Obtaining the Phonon Mean Free Paths of Inhomogeneous Materials using Molecular Dynamics: Dislocation Core

Yandong Sun\textsuperscript{a,c}, Yanguang Zhou\textsuperscript{b}, Ming Hu\textsuperscript{d}, G. Jeffrey Snyder\textsuperscript{e,*}, Ben Xu\textsuperscript{c,*}, and Wei Liu\textsuperscript{a,*},

\textsuperscript{a}Laboratory of Advanced Materials, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China.

\textsuperscript{b}Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Hong Kong, People’s Republic of China.

\textsuperscript{c}State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China.

\textsuperscript{d}Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA.

\textsuperscript{e}Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA.

*Email:
jeff.snyder@northwestern.edu
xuben@mail.tsinghua.edu.cn
weiliu@mail.tsinghua.edu.cn
Abstract

Thermal management is extremely important for designing high-performance devices. The lattice thermal conductivity of materials is strongly dependent on the detailed structural defects at different length scales, particularly point defects like vacancies, line defects like dislocations, and planar defects such as grain boundaries. To evaluate the phonon mean free paths (MFPs), the McKelvey-Shockley phonon Boltzmann's transport equation (BTE) method combined with molecular dynamics simulations has been widely used. However, this method can only provide the aggregate MFPs of the whole sample, it is challenging to extract the MFPs in different regions with various thermal conductivities. In this study, the 1D McKelvey-Shockley phonon BTE method was extended to model thermally inhomogeneous materials, where the contributions of defects to the phonon MFP can be obtained. Then, the method was used to study the phonon scattering with the core structure of edge dislocation. The phonon MFPs in the dislocation core were obtained and consistent with the analytical model in a way that high frequency phonons are likely to be scattered in this area. This method not only advances the knowledge of phonon dislocation scattering but also shows the potential to investigate materials with more complicated components with different phonon behaviors.
Keywords: Phonon, Thermal conductivity, Inhomogeneous materials, dislocation core
1. Introduction

Phonons are the primary heat carriers in materials, especially in semiconductors\(^1\). Enriching the knowledge of phonon transport is important for managing the lattice thermal conductivity (\(\kappa_L\)) of materials to achieve better device performance. The Boltzmann transport equation (BTE)\(^2\), Green's function\(^3\) \(\text{and } 4\), Landauer-Büttiker formalism\(^5\) - \(7\), and molecular dynamics (MD)\(^8\) \(\text{and } 9\) have been developed to model phonon transport in materials. By combining the force constants and eigenvectors from ab initio calculations, the BTE with high orders phonon process, and Green's function can well describe phonon transport in thermally homogeneous materials. Defects have been verified experimentally to effectively decrease the \(\kappa_L\)\(^10\) - \(14\). The combination of point defects, dislocations, interfaces, precipitates, and nanogranular scatter phonons with different wavelengths\(^15\) \(\text{and } 16\). However, ab initio calculations are unsuitable for or incapable of obtaining realistic phonon transport in crystal with defects owing to their small computational size. Defects modeled in ab initio calculations usually have a very high concentration (e.g., point defects) or miss some features of the defect (e.g., the long strain field of dislocations). The computational scale of MD simulations is more than \(10^3\) times larger than that of ab initio calculations; thus, MD is more suitable for simulating phonon transport in crystals with defects.

Non-equilibrium MD (NEMD) simulations have been widely used to study phonon
transport in pure crystals, in crystals with point defects, dislocations, and interfaces, and even in amorphous crystals\textsuperscript{17-21}. The $\kappa_L$ can be directly obtained from a NEMD simulation, but detailed phonon scattering information is missing. To overcome this shortcoming, the frequency-domain direct decomposition method was developed to calculate the spectral heat flux in NEMD simulations\textsuperscript{22, 23}, from which the contributions of different phonons to the total heat flux can be obtained. In addition, the heat flux can also be modeled using the 1D McKelvey-Shockley phonon BTE method\textsuperscript{24-26}, and the phonon mean free paths (MFPs) can be calculated using the length-dependent heat flux results\textsuperscript{27, 28}. However, the traditional method of fitting the phonon MFPs only applies to thermally homogeneous materials, which assumes that the phonon scattering rates are constant throughout the material. Therefore, it is necessary to extend the method to thermally inhomogeneous materials, where the phonon scattering rate varies in the regions containing defects.

