A
Presentation
on
Specific Heat or Heat Capacity of solids
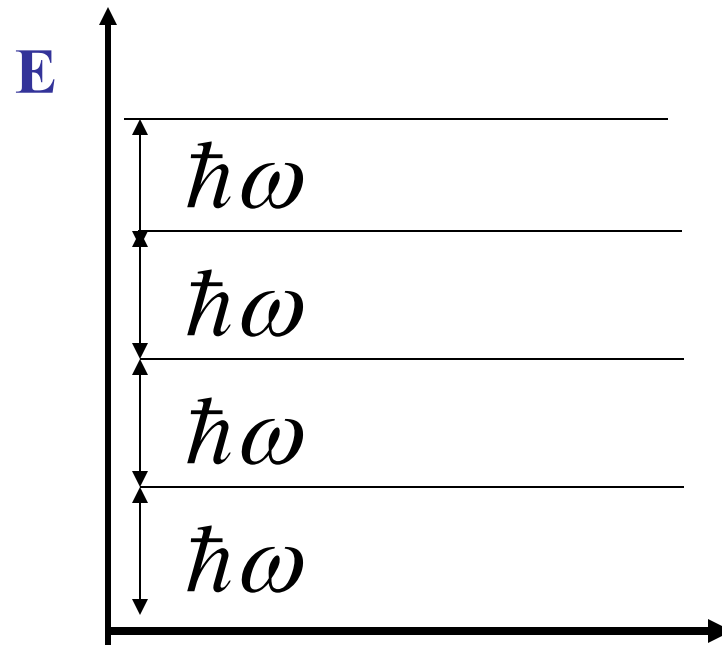
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Quantum Mechanical Simple Harmonic Oscillator

- Quantum mechanical results for a simple harmonic oscillator with classical frequency ω: The energy is quantized

$$E_n = \left(n + \frac{1}{2} \right)\hbar\omega \qquad n = 0,1,2,3,..$$

- **Energy levels are equally spaced!**

Often, we consider E_n as being constructed by adding **n** excitation quanta of energy $\hbar\omega$ to the ground state.

$$E_0 = \frac{1}{2}\hbar\omega$$

← ***Ground state energy of the oscillator.***

If the system makes a transition from a lower energy level to a higher energy level, it is always true that the change in energy is an integer multiple of $\hbar\omega$

Phonon absorption or emission

$$\Delta E = (n - n')\hbar\omega$$

n & n ´ = integers

In complicated processes, such as phonons interacting with electrons or photons, it is known that ***phonons are not conserved.*** That is, they can be created and destroyed during such interactions.

Thermal Energy & Lattice Vibrations

As we've been discussing in detail, the atoms in a crystal vibrate about their equilibrium positions.
This motion produces vibrational waves.

The amplitude of this vibrational motion increases as the temperature increases.

In a solid, the energy associated with these **vibrations** is called
Thermal Energy

- A knowledge of the **thermal energy** is fundamental to obtaining an understanding many of the basic properties of solids. A relevant **question** is how do we calculate this **thermal energy**?

- Also, we would like to know how much thermal energy is available to scatter a conduction electron in a metal or semiconductor. This is important; this scattering contributes to electrical resistance in the material.

- Most important, though, this **thermal energy** plays a fundamental role in determining the

Thermal Properties of a Solid

- A knowledge of how the thermal energy changes with temperature gives an understanding of the heat energy which is necessary to raise the temperature of the material.

- An important, measureable property of a solid is it's

Specific Heat or Heat Capacity

Lattice Vibrational Contribution to the Heat Capacity

The **thermal energy** is the dominant contribution to the heat capacity in most solids. In non-magnetic insulators, it is the only contribution. Some other contributions:

Conduction Electrons in metals & semiconductors.

The magnetic ordering in magnetic materials.

Calculation of the vibrational contribution to the thermal energy & heat capacity of a solid has 2 parts:

1. Evaluation of the contribution of a single vibrational mode.

2. Summation over the frequency distribution of the modes.

Vibrational Specific Heat of Solids

c_p Data at T = 298 K

Table 7·7·1   *Values* of c_p (joules mole^{-1} deg^{-1}) for some solids at T = 298°K*

Solid	c_p	Solid	c_p
Copper	24.5	Aluminum	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulfur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

* "American Institute of Physics Handbook," 2d ed., McGraw-Hill Book Company, New York, 1963, p. 4–48.

Thermal Energy & Heat Capacity
Einstein Model

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

Average 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

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

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

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

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

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

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

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

According to the Binomial expansion for x≪1 where

$$x = -\hbar \omega / k_B T$$

Eqn (*) can be written

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

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

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

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

$$\bar{\varepsilon} = k_B T^2 \left[\frac{2k_B \hbar\omega}{4k_B^2 T^2} + \frac{\frac{\hbar\omega k_B}{k_B^2 T^2} e^{-\hbar\omega/k_B T}}{\left(1 - e^{-\hbar\omega/k_B T} \right)} \right] = \frac{1}{2} \hbar\omega + \frac{\hbar\omega e^{-\hbar\omega/k_B T}}{\left(1 - e^{-\hbar\omega/k_B T} \right)} \qquad \boxed{\frac{\partial}{\partial x} (\ln x) = \frac{x'}{x}}$$

