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ABSTRACT

Following recent molecular dynamic simulations [M. Dinpajooh and A. Nitzan, J. Chem. Phys. **153**, 164903 (2020)], we theoretically analyze how the phonon heat transport along a single polymer chain may be affected by varying the chain configuration. We suggest that phonon scattering controls the phonon heat conduction in strongly compressed (and tangled) chain when multiple random bends act as scattering centers for vibrational phonon modes, which results in the diffusive character of heat transport. As the chain is straightening up, the number of scatterers decreases, and the heat transport acquires nearly ballistic character. To analyze these effects, we introduce a model of a long atomic chain made out of identical atoms where some atoms are put in contact with scatterers and treat the phonon heat transfer through such a system as a multichannel scattering problem. We simulate the changes in the chain configurations by varying the number of the scatterers and mimic a gradual straightening of the chain by a gradual reducing of the number of scatterers attached to the chain atoms. It is demonstrated, in agreement with recently published simulation results, that the phonon thermal conductance shows a threshold-like transition from the limit where nearly all atoms are attached to the scatterers to the opposite limit where the scatterers vanish, which corresponds to a transition from the diffusive to the ballistic phonon transport.

I. INTRODUCTION

Lattice vibrations are the sole carriers of heat currents in insulating materials. Bulk disordered materials such as amorphous polymers and/or glasses are known to be rather poor heat conductors. Nevertheless, the phonon thermal conductance of polymer chains aligned in a crystalline form may far exceed that of their bulk counterparts.[1–4] Specific characteristics of heat transfer in one-dimensional systems including, among others, atomic, alkane, and polymer chains have inspired many works concentrated on analyzing heat conduction in such systems both experimentally[5–9] and theoretically.[10–16] Unceasing interest of the research community in these studies stems in part from the hope of introducing novel applications in nanotechnology. For example, there are grounds to believe that sole polymer chains may be employed in building thermal resistors and nanoscale energy transfer devices.[17–20]

Using molecular dynamics (MD) simulations, it was demonstrated that mechanical stress applied to an amorphous polymer may result in the enhancement of its thermal conductance.[21,22] This happens because the stress sets polymer chains along a certain direction. Similar effect occurs when a strain is applied to a sole polymer chain. As the initially crumpled chain straightens up, its thermal conductance significantly rises.[23,24] A nontrivial feature was demonstrated in the behavior of the phonon thermal conductance κ along a sole polymer chain with controlled end-to-end distance R.[24] It appears that the conductance behavior is quite different in the compressed (when the chain is crumpled) and stretched (straightened) limits, which are characterized by different values of R. At sufficiently small end-to-end distances, κ remains nearly independent on R and rapidly rises when R exceeds a certain threshold value R_0, thus indicating a transition from diffusive to increasingly ballistic phonon heat transport.

MD simulations have been successfully employed to explore transport properties of mesoscale and/or nanoscale systems. However, this method has its limitations. In some cases, MD does not provide means to gain the insight into the physical nature of primary transport mechanisms. Nonequilibrium Green's functions formalism (NEGF) and Boltzmann Transport equations (BTEs) were (and still are) employed to study heat transport through nanoscale systems.[11–13,25–30] Unfortunately, using these methods often one meets significant computational difficulties. An efficient, although heuristic, approach was first developed by Büttiker[31,32] and later successfully used to explore characteristics of electron[33–35] and phonon[11,36] transport avoiding computational problems arising when either NEGF or BTE is employed. In the present work, we use this method to model and analyze the physical mechanisms controlling the behavior of phonon thermal conductance along a long polymer chain with varying configuration.

II. MODEL AND MAIN EQUATIONS

The following analysis is based on a simple model described below. To elucidate and justify this model, we turn back to the original problem treated in an earlier work.[24] When the end-to-end distance R of the polymer chain is significantly smaller than the chain length, one cannot treat the chain as a 1D system. Due to numerous kinks and bends appearing in the crumpled chain, some parts of the latter become strongly tangled. Within the limit of small R, we may consider the whole chain as a single ball-like object. Then, we may separate out an arbitrary single atom out of this ball and treat the remaining atoms as a disordered set. We introduce a phonon bath representing random motions of these atoms. The bath may be considered as a scattering reservoir for the phonons traveling between the walls responsible for the diffusive component of the heat transport, as shown in the lower part of Fig. 1. For greater R, the crumpled chain may include several nearly straightened up pieces alternating with strongly tangled regions. Again, we assume that each of these ball-like regions can be treated as a single atom attached to a phonon bath acting as a scattering reservoir for the traveling phonons. Certainly, there may exist other kinds of scatterers for phonons such as various defects and other imperfections inherent to the chain regardless of its configuration, but we omit them from consideration assuming that the straightened up chain is free from defects and any other disorder. Accordingly, we simulate a molecule/polymer chain by a periodic insulating chain including N identical atoms with masses m and nearest neighbors harmonic interactions characterized by the force constant k. End atoms of the chain are attached to parallel walls, as shown in Fig. 1. The walls are kept at different temperatures (T_L and T_R, respectively). The heat conduction along the chain depends on these temperatures and on the chain stretching configuration. We assume that M atoms ($0 \le M \le N$) are put in contact with scattering reservoirs. Within the Büttiker's model, the physical nature of scatterers is not specified. These reservoirs are solely introduced as technical instruments intended for simulation of dephasing centers. In the considered case, these centers originate from the presence of tangled regions in the compressed polymer chain. The strong chain compression is represented by the case when M takes on values close to N, indicating that nearly all chain atoms are attached to the scatterers. When the chain is straightening up, M reduces and approaches zero for the extended chain.

