limit can be found from the condition that the number of vibrational modes in a crystal is finite and is equal to the number of degrees of freedom of the lattice. Assuming that there are *N* unit cells is the crystal, and there is only one atom in per cell (so that there are *N* atoms in the crystal), the total number of phonon modes is 3*N*. Therefore, we can write

$$\sum_p \int_0^{\omega_D} D(\omega)d\omega = 3N\tag{6.27}$$

where the cutoff frequency ω_D is known as Debye frequency. Assuming that the velocity of the three acoustic modes is independent of polarization and substituting (6.26) in (6.27) we obtain:

$$\omega_D = \left(\frac{6\pi^2 \text{v}^3 N}{V}\right)^{1/3} .\tag{6.28}$$

The cutoff wavevector which corresponds to this frequency is given by

$$q_D = \frac{\omega_D}{\text{v}} = \left(\frac{6\pi^2 N}{V}\right)^{1/3} ,\tag{6.29}$$

so that modes of wavevector larger than q_D are not allowed. This is due to the fact that the number of modes with $q \leq q_D$ exhausts the number of degrees of freedom of the lattice.

The thermal energy is given by Eq. (6.12), so that

$$E = 3\int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 \mathrm{v}^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \,,$$ (6.30)

where a factor of 3 is due to the assumption that the phonon velocity is independent of polarization. This leads to

$$E = \frac{3V\hbar}{2\pi^2 \mathrm{v}^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 \mathrm{v}^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \,,$$ (6.31)

where $x \equiv \hbar\omega / k_B T$ and

$$x_D \equiv \hbar\omega_D / k_B T \equiv \theta_D / T \,.$$ (6.32)

The latter expression defines the Debye temperature

$$\theta_D = \frac{\hbar \mathrm{v}}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{1/3} \,.$$ (6.33)

The total phonon energy is then

$$E = 9Nk_B T \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \,,$$ (6.34)

where N is the number of atoms in the crystal and $x_D \equiv \theta_D / T$.

The heat capacity is most easily found by differentiating the middle expression of (6.31) with respect to the temperature (in Eq.(6.34) we should have to differentiate the upper limit) so that

$$C_V = \frac{3V\hbar^2}{2\pi^2 \mathrm{v}^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2} = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{\left(e^x - 1\right)^2} \,.$$ (6.35)

In the limit $T \gg \theta$, we can expand the expression under the integral and obtain: $C_V = 3Nk_B$. This is exactly the classical value for the heat capacity, which is known from the elementary physics. Recall that according to the elementary thermodynamics the average thermal energy per a degree of freedom is equal to $E = k_B T$. Therefore for a system of N atoms $E = 3Nk_B T$ which results in $C_V = 3Nk_B$. This is known as the *Dulong-Petit* law.

Now consider an opposite limit, i.e. $T \ll \theta$. At very low temperatures we can approximate (6.34) by letting the upper limit go to infinity. We obtain

$$E = 9Nk_B T \left(\frac{T}{\theta_D} \right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1} = 9Nk_B T \left(\frac{T}{\theta_D} \right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} Nk_B T \left(\frac{T}{\theta_D} \right)^3 \,,$$ (6.36)

and therefore

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

(6.37)

We see that within the Debye model at low temperatures the heat capacity is proportional to T^3.

The cubic dependence may be understood from the following qualitative argument. At low temperature, only a few modes are excited. These are the modes whose quantum energy $\hbar\omega$ is less than k_BT. The number of these modes may be estimated by drawing a sphere in the q-space whose frequency $\omega = k_B T / \hbar$, and counting the number of points inside, as shown in Fig. 3. This sphere may be called the *thermal sphere,* in analogy with the Debye sphere discussed above. The number of modes inside the thermal sphere is proportional to $q^3 \sim \omega^3 \sim T^3$. Each mode is fully excited and has an average energy equal to k_BT. Therefore the total energy of excitation is proportional to T^4, which leads to a specific heat proportional to T^3, in agreement with (6.37).
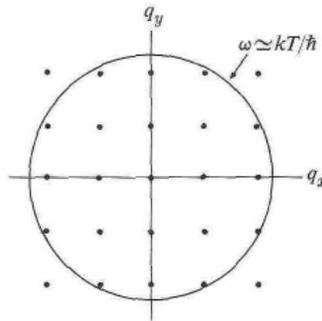

Fig. 3 The thermal sphere which is the frequency contour $\omega = k_B T / \hbar$.

