Chapter 5

Phonons II: Thermal Properties

PHYS 432
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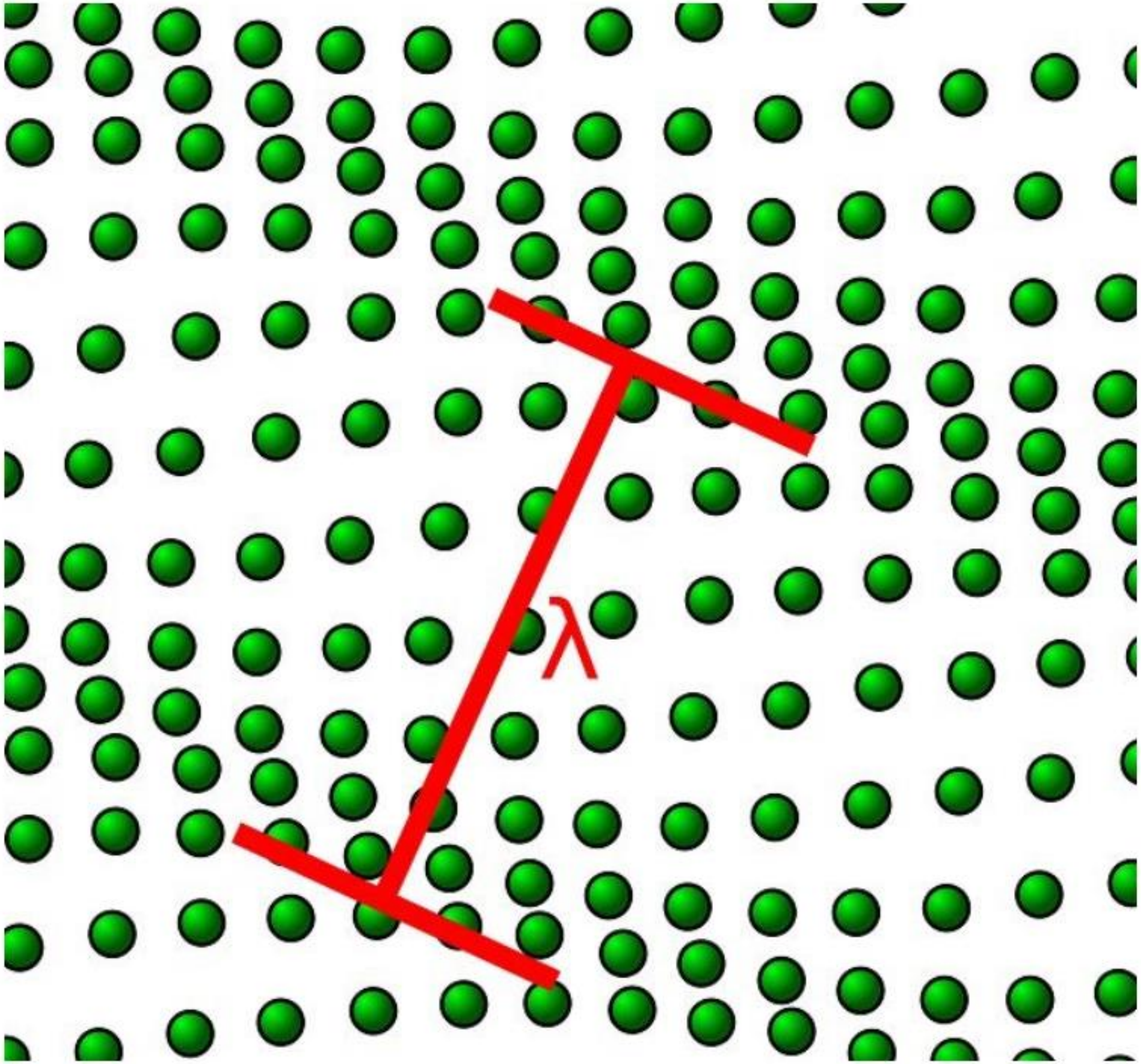
- PHONON HEAT CAPACITY
  - Planck distribution
  - Normal mode enumeration
  - Density of states in one dimension
  - Density of states in three dimensions
  - Debye model for density of states
  - Debye T^3 law
  - Einstein model of the density of states
  - General result for $D(\omega)$
- ANHARMONIC CRYSTAL INTERACTIONS
  - Thermal expansion
- THERMAL CONDUCTIVITY
  - Thermal resistivity of phonon gas
  - Umklapp processes
  - Imperfections

Thermal Phonons

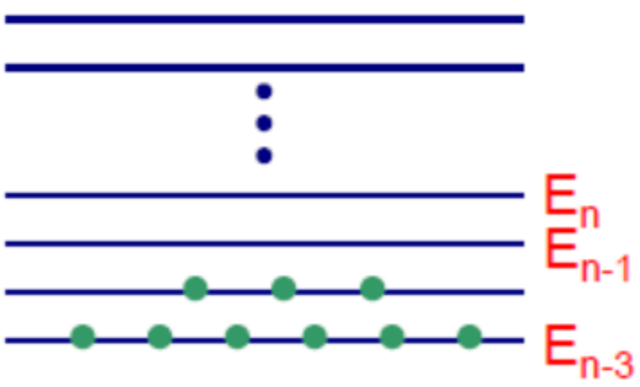
- Phonons dominate thermal properties of materials and affect the electrical transports of conductors by scatterings of electrons.



Thermal Phonons

Phonon generations : How are phonons created or excited in a crystal?

- External perturbations – vibrations or sound transducer
- Scattering of particles – energy transferred into lattice vibrations
- Thermal energy ($K_B T$) – excited at any finite temperature ($T \neq 0K$)



Probability of occupancy at temperature T, $P_n = P_0 e^{-n\hbar\omega/k_B T}$ (Boltzmann factor).

Planck Distribution

- How can we include energies of all phonons in the total energy of the crystal?

- We have to establish rules for counting how many phonons are active at a certain temperature, and then figure out how much energy goes into each phonon mode.

- Consider a set of identical harmonic oscillators in thermal equilibrium. The ratio of the number of oscillators in their (n + 1)th quantum state of excitation to the number in the nth quantum state are determined by the Boltzmann distribution function.

$$N_{n+1}/N_n = e^{-\hbar\omega/\tau}$$

classical physics
(Boltzmann factor)

$$\tau = k_B T$$

Planck Distribution

Let $\quad {}^{N_{n+1}}/_{N_n} = e^{-\hbar\omega/\tau} = c$

$$\Rightarrow N_n = c^n N_0$$

The fraction of the total number of oscillators in the nth quantum state is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{c^n N_0}{\sum_{s=0}^{\infty} c^s N_0} = \frac{c^n}{\sum_{s=0}^{\infty} c^s} = \frac{e^{-n\hbar\omega/\tau}}{\sum_{s=0}^{\infty} e^{-s\hbar\omega/\tau}}$$

Which is the occupation of energy level n: (probability of oscillator being in level n)

Planck Distribution

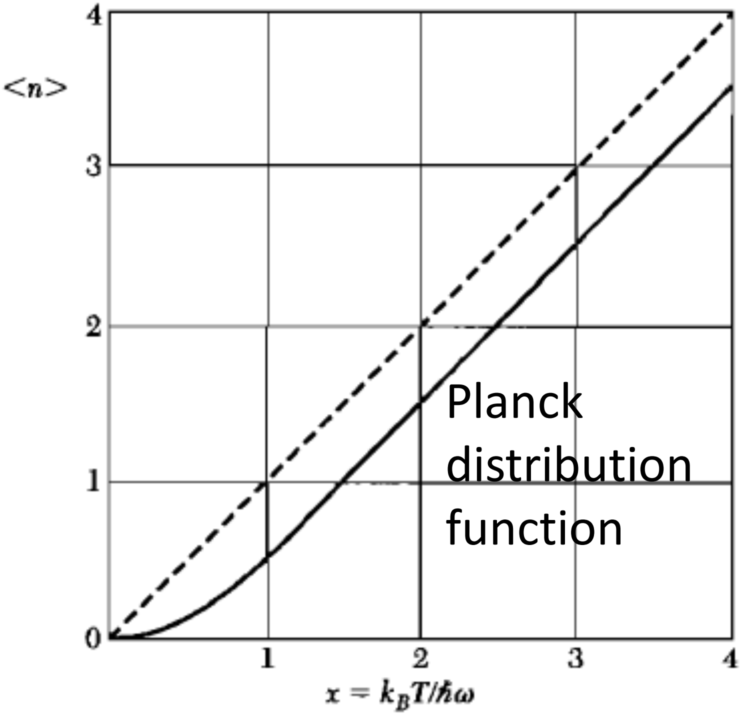
- The average number of phonons excited per mode at ω is

$$< n > = \frac{\sum_s^\infty s\, e^{-s\hbar\omega/\tau}}{\sum_s^\infty e^{-s\hbar\omega/\tau}}$$

- Using the following Tylor series

$$\sum_s x^s = \frac{1}{1-x}\ ; \qquad \sum_s s x^s = x\frac{d}{dx}\sum_s x^s = \frac{x}{(1-x)^2}\ ,$$

$$< n > = \frac{e^{-\hbar\omega/\tau}}{1 - e^{-\hbar\omega/\tau}} = \frac{1}{e^{\hbar\omega/\tau} - 1}$$



Planck distribution function

- PHONON HEAT CAPACITY
- Normal mode enumeration
- Density of states in one, two and three dimensions
- Debye model for density of states

Heat Capacity

- Heat capacity is the measure of how much energy it takes to raise the temperature of a unit mass of an object by a certain amount.

- We know two types of heat capacities: constant volume, C_V, and constant pressure, C_P .

- For an ideal gas $C_P = C_V + R$.

- For solids $C_P = C_V + 9\alpha^2 BVT$, where α is the temperature coefficient of linear expansion, V the volume of the sample, and B the bulk modulus.

- The fractional difference between C_p, and C_V, is usually small in solids and often may be neglected. As $T \to 0$ we see that $C_p = C_V$, provided α and B are constant.

Classical Heat Capacity

For a solid with N atomic oscillators:

$$\overline{E} = N\overline{E}_1 = 3Nk_BT$$

Total energy per mole:

$$\frac{\overline{E}}{n} = \frac{3Nk_BT}{n} = 3N_Ak_BT = 3RT$$

Heat capacity at constant volume per mole is:

$$C_V = \frac{d}{dT}\left(\frac{\overline{E}}{n}\right)_V = 3R \approx 25\,\frac{J}{mol\;K}$$

This is Dulong and Petit law (1819) and approximately obeyed by most solids at high T.

But by the middle of the 19th century it was clear that $C_V \rightarrow 0$ as $T \rightarrow 0$ for solids.

So…what was happening?

Phonon Heat Capacity

- The heat that goes into a solid to raise its temperature shows up as internal vibrational energy U (phonons).
- For metals at low temperatures, the heat capacity is the sum of electronic heat capacity (γT) and phonon heat capacity (βT^3).

$$C = C_{electron} + C_{phonon} = \gamma T + \beta T^3$$

- To determine C_V we need to determine U(T) first.
- Then we can calculate $C_V = (\partial U/\partial T)_V$.

- In calculating U we need to consider the following:

– (1) how many different polarization of vibration are there;

– (2) what is the average number of phonons existing at any T for each polarization of vibration;

– (3) what is the average energy of each phonon.

