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Phonon Scattering in Polyethylene at Low Temperatures

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An expression, valid below 4 °K, for the phonon mean free path in polyethylene is derived through a consideration of the microscopic structure. Above 1 °K, scattering of phonons occurs mainly within the amorphous regions and can be described by a structure scattering term. The amorphous-crystalline boundaries contribute a constant term to the mean free path above 1 °K, but below this temperature, when the phonon wavelength is comparable to the size of the crystallites, it is suggested that the alternation of crystalline and amorphous material should be described by a second structure scattering term. This free path is shown to account for the anomalous temperature variation of the thermal conductivity recently observed below 1.5 °K: No modification to the phonon density of states predicted by the Debye theory is required. A discussion of phonon resonant scattering is also presented.

I. INTRODUCTION

In a recent paper,[1] Giles and Terry reported measurements on the thermal conductivity of polyethylene between 0.5 and 1.4 °K. Their results show considerable deviations from the theoretical model[2,3] which has been used successfully above 1.5 °K and they interpret this behavior in terms of a change in the phonon spectrum: At sufficiently low temperatures the three-dimensional phonon spectrum given by the Debye model should be supplemented by an additional two-dimensional spectrum corresponding to the relative motion of polymer chains, which themselves remain rigid.

There are two aspects of this interpretation which need further discussion: the validity of the Debye expression at these temperatures, and the consistency of the results of Giles and Terry with the earlier measurements. The extension of the Debye theory to an anisotropic crystalline solid is relatively straightforward: The surfaces of constant energy in reciprocal space are ellipsoidal rather than spherical, but the density of states remains proportional to ω^2, where ω is the phonon frequency. Only when the major axis of the ellipsoid meets the Brillouin zone boundary will a two-dimensional density of states proportional to ω be obtained. The results of this simple picture have been confirmed by detailed studies of the phonon spectrum of polyethylene,[4,5] and measurements of specific heat at temperatures[6] below 10 °K, which, when extrapolated to 100% crystallinity, show a cubic variation with temperature. In polyethylene with a large amorphous content, the specific heat contains an additional contribution which has been interpreted as a local mode with a specific heat given by the Einstein expression. Similar local modes have been observed in other amorphous materials,[7] but should not affect the thermal conductivity, except as a possible scattering mechanism. Below 4 °K we may therefore completely describe the acoustic phonons by a density of states of the Debye form: The transition to two-dimensional behavior occurs at considerably higher temperatures.

Between 1 and 4 °K, the thermal conductivity follows the relation

$$\kappa = \frac{k_B^2 TA}{6\pi^2\hbar} \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \frac{dx}{x^2 + (A/l_0)(\hbar v_s/k_B T)^2} , \tag{1}$$

where the phonon free path due to structure scattering is Ak^{-2}, k being the phonon wave number, and a free path l_0 due to scattering from internal boundaries is included. The values of A and l_0 depend to some extent on crystallinity, but the values obtained by different authors[2,3] agree reasonably well for the same degree of crystallinity. Typical values for high-density polyethylene are $A = 10^8$ mm^{-1} and $l_0 = 1$ μm. A increases with crystallinity while l_0 decreases. However, the values used by Giles and Terry differ by an order of magnitude from the above values.

We would like to suggest in this paper that the change in the temperature variation of the thermal conductivity is due not to an additional contribution to the specific heat, but to a change in the mechanism of phonon scattering. Polyethylene is a partly crystalline material, and we do not believe that the scattering can be described by a constant mean free path together with a single-structure scattering term. A more complete picture of the structure of melt-crystallized polyethylene is required.

