Normal modes in three dimensions
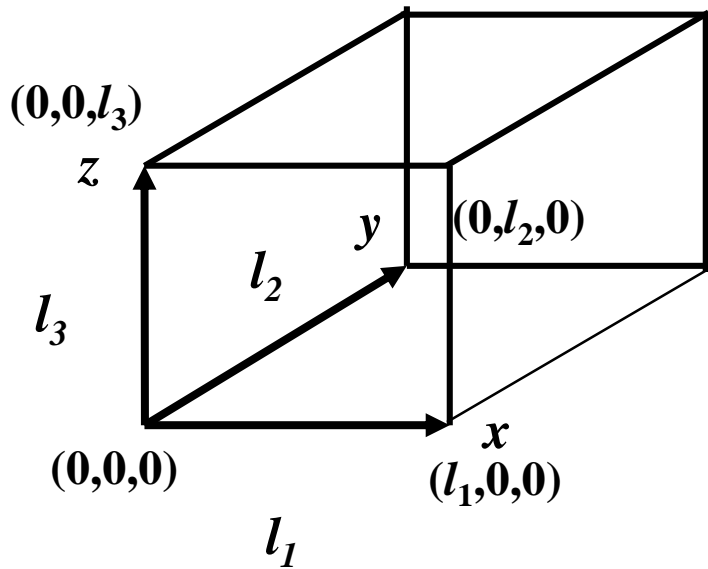
Waves equation in 3 dimensions

- Recall, the wave equation in 3 dimensions can be written as

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2}$$

- The solution of the equation can be found from the method of separation of variables.

- The general solution, i.e., the wave function, is found to be

$$\phi = A \left. {\sin \atop \cos} \right\} k_1 x \left. {\sin \atop \cos} \right\} k_2 y \left. {\sin \atop \cos} \right\} k_3 z \left. {\sin \atop \cos} \right\} ckt$$

Standing waves in rectangular enclosure

• Consider a rectangular enclosure as illustrated in the figure, l_1, l_2 and l_3 are lengths of the sides of the rectangular enclosure.

• The wave function describing the standing waves inside the enclosure have to satisfy the following boundary conditions.

$$\phi = 0 \ @ \begin{cases} x = 0 & x = l_1 \\ y = 0 \ \text{and} & y = l_2 \\ z = 0 & z = l_3 \end{cases}$$

A particular wave function within the rectangular enclosure

- By applying the first boundary condition, $\phi = 0$ @ x = y = z = 0 at all times, the wave function becomes

$$\phi = A \sin k_1 x \sin k_2 y \sin k_3 z \sin kct$$

- Likewise, the application of the second boundary condition, $\phi = 0$ @ x = l_1, y = l_2 and z = l_3 at all times, leads to the particular wave function

$$\phi = A \sin \frac{n_1 \pi}{l_1} x \sin \frac{n_2 \pi}{l_2} y \sin \frac{n_3 \pi}{l_3} z \sin kct$$

- where n_1, n_2 and n_3 are integers.

Normal mode frequency of standing wave in a rectangular enclosure

- Substituting the particular wave function into the 3 D wave equation, we then obtain

$$\left[\left(\frac{n_1\pi}{l_1}\right)^2 + \left(\frac{n_2\pi}{l_2}\right)^2 + \left(\frac{n_3\pi}{l_3}\right)^2\right]\phi = k^2\phi$$

- This leads to

$$\left[\left(\frac{n_1\pi}{l_1}\right)^2 + \left(\frac{n_2\pi}{l_2}\right)^2 + \left(\frac{n_3\pi}{l_3}\right)^2\right] = k^2$$

The allowed standing wave must have wave vectors that satisfy this condition.

- Or

$$\left[\left(\frac{n_1\pi}{l_1}\right)^2 + \left(\frac{n_2\pi}{l_2}\right)^2 + \left(\frac{n_3\pi}{l_3}\right)^2\right] = \left(\frac{2\pi}{\lambda}\right)^2 = \left(\frac{2\pi}{c}\nu\right)^2$$

- Finally, the normal mode frequency ν;

$$\nu = \frac{c}{2}\left[\left(\frac{n_1}{l_1}\right)^2 + \left(\frac{n_2}{l_2}\right)^2 + \left(\frac{n_3}{l_3}\right)^2\right]^{\frac{1}{2}}$$

Normal mode frequency

- Recall the normal mode frequency from the previous slide,

$$\nu_{n_1 n_2 n_3} = \frac{c}{2}\left[\left(\frac{n_1}{l_1}\right)^2 + \left(\frac{n_2}{l_2}\right)^2 + \left(\frac{n_3}{l_3}\right)^2\right]^{\frac{1}{2}}$$

- The labels; i.e., $n_1 n_2 n_3$, need not all have the same value, but can be chosen quite independently of each other. Note that, setting any one of them equal to zero causes the wave function ϕ to vanish.