Numerous experiments have shown that introducing dislocations into thermoelectric materials greatly decreases the thermal conductivity and enhances the figure of merit\textsuperscript{11, 12, 14, 29-32}. Theoretical equations first derived by Klemens\textsuperscript{33, 34} and then improved by Carruthers\textsuperscript{35} in the mid-1950s are used to obtain the scattering rate of phonon-dislocation scattering. The equations are based on the perturbation theory where the perturbation comes from the atom mass missing in the core of the edge dislocation (DC)
and the static strain field (DS) where the phonon relaxation time followed: $\tau_{DC}^{-1} \sim \omega^3$ and $\tau_{DS}^{-1} \sim \omega$. The calculation method provides a potential way for the study of phonon defect scattering. Seeking a computational view of phonon dislocation scattering is important and of great interest.

In this study, NEMD simulations were performed to study phonon transport in a rock salt PbTe crystal with a line of vacancies perpendicular to the heat flux direction which can be seen as the core of the edge dislocation. Thermal inhomogeneities were caused near the position of the dislocation core. The $\kappa_L$ and spectral heat flux was obtained directly from the NEMD results. The $\kappa_L$ of the dislocation core structure model decreased by 19% compared to the pristine structure model. By extending the 1D McKelvey-Shockley flux method to thermally inhomogeneous materials, the frequency ranges of the phonons scattered by the defects and phonon MFPs due to phonon defects scattering were obtained.

2. Methodology

2.1 NEMD Simulations

The LAMMPS$^{36}$ package was used to conduct the NEMD simulations with a timestep of 5 fs. A Buckingham pair potential taken from ref.37 was used to model the interactions between atoms. A total of $4.5 \times 10^6$ steps were performed, corresponding to
a running time of 28 ns. The first 12.5 ns was used to relax the structure with isothermal-isobaric ensemble (NPT) and canonical ensemble (NVT), then the following 15 ns was used to obtain a steady temperature gradient and heat flux. Langevin thermostats were applied to the hot and cold region with damping parameter 0.1 (20 fold of the timestep of the simulation) and keyword tally yes, see the schematic of simulation cell in Fig. 2. The main system region was coupled to microcanonical ensemble (NVE). Time-domain velocity for spectral heat flux calculation and the temperature distribution along the heat flux direction were sampled in the last 1.5 ns.

2.2 Spectral Heat Flux Method

The spectral heat flux \( (Q(\omega)) \) was calculated using the following equation \(^{22,23}\)

\[
Q(\omega) = -\frac{2}{t_{\text{simu}} A \Delta T} \sum_{i \in L, j \in R} \sum_{\alpha, \beta \in \{x,y,z\}} \text{Im} \left( \bar{\nu}_i^\alpha(\omega) K_{ij}^{\alpha\beta} \bar{\nu}_j^\beta(\omega) \right),
\]

where \( t_{\text{simu}} \) is the total simulation time, \( A \) is the area of the cross-section, \( \Delta T \) is the temperature gradient, \( K_{ij}^{\alpha\beta} \) is the second-order interatomic force constant between the atoms distributed on both sides of the dislocation (denoted by \( L \) and \( R \)), \( \bar{\nu}_i^\alpha(\omega) \) and \( \bar{\nu}_j^\beta(\omega) \) are the discrete Fourier-transform velocity of atom \( i \) in direction \( \alpha \) and atom \( j \) in direction \( \beta \), and \( \bar{\nu}_i^\alpha(\omega)^* \) is the complex conjugate of \( \bar{\nu}_i^\alpha(\omega) \); the angular brackets denote the steady-state nonequilibrium ensemble average. The time-domain velocity of
atoms was directly obtained from the NEMD simulations, and the interatomic force constants were obtained by the finite displacement method in MD simulations.

2.3 1 D McKelvey-Shockley Flux Method with Defects

It is possible to use the McKelvey-Shockley phonon BTE method to describe phonon transport in NEMD simulations\(^{24-26}\). A schematic of the McKelvey-Shockley flux method is shown in Fig. 1. Steady-state 1D transport along \(x\) with an infinite \(y-z\) plane was assumed. The forward/backward phonon fluxes \(F^+(x)\) and \(F^-(x + dx)\), respectively) incident on a slab with thickness \(dx\) transmit or reflect with the backscattering probabilities per length, \(\frac{1}{\lambda(\omega)}\), where \(\lambda(\omega)\) is the phonon MFP for backscattering that contributes to the outward fluxes \(F^-(x)\) and \(F^+(x + dx)\). The equations are

