CHAPTER II

THEORY

2.1   The significance of heat conduction

Human appreciation of the conduction of heat begins with the well-known fact that something, a piece of metal for instance, feel cold to the touch while a piece of wood, feel warm. The reason for this is that metal conducts heat away from the body faster than wood. Amongst the things that feel warm because of their low thermal conductivity are furs, skins, and woven cloth used by mankind for protection against external cold.

For elecronic industry considerations, [10] the need to protect certain semiconductor devices from damage due to overheating has led to the semiconductor being mounted on a diamond heat sink, diamond having a higher thermal conductivity around room temperature than any metal. This is an extreme case, but there are many others where efficiency requires the transfer of heat. We sometimes need high, sometimes low thermal conductivity. Often this will be associated with a requirement of good mechanical strength. It will be clear that the existence of data on thermal conductivity and related properties will never suffice to meet the problems posed by technology. What is also needed is theoretical

understanding which will use to predict the thermal conductivity of new materials. In turn the testing of theories will challenge the experimenters to obtain new standards of accuracy in measurement and prediction.

2.2   The definition of heat conduction

To define the word "conduction" [11], it should refer to the concept of atomic and molecular activity. Conduction may be viewed as the transfer of energy from the more energetic to the less energetic particles of a substance due to interactions between the particles.

The physical mechanism [12] of conduction is most easily explained by considering a gas. Consider a gas in which there exists a temperature gradient and assume that there is no bulk motion. The gas may occupy the space between two surfaces that are maintained at different temperatures, as shown in Figure 2.1. We associate the temperature at any point with the energy of the gas molecules in the vicinity of the point. This energy is related to the random translational motion, as well as to the internal rotational and vibrational motions, of the molecules.

Moreover, higher temperatures are associated with higher molecular energies, and when neighboring molecules collides, as they are constantly doing, a transfer of energy from the more energetic to the less energetic molecules must

occur. In the presence of a temperature gradient, energy transfer by conduction must then occur in the direction of decreasing temperature. This transfer is evident from Figure 2.1.
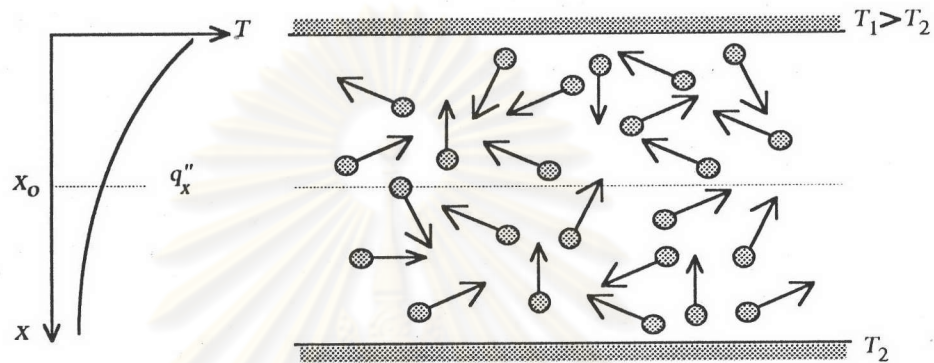

Figure 2.1 Association of conduction heat transfer with diffusion of energy due to melecular activity.

The hypothetical plane at x_o is constantly being crossed by molecules from above and below due to their random motion. However, molecules from above are associated with a higher temperature than those from below, in which case there must be a net transfer of energy in the positive x direction. It may speak of the net transfer of energy by random molecular motion as a diffusion of energy.

The situation is much the same in liquids, although the molecules are more closely spaced and the molecular interactions are stronger and more frequent. Similarly, in a solid, conduction may be attributed to atomic activity in the form of lattice vibrations. The modern view is to ascribe the energy transfer to lattice waves induced by atomic motion. In a nonconductor, the energy transfer is exclusively via these lattice waves; in a conductor it is also due to the transitional motion of the free electrons. We treat the important properties associated with conduction phenomena.

