CRITICALLY ASSESSING THE APPLICATION OF QUANTUM CORRECTIONS TO CLASSICAL THERMAL CONDUCTIVITY PREDICTIONS

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ABSTRACT

Quantum corrections can be used to map the thermal conductivity predicted in a classical framework [e.g., a molecular dynamics (MD) simulation] to a corresponding value in a quantum system. This procedure is accomplished by equating the total energies and energy fluxes of the classical and quantum systems. The validity of these corrections is questionable because they are introduced in an ad hoc manner and are not derived from first principles.

In this work, the validity of these quantum corrections is examined by comparing the thermal conductivity of Stillinger-Weber silicon calculated using a full quantum mechanical treatment to a quantum-corrected value predicted from a classical framework between temperatures of 10 K and 1000 K. The quantum and classical predictions are obtained using anharmonic lattice dynamics calculations. We find discrepancies between the quantum-corrected predictions and the quantum predictions obtained directly. We investigate the causes of these discrepancies and from our findings, conclude that quantum thermal conductivities cannot be predicted by applying simple corrections to the values obtained from a purely classical framework.

INTRODUCTION AND METHOD

Classical molecular dynamics (MD) simulation is a powerful tool for predicting physical behavior and material properties [1–3]. As a general rule, MD simulations are considered valid near and above a material’s Debye temperature, where all of the vibrational (i.e., phonon) modes are fully excited. Molecular dynamics simulations are not valid at lower temperatures, where quantum effects cannot be neglected. To mitigate this limitation, quantum corrections (QCs) have been developed. The purpose of QCs is to map predictions made for a classical system onto corresponding values in a quantum system. Quantum corrections have been derived from first principles for thermodynamic, mechanical, and structural properties (e.g., Helmholtz free energy, entropy, bulk modulus, and pair distribution function) [4–6]. Rigorous QCs for transport properties such as thermal conductivity are more difficult to obtain [7].

The commonly-used QCs for thermal conductivity are based on ad-hoc physical arguments rather than fundamental relations. These QCs are applied to the temperature, \( T \), and the thermal conductivity, \( k \) [8, 9]. The temperature correction is made by equating the total energies of the classical and quantum systems.
The energy equality can be expressed as

\[
3(Nn - 1)k_B T^C = \sum_{\nu} \left[ \hbar \omega_{\nu} f^Q(\nu) + \frac{\hbar \omega_{\nu}^2}{2} \right].
\] (1)

Here, the sums are over all phonon modes denoted by \(N\) wave vectors, \(\mathbf{k}\), and \(3n\) dispersion branches, \(\nu\), the superscripts \(C\) and \(Q\) indicate classical and quantum, \(k_B\) is the Boltzmann constant, \(\hbar\) is the Planck constant divided by \(2\pi\), and \(\omega_{\nu}\) and \(f(\nu)\) are the mode-dependent frequency and equilibrium occupation number. For the quantum system, the equilibrium occupation number is the Bose-Einstein distribution,

\[
f^Q = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T^Q}\right) - 1}.
\] (2)

The term \(\hbar \omega/2\) in Eq. (1) is the zero-point (ZP) energy. The ZP energy has no parallel in a classical system, and, as will be shown, plays an important role in the QCs.

The thermal conductivity correction is

\[
k^Q = k^C \frac{dT^C}{dT^Q},
\] (3)

which arises from equating the heat fluxes obtained from the Fourier law in the classical and quantum systems. The QCs given by Eqs. (1) and (3) have been applied to classical MD thermal conductivity predictions for amorphous silicon [9], crystalline silicon in bulk [10–12] and thin films [13], \(\beta\)-silicon carbide [14], silicon-germanium superlattices [15], carbon nanotubes [16], and various transition metals (the phonon contribution only) [17]. In these studies, some have found that neglecting the ZP energy yields better agreement with experimental data [11, 12, 15] while others find that including the ZP energy is better [9, 13, 14, 16].

The validity of Eqs. (1) and (3) is questionable as they are not derived from fundamental relations and have not been rigorously tested. The doubts regarding these QCs are further exemplified by the non-consensus on whether to include the ZP energy in Eq. (1) or to ignore it [18]. The objective of this work is to rigorously assess the validity of Eqs. (1) and (3). To do so, we self-consistently predict the classical and quantum thermal conductivities of a crystalline Stillinger-Weber (SW) [19] silicon system using the relation

\[
k = \sum_{\mathbf{k}} \sum_{\nu} c_{\nu} m_{\nu}^2 \sum_{\mathbf{g},\mathbf{v}} v_{g,v} \tau(\mathbf{g}),
\] (4)

which is based on the Boltzmann transport equation (BTE) under the relaxation time approximation. In Eq. (4), \(c_{\nu}\) is the phonon specific heat, \(v_{g,v}\) is the group velocity along the [100] direction, and \(\tau\) is the relaxation time. Harmonic and anharmonic lattice dynamics (LD) calculations, which can be performed for both quantum and classical systems, are used to compute all necessary phonon properties. A discussion of the LD techniques is given by Turney et al. [20]. Classical thermal conductivity predictions made using Eq. (4) and classically defined phonon properties have been shown to be equivalent to MD-based predictions at low temperatures [20]. We directly test the accuracy of the QCs by quantum-correcting the LD-based classical thermal conductivity predictions and comparing to the quantum predictions made using Eq. (4) and quantum properties.