II. STRUCTURE OF POLYETHYLENE

The structure of melt-crystallized polyethylene has been discussed in some detail by Keller,[8] and we will summarize his results here. The basic structural unit is the crystallite, of characteristic dimensions 20 nm×0.1 μm×0.1 μm. The chains are parallel to the shortest dimension, indicating that the chains, typically of length 1 μm, are folded back on themselves a large number of times. These folds occupy a surface layer of thickness 1 nm. In the solid, the crystallites are arranged end to end to form a ribbonlike structure. If a sample of polyethylene is allowed to crystallize the ribbons grow out from nucleating centers to form spherulites, the characteristic structures observed under the optical microscope. If, however, crystallization occurs during extrusion, the nucleating centers lie close together on a line parallel to the stress direction and the ribbons grow, with cylindrical symmetry, out from these centers. For low stresses, and in spherulitic polyethylene, the ribbons are twisted with a twist period of from 0.1 to 1 μm, which is of the same order as the separation of the nucleating centers in extruded polyethylene. It should be noted that this picture is a considerable departure from the traditionally accepted structure of extruded polymers in which the chains were assumed to lie along the stress direction. The nature of the material which fills the spaces between these twisted ribbons is still uncertain, but we may assume that it will be disordered to a considerable extent. On a microscopic scale, we may therefore picture the structure as an arrangement of alternate crystalline and amorphous regions both parallel and perpendicular to the stress direction in extruded polyethylene, with a characteristic scale length L of about 0.1 μm. In general, the orientation of neighboring crystallites will not be correlated, and we may expect that as the crystallinity of the polyethylene is increased (by, for example, reducing the number of methyl groups attached to the main chain) not only will the crystallites be larger, but their perfection will also increase.

III. PHONON MEAN FREE PATH

In this section we shall assume that we may treat a phonon as a plane wave with a well-defined wave number $\underline{k}$, and calculate the effective free path due to scattering from the random structure of the polymer. This is the approach taken by previous authors, and we expect that it will be valid at very low temperatures, in the long-wavelength limit. In a structure of the type described for polyethylene, with alternate disordered and crystalline regions, the scattering of phonons will depend on the ratio of the phonon wavelength λ to the scale length L. For $\lambda \ll L$, we may consider the two regions separately, with the dominant scattering occurring in the amorphous region, where we may assume a mean free path for structure scattering of the form Ak^{-2} with A of the order of 0.1 nm, the scale of the disorder in the amorphous polymer. The boundary between crystalline and amorphous regions will contribute a constant free path of the order of 0.1 μm, although this may be reduced by scattering in the interior of the crystallites. When $L \ll \lambda$, however, the two regions cannot be considered separately, and we must define a new structure scattering term Bk^{-2}, with B of order 0.1 μm.

This intuitive approach has been placed on a firmer base by Ziman[9] in his calculation of the phonon mean free path in an amorphous structure. We follow his approach in order to obtain a quantitative estimate of the free path in polyethylene. Each point on the wave front of a plane wave passing through the medium suffers a different phase shift, due to the variations δv_s in the velocity of sound. This leads to a diffraction of radiation from the forward direction, and from the attenuation of the wave we may calculate a mean free path. The step in the argument that reflects the microscopic structure of the materials consists of noting that the variation in the velocity of sound is not purely random. v_s does not change rapidly over a correlation length characteristic of the medium. In polyethylene at long wavelengths we may identify this as the scale length L. The phonon free path due to the alternation of amorphous and crystalline regions is then given by expressions of the form[9]

$$l = \tfrac{1}{4}\pi^{-(7/2)}(v_s/\delta v_s)^2(\lambda^2/L), \qquad \lambda \gg L \ .$$

$$l = \pi^{-(5/2)}(v_s/\delta v_s)^2 L, \qquad \lambda \ll L \ .$$

We may sum these two expressions to provide an interpolation formula

$$l = l_0(1 + \lambda^2/\alpha^2 l_0^2),$$

where

$$l_0 = \pi^{-5/2}(v_s/\delta v_s)^2 L$$

and

$$\alpha = 2\pi^3(\delta v_s/v_s)^2 \ .$$

Including a structure scattering term Ak^{-2} to describe the interior of the amorphous regions, we obtain

$$\frac{1}{l} = \frac{1}{Ak^{-2}} + \frac{1}{l_0[1 + (\lambda^2/\alpha^2 l_0^2)]} \ . \tag{2}$$

If $\lambda \ll L$, this reduces to the free path used in (1). It has been assumed that the scale length L determines the mean free path in both the long- and short-wavelength limits, whereas in reality we should define a length $L_\parallel$ parallel to the phonon propagation direction, which will determine the short-wavelength behavior, and $L_\perp$ which will be important at long wavelengths. As we are concerned here to indicate the effects of the polymer morphology on the thermal conductivity, rather than to attempt a detailed comparison of experiment with theory, the additional analysis will not be performed. A second point should also be noted in connection with

(2). In the calculation we assumed, following Ziman, an exponential correlation between v_s at two different points on the wavefront. This is probably an oversimplification, but is chosen in order to make the problem tractable; in principle an exact correlation function could be used.