- Likewise, the wave function can be expressed with the label $n_1 n_2 n_3$ as follows

$$\phi_{n_1 n_2 n_3} = A\sin\frac{n_1\pi}{l_1}x\sin\frac{n_2\pi}{l_2}y\sin\frac{n_3\pi}{l_3}z\sin kct$$
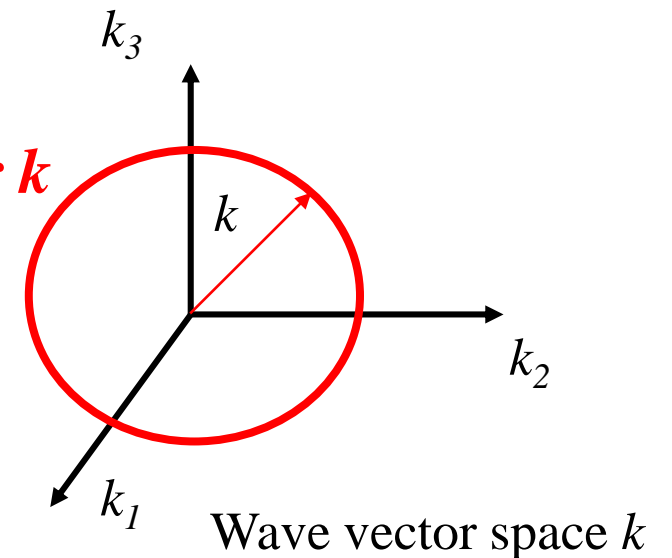
Degenerate standing waves

- Recall the relationship of the wave vectors k, k_1, k_2 and k_3,

$$k^2 = \left[\left(\frac{n_1\pi}{l_1}\right)^2 + \left(\frac{n_2\pi}{l_2}\right)^2 + \left(\frac{n_3\pi}{l_3}\right)^2\right] = \left[k_1^2 + k_2^2 + k_3^2\right]$$
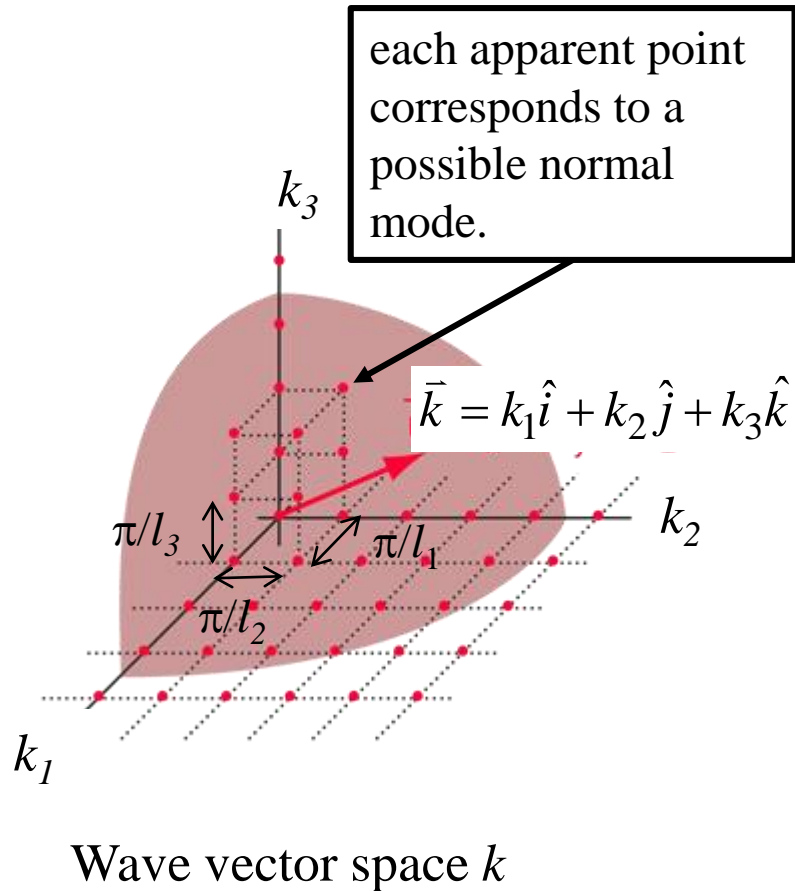
- This implies that standing waves with different composite wave vectors can have the same wave vector k, normal mode frequency and subsequently energy. Those standing wave are called "**degenerate waves functions**".

- For example, if $l_2 = 2l_1$ for any value of n_3, ϕ_{22n_3} and ϕ_{14n_3} are degenerate wave functions.

No. of normal mode frequency in a rectangular enclosure in *k* space

- No. of normal mode frequency, representing the no. of standing waves in the rectangular closure, can be determined from either wave vector space *k* or frequency space *ν*.

- If we start the analysis with the wave vector relation, $k^2 = \left[k_1^2 + k_2^2 + k_3^2 \right] = \left[\left(\frac{n_1 \pi}{l_1} \right)^2 + \left(\frac{n_2 \pi}{l_2} \right)^2 + \left(\frac{n_3 \pi}{l_3} \right)^2 \right]$

- The composite components of the wave vector *k*

  can form three perpendicular axes.

- Also, it is noted that the **maximum magnitude of the wave vector *k***

  has to be within a sphere of radius *k*.