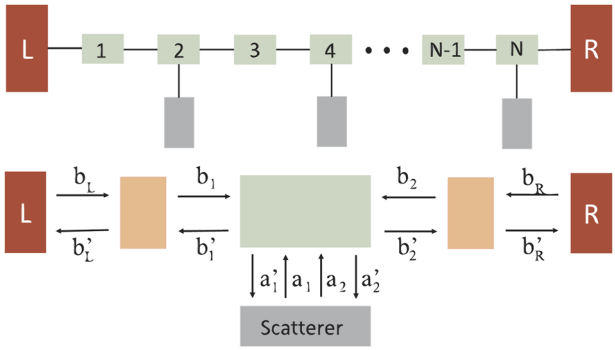

FIG. 1. Top: Schematics of the chosen model for the chain including N atoms placed between two walls. Some atoms represented by green squares are coupled to scattering phonon baths shown as gray squares. Bottom: A single atom placed between the walls and attached to a scattering reservoir. The phonon amplitudes b_L, b_R coming from the left/right wall are partly reflected back to the walls as amplitudes b'_L, b'_R and partly transmitted to the atom as b_1 and b_2. Moreover, amplitudes b'_1 and b'_2 are reflected from the atom, and the amplitudes a_1, a'_1, a_2, a'_2 represent phonon exchange between the atom and the scattering reservoir.

First, we consider ballistic phonon transport along the chain ($M = 0$). The Hamiltonian describing the chain may be written in the form[10]

$$H = \sum_{i=1}^{N} \frac{p_i^2}{m} + \frac{k}{2}\sum_{i=1}^{N-1} (x_i - x_{i+1})^2 + \frac{k}{2}(x_1^2 + x_N^2), \tag{1}$$

where p_i and x_i are the linear momentum and the displacement of the i-th atom in the chain. Atoms' motions are controlled by $N \times N$ dynamical matrix $\mathbf{K}$ whose off-diagonal elements $K_{i,j} = \frac{\partial^2 H}{\partial x_i \partial x_j}$ and diagonal elements are given by the expressions $K_{i,i} = -\sum_{i \neq j} K_{i,j}$.[11] As follows from the adopted Hamiltonian, nonzero matrix elements of the dynamical matrix are $K_{i,i+1} = K_{i+1,i} = -k$ $(1 \le i \le N-1)$ and $K_{i,i} = -2k$ $(1 \le i \le N)$.

The retarded Green's function for the chain $\mathbf{G}^{(r)}(\omega)$ equals[13]

$$\mathbf{G}^{(r)}(\omega) = \left(\omega^2 \mathbf{I} + \tilde{\mathbf{K}} + \frac{i}{2}\mathbf{\Gamma}^L(\omega) + \frac{i}{2}\mathbf{\Gamma}^R(\omega)\right)^{-1}. \tag{2}$$

Here, $\mathbf{I}$ is an $N \times N$ unit matrix, $\tilde{\mathbf{K}} = \frac{1}{m}\mathbf{K}$, and matrices $\mathbf{\Gamma}^{L,R}(\omega) = -2\Im\mathbf{\Sigma}^{L,R}(\omega)$ are self-energy terms describing coupling of the chain end atoms to the left and right walls, respectively. Each of these $N \times N$ matrices has a single nonzero element: $\Gamma^L_{1,1}(\omega) = \gamma^L(\omega)$, $\Gamma^R_{N,N}(\omega) = \gamma^R(\omega)$. In further analysis, we treat the walls as identical Ohmic phonon baths. Then, we may approximate $\gamma^{L,R}(\omega) \equiv \gamma(\omega) \approx \eta\omega_D\omega \exp\left(-\frac{\omega}{\omega_D}\right)$,[12,37–39] ω_D being the analog of Debye frequency for these baths, which controls the position of maximum of their phonon spectral densities. The dimensionless parameter η characterizes the coupling strength between the chain end atoms and the walls and strongly influences heat conduction.

The expression for ballistic phonon transmission may be presented in the following form: $\Xi_b = \mathrm{Tr}\left[\mathbf{\Gamma}^L\mathbf{G}^{[r]}\mathbf{\Gamma}^R\mathbf{G}^{(r)\dagger}\right]$.[11] Within the present model, this expression may be reduced to

$$\Xi_b = \gamma^2(\omega)\left|G^{(r)}_{1,N}(\omega)\right|^2. \tag{3}$$

Here,

$$G^{(r)}_{1,N}(\omega) = \frac{4\zeta\Omega^{2(N-1)}}{(\mu+\zeta)^{N-1}(\mu+\zeta+2i\gamma(\omega))^2-(\mu-\zeta)^{N-1}(\mu-\zeta+2i\gamma(\omega))^2} \tag{4}$$

where $\mu = \omega^2 - \Omega^2$, $\zeta = \sqrt{\lambda^2-\Omega^4}$, and $\Omega = \sqrt{\frac{2k}{m}}$. Note that Eq. (4) resembles the known expression for the electron Green's function associated with propagation of electrons along a periodical chain of identical sites with nearest neighbors coupling.[40] The resemblance originates from similarities in the form of the relevant Green's functions.

We first explore the effect of scatterers on the heat conduction in a simple case when a single atom treated as a harmonic oscillator is attached to the left and right walls and put in contact with a scattering phonon bath, as shown in Fig. 1. Phonon amplitudes ($b_{L,R}$) are emitted from the left/right wall and amplitudes ($b'_{L,R}$) are reflected back to the walls. Moreover, we introduce the incident and outgoing amplitudes for the atom ($b_{1,2}$ and $b'_{1,2}$, respectively) and the amplitudes a_1, a'_1, a_2, a'_2 corresponding to phonon exchange between the atom and the scattering reservoir. The outgoing amplitudes b'_L, b'_R, a'_1, a'_2 are related to the incident ones b_L, b_R, a_1, a_2 by 4×4 matrix $\mathbf{S}^{(1)}$,

$$\begin{bmatrix} b'_L \\ b'_R \\ a'_1 \\ a'_2 \end{bmatrix} = \mathbf{S}^{(1)} \begin{bmatrix} b_L \\ b_R \\ a_1 \\ a_2 \end{bmatrix}. \tag{5}$$

