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## Thermal Properties of Polymers at Low Temperatures

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## Thermal Properties of Polymers at Low Temperatures

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### SUMMARY

The existing measurements and theories of the low-temperature thermal properties, heat capacity, and thermal conductivity of polymers are reviewed with particular attention paid to the differences between partly crystalline and amorphous polymers. The most striking feature of the low-temperature heat capacity of polymers is that in the liquid helium temperature range the heat capacity does not depend upon the cube of the temperature as for other solids. Further, only well below  $1^{\circ}\text{K}$  does the heat capacity approach the value predicted on the basis of the sound velocity. This behavior indicates the presence of a small number of low-frequency modes of vibration in the frequency spectrum. The fact that such anomalous behavior seems linearly related to the crystallinity implies that this behavior is associated with the amorphous structure, perhaps with motions of pendent groups within cavities formed in the amorphous structure. The thermal conductivity of semicrystalline and amorphous polymers differs considerably. Semicrystalline polymers display a temperature dependence of the thermal conductivity similar to that obtained from highly imperfect crystals, the thermal conductivity having a maximum in the temperature range near  $100^{\circ}\text{K}$  which moves to lower temperatures and higher thermal conductivities as the crystallinity is increased. Amorphous polymers display a temperature dependence similar to that obtained for glasses with no maximum but a significant plateau region in the range between 5 and  $15^{\circ}\text{K}$ . The theoretical interpretation of the thermal conductivity of these materials is considered.

## INTRODUCTION

In this paper the low-temperature thermal conductivity and heat capacity of polymers are discussed. Such a discussion may be appropriate at this symposium, first, because the technical utilization of polymers in cryogenic environments often requires some knowledge of these thermal properties (for example, the very low thermal conductivity of polymers may either be a very useful feature or a great nuisance in various applications); and secondly, because of the insights into the nature of the solid-state behavior of polymers that the studies of these properties can give. In our discussion, which examines the experimental and theoretical aspects of the two problems in turn, we concentrate on the heat capacity below about 20°K, as considerable attention has been paid elsewhere to the heat capacity at higher temperature; but our concern with the thermal conductivity will extend to much higher temperatures, as the temperature dependence of this property of polymers has received little attention in the past and we find general patterns emerging only when we examine the thermal conductivity over a wide range of temperatures. Our general plan of attack is to survey briefly the available experimental information, then to present some rather general theoretical orientation suitable for consideration of the available data, and finally to examine in some detail the special cases of polyethylene and polymethyl methacrylate as examples of semicrystalline and amorphous polymers. In our survey we find that the behavior of semicrystalline differs considerably from that of amorphous polymers.

In contrast to the situation which prevails for many other types of materials, very few low-temperature data exist for the heat capacity and thermal conductivity of polymers. In fact, the heat capacity of only the single polymer, polyethylene, is known over a full range of temperatures, while the thermal conductivity of no polymer is known over a full range of temperatures. Thus we devote much attention to developing rather simple models which may be used to try to bridge the gaps in the experimental data.

In our discussion of heat capacity we pay particular attention to the existence of the so-called excess, or low-temperature nonacoustic, heat capacity in amorphous polymers, as the existence of this heat capacity contribution must be recognized if simple models are to be used to extrapolate heat capacity measurements to lower temperatures or if reliable deductions concerning molecular motion are to be made from low-temperature heat capacity studies.

In our discussion of thermal conductivity we pay particular attention to amorphous materials because for these materials the greatest degree of understanding has been achieved. The case of semicrystalline polymers is much more difficult and it is not yet clear that a generally applicable methodology for the interpretation of the thermal conductivity of such materials is currently available, although it is suggested that the best method of approach may be by analogy with the case of crystals with a high defect concentration. Because of this lack of understanding, the chief physical factors, other than crystallinity, which effect the thermal conductivity of semicrystalline polymers have not yet been identified with certainty.

## THE LOW-TEMPERATURE HEAT CAPACITY OF POLYMERS

### The Experimental Situation

In contrast to the wealth of available experimental data on the low-temperature heat capacity of typical inorganic substances, there is a relative scarcity of data on polymeric substances. There is a considerable body of data concerning the heat capacity of a large number of polymers from approximately the liquid hydrogen temperature range, about 20°K, to quite elevated temperatures [1-7], and these data have been subjected to a great deal of analysis to extract thermochemical parameters of interest and often in an effort to extract information concerning the motion of various side groups along the polymer chain [3, 8]. It is not our purpose here to review these data nor the interpretations that have been made of them, but rather to point out some difficulties that may result because of the lack of truly low-temperature data.

From an experimental point of view it is quite understandable that most of the data available lie above 20°K. One of the principal problems in measuring the heat capacity of polymers stems from their very low thermal conductivities, leading to excessive thermal equilibrium times unless special techniques are adopted. The typical experimental approach to this problem is to use a large number of small pieces of polymer (typical size, a few mm<sup>3</sup>) and to effect thermal contact with an exchange gas (typically helium). While this procedure is not objectionable in the temperature range in which it has been used, it is difficult to extend the technique to much lower temperatures without encountering the difficulty of a temperature-dependent absorption of exchange gas on the sample surface leading to misleading data since the heat added to effect a measurement would be divided in an

unknown way between the heat used to actually change the temperature of the material and the heat of desorption of the exchange gas.

The goal of heat capacity measurements is often to obtain thermochemical data. To obtain adequate thermochemical data for many inorganic systems, heat capacity measurements above the hydrogen range quite often suffice, as there are good extrapolation methods for a typical crystalline solid, usually the Debye model, which may be used to extend heat capacity and entropy data toward the absolute zero. However, such extrapolations, although sometimes employed for polymers, are quite unreliable because the Debye approximation is not a good approximation to the heat capacity of polymers in the temperature range near 20°K. As an example we might cite the case of Teflon in which measurements were carried to 15°K and fit to a Debye function [2]. If one compares the measured heat capacity in the liquid helium temperature range [9, 10] with the Debye function extrapolation from 15°K, one finds that the extrapolation is in error by approximately a factor of 2. It is true that such discrepancies really do not contribute too much error to entropy calculations and resultant thermochemical considerations, since the heat capacity at low temperatures is small and even a large error in extrapolation will lead to a small relative error in the entropy. However, such errors indicate that the low-frequency portion of the vibration spectrum is not well understood and should be troubling to anyone wishing to extract information concerning molecular motion from heat capacity data.

The available low-temperature (below 15°K) data on the heat capacity of polymers are summarized in Table 1. As can be seen, for only two polymers, the linear polymer polyethylene [4, 6, 10-12] and the cross-linked epoxy Araldite [13, 14], data are available over a complete range of temperatures to 20°K, and data are available over a truly wide temperature range only for polyethylene. However, a comparison of the existing helium temperature and hydrogen temperature data will probably allow a reasonable extrapolation to be made in the other cases (see, for example, Fig. 6). The low-temperature data fall into two classes, those obtained by direct calorimetric means and those obtained indirectly as a by-product of thermal conductivity measurements.

As mentioned, the low thermal conductivity of polymers presents experimental difficulties for direct heat capacity measurements of large samples. In the case of polyethylene, this problem has been overcome either by the use of a sample consisting of a number of flat disks sandwiched between a number of flat, connected copper plates [11], or by embedding a large number of fine copper wires inside the sample [12].

**Table 1.** Summary of Available Heat Capacity Data on Polymers Below the Liquid Hydrogen Temperature Range

Material	Temperature range, °K	Method <sup>a</sup>	Ref. <sup>b</sup>
Polyethylene	17-60	D	[4]
	20-300	D	[6]
	1-4.5	I	[10]
	1.8-5.3	D	[11]
	2.5-30	D	[12]
Teflon	15-370	D	[2]
	1.4-4.2	D	[9]
	1-4.5	I	[10]
Nylon	1-4.5	I	[10]
	1-4	D	[14]
Kel-F	1-4.5	I	[10]
Polystyrene	16-60	D	[5]
	20-300	D	[7]
	1.4-4.2	D	[9]
	0.5-2	D	[15, 16]
	1-4.2	I	[15, 16]
	1-4.5	I	[17]
Polymethyl methacrylate	17-60	D	[5]
	1.4-4.2	D	[9]
	0.5-2	D	[16]
	1-4.2	I	[16]
	1-4.5	I	[17]
Araldite	1-2	D	[13]
	1.5-20	D	[14]

<sup>a</sup>D = direct, I = indirect.

<sup>b</sup>References are to some measurements at higher temperatures where there is comparable low-temperature data available.

A similar procedure was used for the recent measurements on Araldite [13]; the earlier measurements employed the exchange gas technique [14] and, at least at the low-temperature end, should consequently be viewed with a bit of skepticism. At sufficiently low temperatures, below about 2°K for most polymers, the time required for thermal equilibration becomes quite reasonable, of the order of a few minutes for a sample of about 10-cm length, so that no special techniques are required to promote thermal transfer. Recent measurements below 2°K on polystyrene [15, 16] and polymethylmethacrylate [16] are of this type. In addition, the direct measurements on nylon [13] were made without special techniques to ensure rapid thermal equilibrium. There is no information available concerning the techniques employed by Noer et al. [9], although the exchange gas technique was probably used in this work.

The second class of measurements are those which were obtained through an analysis of the thermal equilibration in measurements of thermal conductivity. In such experiments heat is typically introduced from one end of a rod whose other end is held at a fixed temperature, and the approach to thermal equilibrium is essentially exponential with the time constant proportional to the heat capacity per unit volume. Such measurements are inherently of low accuracy (typically  $\pm 10\%$ ) and below about 1.5°K suffer because of contribution to the time constant by thermal boundary resistance, an effect which may increase the measured value of the heat capacity considerably above the actual value. It is undoubtedly because of this problem that the decrease in  $C/T^3$ , which takes place in polystyrene and polymethyl methacrylate below about 1.5°K, was not detected in work using this technique.