2.3 Thermal conductivity

It is possible to quantify heat transfer processes in terms of appropriate rate equations. These equations may be used to compute the amount of energy being transferred per unit time. For heat conduction, the rate equation is known as Fourier's law. For the one-dimensional plane wall shown in Figure 2.2, having a temperature distribution $T(x)$, the rate equation is expressed as :

$$q''_x = -k \, dT/dx$$

The heat flux q''_x (W/m^2) is the heat transfer rate in the x direction per unit area perpendicular to the direction of transfer, and it is proportional to the temperature gradient, dT/dx , in this direction. The proportionality constant k is a

transport property known as the thermal conductivity (W/mK) and is a characteristic of the material. The minus sign is a consequence of the fact that heat is transferred in the direction of decreasing temperature.
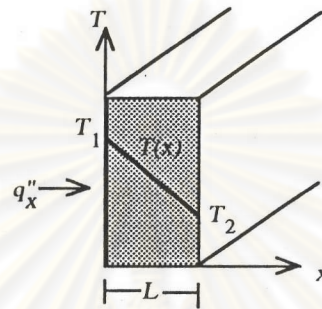

Figure 2.2   One dimensional heat transfer by conduction

Under the steady-state conditions shown in Figure 2.3, where the temperature distribution is linear, the temperature gradient may be expressed as

$$dT/dx \quad = \quad (T_2 - T_1)/L$$

and the heat flux is then

$$q''_x \quad = \quad -k(T_2 - T_1)/L$$

$$\text{or} \quad q''_x \quad = \quad k(T_2 - T_1)/L \quad = \quad k\,\Delta T/L$$
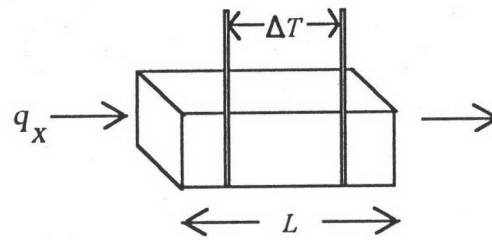
Figure 2.3   Principle of the steady-state longitudinal heat-flow

Note that this equation provides a heat flux, that is, the rate of heat transfer per unit area, The heat transfer rate by conduction, q_X (W), through a plane wall of area A is then the product of the flux and the area, $q_X = A\, q''_X$.

therefore, $q_X = kA\, \Delta T/L$

Fourier's law is phenomenological, that is developed from observed phenomena rather than being derived from the principles. Hence, we view the rate equation as a generalization based on much experimental evidence. For example, consider the steady-state conduction experiment of Figure 2.3 which shows a material having end faces of different temperatures with $T_1 > T_2$ (ΔT). The temperature difference causes conduction heat transfer in the positive x direction. We are able to measure the heat transfer rate q_X , and we seek to determine how q_X or Q depends on the following variables : ΔT, the temperature difference; L or x, the length; and A, the cross-sectional area.

At normal temperature, k is independent of the shape and size of the specimen measured, so that a unique value can be defined at any particular temperature. However, for every non-metallic crystal of normal purity and perfection there is some temperature below which the conductivity, as deduced from normal measurements, is size dependent.

In general, the thermal conductivity of a solid is larger than that of a liquid, which is larger than that of a gas. As illustrated in Figure 2.4.
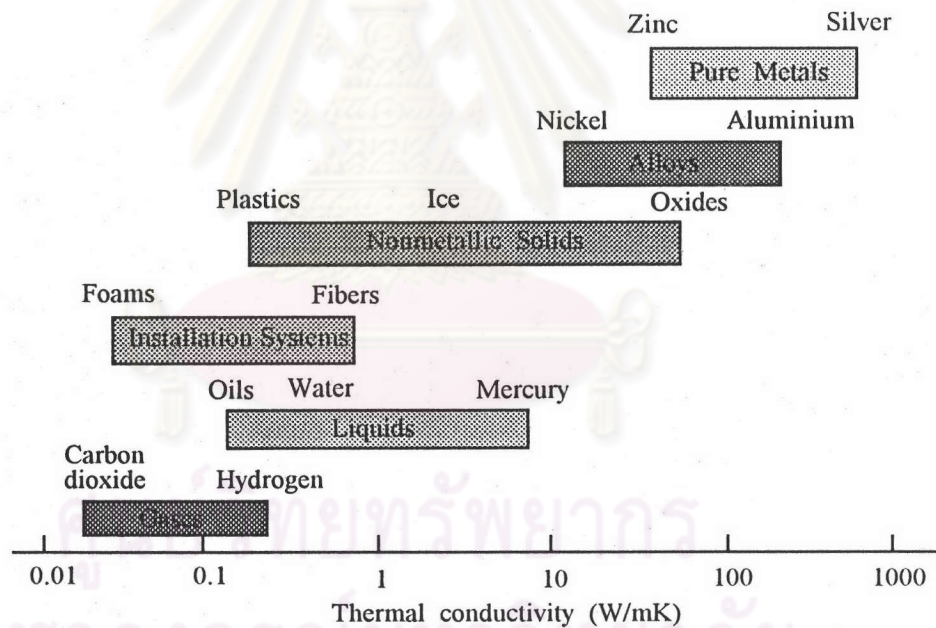