Finally, the result is

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

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

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

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

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

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

The second term in the mean energy is the phonon contribution to the thermal energy.
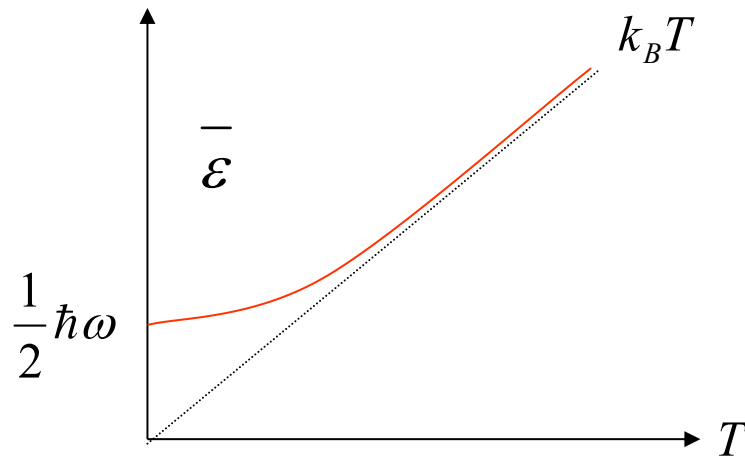
Mean energy of a harmonic oscillator as a function of T
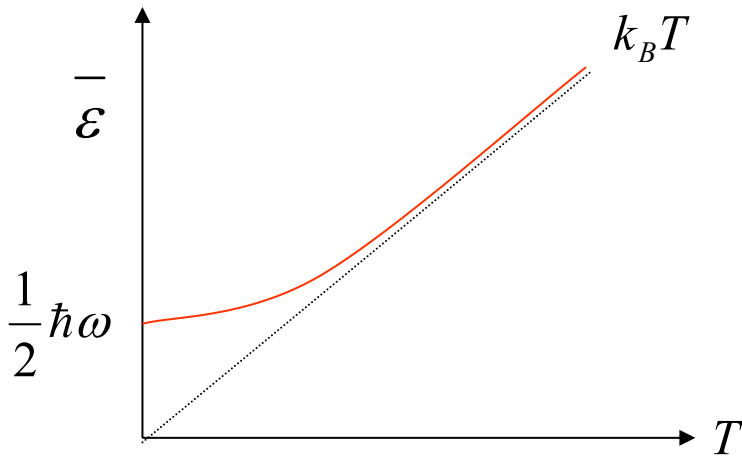
Low Temperature Limit

$$\hbar\omega \succ\succ k_B T$$

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

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

$\dfrac{1}{2}\hbar\omega$

$k_B T$

$\overline{\varepsilon}$

T

<u>High Temperature Limit</u>

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

$\overline{\varepsilon}$ 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 $\overline{\varepsilon}$ is the thermal energy of the classical 1D harmonic oscillator.

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

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

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

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

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

Heat Capacity C

- Heat capacity C can be found by differentiating the average phonon energy

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

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

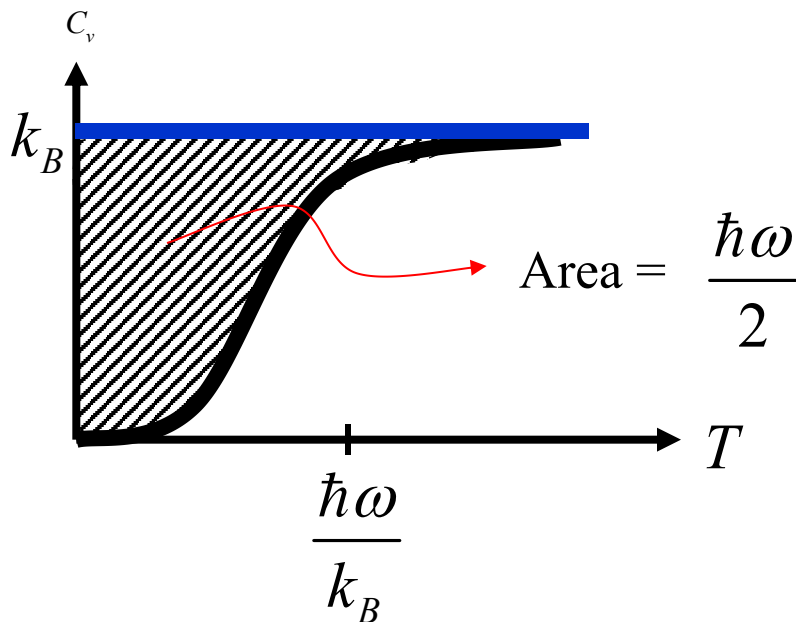$$C_v = k_B \frac{(\hbar\omega)^2}{(k_BT)^2} \frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT} - 1\right)^2}$$

Let $\theta = \dfrac{\hbar\omega}{k}$

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

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


Area = $\dfrac{\hbar\omega}{2}$

Specific heat in this approximation vanishes exponentially at low T and tends to classical value at high temperatures.

These features are common to all quantum systems; the energy tends to the zero-point-energy at low T and to the classical value of Boltzmann constant at high T.

