Phonons – Thermal properties

Till now everything was classical – no quantization, no uncertainty....

WHY DO WE NEED QUANTUM THEORY OF LATTICE VIBRATIONS?

Classical – Dulong Petit law

All energy values are allowed – classical equipartition theorem – energy per degree of freedom is $1/2k_BT$.

Total energy $E = 3N \times 1/2k_BT$

$C = \frac{\partial E}{\partial T} \sim k_B$; independent of temperature! Detailed calculation gives $C = 3Nk_B$
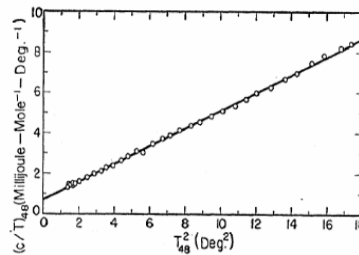
In reality $C \sim aT + bT^3$

Figure 1: Heat capacity of gold

Need quantum theory!

Quantum theory of lattice vibrations:

Hamiltonian for 1D linear chain $\mathcal{H} = \sum_i \frac{p_i^2}{2m} +$ interaction energy

Interaction energy is simple harmonic type $\sim \frac{1}{2} kx^2$

Solve it for N coupled harmonic oscillators – 3N normal modes – each with a characteristic frequency $\omega_p(k)$ where p is the polarization/branch.

Energy of any given mode is $E_{kp} = \left(n_{kp} + \frac{1}{2}\right)\hbar\omega_p(k); \ n_{kp} = 0,1,2 \dots$

- $1/2\hbar\omega_p(k)$ is the zero-point energy
- n_{kp} is called 'excitation number' of the particular mode of pth branch with wavevector k

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Phonons are quanta of ionic displacement field that describes classical sound wave. Analogy with black body radiation - n_i is the number of photons of the ith mode of oscillations of the EM wave.

Total energy of the system $E = \sum_{kp} E_{kp} = \sum_{kp} \left(n_{kp} + \frac{1}{2} \right) \hbar \omega_p(k)$

$n_{kp} = \frac{1}{e^{\beta \hbar \omega_p(k)} - 1}$ is the 'Planck distribution' of the occupation number.

Planck distribution:

Consider an ensemble of identical oscillators at temperature T in thermal equilibrium.

Ratio of number of oscillators in $(n+1)^{th}$ state to the number of them in n^{th} state is

$$\frac{N_{n+1}}{N_n} = e^{-\beta \hbar \omega}$$

So, the average occupation number <n> is:

$$< n > = \frac{\sum_n n e^{-\beta E}}{\sum_n e^{-\beta E}} = \frac{\sum_n n e^{-\beta \hbar \omega \left(n + \frac{1}{2} \right)}}{\sum_n e^{-\beta \hbar \omega \left(n + \frac{1}{2} \right)}}$$

$$< n > = \frac{\sum_n n e^{-\beta \hbar \omega n} e^{-\frac{\beta \hbar \omega}{2}}}{\sum_n e^{-\beta \hbar \omega n} e^{-\frac{\beta \hbar \omega}{2}}} = \frac{\sum_n n e^{-\beta \hbar \omega n}}{\sum_n e^{-\beta \hbar \omega n}} = \frac{\sum_n n x^n}{\sum_n x^n} ; x = e^{-\beta \hbar \omega}$$

$$\langle n \rangle = \frac{\frac{x}{(1-x)^2}}{\frac{1}{1-x}} = \frac{x}{1-x} = \frac{1}{x^{-1} - 1} = \frac{1}{e^{\beta \hbar \omega} - 1}$$

Special case of Bose-Einstein distribution with $\mu = 0$, chemical potential is zero since we do not directly control the total number of phonons (unlike the number of helium atoms is a bath – BE distribution or electrons in a solid –FE distribution), it is determined by the temperature.

Total energy of the system E =
$$\sum_{kp} E_{kp} = \sum_{kp} \left(n_{kp} + \frac{1}{2} \right) \hbar \omega_p(k) = \sum_{kp} \left(\frac{\hbar \omega_p(k)}{e^{\beta \hbar \omega_p(k)} - 1} + \frac{1}{2} \hbar \omega_p(k) \right)$$

Specific heat $C_v = \frac{\partial E}{\partial T} = \sum_{kp} \frac{\partial}{\partial T} \left(\frac{\hbar \omega_p(k)}{e^{\beta \hbar \omega_p(k)} - 1} \right)$

General expression; actual values will depend upon frequency spectrum of the normal modes.

