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Normal Mode Analysis of the Thermal conductivity in Amorphous Polymers: The Importance of Localized Modes

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Abstract: Polymers are a unique class of materials from the perspective of normal mode analysis. Polymers consist of individual chains with repeating units and strong intra-chain covalent bonds, and amorphous arrangements among chains with weak inter-chain van der Waals and for some polymers also electrostatic interactions. Intuitively, this strong heterogeneity in bond strength can give rise to interesting features in the constituent phonons, but such effects have not been studied deeply before. Here, we use lattice dynamics and molecular dynamics to perform modal analysis of the thermal conductivity in amorphous polymers for the first time. We find an abnormally large population of localized modes in amorphous polymers, which is dramatically different from amorphous inorganic materials. Contrary to the common picture of thermal transport, localized modes in amorphous polymers are found to be the dominant contributors to thermal conductivity. We find that a significant portion of the localization happens within individual chains, but heat is dominantly conducted when localized modes involve two chains. These results suggest that even though each polymer is different, localized modes play a key role. The results provide new perspective on why polymer thermal conductivity is generally quite low and gives insight into how to potentially change it.

Keywords: thermal conductivity, amorphous polymer, localization, normal modes, molecular dynamics, lattice dynamics

Introduction

Polymers are one of the most important and widely used classes of materials in modern society. The proliferation of polymers is attributed to their low density, low cost, high resistance to corrosion and the low-energy requirements to manufacture/form them into requisite shapes. In their usage, polymers are commonly amorphous in structure and have thermal conductivities on the order of $0.1 \text{ W m}^{-1} \text{ K}^{-1}$. The low thermal conductivity (TC) of polymers is useful in many contexts (e.g., food containers and structural materials), but also becomes a limitation in other contexts (e.g., electronics packaging, heat exchangers etc.). Prior work^{1–11} showing that the TC of polymers can be increased by two orders of magnitude to the same range as most metals, has prompted interest in understanding and engineering the TC of polymers for new applications, such as heat exchangers¹² and thermally conductive chassis for personal electronics.^{13,14}

1 While the low value of TC for amorphous polymers is generally understood to be
2 associated with their disordered structure, amorphous polymer TC is still an order of
3 magnitude lower than that of amorphous inorganic materials, and the reason why is not
4 entirely clear from a theoretical perspective. For crystalline materials, the TC is usually
5 well explained by the phonon gas model (PGM).^{15–17} However, there is growing evidence
6 to suggest that the PGM is insufficient for understanding the thermal behavior of
7 disordered materials^{18–39}, such as an amorphous polymer. The structural or compositional
8 disorder within disordered materials causes a drastic change in the character of
9 vibrational modes, which are no longer spatially periodic, as they are in crystalline
10 materials.⁴⁰ As a result, the PGM can become ill-suited for describing the behaviors and
11 contributions of phonons/normal modes with non-periodic mode shapes, which we will
12 henceforth refer to as “non-propagating”.

13
14 When a significant fraction of the modes in a material cease to have propagating
15 character, the PGM can fail at describing the TC in ways that cannot be corrected with
16 simple modifications of terms that treat it as a perturbation.⁴¹ This is because there is an
17 intrinsic inapplicability of the PGM physical picture to modes that are non-propagating,
18 since a well-reasoned group velocity or wave vector cannot be assigned to non-
19 propagating modes.²¹ For amorphous materials, Allen-Feldman (AF) proposed a model
20 based on supercell lattice dynamics calculations that naturally classifies modes into three
21 distinct categories, namely propagons, diffusons, and locons.^{19,42,43}

22
23 Propagons are modes that most closely resemble the traditional picture of a phonon,
24 which arises from the periodicity in crystalline materials. Propagons have a well-defined
25 wave vector and a periodic mode shape that can produce a propagating wave packet,⁴⁴
26 and we therefore refer to them herein as propagating. They tend to be low-frequency
27 modes that are delocalized throughout the entire system, and their propagating nature is
28 what allows them to be accurately described by the PGM. Diffusons, while spatially
29 delocalized, exhibit no apparent periodicity in the atomic vibrations/mode shape. Instead,
30 these vibrations appear random, and it is not clear how one could define a wave-vector
31 and/or a group velocity for them. Thus, diffusons are not likely to be well described by the
32 PGM. Finally, locons are spatially localized modes that exist in a portion of the supercell
33 that have their energy highly concentrated onto a subset of atoms. In all previous studies,
34 locons have comprised the smallest group of modes^{21,35,41,45} and they have been
35 assumed to be too localized to contribute to TC in a significant way,^{19,21,30,46–50} although
36 there has been recent evidence that this may not always be the case.³⁵