Expressions for matrix elements of $\mathbf{S}^{(1)}$ are derived in Appendix A. Note that $\mathbf{S}^{(1)}$ has the same form as the scattering matrix derived for the case of electron transport through a single-site bridge linking two leads.[34,35] Accordingly, outgoing energy fluxes may be presented as linear combinations of incoming fluxes,

$$\begin{bmatrix} J'_L \\ J'_R \\ J'_1 \\ J'_2 \end{bmatrix} = \mathbf{T}^{(1)} \begin{bmatrix} J_L \\ J_R \\ J_1 \\ J_2 \end{bmatrix}, \tag{6}$$

where $T^{(1)}_{k,j} = \left|S^{(1)}_{k,j}\right|^2$, $J'_{L,R}$ are the heat fluxes outgoing from the atom to the left/right wall, respectively, $J_{L,R}$ are fluxes coming to the atom from the left/right and J'_1, J_1, J'_2, J_2 appear due to the phonons transferred between the atom and the scatterer. Supposing that heat transport is directed to the right ($J_R = 0$) and the net heat is not coming to/from the scattering reservoir to the atom, we may rearrange Eq. (6) to get the expression for the phonon transmission $\Xi = \frac{J'_R}{J_L}$,

$$\Xi = \Xi_1 + \Xi_2 = \alpha^2\frac{t_L^2t_R^2}{(1+\alpha^2|r_Lr_R|)^2} + \frac{1}{2}\beta^2\frac{t_Lt_R}{1+\alpha^2|r_Lr_R|}. \tag{7}$$

Here, coefficients $t_{L,R}$ describe the transmission between the left/right wall and the atom, $r_{L,R} = i\sqrt{1-t^2_{L,R}}$, the dimensionless parameter α^2 determines the probability for a phonon to avoid scattering, and $\beta^2 = 1-\alpha^2$. Accordingly, the terms Ξ_1 and Ξ_2 denote the ballistic and diffusive components in the phonon transmission. In the case of ballistic transport ($\alpha = 1$), the second term in this expression vanishes. In the diffusive limit $\alpha = 0$, the transmission Ξ is reduced to Ξ_2. Within the Büttiker approach, α is treated as a phenomenological parameter. To find a suitable approximation for this parameter, we must turn to the specifics of the considered problem.

Assuming that the walls are kept at temperatures T_L and T_R and stipulating that there is no heat exchange between the atom and the scatterer, we may determine the temperature $\tilde{T}$ associated with the atom. The corresponding expression is derived in Appendix B. It is shown that in the case $t_L = t_R$ $\tilde{T} = \frac{1}{2}(T_L + T_R)$. In a general case ($t_L \neq t_R$), $\tilde{T}$ is shifted from this position.

In further analysis, we assume that the phonon bath acting as a scatterer is characterized by a continuous spectral function. Particular form of this function may be found based on MD simulations but to qualitatively study the processes of phonon scattering, we may employ a commonly used approximation treating the scatterer as an Ohmic phonon bath whose coupling to the vibrating atom is described by a self-energy term $\delta(\omega)$ similar to that characterizing the coupling of the atom to the walls: $\delta(\omega) \approx \lambda\omega_{Ds}\omega\exp\left(-\frac{\omega}{\omega_{Ds}}\right)$. The value of parameter α is controlled by self-energy terms $\gamma(\omega)$ and $\delta(\omega)$, which makes α dependent on the phonon frequency. It may happen that the Debye frequencies ω_D and ω_{Ds} strongly differ. For example, in the case of metallic walls at the ends of the polymer chain,[41] ω_D could be far below ω_{Ds}. As a result, within the long wavelength limit, $\gamma(\omega)$ would predominate over $\delta(\omega)$ and the effect of scattering on the phonon heat conduction could vanish. Here, however, we concentrate on the situation when ω_D and ω_{DS} are close, so we may apply our model to analyze the interplay between diffusive and ballistic transport. Furthermore, we ignore the difference between ω_D and ω_{Ds} for simplicity. It is natural to expect the phonon heat transport to be nearly ballistic provided that the atom is much stronger coupled to the walls than to the scatterer ($\eta \gg \lambda$) and nearly diffusive in the opposite limit ($\eta \ll \lambda$). Within these limits, α takes on values close to 1 and 0, respectively. Keeping this in mind, we may put forward a simple approximation: $\alpha \approx \frac{\eta}{\eta+\lambda}$, which elucidates its physical meaning.

Now, we turn to the case when the chain includes an arbitrary number N of atoms. In this case, the scattering matrix $\mathbf{S}^{(N)}$ has dimensions $2N+2\times2N+2$. Its elements depend on parameters α_i, β_i ($1 \le N$), which may take on different values for different atoms. Specifically, $\alpha_i = 0$ for all atoms detached from the scatterers.

In Appendix A, we derive recursive relations matching up matrix elements of $\mathbf{S}^{(N-1)}$ and of $\mathbf{S}^{(N)}$. The phonon transmission

accepts the form identical to that of electron transmission through a multisite one-dimensional bridge derived in earlier works,[33,34,42]

$$\Xi = \Xi_1 + \Xi_2 = T_{2,1}^{(N)} + \sum_{i,j=1}^{N} Q_i^{(1)} \left(\mathbf{W}^{-1}\right)_{i,j} Q_j^{(2)}. \tag{8}$$

Here,

$$Q_i^{(1)} = T_{2i+1,1}^{(N)} + T_{2i+2,1}^{(N)}; \qquad Q_j^{(2)} = T_{2,2j+1}^{(N)} + T_{2,2j+2}^{(N)}; \tag{9}$$

W is an $N \times N$ matrix whose elements are given by

$$W_{i,j} = (2 - R_{i,i})\delta_{i,j} - P_{i,j}(1 - \delta_{i,j}), \tag{10}$$

where

$$R_{i,i} = T_{2i+1,2i+1}^{(N)} + T_{2i+2,2i+2}^{(N)} + 2T_{2i+1,2i+2}^{(N)}; \tag{11}$$

$$P_{i,i} = T_{2i+1,2j+1}^{(N)} + T_{2i+1,2j+2}^{(N)} + T_{2i+2,2j+1}^{(N)} + T_{2i+2,2j+2}^{(N)}; \tag{12}$$

$T_{l,m}^{(N)} = \left|S_{l,m}^{(N)}\right|^2$ $(1 \le l, m \le 2N + 2)$ and $\delta_{i,j}$ is the Kronecker symbol. Again, the term Ξ_1 predominates when the effect of phonon scattering on heat conduction is insignificant. In the limit where all α_i approach 1, the second term in Eq. (8) disappears, reducing Ξ to Ξ_1. We stress that these results are derived omitting all anharmonic terms not only from the Hamiltonian Eq. (1) but from the expression for the phonon transmission Eq. (8) as well. As shown below, this harmonic approximation leads to the ballistic character of phonon transport along a stretched chain. In principle, we may retain the diffusive contribution to heat conductance along the stretched chain by including anharmonic terms into the chain Hamiltonian, but such a case was not considered in the present work. Note that temperature profile along the chain is also controlled by the matrix $\mathbf{T}^{(N)}$ as shown in Appendix B.