High temperature limit:

Writing $\omega_p(k)$ as just ω for brevity:

$$C_v = \frac{\partial E}{\partial T} = \sum_{kp} \frac{\partial}{\partial T} \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right)$$

Replace $x = \beta\hbar\omega = \frac{\hbar\omega}{k_B T} \ll 1$

$$\frac{1}{e^x - 1} = \frac{1}{x + \frac{x^2}{2} + \frac{x^3}{6} + \cdots} = \frac{1}{x} \left(\frac{1}{1 + \frac{x}{2} + \frac{x^2}{6} + \cdots} \right) = \frac{1}{x} \left(1 - \frac{x}{2} + \frac{x^2}{12} \cdots \right)$$

$$E = \sum_{all\ modes} \left(\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right) + \sum_{kp} \frac{1}{2} \hbar\omega$$

$$E = \sum_{all\ modes} \left(\frac{\hbar\omega}{\beta\hbar\omega} \right) \left[1 - \frac{\beta\hbar\omega}{2} + \frac{(\beta\hbar\omega)^2}{12} - \cdots \right] + \sum_{kp} \frac{1}{2} \hbar\omega$$

$$E = \sum_{all\ modes} k_B T \left[1 - \frac{\hbar\omega}{2k_B T} + \frac{1}{12} \left(\frac{\hbar\omega}{k_B T} \right)^2 - \cdots \right] + \sum_{kp} \frac{1}{2} \hbar\omega$$

$$C_v = \frac{\partial E}{\partial T} = \sum_{all\ modes} k_B \left[1 - \frac{k_B}{12} \left(\frac{\hbar\omega}{k_B T} \right)^2 + \cdots \right]$$

To first order; $C_v = \sum_{all\ modes} k_B = 3N k_B$; Dulong Petit law; the other terms ignored in the expansion give the correction to the above result.

Low temperature limit:

Make certain assumptions:

1. Replace the summation by an integral over the first Brillouin zone – justified since N is very large, spacing between allowed values of k is very small and the summand does not vary much between two consecutive points.

$$C_v = \frac{\partial E}{\partial T} = \sum_p \frac{\partial}{\partial T} \int \frac{d\mathbf{k}}{(2\pi)^3} \left(\frac{\hbar\omega_p}{e^{\beta\hbar\omega_p} - 1} \right)$$

2. Modes with high frequency $\beta\hbar\omega_p \gg 1$ will make negligible contribution to the integral as these terms die our exponentially – so can completely ignore the optical branches.
3. Replaced the acoustic branch with $\omega(k) = ck$; valid provided the frequency at which the dispersion deviates from linearity is large compared to the temperature.
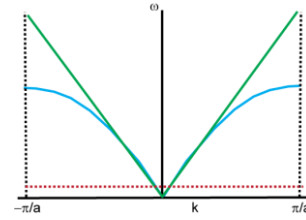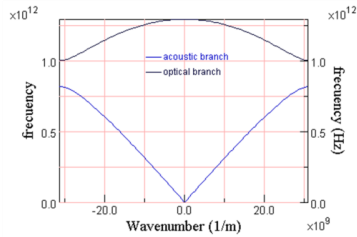
$$C_v = \sum_p \frac{\partial}{\partial T} \int \frac{dk}{(2\pi)^3} \left(\frac{\hbar c k}{e^{\beta \hbar c k} - 1} \right)$$

4. Extend the limit of integral to all k-space – anyway integrand is negligible everywhere except near $k \to 0$.

$$C_v = \sum_p \frac{\partial}{\partial T} \int_0^\infty \frac{dk}{(2\pi)^3} \left(\frac{\hbar c k}{e^{\beta \hbar c k} - 1} \right)$$

$$C_v = \sum_p \frac{\partial}{\partial T} \int_0^\infty \frac{4\pi k^2}{(2\pi)^3} \left(\frac{\hbar c k}{e^{\beta \hbar c k} - 1} \right) dk$$

$$x = \beta \hbar c k$$

$$C_v = \frac{\partial}{\partial T} \left[\frac{3}{2\pi^2} \frac{(k_B T)^4}{(\hbar c)^3} \int_0^\infty dx \left(\frac{x^3}{e^x - 1} \right) \right]$$

The factor 3 is for the three acoustic modes.

$$\boxed{C_v = \frac{\partial}{\partial T} \left[\frac{3}{2\pi^2} \frac{(k_B T)^4}{(\hbar c)^3} \frac{\pi^4}{15} \right] = k_B \frac{2\pi^2}{5} \frac{(k_B T)^3}{(\hbar c)^3} \propto T^3}$$

This result matches to that obtained experimentally for alkali halides to within 1%!!

Specific heat in intermediate temperature range: There is no simple general theory, two good models exist; Debye model and Einstein model.

