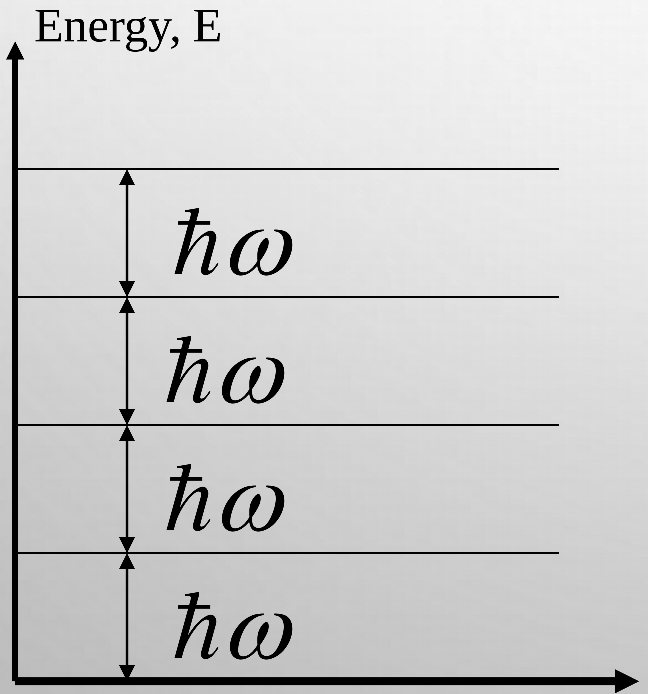
Thermal Properties

Energy Of Harmonic Oscillator

Obtained by in a classical way of considering the normal modes that we have found are independent and harmonic.

$$\boxed{\varepsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega}$$



- Make a transition to Q.M.

- Represents equally spaced energy levels

Energy levels of atoms vibrating at a single frequency ω

It is possible to consider ε_n as constructed by adding n excitation quanta each of energy $\hbar\omega$ to the ground state.

$$\varepsilon_0 = \frac{1}{2}\hbar\omega$$

A transition from a lower energy level to a higher energy level.

$$\Delta\varepsilon = \left(n_2 + \frac{1}{2}\right)\hbar\omega - \left(n_1 + \frac{1}{2}\right)\hbar\omega$$

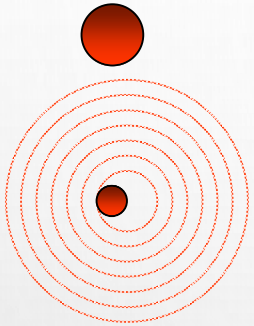
$$\Delta\varepsilon = \underbrace{(n_2 - n_1)}_{unity}\hbar\omega \Rightarrow \Delta\varepsilon = \hbar\omega$$

absorption of phonon

- The converse transition results an emission of phonon with an energy $\hbar\omega$.
- Phonons are quanta of lattice vibrations with an angular frequency of ω .
- Phonons are not localized particles.
- Its momentum is exact, but position can not be determined because of the uncertainity princible.
- However, a slightly localized wavepacket can be considered by combining modes of slightly different ω and λ .

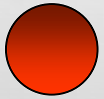
- Phonons are not conserved
- They can be created and destroyed during collisions .

Thermal Energy And Lattice Vibrations



- Atoms vibrate about their equilibrium position.
- They produce vibrational waves.
- This motion is increased as the temperature is raised.

In a solid, the energy associated with this **vibration** and perhaps also with the **rotation** of atoms and molecules is called as ***thermal energy.***



Note: In a gas, the translational motion of atoms and molecules contribute to this energy.

Therefore, the concept of thermal energy is fundamental to an understanding many of the basic properties of solids. We would like to know:

- What is the value of this thermal energy?
- How much is available to scatter a conduction electron in a metal; since this scattering gives rise to electrical resistance.
- The energy can be used to activate a crystallographic or a magnetic transition.
- How the vibrational energy changes with temperature since this gives a measure of the heat energy which is necessary to raise the temperature of the material.
- Recall that the specific heat or heat capacity is the thermal energy which is required to raise the temperature of unit mass or 1gmole by one Kelvin.

Heat capacity from Lattice vibrations

The energy given to lattice vibrations is the dominant contribution to the heat capacity in most solids. In non-magnetic insulators, it is the only contribution.

Other contributions;

- In metals→ from the conduction electrons.
- In magnetic materials→ from magneting ordering.

Atomic vibrations leads to band of normal mode frequencies from zero up to some maximum value. Calculation of the lattice energy and heat capacity of a solid therefore falls into two parts:

i) the evaluation of the contribution of a single mode, and

ii) the summation over the frequency distribution of the modes.

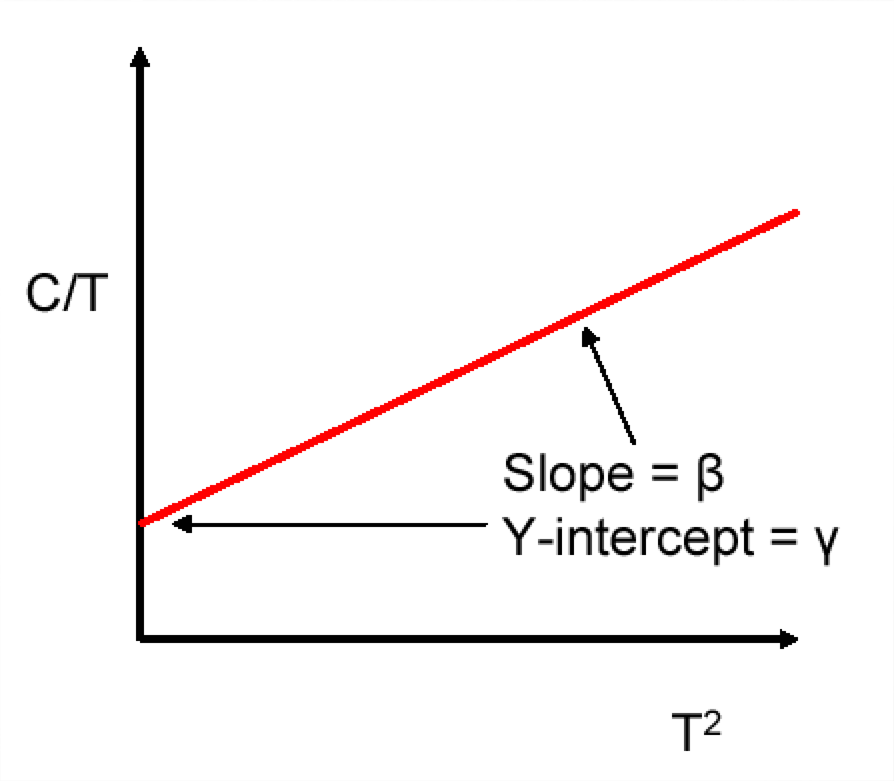
Heat Capacity

You may remember from your study of thermal physics that
the specific heat is the amount of energy per unit mass required to raise the temperature by one degree Celsius.

$Q = mc\Delta T$

Thermodynamic models give us this definition:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$



$$C_v = \gamma T + \beta T^3$$

electrons

phonons

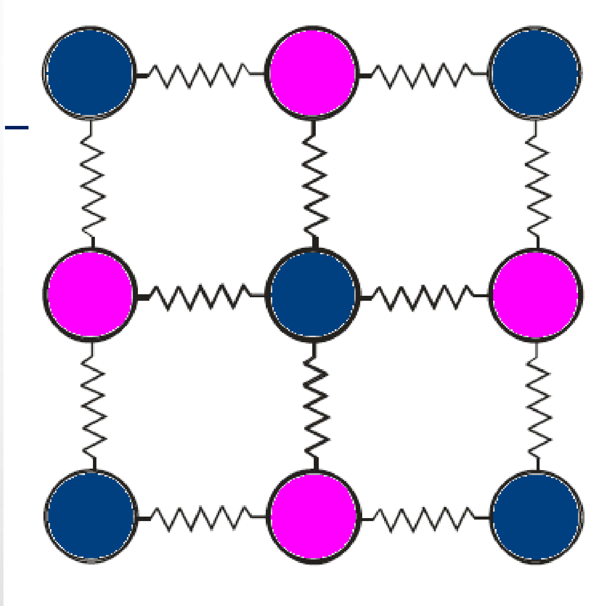
Heat Capacity

Equipartition Theorem (Classical model):

The internal energy of a system of *N* particles is

$$3Nk_BT$$

The mean energy is spread equally over all degrees of freedom, hence the terminology – equipartition.



The solid is one in which each atom is bound to its side by a harmonic force. when the solid is heated, the atoms vibrate around their sites like a set of harmonic oscillators. the average energy for a 1D oscillator is kT. therefore, the averaga energy per atom, regarded as a 3D oscillator, is 3kT,

Monatomic particles have only 3 translational degrees of freedom. They possess no rotational or vibrational degrees of freedom.

$$\bar{\varepsilon} = 3Nk_BT = 3RT$$

where N is avagadro's number, k_B is boltzmann constant and R is the gas constant. the differentiation wrt temperature gives;

1819: Dulong and Petit observed that the specific heat at constant volume for most solids was 3R (~25 J/(K mol)) near room temperature.

$$C_v = \frac{d\bar{\varepsilon}}{dT}$$

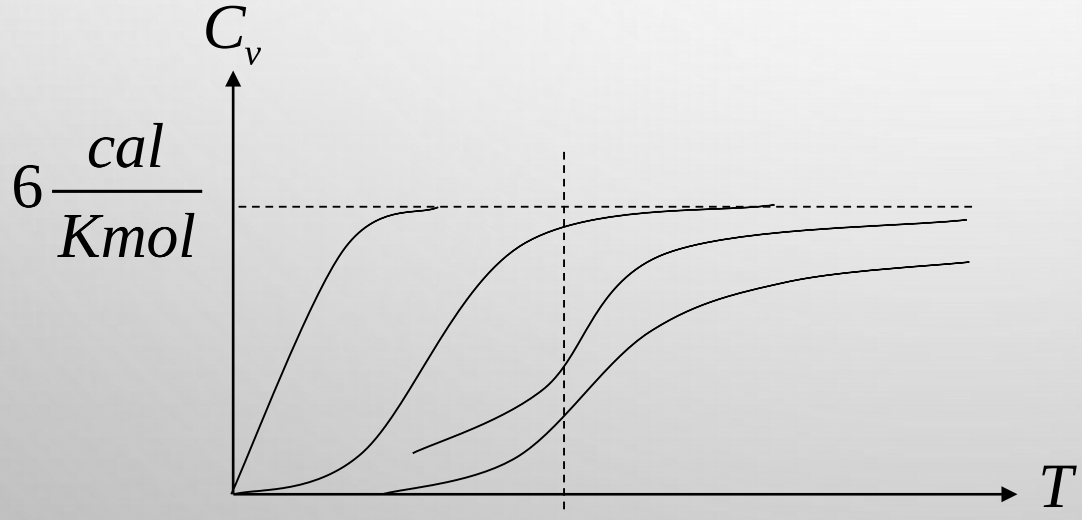
$$C_v = 3R = 3\times 6.02\times 10^{23}(atoms/mole)\times 1.38\times 10^{-23}(J/K)$$

$$Cv = 24.9\frac{J}{(K-mole)};1J = 0.2388Cal \Rightarrow Cv \,\square\, 6\frac{Cal}{(K-mole)}$$

- *At high temperatures*, all crystalline solids have a specific heat of 6 cal/K per mole; they require 6 calories per mole to raise their temperature 1 K.

- This arrangement between observation and classical theory break down if the temperature is not high.

- Observations show that ***at room temperatures and below*** the specific heat of crystalline solids is not a universal constant.



$$\frac{\hbar\omega}{k_B} \longrightarrow C_v = 3R$$

In all of these materials (Pb,Al, Si,and Diamond) specific heat approaches constant value asymptotically at high T’s. But at low T’s, the specific heat decreases towards zero which is in a complete contradiction with the above classical result.

We Need To Use Quantum Statistics To Describe This Properly.

