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On the importance of using exact full phonon dispersions for predicting interfacial thermal conductance of layered materials using diffuse mismatch model

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ABSTRACT
Several models have been employed in the past to estimate interfacial thermal conductance (ITC) for different material interfaces, of which the diffuse mismatch model (DMM) has been generally accepted as reliable for rough material interfaces at high temperature. Even though the DMM has been shown to predict the correct order of magnitude in isotropic material interfaces, it is unable to reproduce the same accuracy for low-dimensional anisotropic layered materials, which have many potential applications. Furthermore, the use of approximated dispersion curves tends to overestimate the ITC. In this work, we propose a new method that utilizes a mode-to-mode comparison within the DMM framework to predict ITC. We employed this model to calculate ITC between layered materials such as MoS$_2$ and graphite and metals such as Al, Au, and Cr. We then compared our values with previous literature data that employ linear dispersion relations and experimental data from time-domain thermoreflectance measurements. This new framework was then used to visualize the phonon focusing effect in anisotropic materials. Further analysis revealed that counting only the three acoustic modes and neglecting the low-frequency optical modes lead to significant underestimation of the ITC using DMM. Our findings indicate that it is imperative to use the exact full phonon dispersion relations in evaluating the ITC for low-dimensional layered materials.

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I. INTRODUCTION
Low-dimensional layered materials such as few-layer graphene, graphite, black phosphorus, and transition metal dichalcogenides (TMDs) have garnered substantial interest in recent years. These materials possess a unique set of electronic, optical, mechanical, and thermal properties, which find applications in nanoelectronics devices, such as integrated circuits, spintronics, flexible electronics, and optoelectronics. The anisotropic nature of these materials renders different structural and thermal transport properties in the cross-plane and basal-plane directions. When metals form interfaces with these materials, a detailed knowledge of the interfacial thermal transport and a reasonable estimation of the interfacial thermal conductance (ITC) is needed for thermal management.

A temperature difference $\Delta T$ exists between two solids in contact, which manifests as the interfacial thermal conductance $G$,

$$G = \frac{Q}{\Delta T},$$

where $Q$ is the heat flux across the interface.

The Diffuse Mismatch Model (DMM) has been extensively used to predict the interfacial thermal conductance in isotropic material interfaces with acceptable accuracy. However, for anisotropic material interfaces, previous applications of the DMM
failed to reproduce the same accuracy due to several assumptions regarding the dispersion curves. An important input of the model is a detailed knowledge of the phonon dispersion relations of the materials involved. For simplicity, the dispersion is usually approximated by three linearized acoustic branches, which has an adverse effect on the accuracy of the DMM. By utilizing the exact dispersion of acoustic phonons to calculate thermal conductance between metal-metal and metal-semiconductor interfaces, the DMM yielded results that varied significantly from the Debye approximation. For layered materials such as graphite, an isotropic phonon dispersion predicts thermal conductance with a high factor of error around 6. A general framework was recently proposed which used an anisotropic Debye dispersion to predict thermal conductance in graphite, Bi$_2$Te$_3$, and high-density polyethylene. This was a significant improvement on the inaccurate isotropic model, which yielded results much closer to experimental values. Following this work, another anisotropic model was proposed which utilized a truncated linear dispersion to predict lattice and interfacial thermal properties. Although it was able to accurately predict thermal conductivity in the basal plane, the interfacial thermal conductance results showed a large discrepancy in comparison with the experimental results. This was due to inaccurate approximations of the group velocity, especially for the flexural acoustic (ZA) mode. We aim to improve upon these models by incorporating the exact full phonon dispersion without approximation into the DMM to accurately predict the interfacial thermal conductance within the DMM framework.

The objective of this work is to calculate the interfacial thermal conductance between layered materials and metals using a new framework involving the DMM. Here, we consider the exact full dispersion of the materials in question without any approximations. We then compared our results with previous anisotropic models and experimental studies. The framework was then used to visualize the phonon focusing effect in anisotropic materials. To demonstrate the usefulness of this new framework, we analyzed the Al-MoS$_2$ interface to obtain temperature-dependent interfacial thermal conductance values, which is lacking in the literature. Another facet of our work involved optical branches that are considered to have negligible contributions to interfacial thermal conductance. We observed that low-frequency optical modes have a significant contribution to thermal conductance in TMDs, which further makes it imperative to use the exact full dispersion relations in the DMM calculations.