Debye model:

Assumptions:

1. Replace all branches of the dispersion by a linear spectrum; $\omega(k) = ck$.
2. Carry out the integration over a sphere of area equal to the area of the Brillouin zones.

$$\frac{(2\pi)^3}{V} N = \frac{4}{3} \pi k_D{}^3; \quad k_D = \left(\frac{6\pi^2 N}{V} \right)^{1/3}$$
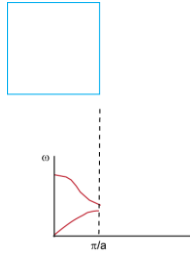
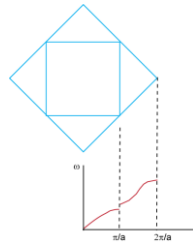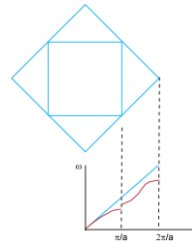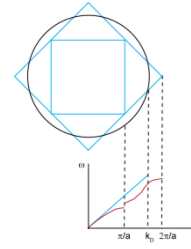**Figure 2: Normal spectrum**   **Figure 3: Spectrum in extended zone scheme**   **Figure 4: Linearized spectrum**   **Figure 5:Debye wavevector**

Calculate the specific heat:

$$C_v = \frac{\partial}{\partial T} \int_0^{k_D} 3 \, \frac{dk}{(2\pi)^3} \left(\frac{\hbar c k}{e^{\beta \hbar c k} - 1} \right)$$

$$C_v = \frac{\partial}{\partial T} \int_0^{k_D} \frac{12\pi k^2}{(2\pi)^3} \left(\frac{\hbar c k}{e^{\beta \hbar c k} - 1} \right) dk$$

$$C_v = \frac{3\hbar c}{2\pi^2} \frac{\partial}{\partial T} \int_0^{k_D} \left(\frac{k^3}{e^{\beta \hbar c k} - 1} \right) dk$$

$$C_v = \frac{3\hbar c}{2\pi^2} \frac{\hbar c}{k_B T^2} \int_0^{k_D} \frac{e^{\beta \hbar c k} k^4}{(e^{\beta \hbar c k} - 1)^2} dk$$

Replace $x = \beta \hbar c k$ in the equation and define Debye temperature $T_D = \frac{\hbar c k_D}{k_B}$.

$$C_v = \frac{3\hbar c}{2\pi^2} \frac{\hbar c}{k_B T^2} \left(\frac{k_B T}{\hbar c} \right)^5 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$C_v = \frac{3k_B}{2\pi^2} \left(\frac{k_B T}{\hbar c} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

$$\boxed{C_v = 9nk_B \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx}$$

At temperatures high compared to T_D; $C_v = 3Nk_B$ - Dulong Petit result

At temperatures low compared to T_D; $C_v = \frac{12\pi^4}{5} nk_B \left(\frac{T}{T_D} \right)^3 \approx 234 \, nk_B \left(\frac{T}{T_D} \right)^3$

T_D plays the same role for phonons as T_F plays for electrons; it divides the high temperature classical regime from the low temperature Quantum regime.

In the case of electrons, $T_F \sim 10^4$ K so only quantum regime is encountered. For phonons T_D ~ 100-1000K, so both classical and quantum behaviour can be seen.

Einstein model:
Einstein model differs from Debye model essentially in the way it treats the Optical modes.
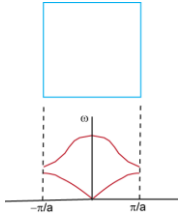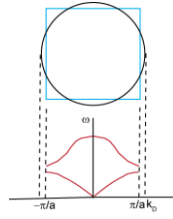
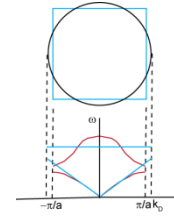| Figure 6: Normal dispersion | Figure 7: Replace by Debye sphere | Figure 8: Linearize the dispersion |

Assumptions:
1. The acoustic modes all have a linear dispersion relation.
2. The optical modes have a constant frequency ω_E independent of k (remember the case $G/K \to 0$).

Acoustic mode contribution to the specific heat remains unchanged.

Optical mode energy $= 3N \frac{\hbar\omega_E}{e^{\beta\hbar\omega_E}-1}$; assuming same dispersion for all three modes.

Specific heat due to Optical modes is $C_v = 3Nk_B \left(\frac{\hbar\omega_E}{k_BT}\right)^2 \frac{e^{\beta\hbar\omega_E}}{(e^{\beta\hbar\omega_E}-1)^2}$

At temperatures high compared to $\hbar\omega_E$; $C_v = 3Nk_B$ - Dulong Petit result

At temperatures low compared to $\hbar\omega_E$; C_v dies off exponentially as it is difficult to excite high energy modes at low temperatures.

Comparison between electronic and lattice specific heats:

Lattice specific heat: $C_v{}^{lat} = \frac{12\pi^4}{5} n_i k_B \left(\frac{T}{T_D}\right)^3$; n_i is the number of ions

Electronic specific heat: $C_v{}^{elec} = \frac{\pi^2}{2} n_e k_B \frac{T}{T_F}$; $n_e = Zn_i$ is the number of ions; Z is valence

$$\frac{C_v{}^{elec}}{C_v{}^{lat}} = \frac{5}{24\pi^2} Z \frac{T_D{}^3}{T^2 T_F}$$

They will be equal at a temperature T_0 where

$$\frac{5}{24\pi^2} Z \frac{T_D{}^3}{T_0{}^2 T_F} = 1$$

$$T_0 = \sqrt{\frac{5Z}{24\pi^2}} \sqrt{\frac{T_D}{T_F}} \; T_D \sim 10K$$

$T_D \sim 300K$ while $T_F \sim 10^4 K$.