- Bosons And Fermions
  - Bosons: Particles That Can Be In The Same Energy State (E.G. Photons, Phonons)
  - Fermions: Particles That Cannot Be In The Same Energy Level (E.G. Electrons)

Phonons

- Quanta Of Lattice Vibrations
- Energies Of Phonons Are Quantized

$$E_{phonon} = \frac{h\nu_s}{\boxed{\lambda}}$$

$\sim a_0 = 10^{-10}$m

$$p_{phonon} = \frac{h}{\lambda}$$

PHOTONS

- Quanta of electromagnetic radiation
- Energies of Photons are quantized as well

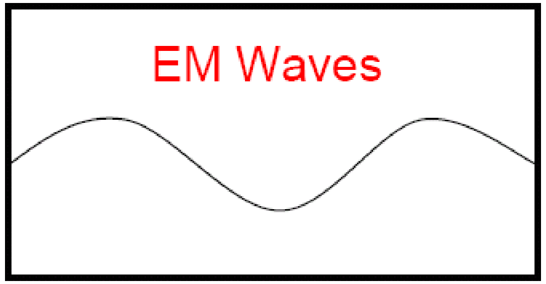
$$E_{photon} = \frac{hc}{\boxed{\lambda}}$$

$\sim 10^{-6}$m

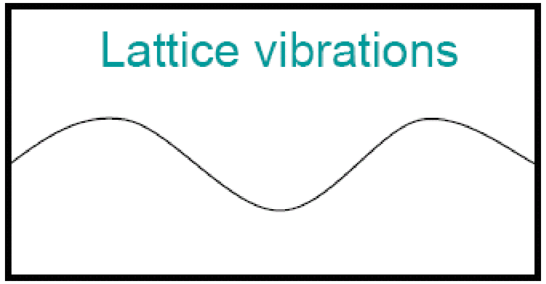
$$p_{photon} = \frac{h}{\lambda}$$

Planck Distribution

- There is an analogy between photons in a cavity and phonons in a solid:



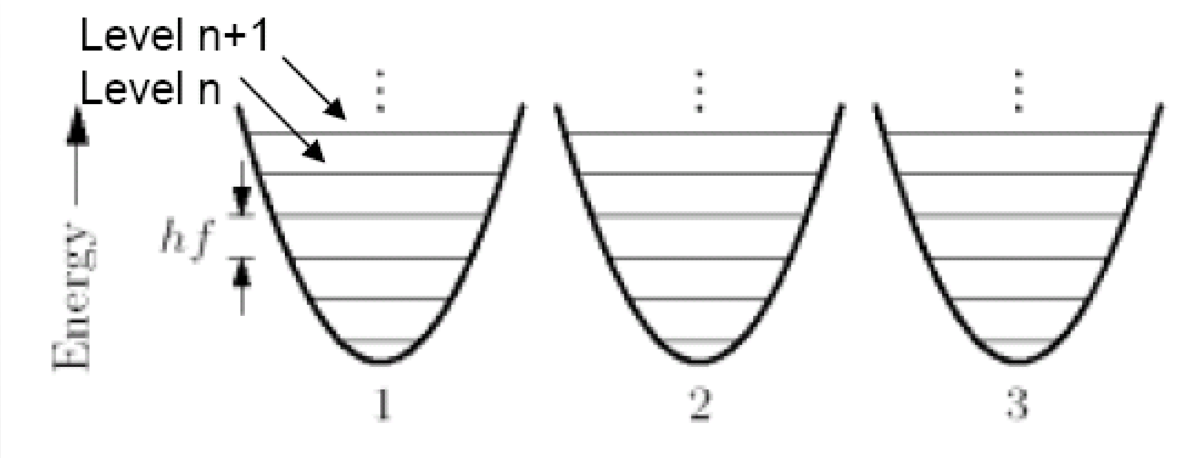
Photons in a cavity



Phonons in a solid

- It turns out that we can use the same rules to treat both photons and phonons. That is why it is said that phonons follow a Planck Distribution of energies.
- Planck figured out how these light wave energy levels were populated as a function of temperature (by considering them to be harmonic oscillators)
- We are going to use the same rules to see how many phonons are occupied at a given temperature (approximate each phonon to be a harmonic oscillator – same energy levels)

Planck Distribution



Series of identical harmonic oscillators
Energy levels = ½ (n+1)$\hbar\omega$ (n is integer)

$$\frac{N_{n+1}}{N_n} = \exp(-\Delta E / kT)$$

Energy difference between n+1 and n
(which is = $\hbar\omega$)

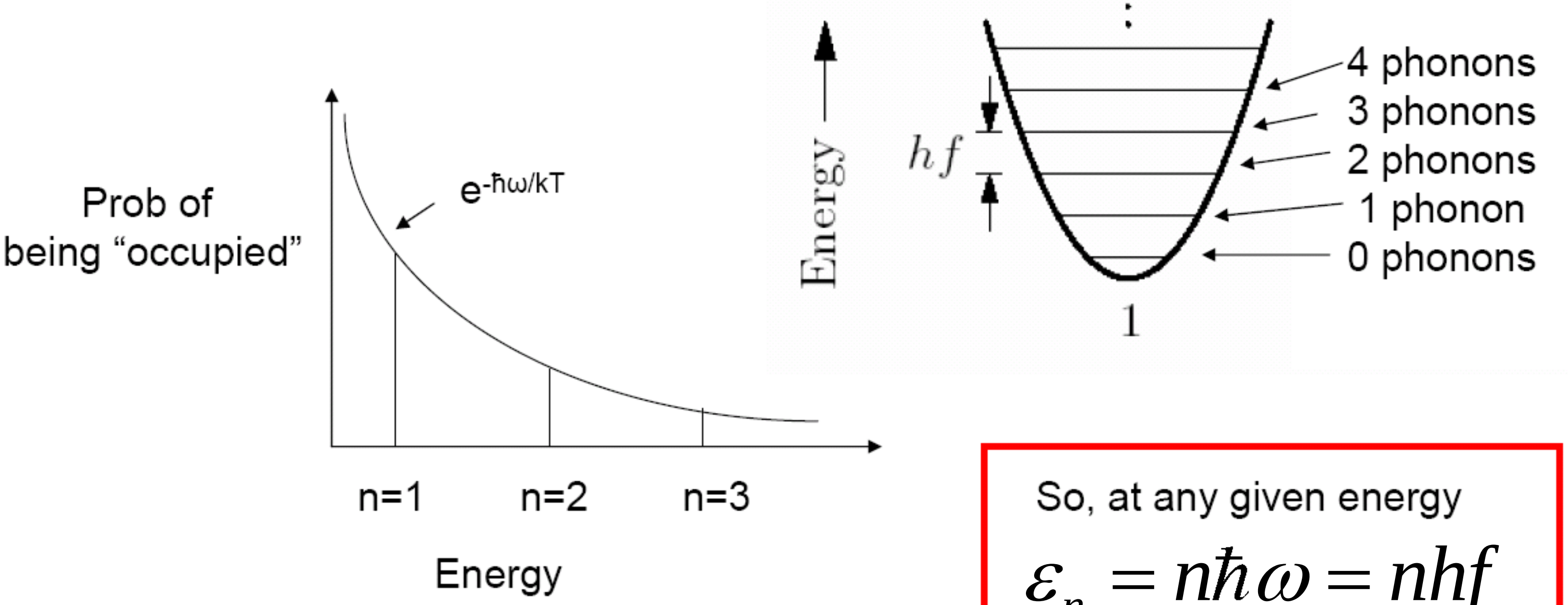
number of phonons in energy level *n*

total number of phonons

$$\frac{N_n}{\sum_0^\infty N_s} = \frac{\exp(-\varepsilon_n / kT)}{\sum_0^\infty \exp(-\varepsilon_s / kT)}$$

all possible energy levels ε_0, ε_1, ε_2, etc.

Planck Distribution



So, at any given energy

$$\varepsilon_n = n\hbar\omega = nhf$$

(above the zero energy level n=0)

Fraction of Phonons at energy *n*

$$= \frac{N_n}{\sum_0^\infty N_n} = \frac{e^{-\varepsilon_n/kT}}{\sum_0^\infty e^{-\varepsilon_n/kT}} = \frac{e^{-n\hbar\omega/kT}}{\sum_0^\infty e^{-n\hbar\omega/kT}}$$

small as n gets large

a constant

Planck Distribution

Average occupied energy level

$$< n >= \frac{\sum_{0}^{\infty} n \exp(-n\hbar\omega / kT)}{\sum_{0}^{\infty} \exp(-n\hbar\omega / kT)}$$

DENOMINATOR

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \Rightarrow \sum_{n=0}^{\infty} e^n = \frac{1}{1-e} \Rightarrow \sum_{n=0}^{\infty} e^{-n\hbar\omega/k_BT} = \frac{1}{1-e^{-\hbar\omega/k_BT}}$$

NUMERATOR

$$\sum_{n=0}^{\infty} nx^n = x\frac{\partial}{\partial x}\left(\sum_{n=0}^{\infty} x^n\right) = x\frac{\partial}{\partial x}\left(\frac{1}{1-x}\right) = \frac{x}{(1-x)^2}$$

$$\boxed{< n >= \frac{x}{1-x} = \frac{1}{\exp(\hbar\omega / kT) - 1}}$$

Energy And Heat Capacity Of A Harmonic Oscillator, Einstein Model

$$\bar{\varepsilon} = \sum_n P_n \varepsilon_n$$

Avarage energy of a harmonic oscillator and hence of a lattice mode of angular frequency at temperature T

Energy of oscillator

$$\varepsilon_n = \left(n + \frac{1}{2} \right) \hbar\omega$$

The probability of the oscillator being in this level as given by the Boltzman factor

$$\exp(-\varepsilon_n / k_B T)$$

$$\boxed{\bar{\varepsilon} = \sum_n P_n \varepsilon_n}$$

$$\bar{\varepsilon} = \frac{\sum_{n=0}^{\infty}\left(n+\frac{1}{2}\right)\hbar\omega \exp\left[-\left(n+\frac{1}{2}\right)\hbar\omega / k_B T\right]}{\sum_{n=0}^{\infty}\exp\left[-\left(n+\frac{1}{2}\right)\hbar\omega / k_B T\right]} \qquad (*)$$

$$z = \sum_{n=0}^{\infty}\exp[-(n+\frac{1}{2})\frac{\hbar\omega}{k_B T}]$$

$$z = e^{-\hbar\omega/2k_B T} + e^{-3\hbar\omega/2k_B T} + e^{-5\hbar\omega/2k_B T} + ...$$

$$z = e^{-\hbar\omega/2k_B T}(1 + e^{-\hbar\omega/k_B T} + e^{-2\hbar\omega/k_B T} + ...$$

$$z = e^{-\hbar\omega/2k_B T}(1 - e^{-\hbar\omega/k_B T})^{-1}$$

According to the Binomial expansion for x«1 where $x = -\hbar\omega / k_B T$

Eqn (*) can be written

$$\bar{\varepsilon} = k_B T^2 \frac{1}{z}\frac{\partial z}{\partial T} = k_B T^2 \frac{\partial}{\partial T}(\ln z)$$

$$\bar{\varepsilon} = k_B T^2 \frac{\partial}{\partial T} \ln\left(\frac{e^{-\hbar\omega/2k_BT}}{1-e^{-\hbar\omega/k_BT}} \right)$$

$$\bar{\varepsilon} = k_B T^2 \frac{\partial}{\partial T} \left[\ln e^{-\hbar\omega/2k_BT} - \ln\left(1-e^{-\hbar\omega/k_BT}\right) \right]$$

$$\bar{\varepsilon} = k_B T^2 \left[\frac{\partial}{\partial T}\left(-\frac{\hbar\omega}{2k_BT} \right) - \frac{\partial}{\partial T} \ln\left(1-e^{-\hbar\omega/k_BT}\right) \right] \Longrightarrow \boxed{\frac{\partial}{\partial x}(\ln x) = \frac{x'}{x}}$$

$$\bar{\varepsilon} = k_B T^2 \left[\frac{2k_B\hbar\omega}{4k_B^2T^2} + \frac{\frac{\hbar\omega k_B}{k_B{}^2T^2} e^{-\hbar\omega/k_BT}}{\left(1-e^{-\hbar\omega/k_BT}\right)} \right] = \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\hbar\omega/k_BT}}{\left(1-e^{-\hbar\omega/k_BT}\right)}$$

$$\boxed{\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}}$$

$$\boxed{\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1}}$$

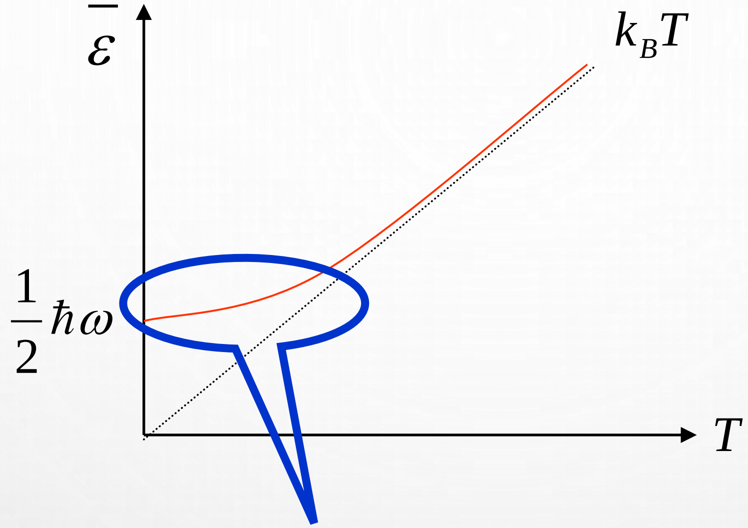
This is the mean energy of phonons.The first term in the above equation is the zero-point energy. As we have mentioned before even at 0ºK atoms vibrate in the crystal and have zero-point energy. This is the minimum energy of the system.