37
38 The AF framework, which describes the contributions of diffusons, has been successfully
39 applied to the explain TC of glasses,^{49–61} amorphous semiconductors,^{24,44,45,62–69} solid
40 solutions,^{70,71} organic compounds,^{72–74} composites,^{75,76} phase change materials,⁷⁷ and
41 low-dimension materials.^{78,79} However, the AF method neglects the contributions of
42 locons altogether. The AF method was extended by Lv and Henry, and termed the Green
43 Kubo Mode Analysis (GKMA)^{21,22,35,80–82} method. GKMA combines the normal modes
44 obtained from supercell lattice dynamics (LD), obtained in the harmonic limit, with the
45 anharmonic trajectory obtained from a molecular dynamics (MD) simulation. This allows
46 one to quantify the contributions from all three classes of modes (i.e., propagons,

diffusons and locons), all in a single and consistent framework with anharmonicity. As a result, GKMA provides a more complete description of mode level TC and can provide useful comparisons to experiments when a quantum correction is used.^{35,80,81,83}

Spatially extended modes can be distinguished from spatially localized modes using the participation ratio (PR), and the extended modes i.e., propagons and diffusons, can be distinguished from each other, using a method developed by Seyf and Henry.⁴⁴ It should be noted that a variety of other approaches also exist to distinguish between propagons and diffusons. Yet, despite significant progress on developing modal analysis methods, there is little, if any, literature reporting their application to resolve the modal contributions to TC in amorphous polymers.

Polymers are special because they can have both strong intra-chain covalent bonds and weak interchain Van der Waals bonds, and for some polymers, electrostatic interactions across chains. From the perspective of normal modes, they're a unique class of materials, because individual chains have repeating structures even the chains are randomly arranged. Besides, via mechanically stretching, it is possible to align the polymer chains without chemical modification to achieve a more ordered structure.^{73,76,77} Thus, polymers provide a means for studying how disorder affects phonon transport in a manner whereby one could theoretically observe a continuous transition from disordered to ordered – all in a single sample. To better understand the physics of phonons/normal modes in polymers, herein we used GKMA, and to the best of our knowledge, this is the first-time supercell LD has been used to study the normal modes in amorphous polymers.

Modeling and Simulations

We performed LD calculations on well-relaxed amorphous polymers to determine the vibrational normal modes. Mode resolved TC was calculated using GKMA with equilibrium MD simulations and the details associated with the relaxation procedure, interatomic potential, and LD/MD are provided in the supplementary information. Three amorphous thermoplastics are studied: amorphous poly(methyl methacrylate) (a-PMMA), amorphous polystyrene (a-PS), and amorphous polyvinyl chloride (a-PVC). All three polymers contain carbon (C) and hydrogen (H), while PMMA contains oxygen (O) atoms, and PVC contains chlorine (Cl). The molecular structure of each monomer is shown below in Fig. 1.

Figure 1 | Chemical structures of thermoplastics in study: a-PMMA (left), a-PS (center), and a-PVC (right).

We chose to study these three thermoplastics for two primary reasons: 1) Due to the nature of thermoplastics, they can be annealed and/or melted using MD to relax the structure without concern about significant changes to the chemical bonding, as opposed to thermosets, which are irreversibly cured. 2) Since there is a practical limit to the number of polymers that can be studied herein, given finite computational resources, we attempted to study thermoplastics with some significant heterogeneity in monomer structure/chemistry. By focusing on these thermoplastics, there will perhaps be some observations that may apply more broadly to thermoplastics in general. Due to the significant differences between the three thermoplastics selected, the findings that hold across all three polymers may have implications for a large number of other thermoplastics, as opposed to the alternative of studying three very chemically similar thermoplastics.

