Interpretation of the Thermal Conductivity of Glasses

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The thermal conductivity of glasses decreases with decreasing temperature, while the conductivity of crystalline substances increases with decreasing temperature. The behavior of glasses is interpreted in terms of an approximately constant free path for the lattice phonons, so that the conductivity decreases roughly with the specific heat. The value of the phonon mean free path at room temperature is of the order of magnitude of the scale of the disorder in the structure of glasses as determined from x-ray evidence—that is, of the order of 7A. This is about the size of the unit cell of the crystalline forms of silica.

IT was pointed out first by Eucken[1] that the temperature dependence of the thermal conductivity of glassy materials is quite different from that of crystalline materials. The thermal conductivity of glasses *decreases* fairly sharply with decreasing temperature, whereas the thermal conductivity of crystalline substances—whether single crystals or polycrystalline—*increases* fairly sharply with decreasing temperature[2] (Fig. 1). A second

FIG. 1. Comparison of thermal conductivity of glasses and crystalline substances. (The data are principally from the Landolt-Börnstein tables. The measurement on Thuringian glass at liquid He temperature is by P. H. Keesom, Physica 11, 339 (1944–46). Other measurements, not shown above, on four glasses at liquid He temperatures have been made by Dr. D. Bijl, and are to be published in Physica. The trend of the conductivity is quite similar in the four glasses measured by Bijl; for example, he finds $K = 1.0 \times 10^{-4}$ cal./cm-sec.-deg. for Monax glass at 1.45°K, while Keesom found for Thuringian glass 0.8×10^{-4} at 1.3°K.)

[1] A. Eucken, Ann. d. Physik (4) 34, 185 (1911).
[2] The thermal conductivity of several single crystals has been found by de Haas and Biermasz to pass through a maximum near the liquid helium range; the fall-off on the low

distinguishing characteristic of the thermal conductivity of glasses is that the spread of values of the conductivity from one glass to another, at a given temperature, is usually smaller than the spread in the care of crystalline substances. A third difference is that the thermal conductivity of glass is considerably lower than for crystalline substances. The point plotted for Thuringian glass at 1.3°K should be particularly noted.

While the mechanism of thermal conduction in crystalline substances is quite well understood in qualitative terms, the corresponding processes in glasses have not previously been considered. It is this subject with which the present paper is concerned, and we shall see that the thermal conductivity data find a natural explanation which is based on the x-ray evidence as to the nature of the glassy state; in fact, the thermal conductivity data may be regarded as a significant additional confirmation of the random lattice theory of glasses, as developed by Zachariasen[3] and Warren.[4]

The present concept of the nature of the glassy state pictures a glass such as fused quartz (SiO_2) as a random, but continuous, network of $Si-O$ bonds. There is a definite structure in vitreous silica, but it is a structure with regard to immediate neighbors rather than a regularly repeating crystalline structure (Fig. 2). The local order which exists in the immediate environment of any atom is the same in vitreous silica as in the crystalline modifications of silica, but fused quartz does not possess the regularly repeating long range order of the crystal. Warren has shown that if we try to interpret the x-ray diffraction pattern of vitreous silica in

temperature side of the maximum has been explained very satisfactorily by Casimir, who showed that the maximum occurs when the phonon mean free path becomes of the same order as the diameter of the test specimen, while at lower temperature the thermal conductivity is approximately proportional to the specific heat. See W. J. de Haas and T. Biermasz, Physica 2, 673 (1935); 4, 752 (1937); 5, 47, 320, 619 (1938); H. B. G. Casimir, Physica 5, 495 (1938); R. E. B. Makinson, Proc. Camb. Phil. Soc. 34, 474 (1938); see also R. Peierls, reference 6.

[3] W. H. Zachariasen, J. Am. Chem. Soc. 54, 3841 (1932).
[4] B. E. Warren, J. App. Phys. 8, 645 (1937); 13, 602 (1942).

terms of the older concept of a glass as composed of small crystallites, rather than as a continuous bonded network, then we must conclude from the width of the diffraction lines that the crystallites are 7A in size. This is, however, just the size of the unit cell of a typical crystalline form of silica, and it is rather meaningless to speak of material as polycrystalline when the crystallites are reduced to single unit cells. The idea of glass as a continuous random network is based on this and a number of other considerations.