The avarage number of phonons is given by Bose-Einstein distribution as

(number of phonons) x (energy of phonon)=(second term in $\bar{\varepsilon}$)

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

The second term in the mean energy is the contribution of phonons to the energy.



Mean energy of a harmonic oscillator as a function of T

low temperature limit

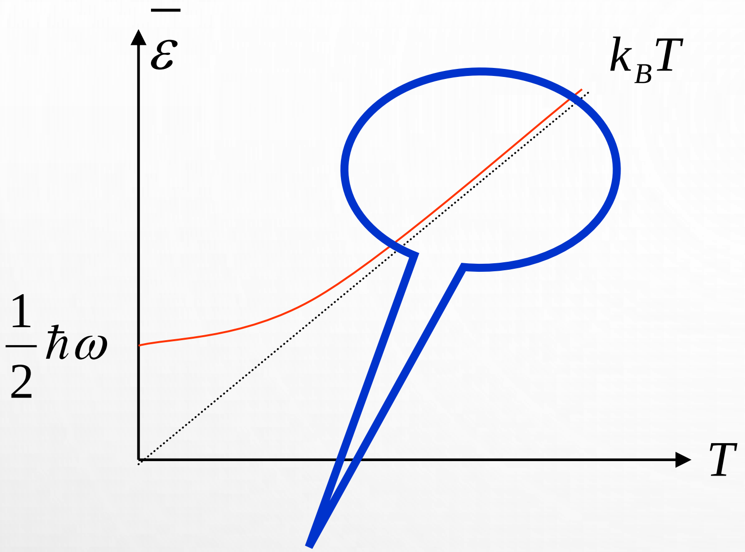
$$\hbar\omega \gg k_B T$$

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega / k_B T} - 1}$$

Since exponential term gets bigger

⇨ $$\bar{\varepsilon} = \frac{1}{2}\hbar\omega$$ ***Zero point energy***

Mean energy of a harmonic oscillator as a function of T



high temperature limit

$$\hbar\omega \ll k_B T$$

- $\bar{\varepsilon}$ is independent of frequency of oscillation.
- This is the classical limit because the energy steps are now small compared with the energy of the harmonic oscillator.
- So that $\bar{\varepsilon}$ is the thermal energy of the classical 1D harmonic oscillator.

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

$$e^{\hbar\omega / k_B T} = 1 + \frac{\hbar\omega}{k_B T}$$

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{1 + \frac{\hbar\omega}{k_B T} - 1}$$

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + k_B T$$

⇓

$$\boxed{\bar{\varepsilon} \approx k_B T}$$

Heat Capacity C

- Heat Capacity c can be found by differentiating the average energy of phonons of

$$\bar{\varepsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/k_BT} - 1}$$

$$C_v = \frac{d\bar{\varepsilon}}{dT} = \frac{-\hbar\omega\frac{-\hbar\omega k_B}{(k_BT)^2}e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \Longrightarrow C_v = k_B\frac{(\hbar\omega)^2}{(k_BT)^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2}$$

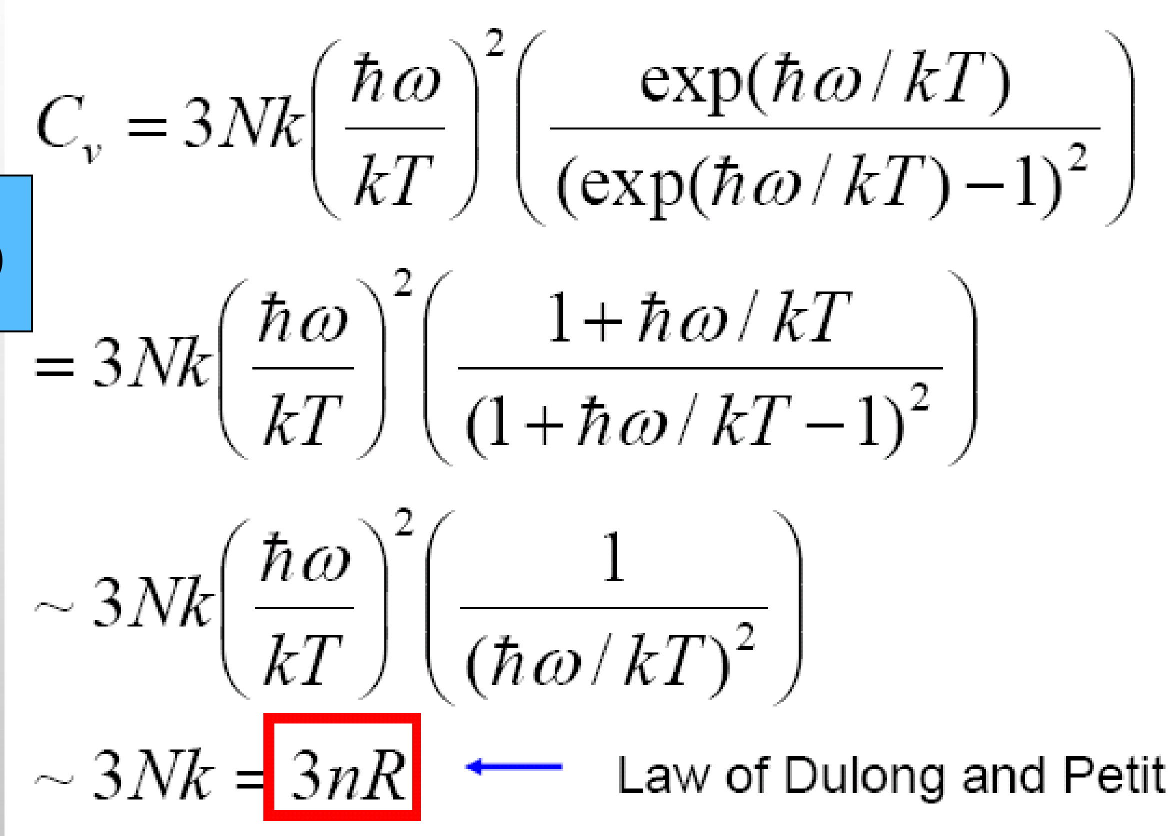
Let $\theta = \frac{\hbar\omega}{k}$ $\Longrightarrow$ $C_v = k_B\left(\frac{\theta}{T}\right)^2\frac{e^{\theta/T}}{\left(e^{\theta/T}-1\right)^2}$

θ is Einestein Temperature

Einstein Model

How did Einstein do?

$$T \rightarrow \infty$$



$$C_v = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\frac{\exp(\hbar\omega/kT)}{(\exp(\hbar\omega/kT)-1)^2}\right)$$

$$= 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\frac{1+\hbar\omega/kT}{(1+\hbar\omega/kT-1)^2}\right)$$

$$\sim 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\frac{1}{(\hbar\omega/kT)^2}\right)$$

$$\sim 3Nk = \boxed{3nR} \quad \leftarrow$$

Law of Dulong and Petit

Einstein Model

How did Einstein do?

$$\boxed{T \to 0\,\mathrm{K}}$$

$$C_v = 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\frac{\exp(\hbar\omega/kT)}{(\exp(\hbar\omega/kT)-1)^2}\right)$$

$$\sim 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\frac{\exp(\hbar\omega/kT)}{(\exp(\hbar\omega/kT))^2}\right)$$

$$\sim 3Nk\left(\frac{\hbar\omega}{kT}\right)^2\left(\exp(-\hbar\omega/kT)\right)$$

$$\sim \left(\exp(-\hbar\omega/kT)\right) \longleftarrow$$

This goes to zero as T goes to zero!

Einstein Heat Capacity Of Solids

- The theory explained by Einstein is the first quantum theory of solids. He made the simplifying assumption that all 3N vibrational modes of a 3D solid of N atoms had the same frequency, so that the whole solid had a heat capacity 3N times

$$C_v = k_B \left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{\left(e^{\theta/T}-1\right)^2}$$

- In this model, the atoms are treated as independent oscillators, but the energy of the oscillators are taken quantum mechanically as

$$\hbar\omega$$

This refers to an isolated oscillator, but the atomic oscillators in a solid are not isolated.they are continually exchanging their energy with their surrounding atoms.

- Even this crude model gave the correct limit at high temperatures, a heat capacity of

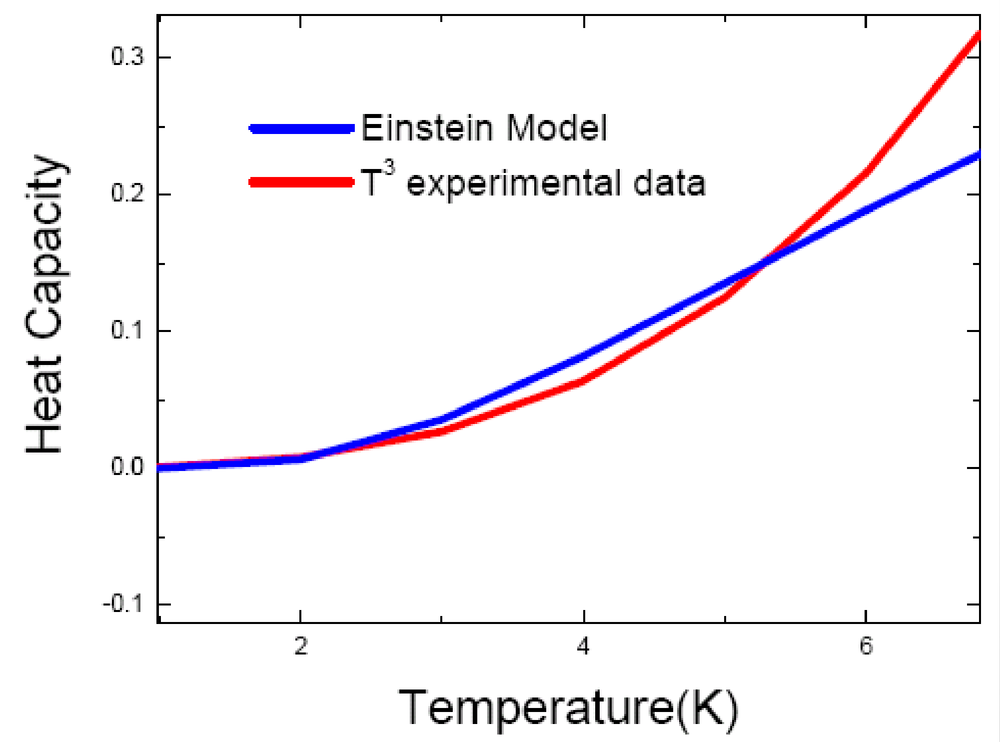
$$3Nk_B = 3R$$

dulong-petit law where R is universal gas constant.

The Discrepancy Of Einstein Model

- Einstein model also gave correctly a Specific Heat tending to zero at absolute zero, but the temperature dependence near T=0 did not agree with experiment.(It is exponential relation)

- Taking into account the actual distribution of vibration frequencies in a solid this discrepancy can be accounted using one dimensional model of monoatomic lattice



The Einstein model failed to identically match the behavior of real solids, but it showed the way.

In real solids, the lattice can vibrate at more than one frequency at a time.