Wave vector space *k*

The lowest normal mode

each apparent point corresponds to a possible normal mode.

$$\vec{k} = k_1\hat{i} + k_2\hat{j} + k_3\hat{k}$$

k_3

π/l_3

π/l_1

π/l_2

k_2

k_1

Wave vector space k

- Consider the lowest normal mode having labels of $n_1n_2n_3 = 111$, the magnitude of the wave vector k becomes

$$k = \left[\left(\frac{\pi}{l_1}\right)^2 + \left(\frac{\pi}{l_2}\right)^2 + \left(\frac{\pi}{l_3}\right)^2\right]^{\frac{1}{2}}$$

- The end point of the lowest normal mode wave vector is at the corner of a rectangular cell having lengths π/l_1, π/l_2, π/l_3 along k_1, k_2 and k_3, respectively, with a volume $\pi^3/l_1l_2l_3$.

- There are as many cells as points since each cell has eight points at its corners and each point serves as a corner to eight cells.

- Therefore, this suggests that the number of modes can be determined from **the ratio of the spherical volume to the volume of a cell**.

- However, only **one octant** of the sphere gives a unique set of normal mode.

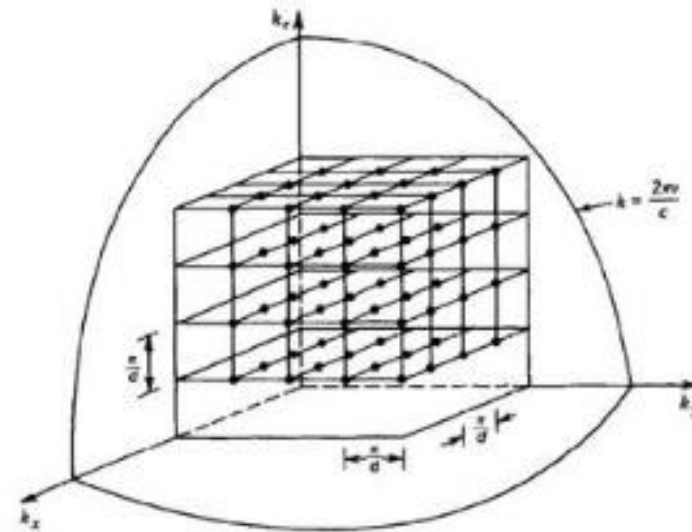# The number of normal modes

- The number of normal modes can be calculated from

$$\text{No. of modes} = \frac{1}{8} \frac{\text{spherical volume}}{\text{volume of a cell}}$$

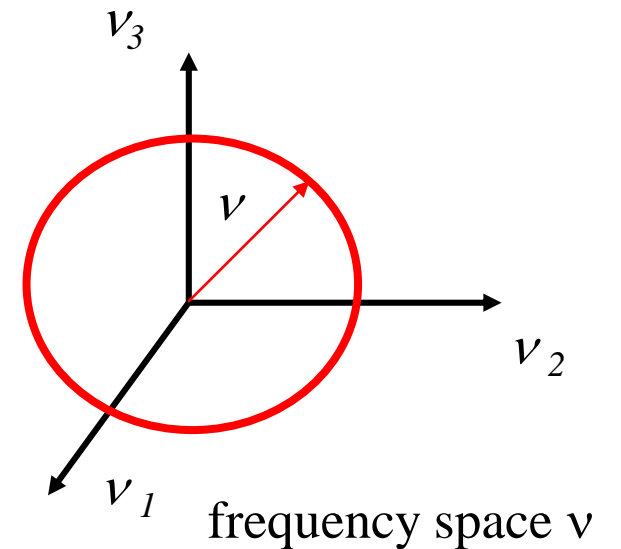Physical space resonator
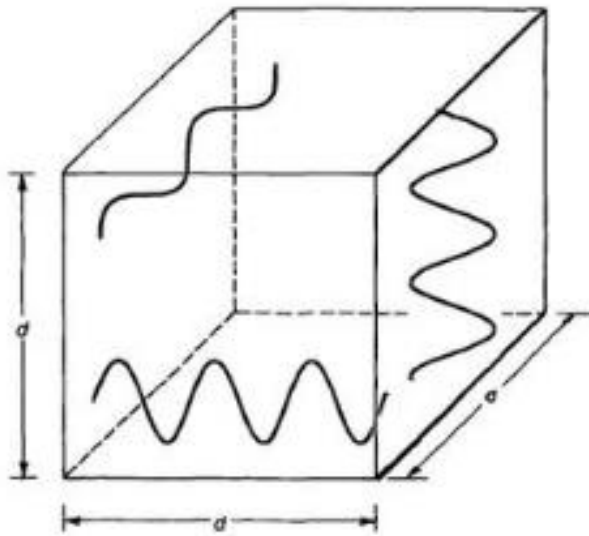
Wave vector space

No. of normal mode frequency in a rectangular enclosure in ν space

- The wave vector space can be transformed into the frequency ν space as follows

$$k^2 = \left[\left(\frac{n_1\pi}{l_1}\right)^2 + \left(\frac{n_2\pi}{l_2}\right)^2 + \left(\frac{n_3\pi}{l_3}\right)^2\right]$$

$$\nu_{n_1 n_2 n_3} = \frac{c}{2}\left[\left(\frac{n_1}{l_1}\right)^2 + \left(\frac{n_2}{l_2}\right)^2 + \left(\frac{n_3}{l_3}\right)^2\right]^{\frac{1}{2}}$$

- Likewise, the frequency space is composed of composite

  frequency components ν_1, ν_2 and ν_3 as shown in the figure.