II. MATERIALS, MODELS, AND COMPUTATIONAL DETAILS

We calculated the interfacial thermal conductance for seven interfaces: Al-Si, Al-graphite, Au-graphite, Cr-graphite, Al-MoS$_2$, Au-MoS$_2$, and Cr-MoS$_2$. We first obtained the phonon dispersions for the materials forming these interfaces using density functional theory (see the supplementary material for details). To calculate the interfacial thermal conductance, we used the DMM framework. For a given interface between two materials A and B, the model assumes that all phonons undergo elastic scattering and lose all memory of their previous state. Let us consider a phonon mode in material A with wave vector $k$ and polarization $i$ that is incident on the interface. The probability that the phonon will be transmitted from A to B is given by $^{24}$

$$\alpha_{A\rightarrow B}(\omega') = \frac{\Delta K_A \left[ \sum_{j} |V(k, j) \cdot \hat{n}| \delta_{\omega(k,j),\omega'} \right]}{\Delta K_A \left[ \sum_{j} |V(k, j) \cdot \hat{n}| \delta_{\omega(k,j),\omega'} + \Delta K_A \left[ \sum_{j} |V(k, j) \cdot \hat{n}| \delta_{\omega(k,j),\omega'} \right] \delta_{\omega(k,j),\omega'}}. \quad (2)$$

where $\Delta K_A$ and $\Delta K_B$ are the volumes of the discretized cells pertaining to the high-resolution Brillouin zones of A and B. The group velocity is given by $V$, and the frequency is denoted by $\omega$. The unit vector normal to the interface is given by $\hat{n}$, and $j$ is the polarization of the phonon in material B. It is important to note here that the Kronecker delta function $\delta_{\omega(k,j),\omega'}$ is unity when the frequencies from the two Brillouin zones are equal and are zero otherwise. It is evident that $\alpha$ is purely a function of the frequency. The transmission probability can now be used to find the interfacial thermal conductance, which is given by $^{24}$

$$G = \frac{1}{2(2\pi)^2} \sum_{k} \int \frac{1}{k_B T^2} \alpha_{A\rightarrow B}(k, i) \times \left( \frac{\hbar \omega(k, i)}{k_B T} \right)^2 |V(k, i) \cdot \hat{n}| \exp \left( \frac{\hbar \omega(k, i)}{k_B T} \right) \left[ \exp \left( \frac{\hbar \omega(k, i)}{k_B T} \right) - 1 \right]^2 dk. \quad (3)$$

Since the phonon loses all memory of its initial state, $\alpha_{A\rightarrow B} = 1 - \alpha_{B\rightarrow A}$. In the calculation of Eqs. (2) and (3), we will set the upper limit of the integration to the maximum frequency of materials A and B. If the phonon modes are not excited at a specific temperature $T$, the contribution to $G$ is negligible due to the Bose-Einstein distribution in Eq. (3).

In order to obtain the correct conductance, we tested different grids for the two Brillouin zones. The choice of the grid depends primarily on the phonon dispersion curves of the respective materials. If the frequency ranges of both A and B are similar, we can select a grid with a similar number of q-points. However, if material A has, for example, a larger frequency range than material B, the number of q-points for A needs to be greater than that for B. Different grids are tested till we obtain $G_{AB} = G_{BA}$. To obtain a quick back-of-the-envelope solution, we can select two grids with the same number of q-points and take the average of $G_{AB}$ and $G_{BA}$. It would yield an interfacial thermal conductance value that lies in the vicinity of the...
III. RESULTS AND DISCUSSION

To ensure reliability, it is important for the dispersion relations to be accurate. We checked the dispersion relations against the literature and experimental data for all materials we studied (see the supplementary material for details). The frequency and group velocity of each mode are fed into our DMM code that calculates the interfacial thermal conductance. Instead of representing these dispersion curves using a polynomial fitting relation, we use a mode-to-mode comparison to determine which phonons are transmitted from material A to material B. To validate our DMM code, we compared our results with another similar model that incorporated the exact dispersion into their calculations for isotropic materials. 