Dulong–Petit model (1819) •

- Atoms on lattice vibrate independently of each other •
- Completely classical •
- Heat capacity independent of temperature (3NkB) •
- Poor agreement with experiment, except at high temperatures

Einstein model (1907) •

- Atoms on lattice vibrate independently of each other •
- Quantum mechanical (vibrations are quantised) •
- Heat Capacity depends on Temperature
- Agreement with experiment good at very high (~3NkB) and very low (~0) temperatures, but not in between

Debye model

Basic idea similar to Einstein model, with one key difference:

Einstein: Energy of system = Phonon Energy x Average number of phonons

Debye: Energy of system = Phonon Energy x Average number of phonons x number of modes

The number and type of modes are the key difference

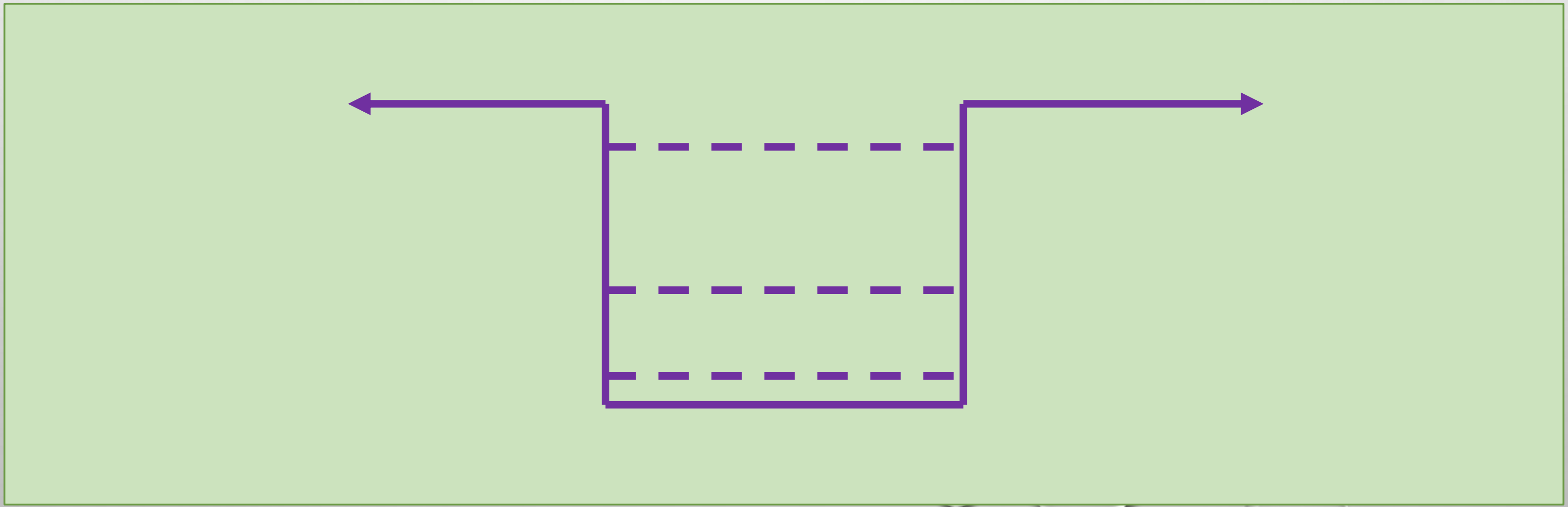
Einstein: number of modes = number of atoms

Debye: each mode has its own k value (and hence frequency)

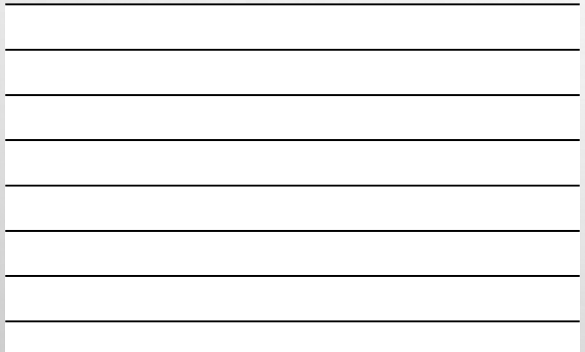
Density Of States

according to Quantum Mechanics if a particle is constrained;

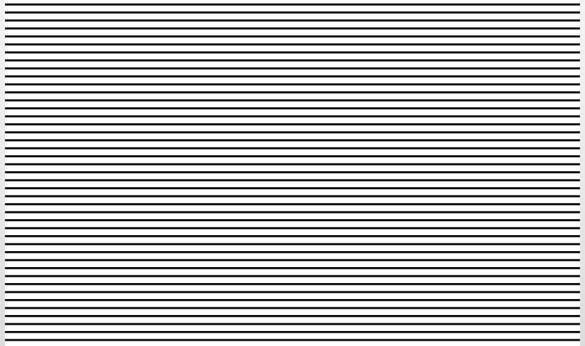
- The energy of particle can only have special discrete energy values.
- It cannot increase infinitely from one value to another.
- It has to go up in steps.



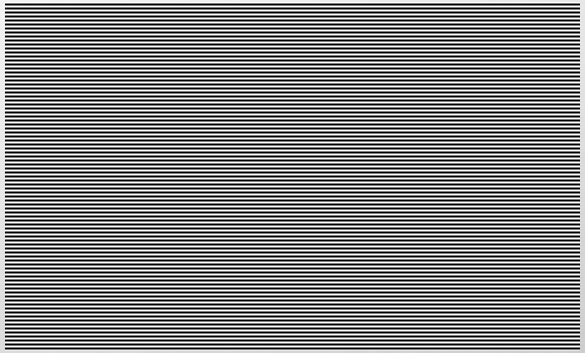
- These steps can be so small depending on the system that the energy can be considered as continuous.
- This is the case of classical mechanics.
- But on atomic scale the energy can only jump by a discrete amount from one value to another.



Definite energy levels



Steps get small



Energy is continuous

- In some cases, each particular energy level can be associated with more than one different state (or wavefunction)
- This energy level is said to be degenerate.

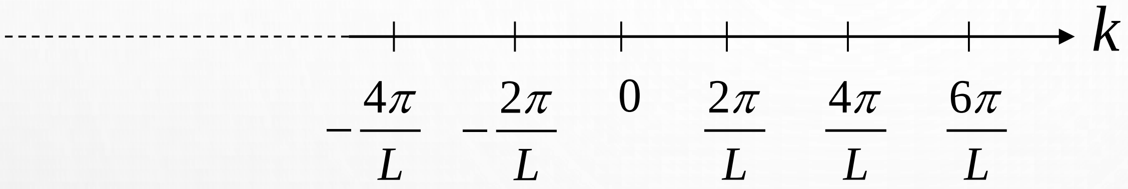
- The density of states $D(\varepsilon)$ is the number of discrete states per unit energy interval, and so that the number of states between ε and $\varepsilon + d\varepsilon$ will be .

$$D(\varepsilon)d\varepsilon$$

There are two sets of waves for solution;

- Running waves
- Standing waves

Running (Travelling) waves:



These allowed k wavenumbers corresponds to the running waves; **all positive and negative values of k are allowed**. By means of periodic boundary condition

$$L = Na = p\lambda \Rightarrow \lambda = \frac{Na}{p} = \frac{2\pi}{k} \Rightarrow k = \frac{2\pi}{Na}\,p \Rightarrow \boxed{k = \frac{2\pi}{L}\,p}$$

an integer

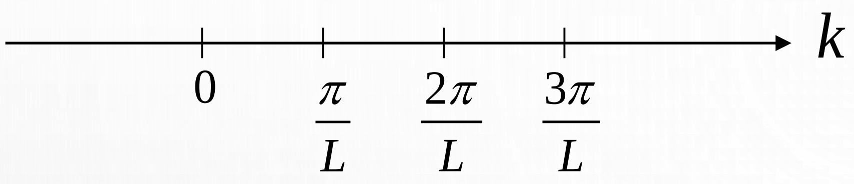
Length of the 1D chain

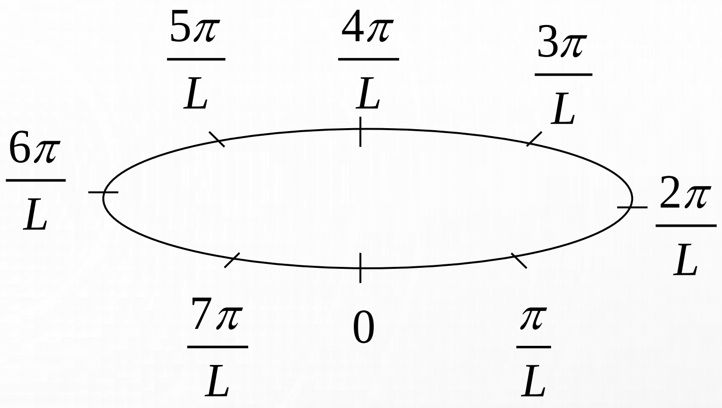
These allowed wavenumbers are uniformly distibuted in k at a density of $D_R(k)$ between k and k+dk.

running waves

$$\boldsymbol{D_R(k)dk = \frac{L}{2\pi}dk}$$

Standing waves:





In some cases it is more suitable to use standing waves,i.e. chain with fixed ends. Therefore we will have an integral number of half wavelengths in the chain;

$$L = \frac{n\lambda}{2}; k = \frac{2\pi}{\lambda} \Rightarrow k = \frac{2\pi n}{2L} \Rightarrow k = \frac{n\pi}{L}$$

These are the allowed wavenumbers for standing waves; only positive values are allowed.

$$k = \frac{2\pi}{L} p \longrightarrow$$

for

running waves

$$k = \frac{\pi}{L} p \longrightarrow$$

for

standing waves

These allowed k’s are uniformly distributed between k and k+dk at a density of $D_s(k)$

$$\boldsymbol{D_s(k)dk = \frac{L}{\pi}dk}$$ ⇒ DOS of standing wave

$$\boldsymbol{D_R(k)dk = \frac{L}{2\pi}dk}$$ ⇒ DOS of running wave

- The *density of standing wave states is twice that of the running waves.*
- However in the case of standing waves only positive values are allowed
- Then the total number of states for both running and standing waves will be the same in a range dk of the magnitude k
- The standing waves have the same dispersion relation as running waves, and for a chain containing N atoms there are exactly N distinct states with k values in the range 0 to π/a .

The Density Of States Per Unit Frequency Range g(ω):

- the number of modes with frequencies ω and ω+dω will be g(ω)dω.
- g(ω) can be written in terms of $D_s(k)$ and $D_R(k)$.

dR modes with frequency from ω to $\omega+d\omega$ corresponds

dn modes with wavenumber from k to $k+dk$

$dn = D_R(k)dk = g(\omega)d\omega$

$dn = D_s(k)dk = g(\omega)d\omega$

Choose standing waves to obtain $g(\omega)$

$$g(\omega) = D_s(k)\frac{dk}{d\omega}$$

Let’s remember dispertion relation for 1D monoatomic lattice

$$\omega^2 = \frac{4K}{m}\sin^2\frac{ka}{2} \Rightarrow \omega = 2\sqrt{\frac{K}{m}}\sin\frac{ka}{2}$$

$$\frac{d\omega}{dk} = \frac{2a}{2}\sqrt{\frac{K}{m}}\cos\frac{ka}{2}$$

$$= a\sqrt{\frac{K}{m}}\cos\frac{ka}{2} \Rightarrow g(\omega) = D_s(k)\frac{1}{a\sqrt{\frac{K}{m}}\cos\frac{ka}{2}}$$

$$g(\omega) = D_s(k)\frac{1}{a}\sqrt{\frac{m}{K}}\frac{1}{\cos\left(\frac{ka}{2}\right)}$$

$$g(\omega) = D_s(k)\frac{1}{a}\sqrt{\frac{m}{K}}\frac{1}{\cos\left(ka/2\right)}$$

$$\sin^2 x + \cos^2 x = 1 \Rightarrow \cos x = \sqrt{1-\sin^2 x}$$

→

$$\cos\left(\frac{ka}{2}\right) = \sqrt{1-\sin^2\left(\frac{ka}{2}\right)}$$

$$g(\omega) = D_s(k)\ \frac{1}{a}\sqrt{\frac{m}{K}}\frac{1}{\sqrt{1-\sin^2\left(\frac{ka}{2}\right)}}\frac{\sqrt{4}}{\sqrt{4}}$$

Multibly and divide

$$g(\omega) = D_s(k)\frac{1}{a}\frac{2}{\sqrt{\frac{4K}{m}-\frac{4K}{m}\sin^2\left(\frac{ka}{2}\right)}}$$

$$g(\omega) = \frac{L}{\pi}\frac{2}{a}\frac{1}{\sqrt{\omega_{\max}^2-\omega^2}}$$

$$\boxed{g(\omega) = \frac{2N}{\pi}\left(\omega_{\max}^2-\omega^2\right)^{-1/2}}$$