To clarify the physical meaning of the coefficients $t_{L,R}$, we consider the limit when scattering effects are omitted. In this limit, the phonon transmission does not depend on N and may be presented as

$$\Xi \equiv \Xi_b = \frac{t_L^2 t_R^2}{(2 - t_L t_R)^2}. \tag{13}$$

This result should agree with the expression for $\Xi_b(\omega)$ given by Eq. (3). Assuming that $t_L = t_R = t$ and comparing Eqs. (3) and (14), we get the relationship $t^2 = 2\frac{\sqrt{\Xi_b(\omega)}}{(1+\sqrt{\Xi_b(\omega)})}$, which enables us to express matrix elements $T_{l,m}^{(N)}$ in terms of the Green's function for the chain given by Eq. (4).

The heat current flowing along the chain provided that the walls are kept at different temperatures may be computed based on phonon transmission as follows:[12,13,38]

$$I = \frac{\hbar}{2\pi}\int_0^\infty d\omega \Xi(\omega)(n_L - n_R). \tag{14}$$

In this expression, $n_{L,R} = \left(\exp\left(\frac{\hbar\omega}{k_B T_{L,R}}\right) - 1\right)^{-1}$ are Bose–Einstein distribution functions for the phonons in the walls and k_B is the Boltzmann constant. We suppose that $T_L > T_R$, so the heat current flows to the right. When the difference between the wall temperatures, ΔT, is small $(\Delta T \ll T_{L,R})$, the phonon heat conductance $\kappa(T) = \frac{J}{\Delta T}$ may be approximated by

$$\kappa(T) = \frac{\hbar^2}{2\pi T^2}\int_0^\infty d\omega \omega^2 \Xi(\omega) \frac{\exp\left(\frac{\hbar\omega}{k_B T}\right)}{\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2}, \tag{15}$$

where $T = \frac{1}{2}(T_L + T_R)$. Our further analysis is based on this expression.

III. RESULTS AND DISCUSSION

We start from exploring phonon heat conduction in the case when the effects of scattering could be neglected $(M = 0)$. In this case, the phonon transmission $\Xi(\omega)$ shows several Lorentzian-type

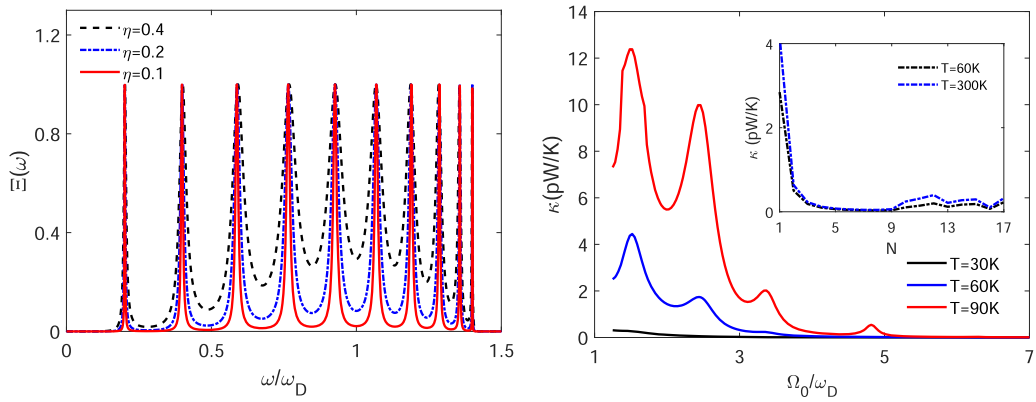

FIG. 2. Phonon transmission for the ballistic transport through a chain made out of identical atoms (left) and dependencies of the ballistic phonon thermal conductance on the elastic properties of the chain plotted at several values of temperature (right). Curves are plotted at $N = 10$, $\omega_D = 0.04$ eV; $\Omega_0 = \sqrt{\frac{k}{m}} = 0.03$ eV, $\eta = 5$ (right panel). The inset in the right panel illustrates the dependencies of the phonon heat conduction κ on the chain length at different temperatures.

resonances occurring at the eigenfrequencies of the chain (ω_i) corresponding to vibrational modes. This is illustrated in Fig. 2. Note that the transmission line shapes may be noticeably affected by the coupling of vibrational phonons to the phonon baths associated with the walls.

Characteristics of heat transport along the chain depend on atom mass m and the elastic constant k. These material parameters along with the number of atoms N determine the eigenfrequencies ω_i. Accordingly, phonon conductance depends on $\Omega_0 = \sqrt{\frac{k}{m}}$. When Ω_0 varies, the eigenfrequencies appear one by one within the frequency range around ω_D where $\gamma(\omega)$ takes on nonzero values, thus giving rise to a sequence of peaks in the phonon conductance superimposed upon a smoothly fading background, as shown in Fig. 2 (right panel). Note that for sufficiently long chains ($N \geq 3$), the phonon heat conductance remains nearly independent of the chain length, in agreement with the corresponding results of earlier works.[10,12]

The nature of heat conduction in solids was theoretically studied in several works.[43–47] It was established that in crystalline solids, ballistic transport is associated with independent motion of phonons whereas diffusive transport results from strong phonon scattering. This simple description cannot be applied to disordered solids and glasses where the standard phonon gas model fails and heat transfer should be described as a motion of specific vibrational modes that are neither plane-wave-like nor localized. Interplay between various mechanisms controlling heat conductance in one-dimensional systems has also been discussed in several works.[23,24,48]

We analyze this issue starting from the case where a single atom treated as a harmonic oscillator is sandwiched between the walls ($N = 1$) and attached to a scatterer ($M = 1$). Results are shown in Fig. 3. We see that when coupling between the atom and the scattering reservoir is weak and the heat transport is nearly ballistic, the term $\Xi_1(\omega)$ gives a predominating contribution to phonon transmission whereas the term $\Xi_2(\omega)$ brings only a small correction. The relation between $\Xi_1(\omega)$ and $\Xi_2(\omega)$ changes when the coupling of the atom to the scatterer strengthens and the diffusive component in the heat transport becomes more pronounced. In the limit of strong coupling ($\lambda \ll \eta$; $\alpha \ll 1$), the probability for a phonon to be scattered (β^2) approaches 1. In this limit, the "diffusive" contribution to the transmission $\Xi_2(\omega)$ exceeds the "ballistic" one, indicating the diffusive nature of heat conduction. In Fig. 3, we also show "diffusive" and "ballistic" components of the phonon transmission κ_1 and κ_2 along with the total transmission $\kappa = \kappa_1 + \kappa_2$. Note that its behavior depends on ω_D. Varying ω_D, we change the relationship between the diffusive and ballistic contributions to heat transport. As a result, κ becomes either an increasing or decreasing function of the parameter α.

