Probing and tuning inelastic phonon conductance across finite-thickness interface

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Received October 15, 2014; accepted November 1, 2014; published online November 25, 2014

Phonon transmission across an interface between dissimilar crystalline solids is calculated using molecular dynamics simulations with interatomic force constants obtained from first principles. The results reveal that, although inelastic phonon transmission right at the geometrical interface can become far greater than the elastic one, its contribution to thermal boundary conductance (TBC) is severely limited by transition regions, where local phonon states at the interface recover the bulk state over a finite thickness. This suggests that TBC can be increased by enhancing phonon equilibration in the transition region, for instance, by phonon scattering, which is demonstrated by increasing the lattice anharmonicity.
Temperature profiles of (a) PbTe/PbS and (b) Si/Ge systems in steady state. The red and blue diamonds indicate the thermostated layers at high and low temperatures. The orange and green dashed lines show the fitting of the temperature profiles in the bulk regions.

Here, \( \xi_i \) is a scalar that is used to evaluate how much the surrounding first-neighbor atoms to the \( i \)th atom resemble those of pure PbS (see Ref. 25 for details). The cubic and quartic IFCs can also be treated in a pairwise fashion since only the nearest neighbors are considered for the anharmonic IFCs. This local virtual crystal approximation has successfully reproduced the substitution alloy effect of lead chalcogenides.\(^{24}\) For the Si/Ge system, we used only the IFCs and lattice constant of the Si crystal because the IFCs of Si and Ge crystals were found to be transferable. Such transferability has been known for harmonic terms,\(^{25,26}\) but we in addition found that this is true also for the cubic terms (see the online supplementary data available at http://stacks.iop.org/APEX/7/121801/mmedia).

A typical EMD simulation was performed for PbTe/PbS and Si/Ge systems in fully periodic cells with sizes of 124.4 \( \times \) 31.11 \( \times \) 31.11 and 216.3 \( \times \) 27.04 \( \times \) 27.04 Å\(^3\), respectively. In an NEMD simulation, the end layers were fixed and the two layers adjacent to them were steadily heated and cooled, and periodic boundary conditions were applied in the cross-sectional directions. In both EMD and NEMD simulations, the size of the system is made sufficiently large to prevent the size effect in the phonon transmission function.\(^{23}\)

Figures 1(a) and 1(b) show temperature profiles of PbTe/PbS and Si/Ge systems obtained by NEMD. TBC can be calculated by dividing the heat flux through the system with the temperature jump at the interface. Here, the temperature jump is identified by extrapolating the linear temperature profile in the bulk region. The bulk temperature gradient is consistent with the bulk thermal conductivity. At the PbTe/PbS interface, temperature discontinuously jumps at the interface, while at the Si/Ge interface, temperature transits continuously over several layers adjacent to the geometrical interface. This indicates that the phonon transmission process through the interface is different between the two systems. In the case of PbTe/PbS [Fig. 2(a)], we can simply describe the system as the interface S directly sandwiched by the two media that effectively have bulk phonon properties. On the other hand, in the case of Si/Ge [Fig. 2(b)], TR extends over a finite thickness around S, which is denoted as \( \alpha \) and \( \beta \).

Now, we calculate the phonon transmission function at S for PbTe/PbS and Si/Ge systems. On the basis of the partial derivative of the Hamiltonian of the subcells divided by the interface, the heat flux between the left (A) and right (B) subcells can be expressed in terms of the cross-correlation of the atomistic velocities (v) and forces on B from A (\( F_{A \rightarrow B} \)) as

\[
\Phi_{ij}^{\text{PbTe/PbS}} = (1 - \xi_i) \Phi_{ij}^{\text{PbTe}} + \xi_i \Phi_{ij}^{\text{PbS}}. \tag{2}
\]

The comparison of PbTe/PbS and Si/Ge reveals a case dependence of the extent of the inelastic channel. In the case of PbTe/PbS, the inelastic channel is more significant compared with the elastic one, and contributes to only about 10% of the total TBC. In contrast, in the case of Si/Ge, the inelastic channel contributes to 70% of the total TBC. We first hypothesized that this is attributable to the difference in lattice anharmonicity, which is expected to widen the inelastic channel. This

\[
J_{\alpha \rightarrow \beta} = \frac{1}{a} \lim_{\tau \to 0} \int \sum_{jB} \langle F_{jA \rightarrow B}^{\alpha} (t + \tau) \cdot v_j(t) \rangle,
\]

where \( a \) is the cross-sectional area. The mode-dependent heat flux can then be obtained by Fourier transformation, and the phonon transmission function can be derived by comparing the Landauer and atomistic expressions of heat flux.\(^{19-21}\)

\[
\Theta(\omega) = \frac{1}{2aK_B T} \text{Re} \left[ \sum_{\alpha, \beta} \sum_{jA, jB} \Phi_{ij}^{\alpha \beta} \left| u_j^\alpha(\omega) \right|^2 - u_j^\beta(\omega) u_j^\beta(\omega) \right]. \tag{4}
\]