To characterize the normal modes in amorphous polymers, we studied the normal modes cumulative density of states (DOS) with different measures of localization in Fig 2. Figure 2a shows the PR versus mode frequency. The PR measures how many atoms are actively involved in a given mode, and therefore is a measure of the degree of localization. The definition of PR can be found in supporting information. Surprisingly, as compared to the modes in amorphous silicon,^{19,44,80} which are similar to the modes in amorphous carbon⁸¹ and amorphous germanium, the modes in amorphous polymers are much more localized than any of the aforementioned amorphous semiconductors. The modes in the polymers studied here have extremely low PR across a broad range of frequencies as shown in Fig. 2a. Based on the PR, the vast majority of the modes are considered locons using the criterion $PR < 0.1$, which is more conservative than the widely used delineation criterion of 0.2 in other studies,^{41,43,44,84} to classify modes as locons. Interestingly, if one were to adopt this less conservative criterion, almost every mode could be considered a locon with $PR < 0.2$ (i.e., 82%, 95%, and 98% of the modes in a-PMMA, a-PS, and a-PVC, respectively).

Figure 2 | Normal modes in amorphous polymers from LD. The results shown come from supercells of a-PMMA with 3000 atoms, a-PS with 3000 atoms, and a-PVC with 1000 atoms. Panel a shows the PR versus frequency for all three polymers. Panel b, c, and d show the cumulative DOS with respect to PR, MSE, and β_2 , respectively. The vertical lines in panel b and c show the delineation between highly localized modes and others, while the vertical line in panel d shows the delineation between modes confined to a single chain vs multiple chains. (Colors online)

Such a high degree of localization, especially at low frequencies has not been observed in any other bulk material to date. However, when visualizing the eigenvectors, which describe the square root mass weighted displacement of each atom, as it participates in a given mode, many of the locons seem to have their eigen vectors spread over a significant portion of the supercell. Several examples of modes with low PR yet high spatial extent for a-PMMA are shown in Supplementary Information (SI) Fig. S2. To better quantify the characteristics of these modes, we created a new descriptor that measures the spatial extension of a mode, termed the mode spatial extent (MSE). MSE measures the size of the spatial region over which participating atoms are distributed, using a unit of length. MSE takes both the eigenvectors and the corresponding atom coordinates into consideration, while PR only measures what fraction of the atoms contain the mode energy. Therefore, MSE describes whether the excited atoms of one mode are spreading over the entire chain/simulation domain or spatially confined to a small region e.g. a

functional group. For each mode, the atomic vibrational amplitude profile with respect to spatial coordinate x (and y, z) is fitted as a two-term Gaussian ($f(x) = a_1 e^{-\left(\frac{x-b_1}{c_1}\right)^2} + a_2 e^{-\left(\frac{x-b_2}{c_2}\right)^2}$), where $f(x)$ is the vibrational amplitude at position x , and a, b are constants. The width of the mode in x direction is calculated as $(c_1 + c_2)/2$. The MSE of one mode is the average of the fitted width in three directions. A Gaussian was chosen based on inspection of the modes, but different trial functions other than a two-term Gaussian were also used and the resulting MSE was not sensitive to the choice of trial function. MSE in essence attempts to quantify how large a mode is, by measuring the size of the region to the participating atoms occupy. Note that the calculation of MSE involves fitting a two-term Gaussian, which might yield values greater than the simulation domain. This is reasonable as in the ideal case the MSE of a periodic mode is infinite. The details of MSE calculation can be found in SI.

In the ensuing analysis, MSE is used as a complimentary descriptor to PR for characterization of mode localization. It should be noted that there are no strict thresholds for either PR or MSE in mode characterization. For PR, the value 0.2 have been suggested for identifying locons,^{44,45,79,84} and 0.1 is used in this study as a more conservative PR cut-off in identification of locons. For MSE, in cases where the MSE is on the order of the atomic spacing or lower (~ 1 Å), the mode can be considered highly spatially localized, while a MSE of 10 Å is closer to the order of the dimensions of the supercell in this work. In Fig. S2, several modes are shown that have low PR (~ 0.01) yet large MSE (~ 100 Å) in a-PMMA. Despite the way the eigenvectors appear upon inspection, the cumulative DOS vs. MSE in Fig. 2c confirms that fact that the majority of modes are in fact spatially localized, with a MSE < 10 Å. For a-PMMA, a-PS, and a-PVC, the fractions of modes with MSE < 10 Å are 75%, 89%, and 89%, respectively.

