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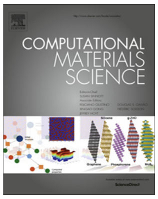

Effect of the accuracy of interatomic force constants on the prediction of lattice thermal conductivity

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ABSTRACT

Solving Peierls-Boltzmann transport equation with interatomic force constants (IFCs) from first-principles calculations has been a widely used method for predicting lattice thermal conductivity of three-dimensional materials. With the increasing research interests in two-dimensional materials, this method is directly applied to them but different works show quite different results. In this work, classical potential was used to investigate the effect of the accuracy of IFCs on the predicted thermal conductivity. Inaccuracies were introduced to the third-order IFCs by generating errors in the input forces. When the force error lies in the typical value of first-principles calculations, the calculated thermal conductivity would be quite different from the benchmark result. It is found that imposing translational invariance conditions cannot always guarantee a better thermal conductivity result. It is also shown that Grüneisen parameters cannot be used as a necessary and sufficient criterion for the accuracy of third-order IFCs in the aspect of predicting thermal conductivity.

1. Introduction

In crystalline semiconductors and insulators, phonons (*i.e.* lattice vibrations) are the major heat carriers, so the thermal conductivity can be calculated with the knowledge of phonon properties. Recently there are growing interests to predict the lattice thermal conductivity by solving Peierls-Boltzmann transport equation (PBTE), either under single mode relaxation time approximation (SMRTA) or with full iterative solution [1,2]. With interatomic force constants (IFCs) extracted from first-principles calculations as the input, this method has been widely used to calculate the thermal conductivity of three-dimensional (3D) materials [3–26]. The good agreement between these calculated values and measured experimental data proves its accuracy and reliability [3–21].

The discovery of ultrahigh thermal conductivity of graphene [27] has stimulated a growing research interest in the thermal conductivity of two-dimensional (2D) materials. The first-principles PBTE method for predicting thermal conductivity has been directly applied to 2D materials like graphene [28–31], silicene [32–35], phosphorene [36–40], MoS_2 [41–43], borophene [44], *etc.* However, previous calculations show quite different results in different works. For example, the predicted thermal conductivity for black phosphorene from SMRTA [36–40] at room temperature along armchair direction varies a lot from 5.46 to 33 W/mK, and the result along zigzag direction spans a rather large range between 15.33 and 83.5 W/mK. Similar discrepancy is also observed in the case of MoS_2, whose thermal conductivity at room temperature was predicted from SMRTA to be 83 W/mK by Li et al. [41] as well as Gu and Yang [42]. In comparison, Yan et al. [43] got a result of 35.5 W/mK with the same method. The lack of consistency in the predicted thermal conductivity may arise from using iterative method instead of SMRTA [30,31], imposing translational invariance conditions to third-order IFCs [15,35], different exchange-correlation functionals used in first-principles calculations [45], enforcing a quadratic branch in the dispersion of 2D materials [44], *etc.* In materials where resistive Umklapp scattering processes dominate in the phonon-phonon scattering, both SMRTA and iterative method should give similar results [1,2]. For graphene, iterative method yields a much larger thermal conductivity value than SMRTA because the momentum-conserving normal scattering processes also play an important role in phonon transport [30,31], which has been explained by the hydrodynamic phonon transport at room temperature [46,47]. Regarding the translational invariance conditions (*i.e.* acoustic sum rules), Lindsay et al. [15] demonstrated that imposing it to third-order IFCs would play an important role in determining thermal conductivity. Our previous results for silicene also showed its importance [32,35]. Transla-

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tional invariance conditions will affect the calculated phonon scattering rate, especially for long-wavelength phonons near the Brillouin zone center. Concerning the exchange-correlation functionals, Jain and McGaughey [45] studied their effects on predicting the thermal conductivity of crystalline silicon from first-principles calculations. Different exchange-correlation functionals could lead to an under-prediction or over-prediction within 20% of the experimental value. Recently, Carrete et al. [44] showed that the second-order IFCs directly extracted from first-principles calculations might yield problematic phonon dispersion curve for 2D materials. The dispersion curve of unstrained 2D materials can be demonstrated to contain a quadratic branch near Brillouin zone center [48] but the second-order IFCs directly extracted from first-principles calculations would yield linear ones. By generating physically sound IFCs, they showed that the thermal conductivity result could be quite different from the value calculated with the raw IFCs from first-principles calculations [44].

Previous discussions explained part of the inconsistency in the predicted thermal conductivity of 2D materials from first-principles calculations. However, with all the above mentioned reasons considered, based on our own testing (unpublished), discrepancy in predicted thermal conductivity could still exist for some 2D materials. As will be shown later, the accuracy of third-order IFCs also plays an important role on the predicted thermal conductivity. For first-principles calculations, the accuracy might be affected by energy cutoff, *k*-point grid, reciprocal space projection technique, aliasing errors, discretization errors, *etc.* [49]. For example, the attainable fractional precision [49] in forces using VASP is 10^{-4}. Currently, the most widely used method to extract IFCs generally takes forces as the input parameter, and uses finite-difference method to calculate the IFCs. The raw IFCs from first-principles calculations often do not satisfy the translational invariance conditions, so these conditions are artificially imposed by adding small compensation to each term. All these processes will induce additional uncertainty to the IFCs, especially the third-order IFCs.