Figure 2.4   Range of thermal conductivity for various states of matter at normal temperature and pressure

2.4   The Measurement of Thermal Conductivity

In the simplest steady-state experimental arrangement, illustrated schematically in Figure 2.3 heat is supplied at one end of the article of uniform cross-sectional area A at a known rate q_x or Q and is removed at the other end. Thermometers are attached at two places along the specimen separated by a distance L, and the temperature difference T is measured. The thermal conductivity is then derived from the relation as :

$$Q \quad = \quad kA\Delta T/L$$

2.5   Standard Method of Test for Thermal Conductivity of Materials by Means of The Guarded Hot Plate (ASTM Designation:C 177-45 ADOPTED, 1945) [24]

Measurements of thermal conductivity generally require careful consideration. Available technique may be divided into steady-state or transient methods. Steady-state methods usually measure the temperature at two different positions. The accepted standard method of tester thermal conductivity of insulation material utilizes the "guarded hot plate" principle. The analysis of materials by guarded hot plate method has been successfully done for many years. This method is quite accurate.

Thermal conductivity of a homogeneous material is the rate of heat flow under steady conditions, through unit area per unit temperature gradient in a direction perpendicular to that area. The relationship can express by the above equation. The method of establishing a fixed thermal difference across the sample is accomplished by placing the sample between two surfaces whose temperature is accurately controlled.

The cold plate temperature is accurately set and controlled by a thermoelectric heat pump driven by a high gain proportional controller. The hot plate is also operated at an accurately controlled temperature. The heat flow through the sample is measured with a heat flow transducer which produces an EMF that is proportional to the heat flow per unit time and area through the sample.

2.6   Thermal conductivity of two-phase system

The conductivity of a two-phase material [25] depends on the conductivities of the matrix and filler, and the volume fraction and geometry of the filler material. In some cases the resistance in the interface between matrix and filler may be of significant influence. However, such a material may be considered to be a three-phase material with the interface as the third phase. The following review of theories will not include interface phenomena.

A particularly simple case is when the filler phase consists of spheres, fibres or rods arranged in the direction of conduction. The conductivity of such materials is described by a parallel coupling of the resistance in the matrix and the filler [15] :

$$1/\rho_e \;=\; (1-\phi)\,/\,\rho_c \;+\; \phi\,/\,\rho_d$$

or because conductivity is the reciprocal of resistivity :

$$k_e \;=\; (1-\phi)\,k_c \;+\; \phi\,k_d$$

In these equations ρ is resistivity and k is conductivity. The subscripts e, c and d refer to the composite, matrix and filler respectively. The volume fraction of filler material is ϕ.

Geometric Mean Model : $\quad k_e \;=\; k_c{}^{\phi} \;+\; k_d{}^{(1-\phi)}$

In the case of a general composite material these mixture rules represent the upper and lower limits of the conductivity. However, if the contrast of the composite material is large, the mixture rules converge to the conductivities of the filler and matrix materials respectively. In this case the equations are useless for the prediction of conductivity. The general case of a particulate filler of

arbitrary size and shape is far more complex and no general theory has yet been developed.

In this chapter are listed some theoretical, semi-empirical or empirical models and a brief description of each basis to elaborate thermal conductivity of different materials as the following :

Behrens Theoretical Model [16]

The theoretical results were based on a field solution to the equation of heat conduction for a composite material with orthorhombic symmetry. Solutions were presented for eliptic filaments in a circular rod lattice :

$$k_e = k_c [(p+1) + (p-1)2\phi] / [(p+1) - (p-1)\phi] ; \quad \text{where } p = k_d / k_c$$

Bruggeman Theoretical Model [16]

Using the assumptions of permeability and field strength, Bruggeman derived the following implicit equation for dilute suspensions of spheres in a homogeneous medium :

$$1-\phi = [(k_d-k_e) / (k_d-k_c)] (k_c/k_e)^{1/3}$$

Halpin-Tsai Theoretical Model [16]