### Theoretical Framework

In principle, the understanding of the heat capacity of solid polymers is a straightforward application of the ideas used to understand the heat capacity of any solid body. Once the spectrum of vibrational states,  $g(\omega)d\omega$ , is known, giving the number of modes of vibration whose frequencies lie between  $\omega$  and  $\omega + d\omega$ , the heat capacity follows at once as

$$C/k = \int_0^\infty g(\omega) \left( \frac{\hbar \omega}{kT} \right)^2 \frac{\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2} d\omega \quad (1)$$

The key assumption in the preceding is that  $g(\omega)$  is known. In favorable cases  $g(\omega)$  may be calculated more or less accurately using the techniques

of lattice dynamics, in which case comparison with experiment is often made by the calculation of the heat capacity through Eq. (1). However, the more usual problem is that from the outset  $g(\omega)$  is not known and one wishes to deduce from the heat capacity as much as one can concerning the vibrational spectrum. Since the heat capacity represents an average over many modes of vibration, very little of the detail of  $g(\omega)$  can be deduced from the heat capacity [18]; only the general features and the limiting behavior at low frequencies can be deduced with any certainty. In this discussion we wish to concentrate on the most general features of the heat capacity and so we deal almost entirely with very simple approximations to  $g(\omega)$  and ignore, for the most part, the insights of those lattice dynamical calculations which have been performed and which are applicable to the problems of polymers.

Before continuing, perhaps it is best to bring up again a point which has been made before [19]. Since the ideas of a vibrational spectrum and the models which are employed in this paper are most often encountered in the context of crystalline solids, their application to polymers, which lack a crystalline structure, may seem novel. However, although a noncrystalline solid does not possess the translational symmetry which characterizes a crystal and greatly simplifies the calculation of its spectrum of vibrations, it does possess a spectrum of normal modes consisting of the coupled oscillations of the primary vibrating units about their local equilibrium positions. Further, in the long-wavelength limit, the details of the atomic structure become unimportant and the modes must be those of an elastic continuum, the basis of the models to be introduced later in this paper.

Aside from the general limitations caused by the fact that heat capacity is determined by an average over many modes, the elucidation of  $g(\omega)$  is often quite difficult in the case of a polymer because of the complicated nature of the repeating unit, which gives rise to the possibility of many differing modes of vibration often characterized by rather low frequencies. These modes, then, contribute significantly to the low-temperature heat capacity of polymers to an extent not often found in other solids.

In our discussion we wish to distinguish between those modes which arise out of a coupling of the translational degrees of freedom of the repeating unit (the acoustic modes), and those modes which stem from the coupling of internal motions of the repeating unit (the optical modes). Since the acoustic modes are characterized by a zero frequency at zero wave number, while the optical modes have a finite frequency at zero wave number, the acoustic modes will eventually dominate the heat capacity, although, as suggested by the discussion in the preceding



paragraph, this domination will often not come until very low temperatures are reached. In this discussion we fix our attention on the contribution of the acoustic modes for several reasons: 1) Their presence is a universal feature of the vibration spectrum of all polymers, while the presence and nature of the optical modes depend on the exact nature of the repeating unit, 2) they eventually dominate the low-temperature heat capacity, and 3) because of the low group velocity usually associated with optical modes, the acoustic modes will dominate the problem of thermal transport in polymers, the subject of the latter part of this paper.

The simplest treatment of the acoustic modes of any solid body is that due to Debye [20] in which one ignores dispersion and relates frequency and wave number by  $\omega = sq$ , where  $s$  is the sound velocity and  $q$  the wave number, for all frequencies. The distribution of vibrational states is then given by

$$g(\omega) = \frac{3N\omega^2}{\omega_D^3} \quad \omega \leq \omega_D \quad (2)$$

for each mode (one longitudinal and two transverse) where the cutoff frequency is introduced to limit the total number of degrees of freedom to the total number of particles in the system ( $N$ ). The Debye model allows us to understand many of the general features of the heat capacity of ordinary solids, particularly the fact that the heat capacity depends on the cube of the temperature at low temperatures.

The Debye model is not completely suitable for application to polymers, even as the first approximation, since it ignores a key feature of the polymer chain, its one-dimensional nature. For long-wavelength excitations many polymer chains will interact with one another through the weak interchain forces and the vibrations will be essentially three-dimensional, so that the Debye model will be satisfactory. However, for shorter wavelengths and higher frequencies there will be many normal modes excited which are essentially vibrations along the chain skeleton and will therefore be essentially one-dimensional in nature. A simple continuum model which allows us to encompass both the three-dimensional and one-dimensional natures of polymers is due to Tarasov [21]. In this model we assume that all of the low-frequency modes are three-dimensional and calculate the frequency spectrum as in the Debye model up to some cutoff frequency,  $\omega_3$ . Higher frequency vibrations are treated as a one-dimensional continuum up to some final cutoff frequency,  $\omega_1$ , which is determined by the requirement that the total number of frequencies be equal to the number of repeating units ( $N$ ). The resulting distribution is then

$$\begin{aligned}
 g(\omega) &= \frac{3N\omega^2}{\omega_1 \omega_3^2} & \omega &\leq \omega_3 \\
 &= \frac{N}{\omega_1} & \omega_3 < \omega &\leq \omega_1
 \end{aligned}
 \tag{3}$$

In this division it is assumed that the fraction  $\omega_3/\omega_1$  of the total number of vibrational states is three-dimensional in nature and the remainder are one-dimensional. The Tarasov approximation for  $g(\omega)$  is shown in Fig. 1a.

When the Tarasov model is used with Eq. (1) to calculate the heat capacity, we find for each mode and for 1 mole of repeating units

$$C/R = D_1(\theta_1/T) - \frac{\theta_3}{\theta_1} [D_1(\theta_3/T) - D_3(\theta_3/T)]
 \tag{4}$$

where  $D_n$  is the  $n$ -dimensional Debye function [22] and the  $\theta$ 's are equivalent temperatures defined by  $\theta_i = \hbar\omega_i/k$ . To find the total heat capacity we must add the results of two transverse and one longitudinal mode, and we do not expect, in general, that the  $\theta$ 's will be the same for longitudinal and transverse modes. This corresponds to the Born, rather than the Debye, cutoff procedure. At low temperatures the three-dimensional modes dominate the calculation, and we find for each mode

$$C/R = \frac{4\pi^4}{5} \frac{T^3}{\theta_3^2 \theta_1}
 \tag{5}$$

At an intermediate temperature,  $T \gtrsim \theta_3 \ll \theta_1$ , all of the three-dimensional vibrations are excited and the one-dimensional modes dominate the temperature dependence of the heat capacity, and we find for each mode

$$C/R = \frac{\pi^2}{3} \frac{T}{\theta_1}
 \tag{6}$$

Thus the Tarasov model predicts the expected cubic dependence of the heat capacity on temperature at low temperatures and a linear dependence at intermediate temperatures. In the cubic temperature dependence region the model is the same as the Debye model so that the heat capacity per unit volume can be related to the sound velocity [23] through

$$c/T^3 = \frac{2\pi^2 k^4}{15 \hbar^3} \left( \frac{1}{S_L^3} + \frac{2}{S_T^3} \right)
 \tag{7}$$

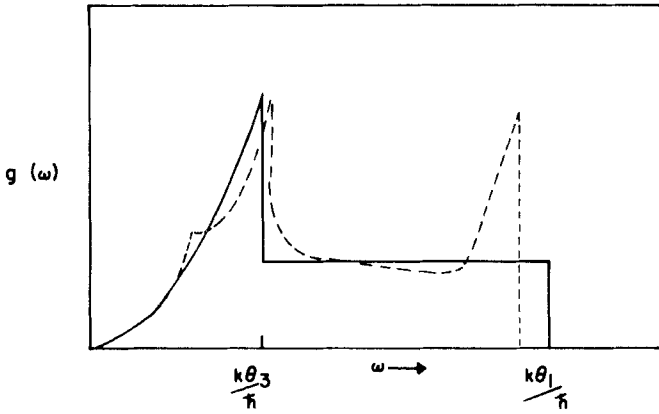


Fig. 1a. The solid line shows the Tarasov approximation to the vibration spectrum for a single acoustic mode. The dashed line shows schematically the results of lattice dynamical calculations for polyethylene and follows the results of Ref. [24].

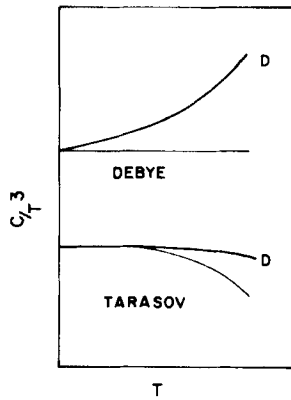


Fig. 1b. We show schematically the low-temperature behavior of  $C/T^3$  in the Debye approximation and a simple solid with dispersion (the upper curve labeled D) to compare it with the behavior obtained from the Tarasov model and a schematic representation of the result of introducing dispersion into the Tarasov model (lower curve labeled D).

where the subscripts stand for longitudinal and transverse and  $c$  is the heat capacity per unit volume. Comparing this with the Tarasov result shows us that

$$\theta_{1i} \theta_{3i}^2 = \frac{6\pi^2 \hbar^3}{k^3} S_1^3 \left( \frac{N}{V} \right) \quad (8)$$

where  $N/V$  is the number of repeating units per unit volume.