- The **maximum normal mode frequency** lies within the sphere

  of radius ν.

frequency space ν

The lowest normal mode frequency

$$\left(\frac{n_1 c}{2l_1} , \frac{n_2 c}{2l_2} , \frac{n_3 c}{2l_3} \right)$$

Vector length gives
allowed frequency

$$\upsilon = \frac{c}{2} \left(\frac{n_1^2}{l_1^2} + \frac{n_2^2}{l_2^2} + \frac{n_3^2}{l_3^2} \right)^{1/2}$$

This lattice cell correspond to the lowest normal mode frequency ν_{111}.
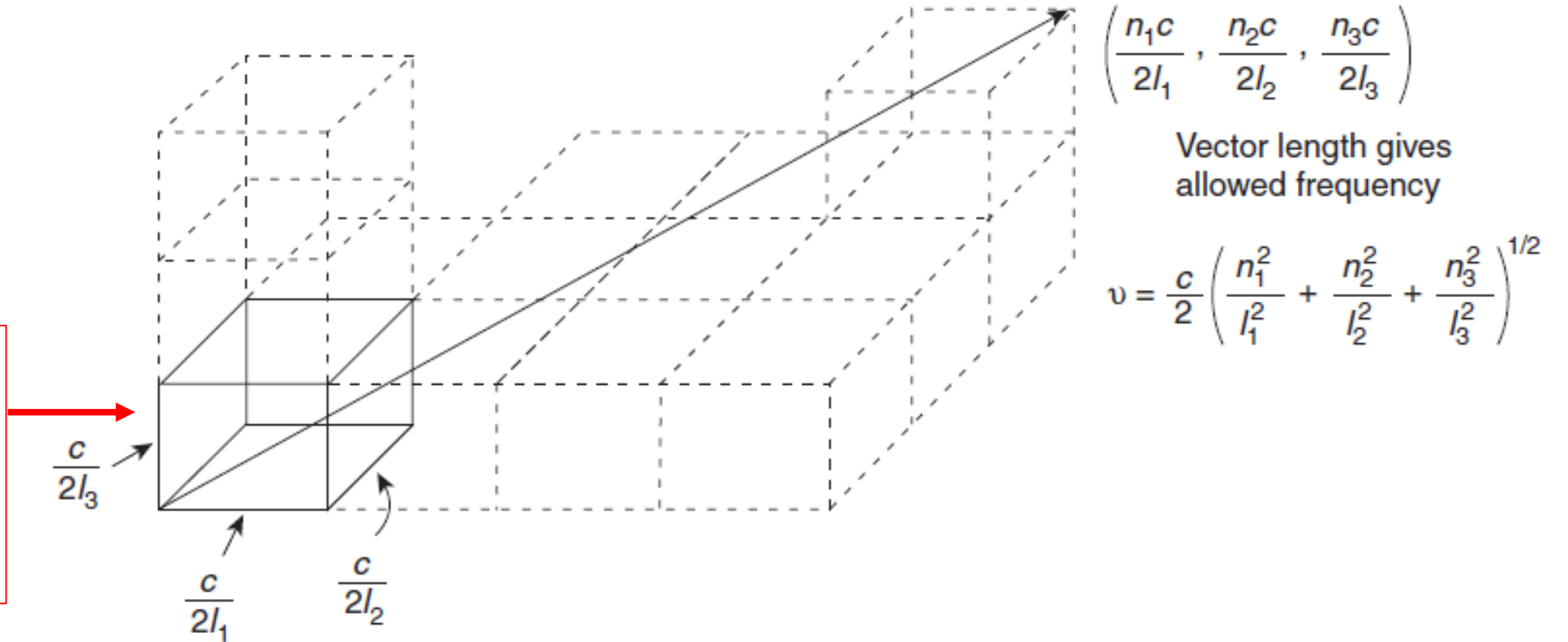
$\frac{c}{2l_3}$

$\frac{c}{2l_1}$

$\frac{c}{2l_2}$

Figure 9.7 Lattice of rectangular cells in frequency space. The length of the vector joining the origin to any cell corner is the value of the frequency of an allowed normal mode. The vector direction gives the propagation direction of that particular mode

How many normal modes can exist in the frequency range ν to ν + dν?

The total normal mode corresponds to the number of possible points (n_1, n_2, n_3) lying in the positive octant between two concentric sphere of radii ν and ν + dν.