Specific heat at constant volume depends on temperature as shown in figure below. At high temperatures the value of C_v is close to 3R, where R is the universal gas constant. Since R is approximately 2 cal/K-mole, at high temperatures C_v is app. 6 cal/K-mole.
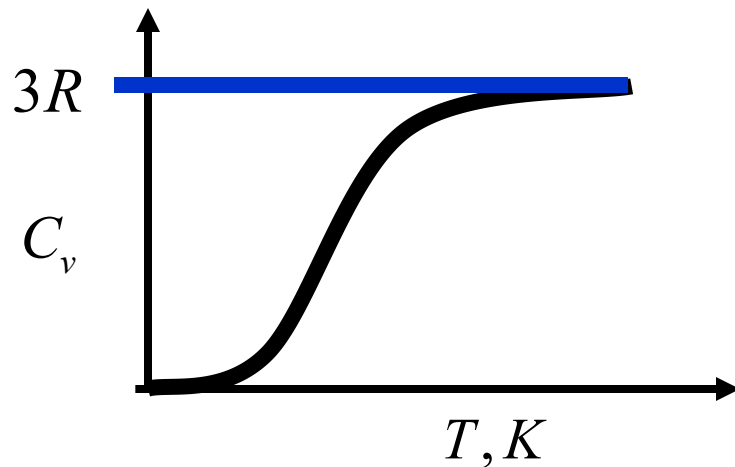
This range usually includes RT. From the figure it is seen that C_v is equal to 3R at high temperatures regardless of the substance. This fact is known as Dulong-Petit law. This law states that specific heat of a given number of atoms of any solid is independent of temperature and is the same for all materials!
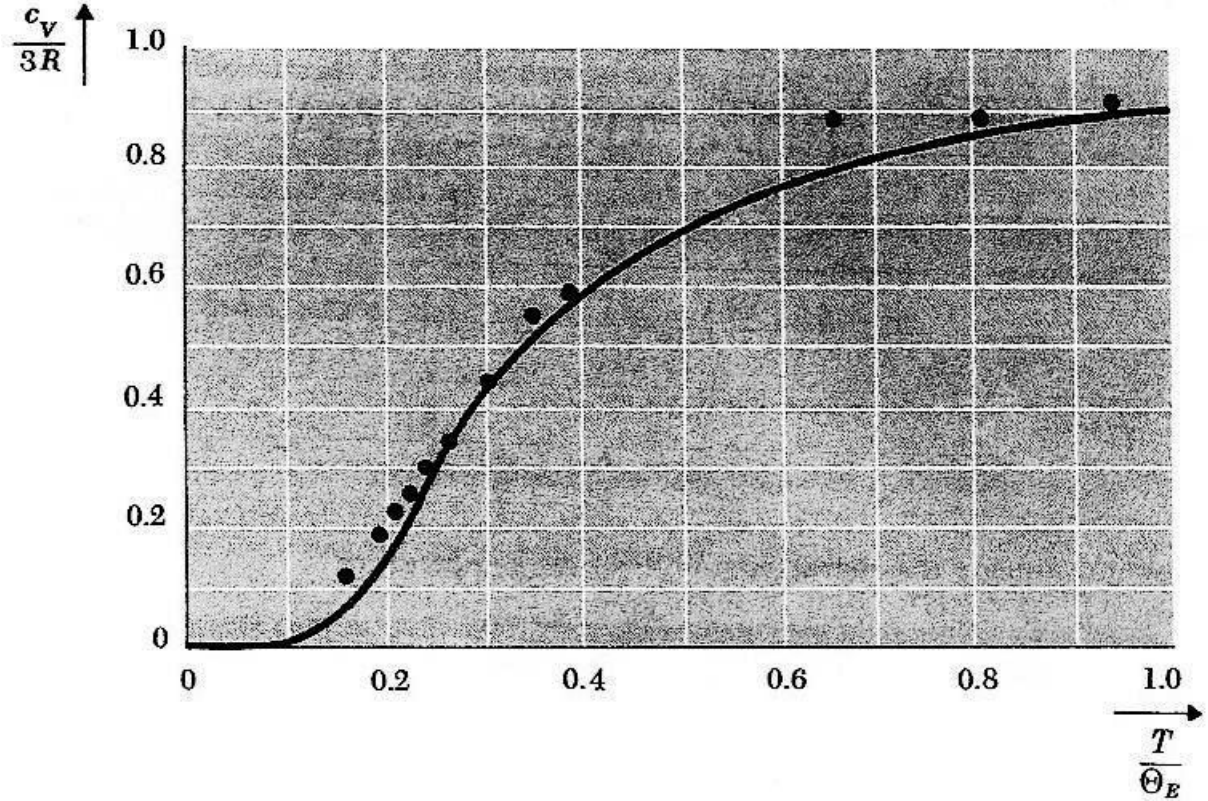
C_v vs T for Diamond

Points:

Experiment

Curve:

Einstein Model
Prediction

Fig. 7·7·1 Temperature dependence of c_v according to the Einstein model. The points are experimental values of c_v for diamond, the fit to the curve being achieved by choosing $\Theta_E = 1320°K$ (after A. Einstein, Ann. Physik, vol. 22, p. 186 (1907)).