Linear term (electronic contribution) in specific heat is seen only at very low temperatures, above that the cubic term (phonon contribution) begins to dominate.

Total specific heat of a crystal:

$$C = C_v{}^{elec} + C_v{}^{lat} = \frac{\pi^2}{2} n_e k_B \frac{T}{T_F} + \frac{12\pi^4}{5} n_i k_B \left(\frac{T}{T_D}\right)^3 \; ; \; n_e = Z n_i$$

Writing C=aT+bT³; C/T = a+bT²

$$a = \frac{\pi^2}{2} n_e k_B \frac{1}{T_F} \text{ and } b = \frac{12\pi^4}{5} n_i k_B \left(\frac{1}{T_D}\right)^3$$

Thus in a plot of C/T as a function of T², the intercept 'a' on the y-axis gives the value of the Fermi temperature (or equivalently Fermi energy) while the slope of the curve 'b' is a measure of the Debye temperature.
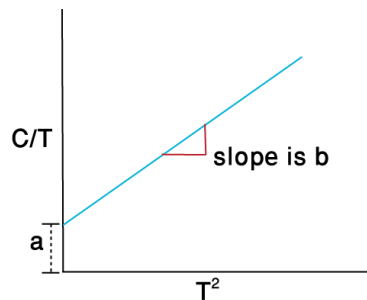

Figure 9: Linear and cubic term in specific heat

Anharhominicity in Phonons

Discussion till now confined to harmonic approximation – potential energy of lattice vibrations had only quadratic terms. We learnt that the lattice waves are normal modes – phonons do not interact with each other; they do not change with time. Its consequences are:

1. The heat capacity becomes T independent for $T > T_D$.
2. There is no thermal expansion of solids.
3. Thermal conductivity of solids is infinite

Conditions not fulfilled in real crystals.

Way out: Include higher order terms in potential energy.

$$U(x) = U_{harm}(x) + U_{anharm}(x) = cx^2 - gx^3 - fx^4 \text{ with c,g and f} > 0$$

This is equivalent to having three or more phonon processes in the Hamiltonian. They can lead to processes like:
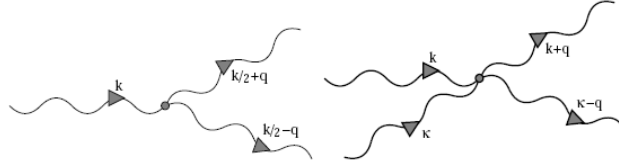
The coefficients g and f are related to the probabilities for having these third order and fourth order processes respectively.

Thermal expansion

Consider the potential energy in terms of the relative displacement x between two ions form their equilibrium position:

$$U(x) = U_{harm}(x) + U_{anharm}(x) = cx^2 - gx^3 - fx^4 \text{ with c,g and f} > 0$$

Average displacement of the ions is:

$$\langle x \rangle = \frac{\int_{-\infty}^{+\infty} dx \, x \exp[-\beta U(x)]}{\int_{-\infty}^{+\infty} dx \, exp[-\beta U(x)]}$$

For small displacements such that $U_{anharm}/k_BT<<0$, we can expand the exponential as:

Numerator:

$$\int dx \, xe^{-\beta(cx^2-gx^3-fx^4)} = \int dx \, x \, e^{-\beta cx^2}e^{\beta gx^3}e^{\beta fx^4}$$

$$\cong \int dx \, x \, e^{-\beta cx^2}(1+\beta gx^3)(1+\beta fx^4) = \int dx \, e^{-\beta cx^2}(x+\beta gx^4+\beta fx^5)$$

$$= \frac{3\pi^{1/2}}{4}\frac{g}{c^{5/2}}\beta^{-3/2}$$

Denominator:

$$\int dx \, e^{-\beta(cx^2-gx^3-fx^4)} = \int dx \, e^{-\beta cx^2}e^{\beta gx^3}e^{\beta fx^4} \cong \int dx \, e^{-\beta cx^2}(1+\beta gx^3)(1+\beta fx^4)$$

$$\cong \int dx \, e^{-\beta cx^2} = \left(\frac{\pi}{c}\right)^{1/2}\beta^{-1/2}$$

So,

$$< x > = \frac{3g}{4c^2}k_BT$$

Note that the thermal expansion does not involve the symmetric term x^4 but only the asymmetric cubic term.
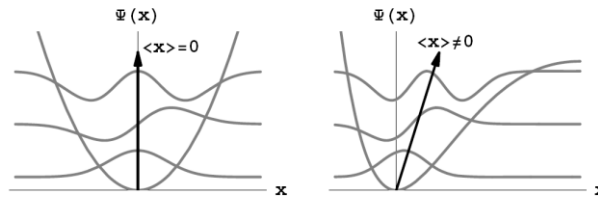
Figure 10:Phonon wavefunctions for (Left) harmonic potential (Right) anharmonic potential

