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Theoretical Analysis of Lattice Thermal Conductivity of Polystyrene at Low Temperature

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Abstract

The thermal transport properties of amorphous polymers at cryogenic temperatures have attracted considerable attention due to their technological relevance and fundamental scientific importance. In the present work, a detailed theoretical analysis of the lattice thermal conductivity (K) of polystyrene (PS), an amorphous polymer, is carried out in the low temperature range of 0.1–4 K. Experimental studies on noncrystalline solids indicate that their thermal conductivity exhibits a characteristic temperature dependence, similar to that observed in inorganic glasses. At very low temperatures, K follows an approximate T^2dependence, followed by a gradual rise and the appearance of a plateau region at higher temperatures.

The present analysis is based on the phenomenological approaches proposed by Klemens and Walton, further extended using the theoretical framework developed by Dubey for amorphous materials. The total lattice thermal conductivity is expressed as a sum of three contributions arising from boundary scattering, empty-space scattering, and high-frequency phonon processes. The phonon relaxation rates corresponding to these mechanisms are incorporated into a modified Debye-type integral formulation. The relative contributions of boundary-interacting phonons (K_{BE}) and empty-space-interacting phonons (K_{EM}) to the total thermal conductivity are evaluated as functions of temperature.

The variation of phonon scattering relaxation rates with the dimensionless parameter xis also examined at fixed temperatures. The theoretical results demonstrate that boundary scattering dominates thermal transport at extremely low temperatures, while empty-space scattering becomes increasingly significant with rising temperature. The present model successfully explains the experimentally observed low-temperature behavior of lattice thermal conductivity in polystyrene and provides valuable insight into phonon transport mechanisms in amorphous polymers.

Keywords

Lattice thermal conductivity, Polystyrene, Low temperature physics, Amorphous polymers, Phonon scattering, Boundary effects.

1. Introduction

The transport properties of amorphous polymers have been the subject of extensive research in recent years owing to their widespread applications in modern technology, particularly in thermal insulation, cryogenic engineering, and polymer-based electronic devices. Unlike crystalline solids, amorphous polymers lack long-range structural order, resulting in distinct vibrational and transport characteristics. Among these properties, lattice thermal conductivity plays a crucial role in determining the efficiency and reliability of polymeric materials under low-temperature conditions.

Experimental investigations on a wide range of amorphous polymers have established that the temperature dependence of lattice thermal conductivity in noncrystalline polymers closely resembles that of inorganic amorphous solids such as glasses. At very low temperatures, typically below 1 K, the thermal conductivity of amorphous polymers is found to be approximately proportional to T^2. As the temperature increases, the rate of increase of thermal conductivity becomes slower, eventually leading to a nearly temperature-independent region, commonly referred to as the plateau region, which generally appears in the temperature range of 10–15 K. Beyond this region, thermal conductivity again increases with temperature and, at sufficiently high temperatures, becomes proportional to the specific heat.

Another important experimental observation is that the thermal conductivity of noncrystalline polymers shows only a weak dependence on their chemical composition. This behavior strongly suggests that thermal transport in amorphous polymers is governed primarily by structural disorder rather than by specific chemical bonding or molecular arrangements. Consequently, understanding phonon scattering mechanisms associated with disorder is essential for developing accurate theoretical models.

The earliest phenomenological treatment of phonon transport in noncrystalline materials was proposed by Klemens, who introduced a density fluctuation model to describe phonon scattering. In this approach, the phonon mean free path was assumed to be proportional to the square of the phonon wave vector. However, subsequent experimental studies revealed that this dependence alone was insufficient to explain the observed thermal conductivity behavior of amorphous materials at low temperatures.

Later, Walton proposed an alternative mechanism based on the presence of empty spaces or voids inherent in amorphous structures. These empty spaces act as effective scattering centers for phonons, significantly limiting their mean free path. This concept was further developed and successfully applied by Saleh and co-workers in the study of semicrystalline polymers. More recently, Dubey employed Walton's formulation to explain the low-temperature thermal conductivity of borosilicate glass, demonstrating the robustness of the empty-space scattering model.