Classical Theory of Heat Capacity of Solids

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, and consequently the energy per mole is

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

where N is Avagadro's number, k_B is Boltzmann constant and R is the gas constant. The differentiation wrt temperature gives;

$$C_v = \frac{d\overline{\varepsilon}}{dT} \qquad\qquad C_v = 3R = 3 \times 6.02 \times 10^{23}(atoms/mole) \times 1.38 \times 10^{-23}(J/K)$$

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

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 the Dulong-Petit law where R is universal gas constant.

$$3Nk_B = 3R$$

• *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.

C_v

$6\dfrac{cal}{Kmol}$

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

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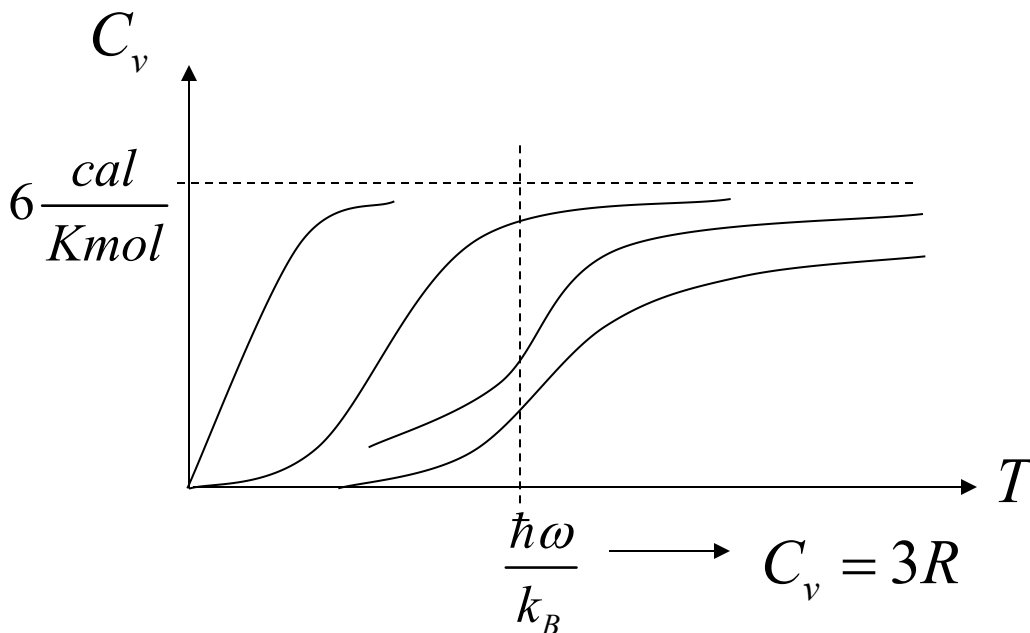
In each of these materials (Pb,Al, Si,and Diamond) specific heat approaches constant value asymptotically at high T. But at low T's, the specific heat decreases towards zero which is in a complete contradiction with the above classical result.

- 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.

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

Thermal Energy & Heat Capacity
Debye Model

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.
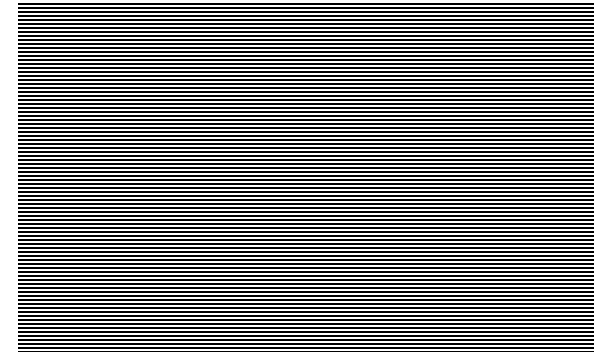
• it has to go up in steps.

- 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
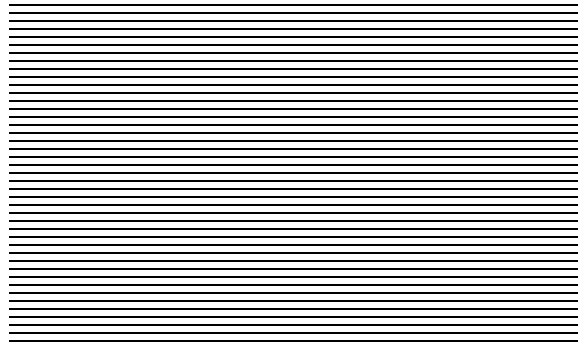
Steps get small

Energy is continuous

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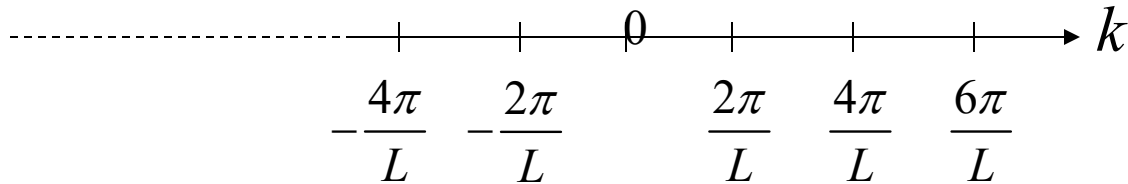- This energy level is said to be degenerate.