Any continuum model, whether Debye or Tarasov, cannot be expected to give a completely accurate picture of the heat capacity of any solid because of the presence of dispersion, so the more detailed and realistic calculations which make use of the actual structure of the solid and the interatomic forces are needed if a complete picture is to be obtained. For polymers, the most complete calculations have been carried out for the case of polyethylene [24, 25] and support, in a very loose sense, the form of  $g(\omega)$  obtained from the Tarasov model. It is not the purpose of this paper to explore the lattice dynamics calculations, but we should like to make one point concerning the effects of dispersion on the heat capacity of polymers. For ordinary solids the Debye model would predict that  $C/T^3$  would become a constant below about  $\theta_D/12$ , although because of the presence of dispersion this often does not occur until  $\theta_D/30$  or at even lower temperatures. The effect of dispersion is to increase the number of low-frequency vibrations over that predicted on the basis of the continuum model and so cause  $C/T^3$  to increase with increasing temperature, as shown in Fig. 1b. In the Tarasov model the presence of the one-dimensional vibrations with their rather low density per unit frequency interval causes  $C/T^3$  to decrease with increasing temperature. The presence of dispersion in the three-dimensional modes causes a competing increase in  $C/T^3$  and as a result one may find that  $C/T^3$  remains nearly constant to a remarkably high value of  $T$ .

### Heat Capacity of Polyethylene

Polyethylene is in many ways an ideal subject with which to study the heat capacity of polymers, as the simple repeating unit does not possess any of the low-lying optical modes which plague the interpretation of the heat capacity of most polymers. The interpretation of the heat capacity in terms of the various vibrational modes has been thoroughly examined on the basis of data existing prior to 1962 [26]. However, the data existing at that time were not such as to permit an examination of the crystallinity

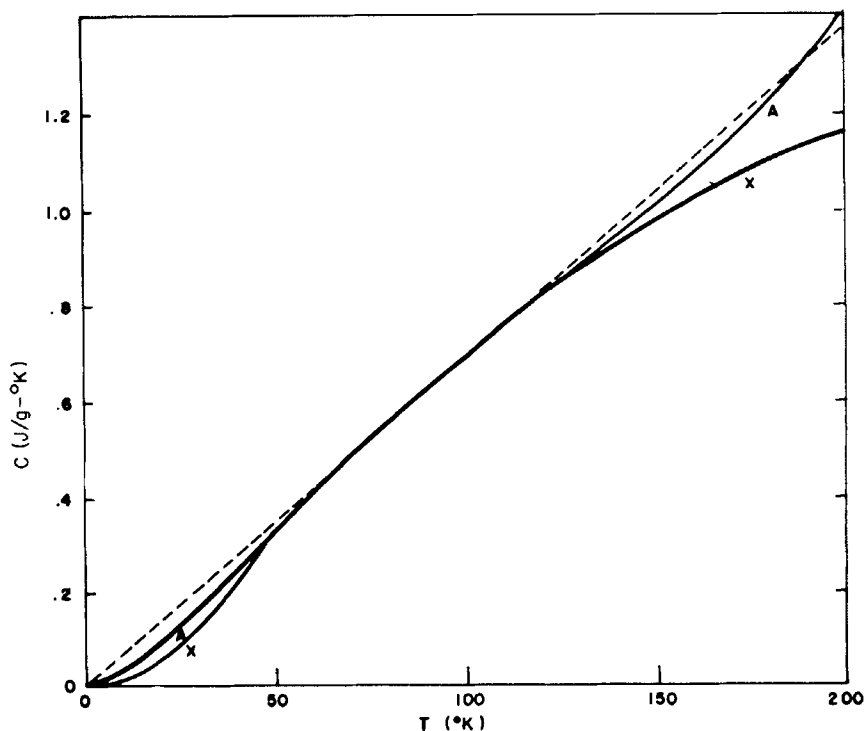


Fig. 2. The heat capacity of crystalline (X) and amorphous (A) polyethylene below 200°K. The dashed line is of the form  $AT$  and shows the linear temperature dependence of the heat capacity between 50 and 100°K. The curves result from a linear extrapolation of the heat capacity versus crystallinity curves at each temperature to 0 and 100% crystallinity.

dependence of the heat capacity below 90°K, so the conclusions reached concerning the low-frequency portion of the vibration spectrum, while correct in form, need some reexamination.

Figure 2 shows the low-temperature heat capacity of amorphous and crystalline polyethylene. These data have been extrapolated from a series of measurements of heat capacity on samples of varying density in which it was found, both at high [27] and low [12] temperatures, that the heat capacity is a linear function of crystallinity. A clear feature of the data is that amorphous and crystalline polyethylene display a significant region (approximately 50-100°K) in which the heat capacity depends linearly on

temperature (shown by the dashed line in Fig. 2) as predicted by the Tarasov model [Eq. (6)]. Further, we see that the same slope, and hence  $\theta_1$  in terms of the continuum model, characterizes polyethylene independent of the density. This latter fact is as expected since the one-dimensional vibrations should, to a first approximation, be independent of the interchain forces and depend only on the intrachain forces and thus be independent of the density.

From Fig. 2 it is seen that the heat capacity of amorphous polyethylene differs from that of crystalline polyethylene both above 110°K and below 50°K. At the high-temperature end, this difference is connected with the glass transition [27]; it is not discussed here as this is a "high-temperature" effect. Below 50°K the difference stems from two sources: (1) The acoustic contribution to the heat capacity is dominated by the three-dimensional vibrations which are quite sensitive to the interchain forces and hence the density, and (2) the existence of nonacoustic vibrations of low frequency associated with the disordered amorphous structure.

The low-temperature behavior of the heat capacity is best studied on the basis of a plot of  $C/T^3$  versus  $T$ , as shown in Fig. 3. We see that such a plot is almost a flat line for crystalline polyethylene below 10°K but displays a distinct "hump" at about 5°K for amorphous polyethylene. The limiting value of  $C/T^3$  for crystalline polyethylene shows good agreement with the value predicted by measurements of the sound velocity through Eq. (7), but there are no sound-velocity measurements with which the amorphous heat capacity data can be compared.

If one attempts to fit the heat capacity to the Tarasov model one finds that the parameters

$$\theta_{1L} = 1655^\circ\text{K}, \theta_{1T} = 707^\circ\text{K}, \theta_{3L} = 223^\circ\text{K}, \theta_{3T} = 134^\circ\text{K}$$

fit the heat capacity to better than 10% up to 100°K. If, as discussed below in connection with the heat capacity of amorphous polymers, one attributes the "hump" in the  $C/T^3$  plot to the presence of a small number of nonacoustic vibrations characterized by a very low frequency (this is discussed in the next section), the Tarasov model will give an equally good fit to amorphous polyethylene using the parameters

$$\theta_{1L} = 1655^\circ\text{K}, \theta_{1T} = 707^\circ\text{K}, \theta_{3L} = 123^\circ\text{K}, \theta_{3T} = 74^\circ\text{K}$$

In keeping with the spirit of the continuum model, we allow only the three-dimensional contributions to be affected by the density.

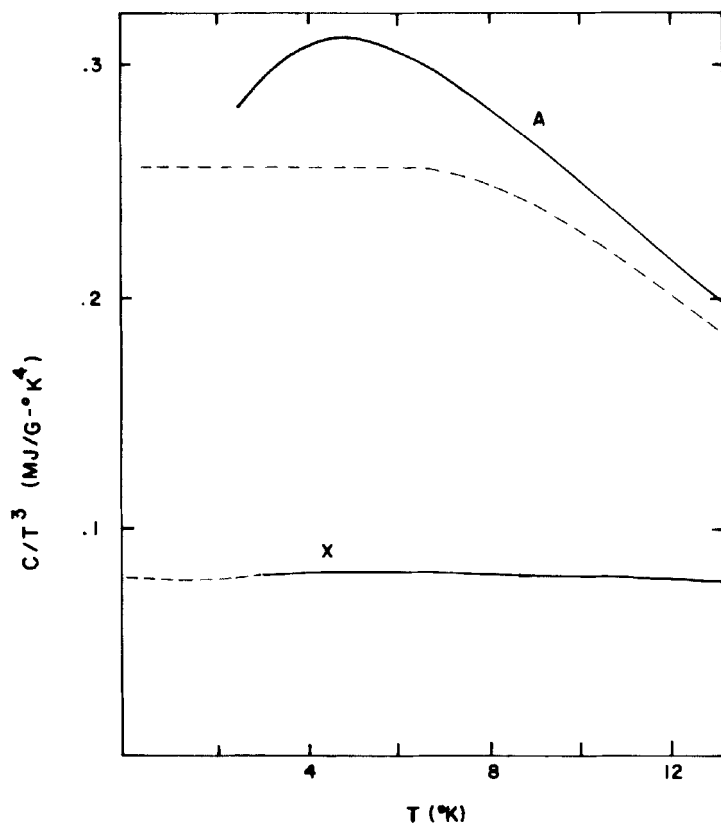


Fig. 3. The low-temperature behavior of the heat capacity of polyethylene is shown in a plot of  $C/T^3$  versus  $T$ . The labels X and A refer to extrapolations to 100 and 0% crystallinity, respectively. The data are taken from Ref. [12]. The dashed lines show the Tarasov fits to the data using the parameters given in the text.

A much better fit to the heat capacity of crystalline polyethylene can be obtained on the basis of lattice dynamical calculations than with the continuum model. Recently Kitagawa and Miyazawa [25] presented calculations based on a lattice dynamical model which give the results shown in Fig. 4, and they show what must be considered excellent agreement with the experimental data. Thus we can say that in the case of crystalline polyethylene, our understanding of the heat capacity is excellent, while in the case of amorphous polyethylene our understanding is still incomplete.