The origin of anharmonicity is explained in Figure 10. Left figure- phonon wavefunctions when the potential is harmonic: the average displacement <x> is zero for all modes. Right figure: the same wavefunctions when the potential in anharmonic: the average displacement increases with phonon energy. Therefore anharmonicity

Dependence of thermal expansion co-efficient on specific heat:

Helmholtz fee energy is defined as:

$$F = U - TS$$

It is related to pressure as: $P = -(\partial F/\partial V)_T$

From TdS = dU + pdV we get

$$T(\partial S/\partial T)_V = (\partial U/\partial T)_V$$

So,

$$P = -\frac{\partial}{\partial V}[U - TS]_T = -\frac{\partial}{\partial V}[U - T\int_0^T \frac{d\acute{T}}{\acute{T}} \frac{\partial}{\partial \acute{T}} U(T\acute{},V)]_T - -(1)$$

From calculations based on harmonic approximation:

$$U = \sum_{k,p} \frac{\hbar\omega_p(k)}{e^{\beta\hbar\omega_p(k)} - 1} + \frac{1}{2}\sum_{k,p} \hbar\omega_p(k) - - - -(2)$$

Combining (1) and (2);

$$P = -\frac{\partial}{\partial V}\left[\frac{1}{2}\sum_{k,p} \hbar\omega_p(k)\right] + \sum_{k,p}\left(-\frac{\partial}{\partial V}(\hbar\omega_p(k))\right)\frac{1}{e^{\beta\hbar\omega_p(k)} - 1}$$

The first term (only term at zero energy) is the volume derivative of the ground state energy. The second term is the volume derivative of the phonon energies.

If harmonic approximation is rigidly correct then the second term vanishes, P does not depend on T at all!!

So, $\left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} = 0$ implying the co-efficient of linear expansion

$$\alpha = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V = 0$$

The co-efficient of thermal expansion for a harmonic lattice is zero!!

Here $B = -V \left(\frac{\partial P}{\partial V} \right)_T$ is the bulk modulus.

Many other thermodynamic anomalies:

1. $C_P = C_v - \frac{T}{V} \frac{(\partial P/\partial T)^2 V}{(\partial P/\partial V)_T} = C_v$; implying the specific heats at constant pressure and constant volume are identical.

2. $\frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} = \frac{C_P}{C_v} = 1$; implying the adiabatic and isothermal compressibilities are identical.

Both these go against experimental results.

As a first order correction, assume that the energy for the anharmonic potential is the same as that we got for the harmonic potential approximation, only now the normal modes depend on the volume of the crystal.

$$\alpha = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V = \frac{1}{3B} \sum_{k,p} \left(-\frac{\partial}{\partial V} (\hbar \omega_p(k)) \right) \frac{\partial}{\partial T} \left(\frac{1}{e^{\beta \hbar \omega_p(k)} - 1} \right) - -(3)$$

Compare with the expression for lattice specific heat per unit volume:

$$c_V{}^{ion} = \frac{1}{V} \frac{\partial}{\partial T} \sum_{k,p} \left(\frac{\hbar \omega_p(k)}{e^{\beta \hbar \omega_p(k)} - 1} \right) = \sum_{k,p} \left(\frac{\hbar \omega_p(k)}{V} \right) \frac{\partial}{\partial T} \frac{1}{e^{\beta \hbar \omega_p(k)} - 1} - -(4)$$

Therefore

$$\alpha = \frac{c_V{}^{ion}}{3B} \frac{\sum_{k,p} \left(-\frac{\partial}{\partial V} (\hbar \omega_p(k)) \right)}{\sum_{k,p} \left(\frac{\hbar \omega_p(k)}{V} \right)} - -(4)$$

For simple dispersion relations like Debye model, we can make further simplifications;

Define a parameter called Gruneisen parameter:

$$\gamma \equiv -\frac{\partial (ln \omega_D)}{\partial (ln V)}$$

$$\boxed{\alpha^{ion} = \frac{\gamma c_V{}^{ion}}{3B} \quad - -(5)}$$

Electrical contribution to the thermal expansion co-efficient:

For electrons the internal energy is related to the pressure by:

$$P = \frac{2U}{3V}$$

$$\alpha^{el} = \frac{1}{3B}\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3B}\frac{2}{3V}\left(\frac{\partial U}{\partial T}\right)_V = \frac{2}{9B}c_V{}^{el}$$

So, net thermal expansion co-efficient is:

$$\boxed{\alpha = \alpha^{ion} + \alpha^{el} = \frac{\gamma c_V{}^{ion}}{3B} + \frac{2}{9B}c_V{}^{el} = \frac{1}{3B}\left(\gamma c_V{}^{ion} + \frac{2}{3}c_V{}^{el}\right) - - - (6)}$$

$\gamma \sim$ 1-2, so the electronic term will make significant contribution only when electronic specific heat is large as compared to the lattice specific heat i.e. at temperatures below 10K.