- The density of states $\rho(\varepsilon)$ 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 $\rho(\varepsilon)d\varepsilon$.

There are two sets of waves for solution;

- Running waves

- Standing waves

<u>Running waves:</u>

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

$$L = Na = p\lambda \Rightarrow \lambda = \frac{Na}{p} = \frac{2\pi}{k} \Rightarrow k = \frac{2\pi}{Na}p \Rightarrow k = \frac{2\pi}{L}p$$
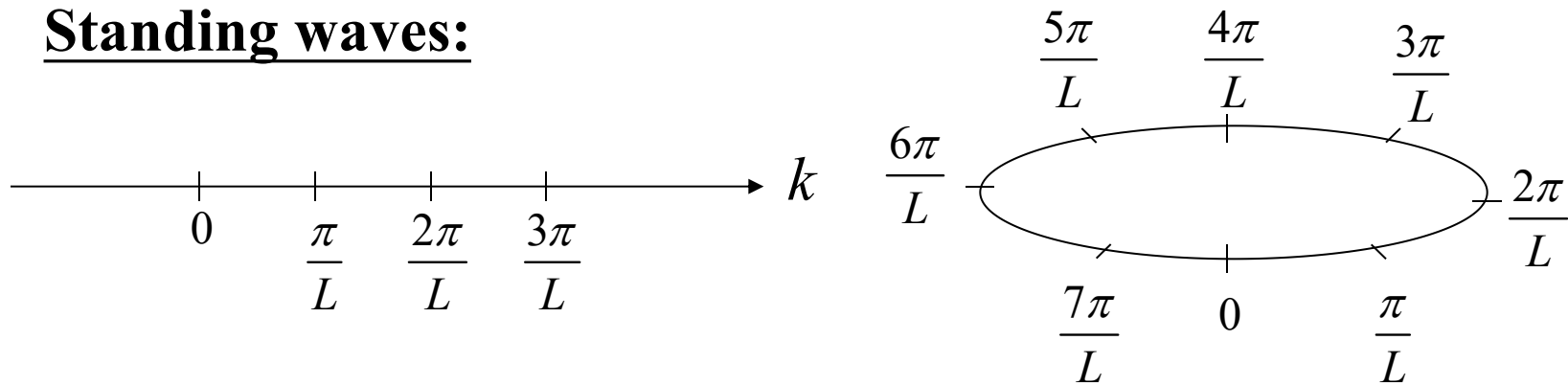
an integer

Length of the 1D chain

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

running waves

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

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.

$$k = \frac{2\pi}{L} p \longrightarrow \quad \text{for running waves}$$

$$k = \frac{\pi}{L} p \longrightarrow \quad \text{for standing waves}$$

These allowed k's are uniformly distributed between k and k+dk at a density of $\rho_S(k)$

$$\rho_S(k)dk = \frac{L}{\pi}dk$$ ➡ DOS of standing wave

$$\rho_R(k)dk = \frac{L}{2\pi}dk$$ ➡ 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(♦):

- The number of modes with frequencies ♦ and ♦+d♦ will be g(♦)d♦.
- g(♦) can be written in terms of □$_S$(k) and □$_R$(k).

dR modes with frequency from ♦ to ♦+d♦   corresponds

dn modes with wavenumber from k to k+dk

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

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

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

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

Let's remember dispertion relation for 1D monoatomic lattice

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

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

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

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

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

$$\sin^2 x + \cos^2 x = 1 \Rightarrow \cos x = \sqrt{1 - \sin^2 x} \qquad \Longrightarrow \qquad \cos\left(\frac{ka}{2}\right) = \sqrt{1 - \sin^2\left(\frac{ka}{2}\right)}$$