For filaments of uniform cross-sectional area arranged in parallel, the thermal conductivity parallel to the filaments was assumed to be :

$$k_e \quad = \quad \phi\, k_d \;+\; (1-\phi)\, k_c$$

Using an analogy between in-plane field equations and boundary conditions to the transverse transport coefficient, the transverse thermal conductivity is :

$$k_e \quad = \quad (\, 1 + \zeta\eta\phi \,)\, /\, (\, 1 - \eta\phi \,)$$

where $\eta \quad = \quad (\, k_d/k_c - 1 \,)\, /\, (k_d/k_c + \zeta\,)$

for plates of width a and thickness b :

$$\zeta \quad = \quad \sqrt{3}\ \log\,(a/b)$$

and for circular or square fibers :

$$\zeta \quad = \quad 1.0$$

Hamilton and Crosser Semi-Theoretical Model [17]

Hamilton and Crosser define the thermal conductivity of a two component mixture as :

$$k_e = [k_c\ (1\text{-}\phi)\mathrm{d}t/\mathrm{d}x \big|_1 + k_d\phi\ \mathrm{d}T/\mathrm{d}x \big|_2] / [(1\text{-}\phi)\mathrm{d}t/\mathrm{d}x \big|_1 + \phi\ \mathrm{d}T/\mathrm{d}x \big|_2] \quad ....*$$

The ratio of thermal gradients can be determined from

$$\mathrm{d}T/\mathrm{d}x \big|_d / \mathrm{d}T/\mathrm{d}x \big|_c = n\,k_c\,/\,k_d + (n\text{-}1)\,k_c$$

which substituted into equation * results in :

$$k_e = k_c[\,k_d + (n\text{-}1)\,k_c - (n\text{-}1)\phi\ (\,k_c\text{-}\,k_d)\,]\,/\,[\,k_d + (n\text{-}1)\,k_c + \phi(\,k_c - k_d\,)]$$

where n is an empirical constant. For a spherical particle Maxwell showed analytically that $n = 3.0$. For nonspherical particles Hamilton and Crosser correlated numerous sets of data with $(0.58 < \psi < 1.0)$:

$$n = 3/\psi$$

where ψ is the sphericity. The sphericity was defined as the ratio of the surface area of a sphere, with a volume equal to that of the particle, to the surface area of the particles.

Harding Semi-Empirical Model [16]

Starting with an elementary conduction, convection, and radiation heat transfer analysis for low density, cellular foam, Harding obtained a semi-empirical relation.

$$k_e = k_c E_s(1-\phi) + k_d\phi + (k_b - k_a)\phi(1-F)(1-0.5R_g V_g^{1/3})M + C_r V_g/\phi[(T_h + T_c + 920)/1000]^3$$

where E_s = dimensionless efficiency fact for heat conduction through foam solids (empirical)

k_a = thermal conductivity of air

k_b = thermal conductivity of blowing agent

R_g = geometric ratio of cut surface exposed per unit foam volume

V_g = volume of gas in average cell

M = mean mole fraction of blowing agent in a cell

C_r = coefficient defining the rate of radiant energy transfer through foam.

Leob Theoretical Model [16]

Leob derived a relationship for the effective thermal conductivity of porous solid as a function of the cross-sectional and longitudinal pore fractions and surface emissivity.

$$k_e = k_c\{1-\phi_c[1-4\gamma\epsilon\sigma\Delta T^3/k_c]/(1+4\gamma\epsilon\sigma\Delta T^3/k_c)[(1-\phi_l)/\phi_l]\}$$

where :

ϕ = cross-sectional porosity

ϕ_l = longitudinal porosity

γ = geometrical factor

ϵ = pore emissivity

σ = Stefan-Boltzman constant

ΔT = temperature difference

This model attempts to compensate for radiation in the direction parallel to heat flow. For an orderly array of pores the above model was incorporated with a series-parallel analysis.

Lewis and Nielsen Semi-Theoretical Model [18]

Lewis and Nielsen have presented a model for thermal conduction in two-phase media by modifying the Halpin-Tsai equation to include the effect of the shape of the particles and the orientation or type of packing for a two-phase system. :

$$k_e \quad = \quad k_c \, [\, (1+AB\phi) \, / \, (1- B\psi\phi) \,]$$

$$\psi \quad = \quad 1+ \quad [\, (1-\phi_m) \, / \, \phi_m^2 \,] \, \phi$$

$$\text{where} \quad B \quad = \quad [\, (k_d / k_c - 1) \, / \, (k_d / k_c +A) \,]$$

$$A \quad = \quad \text{geometrical parameter reflecting the shape of the filler particles}$$

$$\phi_m \quad = \quad \text{the maximum packing fraction of the filler}$$

The Lewis and Nielsen theory was the introduction of the geometry-dependent parameter A [19]. This parameter takes care of the fact that elongated filler particles yield a higher conductivity than spherical particles if the volume ratio ϕ is equal [20]. There is a relation between the aspect ratio of the particles and A. The Lewis and Nielsen theory also includes the concept of a maximum packing fraction of filler particles. The maximum packing fraction, ϕ_m reflects that it is impossible to load more filler material into the matrix than ϕ_m value. Table 2.1 and 2.2 give some values of A and ϕ_m for particles of different shapes.