In Fig. 3, we show the MSE and PR for all three polymers. While generally modes with smaller PR will have a smaller MSE, these results also show that modes with extremely low PR can still have a relatively large MSE, which visually corresponds to some degree of spreading as shown in the examples in Fig. S2. If we combine these two measures, it suggests that there could be a significant amount of locons in amorphous polymers involving atoms over an extended spatial region. In the case of locons (PR < 0.1) in a-PMMA, the MSE calculations indicate 25% of these modes are spatially spread over more than 10 Å (MSE > 10 Å) and 47% of these modes are partially spread with MSE values between 1 -10 Å. Importantly, the results for a-PS and a-PVC are similar, which suggests this may be a general feature of amorphous polymers. For locons in a-PS, 11% have an MSE greater than 10 Å, and 41% have an MSE between 1 and 10 Å. For locons in a-PVC, 14% have an MSE greater than 10 Å, and 58% have an MSE between 1 and 10 Å.

Interestingly, both descriptors offer insights. If a few atoms have eigenvectors much larger than the remainder of the atoms in the supercell, it leads to a low PR. However, if those atoms are separated by a significant distance and/or the remaining atoms exhibit small participation in the mode over a larger region, it can result in a larger MSE. It seems reasonable to postulate that similar results might also be observed for other thermoplastics, and maybe even thermosets. Nonetheless, more materials need to be

studied to confirm or deny this hypothesis. Regardless, the difference between the two descriptors is an indication that perhaps “locons” (specifically, modes with PR < 0.1 and high MSE > 10 Å) may be able to interact with other modes more than previously thought, thereby – contrary to the findings of many previous studies,^{47–50} playing an important role in thermal transport.

Figure 3| Scattering of modes in coordinates of their PR and MSE. The panel a, b, and c shows the modes in a-PMMA, a-PS, and a-PVC respectively. The grayscale shows the value of modal thermal conductivity in units of $\text{W m}^{-1} \text{K}^{-1}$. (Colors online)

The large degree of localization observed in amorphous polymers prompted the hypothesis that it may be possible that modes localize onto individual chains where there

is more homogeneity in bond strength. We therefore evaluated a polymer chain participation ratio (PCPR) as a measure of the involvement of each individual chain in each mode. The definition of PCPR can be found in SI, as it contains a selective summation for PR, that is limited to the atoms on a given polymer chain. Thus, for each polymer chain in a simulation domain, there will be a PCPR value measuring its involvement in a given normal mode. Consequently, we assign M different PCPR values, $PCPR_1, PCPR_2, \dots PCPR_M$, for each individual mode, where M is the number of polymer chains in the supercell. The subscripts, however, do not denote which specific chain a mode is localized onto. Instead, since all of the chains are the same i.e., chemically indistinguishable, the values of the subscripts are sorted by decreasing value. In this way, the $PCPR_1$ value for a given mode will always correspond to the chain that has the largest PCPR for that given mode. The $PCPR_2$ is therefore by definition always smaller than the $PCPR_1$, and it represents the extent of participation the mode has on whichever chain has the 2nd highest participation. The PCPR values then continue in decreasing order of participation, with $PCPR_M$ being the smallest. The PCPR spectrums of three polymers are provided in the SI (see Fig. S3).

With this definition for PCPR, the ratio $\beta_2 = PCPR_2/PCPR_1$ becomes an important quantity, because it describes the extent to which a mode is localized onto more than one chain. For example, when β_2 is less than 0.1, it indicates that at least 53% of the energy of the mode is confined to one polymer chain. Here, it should be noted that there is a somewhat complex relationship between the value of β_2 and the amount of energy confined to a single chain, as explained in the SI. However, most modes with $\beta_2 < 0.1$ have more than 90% of their energy localized onto a single chain. Similarly, the ratio β_k will tell whether there are k chains involved in this mode. The β_2 spectrums of three polymers are shown in Fig. S3d in SI, which suggests a large number of modes have a small β_2 . To better understand this, we show the cumulative DOS with respect to β_2 in Fig. 2d. If we take $\beta_2 < 0.1$, to mean a mode is primarily localized onto a single chain, then for a-PMMA, 52% of the localized modes are localized onto a single chain, and this fraction is 75% for a-PS and 74% for a-PVC. This is a somewhat surprising result, as it shows a strong tendency for modes to localize onto individual chains, which is a special feature of polymers. The strength of covalent bonds are usually three orders of magnitude higher than that of van der Waals interactions. The disparity in bond strength for inter vs. intra chain interactions is rather unique to polymers and possibly some 2D materials (e.g., graphite, MoS₂, W₂Se, Hexagonal BN etc.). Beside, individual chains have repeating units. Such repeating units together with strong bonds likely give rise to strong localization onto an individual chain. It is therefore a reasonable hypothesis that heat flux will primarily circulate within those homogenous substructures, e.g. polymer chains, and barely transmitted among those substructures.