Now, we consider the chain of N atoms assuming that M out of N atoms are put in weak contact with scattering reservoirs. For simplicity, we assume that each scatterer attached to an atom is coupled to it with the same strength λ ($\lambda \ll \eta$). Although each scatterer by itself cannot significantly influence heat transport, their combined effect gets stronger as their number increases. This situation is illustrated in the left panel of Fig. 4 for a short chain ($N = 3$). Again, in the ballistic limit ($M = 0$), $\Xi_1(\omega)$ takes on maximum values and $\Xi_2(\omega)$ vanishes. As the number of attached scatterers rises, the "nearly ballistic" contribution to phonon transmission diminishes whereas the "diffusive" contribution enhances.

These results help to explain the phonon conductance dependencies on the relative number of atoms $\left(\frac{M}{N}\right)$ in contact with the scatterers displayed in the right panel of Fig. 4. When sufficient number of atoms contact the scatterers $\left(\frac{M}{N} > \frac{1}{2}\right)$, the "diffusive" contribution to heat conduction strongly exceeds the "nearly elastic" contribution and controls heat transport along the chain. As the ratio $\frac{M}{N}$ decreases below a certain value, the effect of scatterers sharply reduces. The diffusive component rapidly approaches zero and the transport becomes nearly ballistic. Thus, we conclude that the predominating transport mechanism changes when the relative number of attached scatterers falls below some threshold value. The effect is more pronounced in longer atomic chains. It is worth mentioning that in the ballistic limit, phonon conductance takes on the same value regardless of the chain length, thus confirming the results reported in earlier works.[10,12] Moreover, the effect is sensitive to the coupling between the chain end atoms and the walls as well as to those between atoms, as shown in Fig. 5, and

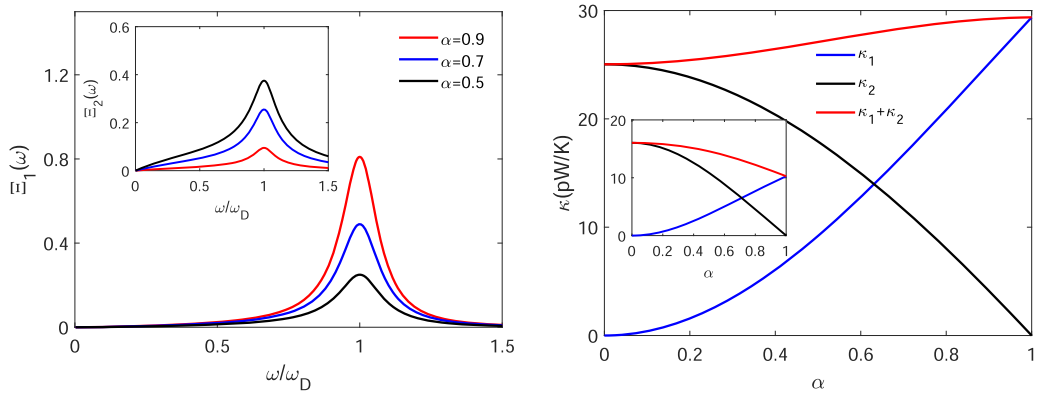

FIG. 3. Left panel: "Ballistic" $\Xi_1(\omega)$ (main body) and "diffusive" $\Xi_2(\omega)$ (inset) contributions to phonon transmission computed for $N = M = 1$, $\omega_D = 0.04$ eV, $\Omega_0 = 0.02$ eV, $\eta = 0.4$. Right panel: "Ballistic" κ_1 and "diffusive" κ_2 contributions to heat conduction computed for $N = M = 1$ assuming that $\omega_D = 0.08$ (main body) and $\omega_D = 0.04$ eV (inset) at $T = 120$ K. The remaining parameters take on the same values as in the left panel.

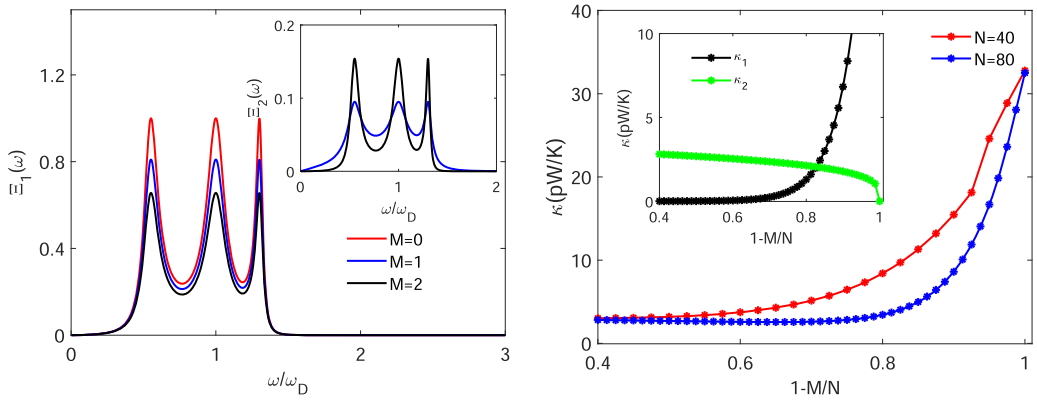

FIG. 4. Left panel: Contributions $\Xi_1(\omega)$ (main body) and $\Xi_2(\omega)$ (inset) to the phonon transmission computed for $N = 3$ and several numbers of scatterers weakly coupled to the atoms. Right panel: Dependencies of phonon conductance through long chains on the number of scatterers M for two different chain lengths. Inset shows contributions to phonon conductance originating from $\Xi_1(\omega)$ and $\Xi_2(\omega)$ for the chain of 80 atoms. Curves are plotted assuming that $\omega_D = 0.04$ eV, $\Omega_0 = 0.02$ eV, $\eta = 0.4$, $\lambda = 0.11$, and $T = 120$ K (right panel).

