

## THERMAL CONDUCTIVITY OF LIQUIDS

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**ABSTRACT.** Considering a liquid near its melting point as an assemblage of a large number of linear harmonic oscillators each vibrating with a frequency  $\nu$  and assuming that communication of thermal energy takes place at each extreme vibration an expression for the thermal conductivity of the liquid at the melting point is deduced, *viz.*,  $K = 2.096 \times 10^5 \sqrt{\frac{\theta}{M V}}$ ,

where  $\theta$ , is the melting point of the liquid on the absolute scale of temperature,  $M$  the molecular weight,  $V$ , the molecular volume. A brief review of the subject is attempted and it is shown that the thermal conductivity  $K$  is intimately connected with the free volume of the liquid at the melting point. Calculated values of thermal conductivity according to the above expression are in agreement with observed values

The thermal conductivity of liquids is a subject which has been without any general theoretical basis. It has been recognised that the mechanism of conduction in liquids must be different from that in a gas. This is evinced for instance by the fact that the thermal conductivity of a liquid decreases with rise of temperature while the thermal conductivity of a gas increases with rise of temperature. In a gas there is transport of the individual atoms from one layer to another with a consequent transfer of energy. Between collisions the atoms are supposed to move freely over a distance large compared with the molecular size and it is essential for the theory that disparity between mean free path and molecular diameter should exist. In the case of liquids there is in the ordinary sense no free path at all, the motion being always in an intense field of intermolecular forces.

Leon Brillouin<sup>1</sup> has given a theory of liquid viscosity in which the fundamental idea is that the impact of molecules gives rise to elastic waves, the effect of which is that neighbouring molecules are successively disturbed from their positions. The theory is an attempt to transfer the general theory developed by Einstein and Debye for specific heats of solids and liquids to the field of liquid viscosity. The final formula which gives the temperature coefficient of viscosity in terms of the thermal conductivity and the velocity of sound fails by a factor of nearly 5,000. In 1923 Bridgman<sup>2</sup> put forward a theory of thermal conduction in liquids in which the energy difference between adjacent molecules in the direction of temperature gradient is to be conceived as handed down a row of molecules with the velocity of sound. He arrived at an expression for the

thermal conductivity  $K$  in terms of the velocity of sound  $V$  and the mean molecular distance. Although this simple picture gives approximately the absolute value of the thermal conductivity at the ordinary temperatures, it does not explain quantitatively the variation of thermal conductivity with temperature. It does not account at all well for the phenomena of thermal conduction under pressure. In 1914 Debye<sup>3</sup> suggested a complicated equation for the conductivity of a solid which can readily be reduced to one exactly like Bridgman's by substituting the liquid values for the solid ones, with the exception that the constant  $\alpha$  in Bridgman's expression is replaced by  $1/2$ . Thus Debye's values are only one quarter of Bridgman's. Kardos<sup>4</sup> has modified Bridgman's theory by allowing for the diameter of the molecules. Kardos introduces in his expression a factor  $\delta$  which is the mean distance between edges of molecules and suggests that as a first approximation  $\delta$  be assumed constant and equal to  $0.95 \times 10^{-8}$  cm. Kardos gives expression to calculate  $\delta$ , viz.,  $\delta = \frac{C_1 \beta^{1/3}}{\sigma}$  where  $C_1$  is the inner repelling force of molecules,  $\beta$  is the volume compressibility,  $\sigma$  the mean molecular distance. An examination of the above relation shows that the equation is dimensionally incorrect and does not seem to have any physical significance. Weber<sup>5</sup> in 1880 suggested an empirical relation connecting the thermal conductivity of liquids with their other properties, namely,  $\frac{K}{\rho C} = \text{constant}$  and later modified to

$$\frac{K}{\rho C} \left( \frac{m}{\rho} \right)^{1/3} = \text{constant}.$$

Here  $\rho$  is the density of the liquid,  $C$  its specific heat, and  $m$  its molecular weight. The factor  $\left( \frac{m}{\rho} \right)^{1/3}$  is seen to be proportional to the mean molecular distance. Weber's own data indicate a surprising constancy of the modified expression but later discussion by Aubel has disclosed considerably greater variations than supposed by Weber. Smith's<sup>6</sup> empirical equation for thermal conductivity involves a number of constants and is sufficiently complicated to merit any discussion.