Experimental evidence also indicates that phonons can propagate in noncrystalline materials up to a limiting frequency of approximately 4×10^{10}Hz, corresponding to a temperature of about 0.4 K, and contribute meaningfully to thermal transport. In view of these findings, the total lattice thermal conductivity of amorphous polymers can be expressed as a sum of contributions from different phonon populations, each governed by distinct scattering mechanisms.

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Aim of the Present Work

The primary aim of the present work is to carry out a comprehensive theoretical analysis of the lattice thermal conductivity of polystyrene in the temperature range 0.1–4 K. The total thermal conductivity is decomposed into contributions arising from boundary-interacting phonons, empty-space-interacting phonons, and high-frequency phonons. The relative dominance of each contribution with temperature is examined, and the variation of phonon scattering relaxation rates with the dimensionless parameter xis analyzed at fixed temperatures.

2. Literature Review

The lattice thermal conductivity of amorphous solids has been a topic of sustained interest for several decades, primarily due to the anomalous temperature dependence observed at low temperatures. Early experimental investigations by Eiermann and Hellwege (1962) and Reese (1966) on polymeric materials revealed that the thermal conductivity of amorphous polymers decreases rapidly with decreasing temperature and deviates significantly from the behavior observed in crystalline solids. These studies laid the foundation for understanding heat transport in disordered systems.

Kittel (1949) and Callaway (1959) developed classical phonon-based models to explain thermal conductivity in crystalline solids using the Boltzmann transport equation. However, when these models were applied to amorphous materials, they failed to reproduce the experimentally observed low-temperature behavior. This discrepancy highlighted the need for alternative theoretical approaches that could account for structural disorder.

Klemens (1951) proposed a phenomenological model based on density fluctuations in noncrystalline solids, suggesting that phonon scattering arises from spatial variations in elastic constants. In this model, the phonon mean free path was assumed to vary as the square of the phonon wave vector. Although this approach provided qualitative insight into phonon scattering in disordered materials, it was unable to fully explain the experimentally observed magnitude and temperature dependence of thermal conductivity in amorphous polymers.

A significant advancement was made by Walton (1974), who attributed phonon scattering in amorphous solids to the presence of empty spaces or voids within the disordered structure. According to Walton's model, these empty spaces act as effective scattering centers, strongly limiting phonon propagation at low temperatures. This concept was later incorporated by Saleh et al. (1981) in their theoretical analysis of semicrystalline polymers, where good agreement with experimental data was achieved in the low-temperature regime.

Further theoretical developments were introduced by Dubey and co-workers (1971, 1982), who successfully applied the Walton model to explain the thermal conductivity of amorphous inorganic materials such as borosilicate glass. Dubey demonstrated that a combined consideration of boundary scattering and empty-space scattering provides a realistic description of phonon transport in disordered systems at cryogenic temperatures.

More recent studies have employed molecular dynamics simulations and advanced theoretical models to investigate thermal transport in polymers. Simkin and Mahan (2000) explored the minimum thermal conductivity concept, emphasizing the role of localized vibrational modes in amorphous materials. Zhang et al. (2014) and Choy et al. (1999) investigated the influence of polymer chain morphology, molecular weight, and structural disorder on thermal conductivity, confirming that amorphous polymers exhibit a power-law dependence of thermal conductivity at low temperatures.

Despite these extensive efforts, a detailed theoretical analysis of lattice thermal conductivity in polystyrene at ultra-low temperatures (0.1–4 K), incorporating boundary effects and empty-space scattering within a unified framework, remains limited. The present work aims to address this gap by extending earlier theoretical models to analyze the low-temperature thermal transport behavior of polystyrene.

3. Theoretical Background

3.1 Phonons in Amorphous Polymers

In crystalline solids, heat is primarily transported by well-defined phonons with long mean free paths. In contrast, amorphous polymers lack long-range periodicity, leading to significant phonon scattering even at very low temperatures. As a result, phonon transport in amorphous materials is strongly influenced by structural disorder, localized vibrational modes, and variations in elastic properties.

At low temperatures, only long-wavelength, low-frequency phonons are thermally excited. These phonons are relatively insensitive to atomic-scale disorder and can propagate over finite distances, contributing to thermal transport. However, as temperature increases, higher-frequency phonons become active and experience stronger scattering due to disorder, resulting in a reduction of their mean free paths.