Phonon Heat Capacity

- The contribution of the phonons to the heat capacity of a crystal is also called the lattice heat capacity and is denoted by C_{lat}.

- The total energy of the phonons at a temperature τ $(= K_B T)$ in a crystal may he written as the sum of energies over all phonon modes $(\omega_{K,p})$ and polarizations (p: TA, TO, LA, LO waves).

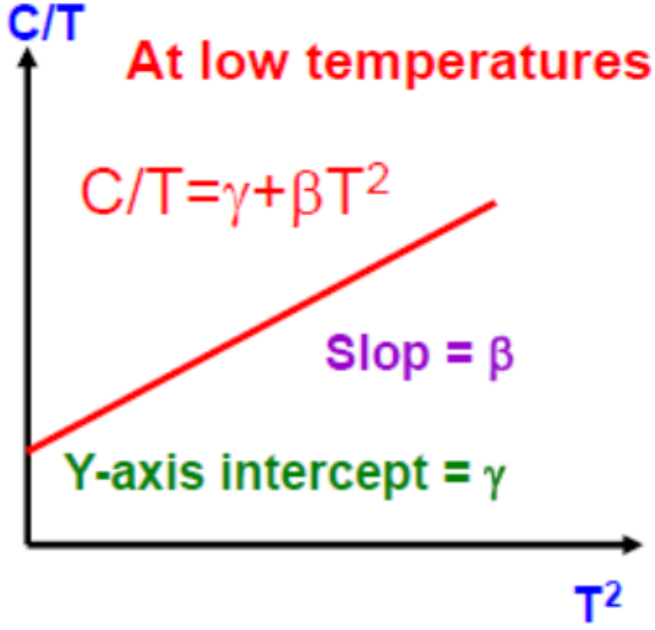
$$U_{lat} = \sum_K \sum_p < n_{K,p} > \hbar\omega_{K,p}$$

$$< n_{K,p} > = \frac{1}{e^{\hbar\omega_{K,p}/\tau} - 1}$$

- For a metal, $C = \gamma T + \beta T^3$

electronic term

lattice term



$C=dU/dT$

Normal Mode Enumeration

- The energy of a collection of oscillators of frequencies $\omega_{K,p}$, in thermal equilibrium is found to be

$$U_{lat} = \sum_{K}\sum_{p} \frac{\hbar\omega_{K,p}}{e^{\hbar\omega_{K,p}/\tau} - 1}$$

- It is convenient to replace the summation over K by an integral.

- If the crystal has $D_p(\omega)d\omega$ modes of a given polarization p in the range ω to $\omega + d\omega$, then the energy can be expressed as

$$U_{lat} = \sum_{p} \int d\omega_K D_p(\omega_K) \frac{\hbar\omega_K}{e^{\hbar\omega_K/\tau} - 1}.$$

- It is understood that ω is a function of K. The subscripts K and *lat* from ω_K and U_{lat} will be dropped.

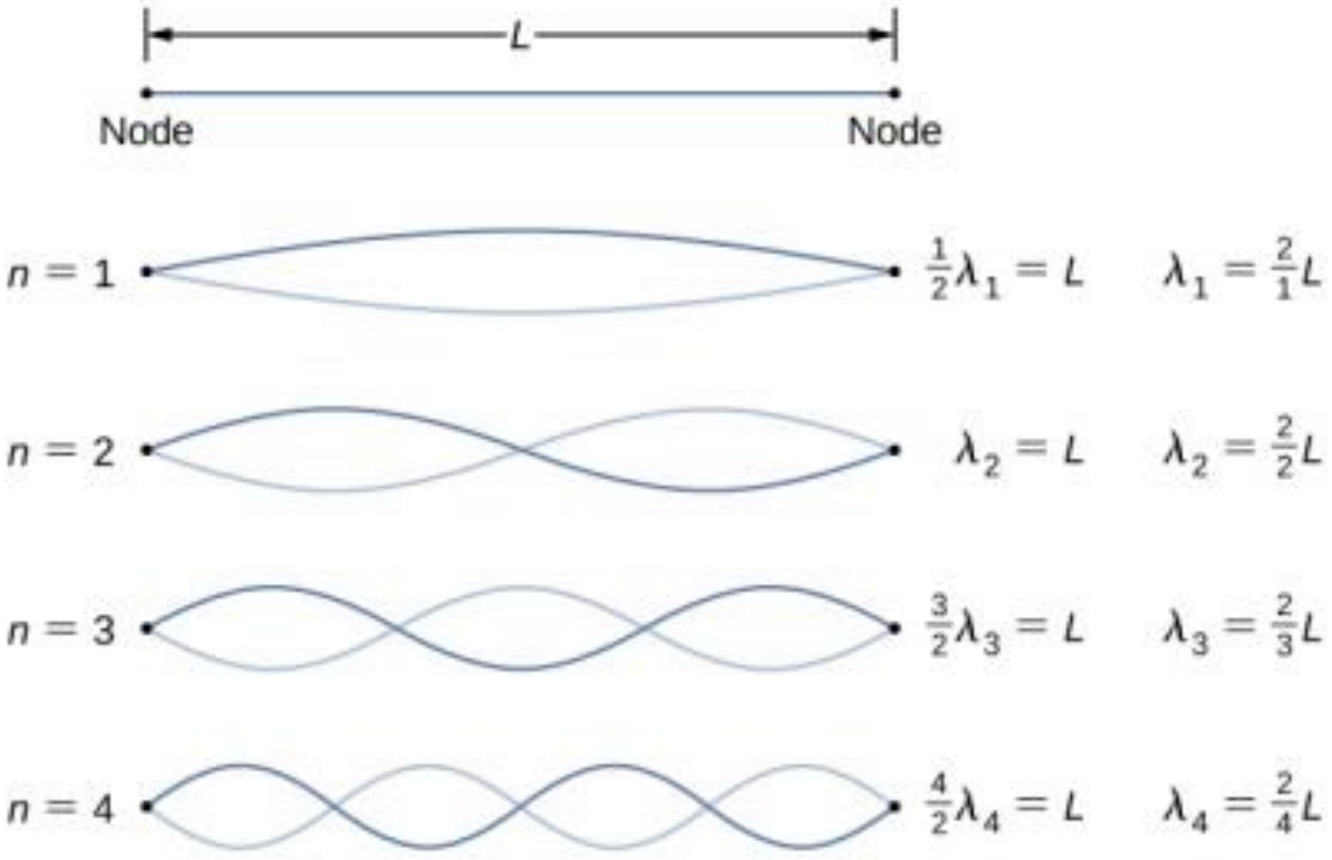
Normal Mode Enumeration

- The lattice heat capacity is found by differentiation with respect to temperature T.

$$C = \frac{\partial U}{\partial T} = k_B \sum_p \int d\omega \; D_p(\omega) \frac{\left(\frac{\hbar\omega}{\tau}\right)^2 \; e^{\hbar\omega/\tau}}{(e^{\hbar\omega/\tau}-1)^2}$$

- **The central problem is to find $\mathbf{D}(\boldsymbol{\omega})$,** the number of modes per unit frequency range. This function is called the density of modes or density of states.

Standing waves on a string



$$\lambda_n = \frac{2}{n}L \quad n = 1, 2, 3, 4, 5 \ldots$$

$$f_n = n\frac{v}{2L} = nf_1 \quad n = 1, 2, 3, 4, 5 \ldots$$

$$f_n = \frac{nv}{2L} = \frac{n}{2L}\sqrt{\frac{T}{\mu}}$$

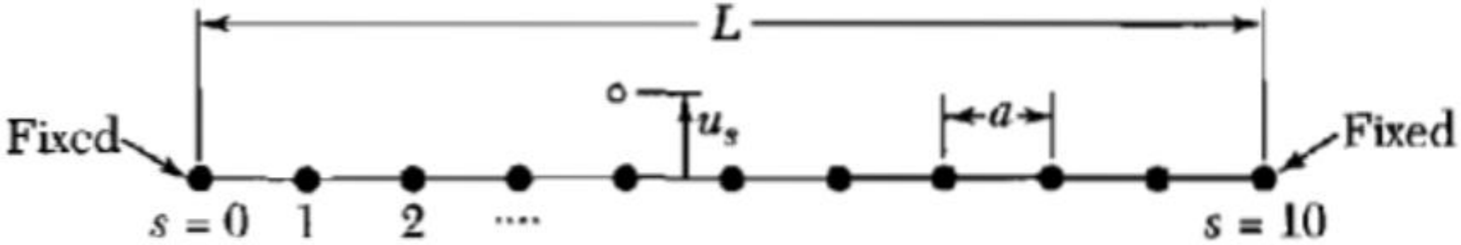
Tension on the string

mass per unit length

length of string

Density of States in One Dimension: Chain with Fixed Ends

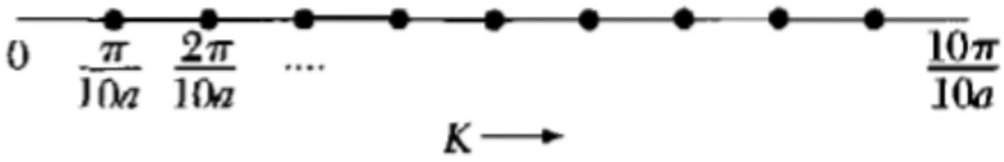
- Consider the boundary value problem for vibrations of a one-dimensional line of length L $(= 10a)$ carrying 11 particles at separation a.



- The particle displacements in the normal modes for longitudinal or transverse displacements are of the form $\boldsymbol{u_s \propto \sin(sKa)}$. This form is automatically zero at the atom at the end s = 0, and the standing waves we choose K to make the displacement zero at the other end s=10.

Density of States in One Dimension: Chain with Fixed Ends

- In the following reciprocal lattice, the dots are not atoms but are the allowed values of K. Of the 11 particles on the line, only 9 are allowed to move, and their most general motion can be expressed in terms of the 9 allowed values of K. This quantization of K has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.



$\sin(sKa) = 0$ → $K(sa) = KL = n\pi$ $\quad$ $n = 1,2,3 \ldots 10$

- Each normal vibrational mode of polarization *p* has the form of a standing wave, where u_s is the displacement of the particle s:

$$u_s = u(0)e^{-i\omega_{K,p}t}\sin(sKa)$$

Density of States in One Dimension: Chain with Fixed Ends

- The wavevector K is restricted by the fixed-end boundary conditions to the values K= π/L, 2π/L, 3π/L, …, 10π/L.

$$u_s = u(0)e^{-i\omega_{K,p}t}\sin(s\pi/10)$$

- For the one-dimensional line there is one mode for each interval ΔK = π/L, so that the number of modes per unit range of K (dN/dK) is L/π for K ≤ π/a, and 0 for K > π/a.

- The total number of modes (N) with the above condition is

$$\frac{dN}{dK}dK = \frac{10a}{\pi}\frac{\pi}{a} = 10$$

Density of States in One Dimension: Chain with Fixed Ends

- Similarly, if we consider a chain of N+1 atoms with the two ends fixed. There will be N-1 atoms allowed to move. The two atoms at the ends will remain at rest.

- The length of the chain is L=N*a*.

- The wavevector K is restricted by the fixed-end boundary conditions to the values K= π/L, 2π/L, 3π/L, …, (N-1)π/L.