It will be seen then that none of the older attempts have led to results which can withstand comparison with experimental results, in particular with the recent high pressure results of Bridgman which enable thermal conductivities at constant volume to be computed. As a result the study has hitherto consisted largely of a collection of more or less well-established empirical relations mostly of limited scope. In general, lack of agreement with experiment is the chief reproach that can be levelled against older theories. The theory of liquids should be approached not as has hitherto been done from the point of view of the kinetic theory of gases, which was constructed to deal with matter where the spaces between the molecules are large compared with the size of the molecules but from

the point of view of the solid state, the density of which is not markedly different from that of the liquid state of the same substance. In a solid the atoms vibrate about mean positions which are fixed. In a liquid at temperatures near the melting point, it is now generally recognized that the atoms vibrate about mean positions which though not fixed move slowly compared with the velocity of the order of magnitude  $\sqrt{\frac{KT}{m}}$  with which the atoms vibrate. The most direct evidence for this is afforded by the specific heat of substances which have within experimental error (7%) the same values (in the neighbourhood of  $3R$ ) for a given substance in the solid and liquid states near the melting point. Further evidence<sup>7</sup> is given by the rates of diffusion of gold in mercury or of thorium B in non-radio-active liquid lead. If one compares the numbers with the formula for the diffusion coefficient  $D$  in gases  $D = \frac{1}{2}lc$  where  $l$  is the mean free path and  $c$  the mean molecular velocity, one finds on setting  $c$  equal to a quantity of the order of magnitude  $\sqrt{\frac{KT}{m}}$  that  $l$  must be taken to be about 1/100 of the inter-atomic distance. A theory of viscosity of liquids has recently been given by Andrade<sup>8</sup> based on the same hypothesis. Based on the same hypothesis a theory of surface tension in liquids<sup>9</sup> at the melting point has been proposed by Sibaiya and Rama Rao.

Let us treat the atoms of the liquid as though they were vibrating about slowly displaced equilibrium positions. We shall also suppose that each atom vibrates with a frequency  $\nu$  which is the same for each atom although it is probable that in a real liquid the frequencies will not all be exactly the same. The arrangement of molecules in the liquid state is not fundamentally dissimilar to the arrangement in the solid state—the difference in the two states being brought about by the large amplitude of vibration of the atoms in the liquid state. Hence a liquid at its melting point is regarded as an assemblage of a number of harmonic oscillators, each vibrating with a frequency  $\nu$  about a slowly displaced equilibrium position and with an amplitude which is comparable with the mean molecular distance. In dealing with the problem of heat conduction in liquids we are concerned with the transport of thermal energy by the molecules. We shall treat the whole system as though there were merely a superimposed disturbance which is transmitted by the molecules, thus neglecting the effect of the superimposed disturbance on the original system. On the basis of the assumptions an estimate of thermal conductivity from other physical data such as can be found in tables can be made. A preliminary report<sup>10</sup> regarding this has already appeared in the "Physical Review." Such an estimate is a desirable feature of any theory of thermal conduction in liquids because the more complicated theories, based on considerations of partition functions, have failed not only to provide such an estimate, but have in general involved undetermined parameters in such a way that any experimental verification is difficult, except in the matter of generalities.

Let there be a thermal energy gradient  $\frac{dE}{dz}$  along the  $z$ -axis. Let us consider layers of molecules parallel to the direction of the thermal energy gradient and the molecules to be vibrating in random directions. We shall suppose that on an average  $1/3$  of the molecules are vibrating along each of three directions perpendicular to one another. The difference of energy between two layers is  $\frac{dE}{dz} \sigma$  where  $\sigma$  is the mean molecular distance. According to our assumption, since the amplitude of vibration is large at the melting point, molecules of one layer come into contact with the molecules of the neighbouring layers at every extreme vibration. When there is a contact (of very brief duration), we shall assume that the excess of thermal energy is communicated. A molecule of a given layer conveying thermal energy crosses a plane normal to the direction of drift twice in every complete vibration. A molecule of the adjacent layer also crosses this plane twice in every complete vibration. If  $\nu$  is the frequency of vibration of the molecule, then the transfer of thermal energy per unit area per unit time is given by  $\frac{4}{3} \nu \frac{1}{\sigma^2} \frac{dE}{dz} \sigma$ , where  $\frac{1}{\sigma^2}$  refers to the number of molecules in unit area. This, by definition, is equal to the product of the coefficient of thermal conduction and the temperature gradient; hence we have

$$K \frac{d\theta}{dz} = \frac{4}{3} \nu \frac{1}{\sigma^2} \frac{dE}{dz} \sigma,$$