\[
\frac{dF^+(x,\omega)}{dx} = -\frac{F^+(x,\omega)}{\lambda(\omega)} + \frac{F^-(x,\omega)}{\lambda(\omega)} \quad (2)
\]

\[
-\frac{dF^-(x,\omega)}{dx} = \frac{F^+(x,\omega)}{\lambda(\omega)} - \frac{F^-(x,\omega)}{\lambda(\omega)}. \quad (3)
\]
Fig. 1 Schematic of the McKelvey-Shockley flux method. The forward/backward phonon fluxes \( F^+(x) \) and \( F^-(x + dx) \), respectively which are incident on a slab with thickness \( dx \) transmit or reflect with the backward scattering probabilities per length \( \frac{1}{\lambda(\omega)} \).

By specifying the incoming fluxes at the boundaries, the forward and backward phonon fluxes can be obtained by solving Eqs. (2) and (3). The boundary conditions are as follows,

\[
F^+(x = 0, \omega) = F_B(\omega, T_H) \quad (4)
\]
\[
F^-(x = L, \omega) = F_B(\omega, T_C), \quad (5)
\]

where \( L \) is the length of the model, and \( F_B(\omega, T_H) \) and \( F_B(\omega, T_C) \) are the incoming phonon fluxes from the hot and cold baths, respectively, (Fig. 2; the interface contact resistance is neglected here). The solutions are

\[
F^+(x, \omega) = F_B(\omega, T_H) - \frac{F(\omega)}{\lambda(\omega)} x \quad (6)
\]
\[
F^-(x, \omega) = F_B(\omega, T_C) - \frac{F(\omega)}{\lambda(\omega)} (x - L), \quad (7)
\]

where the net phonon flux \( F(\omega) = F^+(x, \omega) - F^-(x, \omega) \), which is constant in the steady-state. The forward and backward phonon fluxes vary linearly along the heat flux direction with a slope of \(-\frac{F(\omega)}{\lambda(\omega)}\).

Then, \( F(\omega) \) can be extracted by subtracting Eq. (7) from Eq. (6) and isolating \( F(\omega) \),
The spectral heat flux ($Q(\omega)$) corresponds to multiplying the net phonon flux ($F(\omega)$) by the phonon energy ($\hbar \omega$),

$$Q(\omega) = \frac{1}{1+L/\lambda(\omega)} \hbar \omega \cdot v(\omega) \cdot [F_B(\omega, T_H) - F_B(\omega, T_C)] = \frac{Q_0(\omega)}{1+L/\lambda(\omega)}.$$  \hspace{1cm} (9)

which can be interpreted as the Landauer-Büttiker flux ($Q_0(\omega)$) with an effective transmission function $^{38}$

$$T_{eff}(\omega) = \frac{1}{1+L/\lambda(\omega)}.$$  \hspace{1cm} (10)

The above expression for $Q(\omega)$ can be applied to all length scales and spans from the ballistic to diffusive transport regimes. In the ballistic limit, $L \ll \lambda$ and $T_{eff} \rightarrow 1$, which indicates that all the phonons can achieve ballistic transport through the model without scattering. The population of phonons in the system will be constant; thus, $Q(\omega)$ is independent of the length. In the diffusive limit, $L \gg \lambda$ and $T_{eff} \approx \lambda/L$, which indicates that the population of phonons will change linearly in the system. Therefore, $Q(\omega) \propto 1/L$, which is expected from Fourier’s law. When $L \approx \lambda$, part of the phonons exhibit ballistic transport, while others exhibit diffusive transport.

If the transmission functions of models with different $L$ are calculated, $\lambda(\omega)$ can be obtained by fitting the data to Eq. (10). Alternatively, the spectral heat flux of the $L_1$ model can be used as a reference, and the ratio between the $L$ model and the $L_1$ model can be calculated$^{39}$. The ratio of the $L$ model is
\[ R(\omega, L) = \frac{Q(\omega, L)}{Q(\omega, L)} = 1 + \frac{L-L_1}{\lambda(\omega)+L_1}, \tag{11} \]

where \( R(\omega, L) \) and \( L \) follow linear relationships and \( \lambda(\omega) \) can be obtained by fitting the slope.