- The solution for K = Nπ/L = π/*a* = K_{max} has $u_s \propto \sin(s\pi)$; this permits no motion of any atom, because $\sin(s\pi)$ vanishes at each atom.

- There are $N-1$ allowed independent values of K, which is the number of particles that are allowed to move.

- Each allowed value of K is associated with a standing wave.

Density of States in One Dimension: Chain with Fixed Ends

- For the one-dimensional line there is one mode for each interval ΔK = π/L, so that the number of modes per unit range of K is L/π for K ≤ π/*a*, and 0 for K > π/*a*.

- The total number of modes in the interval dK is (N values of K, as K=0, and N-1 other values)

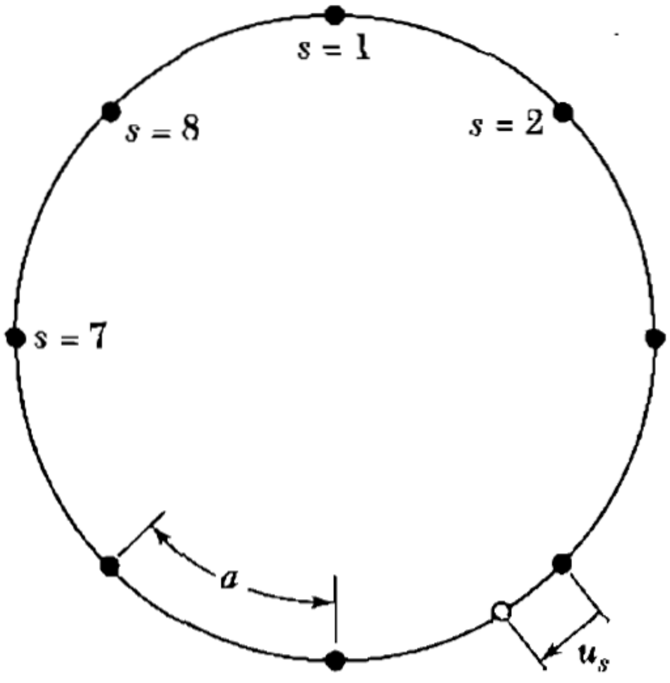
$$N = \frac{L}{\pi} dK$$

- The density of states $D(\omega)$ is defined such that $D(\omega)d\omega$ gives this number of modes in the frequency range dω.

$$D(\omega)d\omega = \frac{L}{\pi} dK = \frac{L}{\pi}\frac{dK}{d\omega} d\omega$$

- Density of states in one-dimensional periodic boundary conditions
- Density of states in two dimensions
- Density of states in three dimensions
- Debye model for density of states
- Debye T^3 law

Density of States in One Dimension: Periodic Boundary Conditions



- For a chain of N atoms with periodic boundary conditions the solutions should be

$$\boldsymbol{u_{s+N} = u_s}$$

- The displacements will be of the form

$$\mathbf{sin}(\boldsymbol{sKa}) \quad \mathbf{or} \quad \mathbf{cos}(\boldsymbol{sKa})$$

- with

$$\boldsymbol{NKa = \pm n2\pi} \;\boldsymbol{\rightarrow K = \pm\frac{n2\pi}{Na}} \boldsymbol{\rightarrow} \mathbf{sin}\left(\boldsymbol{s\frac{n2\pi}{8}}\right)$$

- For the N=8, the allowed independent values of K are 0, $\pm 2\pi/8a$, $\pm 4\pi/8a$, $\pm 6\pi/8a$, and $\pm 8\pi/8a$.

- $\mathbf{sin}(\boldsymbol{sKa}) = 0$ for K= $\pm 8\pi/8a$, so it should be considered one value of K.

- So, there are 8 independent values of K, 0, $\pm 2\pi/8a$, $\pm 4\pi/8a$, $\pm 6\pi/8a$, and $8\pi/8a$. which is equal to the number of particles.

Density of States in One Dimension: Periodic Boundary Conditions

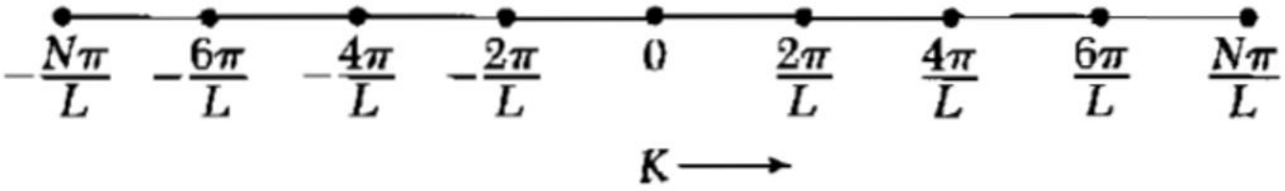


Figure 5 Allowed values of wavevector K for periodic boundary conditions applied to a linear lattice of periodicity $N = 8$ atoms on a line of length L. The $K = 0$ solution is the uniform mode. The special points $\pm N\pi/L$ represent only a single solution because $\exp(i\pi s)$ is identical to $\exp(-i\pi s)$; thus there are eight allowed modes, with displacements of the sth atom proportional to 1, $\exp(\pm i\pi s/4)$, $\exp(\pm i\pi s/2)$, $\exp(\pm i3\pi s/4)$, $\exp(i\pi s)$.

- If we had taken the displacement solutions of the form $\boldsymbol{e^{isKa}}$, then the allowed independent values of K would be 0, $\pm 2\pi/8a$, $\pm 4\pi/8a$, $\pm 6\pi/8a$, and $8\pi/8a$. Which are 8 values, equal to the number of the particles.

- The number of independent values of K for $\boldsymbol{sin(sKa)}$, $\boldsymbol{cos(sKa)}$, *and* $\boldsymbol{e^{isKa}}$ is same, which indicates that the number of independent values of K does not depend on the choice of displacement solution in a normal mode.

Density of States in One Dimension: Periodic Boundary Conditions

- This method gives the same number of modes with an interval $\Delta K = 2\pi/L$ between consecutive values of K.

- The number of modes per unit range of K is $L/2\pi$ for $-\pi/a < K \leq \pi/a$, and 0 otherwise.

- The total number of modes in the interval dK is $\frac{\mathbf{L}}{\mathbf{2\pi}}\mathbf{dK} = \frac{\mathbf{L}}{\mathbf{2\pi}}\frac{\mathbf{2\pi}}{\boldsymbol{a}} = \mathbf{N}$.

- The density of states $D(\omega)$ is defined such that $D(\omega)d\omega$ gives this number of modes in the frequency range $d\omega$.

- Multiplying by 2 for the positive and negative values of K.

$$D(\omega)d\omega = 2\left(\frac{L}{2\pi}\right)\frac{dK}{d\omega}\,d\omega = \left(\frac{L}{\pi}\right)\frac{1}{d\omega/dK}\,d\omega$$

Density of States in One Dimension: Periodic Boundary Conditions

- The group velocity $\frac{d\omega}{dK}$ can be obtained from the dispersion relation.
- When group velocity is zero, there is a singularity in D(ω) (Van Hove singularities).

- Li, Guohong et al. "Observation of Van Hove singularities in twisted graphene layers." ***Nature physics*** 6, no. 2 (2010): 109-113. https://www.nature.com/articles/nphys1463

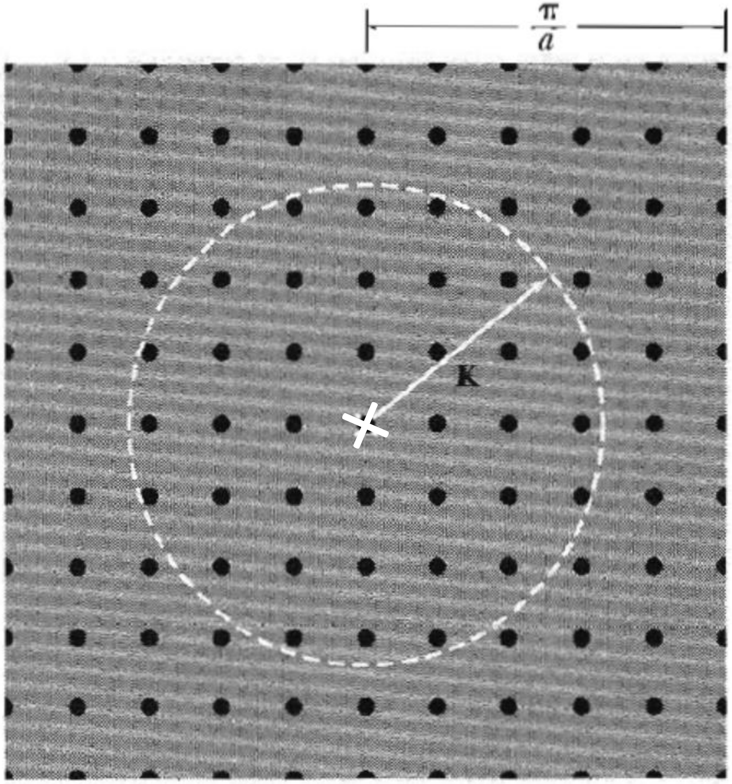
Density of States in Two Dimensions: Periodic Boundary Conditions

Figure shows the allowed values in Fourier space of the phonon wavevector K for a square lattice of lattice constant a, with periodic boundary conditions applied over a square of side L = 10a.

The uniform mode (K=0) is marked with a cross; center of the circle.

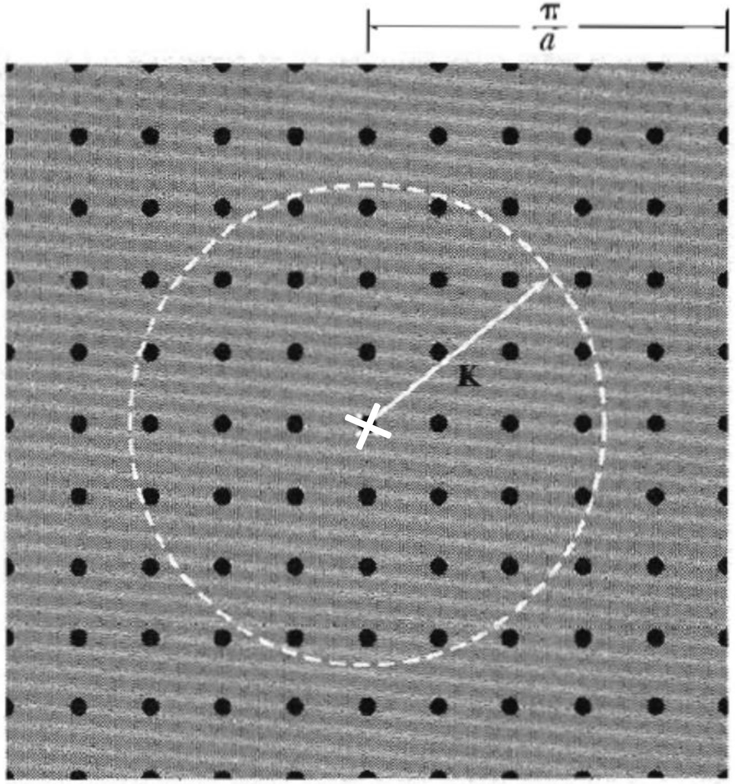
There is one allowed value of K per area in K space.

$$\left(\frac{2\pi}{10a}\right)^2 = \left(\frac{2\pi}{L}\right)^2$$



Density of States in Two Dimensions: Periodic Boundary Conditions

The allowed values of K per unit area of K space is $\left(\frac{L}{2\pi}\right)^2$ for
$-\pi/a < K_x \leq \pi/a$ and $-\pi/a < K_y \leq \pi/a$,
and 0 otherwise.