Conceptually, the homogeneous bond strength and repeating units within an individual chain creates entries within the dynamical matrix of similar magnitude, and presumably the chain/string of atoms that are interconnected with covalent bonds, leads to a natural tendency to delocalize over those bonds for some modes. Conversely, when one encounters the ends of the polymer chains, or monomer's lateral boundaries, there is a discontinuity in bond strength as the next nearest neighboring atoms experience van der

1 Waals or electrostatic interactions, which are much weaker. It then stands to reason that
2 this large change in the bond strength tends to terminate the delocalization of modes, as
3 it becomes difficult for non-covalently bonded, yet neighboring atoms, to vibrate
4 together/collectively at the same high frequencies as those associated with the covalently
5 bonded atoms on a different chain. This observation provides intuition on how heat
6 conduction through amorphous polymers occurs. One might expect that these two groups
7 of modes, i.e., modes confined to a single chain, versus modes that are able to spread
8 across multiple chains, might exhibit different transport characteristics, as the latter
9 category are more likely to couple/share energy between among different chains. This
10 point will become clearer when we discuss thermal conductivity.

11
12 We emphasize again that a-PMMA, a-PS, and a-PVC have significantly different
13 structures i.e., the monomers are comprised of 15, 16, and 6 atoms respectively. PS is
14 the only polymer with an aromatic ring. And the polymers contain different functional
15 groups. However, the observations about the high degree of localization in these
16 polymers are consistent amongst all three and are independent of supercell size (see SI
17 - Fig. S1). Thus, we postulate that it may be also the case that most of the modes in many
18 other amorphous polymers are locons. However, it is not clear to what extent these modes
19 contribute to TC, and if they do, which classifications of modes contribute most (i.e.,
20 modes localized onto individual chains or modes delocalized over multiple chains)?
21 Conventional wisdom, based on the PGM, would suggest that localized modes in general
22 do not contribute much to thermal transport, but if they're the predominant mode type in
23 amorphous polymers, it stands to reason that they may be the dominant contributors to
24 TC, simply because they're the dominant mode type.

25 26 **Contributions to Thermal conductivity**

27
28 In Fig. 4 we show the normalized TC accumulation with respect to PR, MSE, and β_2 ,
29 based on GKMA. Fig.4a shows the locons, defined by $PR < 0.1$, contribute 82%, 95%,
30 and 98% to TC for a-PMMA, a-PS, and a-PVC respectively. Therefore, they are the
31 dominant contributors to thermal transport. This is very different than prior studies, some
32 of which have suggested that locons do not contribute significantly,^{19,21,30,35,46–50} and the
33 highest locon contributions reported by Lv & Henry,³⁵ was only 10%. Note that even
34 though locons dominate the population and hence the TC in amorphous polymers, their
35 contributions are small, yet still comparable, on a per mode basis, to the delocalized
36 modes. For example, in a-PMMA delocalized modes contribute 2 times more on a per
37 mode basis, but in a-PS and a-PVC, the delocalized modes only contribute 20% and 14%
38 more. This provides significant insight into why amorphous polymer TC is much lower
39 than that of amorphous inorganics, namely because amorphous polymers are
40 predominated by locons, which in general, are poor heat conductors. Similar observations
41 can be made using the measure of MSE as shown in Fig. 4b. Modes that are spatially
42 localized ($MSE < 10 \text{ \AA}$) contribute the majority of the TC in amorphous polymers,
43 specifically, 61%, 87%, and 88% for a-PMMA, a-PS, and a-PVC, respectively. This is
44 simply because modes with $MSE < 10 \text{ \AA}$ are the dominate type of modes in amorphous
45 polymers. On a per mode basis, their contributions are smaller yet comparable to the
46 spatially delocalized modes. Figure 4c plots thermal conductivity as a function of β_2 that

represents localized phonons spreading over two chains, and it clearly shows heat is mainly conducted by localized modes able to across chains.