The mechanism of heat conduction in *crystalline substances* has been explained by Debye,[5] Peierls,[6] and others, as sketched below. By analogy with the corresponding expression in the kinetic theory of gases the thermal conductivity K is written

$$K = \tfrac{1}{4}cv\Lambda, \tag{1}$$

where c is the heat capacity per unit volume, v is average velocity of a sound wave (phonon) in the material, and Λ is the mean free path of phonons; the factor $\tfrac{1}{4}$ is somewhat arbitrary. In an ideal infinite crystal lattice the mean free path will be infinite if the lattice interactions are strictly harmonic; finite values of Λ in an ideal crystal lattice are the result of anharmonic terms in the lattice interactions. The anharmonic terms have two effects: they limit the mean free path by coupling together the various lattice vibrations, and by the same mechanism they are able to produce a distribution of phonon frequencies corresponding to thermal equilibrium.

The numerical value of Λ in a perfect crystal will depend on the magnitude of the anharmonic interactions, and also on the total density of phonons, since the greater the density of phonons, the greater are the number of possibilities for a given phonon to interact with other phonons. The phonon density decreases with decreasing temperature, so that we should expect the mean free path and thus the thermal conductivity to increase as we lower the temperature. This feature of the theory is in agreement with the experimental data which suggest that the conductivity of crystalline materials usually varies approximately as $1/T$ over the range of ordinary temperatures.

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In the case of glasses the anharmonic lattice interactions are still responsible for establishing thermal equilibrium among the phonons, but the mean free path which enters into the equation for the conductivity will usually be limited by geo-

[5] P. Debye, in *Vorträge über die kinetische Theorie der Materie und Elektrizität*, by M. Planck *et al.* (B. G. Teubner, Leipzig, 1914).

[6] R. Peierls, Ann. d. Physik (5) **3**, 1055 (1929); M. Blackman, Phil. Mag. **19**, 989 (1935).
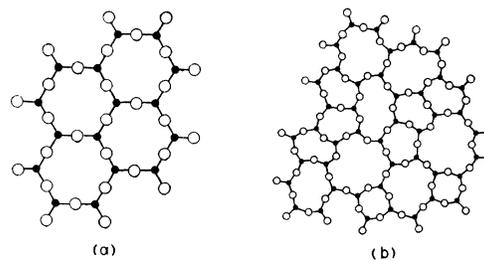
FIG. 2. Schematic two-dimensional figures, after Zachariasen, illustrating the difference between: (a) the regularly repeating structure of a crystal; and (b) the random network of a glass.

metrical effects associated with the disordered nature of the structure.

If, to take an extreme case, the disorder determines a mean free path Λ_0 which is a constant, independent of phonon wave-length and phonon density, then the thermal conductivity may be written as

$$K = \tfrac{1}{4}cv\Lambda_0 \tag{2}$$

so that the ratio K/c is approximately constant. Since the heat capacity decreases with decreasing temperature, the thermal conductivity would also be expected to decrease, on the assumption of constant mean free path.

Values of Λ for glasses are given in Table I, as calculated from the experimental values of the conductivity, heat capacity, density and sound velocity. It is seen that the values of Λ are all of the order of magnitude of the dimensions of a "unit cell"—that is, of the order of 7A.

The phonon free path in quartz glass at room temperature is seen from Table I to be longer than in the other two glasses for which data are given. This result may be accounted for by the presence of foreign atoms introduced in the commercial glasses as "modifiers"; these give additional scattering.

The increase in the phonon free path at low temperatures can be understood as a consequence of
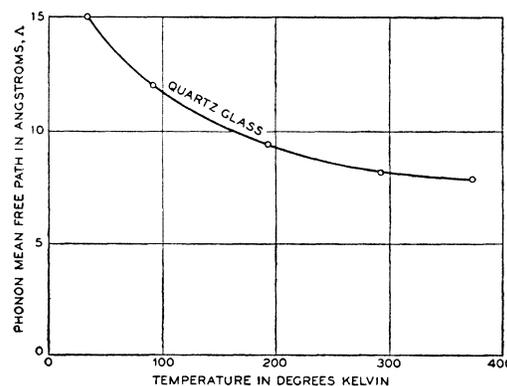
FIG. 3. Phonon mean free path Λ as a function of absolute temperature for quartz glass.