The total number of modes with wavevector less than K is found to be $\left(\frac{L}{2\pi}\right)^2$ time the area of the circle of radius K i.e. $N = \left(\frac{L}{2\pi}\right)^2 \pi K^2$.

$$N = D(\omega)d\omega$$

$$D(\omega) = \frac{dN}{d\omega} = \frac{d}{d\omega}\left[\left(\frac{L}{2\pi}\right)^2 \pi K^2\right]$$

$$D(\omega) = \left(\frac{L}{2\pi}\right)^2 2\pi K \frac{dK}{d\omega}$$

Density of States in Three Dimensions

- We apply periodic boundary conditions over N^3 primitive cells within a cube of side L, so that K is determined by the condition

$$e^{[i(K_x x+K_y y+K_z z)]}=e^{[i(K_x(x+L)+K_y(y+L)+K_z(z+L))]}$$

$$e^{[i(K_x x+K_y y+K_z z)]}=e^{[i(K_x x+K_y y+K_z z)]}e^{[i(K_x L+K_y L+K_z L)]}$$

$$e^{[i(K_x L+K_y L+K_z L)]}=1$$

$$K_x,K_y,K_z=0;\ \pm\frac{2\pi}{L};\ \pm\frac{4\pi}{L};\ldots;\ \pm\frac{N\pi}{L}$$

- Therefore, there is one allowed value of K per volume $\left(\frac{2\pi}{L}\right)^3$ in K space.

- Or the allowed values of K per unit volume of K space, **for each polarization and for each branch** is

$$\left(\frac{L}{2\pi}\right)^3=\frac{V}{8\pi^3}$$

Density of States in Three Dimensions

- For each polarization type, the total number of modes with wavevector less than K is found to be $\left(\frac{L}{2\pi}\right)^3$ times the volume of a sphere of radius K.

$$N = \left(\frac{L}{2\pi}\right)^3 \left(\frac{4\pi K^3}{3}\right) = \frac{VK^3}{6\,\pi^2}$$

- The density of states for each polarization is

$$D(\omega)d\omega = \left(\frac{L}{2\pi}\right)^3 4\pi K^2\, dK$$

$$D(\omega)d\omega = \frac{dN}{d\omega} = \frac{VK^2}{2\pi^2}\left(\frac{dK}{d\omega}\right)d\omega$$

- Debye model for density of states
- Debye T^3 law
- Einstein model of the density of states
- General result for $D(\omega)$

Debye Model for Density of States

- In Debye approximation and in classical elastic continuum, **for each polarization**, the velocity of sound is considered constant.

$$\omega = vK$$

- The density of states for each polarization thus becomes.

$$D(\omega) = \frac{VK^2}{2\pi^2}\left(\frac{dK}{d\omega}\right) = \frac{VK^2}{2\pi^2}\left(\frac{1}{v}\right)$$

$$D(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v^3}\right)$$

- The total density of states for **three polarizations: one longitudinal and two transverse acoustical** is

$$D(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right)$$

Debye Model: Cutoff frequency and wavevector

- Consider a monoatomic lattice with N primitive cells in a specimen.
- For a single polarization the total number of acoustic phonon modes is N.

$$N = \left(\frac{L}{2\pi}\right)^3 \left(\frac{4\pi K^3}{3}\right) = \frac{VK^3}{6\,\pi^2} = \frac{V\omega^3}{6\,\pi^2\ v^3}$$

$$\longrightarrow \quad \omega_D = \left(\frac{6\pi^2 v^3 N}{V}\right)^{1/3} = v\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

$$\longrightarrow \quad \omega_D = vK_D$$

$$\longrightarrow \quad K_D = \left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

- The cutoff wavevector K_D, is the maximum K and corresponds to a cutoff frequencyω_D (maximum frequency) for the N phonon modes.

- At frequencies higher than the cut off frequency the “lattice” unable to “see” the vibration because the wavelength of the vibration is smaller than the basic unit of the atomic arrangement; therefore, the vibration becomes independent from the lattice.

Debye Model for Density of States

- Based on the Debye model the modes of frequency and wavevector larger than ω_D and K_D are not allowed.
- Because the number of modes with $\mathrm{K} \leq K_D$, exhausts the number of degrees of freedom of monatomic lattice.

Debye Model for Density of States

- For a single polarization the lattice energy is

$$U = \int d\omega\, D(\omega) \frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

- Since the density of states for each polarization is $\boldsymbol{D(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v^3}\right)}$, the lattice energy becomes

$$U = \int d\omega \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v^3}\right)\frac{\hbar\omega}{e^{\hbar\omega/\tau} - 1}$$

- **Assuming that the phonon velocity for the one longitudinal and two transverse polarizations is the same,** we multiply the lattice energy by 3 to obtain

$$U = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega\, \frac{\omega^3}{e^{\hbar\omega/\tau} - 1}$$

- Debye model for Heat Capacity
- Debye Model for $T \gg \theta$
- Debye Model for $T << \theta$
- Debye T^3 law
- Einstein Model for Heat Capacity

Debye Model for Heat Capacity

- Let $x = \frac{\hbar\omega}{k_B T}$ and $x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta}{T}$
- Debye temperature is $\theta = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$

$$U = \frac{3V\hbar}{2\pi^2 v^3}\int_0^{\omega_D} d\omega \, \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3}\int_0^{x_D} dx \, \frac{x^3}{e^x - 1} \ ,$$

- For the total number of atoms N, the energy is

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

Debye Model for Heat Capacity

$$C_V = \left.\frac{\partial U}{\partial T}\right|_V = \left(\frac{3V\hbar}{2\pi^2 v^3}\right)\frac{\partial}{\partial T}\left[\int_0^{\omega_D} d\omega \frac{\omega^3}{\exp(\hbar\omega/k_B T)-1}\right]$$

$$= \left(\frac{3V\hbar}{2\pi^2 v^3}\right)\left(-\frac{\hbar}{k_B}\right)\left(-\frac{1}{T^2}\right)\int_0^{\omega_D} d\omega \frac{\omega^4 \exp(\hbar\omega/k_B T)}{\left(\exp(\hbar\omega/k_B T)-1\right)^2}$$

$$= 9Nk_B\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{\left(e^x-1\right)^2}$$

Debye Model for Density of States

- The Debye temperature θ is the temperature of a crystal's highest normal mode of vibration i.e., the highest **temperature** that can be achieved due to a single normal vibration.

- The Debye temperature separates the collective thermal lattice vibration (phonons) from the independent thermal lattice vibration (thermal noise).

- It correlates the elastic properties with the thermodynamic properties such as phonons, thermal expansion, thermal conductivity, specific heat, and lattice enthalpy.

Debye Model for $T \gg \theta$

- For $T \gg \theta$ the heat capacity approaches the classical value of C_V.
- For $T \gg \theta$, $\exp(x) \sim 1 + x$

At high T limit, $x_D = \theta/T \ll 1$

$$\int_0^{x_D} dx\left(\frac{x^3}{e^x-1}\right) \rightarrow \frac{1}{3}(x_D)^3 = \frac{1}{3}\left(\frac{\theta}{T}\right)^3$$

$$\int_0^{x_D} dx\,\frac{x^4 e^x}{\left(e^x-1\right)^2} \rightarrow \frac{1}{3}(x_D)^3 = \frac{1}{3}\left(\frac{\theta}{T}\right)^3$$

i.e., For T >> θ ,

$$\boxed{\begin{array}{l} U \longrightarrow 3Nk_BT \\ C_V \longrightarrow 3Nk_B \end{array}}$$

Dulong and Petit value

Debye T^3 Law (Debye Model for $T \ll \theta$)

- At very low temperatures, $x_D = \frac{\theta}{T} \rightarrow \infty$

$$U = 9Nk_BT\left(\frac{T}{\theta}\right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1}$$

- The integral is

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \int_0^\infty dx\, x^3 \sum_{s=1}^\infty \exp(-sx) = 6 \sum_1^\infty \frac{1}{s^4} = \frac{\pi^4}{15}$$

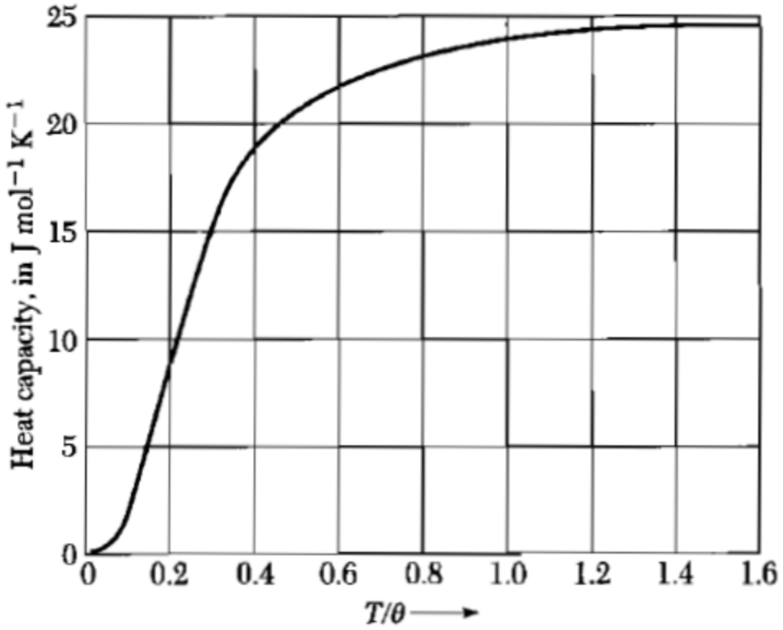
- Use gamma function $\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt$

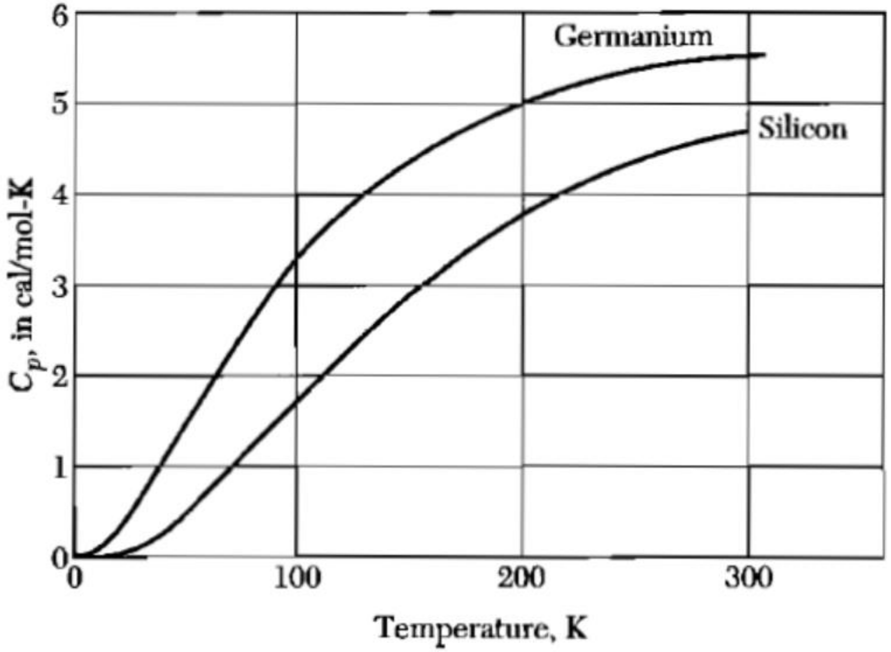
$$U = 3\pi^4 N k_B T^4 / 5\theta^3$$

$$C_V \cong \frac{12\pi^4}{5} Nk_B\left(\frac{T}{\theta}\right)^3 \cong 234\, Nk_B\left(\frac{T}{\theta}\right)^3$$

- This is the Debye T^3 Law.