However, this \( \lambda(\omega) \) fails to give real physical information of mean free path when there is inhomogeneity in the system, which is because of the different phonon scattering rates in different parts of the system. The equations for the 1D McKelvey-Shockley phonon BTE must then be rewritten as a piecewise function, where the averaged backscattering probability per length for two different areas are noted as \( \frac{1}{\lambda_1(\omega)} \) and \( \frac{1}{\lambda(\omega)} \), for areas from \( x_1 \) to \( x_2 \) (area I with defects) and out of it (area II without defects), respectively. The equations for \( F^+(x, \omega) \) are then expressed as

\[
\frac{dF^+(x,\omega)}{dx} = -\frac{F^+(x,\omega)}{\lambda(\omega)} + \frac{F^-(x,\omega)}{\lambda(\omega)}, \quad x < x_1, \quad x > x_2, \tag{12}
\]

\[
\frac{dF^+(x,\omega)}{dx} = -\frac{F^+(x,\omega)}{\lambda_1(\omega)} + \frac{F^-(x,\omega)}{\lambda_1(\omega)}, \quad x_1 < x < x_2, \tag{13}
\]

the same equations are for \( F^-(x, \omega) \).

Under the same boundary conditions as in Eqs. (4) and (5), the following can be obtained,

\[
F(\omega) = \frac{1}{1+L/\lambda(\omega)+d(1/\lambda_1(\omega)-1/\lambda(\omega))} [F_B(\omega,T_H) - F_B(\omega,T_C)], \tag{14}
\]

where \( d \) is the length of the area I (\( d = x_2 - x_1 \)).

The transmission function is

\[
T'_{eff}(\omega) = \frac{1}{1+L/\lambda(\omega)+d(1/\lambda_1(\omega)-1/\lambda(\omega))}, \tag{15}
\]
and the spectral heat flux ratio of the $L$ model is

$$R'(\omega, L) = \frac{Q(\omega, L_1)}{Q(\omega, L)} = 1 + \frac{L - L_1}{\lambda(\omega) + L_1 + d(\lambda(\omega)/\lambda_1(\omega) - 1)}.$$  (16)

Compare to the Eq. (11), the above equation can be written as

$$R'(\omega, L) = \frac{Q(\omega, L_1)}{Q(\omega, L)} = 1 + \frac{L - L_1}{\lambda_{nm}(\omega) + L_1}.$$  (17)

The nominated $\lambda_{nm}(\omega) = \lambda(\omega) + d(\lambda(\omega)/\lambda_1(\omega) - 1)$ can be obtained as a whole, while it is not possible to obtain $\lambda(\omega)$ and $\lambda_1(\omega)$ separately. It must be emphasized that $\lambda_{nm}(\omega)$ does not give the actual phonon MFPs of backscattering for area I, instead, its value implies the difference of phonon MFPs between the area I and II as follows. Thus, it is equal to $\lambda(\omega)$ when $d = 0$; while it is larger than $\lambda(\omega)$ when $\lambda_1(\omega) < \lambda(\omega)$. In most cases, the $\lambda_1(\omega)$ is obtained when the $\lambda_{nm}(\omega)$ and $\lambda(\omega)$ are obtained by the fitting processes. Thus, it is possible to determine the phonons that are scattered in area I by comparing the variety of the nominated phonon MFPs and the phonon MFPs in the pristine model. This extended method can obtain additional information on phonon scattering from defects in thermally inhomogeneous crystals.

### 3. Models

The above method was used to study the phonon scattering from the edge dislocation core. A model with a vacancy line perpendicular to the heat flux direction was built
which can be seen as a core of the edge dislocation. It was 63.15 nm long in the x-direction and had a 9.48 nm × 8.94 nm cross-section with orientations of $\mathbf{u}_x = [\bar{1} \ 1 \ 0]$, $\mathbf{u}_y = [\bar{1} \ \bar{1} \ 2]$, and $\mathbf{u}_z = [1 \ 1 \ 1]$. A line of an equal number of Pb and Te atoms along the z-direction was removed from the center of the model. A schematic of the simulation cell used for the NEMD simulations is shown in Fig. 2. The atoms at each end of the system were fixed. Next to the fixed region, atoms within the length $L_{bath} = 2$ nm of the left and right side were coupled to Langevin thermostats with a dumping parameter of 0.1 (20 times the timestep) and keywords tally yes. The temperature was fixed to 40 K in the hot bath and 0.1 K in the cold bath. The low temperature will reduce the phonon-phonon process which helps to reveal the phonon-defect interactions. In the molecular dynamics simulation, all the phonon modes can be activated no matter how low the temperature is. Even though the phonon distribution will change due to the quantum effect in low temperature, but our work focus on the basic physics of phonon-defect scattering other than to obtain the real phonon scattering processes in material. A virtual interface at the position of the dislocation core was chosen to calculate the spectral heat flux. Two groups of atoms (denoted by L and R) were selected on both sides of the interface, and their velocities were sampled at successive timesteps, which were used to calculate the spectral heat flux. The same simulation procedure was performed for the pristine structure.
Fig. 2 Schematic of the simulation cell used in the NEMD simulations. A virtual interface at the position of the dislocation core of the model was selected, and the velocities of the atoms in the left and right regions of the virtual interface (within 2 nm) were sampled at successive timesteps to calculate the spectral heat flux, $Q$, through the interface.