IV. THERMAL CONDUCTIVITY OF POLYETHYLENE

We may use the complete expression (2) for the phonon mean free path, together with the Debye expression for the density of phonon states, to obtain the thermal conductivity κ. Equation (1) is replaced by

$$\kappa=\frac{1}{6\pi^2}\,\frac{k_B^2 T}{\hbar}\,A\left[\int_0^\infty \frac{x^4 e^x}{(e^x-1)^2}\times\frac{dx}{(A/l_0)(\hbar v_s/k_B T)^2+x^2}+\left(\frac{h v_s}{\alpha k_B T l_0}\right)^2\times\int_0^\infty \frac{x^2 e^x}{(e^x-1)^2}\,\frac{dx}{(A/l_0)(\hbar v_s/k_B T)^2+x^2}\right], \quad (3)$$

where we have neglected $1/\alpha^2 l_0$ in comparison with A. The second integral represents an additional contribution to the thermal conductivity which at low temperatures is proportional to T rather than T^3. Equation (3) has been fitted to the experimental results as shown in Fig. 1. The parameters used to fit the result are $A=2.8\times10^8\ \mathrm{mm}^{-1}$, $l_0=0.2\ \mu\mathrm{m}$, $\alpha=1.4$, using a velocity $v_s=2\times10^3\ \mathrm{m\ sec}^{-1}$, and we should note that these agree significantly better with earlier results than the corresponding parameters of Giles and Terry. From α we may deduce that $(v_s/\delta v_s)$ is about 6, which is in agreement with an order-of-magnitude estimate derived from the velocities of sound in amorphous and crystalline regions.[1,2] Using this value we obtain from l_0 a scale of irregularity of 0.3 μm and from A, which in our interpretation is a measure of the strength of the scattering in the amorphous regions, we may say that the position of the molecules is correlated only to about 3×10^{-11} m. This is rather small, but as the derived value of $(v_s/\delta v_s)^2$ is a measure of the variation of the sound velocity between amorphous and crystalline regions, and is therefore probably a lower bound on $(v_s/\delta v_s)^2$ within the amorphous region, it is not unreasonably so. In addition, the numerical constants are sensitive to the details of the calculation; values of A up to $10^9\ \mathrm{mm}^{-1}$ have been found in certain glasses.[10]

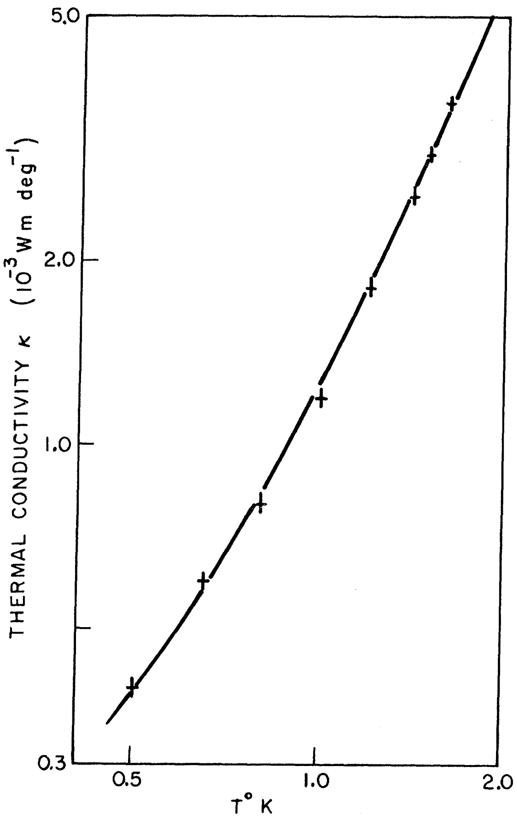

FIG. 1. Solid curve is drawn according to Eq. (2), while the points are representative of the data given in Ref. 1.