True density of states

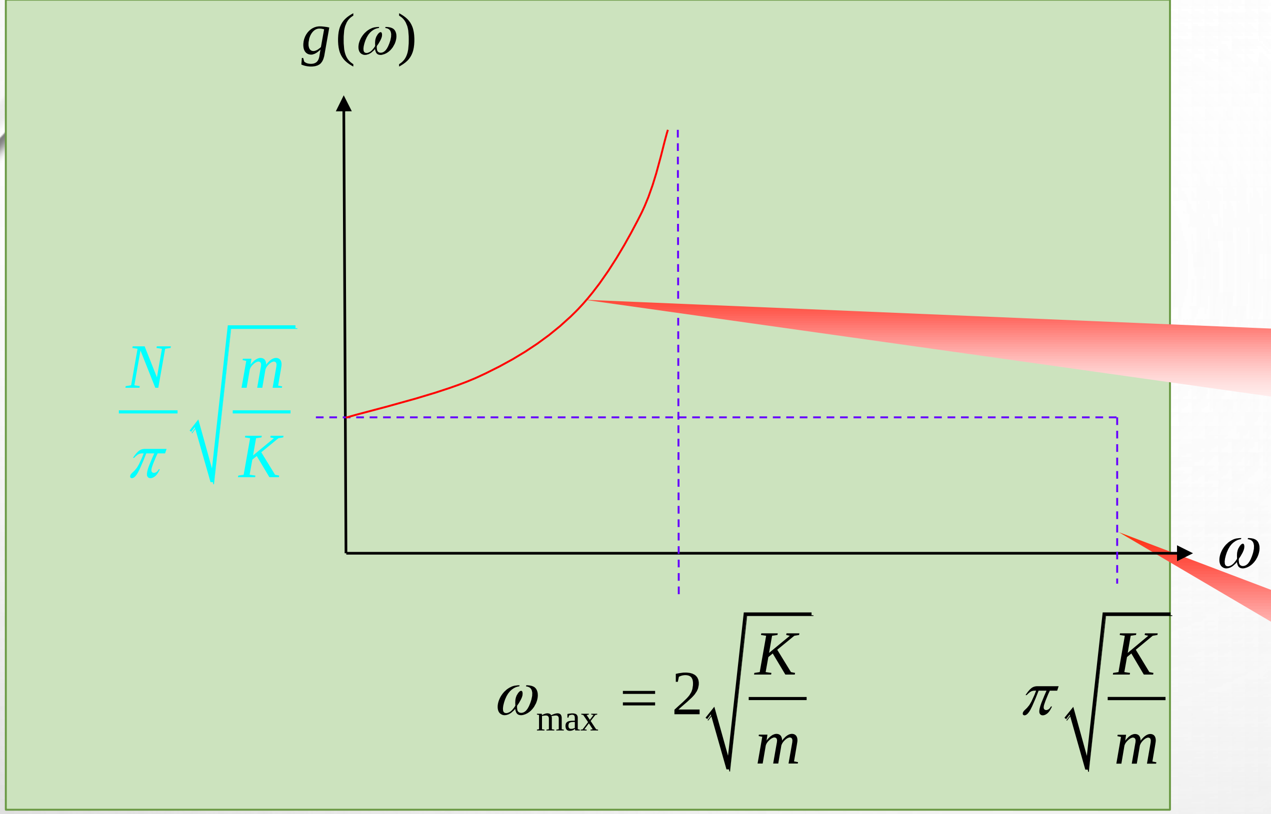
Let’s remember:

$$D_s(k)dk = \frac{L}{\pi}dk$$

$$L = Na$$

$$\omega^2 = \frac{4K}{m}\sin^2\left(\frac{ka}{2}\right)$$

$$\omega_{\max}^2 = \frac{4K}{m}$$



$$g(\omega) = \frac{2N}{\pi}\left(\omega_{\max}^2 - \omega^2\right)^{-1/2}$$

True density of states by means of above equation

constant density of states

True DOS(density of states) tends to infinity at $\omega_{\max} = 2\sqrt{\frac{K}{m}}$

since the group velocity $d\omega/dk$ goes to zero at this value of ω.

Constant density of states can be obtained by ignoring the dispersion of sound at wavelengths comparable to atomic spacing.

The energy of lattice vibrations will then be found by integrating the energy of single oscillator over the distribution of vibration frequencies. Thus

$$\varepsilon = \int_0^\infty \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\times g(\omega)\,d\omega$$

Mean energy of a harmonic oscillator

$$\frac{2N}{\pi}\left(\omega_{\max}^2-\omega^2\right)^{-1/2}$$ for 1D

It should be better to find 3D DOS in order to compare the results with experiment.

$$N(K)=\frac{\frac{4}{3}\pi K^{3}}{\left(\frac{2\pi}{L}\right)^{3}}=\frac{L^{3}}{(2\pi)^{3}}.\frac{4}{3}\pi K^{3}=\frac{V}{(2\pi)^{3}}.\frac{4}{3}\pi K^{3}$$

$$dN(K)=\frac{V}{(2\pi)^{3}}.4\pi K^{2}dK$$

- $D(k)=\dfrac{Vk^{2}}{2\pi^{2}}$ is a new density of states in 3D.This eqn can be obtained by using running waves as well.
- ω(frequency) space can be related to k-space:

$$g(\omega)d\omega=D(k)dk \qquad\qquad g(\omega)=D(k)\frac{dk}{d\omega}$$

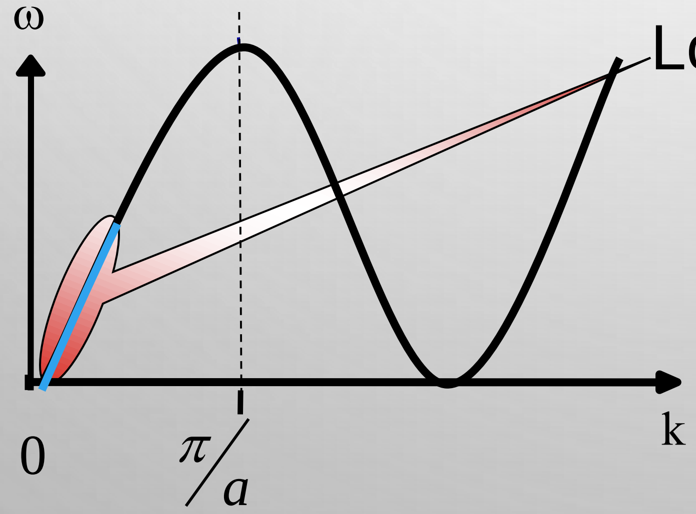
Let’s find C at low and high temperature by means of using the expression of $g(\omega)$.

High And Low Temperature Limits

$\bar{\varepsilon} = 3Nk_BT$ Each of the 3N lattice modes of a crystal containing N atoms ⇒ $C = \frac{d\bar{\varepsilon}}{dT}$ ⇒ $C = 3Nk_B$

- this result is true only if $T \gg \frac{\hbar\omega}{k_B} \longrightarrow \theta$

- At low T's only lattice modes having low frequencies can be excited from their ground states;



Low frequency ⇒ long λ

⇓

sound waves

$\omega = v_s k$ ⇒ $v_s = \frac{\omega}{k}$

$$v_s = \frac{\omega}{k} \Rightarrow \frac{k}{\omega} = \frac{1}{v_s} \Rightarrow \frac{dk}{d\omega} = \frac{1}{v_s}$$

and

$$g(\omega) = \frac{Vk^2}{2\pi^2}\frac{dk}{d\omega}$$

$$g(\omega) = \frac{V\left(\frac{\omega^2}{v_s^2}\right)}{2\pi^2}\frac{1}{v_s}$$ *at low T's*

v_s depends on the direction and there are two transverse, one longitudinal acoustic branch:

$$g(\omega) = \frac{V\omega^2}{2\pi^2}\frac{1}{v_s^3} \Rightarrow g(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

Velocities of sound in longitudinal and transverse direction

$$\varepsilon=\int_0^\infty\left(\frac{1}{2}\hbar\omega+\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\times g(\omega)\,d\omega$$

Zero point energy= ε_z

$$\varepsilon=\int_0^\infty\left(\frac{1}{2}\hbar\omega+\frac{\hbar\omega}{e^{\hbar\omega/kT}-1}\right)\times\frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)d\omega$$

$$\varepsilon=\varepsilon_z+\left[\frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\right]\left(\int_0^\infty\frac{\hbar\omega^3}{\left(e^{\hbar\omega/kT}-1\right)}d\omega\right)$$

$$\int_0^\infty\frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1}d\omega=\int_0^\infty\frac{\cancel{\hbar}\left(\frac{k_BT}{\hbar}\right)^3x^3}{e^x-1}\frac{k_BT}{\cancel{\hbar}}dx$$

$$\int_0^\infty\frac{\hbar\omega^3}{e^{\hbar\omega/kT}-1}d\omega=\frac{(k_BT)^4}{\hbar^3}\underbrace{\int_0^\infty\frac{x^3}{e^x-1}dx}_{\pi^4/15}$$

$$\varepsilon=\varepsilon_z+\frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\frac{(k_BT)^4}{\hbar^3}\frac{\pi^4}{15}$$

$$C_v=\frac{d\varepsilon}{dT}=\frac{V\pi^2}{30\hbar^3}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)k_B{}^4\,4T^3$$

$$x=\frac{\hbar\omega}{k_BT}$$

$$\omega=\frac{k_BT}{\hbar}x$$

$$d\omega=\frac{k_BT}{\hbar}dx$$

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

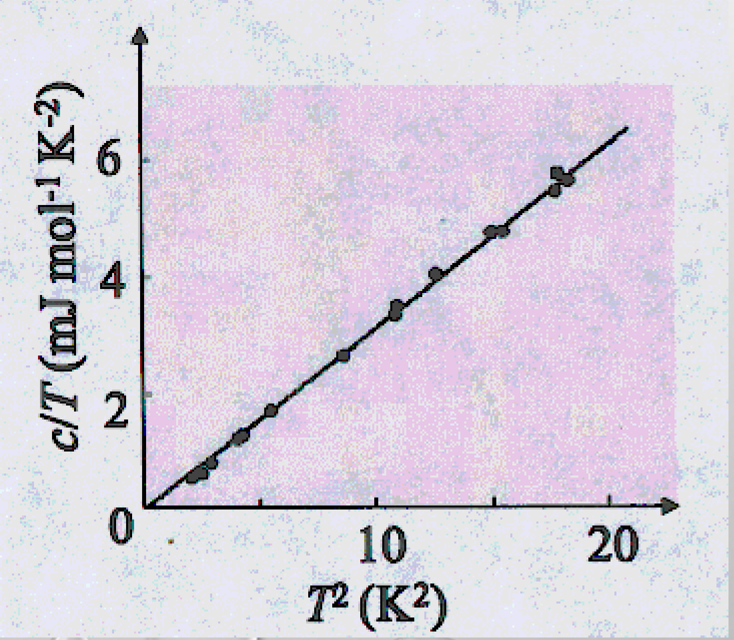
at low temperatures

$$C_v=\frac{d\varepsilon}{dT}=\frac{2}{15}V\pi^2k_B\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\left(\frac{k_BT}{\hbar}\right)^3$$

How Good İs The Debye Approximation At Low T?

$$C_v = \frac{d\varepsilon}{dT} = \frac{2}{15} V \pi^2 k_B \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \left(\frac{k_B T}{\hbar} \right)^3$$

The lattice heat capacity of solids thus varies as T^3 at low temperatures; this is referred to as the Debye T^3 law. Figure illustrates the excellent aggrement of this prediction with experiment for a non-magnetic insulator. The heat capacity vanishes more slowly than the exponential behaviour of a single harmonic oscillator because the vibration spectrum extends down to zero frequency.



The Debye İnterpolation Scheme

the calculation of $g(\omega)$ is a very heavy calculation for 3D, so it must be calculated numerically.