4. Results and Discussion

4.1 Temperature Distribution and Thermal Conductivity

The temperature distributions along the heat flux direction in the dislocation core structure DC Model and pristine structure P Model are shown in Fig. 3. There was a linear temperature distribution in the thermally homogeneous P Model. In contrast, there was a sharp reduction in temperature at the dislocation core in the DC Model. The dislocation core area led to thermal inhomogeneities in the crystal; thus, a higher temperature gradient was necessary to maintain the same heat flux as that in other parts of the system. The temperature drops also occurred near the baths because some
phonons will demonstrate ballistic transport through the sample without any scattering when their phonon MFP is comparable to the length of the model. The shape of the temperature profiles can be well interpreted by the McKelvey-Shockley phonon BTE method. The ballistic thermal phonons will not change the phonon population in the system, thus generating a flat temperature distribution. When combined with the linear temperature distribution due to diffusive phonons, a temperature distribution with drops near the baths and linear behavior elsewhere in the system is formed.

![Graphs showing temperature distributions](image)

Fig. 3 (a) Temperature distributions of the dislocation core structure DC Model and pristine structure P Model in the NEMD simulations. (b) Magnified view showing of the sharp reduction in temperature near the line of vacancies (grey rectangle region in (a)).

The thermal conductivity $\kappa_L$ was calculated directly from the Fourier’s law, and the results are shown in Tab. 1. The temperature gradient was calculated over the entire region rather than the dislocation core area in the DC Model. The $\kappa_L$ decreased by 19.2%
due to the addition of the dislocation core.

|                  | Heat Flux, $J_Q$ (GW/m²) | Temperature Gradient, $\partial T/\partial x$ (K/nm) | Thermal Conductivity, $\kappa_L$ (W/(m·K)) |
|------------------|--------------------------|---------------------------------------------------|------------------------------------------|
| DC Model         | 4.30                     | 0.331                                             | 13.0                                     |
| P Model          | 4.57                     | 0.287                                             | 15.9                                     |
| DC/P Ratio       | 94.1%                    | -                                                 | 81.8%                                    |

### 4.2 Spectral Heat Flux

Before the newly developed 1D McKelvey-Shockley flux method can be applied to calculate the phonon MFPs, the spectral heat flux ($Q(\omega)$) through the two models must be investigated first. $Q(\omega)$ is related to the thermal conductivity of the materials, from which the amount of heat transferred by different frequency phonons in the material can be determined (see Fig. 4(a)). The heat flux is less in the frequency range of 1 to 2 THz in the dislocation core structure DC Model compared with the pristine structure P model, which indicates that these frequency range phonons were influenced by the dislocation core. Normalized spectral heat fluxes ($q(\omega)$) were obtained by dividing by the total heat flux (shown in Fig. 4(b)), from which the proportion of the contribution to the heat flux from different frequency phonons can be determined. $q(\omega)$ did not change for
frequency less than 1.6 THz and had the same shape as the phonon density of state (DOS) (Fig. A1 in Appendix) because the phonons in this frequency range could achieve ballistic transport through the model without scattering when their MFP was much longer than the length of the simulation model. The proportions that different phonons contributed to the heat flux in the DC Model and P Model were almost identical except for a small decrease in the 1.60-1.80 THz frequency range and a small increase at high frequencies. From Eq. (9), the change in $Q(\omega)$ is related to the phonon MFPs ($\lambda(\omega)$) and the phonon group velocity ($v(\omega)$). Thus, the phonon MFPs must be obtained.