Debye Model for Heat Capacity





- Heat capacity C_V, of a solid, according to the Debye approximation is shown. The region of the T^3 law is below 0.1θ. The asymptotic value at high values of T/θ is $3R$.

- Heat capacity of silicon and germanium follow the same pattern as predicted by the Debye model.

Debye Model at low T: Theory vs. Expt.

Quite impressive agreement with predicted $C_V \propto T^3$ dependence for Ar! (noble gas solid)

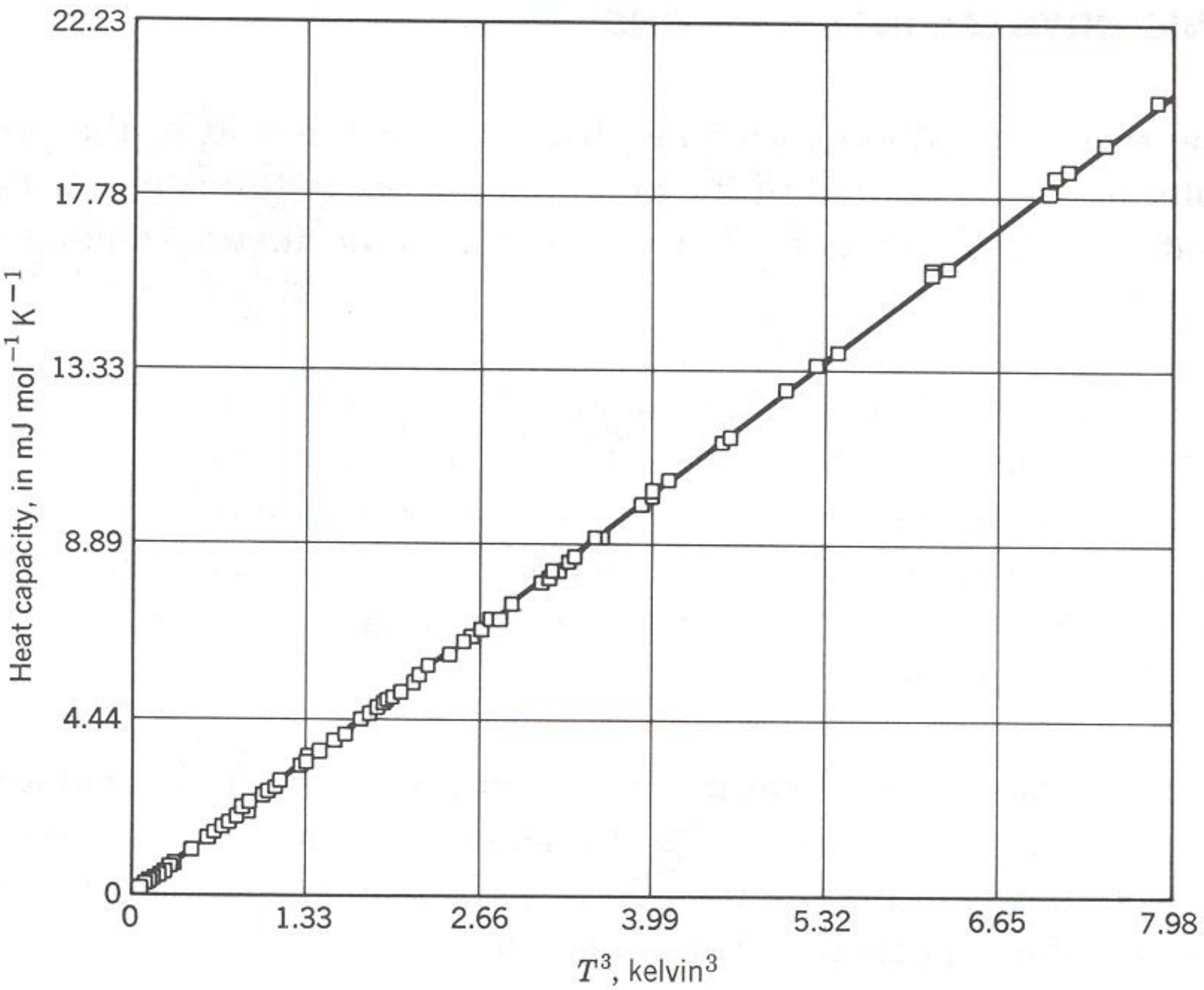
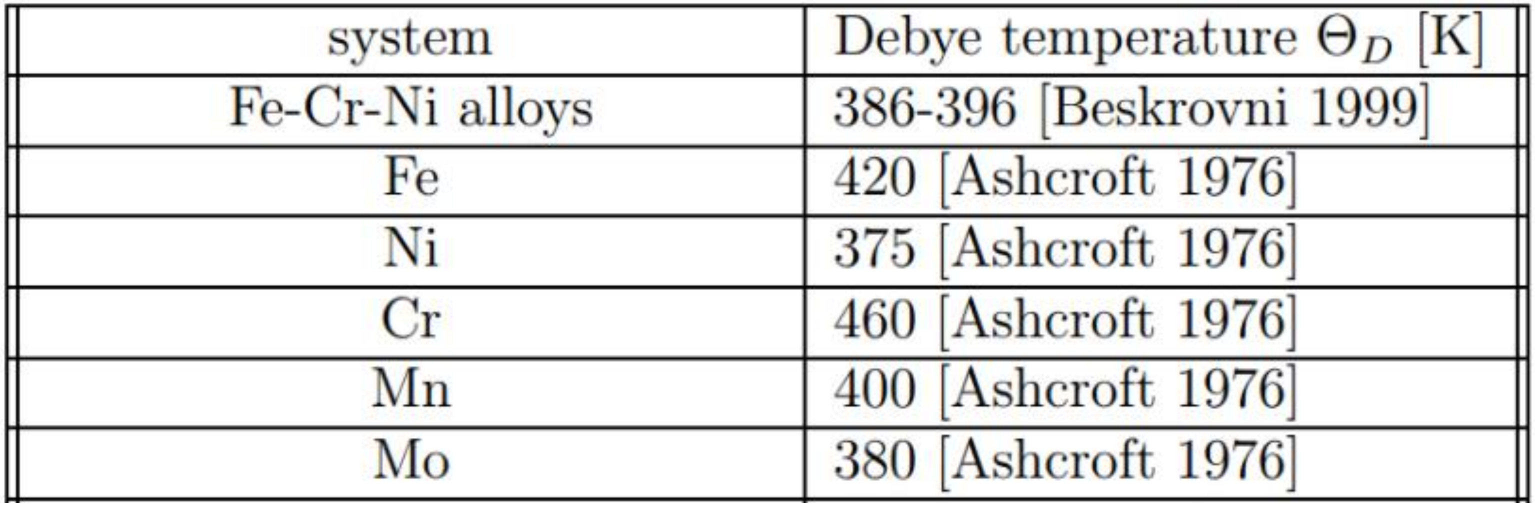


Figure 11 Low temperature heat capacity of solid argon, plotted against T^3. In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta_0 = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

Debye T^3 Law

- At sufficiently low temperature the T^3 approximation is quite good; that when only long wavelength acoustic modes are thermally excited.
- The energy of the short wavelength modes (for which this approximation fails) is too high for them to be populated significantly.
- For actual crystals the temperatures at which the T^3 approximation holds are quite low. It may be necessary to be below $T = \theta/50$ to get reasonably pure T^3 behavior.



system	Debye temperature Θ_D [K]
Fe-Cr-Ni alloys	386-396 [Beskrovni 1999]
Fe	420 [Ashcroft 1976]
Ni	375 [Ashcroft 1976]
Cr	460 [Ashcroft 1976]
Mn	400 [Ashcroft 1976]
Mo	380 [Ashcroft 1976]

Debye T^3 Law

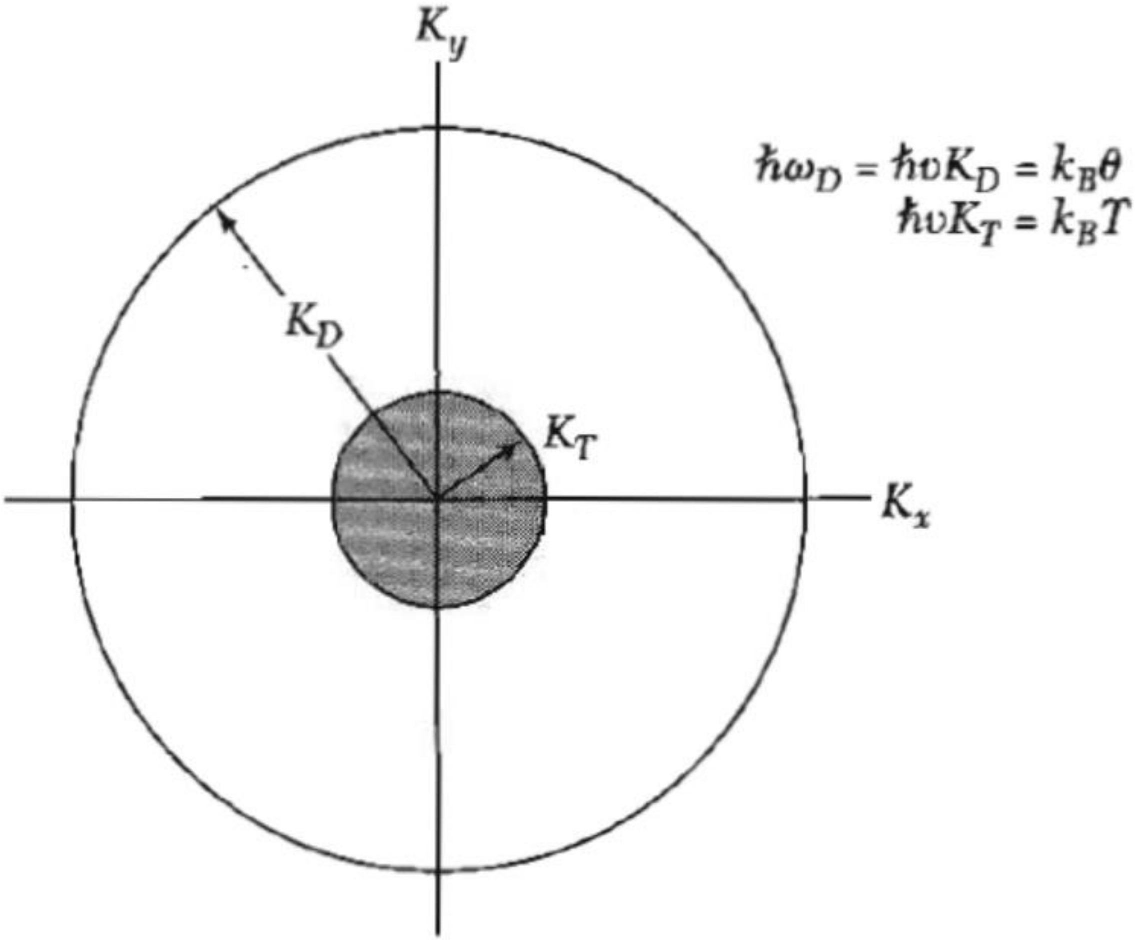
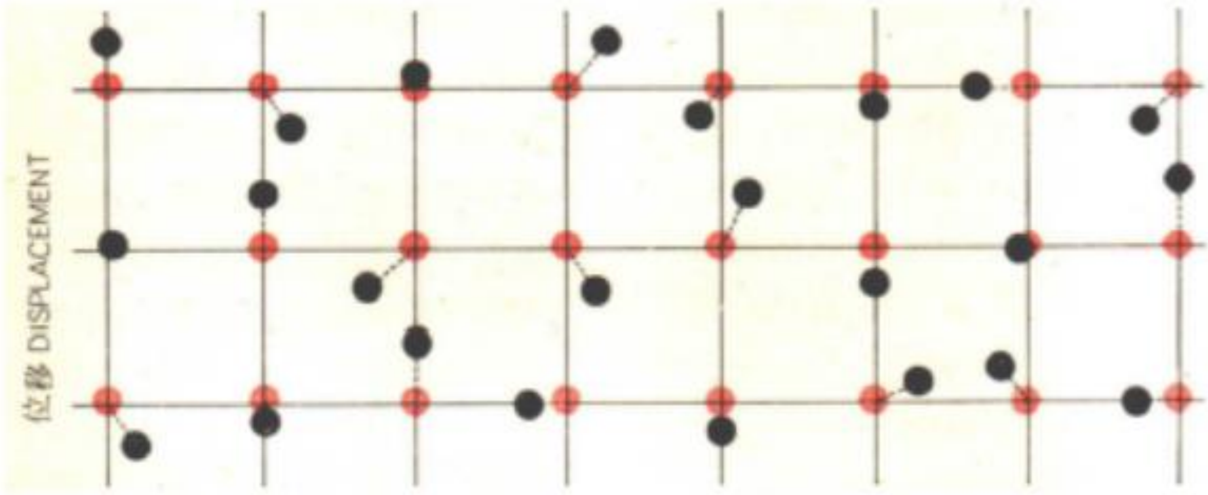