• The total number of possible points or cell will be

$$\frac{1}{8} \frac{\left(\text{volume of spherical shell}\right)}{\text{volume of a cell}} = \frac{4\pi\nu^2 d\nu}{8} \cdot \frac{8l_1l_2l_3}{c^3}$$

This came from the volume of the fundamental mode, $c^3/8l_1l_2l_3$.

$$= 4\pi l_1l_2l_3 \cdot \frac{\nu^2 d\nu}{c^3}$$

• Note that the **mode density** is given by $\dfrac{4\pi\nu^2 d\nu}{c^3}$ in the frequency range ν to ν + dν per unit volume of enclosure.

Review of the specific heat of a solid

- By definition, the **specific heat** is the amount of heat energy that must be supplied to a mole of solid to raise its temperature by one degree.

- The amount of head also increases the internal energy of the solid.

- Therefore, the variation of the internal energy E with the temperature T is the molar specific heat capacity of the solid and can be expressed as $c = \frac{\partial E}{\partial T}$.

- **This suggests that the molar specific heat capacity is not constant and varied with the temperature**.

Heat Capacity
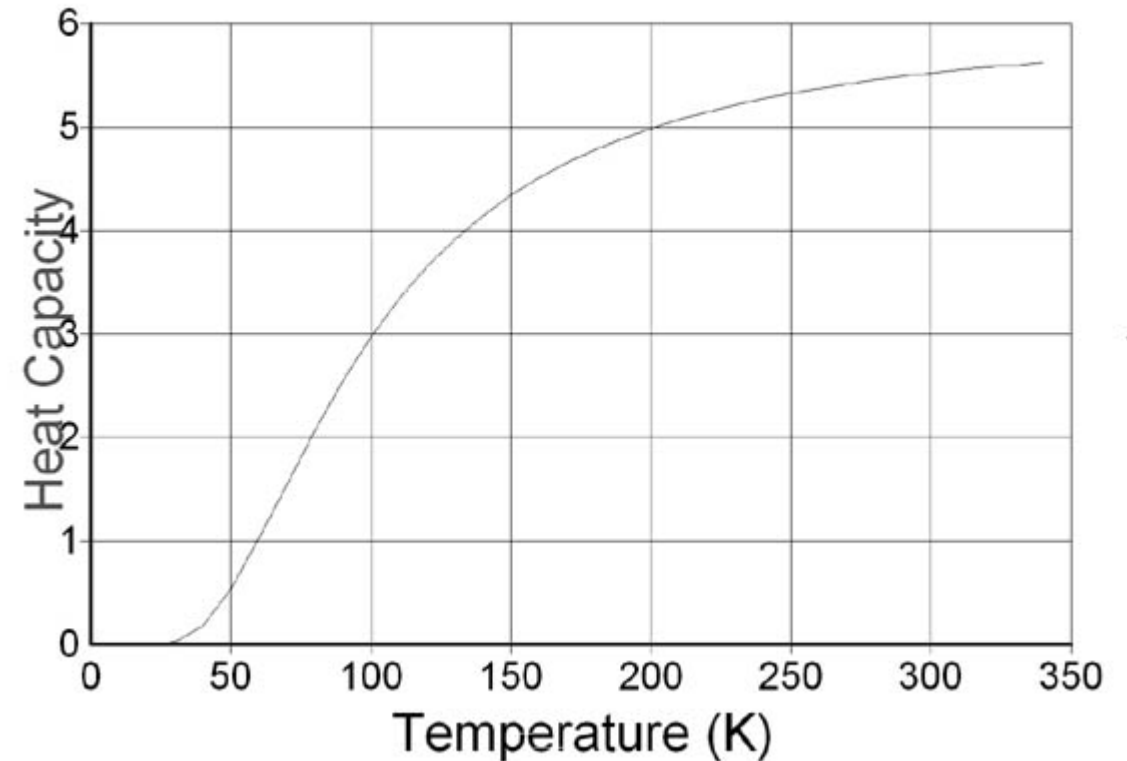
Application of mode density :
Debye theory of specific heat of a solid

- Debye considered the thermal vibrations of atoms in a solid lattice correspond to the internal energy.

- To determine the energy, first of all the possible mode density in the frequency interval ν to $\nu + d\nu$ has to be determined.

- In Debye's model, each atom was allowed two transverse vibrations (perpendicular planes of polarization) and one longitudinal vibration.

- This gives the number of possible modes to be

$$dn = 4\pi\nu^2 d\nu \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right)$$

C_T and C_L are the transverse and longitudinal velocities.

Debye's approximation

- Once the mode density in the frequency range ν to $\nu + d\nu$ and an average energy (from Planck's law) are known. The total energy for a solid volume V_A is then

$$V_A \bar{\varepsilon}\, dn = V_A \cdot \frac{h\nu}{e^{h\nu/kT} - 1} \cdot 4\pi\nu^2 \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) d\nu$$

- Where the average energy per oscillator is given by

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

Debye's approximation (cont.)