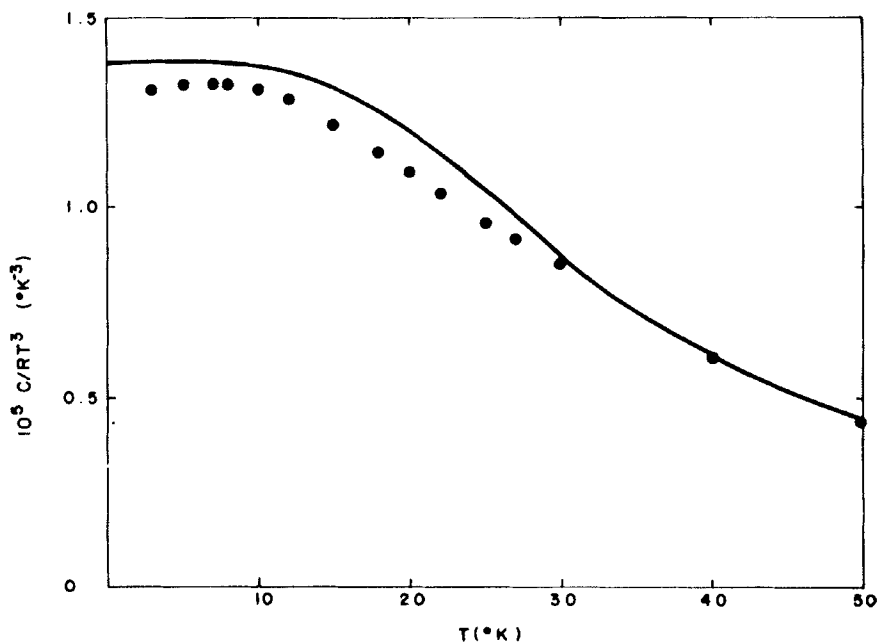


Fig. 4. A comparison of the results of the lattice dynamics calculation of Kitagawa and Miyazawa [25] with the heat capacity of crystalline polyethylene. The solid line is the calculated behavior while the solid points give some of the experimental results.

### Heat Capacity of Amorphous Polymers

It is unlikely that a comparison with a microscopic calculation of the heat capacity, such as is possible in the case of polyethylene, will soon be possible for any amorphous material. Thus in the following we concentrate on only the most general features of the low-temperature heat capacity. A prominent feature in the plot of  $C/T^3$  versus  $T$  for amorphous polyethylene (Fig. 3) is the distinct hump centered at about 5°K. Similar features have been found in the heat capacity of other amorphous materials, vitreous silica [28, 29], vitreous germania [30], and glycerol glass [31], and they have been attributed to a small number of low-frequency optical modes associated in some manner with the amorphous structure. In an analogous manner it was found that the heat capacity of amorphous polyethylene could be accounted for by the combination of a Tarasov spectrum (dashed



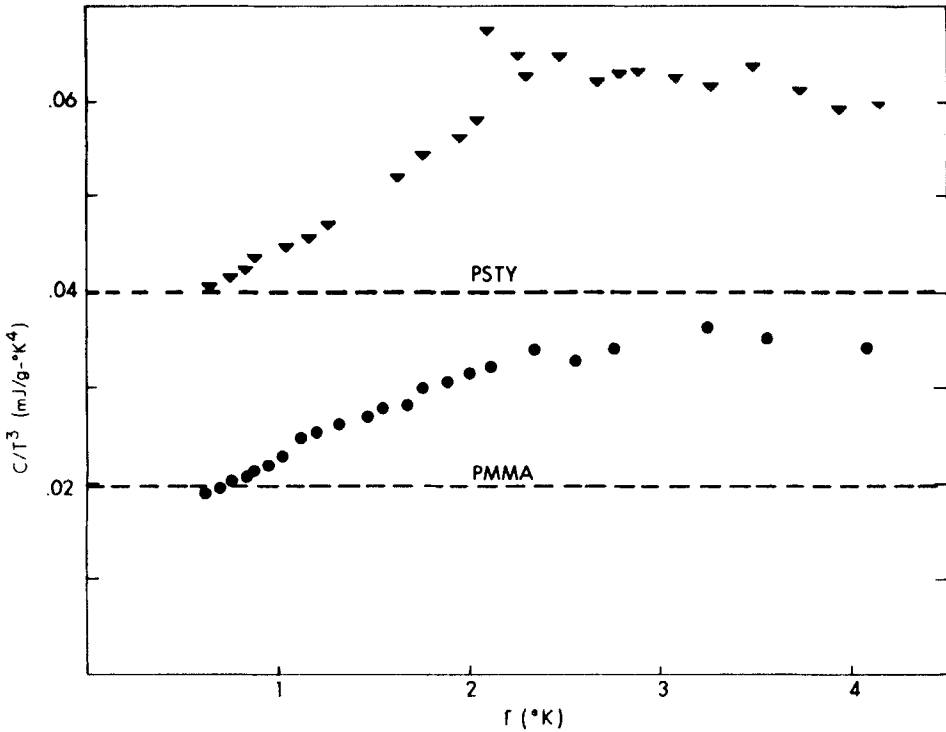


Fig. 5. A representation of the low-temperature heat capacity of polystyrene (PSTY and  $\blacktriangledown$ ) and polymethyl methacrylate (PMMA and  $\bullet$ ). The data are taken from Ref. [16] and the dashed lines represent the contribution of acoustic modes calculated from the sound velocity using Eq. (7).

line in Fig. 3) and a small number (0.17% of the repeating units) of vibrations having a characteristic temperature of 23°K [12, 32].

At about the same time as the polyethylene heat capacity measurements became available, low-temperature sound-velocity measurements on polymethyl methacrylate (PMMA) and polystyrene were made and the results were compared with the heat capacity using Eq. (7) [33]. The result of this comparison was that the measured heat capacity was found to be considerably larger in the liquid-helium temperature range than could be accounted for by the acoustic vibrations, implying the existence of low-temperature nonacoustic contributions to the heat capacity (this contribution is sometimes referred to as excess heat capacity). Recently, this

suggestion has been tested by heat capacity measurements of these materials below 1°K, the results of which are shown in Fig. 5 [15, 16]. These measurements display a clear decrease in  $C/T^3$  taking place below about 1.5°K and are consistent with the limiting value predicted from the sound-velocity measurements through Eq. (7). Thus, for these two polymers, and probably also in the case of amorphous polyethylene, there is considerable evidence for the existence of nonacoustic contributions to the heat capacity in the liquid-helium temperature range.

The physical interpretation of the nonacoustic contributions to the low-temperature heat capacity are not at all clear and can probably never be clarified solely through calorimetric data. From a purely descriptive point of view it is possible to account for the heat capacity excess by postulating a small number of vibrations having one or more discrete, low frequencies. The parameters deduced for a number of amorphous materials are presented in Table 2. From this tabulation we see that the number of vibrations is rather small, of the order of 1% of the total number of vibrating units, and the characteristic frequency is rather low, of the order of  $10\text{ cm}^{-1}$ . In the case of vitreous silica there is evidence that these modes are Raman active [29], leading to their characterization as optical modes.

One possible interpretation of such low-frequency modes has been offered by postulating that there are cavities in the amorphous structure with one or more vibrating units loosely bound inside the cavity [34]. In the case of polymers the most likely such unit is a pendent group (perhaps one of the methyl groups in the case of PMMA) or a short branch. Certainly the nearness of the characteristic temperatures for the case of polyethylene and PMMA can be taken to support the contention that the vibrating unit in this case is a methyl group (pendent methyl groups are a possible branch in amorphous polyethylene, and, in one of the heat capacity samples from which the data shown in Fig. 3 were deduced, methyl groups were deliberately added to the polyethylene chain to impede crystallization). This argument is made even stronger if the reanalysis of the Tucker and Reese [12] data made by Morrison and Newsham [32] is used, as they conclude that a characteristic temperature of 17°K, approximately the same as in PMMA, is the best single frequency needed to fit the heat capacity excess. In the case of polystyrene it may be that the pendent group involved could be the phenyl ring, but because of its size it may be unlikely that a sufficiently large cavity could occur. Further, the comparison of the dominant characteristic frequencies involved with the cases of PMMA and polyethylene shows that it is likely that the vibrating unit in the case of polystyrene has a mass not much more than

**Table 2.** Parameters Characterizing the Low-Temperature Nonacoustic Contribution to the Heat Capacity of Some Amorphous Materials

Material	$N_0/N^a$	$\theta^b, ^\circ\text{K}$
Amorphous polyethylene	0.0017	23
Polymethyl methacrylate	0.0106	17
	0.0005	7.5
Polystyrene	0.0078	13
	0.00006	5
Vitreous silica	0.014	58
	0.002	32
	0.00008	13
Vitreous germania	0.004	38

<sup>a</sup>Ratio of number of low-frequency optical modes to the total number of primary vibrating units (repeating in the case of polymers).

<sup>b</sup>Equivalent temperature of the frequency of oscillation of these modes needed to account for the heat capacity. Where more than one characteristic temperature is given, more than one discrete frequency is required to satisfactorily fit the heat capacity.

twice that in the case of the other two polymers. Thus, chain ends or branches may be needed to account for the vibrating unit in this case.

It is perhaps attractive to postulate that these low-temperature heat capacity anomalies are associated with the low-temperature mechanical relaxation peaks found in PMMA and polystyrene, and they are tentatively identified with motions of methyl and phenyl groups, respectively [35-38]. However, both the association and the identification must at present be considered conjectural.