Fig. 4 (a) Spectral heat fluxes ($Q(\omega)$) of the dislocation core structure DC Model and pristine structure P Model, from which the contributions from different phonons to the total heat flux can be determined. (b) Normalized spectral heat fluxes ($q(\omega)$) obtained from (a) by dividing by the total heat flux, from which the proportions of different frequency phonons contributing to the heat flux can be determined. All the curves are smoothed with a width $\Delta\omega = 0.0244$ THz.
4.3 Fitting the Phonon MFPs

The phonon MFPs can be obtained from the length-dependent heat flux\(^{22, 23}\). As mentioned previously, there are two areas in the dislocation core model (DC Model). In area I with dislocation core, there is phonon-phonon scattering and phonon dislocation core scattering. In area II without dislocation core, there is only phonon-phonon scattering which is identical to the scattering process in the pristine model (P Model). According to Matthiessen’s rule, the backward scattering probabilities per length in area I (1/\(\lambda_1\)) satisfy

\[
\frac{1}{\lambda_1(\omega)} = \frac{1}{\lambda_P(\omega)} + \frac{1}{\lambda_{DC}(\omega)}
\]

(18)

where \(\lambda_P(\omega)\) and \(\lambda_{DC}(\omega)\) are the phonon MFPs for backward scattering from phonon-phonon scattering and phonon dislocation core scattering, respectively. Combining Eqs. (17) and (18) yields

\[
\lambda_{nm}(\omega) = \lambda_P(\omega) + \frac{d}{\lambda_{DC}(\omega)} \frac{\lambda_P(\omega)}{\lambda_{DC}(\omega)},
\]

(19)

where \(\lambda_P(\omega) = \lambda(\omega)\). The \(d\) is the length of area I and can be obtained from the temperature distribution in Fig. 3 (a). It starts from the position where temperature distribution begins to deviate from the linear distribution and ends in the position where temperature distribution backs to the linear distribution.

The fitted phonon MFPs for backward scattering (\(\lambda_{nm}(\omega)\)) in the dislocation core structure DC Model and the phonon MFPs for backward scattering (\(\lambda(\omega)\)) in the pristine
structure P Model are shown in Fig. 5 (a). The length-dependent spectral heat flux results are shown in Fig. A2 in Appendix. According to the analysis in the Methodology section, if the phonons are scattered in the area with defects, \( \lambda_{nm}(\omega) \) will be larger than the \( \lambda(\omega) \) of the P Model. It was observed that \( \lambda_{nm}(\omega) \) of the DC Model visibly increased when the frequency was higher than 2.1 THz, which indicates that, in this frequency range, phonons were significantly scattered by the dislocation core. By substituting \( \lambda(\omega) \) from the P Model and \( \lambda_{nm}(\omega) \) from the DC Model into the Eq. (19), the phonon MFPs for backscattering from phonon dislocation core scattering can be obtained. Here, only the average results were used to calculate the phonon MFPs instead of the whole data in the confidence intervals, and the negative values were omitted. The regular phonon MFPs were 75% smaller than the phonon MFPs for backscattering\(^{40}\), as shown in Fig. 5(b). The result is consistent with the analytical theory\(^{33-35}\) that \( \lambda(\omega) \sim \omega^{-3} \) for phonon dislocation core scattering, but a constant group velocity is being assumed here and the relationship is greatly related to the spacing between the dislocation cores\(^{41}\).

Most of the high frequency phonons were scattered by the dislocation core, but their contributions to the total heat flux increased according to the analysis in section 4.2. This is because there was a larger temperature gradient at the position of dislocation core in the DC Model. It was also found that the contribution from the medium frequency phonons decreased when they were scattered less by the dislocation core.
From Eq. (9), the change in $Q(\omega)$ is not only related to the phonon MFPs ($\lambda(\omega)$) but also to the phonon group velocity ($v(\omega)$). Therefore, it is necessary to check the change in the phonon group velocity after introducing the dislocation core.

![Graph](image.png)

**Fig. 5 (a)** Nominated phonon MFPs and phonon MFPs for the dislocation core structure DC Model and pristine structure P Model with 95% confidence intervals from the fitting processes mentioned in the Methodology section. High frequency phonons are significantly scattered by the dislocation core.

**Fig. 5 (b)** Phonon MFPs introduced by phonon dislocation core scattering assuming Mathiessen’s rule, Eq 18. Here, only the average results in (a) were used to calculate the phonon MFPs instead of the whole data in confidence intervals, and the negative values were omitted.