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

Multibly and divide

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

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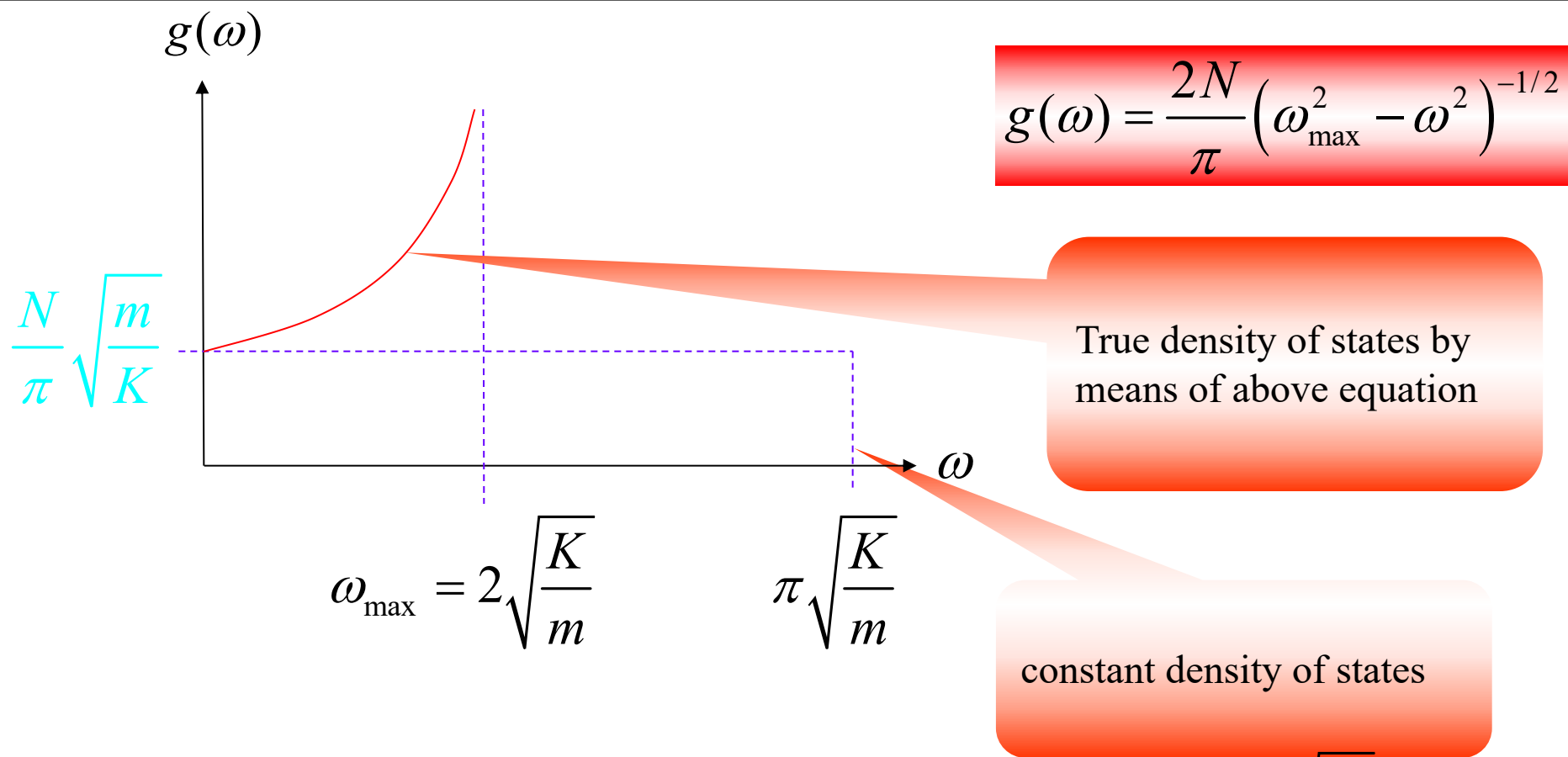
True density of states

Let's remember:

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

$$L = Na$$

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

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

$g(\omega)$

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

$\frac{N}{\pi}\sqrt{\frac{m}{K}}$

True density of states by means of above equation

ω

$\omega_{max} = 2\sqrt{\frac{K}{m}}$

$\pi\sqrt{\frac{K}{m}}$

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

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

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

Mean energy of a harmonic oscillator

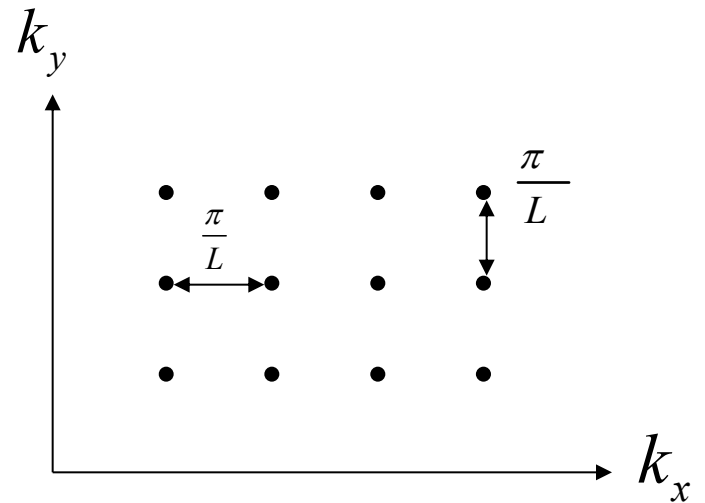One can obtain same expression of $g(\omega)$ by means of using running waves.

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

3D DOS

- Let's do it first for 2D

- Then for 3D.

- Consider a crystal in the shape of 2D box with crystal lengths of L.
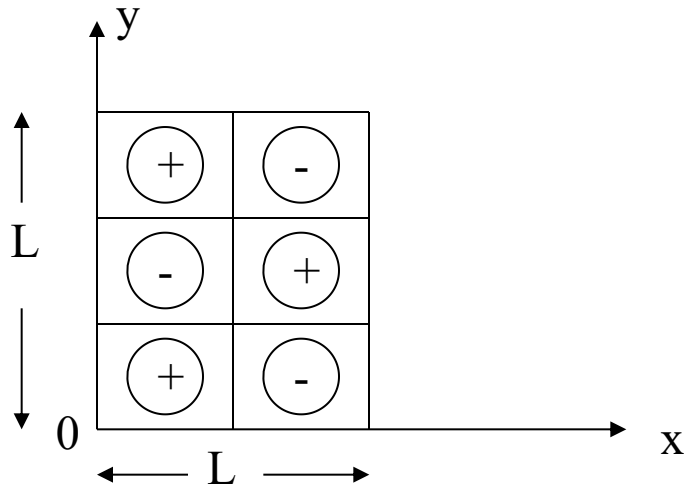
Standing wave pattern for a 2D box

Configuration in k-space

- Let's calculate the number of modes within a range of wavevector k.