In metals α vanishes linearly with temperature (dominated by α^{el}) while in insulators it vanishes as T^3 (determined by α^{ion}) – these have been experimentally verified.
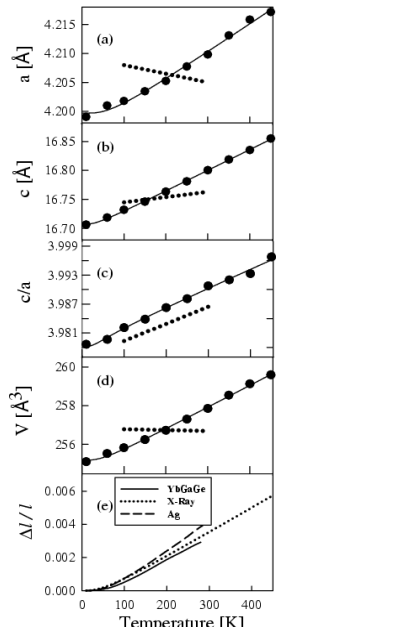

Figure 11: Temperature dependence of the (a,b) lattice constants, (c) the c/a ratio and (d) the unit cell volume in YbGaGe. Solid lines are fits to Debye model. Ref: G. K. White *Proc. Roy. Soc. London,* **A286,** 204 (1964).
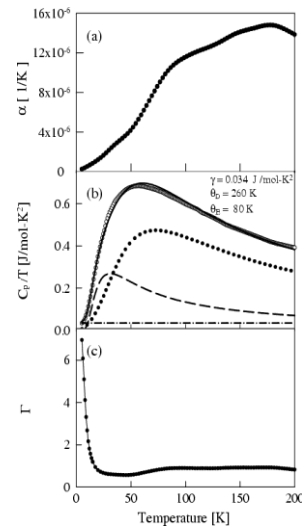

Figure 12: (a) Temperature dependence of thermal-expansion coefficient α in YbGaGe (b) Temperature dependence of the heat capacity (open symbols) together with the fitting results (solid line) using Debye phonons with the cut off energy of T_D =260K (dotted line); Einstein phonons centered at T_E = 80K (dashed line) on top of the electronic contribution (dash-dotted line) (c) Temperature dependence of Grüneisen parameter. Ref: G. K. White *Proc. Roy. Soc. London,* A286, 204 (1964).

Thermal conductivity

Without collisions there will be no thermal equilibrium, thermal conductivity will be infinite. For harmonic crystal, there is no collision between phonons; only factors limiting the thermal conductivity are geometrical scattering of phonons by the boundary of the crystal and defects in the crystal.

In ordinary gas two particle collision lead to equilibrium, so how does phonon 'gas' differ from the ordinary gas of molecules?

The main difference is that phonon number need not be conserved – so the analogue of phonon gas is not molecules confined in a vessel (see fig. 4) but rather molecules flowing freely through a tube carrying heat across it without any temperature gradient (see fig. 5).
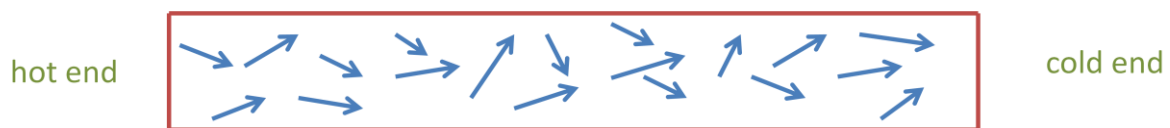

Figure 13: Gas flow in a closed tube: no mass flow permitted - energy transported from left to right with no thermal gradient - finite thermal conductivity.
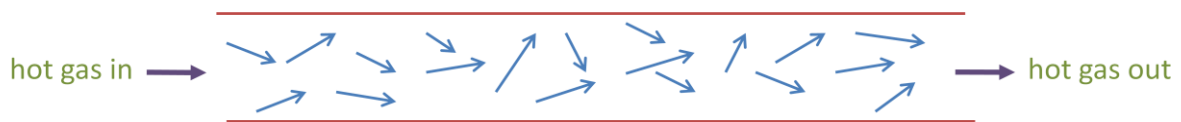

Figure 14: Gas flow in open tube: energy transported from left to right with no thermal gradient; thermal conductivity infinite

Consider a rod with the two ends maintained at different temperatures. Thermal conductivity κ is defined as the energy transmitted per unit time across unit area per unit temperature gradient.

$$j = -\kappa \frac{dT}{dx}$$

Dependence of κ on dT/dx implies that the thermal energy transfer is a random process involving scattering – introduces mean free path of phonons in the problem. If the process was ballistic, it would involve only dT between the two ends and not the gradient.

We make a relaxation time kind of approximation: the energy contributed by a phonon at a point is decided by where it has had its last collision. So phonons coming from the high temperature end bring more energy than those coming from the low temperature end. Thus, although there is no net number flux, there can be energy flux travelling from the high T end to the low T end.

