

Thermal Expansion:-

The origin of thermal expansion can be understood by considering the effect of anharmonic terms in the potential energy of the mean separation of a pair of atoms at any temperature T . The potential energy of the atoms at a displacement x from the equilibrium separation at 0°K can be written as,

$$U(x) = cx^2 - gx^3 - fx^4.$$

where c , g & f are all positive. Then the term x^3 represents the asymmetry of the mutual repulsion of the atoms, and the term x^4 represents the softening of the vibration, at large amplitudes.

By Boltzmann's distribution function, the average displacement can be calculated and it gives the possible values of x according to their thermodynamic probability. Hence

$$\bar{x} = \frac{\int_0^{\infty} x e^{-U(x)/kT} dx}{\int_0^{\infty} e^{-U(x)/kT} dx}$$

$$\bar{x} = \frac{\int_{-\infty}^{\infty} x e^{-U(x)/kT} dx}{\int_{-\infty}^{\infty} e^{-U(x)/kT} dx}$$

for small displacements. The anharmonic terms in the energy are small as compared with RT . Hence, expanding the integrands we have

$$\int n e^{-U/KT} dn \approx \int \exp(-cn^2/KT) \left[n + \frac{gn^4}{KT} + \frac{fn^5}{KT} \right] dn$$

$$= \left(\frac{g}{RT} \right) \left(\frac{RT}{c} \right)^{5/2} \left(\frac{3\pi^{1/2}}{4} \right) \quad \text{--- (1)}$$

$$\int e^{-U/KT} dn \approx \int \exp(-cn^2/KT) dn$$

$$= \left(\frac{\pi KT}{c} \right)^{1/2} \quad \text{--- (2)}$$

so that $\bar{n} = \frac{2Eg}{4c^2} \quad \text{--- (3)}$

This gives a constant value of a temperature coefficient of thermal expansion since RT represents classically the mean energy \bar{E} of the oscillation in the harmonic approximation.

eq (3) can be written as

$$\bar{\pi} = \frac{3\bar{E}_g}{4C^2}$$

If we substitute the energy

$$\bar{E} = \hbar\omega / \exp(\hbar\omega / kT) - 1$$

of harmonic oscillator in quantum mechanics we would get the quantum mechanical result we can therefore expect the thermal expansion coefficient to decrease rather abruptly as the temperature goes below the characteristic temperature of the oscillator and to go to zero as $T \rightarrow 0K$ as is actually observed. A/c to the third law of thermodynamics also the thermal expansion coefficient vanishes as the absolute temperature tends to $0K$.

Thermal Conductivity of Solids

In the case of steady state flow of heat along a long rod having a temperature gradient dT/dx , the flux of thermal energy or, the energy transmitted across unit time is given by.

$$Q = K \cdot \frac{dT}{dx},$$

where K is the thermal conductivity coefficient. This equation shows that the process is random i.e., the energy diffuses through the specimen, suffering frequent collisions, besides entering one end and travelling directly to the other end along straight paths. Without diffusion, the expression will depend only upon the difference of temperature between the ends of the specimen and not upon the temperature gradient. From the kinetic theory of gases, we know that

$$K = \frac{1}{3} C_v \lambda \bar{c}.$$

where C_v is the heat capacity per unit volume, λ is the mean free path of a particle between collisions and

c is the average particle velocity. This result also holds good for a distribution of phonons provided that the velocity c is supposed to refer to an average phonon velocity i.e., to an average sound velocity in the solid or crystal.

The thermal conductivity of solids can be most easily understood by regarding the crystal as a container enclosing a 'gas of phonons'. This is found to behave like an ideal monoatomic gas. We can, therefore, deduce a formula for the thermal conductivity of monoatomic gas and then it may be applied to the lattice of a crystal solid.

Let us first find the number of particles of an ideal gas having velocity in the range dv about v , which cross an element of area ds per second from a direction lying within an angular range $d\theta$ about a polar angle θ . This number is just half the number within that velocity range inside a column of cross-section of $ds \cos \theta$ (the projection of the area ds on a plane normal to

the θ -direction) which lies within a distance of v cms, from the element of area itself because the other half may go in the opposite direction.

This is shown in Fig 7 here. If $n(v) dv$ be the number of particles per unit volume having velocity in the range dv about v , then the number crossing the element of an area is

$$dn = \frac{1}{2} v \cdot n(v) dv \cdot \frac{4\pi \sin\theta d\theta \cdot ds \cos\theta}{4\pi}$$

$$= \frac{1}{2} v \cdot n(v) \sin\theta \cos\theta dv d\theta ds.$$

The factor having $\sin\theta$ represents the ratio of the solid angle subtended by the element $d\theta$ about θ to the solid angle 4π subtended by all space. Integrating over v , using Maxwell-Boltzmann's distribution and knowing that the velocity distribution is independent of θ , we get

$$n(\theta) d\theta = \frac{1}{2} n \bar{c} \sin\theta \cos\theta ds$$

where $\bar{c} = \sqrt{\left(\frac{8KT}{\pi m}\right)}$

Here it may be noted that the

use of so statistical distribution is an approximation because thermal conduction always involves a flow of energy and temperature gradient and so we are dealing with a system which is not in thermal equilibrium. Such distribution apply to system at equilibrium.

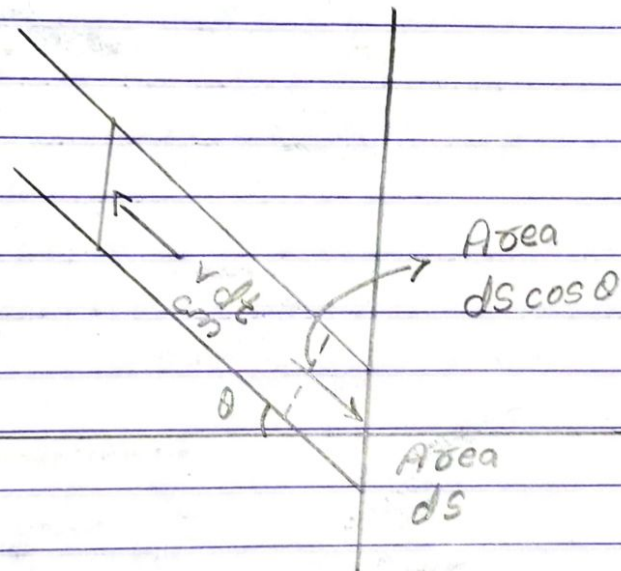


Fig 7.7