Figure 10 To obtain a qualitative explanation of the Debye T^3 law, we suppose that all phonon modes of wavevector less than K_T have the classical thermal energy k_BT and that modes between K_T and the Debye cutoff K_D are not excited at all. Of the $3N$ possible modes, the fraction excited is $(K_T/K_D)^3 = (T/\theta)^3$, because this is the ratio of the volume of the inner sphere to the outer sphere. The energy is $U \approx k_BT \cdot 3N(T/\theta)^3$, and the heat capacity is $C_V = \partial U/\partial T = 12Nk_B(T/\theta)^3$.

Einstein Model for the Density of States

Assume that

1. each atom vibrates independently of each other, and
2. every atom has the same vibration frequency ω_0



- The DOS can be written as

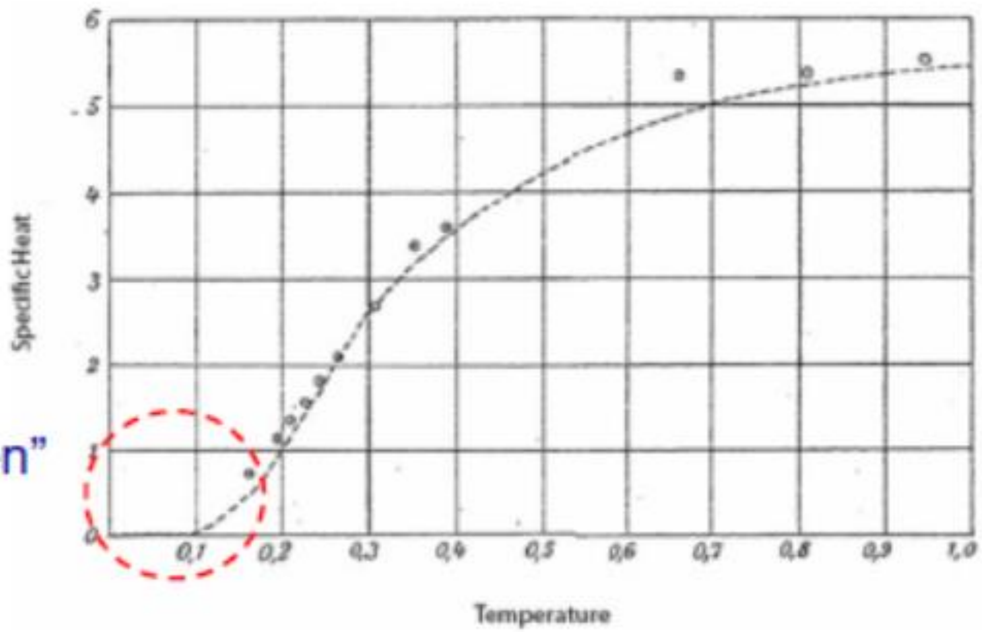
$$D(\omega) = \underset{\uparrow}{3N}\,\delta(\omega - \omega_0)$$

3 dim ×
number of atoms

Einstein Model for the Density of States

$$U = 3N\left(\langle n\rangle + \frac{1}{2}\right)\hbar\omega_0 = 3N\frac{\hbar\omega_0}{\exp(\hbar\omega_0 / kT) - 1} + 3N\frac{\hbar\omega_0}{2}$$

$$C_V = (\partial U / \partial T)_V = 3Nk\left(\frac{\hbar\omega_0}{kT}\right)^2 \frac{e^{\hbar\omega_0/kT}}{\left(e^{\hbar\omega_0/kT} - 1\right)^2}$$



vibration is “frozen” at low T

Data of diamond from Einstein’s 1907 paper.

Einstein Model for T $\gg \hbar\omega/k_B$

- For $T \gg \hbar\omega/k_B$ the heat capacity in Einstein model also approaches the classical value of C_V.
- For $T \gg \hbar\omega/k_B$, $\exp(x) \sim 1 + x$

$$U = 3N \frac{\hbar\omega}{\hbar\omega/k_B T} = 3Nk_B T$$

- The heat capacity is

$$C_V = 3Nk_B$$

- Dulong–Petit law for the classical heat capacity.

Einstein Model for T $\ll \hbar\omega/k_B$

$$U = 3N\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1} \approx 3N\hbar\omega e^{-\hbar\omega/k_BT}$$

- $e^{\hbar\omega/k_BT} - 1 \approx e^{\hbar\omega/k_BT}$

$$C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\hbar\omega/k_BT}$$

- At low temperatures, the $e^{-\hbar\omega/k_BT}$ is more important than the $\left(\frac{\hbar\omega}{k_BT}\right)^2$, therefore C_V decreases as $e^{-\hbar\omega/k_BT}$, whereas the experimental form of the phonon contribution is known to be T^3 as accounted for by the Debye model treated above. The Einstein model, however, is often used to approximate the optical phonon part of the phonon spectrum.

- General Result for D(ω)
- Anharmonic Crystal Interactions
- Thermal Conductivity
- Umklapp Processes
- Imperfections

General Result for D(ω)

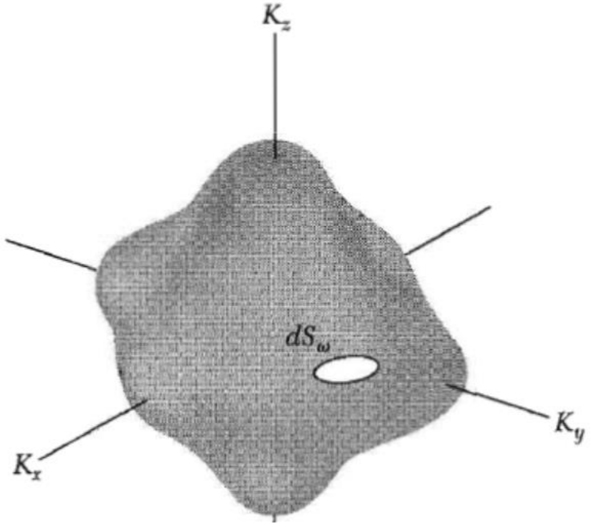
- We want to find a general expression for D(ω), the number of states (allowed values of K) per unit frequency range, given the phonon dispersion relation ω(K).

$$D(\omega)d\omega = \left(\frac{L}{2\pi}\right)^3 \int_{shell} d^3K$$

- This integral is over the volume of the shell in K space hounded by the two surfaces on which the phonon frequency is constant, one surface on which the frequency is ω and the other on which the frequency ω+$d\omega$.

- With a perpendicular distance to the middle of the two surfaces $dK_\perp$ and for an arbitrary surface S_ω

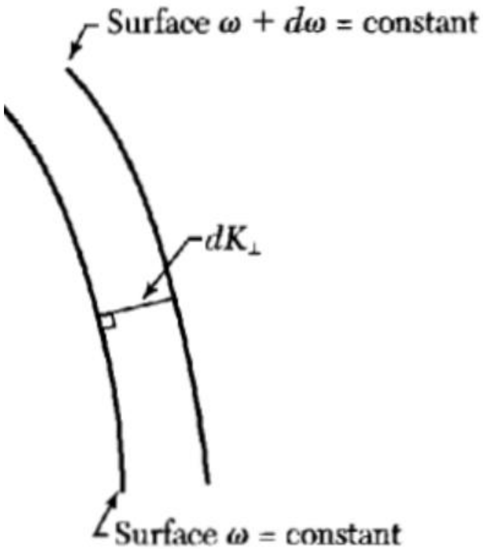
$$\int_{shell} d^3K = \int dS_\omega dK_\perp$$



General Result for D(ω)