We now proceed to the main objective of this work, i.e., calculating thermal conductance for interfaces between layered materials and metals. Using the actual dispersion, we calculated interfacial thermal conductance of Al-graphite, Au-graphite, and Cr-graphite interfaces, which are listed in Table I. The converged q-grid for Au-graphite calculations are 50 × 50 × 20 and 30 × 30 × 30, respectively. Whereas for the Al-graphite interface, grids of 40 × 40 × 20 and 40 × 40 × 20 yielded convergence. The results were then compared with previous anisotropic models and experimental measurements, as shown in Figs. 2(a) and 2(b). For the Al-graphite interface, Chen’s model predicted the conductance values as 346 MW/m² K. Hongkun’s model predicted the value as 133 MW/m² K, and the experimental results yielded a value of 49 MW/m² K for measurements by Schmidt et al. Our model calculated thermal conductance as 98 MW/m² K. While Chen’s and Hongkun’s anisotropic DMM predicted the value of thermal conductance as 300 MW/m² K and 68 MW/m² K, respectively, for Au-graphite interface at room temperature, our model calculates the conductance as 56 MW/m² K, which is significantly closer to the experimental value of 30 MW/m² K. As mentioned earlier, the experimental results heavily depend on the quality of the sample, and it is therefore important to note that our model does reasonably well to project interfacial thermal conductance values that have the same order of magnitude as the true thermal conductance. Even though our model slightly overpredicts thermal conductance, it can still be regarded as a good framework to study interfacial thermal transport between layered materials and metals. It can also be extended for determining the phonon contribution to the thermal conductance of semiconductor interfaces, as long as we have an exact full phonon dispersion to work with since the crux of our model is using a mode-to-mode comparison.

We now take an in-depth look at the reason for the improved accuracy of our model and the factors that govern thermal transport in anisotropic materials. Previous models have used approximate representations of acoustic branches to reduce complexity while sacrificing accuracy. In reality, these approximations lead to the inclusion of artificial modes with unrealistic group velocities. It is well known that flexural phonons (ZA) have a significant contribution to thermal conductance in the cross-plane direction. For example, in graphene, flexural modes have 70%–80% contribution to thermal conductance in the cross-plane direction. For layered materials and metals, it can also be extended for determining thermal conductance for interfaces between layered materials and metals. Using the actual dispersion, we calculated interfacial thermal conductance of Al-graphite, Au-graphite, and Cr-graphite interfaces, which are listed in Table I. The converged q-grid for Au-graphite calculations are 50 × 50 × 20 and 30 × 30 × 30, respectively. 

As shown in Fig. 1, for the interfacial thermal conductance of an Al-Si interface, the previous model predicted a thermal conductance of 270 MW/m² K at room temperature, whereas our model calculated the thermal conductance as 304 MW/m² K. The values converged for a q-grid of 50 × 50 × 50 applied to the Brillouin zone of both materials involved. The converged q-grid for the Al-Si interface using transient thermoreflectance measurements is around 360 ± 40 MW/m² K at 300 K. The Si surface in this reference was cleaned by hydrogen fluoride, so the native oxide usually at the interface was removed. The departure of our values from the experimental results can be attributed to the assumption of elastic scattering in the DMM. Since Reddy et al. used only acoustic modes for the thermal conductance calculations, the predicted values slightly differ for the full-dispersion model.

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to thermal conductance by virtue of the symmetry selection rule, which leads to the restriction of certain scattering mechanisms. Figure 3 demonstrates a comparison of the ZA branch of graphite used in our model with that used in Hongkun’s model. The difference is clearly visible here, as the truncated dispersion fails to capture the original curvature of the ZA branch. The calculation of the transmission coefficient relies on matching the dispersion curves of the two materials forming the interface. The use of actual dispersion relations avoids the inclusion of any artificial modes and therefore leads to improved accuracy. For the Au-graphite interface, if we were to pick a random mode from the LA branch of Au as shown in Fig. 3 and match it with the ZA mode of graphite, we can observe a difference in the wave vectors and group velocity for the two models.