To compare these predictions with experimental results one should know the Debye temperature. This temperature is normally determined by fitting experimental data. Fig.4 shows the fitted data versus the reduced temperature T/θ. You see that the curve is *universal*; it is the same for different substances. The agreement between the calculated and experimental data is remarkable.
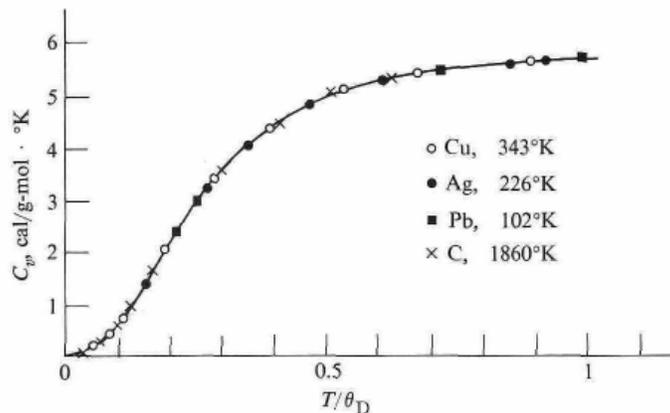

Fig. 4. Specific heats versus reduced temperature for four substances.

Einstein model

Within the Einstein model the density of states is approximated by a delta function at some frequency ω_E, i.e

$$D(\omega) = N\delta(\omega - \omega_E),$$ (6.38)

where N is the total number of atoms (oscillators). ω_E is known as the Einstein frequency. The thermal energy of the system (6.12) is then

$$E = \frac{3N\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1},$$ (6.39)

where a factor of 3 reflects the fact that there are three degree of freedom for each oscillator. The heat capacity is then

$$C_V = \frac{\partial E}{\partial T} = 3Nk_B \left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E/k_B T}}{\left(e^{\hbar\omega_E/k_B T} - 1\right)^2}.$$ (6.40)

The high temperature limit for the Einstein model is the same as that for the Debye model, i.e. $C_V = 3Nk_B$, which is the Dulong-Petit law. At low temperatures however (6.40) decreases as $C_V \sim e^{-\hbar\omega_E/k_B T}$, which is different from the Debye T^3 low. The reason for this disagreement is that at low temperatures only acoustic phonons are populated and the Debye model is much better approximation that the Einstein model. The Einstein model is often used to approximate the optical phonon part of the phonon spectrum.

Concluding our discussion about the heat capacity we note that a real density of vibrational modes could be much more complicated than those described by the Debye and Einstein models. Fig.5 shows the density of states for Cu. The dashed line is the Debye approximation. The Einstein approximation would a delta peak at some frequency. At low frequencies the density of states varies quadratically with the frequency, which is due to acoustic modes and similar to that within the Debye approximation. At higher frequencies there is a peak which is due to optical modes. This density of states has to be included in order to obtain quantitative description of experimental data.
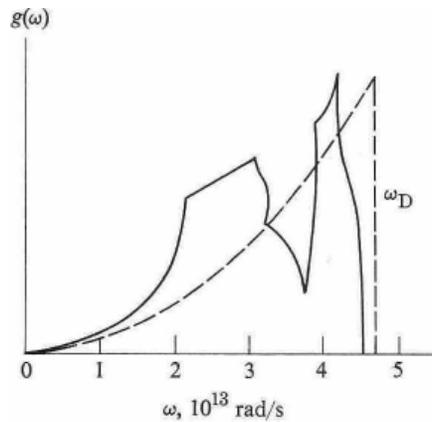

Fig. 5. Total density of states for Cu, as deduced from data on neutron scattering. Dashed curve is the Debye approximation, which has the same area (under the curve) as the solid curve.