Measurements of l_0 in a range of different types of polyethylene[1,2] have shown that the mean free path increases with decreasing crystallinity. This has been interpreted as a change in the spherulite radius, but this is inapplicable if we consider the boundary between crystalline and amorphous regions, rather than between spherulites, to be the main cause of boundary scattering. However, the factor $(v_s/\delta v_s)^2$ also decreases with increasing crystallinity. As the crystallite size changes only slightly with crystallinity this leads to a mean free path l_0 which, as observed, decreases with increasing crystallinity. This model also predicts the observed increase of A with crystallinity. The mean free path Ak^{-2} describes an average scattering due to the interior of the amorphous regions. As the crystallinity increases the phonons spend less time within the amorphous material, the effectiveness of the structure scattering within these regions decreases, and so the mean free path increases. This effect should of course be taken into account when deriving a correlation length within the amorphous regions by using the value of A extrapolated to zero crystallinity.

V. PHONON RESONANT SCATTERING

The experimental results show a strong similarity with measurements of the thermal conductivity of impurity-doped alkali halides in the same temperature range,[11] and it is interesting to note that there is evidence of a phonon resonant scattering center in polyethylene. Studies of the dielectric properties of polyethylene at liquid-helium temperatures[12,13] have indicated the presence of a tunnelling state which has been ascribed to the rotation of a hydroxyl group attached to the polyethylene chain. The ground-state energy level is split into two levels separated by about 10^{-4} eV, corresponding to the dominant phonon frequency at 1 °K. A calculation of the effective free path has been made by a number of authors,[14-16] who relate the phonon relaxation time τ_{ph} to the lifetime Γ of the defect state by

$$\tau_{ph}^{-1} = \Gamma^{-1} \frac{2\pi^2 \hbar v_s^3}{\omega^2} N(\omega) \tanh^2 \frac{\hbar\omega}{2k_B T} ,$$

where $N(\omega)$ is the number of defect centers with splitting between ω and $\omega + d\omega$. For commercial polyethylene we may estimate the total number of defect centers[13] as 10^{23} m^{-3}, spread over an energy range of 10^{-4} eV, so

$$\tau_{ph}^{-1} \sim 20\Gamma^{-1} .$$

Now at 1 °K the dielectric relaxation time is 1.7×10^{-4} sec, so that using this as a value for Γ we obtain $\tau_{ph} \sim 10^{-5}$ sec, leading to a phonon free path of about 10 mm. This is much greater than the corresponding terms for structure or boundary scattering, and so it appears that we may neglect the phonon resonant scattering. In the case of OH^- in KCl, the corresponding value for the dielectric relaxation time is 10^{-8} sec, giving a phonon free path of 0.1 μm, and hence an observable drop in the thermal conductivity.

We cannot, of course, rule out the possibility of resonant scattering by other groups. In certain amorphous polymers a temperature dependence of the thermal conductivity[17] not unlike that seen in polyethylene, although occurring at higher temperatures (5 °K), has been convincingly explained in terms of phonon resonant scattering,[18] although alternative explanations have also been put forward.[14] In these amorphous polymers, however, as in amorphous silica, there is a considerable discrepancy between the measured heat capacity and that predicted on the basis of the acoustic properties of the material,[19] and this has been ascribed to the localized modes which also act as resonant scattering centers. In crystalline polyethylene, as in other crystalline polymers, this discrepancy is much less,[6] indicating a much smaller number of local modes. The experimental results on the specific heat of polyethylene, as mentioned previously, show an anomaly at 15 °K, but this is at too high a frequency to affect the thermal conductivity below 1 °K.

Further experiments on the thermal conductivity of polymers, particularly in conjunction with specific-heat measurements in materials of different crystallinity, are required before any conclusions can be drawn concerning the importance of phonon resonant scattering.

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