For one mode, this discrepancy might seem negligible, but when we calculate the total conductance, it manifests as a significant overestimation of the calculated values. We avoid this overestimation by using a mode-to-mode comparison to determine which phonons are truly transmitted. This new approach will enable researchers to gain a clear picture of the contribution of each mode to thermal transport across the interface.

Figure 4(a) shows the propagation directions of each phonon for the acoustic branches of graphite. We can observe that the majority of phonons are inclined to travel in the in-plane direction, signified by the density of the velocity vectors. Figure 4(b) shows the directions of the phonons for Al. Due to its isotropic nature, we can observe that the group velocity vectors are distributed almost evenly in all directions. Whereas for graphite, a large number of phonons have group velocity vectors directed in nearly the same direction, which is known as the phonon focusing effect. Figure 4 acts as an effective method to visualize this effect by utilizing the exact full dispersion of the materials involved. In Al, the phonon focusing effect is absent due to strong bonding interactions along all directions. Whereas in graphite, due to the weak interlayer coupling between the layers, the number of phonon velocity vectors fades from the ab-plane to the c-plane. This visualization of the phonon focusing effect further advocates for the accuracy of our anisotropic model and strengthens the argument that it can be employed to study interfacial thermal conductance of all anisotropic materials.

To illustrate the scope of our model, we calculated thermal conductance for the Al-MoS$_2$ interface as shown in Fig. 5. Our model calculated the value as 56 MW/m$^2$K at room temperature. We further measured interfacial thermal conductance between Al and MoS$_2$ ourselves from 100 to 300 K using the time-domain thermoreflectance (TDTR) setup in our laboratory at North Carolina State University. The experimental details can be found in the literature and supplementary material. The measured interfacial thermal conductance between Al and MoS$_2$ at 300 K is 43 ± 5 MW/m$^2$K.
The conductance decreases to $23 \pm 3$ MW/m$^2$ K when the temperature drops to 100 K. The value of the measured conductance at room temperature is lower than our model, while the temperature-dependent data align closer to the model predictions. These values fare well with previous TDTR measurements that yielded values of $56 \pm 6$ MW/m$^2$ K, $25 \pm 3$ MW/m$^2$ K, and $42 \pm 5$ MW/m$^2$ K at room temperature for different samples.\textsuperscript{39–41}

It is imperative that for any future analysis of thermal transport in such materials, we incorporate the exact full dispersion into the model. We note that the DMM does not account for the inelastic scattering, so the calculated interfacial thermal conductance value may deviate from the experimental value, especially in materials with a large mismatch in their frequency spectra. Although the exclusion of factors such as inelastic scattering, interfacial bonding, and surface effects are responsible for the overprediction of thermal conductance,\textsuperscript{28,30,45–47} our model can still act as a simple framework that can be used to effectively study thermal transport in anisotropic materials.

**IV. SUMMARY**

In summary, we calculated interfacial thermal conductance for Al-Si, Al-graphite, Au-graphite, Cr-graphite, Al-MoS$_2$, Au-MoS$_2$, and Cr-MoS$_2$ interfaces. We found that our results agreed reasonably well with experimental values. The incorporation of exact full dispersion relations without any approximations to the group velocities was critical to the accuracy of the results. Furthermore, we discovered that for layered materials, optical phonons have a significant contribution to interfacial thermal conductance. The phonon dispersion for most metals is readily available, which opens up the possibility of studying several interfaces between metals and layered materials. As the only inputs for the model are the phonon dispersion relations of the two crystalline materials forming the interface, we can apply this model to create a database of interfacial thermal conductance values which can find use in thermal management in several applications, such as optoelectronics, thermoelectric devices, spintronics, and stretchable electronics and nanotransistors.

**SUPPLEMENTARY MATERIAL**

See the supplementary material for calculation details of phonon dispersions and grid convergence check. The experimental details for TDTR are also included.

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