- Standing waves are choosen but running waves will lead same expressions.

- Standing waves will be of the form

$$U = U_0 \sin\left(k_x x\right) \sin\left(k_y y\right)$$
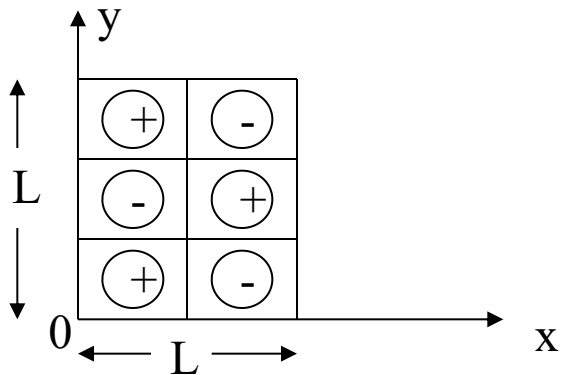
- Assuming the boundary conditions of

  - Vibration amplitude should vanish at edges of
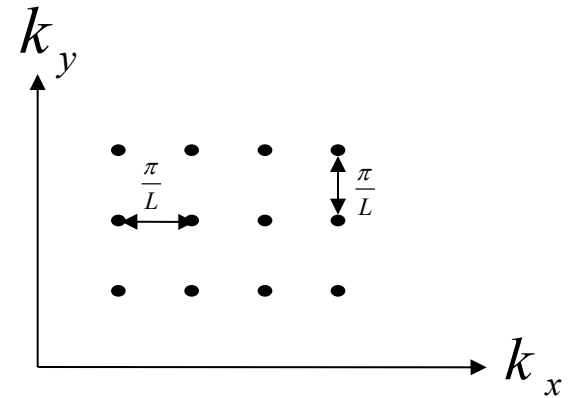
$$x = 0;\, y = 0;\, x = L;\, y = L$$

Choosing

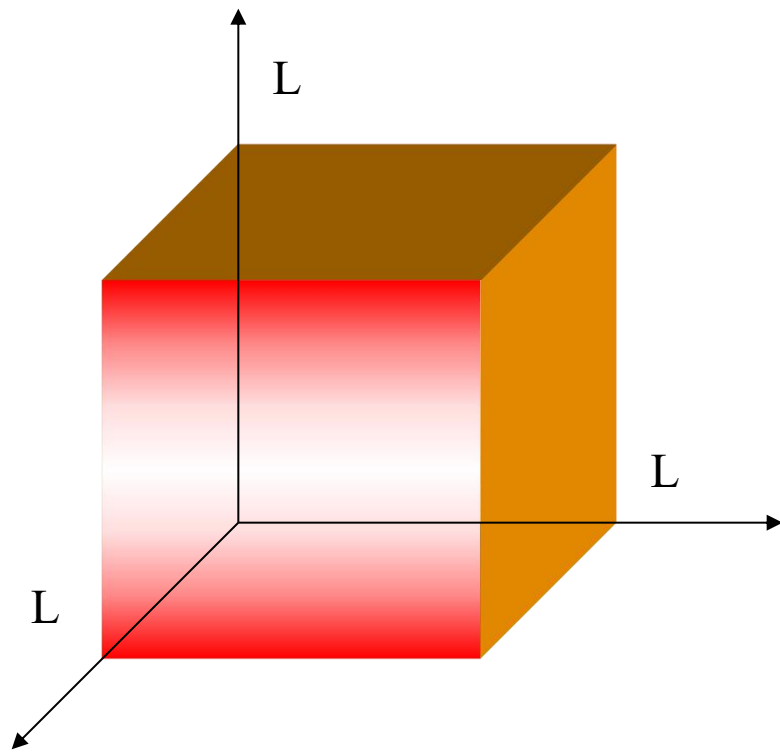*positive integer*

$$k_x = \frac{p\pi}{L};\, k_y = \frac{q\pi}{L}$$

Standing wave pattern for a 2D box

Configuration in k-space

- The allowed k values lie on a square lattice of side π/L in the positive quadrant of k-space.

- These values will so be distributed uniformly with a density of $(L/\pi)^2$ per unit area.

- This result can be extended to 3D.