As evidence in support of the pendent group in a cavity model we might cite the observation that the cross-linking of polystyrene by electron irradiation caused about a 25% reduction of the heat capacity in the helium temperature range [39], a reduction which can be accepted as the reduction of the number of loosely bound units participating in these nonacoustic, low-frequency vibrations. The particle in a cavity model is not, however, the only model which can explain the observations, as the analysis of the heat capacity which leads to the assignments in Table 2 is in no way a uniquely

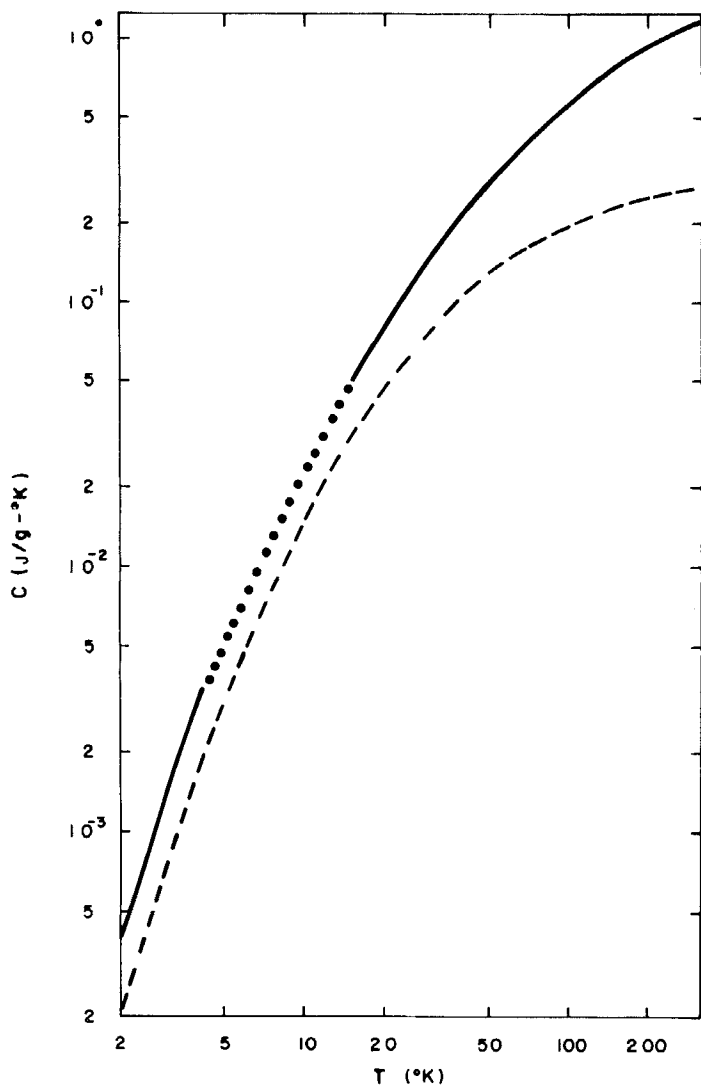


Fig. 6. The heat capacity of polymethyl methacrylate. The low-temperature data (solid lines) are taken from Refs. [16] and [17], while the higher-temperature data are taken from Refs. [5] and [41]. The dotted line shows an interpolation while the dashed line shows the acoustic contribution to the heat capacity as calculated from the Tarasov model using the parameters given in the text.

determined analysis. In the case of vitreous silica, at least, there is as much evidence that the low-temperature heat capacity excess may be associated with vibrations about distorted bonds as with "particle in a cavity" vibrations.

Let us now turn from an examination of the low-temperature excess heat capacity to the total heat capacity of PMMA. The heat capacity has been presented in Fig. 6, with the dotted line showing the interpolation between the existing data in the helium temperature region [16, 17] and the lowest temperature data of Sochava [5]. An exact analysis of the heat capacity is made quite difficult both because of the low-temperature excess and because of a number of other low-frequency modes associated with the complicated repeating unit. A particular trouble spot in the analysis of the low-temperature heat capacity is the mode giving rise to the Raman line at  $84\text{ cm}^{-1}$ , which is thought to be associated with rotations of the pendent methyl group [40]. However, there are many other low-frequency optical modes which contribute significantly to the heat capacity by  $100^\circ\text{K}$  [41]. One can attempt to divide the heat capacity into contributions due to the acoustic modes and optical modes associated with the measured Raman lines, although such a procedure is full of pitfalls since neither the distribution in frequencies of the various optical modes nor the correct parameters for describing the transition from hindered to free rotation is in any way certain, nor is the contribution of the acoustic modes determined in any firm manner. In our analysis of the thermal conductivity of PMMA we need some estimate of the contribution to the heat capacity due to acoustic modes. Rather than attempt the division mentioned above, a simple and grossly approximate alternative has been adopted. We have assumed that the acoustic contribution can be accounted for by the Tarasov model. Since the limiting frequency  $\omega_1$  is related to the limiting frequency for vibrations of the repeating unit with spring constants characteristic of the C—C bond, we have scaled the one-dimensional Tarasov temperatures obtained for amorphous polyethylene according to

$$\frac{\theta_i}{\theta_j} = \frac{\omega_{\max\ i}}{\omega_{\max\ j}} = \left(\frac{m_j}{m_i}\right)^{1/2}$$

where  $m$  is the mass of the repeating unit. The sound-velocity measurements were then used to determine  $\theta_3$  through Eq. (8). The resulting Tarasov parameters were

$$\theta_{1L} = 620^{\circ}\text{K}, \theta_{1T} = 264^{\circ}\text{K}, \theta_{3T} = 51^{\circ}\text{K}, \theta_{3L} = 88.4^{\circ}\text{K}$$

and the resulting acoustic contribution is shown as the dashed line in Fig. 6.

## THE LOW-TEMPERATURE THERMAL CONDUCTIVITY OF POLYMERS

### The Experimental Situation

Most discussions of the thermal conductivity of polymers have concentrated on an understanding of the behavior in the vicinity of room temperatures [42-45]; however, as is the case with crystals, confirmation of the ideas developed and further insight into the process which controls heat conduction come by an extension of the analysis to lower temperatures. However, this extension is hampered by a lack of data which cover a complete range of temperature, as such measurements do not exist for any polymer at the present time. The data presently available do allow us to make a reasonable interpolation between existing data sets in favorable cases and also allow us to draw some broad general conclusions concerning the factors which are important in determining the thermal conductivity of polymers.

The available data fall into two rather natural classes: that taken at low temperatures, below about  $25^{\circ}\text{K}$  [46-49] and mostly below  $4^{\circ}\text{K}$  [10, 15-17, 40, 51], which were obtained on long, rod-shaped samples, and the data in the range above liquid nitrogen temperatures, about  $80^{\circ}\text{K}$  to room temperature and above [52, 54], which were taken with flat, plate-like samples. The change in technique between the two temperature ranges is primarily necessary to guard against radiative heat loss at the higher temperatures, a need which does not exist in any serious sense in the lower-temperature range. There do not exist at present any measurements which bridge these two temperature ranges. A summary of the available data on the low-temperature thermal conductivity of polymers is given in Table 3.

Figure 7 shows the general features of the temperature dependence of the thermal conductivity of polymers. There are two basically different types of behavior illustrated. Semicrystalline polymers, illustrated by polyethylene, show a marked density dependence of the thermal conductivity and display a weak increase in the thermal conductivity with decreasing temperatures to about  $100^{\circ}\text{K}$ , after which point the thermal conductivity decreases. The maximum moves to lower temperatures and higher thermal

**Table 3.** Summary of Measurements of the Low-Temperature Thermal Conductivity of Polymers.

Material	Temperature range, °K	Ref.
Polyethylene	80-350	[52, 53, 54]
	1-4.5	[10]
	1-35	[49]
	0.4-4	[51]
Polytetrafluoroethylene	5-20, 80	[48]
	0.1-1	[50]
	1-4.5	[10]
	80-350	[52, 53]
Polychlorotrifluoroethylene	80-350	[52, 53]
	0.2-1	[50]
	1-4.5	[10]
Nylon	2-20	[47]
	0.2-0.7	[50]
	1-4.5	[10]
	1-20	[49]
Polyethylene terephthalate	80-325	[52, 53]
Polycarbonate	80-425	[54]
Polyoxymethylene	80-370	[54]
Polymethyl methacrylate	2-23	[46]
	80-325	[53, 54]
	1-4.5	[17]
	0.4-4	[16]
Polystyrene	1-4.5	[17]
	0.4-4	[16]
Polyvinyl acetate	0.4-4	[16]
	80-370	[52, 53]

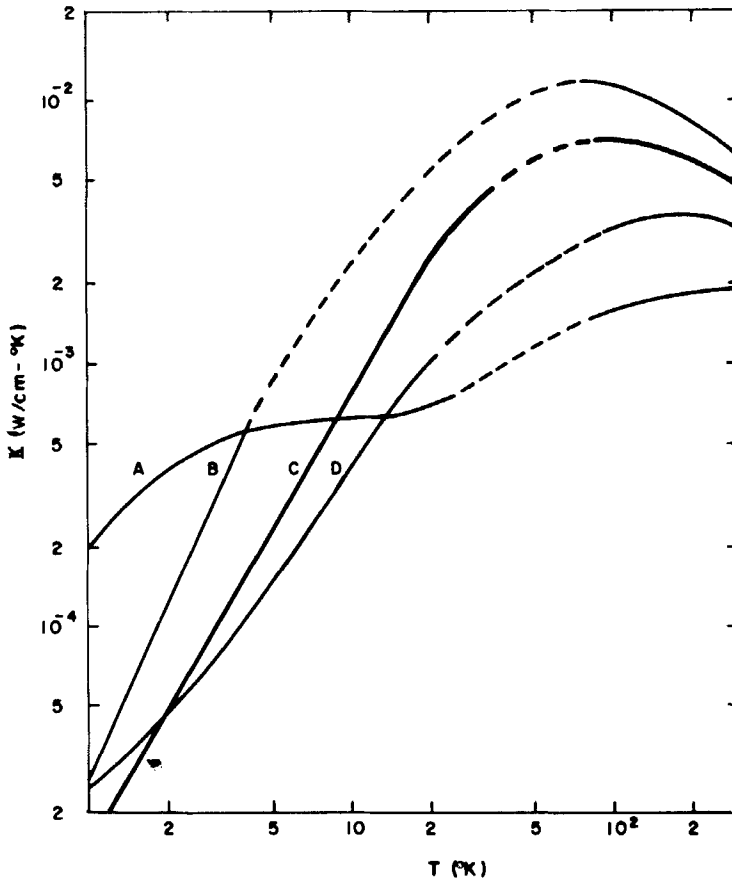


Fig. 7. The thermal conductivity of various polymers. Curve A shows the thermal conductivity of PMMA; curves B, C, and D show the thermal conductivity of polyethylene of densities approximately 0.98, 0.96, and 0.92 g/cm<sup>3</sup>, respectively. The dashed lines show interpolations and the solid lines show where data are available.

conductivities as the density is increased. Amorphous polymers, as illustrated by PMMA, show a considerably different temperature dependence; the thermal conductivity continually decreases with decreasing temperature. The temperature dependence between room temperature and liquid nitrogen temperatures is rather slow, but it is hypothesized that the temperature dependence becomes stronger in the vicinity of 50°K. There is a significant



region, from about 4 to 15°K, in which the thermal conductivity is essentially temperature independent. Below this temperature-independent region, the thermal conductivity again decreases with decreasing temperature. In contrast to the case of semicrystalline polymers in which large changes in the thermal conductivity, primarily associated with density changes, occur from sample to sample, the thermal conductivity of a given amorphous polymer seems to vary little from sample to sample. There is a very weak dependence of the thermal conductivity on molecular weight, which has been observed at room temperature [43, 55, 56] and possibly also at lower temperatures [16]. In addition, the thermal conductivity can be affected through orientation of the polymer chains through frozen-in strain [52, 57, 58] or by extrusion [59]. In either case such orientation increases the thermal conductivity in the direction of the chain orientation. Such orientation effects are either absent or greatly reduced in the helium temperature range, as evidenced by the fact that measurements on strained [17] and extruded [46] samples of PMMA display nearly the same thermal conductivity in the helium temperature range as do cast samples.