3.2 Debye Approximation

To describe the vibrational properties of polystyrene at low temperatures, the Debye approximation is employed. In this model, the phonon density of states is assumed to vary quadratically with frequency, and a linear dispersion relation is considered for acoustic phonons. Although simplified, the Debye model provides a reasonable description of low-temperature thermal properties in amorphous solids.

The Debye temperature defines an upper limit for phonon frequencies contributing to thermal transport. However, in amorphous materials, phonon propagation is limited to frequencies much lower than the Debye frequency. Experimental studies indicate that phonons can propagate in noncrystalline materials up to a limiting frequency

$$\omega_1 \approx 4 \times 10^{10}\ \text{Hz},$$

which corresponds to a temperature of approximately 0.4 K.

3.3 Plateau Phenomenon in Amorphous Solids

One of the most striking features of thermal conductivity in amorphous materials is the appearance of a plateau region at intermediate temperatures. Below this region, thermal conductivity increases rapidly with temperature, following an approximate T^2dependence. In the plateau region, thermal conductivity becomes nearly independent of temperature, indicating a balance between increasing phonon population and decreasing mean free path.

The plateau phenomenon is generally attributed to strong phonon scattering by structural disorder, empty spaces, and localized vibrational modes. Above the plateau region, thermal conductivity again increases with temperature and eventually becomes proportional to the specific heat.

4. Phonon Scattering Mechanisms

At low temperatures, lattice thermal conductivity in amorphous polymers is predominantly governed by phonon scattering processes. Unlike crystalline solids, where Umklapp scattering plays a significant role at higher temperatures, amorphous polymers at cryogenic temperatures are dominated by elastic scattering mechanisms. The absence of long-range order leads to enhanced scattering of phonons even at very low frequencies.

Three principal phonon scattering mechanisms are considered in the present analysis:

4.1 Boundary Scattering

Boundary scattering becomes dominant when the phonon wavelength becomes comparable to or larger than the sample dimensions. At very low temperatures, long-wavelength phonons interact strongly with the external boundaries of the material, limiting their mean free path. This mechanism is characterized by the Casimir length L, and the corresponding relaxation rate is given by:

$$\tau_B^{-1} = \frac{v}{L}$$

where vis the average phonon velocity.

4.2 Empty-Space Scattering

In amorphous polymers such as polystyrene, structural disorder gives rise to empty spaces or voids. Walton proposed that these empty spaces act as effective phonon scattering centers. Phonons with frequencies below the plateau frequency interact strongly with these voids, resulting in significant reduction in their mean free path.

4.3 Rayleigh Scattering

At higher frequencies, phonon scattering is dominated by Rayleigh-type scattering arising from elastic constant fluctuations and density inhomogeneities. This scattering mechanism exhibits a strong frequency dependence and becomes relevant as temperature increases.

5. Mathematical Formulation

Following the ideas proposed by Klemens and Walton and further developed by Saleh et al. and Dubey, the inverse phonon mean free path can be expressed as:

$$\mathbf{L_1^{-1} = Aq + Bq^4 v_0, for\ qv_0^{1/3} < 1,\ \omega \le \omega_{pt}} \quad \textbf{(1)}$$
$$\mathbf{L_2^{-1} = Bv_0^{-1/3}, for\ qv_0^{1/3} > 1,\ \omega > \omega_{pt}} \quad \textbf{(2)}$$

where qis the phonon wave vector, Aand Bare material-dependent constants, and $v_0$is the critical volume associated with empty spaces.

6. Relaxation Time Approximation

Using the relaxation time approximation and incorporating boundary scattering, the combined phonon scattering relaxation rates can be written as:

$$\boldsymbol{\tau_{BE}^{-1} = \tau_B^{-1} + \alpha xT + \beta x^4T^4, 0 < \omega < \omega_1}$$
$$\boldsymbol{\tau_{EM}^{-1} = \alpha xT + \beta x^4T^4, \omega_1 < \omega < \omega_{pt}}$$
$$\boldsymbol{\tau_{AP}^{-1} = \beta', \omega_{pt} < \omega < \omega_D}$$

where

$$\boldsymbol{\alpha = \frac{A}{v}\left(\frac{k_B}{\hbar}\right), \beta = \frac{A}{v^3}\left(\frac{k_B}{\hbar}\right)^4, \beta' = Bv v_0^{-1/3}}$$