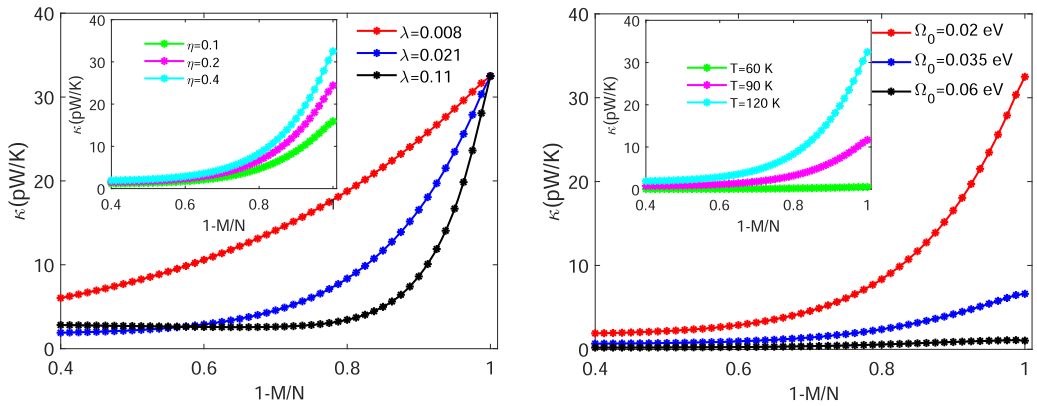

FIG. 5. Heat conduction of an $N = 80$ atom chain plotted as a function of the fraction of scatterers at $T = 120$ K, $\omega_D = 0.04$ eV, $\Omega_0 = 0.02$ eV, $\eta = 0.4$, $\lambda = 0.021$ (insets). Left panel: Effect of coupling of chain atoms to the scatterers (main body) and to the phonon baths associated with the walls (inset) on the phonon heat conductance. Right panel: Effect of material parameters of the chain (main body) and temperature (inset) on the phonon conductance.

is consistent with the MD simulation results of Ref. 24. This is an obvious consequence of the part taken by phonon baths in controlling characteristics of the heat conduction along the chains. The effect of temperature originates from temperature dependencies of Bose–Einstein distribution functions appearing in the expression for heat current. However, these factors do not give rise to qualitative changes in heat conduction.

IV. CONCLUSIONS

The present work was motivated by MD based calculations of phonon thermal conductance along single polymer chains whose configurations were varied by mechanical strain.[24] It was shown that when an initially compressed chain is straightened by a mechanical strain, a threshold-like configuration transition from the diffusive to the ballistic phonon transport occurs. To explain this peculiar behavior of phonon conductance, it was suggested[24] that random bends formed in the compressed chain may act as scattering centers for phonons. When the chain end-to-end distance R is small, the chain is a tangle of randomly distributed atoms. Many of them interact not only with their nearest neighbors but with other atoms located nearby due to the presence of multiple bends. When R increases, the chain untangles and the number of scattering centers gradually fades away, thus reducing their effect on phonon transport.

To better visualize this process, we employ a model simulating a single polymer chain or a long molecule by an atomic chain including N atoms with nearest neighbor interactions placed in between two walls. We mimic the wire compression by introducing M scattering phonon reservoirs attached to a few atoms $(M \leq N)$. Moreover, we assume that the coupling between a single atom and the attached scatterer is weak $(\lambda \ll \eta)$ whereas their combined effect on the heat transport may be significant provided that $M \sim N$. The chain untangling resulting from its stretching is simulated by reducing the number of scatterers. As long as the chain remains highly disordered and the relative number of scatterers $\left(\frac{M}{N}\right)$ is close to 1, the diffusive transport mechanism predominates, making the heat

conductance almost insensitive to $\left(\frac{M}{N}\right)$ value. However, when the chain straightens up and fewer scatterers remain, a transition from diffusive to nearly ballistic transport occurs. In sufficiently long chains, the transition shows a threshold-like character. Thus, the model gives means to reproduce and explain the heat conduction behavior earlier predicted based on MD simulations.[24]

The proposed explanation may need further development and improvement in view of the analysis of heat transfer in disordered solids and/or glasses, which suggests that the diffusive nature of phonon transport in such materials may originate from more complex mechanisms.[43–47] As mentioned before, for many amorphous systems thermal transport is carried by specific vibrational modes (called diffusons) that are neither plane-wave-like nor localized. Modes of this nature have been found for perfluoronated alkanes.[48] Perhaps, similar modes could appear in crumpled polymer chains and significantly affect the heat conduction. This possibility as well as the effect of anharmonicities and the case when Debye frequencies of the walls and those of the scatterers strongly differ[41] could be a subject of future studies.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Natalya A. Zimbovskaya: Formal analysis (equal); Writing – original draft (lead). **Abraham Nitzan**: Conceptualization (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

APPENDIX A: EXPRESSIONS FOR THE SCATTERING MATRIX ELEMENTS

To derive the expression for matrix **S**, we start from the case when a single atom represented by a harmonic oscillator is placed between the walls. The relationships between the amplitudes b_L, b'_L and b_1, b'_1 and between the amplitudes b_2, b'_2 and b_R, b'_R corresponding to the phonon transfer from the left wall to the atom and from the atom to the right wall shown in Fig. 1 could be presented as follows:

$$\begin{bmatrix} b_1 \\ b'_1 \end{bmatrix} = \frac{1}{t_L}\begin{bmatrix} 1 & -r_L \\ r_L & 1 \end{bmatrix}\begin{bmatrix} b_L \\ b'_l \end{bmatrix}; \tag{A1}$$

$$\begin{bmatrix} b'_R \\ b_R \end{bmatrix} = \frac{1}{t_R}\begin{bmatrix} 1 & -r_R \\ r_R & 1 \end{bmatrix}\begin{bmatrix} b'_2 \\ b_2 \end{bmatrix}. \tag{A2}$$

Here, the coefficients $t_{L,R}$ describe the effect of driving the atom by the phonon mode coming from the left/right and $r_{L,R} = i\sqrt{1 - t^2_{L,R}}$.