- The gradient of ω, which is $\nabla_K \omega$, is also normal to the surface ω constant, and the difference in frequency between the two surfaces connected by $dK_\perp$ is given by

$$|\nabla_K \omega| dK_\perp = d\omega$$



- Thus the element of the volume

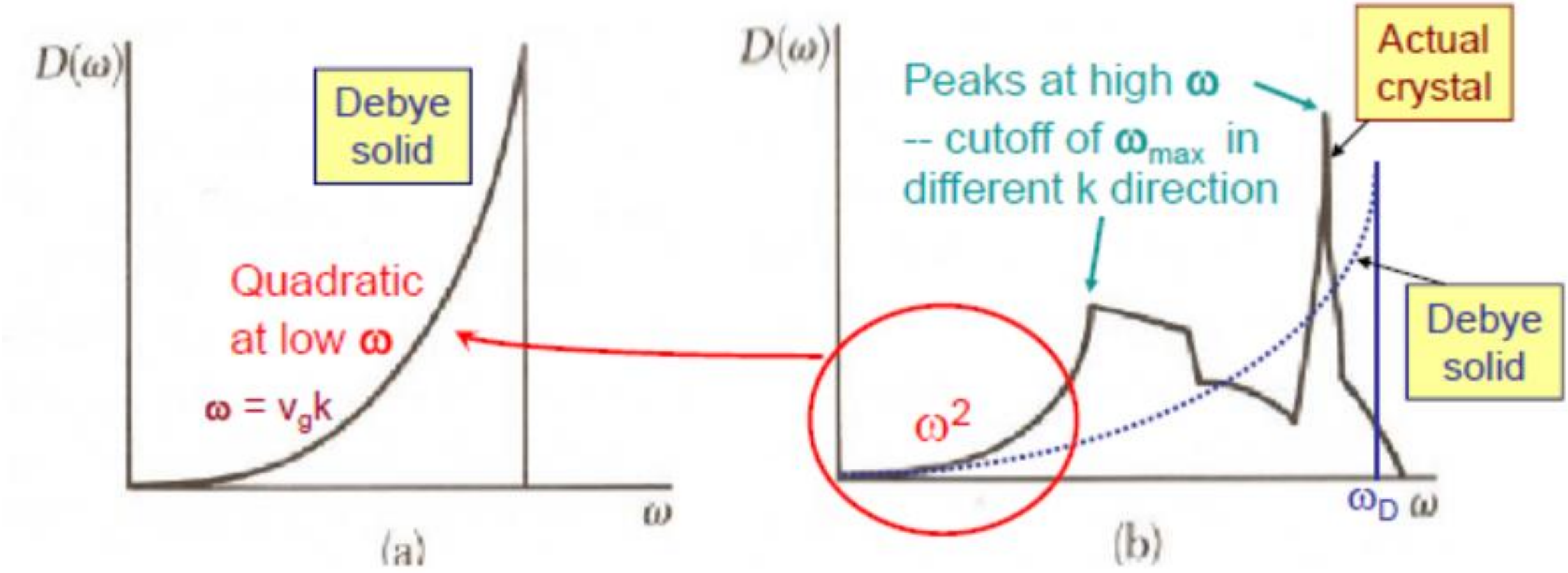
$$dS_\omega dK_\perp = dS_\omega \frac{d\omega}{|\nabla_K \omega|} = dS_\omega \frac{d\omega}{v_g}$$

$$D(\omega) d\omega = \left(\frac{L}{2\pi}\right)^3 \int dS_\omega \frac{d\omega}{v_g}$$

- For a cubic crystal $V = L^3$ and divide both sides by $d\omega$

$$D(\omega) = \frac{V}{(2\pi)^3} \int_{surface} \frac{dS_\omega}{v_g}$$

General Result for D(ω)



- There is a special interest in the contribution to D(*ω*) from points at which the group velocity is zero i.e. many states are available at the same energy. Such critical points in the Brillouin zone produce singularities (known as Van Hove singularities) in the distribution function.

ANHARMONIC CRYSTAL INTERACTIONS

So far only harmonic oscillators have been discussed with small deformations that obey Hook's law ($F = -kx$). The restoring potential energy is $U = \frac{1}{2}kx^2$.

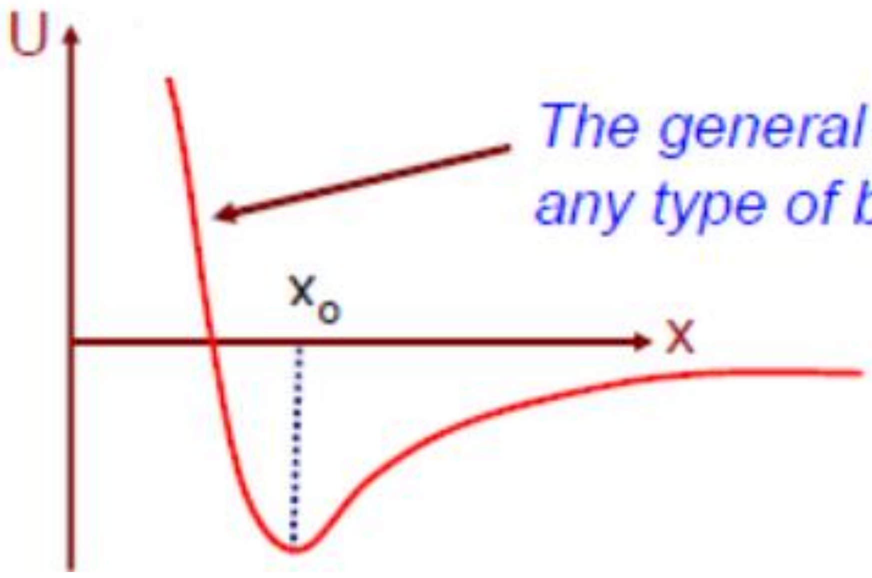
- However, real systems have anharmonic effects thus the related terms should be included in the equations of motion.

- What we have assumed for the harmonic oscillators is that:

– Two lattice waves do not interact.
– Adiabatic and isothermal elastic constants are equal.
– A single wave does not decay or change its form with time.
– There is no thermal expansion in the crystals.
– The force (elastic) constants between the atoms do not change as a function of temperature or pressure.
– The heat capacity becomes constant at high temperatures $C_V = 3R$.

In real crystals, none of these consequences can be satisfied accurately. The deviations may be attributed to the neglect of anharmonic (higher than quadratic) terms in the interatomic displacements.

ANHARMONIC CRYSTAL INTERACTIONS



The general shape applies for any type of binding

$$U(x) = U(x_o) + \left.\frac{\partial U}{\partial x}\right|_{x_o} (x - x_o) + \frac{1}{2}\left.\frac{\partial^2 U}{\partial x^2}\right|_{x_o} (x - x_o)^2 + \frac{1}{6}\left.\frac{\partial^3 U}{\partial x^3}\right|_{x_o} (x - x_o)^3 + \ldots$$

$$\Delta U(x) = U(x)\text{-}U(x_o) = \frac{1}{2}\left.\frac{\partial^2 U}{\partial x^2}\right|_{x_o} (x - x_o)^2 + \frac{1}{6}\left.\frac{\partial^3 U}{\partial x^3}\right|_{x_o} (x - x_o)^3 + \ldots$$

Reset the equilibrium, let displacement x-x_o → x

$$U(x) = cx^2 \boxed{-gx^3 - fx^4 \ldots}$$

harmonic term

anharmonic term

Thermal Expansion

As a solid is heated up, the lattice expands (due to the average displacement of the atoms increasing with thermal energy which causes fluctuation of x from x_o.

$$\langle x\rangle = \frac{\int_{-\infty}^{\infty} dx\, x \exp[-\frac{U(x)}{k_B T}]}{\int_{-\infty}^{\infty} dx \exp[-\frac{U(x)}{k_B T}]} \cong \frac{\int_{-\infty}^{\infty} dx\, x \exp[-\frac{cx^2 - gx^3 - fx^4}{k_B T}]}{\int_{-\infty}^{\infty} dx \exp[-\frac{cx^2 - gx^3 - fx^4}{k_B T}]}$$

$$\exp\left(-\frac{cx^2 - gx^3 - fx^4}{k_B T}\right) = \exp\left(-\frac{cx^2}{k_B T}\right)\exp\left(\frac{gx^3}{k_B T} + \frac{fx^4}{k_B T}\right)$$

anharmonic term gives the net change of <x>

high T limit

$$\cong \exp\left(-\frac{cx^2}{k_B T}\right)\left(1 + \frac{gx^3}{k_B T} + \frac{fx^4}{k_B T}\right)$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

- In lowest order, the thermal expansion does not involve the symmetric fx^4 in U(x), but only the antisymmetric term gx^3.

Thermal Expansion

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

- The first integrand contains odd term x, therefore is zero with the symmetric limits. Use $\beta c x^2 = y$ and apply the gamma function $\Gamma(z) = \int_0^\infty e^{-t} t^{z-1} dt$ on the second integral.

$$\int_{-\infty}^{\infty} dx\, x\, e^{-\beta U(x)} = 2\beta g \int_{0}^{\infty} dx\, e^{-\beta c x^2}(x^4) = \frac{3\beta g}{4} \frac{\sqrt{\pi}}{(\beta c)^{\frac{5}{2}}}$$

- Similarly the other integral is

$$\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)} = \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2}(1+\beta g x^3) = \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2}$$

- Apply the gamma function on the first integral. The second integrand contains odd term x^3, therefore is zero with the symmetric limits.

Thermal Expansion

$$\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)} = \int_{-\infty}^{\infty} dx\, e^{-\beta c x^2} = 2\int_{0}^{\infty} dx\, e^{-\beta c x^2}$$

- Use $\beta c x^2 = y$, then apply the gamma function on the integral.

$$\int_{-\infty}^{\infty} dx\, e^{-\beta U(x)} = \frac{\sqrt{\pi}}{(\beta c)^{\frac{1}{2}}}$$

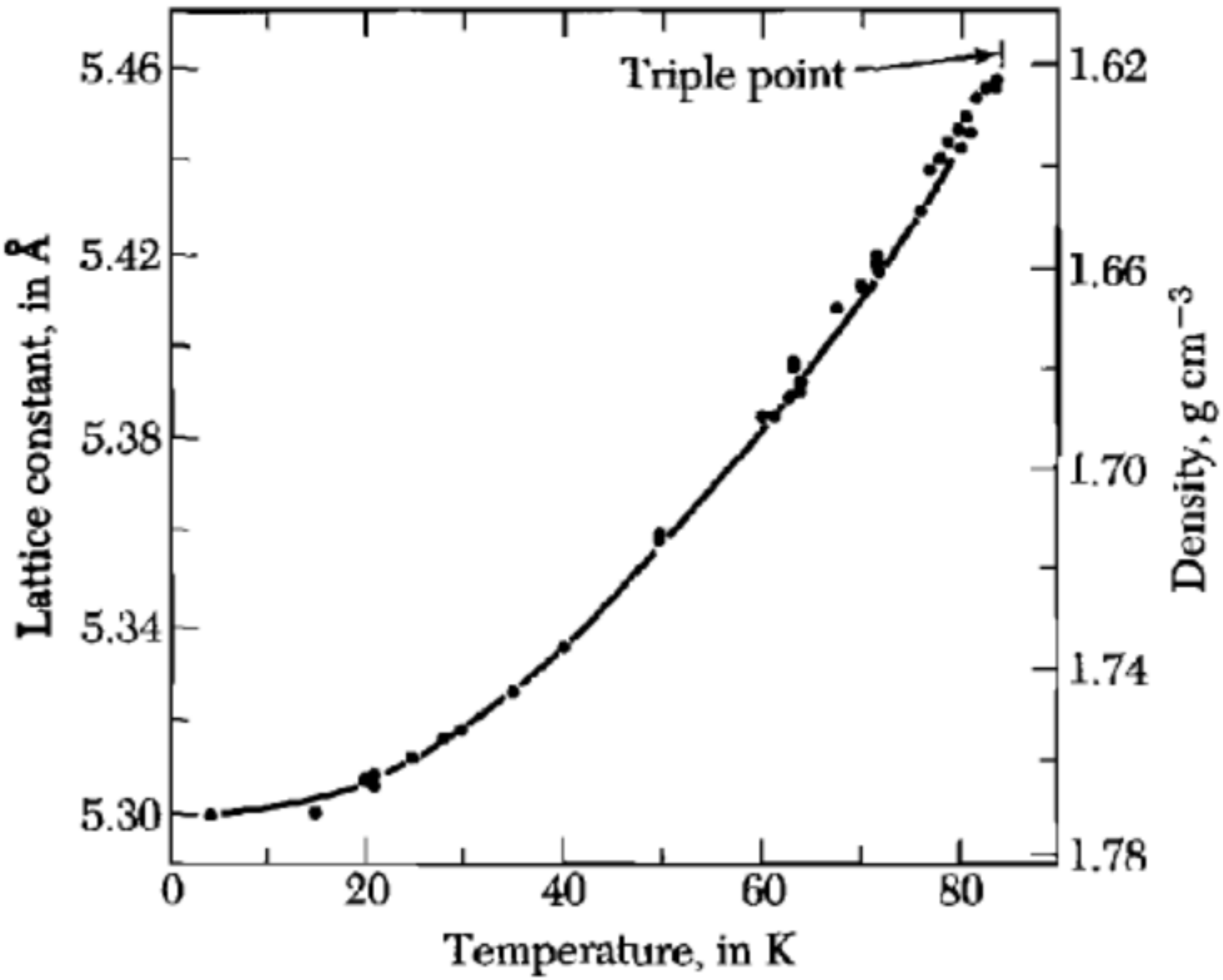
- Put the two values in the equation of the average displacement.

$$\langle x \rangle = \frac{(3\pi^{1/2}/4)(g/c^{5/2})(k_B T)^{3/2}}{(\pi/c)^{1/2}(k_B T)^{1/2}} = \boxed{\frac{3g}{4c^2} k_B} T$$

linear dependence of T

Coefficient of linear expansion

Thermal Expansion



Lattice constant of solid argon as a function of temperature.