### Theoretical Framework

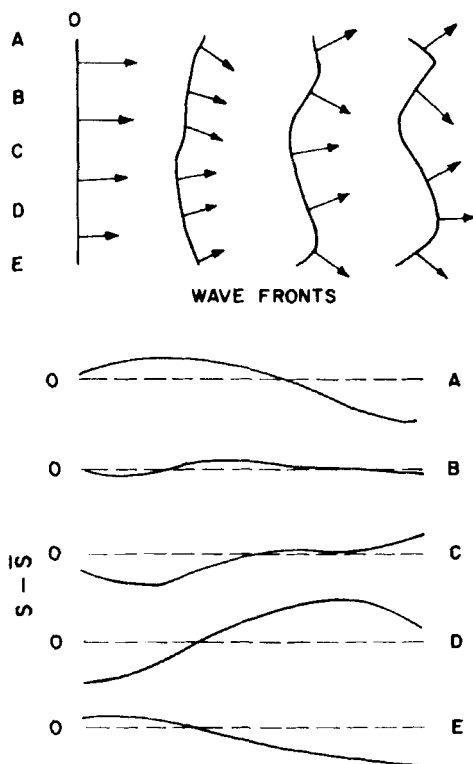
Theories of the thermal conductivity of polymers are of two sorts, those modeled on liquid-state theory [42, 43], which consider energy transfer between repeating units through the chemical bonds, either primary or secondary, as individual uncorrelated events, and those modeled on solid-state theory, which discuss the collective motion of the repeating units and introduce scattering phenomena which limit the range of the energy transport [60]. At low temperatures, where the excitations are vibrations with wavelengths much longer than the distance between the repeating units, a suitable theory must be of the second type. However, it is found for amorphous polymers that at higher temperatures the mean free path becomes of the order of the distance between repeating units (discussed under Thermal Conductivity of Amorphous Polymers), so that the results of the collective mode theory reduce to those of the liquid-like theories. In this case the former class of theory is undoubtedly the more nearly correct way of describing the situation, since a criterion for the validity of the collective picture is that the mean free path should be much longer than the interparticle distances so that the collective modes can be well defined. As we are primarily interested in low-temperature behavior, we shall concentrate our attention on the second class of theories. It is probable that this type of theory is also the best approach in the case of semicrystalline polymers.

The collective approach is to discuss heat transport in terms of a gas of phonons, the thermal conductivity being given by [61]

$$\mathcal{K} = \alpha c_s \Lambda \quad (9)$$

where  $c$  is the (phonon) heat capacity per unit volume,  $s$  is the phonon group velocity,  $\Lambda$  is the mean free path, and  $\alpha$  is the average of  $\cos^2\theta$  ( $\theta$  is the angle between the mean free path and the transport direction) which is  $1/3$  except in the case of oriented polymers. The essence of the problem is to compute the mean free path. There are two primary types of events which determine the mean free path: interactions between phonons and interactions of phonons with defects. For most solids, and perhaps for semicrystalline polymers, phonon-phonon interaction dominates the behavior at high temperature and leads to a thermal conductivity proportional to  $1/T$ . As only so-called umklapp processes contribute directly to the thermal resistance, a process which becomes much less probable at temperatures significantly below the Debye temperature; the mean free path due to phonon-phonon interactions increases as an exponential in  $1/T$  at low temperatures. Eventually, as the phonon-phonon mean free path lengthens, the presence of various defects limits the mean free path and the thermal conductivity begins decreasing, reflecting the fact that the heat capacity decreases with temperature. Differing types of defects yield mean free paths with differing temperature dependences, so, at least in the ideal case, the type of defect which dominates the thermal resistance can be identified. These considerations, which are those normally applied to crystalline solids, lead to a thermal conductivity which initially increases with decreasing temperatures, reaches a maximum at a temperature which decreases with decreasing number of defects, and then decreases toward zero with a temperature dependence which depends upon the type of defects present [61, 62]. As these considerations have been thoroughly explored by a number of other workers, they are not discussed further here.

It is possible to extend the collective model used above to the case of noncrystalline solids, but because such solids lack translational symmetry and thus do not exhibit umklapp processes, the arguments need to be considerably modified. The first major attempt at this extension was made by Klemens [61], who argued that the elastic disorder of the glassy structure would be the source of phonon scattering at all temperatures and termed the resulting process "structure scattering." The essential idea behind structure scattering is shown in Fig. 8, in which we follow the distortion of an initially plane wave (phonon) as it passes through regions of varying



**Fig. 8.** A schematic representation of the process of structure scattering. The upper part of the figure shows the shape of the wavefronts at approximately one-wavelength intervals. The arrows show the direction of energy flow at each point. The lower part of the figure shows sketches of the deviation of the sound velocity from the average at positions A through E shown on the upper figure. In this case, the elastic correlation length and the wavelength are of the same order of magnitude.

sound velocity. For the situation pictured, the phonon is substantially scattered, in the sense that the directions of energy flow are considerably different from the initial direction of energy flow by the time that it has progressed a distance of three wavelengths. In discussing structure scattering, the most important feature is the relation between the phonon wavelength and the elastic correlation length, taken to be of the order of a wavelength in Fig. 8. When the phonon wavelength and the elastic correlation length are of

the same order, the phonon is scattered quickly and the mean free path is of the order of the elastic correlation length. If, on the other hand, the wavelength is much longer than the elastic correlation length, the resulting distortions between successive wavefronts are much less severe, as considerable averaging over the elastic disorder takes place. Initially, Klemens used a heuristic argument to show that in the case of long wavelengths the mean free path for a phonon with wave vector  $q$  would be given by

$$\Lambda = \frac{A}{aq^2} \tag{10}$$

where  $a$  is the distance between vibrating units and  $A$  is a constant characterizing the elastic correlation length. This result predicts that the limiting low-temperature behavior of the thermal conductivity will be proportional to  $T$ .

Klemens' initial arguments have since been considerably refined both by Klemens [19, 63, 64] and by Ziman [62]. In particular, using the techniques developed to treat the problem of radio propagation through a random atmosphere, Ziman shows, after correcting an error of a factor of  $\pi$  which appears in Klemens' results, that at long wavelengths the mean free path is given by

$$\Lambda = \frac{z}{\overline{\Phi^2}(z)} \tag{11}$$

where  $\overline{\Phi^2}(z)$  is the mean square deviation in phase compared with propagation through a uniform medium which develops in propagation through a distance  $z$  in the disordered medium. If one assumes that the correlations are Gaussian in the sense that

$$\delta S(\mathbf{R} + \mathbf{r}) \delta S(\mathbf{r}) \propto \exp [-R^2/L^2]$$

where  $\delta S(\mathbf{r})$  is the deviation of the sound velocity at position  $\mathbf{r}$  from the average velocity, one obtains the result

$$\Lambda = \frac{S_0^2}{\delta \overline{S}^2} \frac{1}{\pi^{1/2} L q^2} , \quad \frac{A}{a} = \frac{1}{\pi^{1/2} L} \frac{S_0^2}{\delta \overline{S}^2} \tag{12}$$

and if one assumes that the correlations are exponential,

$$\delta S(\mathbf{R} + \mathbf{r}) \delta S(\mathbf{r}) \propto \exp [-R/L]$$

one finds that

$$\Lambda = \frac{1}{2Lq^2} \frac{S_0^2}{\delta \bar{S}^2}, \quad \frac{A}{a} = \frac{1}{2L} \frac{S_0^2}{\delta \bar{S}^2} \quad (13)$$

where  $S_0$  is the mean sound velocity and  $\delta \bar{S}^2$  is the mean square deviation of the sound velocity. Klemens [19] has pointed out that if the correlations have other than spherical symmetry a different wave number dependence than  $1/q^2$ , and hence a different limiting temperature dependence of the thermal conductivity than linear in  $T$ , results.