Temperature at two ends of a one dimensional rod are $(T+\Delta T)$ and T. The temperature at point x is $T(x)$ and the energy at that point is $E(T[x])$. Half the phonons arriving at a point x

are from the high temperature side each carrying an energy $E(T[x- v_x\tau])$, the other half are from the low-T side and carry an energy $E(T[x+v_x\tau])$. Number of phonons arriving at x per unit time per unit area of cross section is $1/2 \, n \, v_x$, where v_x is the phonon speed in x direction. So net energy flux is:

$$j = \frac{1}{2}nv[E(T[x - v_x\tau]) - E(T[(x + v_x\tau)])] = nv_x{}^2\tau\frac{dE}{dT}\left(-\frac{dT}{dx}\right) = -\frac{1}{3}v^2\tau C_v\frac{dT}{dx}$$

$$\kappa = \frac{1}{3}C_v v^2\tau = \frac{1}{3}C_v lv = \frac{1}{3}C_v v^2\tau --- (7)$$

Lattice thermal conductivity of a crystal is determined by two contributions – specific heat and the mean free path of phonons.

Mean free path of phonons is determined two factors: (a) rate of scattering with other phonons and (b) scattering with static impurities or boundaries of the crystal. Scattering form other phonons can be classified into two types depending on the energies involved:
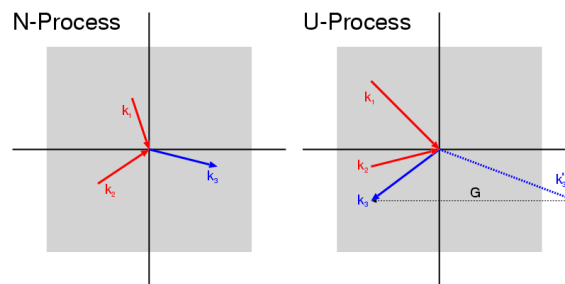

Figure 15: (left figure) N-process and (right figure) U-process in phonon scattering

N-process: Consider a three-phonon scattering process. If the initial energies of the phonons involved in the process is small as compared to $\hbar\omega_D$ then (since energy is conserved in the process) the final energies of the phonons will also be small as compared to $\hbar\omega_D$. Thus all the wave-vectors involved in the process will small as compared to the reciprocal wave-vector (which is of the same order as the Debye wave-vector). So, in the equation;

$$k_1 + k_2 = k_3 + G$$

the reciprocal lattice vector G is identically zero; crystal momentum is exactly conserved in the process. This is called a normal process or an *N-process*. Such processes cannot change the crystal momentum. In equilibrium the net crystal momentum

$$\sum_{k,p}\hbar k n_p(k) = \sum_{k,p}\frac{\hbar k}{e^{\beta\hbar\omega_p(k)} - 1} = 0$$

Thus if we start with a non-equilibrium phonon distribution, N-processes cannot bring about thermal equilibrium – it can be shown that if there were only N-processes the thermal conductivity of a crystal would have been infinite.

Analogous to the flow of gas in a cylinder with open ends – thermal energy is transported from one end to another without a thermal gradient.

U-process (Umklapp process): For scattering events where the initial phonon momenta are not small as compared to k_D; the value of the reciprocal lattice vector required to bring back the final phonon state into the first Brillouin zone will be non-zero. Hence for such scattering events crystal momentum is conserved only to within a reciprocal lattice vector and this gives finite thermal resistance to the crystal.

How does the phonon mean free path depend on temperature?

High temperature limit ($T/T_D \gg 1$): The probability that a phonon will suffer a collision is directly proportional to the number of other phonons present. At high T, the equilibrium number of phonons is:

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \cong \frac{k_B T}{\hbar \omega}$$

So the mean free path should go as 1/T. Since C_V is constant in this temperature range, the entire temperature dependence of κ comes from temperature dependence of l. Thus,

$$\kappa \sim 1/T$$

Low temperature limit ($T/T_D \ll 1$): Thermal conductivity of a perfect infinite crystal is finite at low temperatures only because of U-processes. For U-process at least one of the initial phonons must have energy comparable to $\hbar \omega_D$. At $T/T_D \ll 1$, the number of such phonons is

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \cong \frac{1}{e^{T_D/T} - 1} \sim e^{-T_D/T}$$

As T decreases, the number of phonons that can take part in U-process falls exponentially. Thermal conductivity is inversely proportional to the number of U-processes, so the effective relaxation time for thermal scattering goes as:

$$\tau \sim e^{T_D/T}$$

Thus as T decreases, κ shows an exponential increase till the mean free path becomes comparable to that due to scattering from static imperfections/boundary of the crystal. Below this temperature, l becomes T independent and κ is determined solely by the temperature dependence of specific heat.