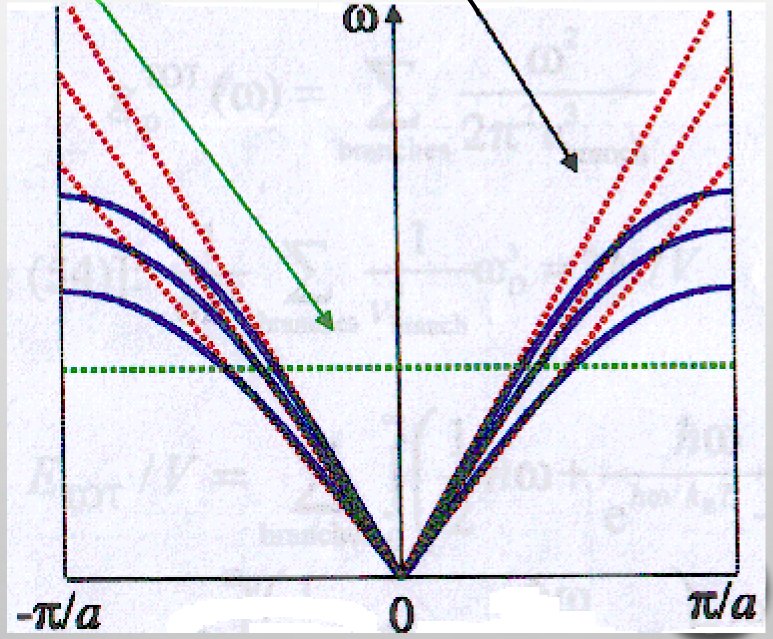
debye obtained a good approximation to the resulting heat capacity by neglecting the dispersion of the acoustic waves, i.e. assuming

$$\omega = \upsilon_s k$$

for arbitrary wavenumber. ın a one dimensional crystal this is equivalent to taking $g(\omega)$ as given by the broken line of density of states figure rather than full curve. debye’s approximation gives the correct answer in either the high and low temperature limits, and the language associated with it is still widely used today.

The Debye approximation has two main steps:

1. approximate the dispersion relation of any branch by a linear extrapolation of the small k behaviour:



Einstein approximation to the dispersion

Debye approximation to the dispersion

$$\omega = vk$$

Debye Cut-off Frequency ω_D

2. ensure the correct number of modes by imposing a cut-off frequency ω_D , above which there are no modes. the cut-off freqency is chosen to make the total number of lattice modes correct. since there are 3N lattice vibration modes in a crystal having N atoms, we choose ω_D so that

$$\int_0^{\omega_D} g(\omega)d\omega = 3N$$

$$g(\omega)=\frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)$$

$$\frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\int_0^{\omega_D}\omega^2 d\omega=3N$$

$$\frac{V}{6\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)\omega_D^3=3N \Longrightarrow \frac{V}{2\pi^2}\left(\frac{1}{v_L^3}+\frac{2}{v_T^3}\right)=\frac{3N}{\omega_D^3}3=\frac{9N}{\omega_D^3}$$

$$g(\omega)=\frac{9N}{\omega_D^3}\omega^2$$

$$g(\omega)\propto\omega^2$$

the lattice vibration energy of

$$E=\int_0^\infty\left(\frac{1}{2}\hbar\omega+\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\right)g(\omega)d\omega$$

becomes

$$E=\frac{9N}{\omega_D^3}\int_0^{\omega_D}\left(\frac{1}{2}\hbar\omega+\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\right)\omega^2d\omega=\frac{9N}{\omega_D^3}\left[\int_0^{\omega_D}\frac{\hbar\omega^3}{2}d\omega+\int_0^{\omega_D}\frac{\hbar\omega^3}{e^{\hbar\omega/k_BT}-1}d\omega\right]$$

and

$$E=\frac{9}{8}N\hbar\omega_D+\frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3d\omega}{e^{\hbar\omega/k_BT}-1}$$

first term is the estimate of the zero point energy, and all T dependence is in the second term. the heat capacity is obtained by differentiating above eqn wrt temperature.

The heat capacity is $C = \frac{dE}{dT}$

$$E = \frac{9}{8} N\hbar\omega_D + \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_BT} - 1} \Rightarrow C_D = \frac{dE}{dT} = \frac{9N}{\omega_D^3}\int_0^{\omega_D} \frac{\hbar^2\omega^4}{k_BT^2}\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2} d\omega$$

Let's convert this complicated integral into an expression for the specific heat changing variables to x

$$x = \frac{\hbar\omega}{k_BT} \longrightarrow \frac{d\omega}{dx} = \frac{kT}{\hbar} \qquad \omega = \frac{kT}{\hbar}x$$

and define the Debye temperature Θ_D

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

The Debye prediction for lattice specific heat

$$C_D = \frac{dE}{dT} = \frac{9N}{\omega_D^3}\frac{k_B T}{\hbar}\left(\frac{k_B T}{\hbar}\right)^4\left(\frac{\hbar^2}{k_B T^2}\right)\int_0^{\Theta_D/T}\frac{x^4 e^x}{\left(e^x - 1\right)^2}dx$$

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

where $\Theta_D = \frac{\hbar\omega_D}{k_B}$

How does C_D limit at high and low temperatures?

High temperature

- $T \gg \Theta_D$

X is always small

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

$$\frac{x^4 e^x}{\left(e^x - 1\right)^2} = \frac{x^4(1+x)}{\left(1+x-1\right)^2} = \frac{x^4(1+x)}{x^2} = x^2$$

$$T \gg \Theta_D \Rightarrow C_D \cong 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} x^2 dx = 3Nk_B$$

How does C_D limit at high and low temperatures?

Low temperature

- $T \ll \Theta_D$

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N}{\omega_D^3}\int_0^{\omega_D}\frac{\hbar\omega^3 d\omega}{e^{\hbar\omega/k_BT}-1}$$

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\left(\frac{k_BT}{\hbar}\right)^3\frac{x^3}{e^x-1}\frac{kT\,dx}{\hbar}$$

For low temperature the upper limit of the integral is infinite; the integral is then a known integral of

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

x is very large

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D}\left(\frac{kT}{\hbar}\right)^4\int_0^\infty\frac{x^3}{e^x-1}dx$$

$$E = \frac{9}{8}N\hbar\omega_D + \frac{9N\hbar}{\omega_D^3}\frac{\pi^4}{15}\left(\frac{kT}{\hbar}\right)^4$$

$$C_D = 0 + \frac{9N\hbar}{\omega_D^3}\frac{\pi^4}{15}\left(\frac{k}{\hbar}\right)^4 4T^3$$

$$\Theta_D = \frac{\hbar\omega_D}{k_B}$$

We obtain the Debye T^3 law in the form

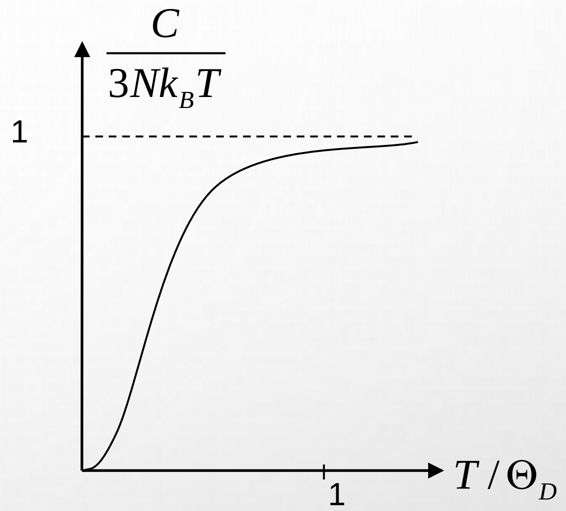
$$C_D \cong \frac{12Nk_B\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3$$

Lattice Heat Capacity Due To Debye İnterpolation Scheme

figure shows the heat capacity between the two limits of high and low t as predicted by the debye interpolation formula.

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

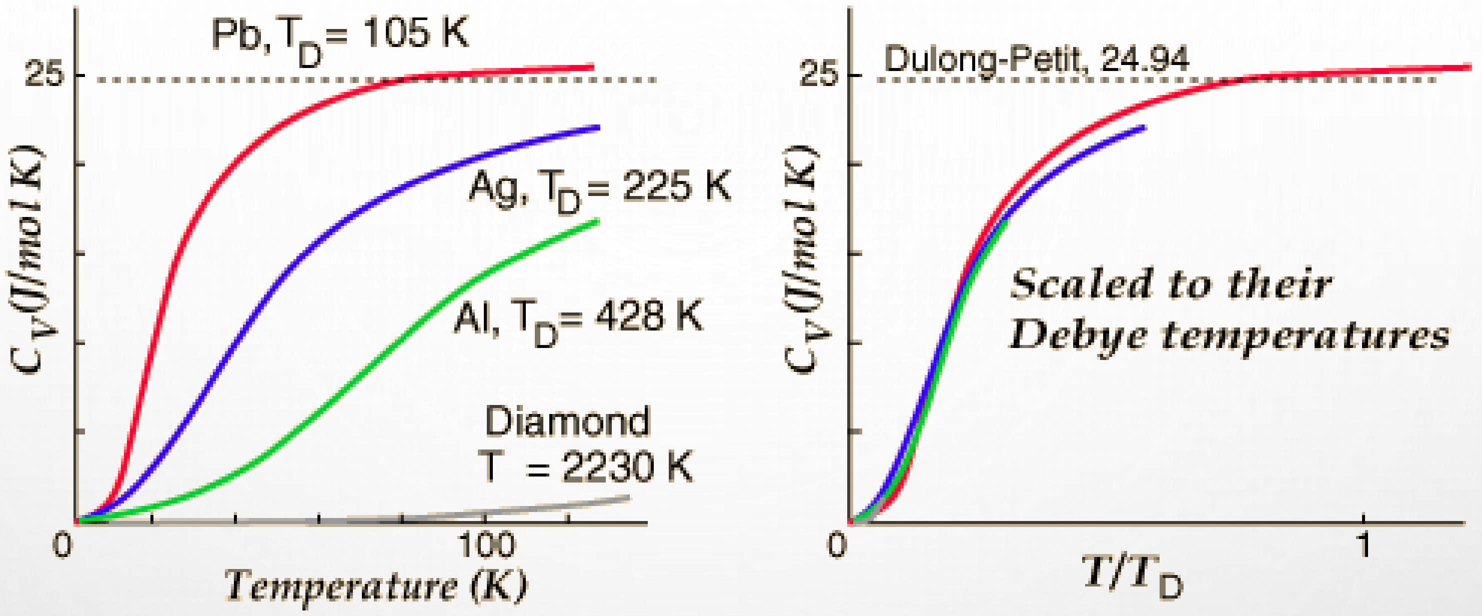
Because it is exact in both high and low T limits the Debye formula gives quite a good representation of the heat capacity of most solids, even though the *actual phonon-density of states curve may differ* appreciably from the Debye assumption.



Lattice heat capacity of a solid as predicted by the Debye interpolation scheme

Debye frequency and Debye temperature scale with the velocity of sound in the solid. So solids with low densities and large elastic moduli have high Θ_D . Values of for Θ_D various solids is given in table. Debye energy $\hbar\omega_D$ can be used to estimate the maximum phonon energy in a solid.

Solid	Ar	Na	Cs	Fe	Cu	Pb	C	KCl
$\Theta_D(K)$	93	158	38	457	343	105	2230	235



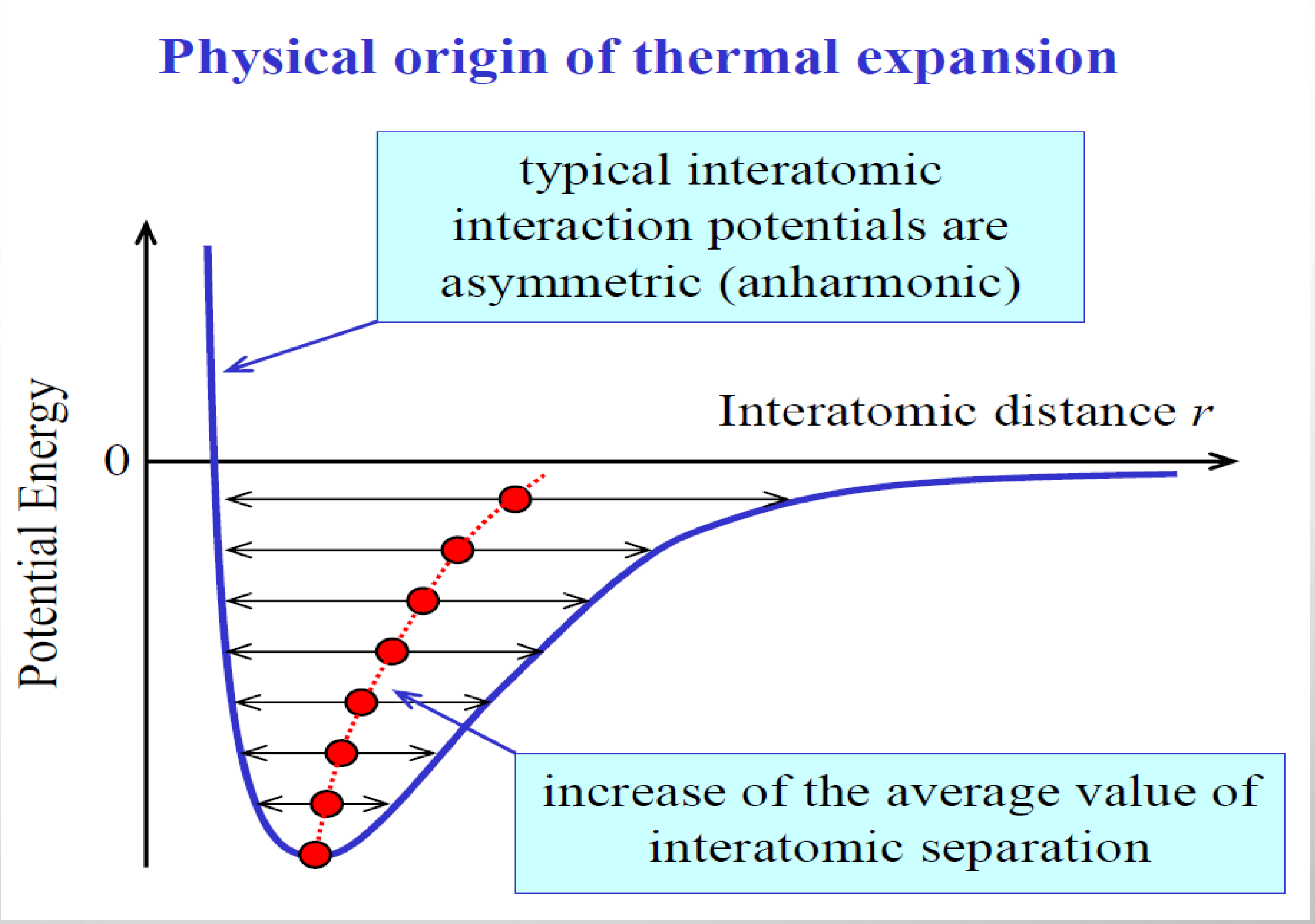
Specific Heats of Lead, Silver, Aluminum and Diamond