- The total energy per one mole of atoms of the solid over all permitted frequencies is then

$$E_A = \int V_A \bar{\varepsilon}\, dn = 4\pi V_A \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \int_0^{\nu_m} \frac{h\nu^3}{e^{h\nu/kT} - 1}\, d\nu$$

- Where ν_m is the maximum frequency of the oscillations.
- The total number of oscillation modes for one mole of the solid of volume V_A can be written in terms of the maximum frequency of the oscillations as follows:

$$\int dn = 3N = 4\pi V_A \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \int_0^{\nu_m} \nu^2\, d\nu = \frac{4\pi V_A}{3} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \nu_m^3$$

- In 1 mole, there are N atoms (= Avogrado's number)
- Each atom has 3 allowed oscillation modes.

Debye's approximation (cont.)

• Rearrange the total number of oscillation modes from the previous slide

$$\int dn = 3N = 4\pi V_A \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \int_0^{\nu_m} \nu^2 d\nu = \frac{4\pi V_A}{3} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right) \nu_m^3$$

• We then end up with $\quad \nu_m = \left(\frac{9N}{4\pi V_A} \right)^{\frac{1}{3}} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3} \right)^{-\frac{1}{3}}$ which represents the maximum frequency of the oscillation mode which can propagate in solid.

Debye's approximation (cont.)

- The last equation in the previous slide gives a new form of E_A as

$$E_A = \frac{9N}{v_m^3} \int_0^{v_m} \frac{v^2}{e^{hv/kT} - 1} \, dv$$

- The molar specific heat of the substance at constant volume can be determine once the variation of E_A with temperature has been found.

- In general, the specific heat is calculated from $\quad c_V = \left(\frac{\partial E_A}{\partial T} \right)$

- The specific heat of aluminum calculated by this model is compared with experiment results shown in the next slide.
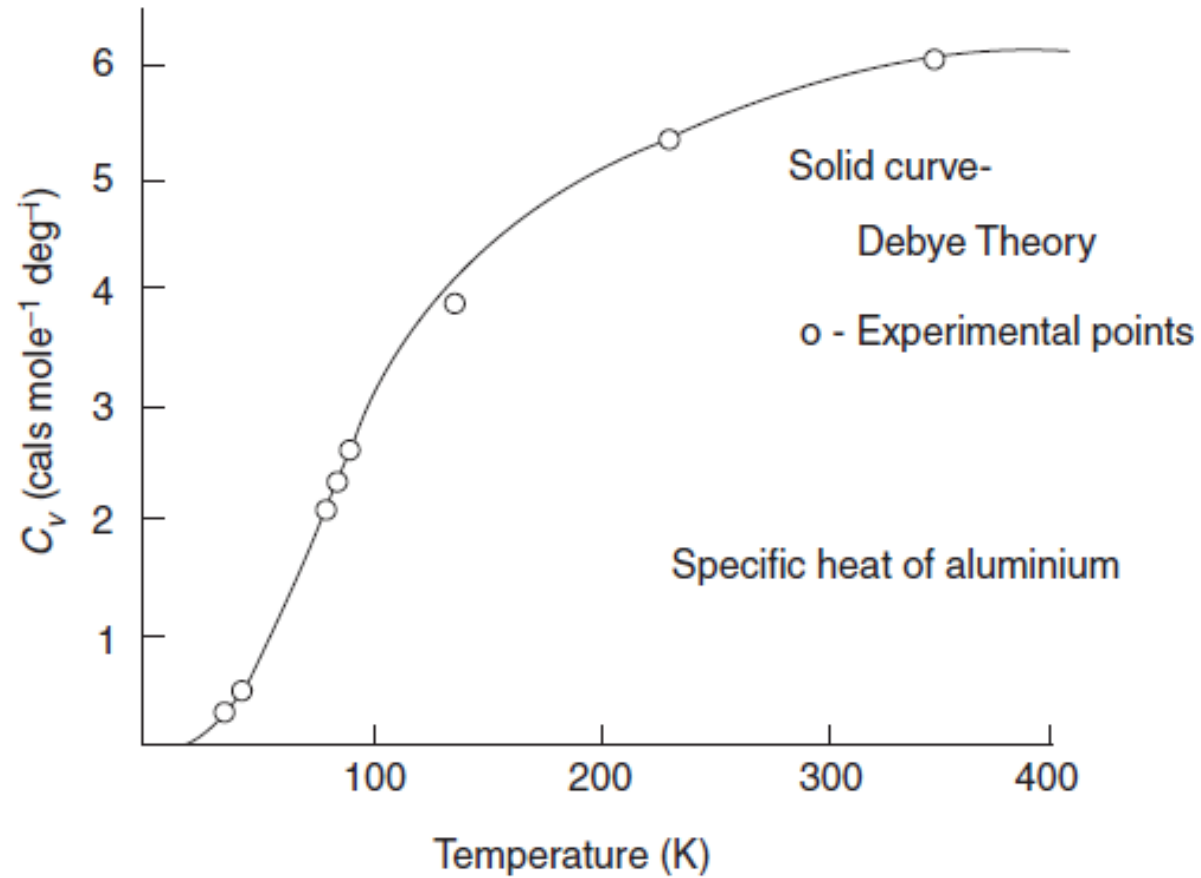
Figure 9.9 Debye theory of specific heat of solids. Experimental values versus theoretical curve for aluminium

Calculation of specific heat

•Recall the total energy of normal oscillating modes,

$$E_A = \frac{9N}{v_m^3} \int_0^{v_m} \frac{v^2}{e^{hv/kT}-1}\, dv$$

•Let $\dfrac{hv}{kT} = x$ and $\dfrac{hv_m}{kT} = x_m$.