### 4.4 Change in the Group Velocity

Defects and strain might also reduce the phonon velocity which has been correlated with much of the reduction in thermal conductivity observed in nanostructured PbTe materials\textsuperscript{41}. To investigate whether a change in phonon velocity also occurs, a model...
with $8 \times 8 \times 4$ unit cells in the $x$, $y$, and $z$ directions (lattice vectors of the unit cell), respectively, was built, and a line of atoms along the $z$-direction in the center of the model was removed to generate the dislocation core. A lattice dynamic calculation was conducted using Phonopy\textsuperscript{42} software, and the force constants were calculated from MD simulations with the same atomic potential that was used for the previous simulations. The group velocities of the dislocation core structure model and the corresponding pristine structure model are shown in Fig. 6. The group velocity of medium frequency phonons was greatly suppressed owing to the dislocation core. Thus, the amount of heat transferred by medium frequency phonons decreased even though they were not significantly scattered by the dislocation core.
Fig. 6 Group velocities of the phonons of the dislocation core structure DC Model and pristine structure P Model from lattice dynamic calculations. The group velocity of the medium frequency phonons was greatly suppressed because of the dislocation core.

5. Conclusion

In this study, the McKelvey-Shockley phonon BTE method was extended to inhomogeneous materials with defects, and the phonon MFPs from phonon defect scattering were obtained. In inhomogeneous materials, it was argued that the MFP had
contributions from both the homogenous and inhomogeneous (defect-containing) regions. The method was used to study the phonon scattering with the dislocation core. The variations in the phonon group velocity primarily lead to the thermal conductivity decrease, and the variations in the MFPs with respect to different frequencies due to the dislocation core structure were demonstrated which was consistent with the analytical theory that high frequency phonons are more likely scattered by dislocation core. Based on these results, this method illuminates the scattering mechanism of phonon transport in materials with inhomogeneous distributions of structures. Moreover, the method not only advances the knowledge of phonon dislocation scattering but also shows the potential to investigate materials with more complicated components with different phonon behaviors.

**Data availability**

The datasets generated during and/or analyzed during this study are available from the corresponding author on reasonable request.

**Code availability**

The codes used in this study are available from the corresponding author on reasonable request.

**Acknowledgment**
Y.D.S. thanks Dr. Shiyao Liu for polishing the language. Simulations were performed with computing resources granted by the National Supercomputer Center in Tianjin under project TianHe-1(A) and Quest High-Performance Computing Cluster at Northwestern University. The research reported in this publication was supported by the NSFC under grant No. 52072209, Basic Science Center Project of NSFC under grant No.51788104 and by the Tsinghua National Laboratory for Information Science and Technology. G. Jeff Snyder acknowledges support from award 70NANB19H005 from U.S. Department of Commerce, National Institute of Standards and Technology as part of the Center for Hierarchical Materials Design (CHiMaD). Y.D.S acknowledges support from Tsinghua University Short-term Overseas Exchange Fund.

Appendix:
Fig. A1 Phonon DOS of the dislocation core structure DC Model and pristine structure P Model. The phonon DOS was calculated from the FFT of the velocity autocorrelation function of atoms in the selected volume containing the dislocation core in the DC Model and the corresponding position in the P Model.

![Phonon DOS](image)

**Author contributions**

Y.D.S. performed MD simulations, data processing, result analysis, and manuscript writing. Y.G.Z., M.H., B.X., W.L., and J. S. participated in the discussion and interpretation of results and contributed to editing the manuscript.