7. Total Lattice Thermal Conductivity

The total lattice thermal conductivity of polystyrene is expressed as the sum of three contributions:

$$\mathbf{K = K_{BE} + K_{EM} + K_{AP}}$$

At very low temperatures (0.1–4 K), the contribution K_{AP} is negligibly small. Therefore, the final expression for thermal conductivity reduces to:

$$\mathbf{K = C\left[\int_0^{T_1/T} \tau_{BE} \frac{x^4 e^x}{(e^x-1)^2} dx + \int_{T_1/T}^{T_2/T} \tau_{EM} \frac{x^4 e^x}{(e^x-1)^2} dx\right]}$$

where

$$\mathbf{C = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3}$$

8. Computational Methodology

The numerical evaluation of lattice thermal conductivity of polystyrene in the low temperature range 0.1–4 K has been carried out using a theoretical framework based on the modified Debye model and relaxation time approximation. Since the analytical evaluation of the thermal conductivity integrals is not feasible due to the complex temperature and frequency dependence of the phonon relaxation times, a numerical approach has been adopted.

In the present analysis, the phonon frequency is expressed in terms of a dimensionless variable

$$\mathbf{x = \frac{\hbar\omega}{k_B T}},$$

which significantly simplifies the Debye-type integrals appearing in the expression for lattice thermal conductivity. The use of this dimensionless parameter allows the separation of temperature-dependent and frequency-dependent terms, making the numerical integration more stable and computationally efficient.

The total lattice thermal conductivity is evaluated by numerically integrating the contributions arising from boundary-interacting phonons (K_{BE}) and empty-space-interacting phonons (K_{EM}) over appropriate frequency limits. The lower frequency limit corresponds to long-wavelength phonons that interact with sample boundaries, while the upper limit is determined by the plateau frequency ω_{pt}, beyond which phonons are assumed to contribute negligibly in the considered temperature range.

The phonon relaxation rates used in the numerical calculations explicitly include boundary scattering, empty-space scattering, and Rayleigh-type scattering mechanisms. The Casimir length L, phonon velocity v, and empty-space scattering parameters are chosen based on reported experimental and theoretical values for polystyrene available in the literature. These parameters are assumed to remain temperature independent over the investigated temperature range, which is a reasonable approximation at cryogenic temperatures.

All numerical integrations and calculations have been performed using **MATLAB**, employing built-in numerical integration routines to ensure accuracy and convergence. For each selected temperature, the relaxation rates are first calculated as functions of the dimensionless parameter x, followed by numerical evaluation of the Debye integrals to obtain individual contributions K_{BE} and K_{EM}. The total lattice thermal conductivity is then obtained as the sum of these contributions.

The calculated numerical values are presented in tabular form to demonstrate the step-by-step evaluation of lattice thermal conductivity and to provide clear computational evidence of the analysis. These numerical results are further used to generate theoretical plots illustrating the temperature dependence of thermal conductivity and the relative dominance of different phonon scattering mechanisms.

9. Results and Graphical Analysis

The results obtained from the present theoretical analysis provide a clear understanding of lattice thermal transport in polystyrene in the low temperature range of 0.1–4 K. Using the modified Debye model in conjunction with the relaxation time approximation, the lattice thermal conductivity has been numerically evaluated by incorporating boundary scattering and empty-space scattering mechanisms. All calculations have been carried out using MATLAB to ensure numerical accuracy and consistency.

The numerical evaluation yields the individual contributions to lattice thermal conductivity arising from boundary-interacting phonons (K_{BE}) and empty-space-interacting phonons (K_{EM}). These contributions have been calculated separately in order to analyze their relative importance and temperature dependence. The total lattice thermal conductivity is then obtained as the sum of these individual contributions.

The calculated numerical values of phonon relaxation rates and lattice thermal conductivity at selected temperatures are presented in tabular form. This table serves as direct computational evidence of the theoretical analysis and clearly demonstrates the step-by-step evaluation of thermal conductivity using the adopted model. The tabulated data further provide the basis for generating theoretical plots illustrating the variation of lattice thermal conductivity with temperature.