Structure scattering then results in a mean free path of the order of  $Aa$  for short wavelengths and inversely proportional to  $q^2$  at long wavelengths. However, Klemens [61] found that in order to account for the plateau in the thermal conductivity of silica glass it was necessary to assume that  $A$  was much smaller for transverse waves than for longitudinal waves. Examining Eqs. (12) and (13) we see that a factor of about 4 in this direction is obtained from the fact that typical transverse sound velocities are about half the typical longitudinal sound velocities, but in order to explain the reduction of about 100 required, one must hypothesize that the variations in transverse sound velocity in the glassy medium are much greater than the variations in longitudinal sound velocity. As a result of this assumption, longitudinal waves completely dominate the low-temperature thermal conductivity, but one also must account for normal processes in which longitudinal waves are scattered into transverse waves which are quickly scattered. This conversion from longitudinal to transverse limits the mean free path and causes a low-temperature plateau in the thermal conductivity. To account for this process, Klemens wrote

$$\mathcal{K} = \mathcal{K}_L + \frac{1}{3} S_T C \Lambda_T \quad (14)$$

where  $\mathcal{K}_L$  is the contribution due to longitudinal waves and is of the form

$$\mathcal{K}_L = \frac{A_L}{a} f(T/T_0)$$

where  $T_0$  is a temperature characterizing the conversion of longitudinal to transverse phonons, the function  $f$  is given in Klemens' original paper, and the second term represents the short mean free path contribution due to

the transverse waves so that  $\Lambda_T = A_T a$ . When an attempt to make the same type of analysis of the thermal conductivity of amorphous polymers was made [60], it was found that a better fit could be obtained if a further partition of the vibration spectrum between three- and one-dimensional modes was made as in the Tarasov model. In this case the thermal conductivity was written as

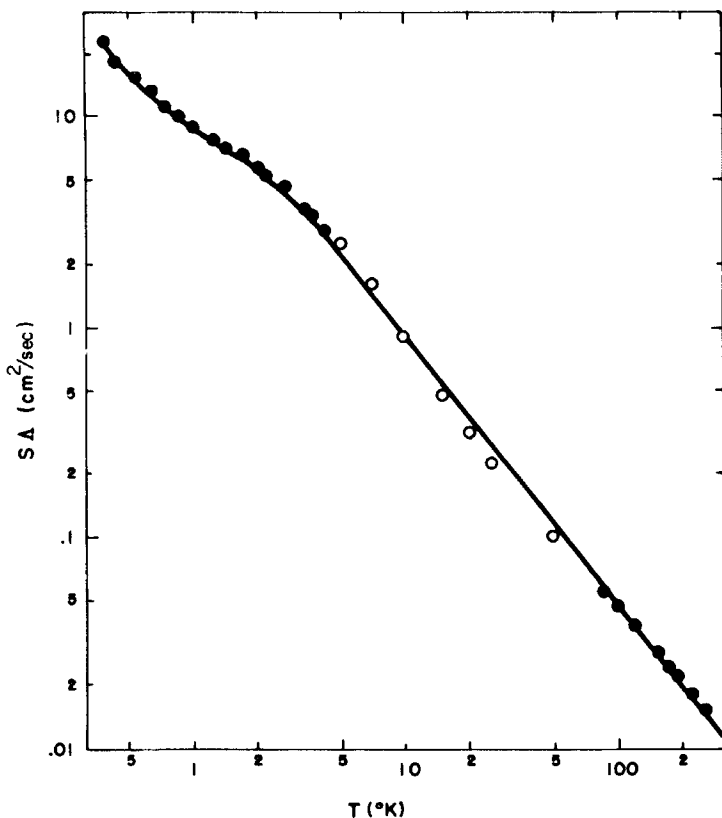
$$\mathcal{K} = \mathcal{K}_L + \frac{1}{3} S_T C_3 \Lambda_T + \alpha S_1 C_1 \Lambda_1 \quad (15)$$

where we have distinguished between the contributions to the heat capacity by three- and one-dimensional modes, and  $\alpha$  is as defined in Eq. (9).

Recently it has been suggested that the plateau in thermal conductivity at low temperatures, which seems characteristic of amorphous substances, results from resonant scattering from the modes which give rise to the excess heat capacity rather than from a gross difference between the scattering of longitudinal and transverse waves [65]. In this theory, modes of low frequency are still scattered by structure scattering so the very-low-temperature behavior is not changed from Klemens' theory. Further, as presently constituted, the numerical results of this theory differ little, except in terms of interpretation, from Klemens' original calculations. The main difference is a slight change in the form of  $f$  which occurs in  $\mathcal{K}_L$  and a reinterpretation of  $S_T C \Lambda_T$  as referring only to that part of the heat capacity associated with modes with frequencies equal to or above the resonant scattering frequency.

### The Thermal Conductivity of Semicrystalline Polymers

As an example of a semicrystalline polymer we consider polyethylene, which shows typical behavior, since more data are available for this material than for any other semicrystalline polymer. As shown in Fig. 7, the thermal conductivity depends markedly on density and displays, more or less, the features expected for the thermal conductivity of a crystalline solid. In fact, the curves in Fig. 7 show a striking similarity to the results of measurements of the thermal conduction of neutron-irradiated quartz [64]. At high temperatures the thermal conductivity varies approximately as  $1/T$ , although the marked density dependence may indicate that the mean free path is not solely limited in this temperature range by an intrinsic phonon-phonon scattering process. There is a maximum in the thermal conductivity which occurs in the vicinity of  $100^\circ\text{K}$  and which moves to



**Fig. 9.** The mean free path for polyethylene (density approximately  $0.98 \text{ g/cm}^3$ ) shown as  $3\mathcal{H}/c = S\Lambda$ . ●, actual data; ○, obtained by interpolation. The low-temperature data are by Salinger [51] and the high-temperature data are by Eierman [54].

lower temperatures and higher thermal conductivities as the density is increased. These features lead us to suspect that the proper interpretation of the thermal conductivity of semicrystalline polymers is to be found in the same techniques of analysis as are applied to crystalline solids.

The mean free path deduced from the data by the application of Eq. (9) to the data for the most highly crystalline samples available is shown in Fig. 9. The mean free path increases slowly with decreasing temperature, approximately as  $1/T$ . We do not attempt in this paper to make an analysis of the thermal conductivity beyond noting this fact.

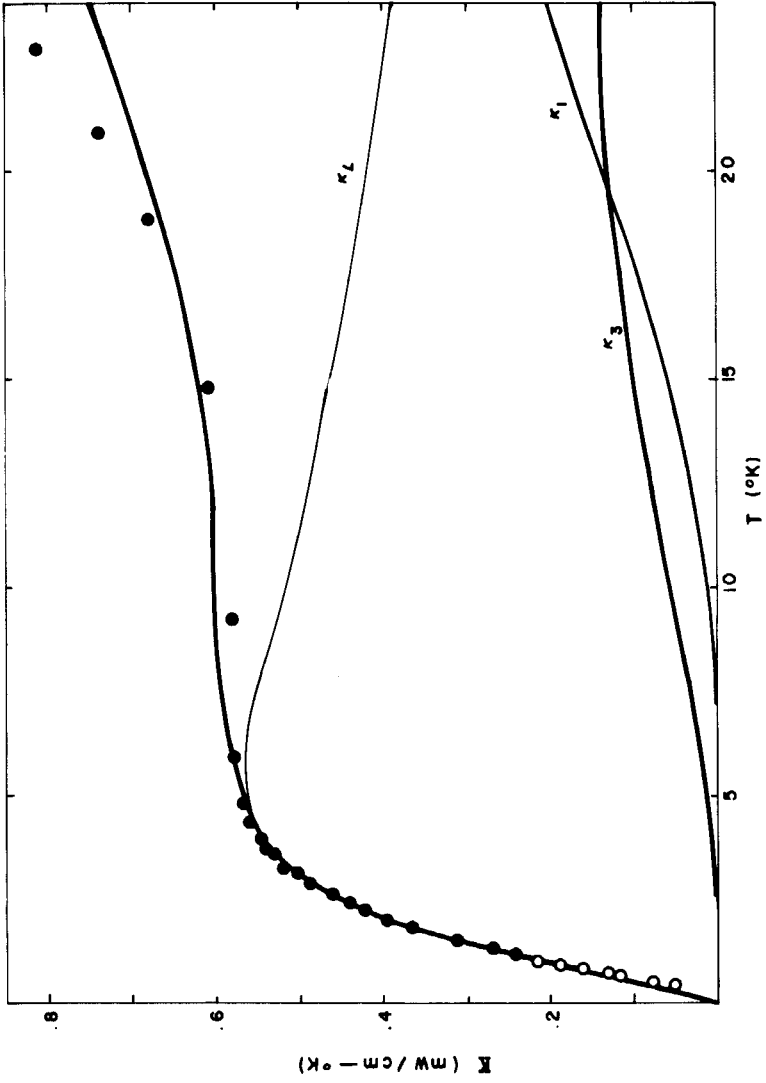
Various attempts have been made to interpret thermal conductivity of semicrystalline polymers as a result of a combination of crystalline and amorphous regions. Hansen and Ho [43] attempted to fit the thermal conductivity to a linear function of the crystallinity, while Eierman [42] attempted to employ the Maxwell formula for the conductivity of a mixture, assuming a model of a number of crystallites embedded in a matrix of amorphous material. In each case the application was made in an attempt to extract the thermal conductivities of "amorphous" and "crystalline" polyethylenes. We should like to point out that neither of these techniques is generally valid. While a linear relationship between crystallinity and thermal conductivity can be established at room temperature, no simple relationship between crystallinity and thermal conductivity exists at lower temperatures, so the procedure of Hansen and Ho lacks even operational significance except in a limited range of temperature. The application of the Maxwell formula, which assumes that the inclusions are small and widely separated, to a polymer with a high degree of crystallinity seems highly doubtful even if the underlying picture—that of a semicrystalline polymer constituted of crystalline and amorphous regions—is a correct one [66]. Further, applications of the formula developed by Eierman predict that at low temperatures the thermal conductivity should be dominated by the amorphous behavior, since, as shown by Fig. 7, amorphous polymers have a higher thermal conductivity than do semicrystalline polymers at low temperatures, while in fact this does not seem to be true. Thus, Eierman's method seems equally dubious as a general procedure.

A different approach to the analysis of the low-temperature thermal conductivity of semicrystalline polymers has been made in which one attempts to fit the thermal conductivity to a combination of structure scattering and scattering characterized by a temperature-independent mean free path [12, 49]. While it is possible to obtain rather good fits of the data to this model, the validity of the model must remain in doubt as the analysis is in no way a unique one. Using this model, Tucker and Reese [12] found a good correlation between the temperature-independent mean free path and the average spherulite size, but this correlation has not been found in more recent work [49], so the earlier results were probably fortuitous.