**Competing interests**
The authors declare no competing interests.

References

1. T. M. Tritt, *Thermal conductivity: theory, properties, and applications*. (Springer Science & Business Media, 2005).
2. J. Y. Murthy, S. V. Narumanchi, P.-G. Jose'A, T. Wang, C. Ni and S. R. Mathur, International Journal for Multiscale Computational Engineering 3 (1) (2005).
3. N. Mingo, Physical Review B 74 (12), 125402 (2006).
4. J.-S. Wang, J. Wang and N. Zeng, Physical Review B 74 (3), 033408 (2006).
5. M. Büttiker, Physical Review B 46 (19), 12485 (1992).
6. R. Landauer, Philosophical magazine 21 (172), 863-867 (1970).
7. N. Mingo and L. Yang, Physical Review B 68 (24), 245406 (2003).
8. F. Müller-Plathe, The Journal of chemical physics 106 (14), 6082-6085 (1997).
9. S. G. Volz and G. Chen, Physical Review B 61 (4), 2651 (2000).
10. Y. Pei, A. LaLonde, S. Iwanaga and G. J. Snyder, Energy & Environmental Science 4 (6), 2085-2089 (2011).
11. J. He, S. N. Girard, M. G. Kanatzidis and V. P. Dravid, Advanced Functional Materials 20 (5), 764-772 (2010).
12. S. I. Kim, K. H. Lee, H. A. Mun, H. S. Kim, S. W. Hwang, J. W. Roh, D. J. Yang, W. H. Shin, X. S. Li, Y. H. Lee, G. J. Snyder and S. W. Kim, Science 348 (6230), 109-114 (2015).
13. D. Medlin and G. Snyder, Current Opinion in Colloid & Interface Science 14 (4), 226-235 (2009).
14. Y. Wu, Z. Chen, P. Nan, F. Xiong, S. Lin, X. Zhang, Y. Chen, L. Chen, B. Ge and Y. Pei, Joule 3 (5), 1276-1288 (2019).
15. G. J. Snyder and E. S. Toberer, in *materials for sustainable energy: a collection of peer-reviewed research and review articles from Nature Publishing Group* (World Scientific, 2011), pp. 101-110.
16. E. S. Toberer, A. Zevalkink and G. J. Snyder, Journal of Materials Chemistry 21 (40), 15843-15852 (2011).
17. D. J. Evans, Physics Letters A 91 (9), 457-460 (1982).
18. D. Bedrov and G. D. Smith, The Journal of Chemical Physics 113 (18), 8080-8084 (2000).
19. Y. Sun, Y. Zhou, J. Han, W. Liu, C. Nan, Y. Lin, M. Hu and B. Xu, npj Computational Materials 5 (1) (2019).
20. T. Ikeshoji and B. Hafskjold, Molecular Physics 81 (2), 251-261 (1994).
21. Z. Huang, Z. Tang, J. Yu and S. Bai, Physica B: Condensed Matter 404 (12-13), 1790-1793 (2009).
22. Y. Chalopin and S. Volz, Applied Physics Letters 103 (5) (2013).
23. Y. Zhou, X. Zhang and M. Hu, Nanoscale 8 (4), 1994-2002 (2016).
24. J. P. McKelvey, R. L. Longini and T. P. Brody, Physical Review 123 (1), 51-57 (1961).
25. W. Shockley, Physical Review 125 (5), 1570-1576 (1962).
26. J. Maassen and M. Lundstrom, Journal of Applied Physics 117 (3), 035104 (2015).
27. K. Sääskilahti, J. Oksanen, S. Volz and J. Tulkki, Physical Review B 92 (24), 245411 (2015).
28. K. Sääskilahti, J. Oksanen and J. Tulkki, Physical Review E 88 (1), 012128 (2013).
29. Y. Wu, P. Nan, Z. Chen, Z. Zeng, R. Liu, H. Dong, L. Xie, Y. Xiao, Z. Chen, H. Gu, W. Li, Y. Chen, B. Ge and Y. Pei, Advanced Science (2020).
30. R. Hanus, M. T. Agne, A. J. E. Rettie, Z. Chen, G. Tan, D. Y. Chung, M. G. Kanatzidis, Y. Pei, P. W. Voorhees and G. J. Snyder, Adv Mater 31 (21), e1900108 (2019).
31. Y. Pan, U. Aydemir, J. A. Grovogui, I. T. Witting, R. Hanus, Y. Xu, J. Wu, C. F. Wu, F. H. Sun, H. L. Zhuang, J. F. Dong, J. F. Li, V. P. Dravid and G. J. Snyder, Adv Mater, e1802016 (2018).
32. Z. Chen, B. Ge, W. Li, S. Lin, J. Shen, Y. Chang, R. Hanus, G. J. Snyder and Y. Pei, Nat Commun 8, 13828 (2017).
33. P. G. Klemens, Proceedings of the Physical Society. Section A 68 (12) (1955).
34. P. G. Klemens, (1958), pp. 1-98.
35. P. Carruthers, Physical Review 114 (4), 995-1001 (1959).
36. S. Plimpton, 1993.
37. J. F. Troncoso, P. Aguado-Puente and J. Kohanoff, J Phys Condens Matter 32 (4), 045701 (2020).
38. L. G. Rego and G. Kirczenow, Physical Review Letters 81 (1), 232 (1998).
39. S. Xiong, D. Selli, S. Neogi and D. Donadio, Physical Review B 95 (18) (2017).
40. C. Jeong, R. Kim, M. Luisier, S. Datta and M. Lundstrom, Journal of Applied Physics 107 (2), 023707 (2010).
41. R. Hanus, A. Garg and G. J. Snyder, Communications Physics 1 (1) (2018).
42. A. Togo and I. Tanaka, Scripta Materialia 108, 1-5 (2015).