- Umklapp Processes
- Imperfections
- Chapter 6: Free Electron Fermi Gas

Thermal Conductivity

Ballistic No interaction/scattering

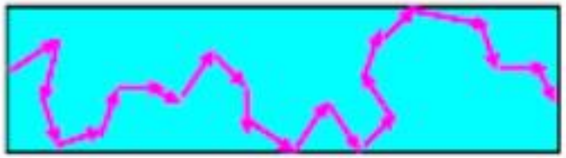
In harmonic approximation in perfect, infinite crystal,
Expect no scattering → phonon modes are uncoupled,
independent plane waves and standing waves

$$v = v_g = \frac{d\omega}{dK}$$

Diffusion Phonons scatter, random walk through crystal

Phonons scatter in real crystals.

Scattering processes :
- ✓ boundary scattering
- ✓ defect scattering
- ✓ phonon-phonon scattering



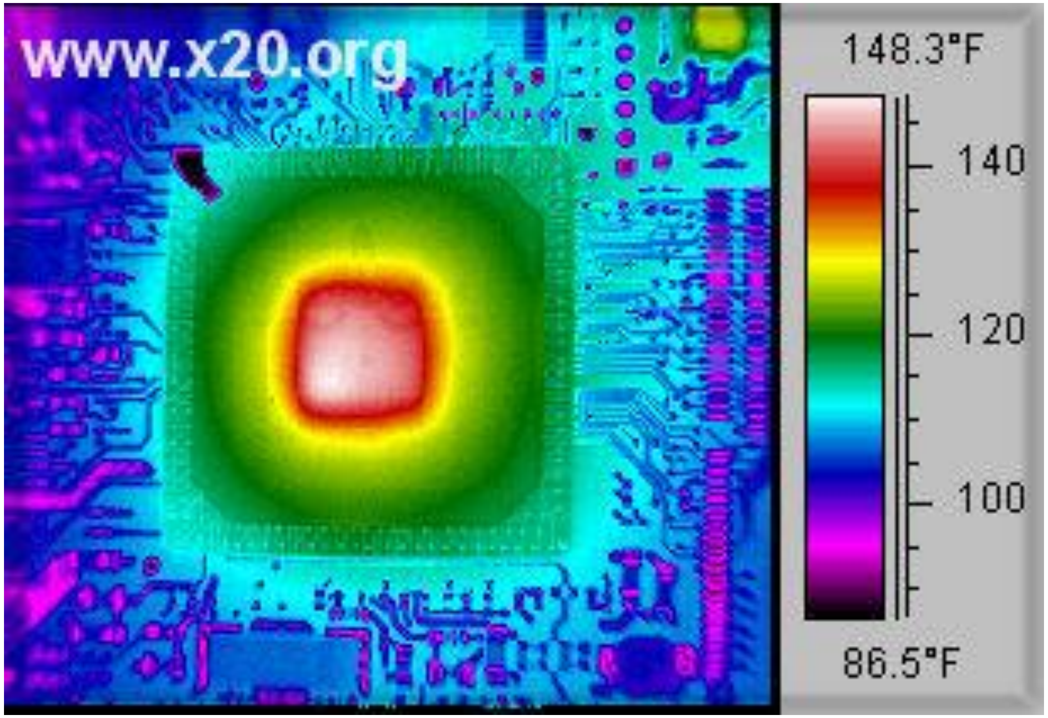
$$v \ll v_g = \frac{d\omega}{dK}$$

Thermal Conductivity

Atomic view: Electronic and/or Atomic vibrations in hotter region carry energy (vibrations) to cooler regions.

In a metal, electrons are free and thus dominate thermal conductivity.

In a ceramic, electrons are localized and phonons carry thermal energy.



Thermal Conductivity

- The thermal energy flux (j) for a steady-state heat flow for a long slab with temperature gradient dT/dx and thermal conductivity K is
$$j = -K\frac{dT}{dx}.$$
- We want to derive the above relation from elementary kinetic theory of phonons.

- The flux of particles in the $+x$ direction is $\frac{1}{2}n\langle|v_x|\rangle$ and in equilibrium there is a flux of equal magnitude in the opposite direction. So the total flux is $n\langle|v_x|\rangle$. The n represents molecular concentration (molecules/volume).

- If c is the heat capacity of a particle, then in moving from a region at local temperature $T + \Delta T$ to a region at local temperature T, the particle will give up energy $E = c\Delta T$.

- The total thermal energy flux (energy/area.time) along x-axis is
$$j = -n\langle|v_x|\rangle\, c\Delta T.$$

Thermal Conductivity

- If ΔT between the ends of a free path l of the particle is given by

$$\Delta T = \frac{dT}{dx} l = \frac{dT}{dx} v_x \tau$$

- where τ is the average time between collisions.

- The total flux of energy along x-axis is therefore

$$j = -n\langle |v_x| \rangle\, c\Delta T = -n\langle v_x^2 \rangle\, c\tau \frac{dT}{dx}$$

For symmetric mean particle velocity in the three directions $\langle v_x^2 \rangle = \frac{1}{3} v^2$

$$j = -\frac{1}{3} n v^2 c\tau \frac{dT}{dx} = -\frac{1}{3} nvcl \frac{dT}{dx} = -\frac{1}{3} Cvl \frac{dT}{dx}$$

$$\boldsymbol{j = -K\frac{dT}{dx}}, \qquad \boldsymbol{where\ K = \frac{1}{3} Cvl}, \qquad \boldsymbol{C = nc}$$

Thermal Resistivity of Phonon Gas

- The phonon mean free path *l* is determined principally by two processes, geometrical scattering and scattering by other phonons.

- If the forces between atoms were purely harmonic, there will be no collisions between different phonons, and the mean free path will be limited solely by collisions of a phonon with the crystal boundary, and by lattice imperfections.

- With anharmonic lattice interactions, there is a coupling between different phonons which limits the value of the mean free path, hence increase thermal resistivity. Thus the mean free path become inversely proportional to the temperature.

$$l \propto 1/T$$

Phonon-phonon scattering

phonon displaces atom which changes the force constant (anharmonic terms)

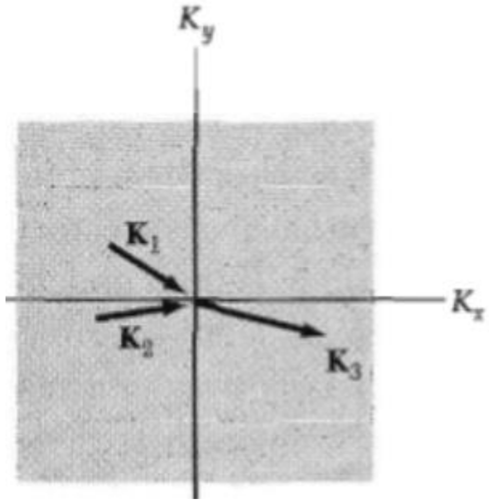
→ scatter other phonons

three phonon process

Normal processes : all ks are in BZ

$$\mathbf{K}_1 + \mathbf{K}_2 = \mathbf{K}_3$$

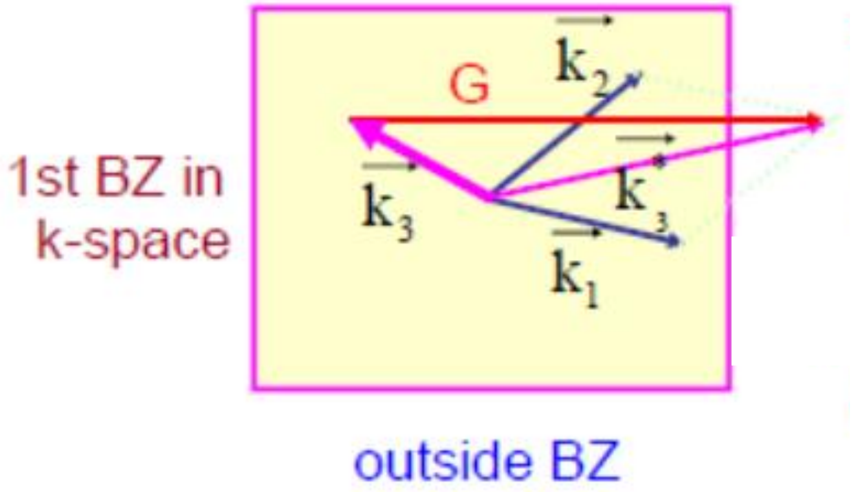
1st BZ in k-space



Total momentum of the phonon gas is conserved by such collision

In the **normal processes (N-processes),** the two interacting phonons have smaller wavevectors. The third wavevector is small, pointing in the resultant direction, and lies in the 1st Brillouin zone. In N-processes the momentum is conserved.

Umklapp processes : k_3^* is outside BZ



"Folding over"

The only meaningful phonon K's lie in the 1st BZ, so any longer K must be brought back into the 1st BZ by adding a G.

$$K_1 + K_2 = K_3^* \rightarrow \quad K_3 + G = K_3^* \rightarrow \quad K_1 + K_2 = K_3 + G$$

- In the **Umklapp processes (U-processes),** the two interacting phonons have larger wavevectors. The third wavevector is larger and goes into higher Brillouin zones. In order to bring it back to the 1st Brillouin zone, one should add G to it.

- The addition of G means that phonons interact with the crystal.

- In the Umklapp processes, phonons exchange energy with the crystal. Increase thermal resistance to the heat flow.

Imperfections

- Geometrical effects such as impurities, grain boundaries etc. may also be important in limiting the mean free path.

- At low temperatures, the mean free path *l* and hence thermal conductivity are limited only by the size of the specimen.

- The size effect enters whenever the phonon mean free path becomes comparable with the diameter of the specimen.

$$K \approx CvD$$

- Where C is the heat capacity, v is velocity of phonons, and D is the diameter of the specimen.

- Since at low temperature $C \propto T^3$, therefore thermal conductivity is also $K \propto T^3$.