Table I. Calculation of the phonon mean free path Λ for glasses.*

Material	Temp.	K	c'	ρvl	⟨ρv⟩	Λ
Quartz glass	100°C	(0.0037)	0.194	——	(0.97×10⁶)	7.8A
	room	0.0034	0.172	1.45×10⁶	(0.97×10⁶)	8.1
	−80°C	0.00275	0.12	——	(0.97×10⁶)	9.5
	−180°C	0.0017	0.059	——	(0.97×10⁶)	12.0
	−238°C	(0.0009)	0.014	——	(0.97×10⁶)	15.0
Crown glass	room	0.00163	0.161	1.41×10⁶	0.94×10⁶	4.2
Flint glass	room	0.00143	0.117	1.54×10⁶	1.02×10⁶	4.8

* For purposes of comparison we may mention that Λ for a quartz crystal (‖ axis) is of the order of 700A at −190°C. The data used above are taken from the *Landolt-Börnstein Tabellen* and from Bergmann *Der Ultraschall*. K is in cal./cm-sec.-deg.; c' is in cal./g-deg.; ρv is in g/cm²-sec.; the mean value $\langle \rho v \rangle$ is arbitrarily taken as $\frac{2}{3}$ of the value ρv for longitudinal waves.

the more uniform propagation conditions which obtain when the wave-length of the dominant phonons becomes substantially larger than the dimensions of a unit cell of the glass. The mean free path may be expected to begin to increase when the temperature drops significantly below the value given by

$$kT_0 = hv/D$$

where D is the unit cell length. For glasses

$$T_0 \approx \frac{(6.6 \times 10^{-27})(4 \times 10^5)}{(1.4 \times 10^{-16})(7 \times 10^{-8})} \approx 270°\text{K},$$

and this value is more or less in agreement with experiment (see Fig. 3, where Λ vs. T is plotted for quartz glass).

There are several ways in which we can understand qualitatively the mechanism by which a disordered structure limits the free path of a phonon of wave-length λ appreciably smaller than the scale D of the disorder.

1. One method is based on the distinction between plane elastic waves and normal modes of vibration. In a regular periodic lattice the normal modes of vibration are essentially identical with plane waves, so that in an infinite medium a plane wave will, if we neglect anharmonic interactions, propagate indefinitely without loss of energy to other modes of vibration. But in a disordered lattice the normal modes are no longer plane waves: if we set up a plane wave it will soon become highly distorted, as the original wave may be viewed as the sum of a number of normal modes with various eigenfrequencies. The resulting distortion may be

described approximately in terms of a mean free path.

2. Another method is based on a consideration of Fig. 1b which shows the random network of a glass. A plane elastic deformation started along one side of the network will not propagate in plane form, since different portions of the original plane deformation will travel down bond linkages of different overall length, leading to phase destruction and to distortion of the character of the deformation.

3. Another approach to the problem utilizes the concepts which have been developed by the present author,[7] and by Mason and McSkimin,[8] in analyzing the results of measurements of the attenuation of ultrasonic waves (~20 mc/sec.) in polycrystalline solids. It is found experimentally that when the wave-length is much smaller than the grain size the "free path" is a constant, independent of frequency. We have the following physical picture of the mechanism responsible for a constant Λ_0 in this limit: the sound wave loses a certain proportion of its energy by reflection at each interface between adjacent crystal grains. The intensity penetrating a distance x will be reduced with respect to the incident intensity by a factor of the order of $e^{-Rx/D}$, where D is the grain size, and R is the reflection coefficient. The phonon free path here is then $\Lambda_0 = D/R$.

It should be mentioned that the viewpoint developed in the present paper is applicable to heat conduction in liquids, as it is well known that in liquids the phonon free paths are of molecular dimensions, and that the lattice structure is in some respects similar to that of a disordered solid.

[7] C. Kittel, "Ultrasonics research and the properties of matter," Reports on Progress in Physics 11, 205–247 (1946–1947).

[8] W. P. Mason and H. J. McSkimin, J. Acous. Soc. Am. 19, 464–474 (1947); also J. App. Phys. 19, 940–946 (1948).