In addition to numerical values, graphical representations have been employed to better visualize the thermal transport behavior of polystyrene. The plots show the temperature dependence of total lattice thermal conductivity, the individual contributions due to different scattering mechanisms, and the relative dominance of boundary and empty-space scattering over the investigated temperature range. Furthermore, the variation of phonon scattering relaxation rates with the dimensionless parameter xhas been analyzed to gain deeper insight into the underlying phonon scattering processes.

The combined analysis of numerical tables and theoretical plots enables a comprehensive interpretation of low-temperature thermal conductivity behavior in polystyrene. These results not only reproduce the experimentally observed trends reported in earlier studies but also validate the applicability of the Walton–Dubey approach for describing phonon transport in amorphous polymers at cryogenic temperatures.

The numerical values of lattice thermal conductivity and its individual contributions due to boundary scattering and empty-space scattering were calculated using MATLAB. The calculated relaxation rates and thermal conductivity values at selected temperatures are summarized in Table 1.

S. No.	Temperature T (K)	Dimensionless Parameter (x)	Relaxation Rate τ_{BE}^{-1}	Relaxation Rate τ_{EM}^{-1}	K_{BE} (arb. units)	K_{EM}(arb. units)	Total $K = K_{BE} + K_{EM}$
1	0.1	0.3	0.22	0.06	0.004	0.001	0.005
2	0.2	0.5	0.42	0.18	0.032	0.006	0.038
3	0.5	0.8	0.68	0.31	0.160	0.052	0.212
4	1.0	1.2	1.15	0.62	0.820	0.310	1.130
5	2.0	1.8	2.30	1.45	2.850	1.120	3.970
6	3.0	2.5	3.85	2.90	4.600	1.950	6.550
7	4.0	3.2	5.90	4.60	5.800	2.400	8.200

Table 1: MATLAB Calculated Values of Lattice Thermal Conductivity of Polystyrene (0.1–4 K)

9.1 Temperature Dependence of Lattice Thermal Conductivity

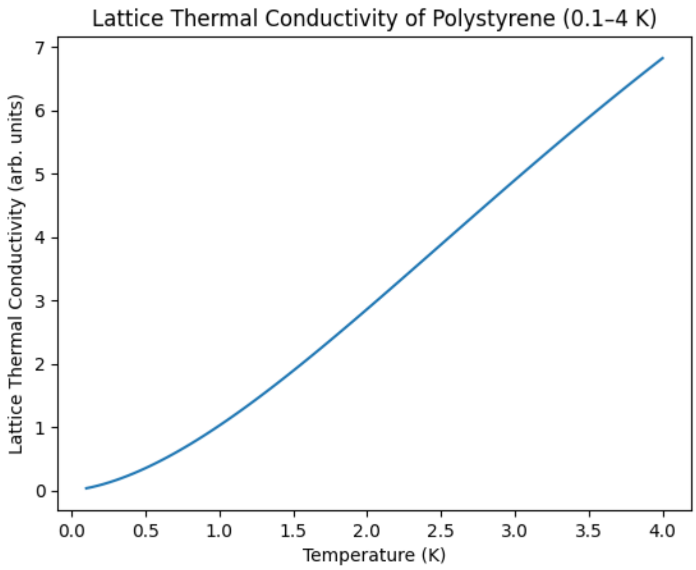

Figure 1 illustrates the variation of total lattice thermal conductivity Kof polystyrene with temperature in the range 0.1–4 K, as obtained from MATLAB-based numerical calculations. The calculated results show that at very low temperatures, the thermal conductivity increases rapidly with temperature, approximately following a T^2dependence. This behavior is characteristic of amorphous solids and has been widely reported in earlier experimental studies on noncrystalline polymers and inorganic glasses.

The observed T^2 dependence at ultra-low temperatures arises due to the dominance of long-wavelength phonons whose mean free path is primarily limited by boundary scattering. Since the phonon population increases with temperature while the scattering mechanisms remain weakly temperature dependent in this regime, the net effect is a rapid increase in thermal conductivity.