Octant of the crystal:

k_x,k_y,k_z(all have positive values)

The number of standing waves;

$$\rho_s\left(k\right)d^3k=\left(\frac{L}{\pi}\right)^3 d^3k=\frac{V}{\pi^3}d^3k$$
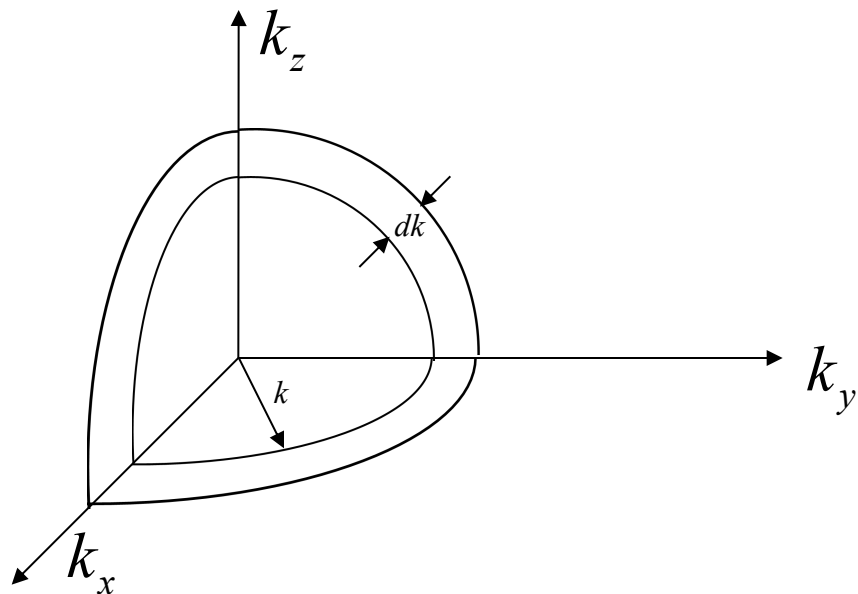
L/π

$$\frac{1}{8}\times 4\pi k^2 dk$$

$$\rho_s\left(k\right)d^3k=\frac{V}{\pi^3}\frac{1}{8}\times 4\pi k^2 dk$$

$$\rho_s\left(k\right)d^3k=\frac{Vk^2}{2\pi^2}dk$$

$$\rho_S\left(k\right)=\frac{Vk^2}{2\pi^2}$$

- $\rho(k) = \dfrac{Vk^2}{2\pi^2}$ is a new density of states defined as the number of

states per unit magnitude of in 3D.This eqn can be obtained by

using running waves as well.

- ◆(frequency) space can be related to k-space:

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

Let's find C at low and high temperature by means of using the

expression of $\quad g(.\omega)$

High and Low Temperature Limits

$$\overline{\varepsilon} = 3Nk_BT$$

Each of the 3N lattice modes of a crystal containing N atoms

➡️

$$C = \frac{d\overline{\varepsilon}}{dT}$$

➡️

$$C = 3Nk_B$$

- This result is true only if $T \gg \dfrac{\hbar\omega}{k_B}$ ➡️ θ

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

0

π/a

k
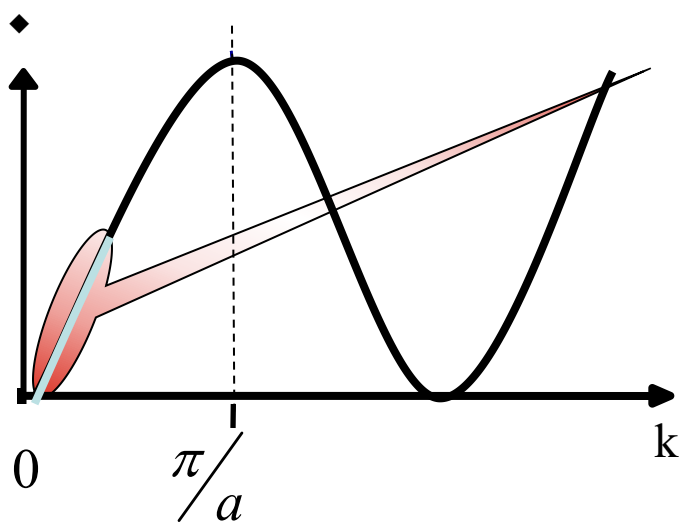
Low frequency ➡️ long ●

⬇️

sound waves

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

$$v_s = \frac{\omega}{k} \Rightarrow \frac{k}{\omega} = \frac{1}{v_s} \Rightarrow \frac{dk}{d\omega} = \boxed{\frac{1}{v_s}} \quad \text{and} \quad g(\omega) = \frac{Vk^2}{2\pi^2}\boxed{\frac{dk}{d\omega}}$$

$$g(\omega) = \frac{V\left(\dfrac{\omega^2}{v_s^2}\right)}{2\pi^2}\frac{1}{v_s} \quad \text{at low } T$$

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

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

Velocities of sound in longitudinal and transverse direction

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

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

$$x = \frac{\hbar\omega}{k_B T}$$

$$\omega = \frac{k_B T}{\hbar} x$$

$$d\omega = \frac{k_B T}{\hbar} dx$$

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

$$\varepsilon = \varepsilon_z + \frac{V}{2\pi^2} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \frac{(k_B T)^4}{\hbar^3} \frac{\pi^4}{15} \int_0^\infty \frac{\hbar\omega^3}{e^{\hbar\omega/kT} - 1} d\omega = \int_0^\infty \frac{\hbar \left(\frac{k_B T}{\hbar} \right)^3 x^3}{e^x - 1} \frac{k_B T}{\hbar} dx$$

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

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

at low temperatures