So, at very low temperatures, thermal conductivity will be determined by C_v and will go as T^3. As temperature increases, U-processes begin to appear and will gradually make the mean free path smaller than the sample dimensions. Thermal conductivity at this point reach a maximum and then begin to fall exponentially with temperature as $e^{T_D/T}$. At higher

temperatures, the exponential fall is replaced by a slower *1/T* power law fall of κ with increasing *T*.
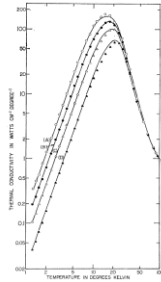

Figure 16: Thermal conductivity of LiF; Mean crystal widths: (A) 7.25 mm, (B) 4.00 mm, (C) 2.14 mm, (D) 1.06 mm. Ref: P. D. Thacher *Phys. Rev*. 156, 975–988 (1967).
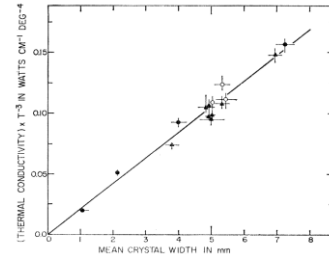

Figure 17: Low-temperature thermal conductivity K divided by T³ and plotted against mean crystal width. Ref: P. D. Thacher *Phys. Rev*. 156, 975–988 (1967).

Phonons – measuring dispersion relations

By either neutron scattering or EM wave scattering.

For neutrons: $E=p^2/2m$; For phonons: $E=pc$.

Focus on neutron scattering:

They are charge neutral and interact only with the ion core. The interaction with electrons is only through weak magnetic coupling of their magnetic moment with that of the electrons.

Neutrons incident with energy $E = \frac{p2}{2m}$ - interact with the lattice -emerge with energy $\acute{E} = \frac{\acute{p}2}{2m}$

Initial phonon number n_{ks}, final phonon number $\acute{n}_{ks}$

From energy conservation:

$$E + \hbar \sum \omega_s(k)n_{ks} = \acute{E} + \hbar \sum \omega_s(k)\acute{n}_{ks}$$

$$\acute{E} = E - \hbar \sum \omega_s(k)(\acute{n}_{ks} - n_{ks}) = E - \hbar \sum \omega_s(k)\Delta n_{ks} - (1)$$

From momentum conservation:

$$\vec{p}\,' = \vec{p} - \hbar \sum \vec{k}\Delta n_{ks} + \hbar\vec{G} - (2)$$

Zero phonon scattering process Δn=0:

$$\vec{p}\,' = \vec{p} + \hbar\vec{G}$$

$$\vec{K}\,' = \vec{K} + \vec{G} \; ; p = \hbar K \text{ and } \acute{p} = \hbar\acute{K}$$

This is the Laue condition for reflection of a plane wave incident on the crystal – no new information.

One phonon scattering process $\Delta n = \pm 1$:

Consider the case where one phonon is absorbed, $\Delta n = 1$

$$E' = E + \hbar\omega_s(k)$$

$$\vec{p}' = \vec{p} + \hbar\vec{k} + \hbar\vec{G}$$

$$\frac{p'^2}{2m} = \frac{p^2}{2m} + \hbar\omega_s\left(\frac{\vec{p}' - \vec{p}}{\hbar} - \frac{\vec{G}}{\hbar}\right) = \frac{p^2}{2m} + \hbar\omega_s\left(\frac{\vec{p}' - \vec{p}}{\hbar}\right)$$

since $\hbar\omega$ is a periodic function in G.

$\vec{p}$ is known. Measure the number of neutrons emerging in a specific direction with a specific momentum, so $\overrightarrow{(p' - p)}$ and $\left(E' - E\right)$ can be calculated.

Tells us that the crystal has a normal mode of frequency $\left(E' - E\right)/\hbar$ and wavevector $\pm(p' - p)/\hbar$ - can map out the entire phonon spectrum this way.

Two phonon scattering process $\Delta n = \pm 2$:

$$E' = E + \hbar\omega_s^1(k) + \hbar\omega_s^2(k)$$

$$\vec{p}' = \vec{p} + \hbar\vec{k}^1 + \hbar\vec{k}^2 + \hbar\vec{G}$$

Too many unknowns, many possible solution – forms the background of the spectrum. So discrete peaks in the scattering spectrum can be seen only for one-phonon processes; multi-phonon scattering events give a continuous distribution of energies in any direction.
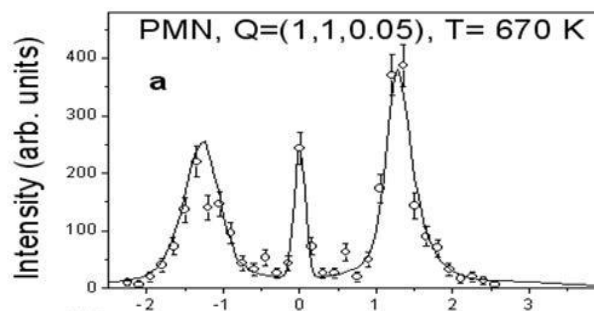
The one-phonon scattering peaks have a finite width. This is due to the fact that the harmonic analysis is only an approximation; phonons have a finite lifetime. If the crystal is in some state at a given time, it will evolve to some other state over time as the phonons are not the steady state solutions of the exact Hamiltonian but only an approximate one. The finite lifetime τ gives an energy uncertainty $\hbar/\tau$ in the peak positions.