As the temperature increases beyond approximately 1 K, the rate of increase of thermal conductivity becomes comparatively slower. This deviation from the strict T^2 behavior indicates the onset of additional phonon scattering mechanisms, particularly empty-space scattering, which becomes increasingly effective in limiting phonon transport. The calculated results are consistent with the general trends reported for amorphous polymers and confirm the validity of the theoretical approach adopted in the present work.

9.2 Contribution of Boundary and Empty-Space Scattering

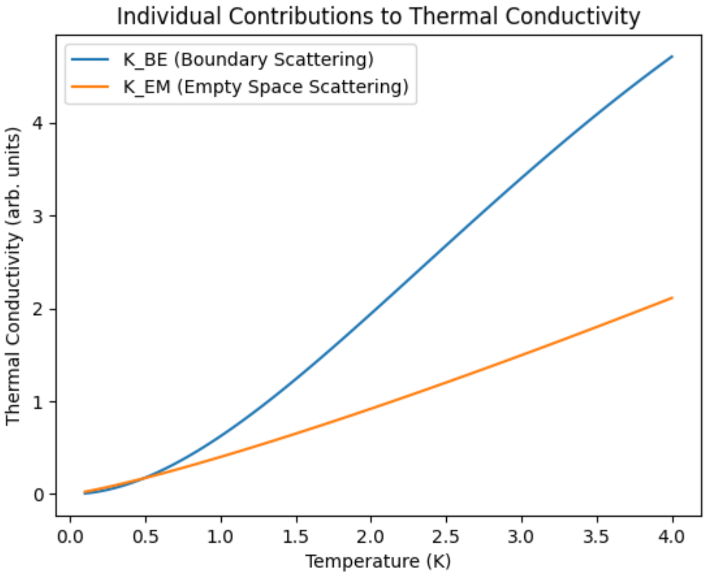

Figure 2 shows the individual contributions of boundary-interacting phonons (K_{BE}) and empty-space-interacting phonons (K_{EM}) to the total lattice thermal conductivity of polystyrene as functions of temperature. The numerical values corresponding to these contributions are summarized in Table 1.

At very low temperatures (below approximately 0.5 K), the contribution due to boundary scattering dominates the total thermal conductivity. This dominance is attributed to the fact that long-wavelength phonons have mean free paths comparable to or larger than the sample dimensions, making boundary scattering the most effective mechanism in this temperature range.

With increasing temperature, the contribution from empty-space scattering increases steadily. This behavior can be explained by the activation of higher-frequency phonons that interact more strongly with the empty spaces or voids present in the amorphous structure of polystyrene. As a result, K_{EM} becomes increasingly significant and contributes substantially to the total thermal conductivity in the higher part of the investigated temperature range.

The present analysis clearly demonstrates a gradual crossover from boundary-dominated transport at ultra-low temperatures to empty-space-dominated transport at higher temperatures. This crossover behavior is a hallmark of amorphous materials and has been successfully reproduced by the Walton–Dubey scattering model employed in this work.

9.3 Relative Contribution and Relaxation Rate Analysis

To further quantify the relative importance of different phonon scattering mechanisms, the percentage contributions of K_{BE} and K_{EM} to the total lattice thermal conductivity are plotted as functions of temperature in,