In this work, we will discuss how the accuracy of IFCs could affect the predicted lattice thermal conductivity values. Due to the large uncertainty in first-principles calculations, we used classical potential to do such an investigation. Classical potential has the advantage that it has an explicit analytical form, so that the error only comes from numerical computation and can be reduced to a negligible amount to get an “accurate” thermal conductivity result as benchmark. Based on the benchmark case from classical potential, inaccuracies are artificially introduced to third-order IFCs and effects of these inaccuracies on the predicted thermal conductivity are investigated. SMRTA is used to calculate thermal conductivity due to the computational cost consideration and also because phonon relaxation time is well defined with this approach. Previously, Grüneisen parameters have been used as a simple test for the accuracy of the third-order IFCs [28]. The applicability of this criterion is also examined. Our result will shed some light on predicting thermal conductivity from first-principles calculations. In what follows, we describe the simulation methods and details in Section 2. Simulation results for silicon, graphene, and silicene are shown in Section 3. Discussions about our results and first-principles calculations are presented in Section 4. Our conclusions are summarized in Section 5.

2. Simulation methods and details

2.1. Single mode relaxation time approximation method

For a periodic crystal structure under equilibrium state, the potential energy can be expanded as the Taylor series [50,51]

$$U = U_0 + \frac{1}{2!}\sum_{ij,\alpha\beta}\Phi_{ij}^{\alpha\beta}u_i^{\alpha}u_j^{\beta} + \frac{1}{3!}\sum_{ijk,\alpha\beta\gamma}\Psi_{ijk}^{\alpha\beta\gamma}u_i^{\alpha}u_j^{\beta}u_k^{\gamma} + \cdots, \tag{1}$$

where U_0 is the equilibrium potential energy. u_i^{α}, u_j^{β}, and u_k^{γ} are the displacements of i-th atom in α direction, j-th atom in β direction, and k-th atom in γ direction, respectively. $\Phi_{ij}^{\alpha\beta}$ is the second-order IFC and $\Psi_{ijk}^{\alpha\beta\gamma}$ is the third-order IFC. Even higher-order IFCs are neglected in this equation. Physically correct second-order and third-order IFCs have to satisfy the point/space group symmetry relations, translational invariance conditions, and rotational invariance conditions, which are shown in the Appendix A. Comparison of Grüneisen parameters from second-order and third-order IFCs has been used as a simple test for the accuracy of third-order IFCs. The calculation of Grüneisen parameters and the definition of relative difference are also shown in the Appendix A. The force acting on each atom is $\boldsymbol{F}_i = -\nabla_i U$ and for a structure under equilibrium state, $\boldsymbol{F}_i = \boldsymbol{0}$. With the IFCs as the input, the thermal conductivity of semiconducting or insulating materials can be calculated from SMRTA with the following equation

$$\kappa_l^{\alpha\beta} = \sum_{\lambda} c_{ph,\lambda} v_{\lambda}^{\alpha} v_{\lambda}^{\beta} \tau_{\lambda}, \tag{2}$$

where λ denotes different phonon modes that can be distinguished by wave vector $\boldsymbol{q}$ and phonon branch ν. $c_{ph,\lambda}$ is the volumetric phonon specific heat. v_{λ}^{α} and v_{λ}^{β} are the phonon group velocities in α and β direction, respectively. $c_{ph,\lambda}$ and $\boldsymbol{v}_{\lambda}$ can be calculated with the second-order IFCs as the input [52]. τ_{λ} is the phonon relaxation time, *i.e.* the inverse of phonon scattering rate. In our calculation of τ_{λ}, only phonon-phonon scattering is considered. More specifically, only three-phonon scattering is considered. τ_{λ} can be calculated with both second-order and third-order IFCs as the input. For more details about the method we refer the reader to Refs. [52–54].

2.2. Simulation details

The second-order and third-order IFCs as the input for SMRTA method were calculated from classical potential. Careful tests were carried out to reduce the numerical error. GULP package [55] was first used to optimize the primitive unit cell of silicon, graphene, or silicene. After that, a supercell was constructed and the lattice constant was re-optimized with LAMMPS package [56]. In this re-optimization process, the bisection method was used to find the lattice constant corresponding to the lowest energy state. Forces acting on each atom were computed from LAMMPS through the analytical derivatives of the potential function [57], which would be free of truncation error coming from numerical differentiation. As the input for calculating IFCs, forces were output with sixteen significant digits to retain accuracy. In order to reduce the truncation error, fourth order accuracy method was used instead of central difference method (see the Appendix A for the details) to compute the second-order and third-order IFCs with our own in-house code and revised THIRDORDER.PY [54], respectively. These third-order IFCs were not modified by adding small compensation because they already satisfied translational invariance conditions to a reasonable extent. Point/Space group symmetry conditions were enforced and utilized to reduce computational cost. These IFCs were then used to obtain the benchmark thermal conductivity. In fact, modified third-order IFCs that have translational invariance conditions imposed were also generated for the purpose of comparison. Inaccuracies in the third-order IFCs were simulated by either truncating digits or adding random numbers to the forces. The force errors were put in the irreducible set of IFCs before point/space group symmetry operations in order to make sure that the full set satisfies symmetry conditions. For truncation