Thermal Conductivity

When the two ends of the sample of a given material are at two different temperatures, T_1 and T_2 ($T_2 > T_1$), heat flows down the thermal gradient, i.e. from the hotter to the cooler end. Observations show that the *heat current density j* (amount of heat flowing across unit area per unit time) is proportional to the temperature gradient (dT/dx). That is,

$$j = -K\frac{dT}{dx}. \tag{6.41}$$

The proportionality constant K, known as the *thermal conductivity,* is a measure of the ease of transmission of heat across the bar (the minus sign is included so that K is a positive quantity).

Heat may be transmitted in the material by several independent agents. In metals, for example, the heat is carried both by electrons and phonons, although the contribution of the electrons is much larger. In insulators, on the other hand, heat is transmitted entirely by phonons, since there are no mobile electrons in these substances. Here we consider only transmission by phonons.

When we discuss transmission of heat by phonons, it is convenient to think of these as forming a phonon gas. In every region of space there are phonons traveling randomly in all directions, corresponding to all the q's in the Brillouin zone, much like the molecules in an ordinary gas. The concentration of phonons at the hotter end of the sample is larger and they move to the cooler end. The advantage of using this gas model is that many of the familiar concepts of the kinetic theory of gases can also be applied here. In particular, thermal conductivity is given by

$$K = \frac{1}{3}C_V \mathrm{v}l \tag{6.42}$$

where C_V is the specific heat per unit volume, v the velocity of the particle, and l its *mean free path*. In the present case, v and l refer, of course, to the velocity and the mean free path of the phonon, respectively. The mean free path is defined as the average distance between two consecutive scattering events, so that $l = \mathrm{v}\tau$, where τ is the average time between collisions which is called *collision time* or *relaxation time*.

Let us give a qualitative explanation for Eq.(6.42). For simplicity we consider a one-dimensional picture, in which phonons can move only along the x axis. We assume that a temperature gradient is imposed along the x axis. We also assume that collisions between phonons maintain local thermodynamic equilibrium, so that we can assign local thermal energy density to a particular point of the sample $E[T(x)]$. The phonons which originate from this point have this energy on average. At a given point x half the phonons come from the high temperature side and half phonons come from the low temperature side. The phonons which arrive to this point from the high-temperature side will, on the average, have had their last collision at point $x-l$, and will therefore carry a thermal energy density of $E[T(x-l)]$. Their contribution to the thermal current density at point x will therefore be the ½v$E[T(x-l)]$. The phonons arriving at x from the low temperature side, on the other hand, will contribute $-$½v$E[T(x+l)]$, since they come from the positive x-direction and are moving toward negative x. Adding these together gives

$$j = \text{½v}E\big[T(x-l)\big] - \text{½v}E\big[T(x+l)\big]. \tag{6.43}$$

Provided that the variation in the temperature over the mean free path is very small we may expand this about the point x to find:

$$j = \mathrm{v}l\frac{dE}{dT}\left(-\frac{dT}{dx}\right) = \mathrm{v}^2\tau\frac{dE}{dT}\left(-\frac{dT}{dx}\right) \qquad (6.44)$$

This result can be easily generalized to the three dimensional case. We need to replace v by the x-component v_x, and then average over all the angles. Since $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = 1/3v^2$ and since

$C_V = \dfrac{dE}{dT}$ is the heat capacity, we obtain

$$j = \frac{1}{3}C_V \mathrm{v}l\left(-\frac{dT}{dx}\right), \qquad (6.45)$$

where v is the phonon velocity.

Let us now discuss the dependence of the thermal conductivity j on temperature. The dependence of C_V on temperature has already been studied in detail, while the velocity v is found to be essentially insensitive to temperature. The mean free path l depends strongly on temperature. Indeed, l is the average distance the phonon travels between two successive collisions. Three important mechanisms may be distinguished: (a) The collision of a phonon with other phonons, (b) the collision of a phonon with imperfections in the crystal, such as impurities and dislocations, and (c) the collision of a phonon with the external boundaries of the sample.

Consider a collision of type (a). The phonon-phonon scattering is due to the *anharmonic* interaction between them. When the atomic displacements become appreciable, this gives rise to anharmonic coupling between the phonons, causing their mutual scattering.