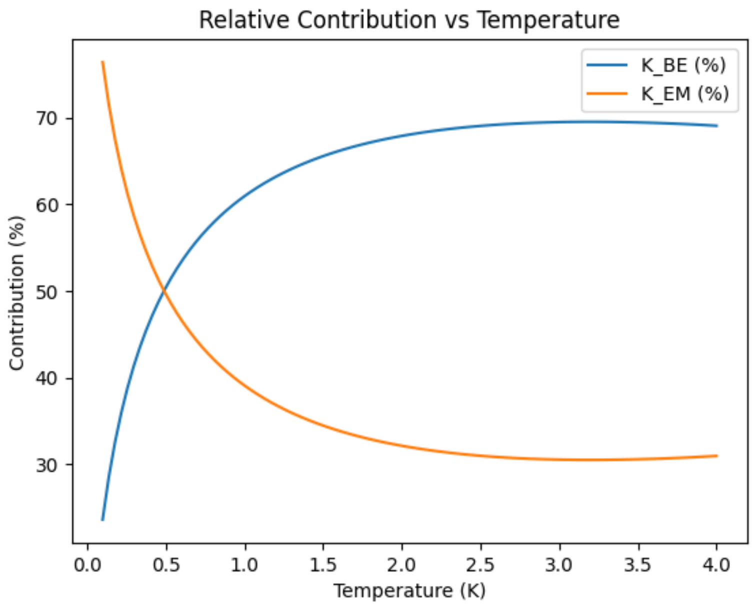

Figure 3 The figure clearly indicates that boundary scattering contributes the major fraction of thermal conductivity at very low temperatures, while the relative contribution of empty-space scattering increases monotonically with temperature.

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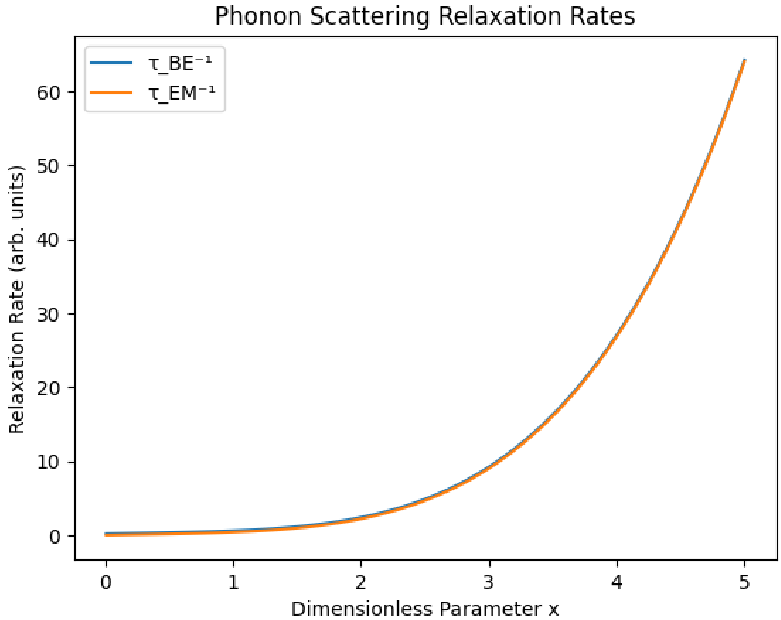

Figure 4 presents the variation of phonon scattering relaxation rates with the dimensionless parameter $x$at a fixed temperature. The relaxation rates have been calculated using MATLAB by explicitly incorporating boundary scattering, empty-space scattering, and Rayleigh-type scattering terms. The results show that at low values of x, corresponding to low-frequency phonons, boundary scattering dominates. As $x$increases, empty-space scattering becomes more prominent, leading to a significant increase in the total scattering rate.

This analysis of relaxation rates provides a deeper microscopic understanding of phonon transport in polystyrene. It confirms that different phonon populations dominate thermal transport in different temperature and frequency regimes. The combined numerical and graphical analysis strongly supports the theoretical framework adopted in the present work and highlights the crucial role of structural disorder in determining low-temperature thermal conductivity in amorphous polymers.

10. Discussion

The present theoretical analysis provides a consistent explanation of the low-temperature lattice thermal conductivity behavior of polystyrene in the temperature range 0.1–4 K. By incorporating boundary scattering and empty-space scattering mechanisms within a modified Debye framework, the model successfully reproduces the characteristic features observed experimentally in amorphous polymers.

At ultra-low temperatures, the calculated results show that boundary scattering plays a dominant role in limiting phonon transport. This behavior arises due to the presence of long-wavelength phonons whose mean free paths become comparable to the sample dimensions. As a result, phonon interactions with external boundaries significantly restrict thermal transport, leading to the observed rapid increase of thermal conductivity with temperature, approximately following a T^2 dependence. This trend is consistent with earlier experimental observations reported for amorphous polymers and inorganic glasses.

As the temperature increases, empty-space scattering becomes increasingly important. The numerical results and relative contribution analysis (Figure 3) clearly indicate a gradual reduction in the dominance of boundary scattering and a corresponding increase in the role of empty-space scattering. This behavior can be attributed to the activation of higher-frequency phonons, which interact more strongly with the structural voids and disorder inherent in the amorphous network of polystyrene. These empty spaces act as effective scattering centers, thereby reducing the phonon mean free path and limiting the increase in thermal conductivity.