Anharmonic Effects

- Any real crystal resists compression to a smaller volume than its equilibrium value more strongly than expansion due to a larger volume.
- This is due to the shape of the interatomic potential curve.
- This is a departure from hooke's law, since harmonic application does not produce this property.
- This is an anharmonic effect due to the higher order terms in potential which are ignored in harmonic approximation.

- Thermal expansion is an example to the anharmonic effect.
- In harmonic approximation phonons do not interact with each other, in the absence of boundaries, lattice defects and impurities (which also scatter the phonons), the thermal conductivity is infinite.
- In anharmonic effect phonons collide with each other and these collisions limit thermal conductivity which is due to the flow of phonons.

Rising temperature results in the increase of the average amplitude of atomic vibrations. For an anharmonic potential, this corresponds to the increase in the average value of interatomic separation, i.e. thermal expansion.

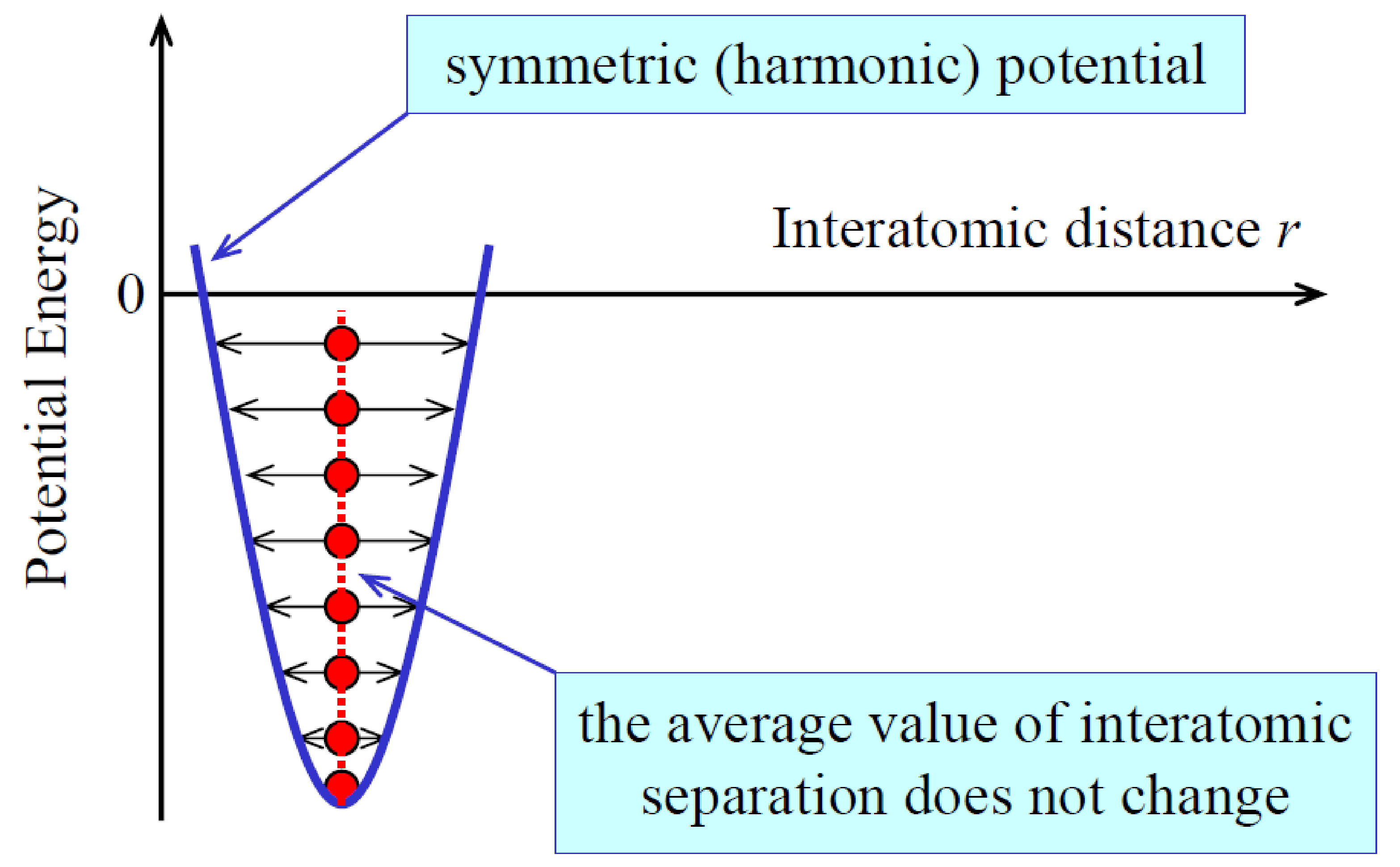


Physical origin of thermal expansion

typical interatomic interaction potentials are asymmetric (anharmonic)

increase of the average value of interatomic separation

Thermal expansion is related to the asymmetric (anharmonic) shape of interatomic potential. If the interatomic potential is symmetric (harmonic), the average value of interatomic separation does not change, i.e. no thermal expansion.

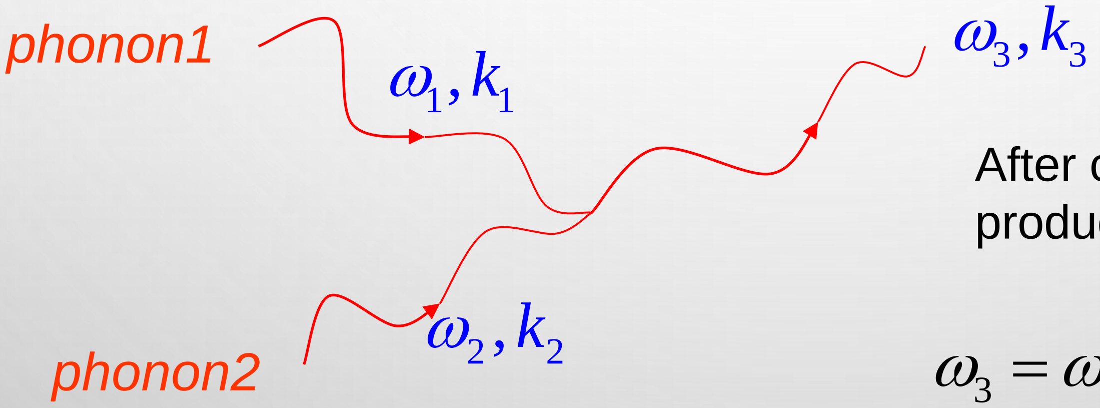


symmetric (harmonic) potential

the average value of interatomic separation does not change

Phonon–phonon Collisions

The coupling of normal modes by the unharmonic terms in the interatomic forces can be pictured as collisions between the phonons associated with the modes. A typical collision process of



After collision another phonon is produced

$\omega_3 = \omega_1 + \omega_2$ and $k_3 = k_1 + k_2$

$\hbar\omega_3 = \hbar\omega_1 + \hbar\omega_2$ ➡ conservation of energy

$\hbar k_3 = \hbar k_1 + \hbar k_2$ ➡ conservation of momentum

Phonons are represented by wavenumbers with

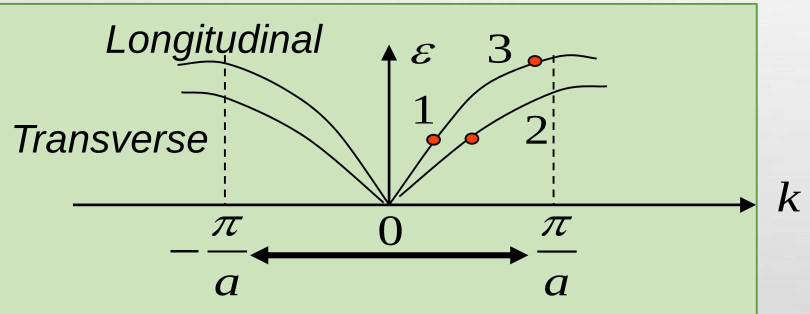
$$-\frac{\pi}{a} \le k \le \frac{\pi}{a}$$

If k_3 lies outside this range add a suitable multible of $\frac{2\pi}{a}$ to bring it back within the range of $-\frac{\pi}{a} \le k \le \frac{\pi}{a}$. Then, $k_3 = k_1 + k_2$ becomes

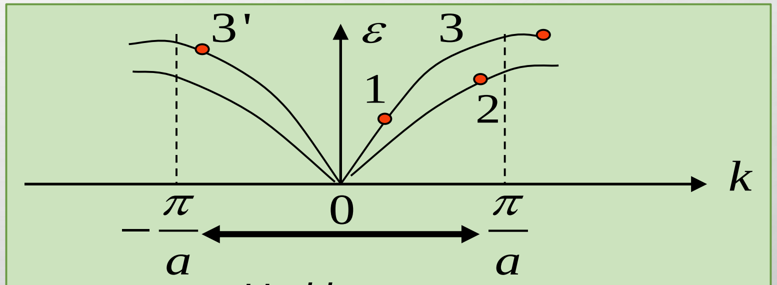
This phonon is indistinguishable
from a phonon with wavevector k_3

$$\boxed{k_3 \pm \frac{n2\pi}{a}} = k_1 + k_2$$

where k_1, k_2 , and k_3 are all in the above range.



$n = 0 \Rightarrow$ Normal process



$n \ne 0 \Rightarrow$ Umklapp process

(due to anharmonic effects)

Phonon3 has $|k| \prec \frac{\pi}{a}$; Phonon3 has $|k| \succ \frac{\pi}{a}$ and Phonon3=Phonon3'

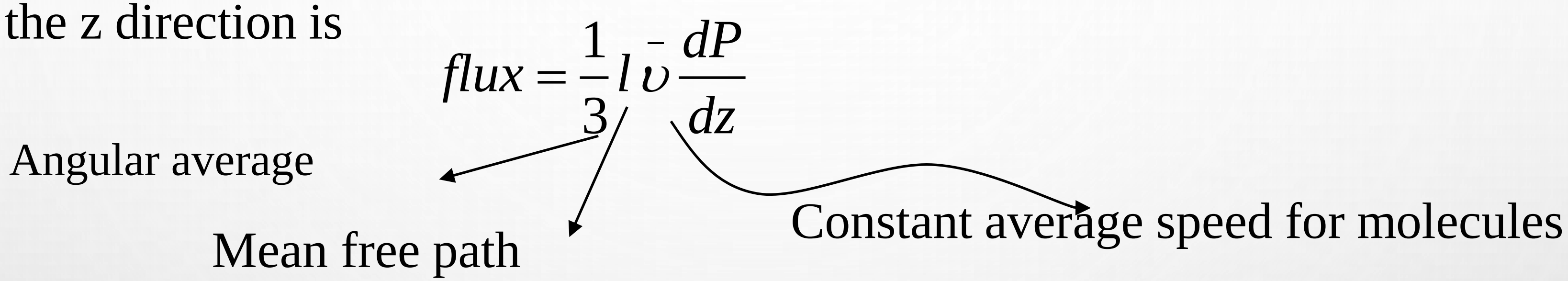
Thermal Conduction By Phonons

- Thermal conductivity is the property of a material's ability to conduct heat.
- A flow of heat takes place from a hotter region to a cooler region when there is a temperature gradient in a solid.
- The most important contribution to thermal conduction comes from the flow of phonons in an electrically insulating solid.
- ***Transport property*** is an example of thermal conduction.
- ***Transport property is*** the process in which the flow of some quantity occurs.
- ***Thermal conductivity*** is a transport coefficient and it describes the flow.
- The thermal conductivity of a phonon gas in a solid will be calculated by means of the elementary kinetic theory of the transport coefficients of gases.