Here, \( \omega \) and \( K_B \) are the phonon frequency and Boltzmann constant, respectively. Note that anharmonic effects are fully incorporated through the anharmonic IFCs in Eq. (1). The transmission here is essentially a frequency-dependent thermal conductance, and thus TBC can be calculated by integrating the transmission function over frequency:

\[
K = k_B \int_0^\infty \Theta(\omega) \, d\omega. \tag{5}
\]

Note that the sign of \( J_{\alpha \rightarrow \beta} \) can also be negative and becomes zero when averaged in time since the simulation is at equilibrium. Therefore, as an empirical treatment, we take the absolute value of the calculated quantity in Eq. (4) with an intention to consider phonon transmission in the same direction with \( J_{\alpha \rightarrow \beta} \).

Figures 3(a) and 3(b) show transmission functions of PbTe/PbS and Si/Ge interfaces at 300 K, respectively. The frequency domain can be divided into two regimes: (I) \( 0 < \omega < \omega_{L_{\text{max}}}^2 \) and (II) \( \omega_{L_{\text{max}}}^2 < \omega < \omega_{H_{\text{max}}}^2 \), where L and H are the materials with lower and higher phonon frequencies. Note that the maximum frequency here is determined on the basis of the bulk density of states of each material. In current cases, L is PbTe or Ge, and H is PbS or Si. The transmission function in regime (I) is attributed to elastic phonon scattering, i.e., the phonons incoming to and outgoing from the interface have the same frequency ("elastic channel"). On the other hand, in regime (II), inelastic scattering contributes to the transmission ("inelastic channel"). Note that the inelastic process can also contribute to the transmission function in regime (I), but, nevertheless, the transmission function in regime (II) is a good indication of the contribution of the inelastic channel.
was checked by varying the anharmonicity at S by turning on and off the anharmonic terms in Eq. (1). However, it had a negligible influence on the transmission function, which is consistent with a recent observation by NEMD.29) We then turned to the local phonon density of states (DOS), which was investigated for each layer by calculating the power spectra of atom velocities. As shown in Fig. 4(a), the DOS on the Ge side of S (0th layer) exhibits a peak that extends beyond the cutoff frequency of bulk Ge. A similar peak is observed on the Si side, which agrees with the peak position in the phonon transmission function [Fig. 3(b)], suggesting that the inelastic channel is associated with the local phonon states at S.

In the case of PbTe/PbS, the TBCs calculated by EMD (0.33 GW m⁻²K⁻¹) and NEMD (0.34 GW m⁻²K⁻¹) were in excellent agreement. Contrastingly, in the case of Si/Ge, the TBCs calculated by EMD (2.8 GW m⁻²K⁻¹) and NEMD (0.27 GW m⁻²K⁻¹) resulted in an order of magnitude difference. The TBC obtained by our NEMD is in good agreement with the values obtained by lattice dynamics (0.28 GW m⁻²K⁻¹)8) and NEMD (0.32 GW m⁻²K⁻¹)11) using the empirical Stillinger Weber potential, and recent NEGF calculation using first-principles-based IFCs similar to this work (0.28 GW m⁻²K⁻¹).30)

The difference between the TBCs calculated by EMD and NEMD for Si/Ge should be due to TR, which is included in NEMD but not in EMD. Now, we postulate the picture of TBC in Fig. 2(b) introducing the additional vertical interfaces A’ (B’) between bulk and α (β). In this picture, the process of interfacial thermal transport from Si to Ge takes place as phonons transmit (i) from bulk Si to α according to the transmission function at A’, (ii) from α to β according to its transmission function at S, and (iii) from β to bulk Ge according to the transmission function at B’. Note that from the viewpoint of the Landauer theory, we ignore phonon scatterings inside α and β assuming ballistic transport.

Now, the question is how to define the thicknesses of α and β. In this work, we take the decay length of the correlation coefficient between the layer at S and layers along the direction of heat flux. Similarly to the transmission function, the thickness of TR is expected to depend on phonon modes, which is evaluated here as a frequency-dependent property. The frequency-dependent correlation coefficient $h(l, \omega)$ is calculated as

$$ h(l, \omega) = \frac{C_{11}(\omega) \cdot C_{00}(\omega)}{C_{00}(\omega) \cdot C_{00}(\omega)}, $$

where $C$ is the cross spectrum defined as

$$ C_{mn}(\omega) = \sum_{i,j} \sum_{j,n} v_i(\omega) \cdot v_j(\omega). $$

Here, $m$ and $n$ are the layer indices (0, 1, . . .) counted from the layer at S. The thickness of TR, $L(\omega)$, is then obtained by fitting an exponential function, $h(q, \omega) = \exp[-l/L(\omega)]$. The calculated $L(\omega)$ on the Si and Ge sides [Fig. 4(b)] ranges from 2 to 1000 layers depending on the phonon frequency. This means that the surface states are localized near S for high-frequency phonons and extend for a significantly long distance for low-frequency ones. Note that the results did not change with the system size.