Suppose that two phonons of vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ collide, and produce a third phonon of vector $\mathbf{q}_3$. Since momentum must be conserved, it follows that $\mathbf{q}_3 = \mathbf{q}_1 + \mathbf{q}_2$. Although both $\mathbf{q}_1$ and $\mathbf{q}_2$ lie inside the Brillouin zone, $\mathbf{q}_3$ may not do so. If it does, then the momentum of the system before and after collision is the same. Such a process has no effect at all on thermal resistivity, as it has no effect on the flow of the phonon system as a whole. It is called a *normal* process.
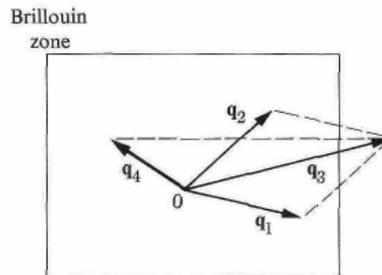

Fig. 6 Umklapp process

By contrast, if $\mathbf{q}_3$ lies outside the BZ, such a vector is not physically meaningful according to our convention. We reduce it to its equivalent $\mathbf{q}_4$ inside the first BZ, where $\mathbf{q}_3 = \mathbf{q}_4 + \mathbf{G}$ and $\mathbf{G}$ is the appropriate reciprocal lattice vector. As is seen from Fig.6, the phonon $\mathbf{q}_4$ produced by the collision travels in a direction almost opposite to either of the original phonons $\mathbf{q}_1$ and $\mathbf{q}_2$. The difference in momentum is transferred to the center of mass of the lattice. This type of process is highly efficient in

changing the momentum of the phonon, and is responsible for phonon scattering at high temperatures. It is known as the *umklapp process* (German for "flipping over").

Phonon-phonon collisions become particularly important at high temperature, at which the atomic displacements are large. In this region, the corresponding mean free path is inversely proportional to the temperature, that is, $l \sim 1/T$. This is reasonable, since the larger T is, the greater the number of phonons participating in the collision.

The second mechanism (b) which results in phonon scattering results from defects and impurities. Real crystals are never perfect and there are always crystal imperfections in the crystal lattice, such as impurities and defects, which scatter phonons because they partially destroy the perfect periodicity of the crystal.

At very low temperature (say below 10^0K), both phonon-phonon and phonon-imperfection collisions become ineffective, because, in the former case, there are only a few phonons present, and in the latter the few phonons which are excited at this low temperature are long-wavelength ones. These are not effectively scattered by objects such as impurities, which are much smaller in size than the wavelength. In the low-temperature region, the primary scattering mechanism is the external boundary of the specimen, which leads to the so-called *size* or *geometrical effects*. This mechanism becomes effective because the wavelengths of the excited phonons are very long - comparable, in fact, to the size of the specimen. The mean free path here is $l \sim L$, where L is roughly equal to the diameter of the specimen, and is therefore independent of temperature.

Figure 7 illustrates the temperature dependence of thermal conductivity K. At low temperature $K \sim T^3$, the dependence resulting entirely from the specific heat C_V, while at high temperature $K \sim 1/T$, the dependence now being entirely due to l.
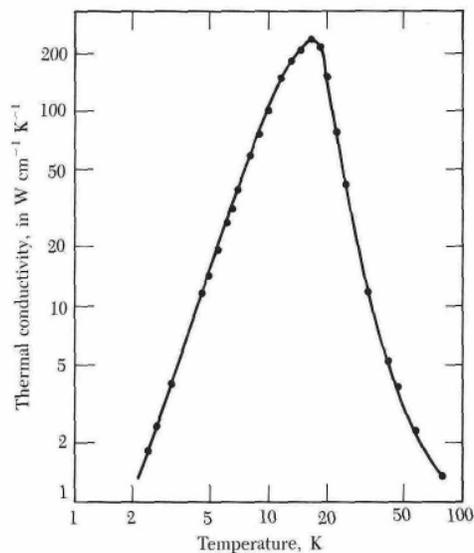

Fig.7. Thermal conductivity of a highly purified crystal of sodium fluoride.