If the atom is put in contact with a scatterer, the outgoing amplitudes from the scatterer amplitudes b'_1, b'_2, a'_1, a'_2 are related to the incoming amplitudes b_1, b_2, a_1, a_2 (see Fig. 1) by the 4×4 matrix[32]

$$\begin{bmatrix} b'_1 \\ b'_2 \\ a'_1 \\ a'_2 \end{bmatrix} = \begin{bmatrix} 0 & \alpha & \beta & 0 \\ \alpha & 0 & 0 & \beta \\ \beta & 0 & 0 & -\alpha \\ 0 & \beta & -\alpha & 0 \end{bmatrix}\begin{bmatrix} b_1 \\ b_2 \\ a_1 \\ a_2 \end{bmatrix}, \tag{A3}$$

where the dimensionless parameter $\alpha = \sqrt{1 - \beta^2}$ gives the probability for the transferred phonon to avoid contact with the scatterer. Using Eqs. (A1) and (A2), we eliminate the amplitudes b_1, b_2, b'_1, b'_2 from Eq. (A3) and get the relationship

$$\begin{bmatrix} b'_L \\ b'_R \\ a'_1 \\ a'_2 \end{bmatrix} = \mathbf{S}^{(1)}\begin{bmatrix} b_L \\ b_R \\ a_1 \\ a_2 \end{bmatrix}. \tag{A4}$$

In this expression, the 4×4 scattering matrix $\mathbf{S}^{(1)}$ has the form[35]

$$Z^{(1)}\mathbf{S}^{(1)} = \begin{bmatrix} -r_L - \alpha^2 r_R & \alpha t_L t_R & \beta t_L & -\alpha\beta t_L r_R \\ \alpha t_L t_R & -r_R - \alpha^2 r_L & -\alpha\beta r_L t_R & \beta t_R \\ \beta t_L & -\alpha\beta r_L t_R & -\beta^2 r_L & -\alpha r_L r_R + \alpha \\ -\alpha\beta t_L r_R & \beta t_R & -\alpha r_L r_R + \alpha & -\beta^2 r_R \end{bmatrix}, \tag{A5}$$

where $Z^{(1)} = 1 - \alpha^2 r_L r_R$.

Now, we derive recursive relations that should be used to find the expression for the scattering matrix $\mathbf{S}^{(N)}$ corresponding to the chain including N atoms following the same way as was used in the case of incoherent electron transport along a multisite bridge.[34,35] The matrix $\mathbf{S}^{(N)}$ has $2N + 2 \times 2N + 2$ dimensions and its elements depend on parameters α_i, β_i $(1 \le i \le N)$. To bring into correlation the scattering matrices $\mathbf{S}^{(N-1)}$ and $\mathbf{S}^{(N)}$, we split the considered system into two parts. The first subsystem includes the left wall and $N - 1$ atoms and the second one includes a single extra atom at the

right end of the chain and the right wall. The relationship between outgoing and incoming amplitudes for this subsystem has the form

$$\begin{bmatrix} b'_L \\ b'_N \\ a'_1 \\ a'_2 \\ \vdots \\ a'_{2N-1} \\ a'_{2N} \end{bmatrix} = \tilde{\mathbf{S}}^{(N-1)} \begin{bmatrix} b_L \\ b_N \\ a_1 \\ a_2 \\ \vdots \\ a_{2N-1} \\ a_{2N} \end{bmatrix}. \tag{A6}$$

The right side of the first subsystem is transparent, so the expression for $\tilde{\mathbf{S}}^{(N-1)}$ could be obtained by putting $t_R = 1, r_R = 0$ in the expression for the matrix $\mathbf{S}^{(N-1)}$. Specifically,

$$\tilde{\mathbf{S}}^{(1)} = \begin{bmatrix} -r_L & \alpha_1 t_L & \beta_1 t_L & 0 \\ \alpha_1 t_L & -\alpha_1^2 r_L & -\alpha_1\beta_1 r_L & \beta_1 \\ \beta_1 t_L & -\alpha_1\beta_1 r_L & -\beta_1^2 r_L & \alpha_1 \\ 0 & \beta_1 & \alpha_1 & 0 \end{bmatrix}. \tag{A7}$$

For the second subsystem whose left side is transparent ($t_L = 1$), we get

$$\begin{bmatrix} b_N \\ b'_R \\ 0 \\ \vdots \\ 0 \\ a'_{2N+1} \\ a'_{2N+2} \end{bmatrix} = \mathbf{U}^{(N)} \begin{bmatrix} b'_N \\ b_R \\ 0 \\ \vdots \\ 0 \\ a_{2N+1} \\ a_{2N+2} \end{bmatrix}, \tag{A8}$$

where both vectors have dimensions $2N + 2 \times 1$ and $2N + 2 \times 2N + 2$ matrix $\mathbf{U}$ equals

$$\tilde{\mathbf{U}}^{(N)} = \begin{bmatrix} -\alpha_N^2 r_R & \alpha_N t_R & 0 & \cdots & \beta_N & -\alpha_N\beta_N r_R \\ \alpha_N t_R & -r_R & 0 & \cdots & 0 & \beta_N t_R \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \beta_N & 0 & \cdots & \cdots & 0 & -\alpha_N \\ -\alpha_N\beta_N r_R & \beta_N t_R & 0 & \cdots & -\alpha_N & -\beta_N^2 r_R \end{bmatrix}. \tag{A9}$$

Using Eqs. (A8) and (A9) to eliminate the amplitudes b'_N and b_N, we get the following recursive relations for the matrix elements of $\mathbf{S}^{(N)}$:

$$S^{(N)}_{i,n} = U^{(N)}_{i,n} + \frac{U^{(N)}_{i,1}\tilde{S}^{(N-1)}_{2,2}U^{(N)}_{1,n}}{Z_N}, \tag{A10}$$

where $i, n = 2, 2N + 1, 2N + 2$;

$$S^{(N)}_{k,l} = \tilde{S}^{(N-1)}_{k,l} + \frac{U^{(N)}_{1,1}\tilde{S}^{(N-1)}_{k,2}\tilde{S}^{(N-1)}_{2,l}}{Z_N}, \tag{A11}$$

where $k, l = 1, 3, 4, \ldots, 2N - 1, 2N$; and

$$S^{(N)}_{i,k} = \frac{U^{(N)}_{1,i}\tilde{S}^{(N-1)}_{2,k}}{Z_N}. \tag{A12}$$

In these expressions, $Z_N = 1 - U^{(N)}_{11}\tilde{S}^{(N-1)}_{22} \equiv 1 - \left(\Pi_{i=1}^{N}\alpha_i^2\right)r_L r_R$.