*i.e.*, 
$$K = \frac{4}{3} \frac{\nu}{\sigma} \frac{dE}{d\theta}.$$

The average energy (both kinetic and potential) of a vibrating molecule is  $3k\theta$ , where  $k$  is Boltzmann constant; hence we have

$$K = \frac{4k\nu}{\sigma}.$$

For  $\nu$  we substitute the Lindemann expression, *viz.*,

$$\nu = 2.8 \times 10^{12} \sqrt{\frac{\theta_m}{MV^{\frac{2}{3}}}}$$

where  $\theta_m$  is the melting point on the absolute scale of temperature,  $V$ , the molecular volume and  $M$  the molecular weight. Lindemann's theory is based upon Einstein's formula for the frequency of vibration of an individual atom in a regular array which implicitly assumes a single frequency  $\nu$ . Lindemann assumes

a simple harmonic vibration characterized by  $m \frac{d^2x}{dt^2} = -\alpha x$ , and  $v = \frac{1}{2\pi} \sqrt{\frac{\alpha}{m}}$ ,

which gives a maximum kinetic energy  $\frac{1}{2} \alpha \Lambda^2 = \frac{h\nu}{e^{k\theta_s} - 1}$ , where  $\Lambda$  is the

amplitude of the vibration. Lindemann assumes that melting takes place when the vibration amplitude attains a value  $1/2S\sigma$  where  $\sigma$  is the mean molecular distance and  $S\sigma$  the distance between the peripheries of the atoms in their equilibrium positions. Then

$$v^2 = \frac{2}{\pi^2 S^2 \sigma^2 m} \frac{h\nu}{e^{k\theta_s} - 1}$$

Lindemann takes  $\frac{h\nu}{k\theta_s}$  small, so that as a first approximation

$$v^2 = \frac{2}{\pi^2 S^2 \sigma^2 m} k\theta_s$$

$$v = \frac{1}{\pi S} \sqrt{\frac{2R\theta_s}{M\sigma^2}}$$

where  $M$  is the molecular weight, and  $R$  is the gas constant. This is further written in terms of the molecular volume  $V_s$  because  $\sigma^3$  is proportional to  $V_s$ , hence we have finally

$$v = c \left( \frac{\theta_s}{MV_s^{2/3}} \right)^{1/2}$$

The value of  $S$  being unknown, Lindemann found  $c$  by comparison with the best values for  $v$  found by other methods for certain bodies. This naturally involves the assumption that  $S$  is the same for all substances or in other words that Grüneisen's rule is true, which states that for all simple solids increase in volume from absolute zero to melting point is about the same fraction of the volume, viz., 7.5 per cent. Above all Lindemann's formula involves  $S$  which is a measure of the free volume so that  $v$  involves this quantity.

For  $\sigma$  we substitute  $\left( \frac{3V_s}{4\pi N} \right)^{1/3}$  where  $N$  is Avogadro number. It then

follows that the thermal conductivity  $K$  at the melting point is given by

$$K = 2.096 \times 10^5 \left( \frac{\theta_s}{MV_s^{2/3}} \right)^{1/2}$$

The constant  $2.096 \times 10^4$  involves the factor  $S$  which has been assumed to be the same for all types of molecules. This is hardly justified when we consider different shapes of molecules. The constant may have to be modified when more precise methods of calculation are available. In Table I are given the calculated and the observed values of thermal conductivity. In some cases, where the variation of thermal conductivity with temperature has been studied, the extrapolated values at the melting point are recorded. As regards liquid metals they stand in a class by themselves because the contribution of the electrons in the metal in the process of thermal conduction has to be dealt with, which really forms the major contribution for thermal conduction in metals. In the present investigation only dielectric liquids are considered.

TABLE I

Substance	Melting point in °K	Thermal conductivity at melting point	
		Calculated	Observed
Carbon tetrachloride	443	1.315	1.124
Aniline	265	1.730	1.720
Chloroform	203	1.591	1.382
Diethyl ether	150	1.590	1.380
Benzene	278.1	2.012	1.677
Chloro-benzene	227.8	1.425	1.501
Fluoro-benzene	231.8	1.615	1.580
Bromo benzene	242.4	1.205	1.330
Iodo-benzene	241.6	1.014	1.230
Acetic acid	280	1.900	1.970
Liquid sulphur	388	1.350	1.810
„ oxygen	54	3.170	2.001
„ nitrogen	62.5	3.040	2.075

The calculated values are of the right order and places the conductivities of substances like liquid sulphur, oxygen and nitrogen in the right sequence of magnitude and gives their relative magnitudes.

The question of the variation of thermal conductivity with pressure and temperature will be dealt with separately. Also the relation between the liquid

structure and the constant occurring in Lindemann's formula will be considered in a separate paper.

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