Table 2.1   Values for the shape parameter A in the Lewis and Nielsen semi-
theoretical model of conduction in composite system [21]

Type of dispersed phase	Direction of heat flow	A
Cubes	Any	2.00
Spheres	Any	1.50
Aggregated of spheres	Any	$(2.5/\phi_a) - 1$
Randomly oriented rods Aspect ratio = 2	Any	1.58
Randomly oriented rods Aspect ratio = 4	Any	2.08
Randomly oriented rods Aspect ratio = 6	Any	2.80
Randomly oriented rods Aspect ratio = 10	Any	4.93
Randomly oriented rods Aspect ratio = 15	Any	8.38
Uniaxially oriented fibers	Parallel to fibers	2L/D
Uniaxially oriented fibers	Perpendicular to fibers	0.5

Table 2.2 Values for the maximum packing fraction   in the Lewis and Nielsen

semi-theoretical model [21]

Particle Shape	Type of Packing	ϕ_m
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.6
Spheres	Simple cubic	0.524
Spheres	Random close	0.637
Rods or fibers	Uniaxial hexagonal close	0.907
Rods or fibers	Uniaxial simple close	0.785
Rods or fibers	Uniaxial random	0.82
Rods or fibers	Three dimensional random	0.52

Maxwell Theoretical Model [21]

Maxwell used the potential theory to obtain an "exact" solution for the conductivity of randomly distributed and non-interacting homogeneous spheres in a homogeneous continuous medium :

$$k_e = k_c \left[k_d + 2k_e + 2\phi(k_d - k_c) / k_d + 2k_e - \phi(k_d - k_c) \right]$$

Norton Empirical Model [22]

Norton's techniques were based upon the following assumption. The polymer matrix which makes up the foam network is so complex that it would be impossible to model the conductive and radiative energy transfer within the foam. The thermal conductivity of a polymer foam with a known gas content is experimentally measured. Subtracting the thermal conductivity of the gas assuming it had the same total volume would give the "effective" conductivity of the polymer for that particular structure and density.

$$k_{effpolymer} = k_{measured} - k_{gas}$$

The thermal conductivity of the foam with a different gas is then assumed to be

$$k_{foam} \quad = \quad k_{effpolymer} + k_{gas}$$

Peterson and Hermans Semi-Theoretical Model [16]

Peterson and Hermans derived a general theory for the dielectric constants of a dilute suspension of spheres in a continuum. By direct analogy between heat transfer and electrostatics.

$$k_e = k_c [1+3\gamma\phi + 3\gamma^2 (1+\gamma/4+\gamma^2/256+.....)\phi^2 + ...]$$

where $\gamma = (k_d - k_c) / (2k_c + k_d)$

Progelhof and Throne Empirical Model [16]

By curve fitting the experimental data for several foamed plastics they found that the following empirical equation fit the data best :

$$k_e = k_d [1+A (\rho/\rho_o)^B]$$

where $A = k_c / k_d$

and B is an empirical constant

Ratcliffe Empirical Model [16]

He presents a geometric mean correlation for determination of thermal conductivity of two-phase system as followed :

$$k_e = k_c{}^\phi \; k_d{}^{(1-\phi)}$$

Springer and Tsai Semi-Theoretical Model [23]

The thermal conductivity of a composite with unidirectional filaments in the direction along the filaments (parallel model)

$$k_e = k_c [\, \phi \, k_d/k_c + (1-\phi)]$$

In the direction normal to the filament an analogy between the response of a unidirectional composite to longitudinal shear loading and heat transfer results in:

$$k_e = k_c [(1-s/2b)+a/b \int_0^S dy \,/ (2a-h)+k_c \,/k_d \,]$$

where s = maximum transverse dimension of filament, h = width of the filament, and a,b = dimensions of elemental volume in which filament is mounted.