•The total energy becomes

•Introduce the Debye temperature θ_D: $\theta_D = \dfrac{hv_m}{k}$ and this leads to $x_m = \dfrac{hv_m}{kT} = \dfrac{\theta_D}{T}$.

•Eventually, the integral can be written as

High and Low temperature Limits

•The integral in the previous slide can be assessed in the high and low limits as follows.

•**High temperature limit : T >> θ$_D$**,

•For very high temperatures, x is small and we can make the approximation : $e^x \approx 1 + x$.

•The integral becomes

$$E_A = 9N\text{kT}\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1}$$

•   So that the specific heat at high temperature limit : $c_v = \frac{\partial E}{\partial T} = $

# High and Low temperature Limits (cont.)

- **Low temperature limit : T >> θ$_D$,**

- For very low temperature, the upper limit is infinity, this gives $\int_0^\infty x^3 \frac{dx}{e^x-1} = \frac{\pi^4}{15}$.

- The total energy becomes

$$E_A = 9\text{NkT}\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x-1} = 9\text{NkT}\left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3}{5}\pi^4 NkT\left(\frac{T}{\theta_D}\right)^3$$

- This shows that the energy f the solid becomes proportional to T^4.

- Now the specific heat is $c_v = \left(\frac{12}{5}\right)\pi^4 NkT\left(\frac{T}{\theta_D}\right)^3 = 1940\left(\frac{T}{\theta_D}\right)^3$.

- The C$_v$ varies as T^3 and this is the famous Debye's T3 law. There is excellent agreement between theory and the experiments performed on a large number of element solids as well as compounds.
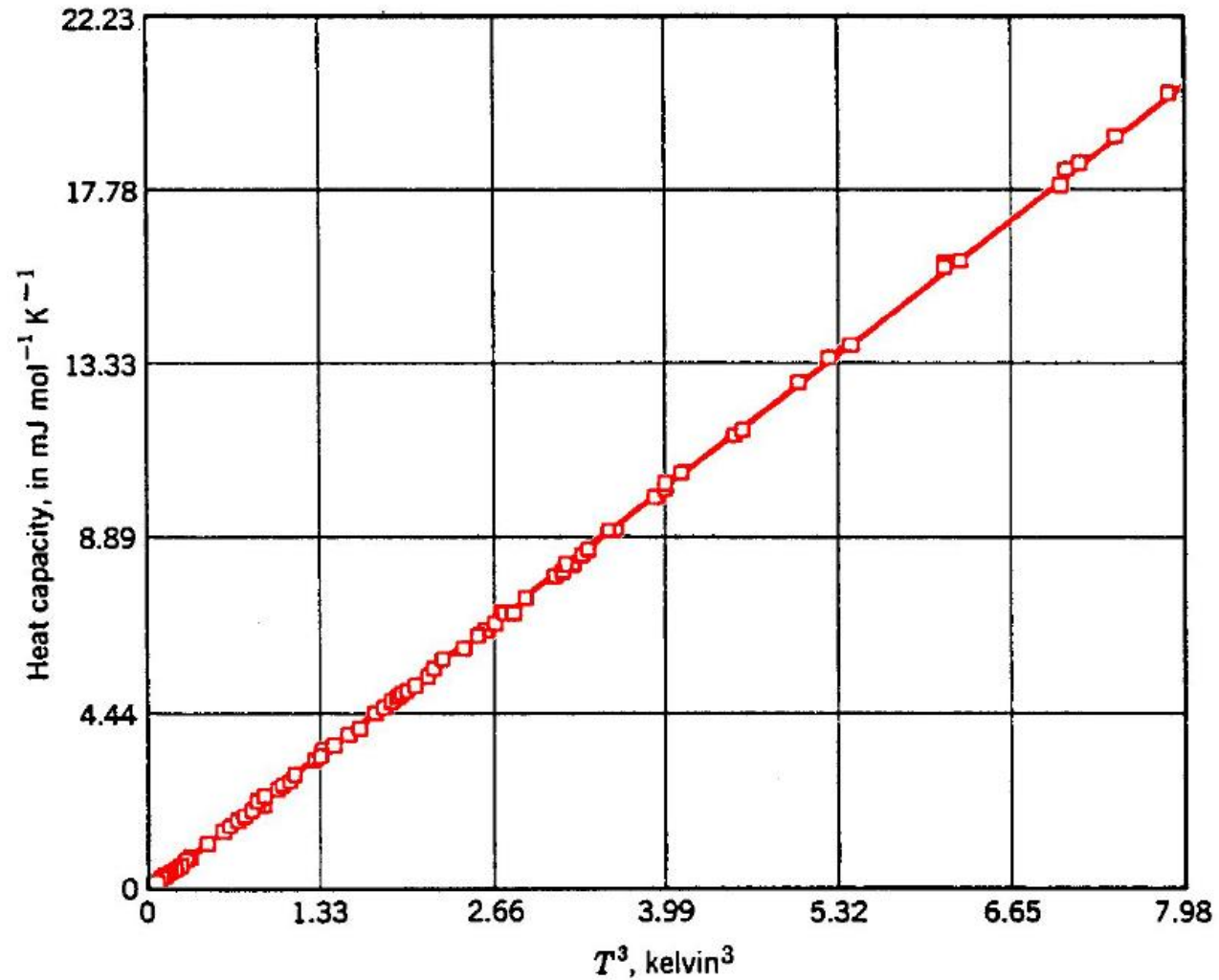
The low-temperature heat capacity of solid argon compared with the Debye T^3 prediction with $\Theta_D = 92$ K (solid line).