APPENDIX B: TEMPERATURE PROFILE ALONG THE CHAIN

To find the temperature $\tilde{T}$ associated with the scatterer in the case of a single atom put between the walls, we assume that there is no heat exchange between the atom and the scatterer, that is, $J_1 + J_2 = J'_1 + J'_2 = 0$. Expressions for the heat currents J_1 and J_2 may be written in the form

$$J_1 = C\left[\left(1 - T^{(1)}_{3,3} - T^{(1)}_{3,4}\right)\left(\tilde{T} - T_R\right) - T^{(1)}_{3,1}\left(T_L - T_R\right)\right], \tag{B1}$$

$$J_2 = C\left[\left(1 - T^{(1)}_{4,4} - T^{(1)}_{4,3}\right)\left(\tilde{T} - T_R\right) - T^{(1)}_{4,1}\left(T_L - T_R\right)\right], \tag{B2}$$

where C is a constant, $T^{(1)}_{i,k} = \left|S^{(1)}_{i,k}\right|^2$, and matrix elements $S^{(1)}_{i,k}$ are determined by Eq. (A5). Note that Eqs. (B1) and (B2) resemble the corresponding expressions for electron currents derived in Büttiker's work.[32] Using the equation $J_1 + J_2 = 0$ and unitary relations $T^{(1)}_{1,4} + T^{(1)}_{2,4} + T^{(1)}_{3,4} + T^{(1)}_{4,4} = 1$ and $T^{(1)}_{1,3} + T^{(1)}_{2,3} + T^{(1)}_{3,3} + T^{(1)}_{4,3} = 1$, we get $\tilde{T} = \mu T_L + \nu T_R$, where

$$\mu = \frac{T^{(1)}_{1,3} + T^{(1)}_{1,4}}{T^{(1)}_{1,3} + T^{(1)}_{2,3} + T^{(1)}_{1,4} + T^{(1)}_{2,4}}; \tag{B3}$$

$$\nu = \frac{T^{(1)}_{2,3} + T^{(1)}_{2,4}}{T^{(1)}_{1,3} + T^{(1)}_{2,3} + T^{(1)}_{1,4} + T^{(1)}_{2,4}}. \tag{B4}$$

Substituting expressions for the relevant matrix elements $T_{i,k}$, we rewrite these coefficients in the form

$$\mu = \frac{t_L^2\left(1 + \alpha^2|r_R|^2\right)}{t_L^2\left(1 + \alpha^2|r_R|^2\right) + t_R^2\left(1 + \alpha^2|r_L|^2\right)}; \tag{B5}$$

$$\nu = \frac{t_R^2\left(1 + \alpha^2|r_L|^2\right)}{t_L^2\left(1 + \alpha^2|r_R|^2\right) + t_R^2\left(1 + \alpha^2|r_L|^2\right)}. \tag{B6}$$

For a symmetrically coupled system ($t_L = t_R$), $\mu = \nu = \frac{1}{2}$ and $\tilde{T} = \frac{1}{2}(T_L + T_R)$.

To find a steady state temperature profile along the chain, we ascribe the temperature $\tilde{T}_i$ $(1 \le i \le N)$ to the place were i-th atom is situated. Thus, the temperature profile is determined by the set of these temperatures. Assuming for certainty that $T_L > T_R$, we may write $T_L > \tilde{T}_1 > \ldots > \tilde{T}_{i-1} > \tilde{T}_i > \tilde{T}_{i+1} > \ldots > \tilde{T}_N > T_R$. Suppose that the i-th atom is put in contact with the scatterer by

means of two channels as in the case of the previously considered single atom shown in Fig. 1. The heat currents coming from the scatterer (J_{2i-1}, J_{2i}) may be written in the form

$$J_{2i-1} = C\left(J'_{2i-1} - J''_{2i-1}\right) \qquad J_{2i} = C\left(J'_{2i} - J''_{2i}\right), \tag{B7}$$

where

$$J'_{2i-1} = \left(1 - T^{(N)}_{2i+1,2i+1} - T^{(N)}_{2i+1;2i+2}\right)\left(\tilde{T}_i - \tilde{T}_{i+1}\right), \tag{B8}$$

$$J''_{2i-1} = T^{(N)}_{2i+1,1}\left(\tilde{T}_{i-1} - \tilde{T}_{i+1}\right), \tag{B9}$$

$$J'_{2i} = \left(1 - T^{(N)}_{2i+2,2i+2} - T^{(N)}_{2i+2;2i+1}\right)\left(\tilde{T}_i - \tilde{T}_{i+1}\right), \tag{B10}$$

$$J''_{2i} = T^{(N)}_{2i+2,1}\left(\tilde{T}_{i-1} - \tilde{T}_{i+1}\right). \tag{B11}$$

Assuming that there is no net heat current flowing from the scatterer to the chain or back, the heat currents coming from the scatterer obey the equation $J_{2i-1} + J_{2i} = 0$, leading to the set of linear equations $(1 \le i \le N)$,

$$\tilde{T}_i = \tilde{T}_{i-1}\frac{K^{(1)}_i}{R_{i,i}} + \tilde{T}_{i+1}\left(1 - \frac{K^{(1)}_i}{R_{i,i}}\right), \tag{B12}$$

where $\tilde{T}_0 = T_L$ and $\tilde{T}_{N+1} = T_R$. Solving these equations, we may find the temperature profile along the chain.

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