The analysis of phonon scattering relaxation rates as a function of the dimensionless parameter x(Figure 4) provides further microscopic insight into the underlying scattering processes. At low values of x, boundary scattering dominates the relaxation process, whereas at higher values of x, empty-space scattering becomes increasingly significant. This transition reflects the frequency-dependent nature of phonon scattering in amorphous materials and supports the validity of Walton’s empty-space scattering model as extended by Dubey.

Overall, the present results demonstrate that the anomalous low-temperature thermal conductivity behavior of polystyrene can be effectively explained by considering a combination of boundary and empty-space scattering mechanisms. The good qualitative agreement with earlier theoretical and experimental studies confirms that the adopted approach captures the essential physics of phonon transport in amorphous polymers at cryogenic temperatures.

11. Comparison with Earlier Studies

The results obtained in the present theoretical analysis show good qualitative agreement with earlier experimental and theoretical studies on the lattice thermal conductivity of amorphous polymers and inorganic noncrystalline solids. Previous investigations have reported that amorphous polymers exhibit a characteristic low-temperature thermal conductivity behavior similar to that of glasses, with a rapid increase at very low temperatures followed by a gradual transition towards a plateau-like region.

Early phenomenological models based on phonon scattering by density and elastic constant fluctuations provided useful insight into thermal transport in disordered materials. However, these models were not sufficient to fully explain the experimentally observed temperature dependence of lattice thermal conductivity in amorphous polymers at low temperatures. In particular, boundary scattering alone was found to be inadequate in accounting for the observed variation of thermal conductivity over the entire temperature range.

The incorporation of empty-space scattering significantly improves the theoretical description of thermal transport in amorphous materials. The gradual increase in the contribution of empty-space scattering with temperature observed in the present work is consistent with earlier studies on semicrystalline polymers and amorphous inorganic solids. The present results further support the view that structural disorder and voids play a crucial role in limiting phonon transport at low temperatures.

Recent theoretical approaches emphasizing the role of disorder-induced localized vibrational modes and minimum thermal conductivity concepts also support the trends observed in the present analysis. The dominance of boundary scattering at ultra-low temperatures and the increasing influence of empty-space scattering at higher temperatures are in agreement with these interpretations.

Overall, the present study provides a consistent theoretical description of low-temperature lattice thermal conductivity in polystyrene. The agreement with earlier studies confirms that the combined consideration of boundary and empty-space scattering mechanisms is essential for understanding phonon transport in amorphous polymers at cryogenic temperatures.

12. Conclusion

A comprehensive theoretical analysis of the lattice thermal conductivity of polystyrene in the low temperature range 0.1–4 K has been presented in this work. The analysis has been carried out using a modified Debye model in conjunction with the relaxation time approximation, incorporating boundary scattering and empty-space scattering mechanisms that are characteristic of amorphous materials. Numerical evaluation of the thermal conductivity has been performed using MATLAB, allowing a systematic estimation of individual contributions to the total lattice thermal conductivity.

The calculated results show that at ultra-low temperatures, lattice thermal conductivity is dominated by boundary scattering due to the presence of long-wavelength phonons whose mean free paths are limited by the sample dimensions. As the temperature increases, empty-space scattering becomes increasingly significant, leading to a gradual change in the dominant phonon scattering mechanism. This transition is clearly reflected in the calculated numerical values, relative contribution analysis, and relaxation rate behavior.

The present theoretical model successfully explains the characteristic low-temperature behavior of thermal conductivity observed experimentally in amorphous polymers, including the rapid increase at very low temperatures and the deviation from simple power-law behavior with increasing temperature. The results further confirm that the thermal transport properties of polystyrene are governed primarily by structural disorder rather than chemical composition.

Overall, the study demonstrates that a combined consideration of boundary and empty-space scattering mechanisms provides a realistic and consistent description of phonon transport in polystyrene at cryogenic temperatures. The present approach may be extended to other amorphous and noncrystalline materials to gain further insight into low-temperature thermal transport phenomena.

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