### Thermal Conductivity of Amorphous Polymers

The thermal conductivity of PMMA which is shown in Fig. 7 is typical of the temperature dependence of the thermal conductivity of amorphous





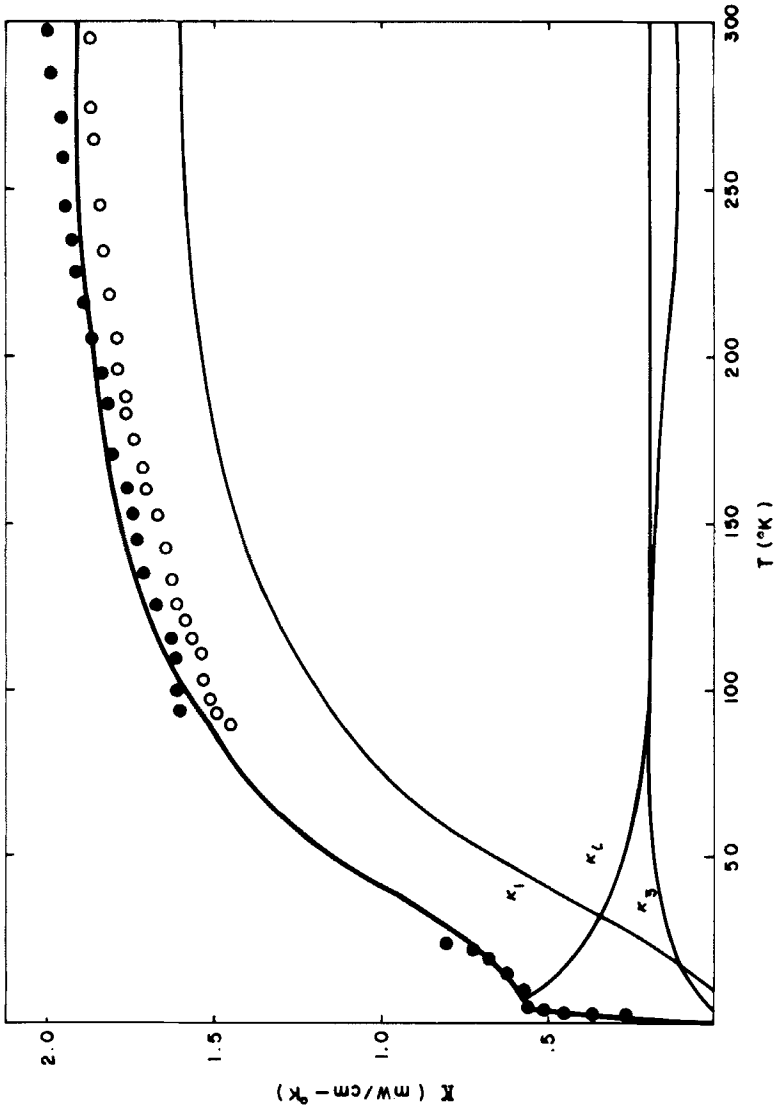


Fig. 10. The thermal conductivity of PMMA as fit by Eq. (15) using the parameters given in the text.  $\circ$  in Fig. 10a are taken from Ref [16]; the higher-temperature data were taken on a different sample and are reported in Refs. [17] and [46]. The higher-temperature data in Fig. 10b are taken from Eierman [52, 54] and were presumably taken on different samples. The calculated curves represent the longitudinal three-dimensional vibration contribution,  $\kappa_L$ , the transverse three-dimensional contribution,  $\kappa_3$ , and the one-dimensional contribution,  $\kappa_1$ .

polymers. As the majority of data are available for the case of PMMA, we restrict our attention to this single example. The temperature dependence is quite different from that in the case of semicrystalline polymers in that the thermal conductivity does not exhibit a peak and there is a significant plateau region from about 4 to 15°K. In the region below about 2°K the temperature dependence appears to approach the linear dependence predicted by the structure scattering theories. However, measurements below 1° show that the temperature dependence becomes faster than linear below about 0.7°K [16].

Equation (15) can be fit to the available data for PMMA and gives a rather satisfactory fit at all temperatures, as shown by Fig. 10. This analysis is slightly different than that given previously [60] in that a slightly different estimate of the heat capacity (namely, that given under Heat Capacity of Amorphous Polymers) was used. This estimate of the heat capacity yields a slightly better fit to the thermal conductivity than was obtained before, primarily because the effects of the low-temperature heat capacity excess have been included and a better account of the one-dimensional modes has been made as a result. In this fit we have used the following set of parameters:

$$\frac{A}{a} = 2.224 \times 10^9 \text{ cm}^{-1}, T_0 = 7.0, \Lambda_T = 7.1 \text{ \AA}, S_1 \Lambda_1 = 2.18 \times 10^{-2} \text{ cm}^2/\text{sec}.$$

The fit differs but slightly from that obtained previously. If we estimate  $a$  from the density as 7.5 Å, we find that  $\Lambda_T$  is approximately 1 and  $\Lambda_L$  is approximately 168. If we estimate  $s_1$  from the one-dimensional Tarasov parameters given under Heat Capacity of Amorphous Polymers, we find

$$S_1 = \frac{1}{3}(S_{1L} + 2S_{1T}) = 3.9 \times 10^5 \text{ cm/sec}$$

so that  $\Lambda_1 = 5.6 \text{ \AA}$ , somewhere between two and three times the distance between repeating units.

As shown in Fig. 10, the one-dimensional modes contribute the most to the thermal conductivity above nitrogen temperature but very little in the helium temperature range. Thus we would expect that orientation of the polymer chains, and hence  $\Lambda_1$ , would cause an increase in the thermal conductivity according to

$$\mathcal{H} = \mathcal{H}_L + \frac{1}{3} S_T C_3 \Lambda_T + \alpha(\epsilon) S_1 C_1 \Lambda_1$$

where  $\epsilon$  is the stretching ratio. This discussion is equivalent at this point to that given by Henning [58] and so it is not pursued further here. However, we see that the observations of sizable orientation effects at nitrogen temperatures and above and negligible orientation effects in the helium temperature range support the model. Since the data shown in Fig. 10a were taken on an extruded sample, while  $\Lambda_1$  was chosen to fit the higher temperature data which were not taken on extruded samples, the fact that the data rise even faster than the calculation above 20°K may be further supported for this model, as a slightly larger value of  $\alpha$  than 1/3 ought to be used for the one-dimensional contribution for the extruded sample.

We may also compare the value of  $A/a$  obtained above with that obtained using either Eq. (12 or Eq. (13). As the numerical factors do not differ too much, which model is used is not too important. Although this comparison has not previously been made, it is possible in principle and is illustrated by the following. There are existing data on light scattering by dielectric constant fluctuations in a Lucite sample [67], which were fit to the exponential correlation function, so that Eq. (13) is the appropriate expression to use. The dielectric constant fluctuations responsible for the light scattering can be related to density fluctuations through the Clausius-Mossotti equation, and the density fluctuations can be related to the sound-velocity fluctuations by the empirical Rama Rao [68] expression

$$\frac{ds}{s} = D \frac{d\rho}{\rho}$$

where  $\rho$  is the density and  $D$  is an empirical constant which is approximately 6 for PMMA. Calculating  $A/a$  from the Debye-Bueche light-scattering data we find a value of  $10^{10} \text{ cm}^{-1}$ . As the light-scattering data refer to a different sample than do the thermal conductivity data, we do not know whether to be pleased or worried by the fact that this value is within a factor of about 4 of that needed to fit the thermal conductivity (for other PMMA samples, values of  $A/a$  as high as  $3.7 \times 10^9 \text{ cm}^{-1}$  have been obtained). It would certainly be interesting to perform both light-scattering and thermal conductivity experiments on the same sample.

More troubling at the present stage of our understanding than the lack of numerical agreement between the calculation attempted above and the thermal conductivity measurements is the fact that below 1°K the temperature dependence becomes more rapid than linear. This difficulty could be ascribed to the presence of an additional scattering mechanism, perhaps internal boundaries, as in the case of silica glasses [69], although the size

of the internal boundaries required, about  $10^{-2}$  cm, makes this analysis somewhat questionable. Also, the more rapid than linear temperature dependence could signal a symmetry of elastic correlations other than spherical. An additional possibility is suggested by the fact that there may be a weak effect of the molecular weight on the helium temperature conductivity and the fact that the most populated thermal wavelengths at temperatures near  $1^{\circ}\text{K}$  are of the order of random coil dimensions of the polymer molecules. This suggestion is that upon lowering the temperature, the phonon wavelength increases sufficiently to sample a different class of elastic correlations than those sampled at high temperatures.

In summary, although it appears that our understanding of the thermal conductivity of amorphous polymers is better than our understanding of semicrystalline polymers, there are still many unanswered questions which should be considered.

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#### Discussion of Paper by W. Reese

##### Thermal Properties of Polymers at Low Temperatures

J. A. Sauer: For the PE sample which showed excess specific heat at low temperatures, how many methyl groups were Present in the sample?

W. Reese: About one per 100 CH<sub>2</sub>.

A. M. Hermann: Do you know of any thermal conductivity studies on polymers that are good electronic conductors such as TCNQ polymeric salts? I have specific reference to the fact that in metals, the thermal conductivity is predominated by electronic contributions at low temperatures.

W. Reese: There have been, to my knowledge, no measurements. This is, of course, an interesting problem and just serves to point out the primitive state of our knowledge.

M. Shen: Did you have the occasion to measure heat capacity of polymer single crystals at very low temperatures?

W. Reese: No, since there are severe problems with the availability of samples of sufficient size. The technique for the small crystals available, either exchange gas or DTA, both seem to have defects as applied to very-low-temperature measurements. Above 90°K, Wunderlich has made measurements, using DTA, on single crystals and obtained results in agreement with the extrapolations.