Kinetic Theory

In the elementary kinetic theory of gases, the steady state flux of a property P

İn the z direction is



$$flux = \frac{1}{3} l \bar{\upsilon} \frac{dP}{dz}$$

Angular average

Mean free path

Constant average speed for molecules

In the simplest case where P is the number density of particles the transport coefficient obtained from above eqn. is the ***diffusion coefficient*** $D = \frac{1}{3} l \bar{\upsilon}$.

If P is the energy density E then the flux W is the heat flow per unit area so that

$$W = \frac{1}{3} l \bar{\upsilon} \frac{dE}{dz} = \frac{1}{3} l \bar{\upsilon} \frac{dE}{dT} \frac{dT}{dz}$$

Now dE/dT is the specific heat C per unit volume, so that the thermal conductivity;

$K = \frac{1}{3} l \bar{\upsilon} C \longrightarrow$ Works well for a phonon gas

Heat Conduction İn A Phonon And Real Gas

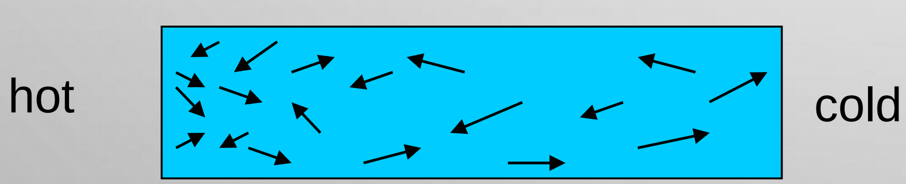
The Essential Differences Between The Processes Of Heat Conduction İn A Phonon And Real Gas;

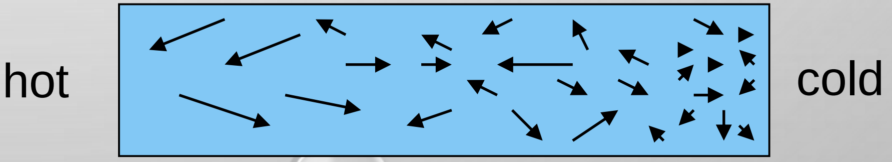
Phonon gas

- Speed is approximately constant.
- Both the number density and energy density is greater at the hot end.
- Heat flow is primarily due to phonon flow with phonons being *created* at the hot end and *destroyed* at the cold end

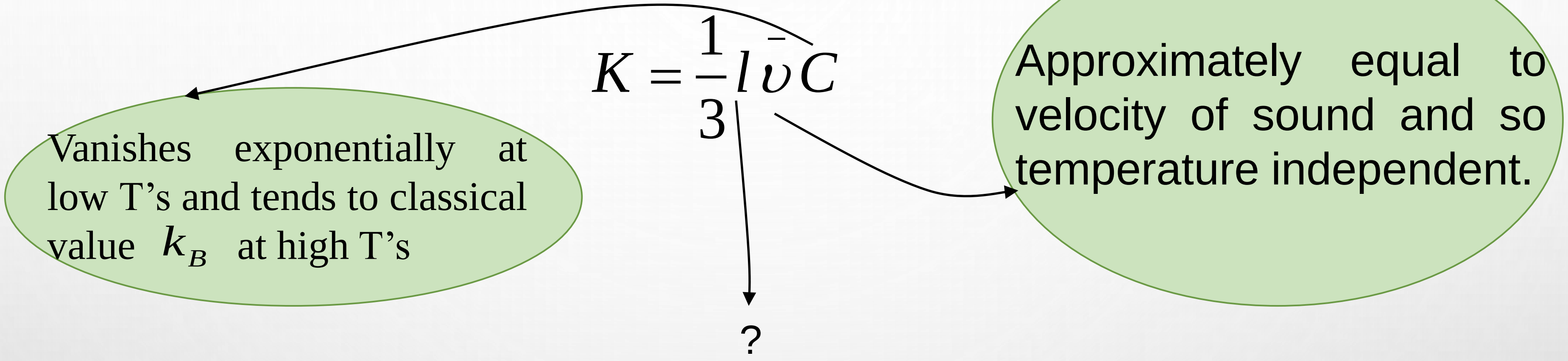
Real gas

- No flow of particles
- Average velocity and kinetic energy per particle are greater at the hot end, but the number density is greater at the cold end, and the energy density is uniform due to the uniform pressure.
- Heat flow is solely by transfer of kinetic energy from one particle to another in collisions which is a minor effect in phonon case.





Temperature Dependence Of Thermal Conductivity K



$$K = \frac{1}{3} l \bar{\upsilon} C$$

Vanishes exponentially at low T's and tends to classical value k_B at high T's

?

Approximately equal to velocity of sound and so temperature independent.

- Temperature dependence of phonon mean free length is determined by phonon-phonon collisions at low temperatures
- Since the heat flow is associated with a flow of phonons, the most effective collisions for limiting the flow are those in which the phonon group velocity is reversed. It is the Umklapp processes that have this property, and these are important in limiting the thermal conductivity

Conduction At High Temperatures

- At temperatures much greater then the debye temperature Θ_D the heat capacity is given by temperature-independent classical result of

$$C = 3Nk_B$$

- The rate of collisions of two phonons $\propto$ phonon density.

- If collisions involving larger number of phonons are important, however, then the scattering rate will increase more rapidly than this with phonon density.

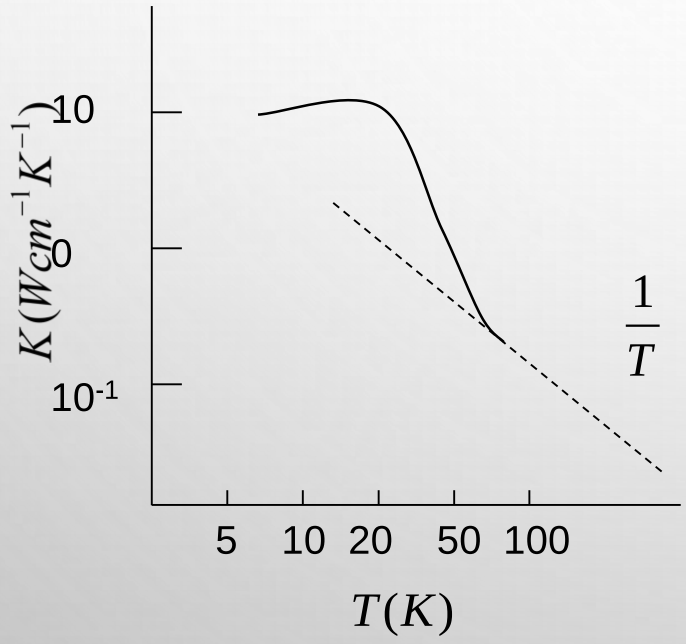
- At high temperatures the average phonon density is constant and

the total lattice energy $\propto$ T ; phonon number $\propto$ T , so

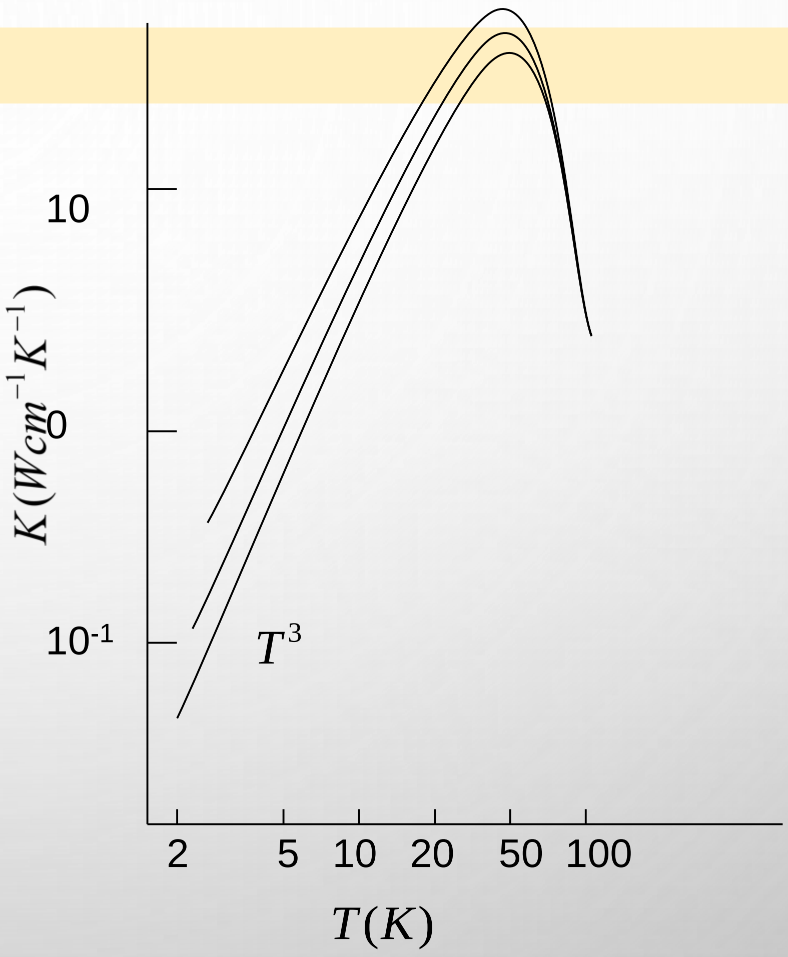
scattering rate $\propto$ T and mean free length $\propto$ T^{-1}

Then the thermal conductivity of $K = \frac{1}{3} l \bar{\upsilon} C \quad \propto \quad \dot{T}^{-1}$

- Experimental results do tend towards this behaviour at high temperatures as shown in figure (a).



(a)Thermal conductivity of a quartz crystal



(b)Thermal conductivity of artificial sapphire rods of different diameters

Conduction At İntermediate Temperatures

Referring figure a

At T< θ_D; the conductivity rises more steeply with falling temperature, although the heat capacity is falling in this region. Why?

⇩

This is due to the fact that umklapp processes which will only occur if there are phonons of sufficient energy to create a phonon with $k_3 > \pi / a$. so

⇩

Energy of phonon must be $\propto$ the debye energy ($k\theta_D$)

⇩

the energy of relevant phonons is thus not sharply defined but their number is expected to vary roughly as

$e^{-\theta_D / bT}$ when $T < \theta_D$,

Where b is a number of order unity 2 or 3. Then $l \propto e^{\theta_D / bT}$

This exponential factor dominates any low power of T in thermal conductivity,

Such as a factor of T^3 from the heat capacity.

Conduction At Low Temperatures

l For phonon-phonon collisions becomes very long at low T’s and eventually exceeds the size of the solid, because

Number of high energy phonons necessary for umklapp processes decay exponentially as

$$e^{-\theta_D/bT}$$

l İs then limited by collisions with the specimen surface, i.E.

$l \propto$ Specimen diameter

T dependence of k comes from C_v which obeys T^3 law in this region

$$C_D \cong \frac{12Nk_B\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3$$

Temperature dependence of C_v dominates.

Size Effect

- When the mean free path becomes comparable to the dimensions of the sample, transport coefficient depends on the shape and size of the crystal. This is known as a ***size effect.***

- If the specimen is not a perfect crystal and contains imperfections such as dislocations, grain boundaries and impurities, then these will also scatter phonons. At the very lowest t's the dominant phonon wavelength becomes so long that these imperfections are not effective scatterers, so;

  The thermal conductivity has a T^3 dependence at these temperatures.

- The maximum conductivity between T^3 and $e^{\theta_D / bT}$ region is controlled by imperfections.

- For an impure or polycrystalline specimen the maximum can be broad and low [figure (a)], whereas for a carefully prepared single crystal, as illustrated in figure(b) , the maximum is quite sharp and conductivity reaches a very high value, of the order that of the metallic copper in which the conductivity is predominantly due to conduction electrons.