Debye theory works well for a wide range of materials.
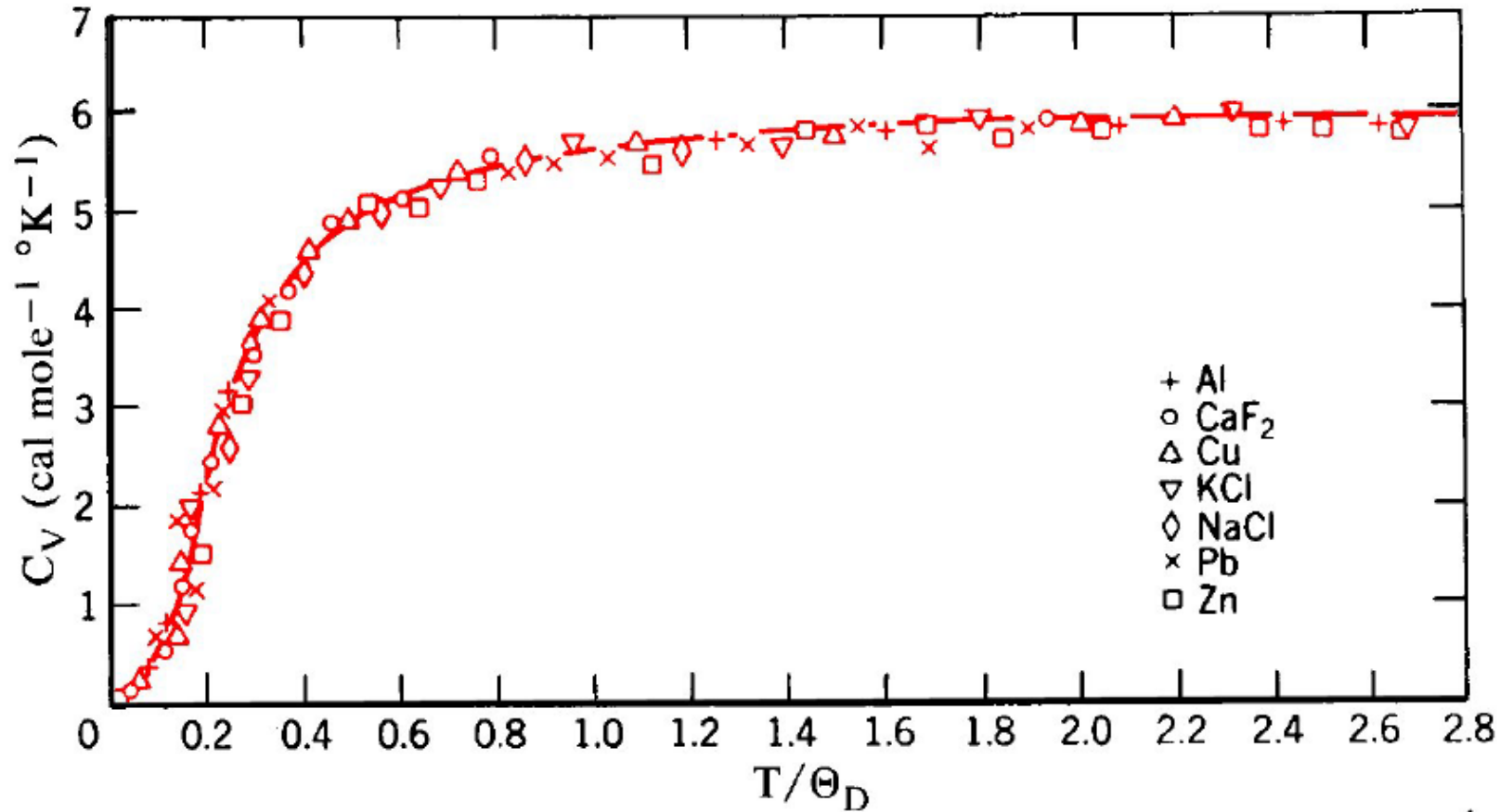
Heat capacity vs. reduced temperature for a number of materials.

Homework #10

Problem 9.11, 9.12