We then calculate the total phonon transmission function of the entire TR consisting of the series of TBC at A’, S, and B’. The inverse of the total phonon transmission function is calculated as the series sum:

$$ \frac{1}{\Theta_{total}(\omega)} = \frac{1}{\Theta_A(\omega, L_S(\omega))} + \frac{1}{\Theta_B(\omega, L_G(\omega))}. $$

One technical problem here is that $L$ of some low-frequency phonons exceed the half of the simulation cell (40 layers). This was remedied by cutting off $L$ of the low-frequency phonons at 40 layers since their contribution to TBC is minor compared with the rest, as can be seen in the transmission function [Fig. 3(b)]. This was confirmed by varying the length of the system, which made a negligible difference in TBC. This also means that the effective thermal interface is still a local property near S and justifies the linear extrapolation carried out in NEMD on extracting TBC.

The obtained total phonon transmission function including TR is shown in Fig. 4(c). Furthermore, the TBC calculated from the transmission function is plotted in Fig. 4(d) together with that obtained by NEMD for different temperatures. Figure 4(d) clearly shows that by taking the total transmission into account, the TBC calculated by EMD agrees with that calculated by NEMD. Firstly, this suggests the validity of the
series resistance model in Fig. 2. Secondly, this confirms that an order of magnitude difference between the Si/Ge-TBCs calculated by EMD (2.8 GW m⁻² K⁻¹) and NEMD (0.27 GW m⁻² K⁻¹) is due to the missing contribution from TR. On the other hand, for PbTe/PbS, L is sufficiently small such that the phonon transmission at S describes TBC well.

It is interesting to note that the obtained TBC at S (2.8 GW m⁻² K⁻¹) is in reasonable agreement with the thermal conductance of the Si/Ge superlattice: ~2 GW m⁻² K⁻¹ per layer (i.e., per interface) measured in experiments. This makes sense if we think that the obtained thermal conductance per layer is similar to the TBC at S because the superlattice period thickness (3 and 4.4 nm in Refs. 31 and 32, respectively) is smaller than L. This may explain the reported discrepancy between the calculated TBC of the Si/Ge interface and those extracted from the superlattice experiments.

The total phonon transmission function of the Si/Ge interface in Fig. 4(c) shows that despite the dominant contribution from the inelastic channel to the phonon transmission across S [Fig. 3(b)], the overall TBC is still dominated by the elastic channel. This is because the thermal resistance between the bulk and TR (A' and B') screens the high-frequency phonons before reaching S, even though the inelastic channel at S has a potential to transmit high-frequency phonons. This also means that the phonon distribution in the TR is strongly nonequilibrium and is skewed towards low frequency; otherwise, the inelastic channel will be utilized.

The above discussion suggests that if we are to promote heat conduction across the interface, one way of making better use of the inelastic channel is to equilibrate the phonon distribution in TR, for instance, by enhancing phonon–phonon scattering in the boundary regime. Here, we have demonstrated it by increasing the anharmonicity in TR by scaling the anharmonic IFCs with a constant value $\gamma$ (= 1.0, 1.1, 1.2, and 1.5). This approach is convenient for proof of principles since the eigenstates do not change. As shown in Fig. 5, increasing $\gamma$ significantly reduces the temperature drop at the interface, as expected. As a result, TBC significantly and monotonically increases (0.27, 0.31, 0.34, and 0.37 GW m⁻² K⁻¹, respectively) with $\gamma$. This clearly demonstrates the controllability of TBC by utilizing the inelastic channel.

In summary, we calculated the frequency-dependent phonon transmission function of PbTe/PbS and Si/Ge interfaces by EMD using first-principles-based IFCs. The comparative study of EMD and NEMD suggests that TBC through the Si/Ge interface with finite-thickness TR can be well described by a series model of thermal resistance between the bulk and the TR and that right at the interface. Although the phonon transmission function at the interface exhibits potential to transport heat through the inelastic channel, the total transmission is bottlenecked by the transmission between the bulk and the transient region.

TR here can be considered as a characteristic length within which the lattice vibration remains coherent with that of the geometrical interface, and thus the interface becomes sharp/thick when this coherent length is small/large. While the length depends on the materials and their combination, it should roughly scale with bulk phonon mean free paths, i.e., thermal conductivities of the materials. This discussion is consistent with the fact that Si and Ge have higher thermal conductivities than PbTe and PbS.

The inelastic channel can be more effectively utilized by enhancing phonon equilibration in TR, for instance, through phonon–phonon scattering, which is demonstrated by increasing the anharmonicity in TR. The current work suggests the possibility of controlling TBC by utilizing the inelastic channel. Such enhancement of phonon equilibration can also be realized by introducing impurities and defects in TR, which may be more practical in the actual material development.

Acknowledgments This work is partially supported by JST, PRESTO, and JSPS KAKENHI Grant Number 2679009.

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