Figure 4| Normalized cumulative TC with respect to modal frequency (panel a), PR (panel b), and β_2 (panel c). The vertical lines in panel a and b show the separations of locons, while the vertical line in panel c shows the separation of modes confined onto a single chain. For locons defined as modes with PR below 0.1, they contribute 82%, 95%, and 98% of the total TC in a-PMMA, a-PS, and a-PVC, respectively. (Colors online)

With this mode-resolved TC, we calculated the temperature dependent TC with quantum correction. In Fig. 5, the quantum corrected temperature dependent TC for the three polymers studied is compared with experimental values for a-PMMA,^{85–87} a-PS,^{88–90} and a-PVC.⁹¹

Figure 5] Temperature dependent TC from GKMA with quantum correction. Solid lines are calculated results, dots are experimental values reported in literatures. (Colors online)

The GKMA results show the correct qualitative trends, although there are significant quantitative discrepancies at different temperatures. The calculations underestimate the TC for α -PMMA and α -PVC, while slightly overestimate that of α -PS. We believe the reason can be attributed to a combination of the difference of polymer molecular weights (MW) and size effects. It is known that for polymers, the TC has a strong positive dependence on its MW.⁹² Due to the limitations of computational power, the MW of α -PMMA, α -PVC, and α -PS are 5,000, 1,696, and 7,813 g/mol in our simulations (every chain contains 200 repeating units), which are orders of magnitudes smaller than the MW of the common products of these polymers. Nevertheless, obtaining good quantitative agreement in temperature dependence of TC is not the main objective here, but the TC results seem to suggest that the mode level observations made in our simulation could still be meaningful and provide important insights for understanding the thermal transport in amorphous polymers.

Although delocalized modes contribute more to TC than locons on a per mode basis, interestingly, the most active modes with the highest TC contributions are strongly localized. As shown in Fig. 3, the modes with highest modal TC are more likely to be localized. It is clear that for all three polymers in study, the modes with highest modal TC appear in the regime with low PR and low MSE. Similar observations are found in the modal TC spectrums shown in SI Fig. S4, where the TC outliers are strongly localized. We summarized the average modal TC value of strongly localized modes (SLM) defined as having $PR < 0.01$ and $MSE < 3 \text{ \AA}$, versus that of other modes (non-SLM) that do not satisfy this criterion, in Table1. For all three polymers in study, the average modal TC values of SLM are found to outperform that of non-SLM.

Table 1| The number and average modal TC values of SLM with $PR < 0.01$ and $MSE < 3 \text{ \AA}$ and non-SLM modes in amorphous polymers.

	a-PMMA	a-PS	a-PVC
Fraction of SLM	42.1%	63.5%	36.0%
Avg. TC of SLM	$13.2 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$	$23.6 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$	$8.0 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$
Fraction of non-SLM	57.9%	36.5%	63.0%
Avg. TC of non-SLM	$7.4 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$	$16.4 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$	$7.8 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$
SLM/non-SLM Avg. TC ratio	176%	143.9%	107.0%

This finding suggests that there is a group of locons participating in thermal transport more actively than the others. Note that this observation is not in conflict with our previous statement that delocalized modes contribute more to thermal transport on a per mode basis. To explain what is special about these active locons, we studied how the locons are localized in polymer structures. In a-PMMA for example, we notice there are a few modes involving two chains with large ($> 10^{-5}$) PCPR₂'s and low ($< 10^{-10}$) PCPR₃'s around 50 THz, where most modes in the same frequency range are confined to a single chain, and no modes are spread across three or more chains. There are a total of 62 out of 9024 of such modes that are delocalized onto a second chain but not a third chain. Interestingly, the average magnitude of these 62 modes' TC is $18.4 \times 10^{-5} \text{ Wm}^{-1}\text{K}^{-1}$. This value is 60% higher than the average magnitude of TC for SLM with both a low PR and MSE and nearly twice the average magnitude of all mode in a-PMMA. Generally, we have found most of the locons are confined onto a single chain, as suggested by the more-than-half cumulative contribution to DOS by modes with $\beta_2 < 0.1$ in Fig. 2d. As shown in the cumulative TC contribution with respect to β_2 in Fig. 4c, however, modes confined onto a single chain only comprise less than half of the total TC, despite their populations being more than half (Fig. 2d). Even if we exclude the contributions from the minority of delocalized modes and focus on the locons, the contribution to TC from locons localized onto multiple chains (i.e., for modes with $PR < 0.1$ yet $\beta_2 > 0.1$), is still higher than the modes localized onto a single chain, as summarized in Tab. 2. The unbalanced contribution in DOS and TC suggests that the locons localized onto multiple chains contribute more than the locons localized onto a single chain.

Table 2| The cumulative DOS and TC contribution of locons localized onto multiple chains.

	a-PMMA	a-PS	a-PVC
Cumulative DOS	48.4%	24.7%	28.6%
Cumulative TC	54.2%	52.9%	29.2%

Therefore, we conclude that the modes with very large TC values are more likely to be strongly localized modes and as a result, the average TC value of the strongly localized modes (SLM) is slightly higher than other modes. And the locons that spread onto multiple chains contribute more to thermal transport than the ones confined onto single chains,

even though the later type of locons are the majority in amorphous polymers. These findings differ from the behavior of locons in other disordered materials.

Conclusions

In this work, we studied the normal modes and TC of three amorphous polymers (i.e., a-PMMA, a-PS, and a-PVC) using LD and GKMA. The results show that in all three amorphous polymers studied, locons are the predominant mode type, comprising more than 90% of the modes. GKMA results showed that even though locons in previously studied systems have exhibited negligible/small contributions, here, since they are the predominant mode type, their contributions comprise more than 80% of the TC. This shows that locons can play an important role in amorphous polymers, although their contributions are much smaller on a per mode basis, by comparison to delocalized modes. Deeper investigation of the character of locon modes showed that 10-30% still involve some participation of atoms over a large region. Such modes are still locons in the sense that their energy is concentrated on a small subset of atoms, but this energy can still be spread over a spatial region comparable to the size of the supercell (i.e., $> 10\text{\AA}$). The introduction of a new descriptor, termed the MSE facilitated quantification of the length scale over which such modes are spread.

Further modal analysis showed that a major fraction of the localized modes are localized onto a single polymer chain, as quantified by the value β_2 . This is presumed to be caused by the inhomogeneity in bond strength between intra and inter chain interactions. Calculations of β_2 for the different polymers showed that for more than half of the localized modes, greater than half of their energy was confined to a single polymer chain. The minority of locons that are nested onto multiple chains, however, have a larger average TC than the main type of locons that are localized onto a single chain, suggesting that these modes serve as bridges across the chain-chain boundaries through van der Waals interaction. Interestingly, this seems to be an important heat transport channel for amorphous polymers, even though it happens through locons.

Furthermore, the localized nature of the modes in amorphous polymers offers an explanation for why their TC is about an order of magnitude smaller than that of amorphous semiconductors. Notably, since localized mode contributions are in general smaller than that of delocalized modes, having a material with predominantly locons translates to an expectation of low TC. Thus, the results herein have provided several new insights in amorphous polymers, namely: (1) that most of the modes are locons, of which a large fraction are localized onto individual chains; (2) Strongly localized modes can still be active in thermal transport by having the highest modal TC values in amorphous polymers; (3) Although most modes are localized, the modes with the largest contributions to TC are modes that span more than one chain and conceivably serve as bridges between chains, implying that the bottleneck for transport is the weaker inter-chain interactions; (4) Amorphous polymer TC is likely lower than that of amorphous semiconductors, in general, because of the large number of locons. It then follows as a natural hypothesis that what likely causes the dramatic increase in TC that can occur with mechanical stretching of polymers, is the conversion of locons to diffusons and propagons,

which correspondingly have larger contributions on a per mode basis. It is from this perspective, that considerable follow-up work is needed to better understand the extent to which the aforementioned findings are generalizable to amorphous thermoplastics, and even possibly some thermosets.

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Contributions

F.D., B.L., and A.H. conceived the idea and supervised the work, along with G.C. F.D. and B.L. performed the simulations. All authors contributed to the analyses, discussions, and writing of the manuscript.

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