RESULTS

The predicted SW silicon thermal conductivities are plotted in Fig. 1 for the quantum and classical systems between temperatures of 10 and 1000 K. The quantum and classical predictions converge at high temperature, as they must. The low-temperature thermal conductivity behavior is also as expected. The quantum thermal conductivity peaks at a temperature of 30 K then approaches zero as the temperature goes to zero. The classical thermal conductivity prediction increases monotonically as the temperature decreases, approaching infinity at zero-temperature. For temperatures less than 100 K, phonon scattering from defects, isotopes, and boundaries is important [21]. We have neglected these scattering mechanisms, resulting in very large thermal conductivity values at these temperatures. We note that Broido et al. predicted the thermal conductivity of SW silicon using a method related to the LD method presented here with these additional scattering mechanisms included [21].

The temperature mapping from the classical system to the quantum system defined by Eq. (1) when the ZP energy is (i) considered and (ii) neglected is plotted in Fig. 2. Also plotted is the scaling factor, \(dT^C/dT^Q\), defined by Eq. (3). This factor is independent of the ZP energy and is always less than one. The temperature mapping depends strongly on the inclusion or exclusion of the ZP energy. For the same quantum temperature, the classical temperatures for the two cases are offset by the average ZP energy divided by \(k_B\), which is 270 K for SW silicon. When the ZP energy is included, the corrected temperature is greater than the quantum temperature, the corrected and quantum temperatures converge in the high-temperature \((i.e.\,\text{classical})\) limit, and a classical system below a temperature of 270 K has no quantum counterpart. When the ZP energy is excluded, the corrected temperature is less than the quantum temperature and the corrected and quantum temperatures do not converge in the high-temperature limit but are separated by 270 K. The effect of the QCs on the thermal conductivity prediction is shown in Fig. 1, where we plot the quantum-corrected classical predictions. Neglecting the ZP energy causes the QCs to increase the thermal conductivity. Including the ZP energy causes the clas-
quantum conductivities to shift downward, away from the quantum predictions. For QCs to be valid, the corrected classical predictions must (i) converge to the quantum predictions at high temperature and (ii) provide a better estimation of the quantum thermal conductivity than the uncorrected classical predictions. Our four sets of thermal conductivity predictions (quantum, classical, and two sets of quantum-corrected classical values) do converge at high temperature, though the convergence is slow for both sets of quantum-corrected values. At the SW silicon Debye temperature of 710 K [22], the corrected thermal conductivities with and without the ZP energy are 10% lower and 30% higher than the quantum value, while the uncorrected classical prediction is within 5% of the quantum value. In fact, for temperatures above 200 K, neither of the QC approaches improves upon the agreement between the uncorrected classical value and the quantum value. When including the ZP energy, a maximum in the thermal conductivity is predicted, however, the location and magnitude of this maximum are clearly wrong. From these observations, we conclude that the QCs prescribed by Eqs. (1) and (3), with the ZP energy either included or neglected, do not properly account for quantum effects. These QCs even fail at high temperatures, where quantum effects are small.

The reasons why the QCs given by Eqs. (1) and (3) fail can be deduced by considering the mode-dependence of the phonon properties (ω, c_{ph}, v_{g,x}, and τ). In Fig. 3, we plot the contribution to the thermal conductivity versus phonon frequency, both scaled by their maximum values, for temperatures of 10, 100, and 500 K. When plotted this way, the results for the classical systems collapse to a single, temperature-independent curve. For the quantum system, however, the low-frequency phonons increasingly dominate the thermal conductivity as the temperature decreases. This effect is due to the temperature-dependence of the occupation number, which effectively freezes out the high-frequency modes at low temperatures. Applying the QCs given by Eqs. (1) and (3) shifts the thermal conductivity by a temperature-dependent scale factor. Yet, we see from Fig. 3 that the frequency-dependence of the mode contribution is strongly

Figure 1. THERMAL CONDUCTIVITY PREDICTIONS FOR THE QUANTUM AND CLASSICAL SYSTEMS AND THE QUANTUM-CORRECTED CLASSICAL PREDICTION USING THE ZP ENERGY (QCs w/ ZP) AND NEGLECTING IT (QCs w/o ZP).

Figure 2. MAPPING BETWEEN QUANTUM AND CLASSICAL TEMPERATURES WITH AND WITHOUT THE ZP ENERGY AND dT^C/dT^Q FOR THE QCS AS DEFINED BY Eqs. (1) AND (3).
temperature-dependent. The thermal conductivity thus cannot be properly corrected by applying a system-level scaling factor.

We attribute the apparent successes of the QCs to the inaccuracy of interatomic potentials and the fact that the thermal conductivity prediction can be decreased or increased by including or neglecting the ZP energy. Using an approach related to the LD method used here, Broido and co-workers found that a fully quantum-mechanical treatment of SW silicon does not match the experimental thermal conductivity data, [21] while the same treatment using input from density-function theory calculations does. [23]

CONCLUSIONS

We have assessed the validity of the commonly-used QCs for thermal conductivity by using harmonic and anharmonic LD calculations to self-consistently predict the quantum and classical thermal conductivities of SW silicon. Applying the QCs to the classical predictions, with or without the ZP energy, does not bring them into better agreement with the quantum predictions compared to the uncorrected classical values above temperatures of 200 K. When neglecting the ZP energy, the quantum-corrected temperature does not approach the quantum temperature in the high-temperature limit. When the ZP energy is included, the corrected thermal conductivity shifts in the wrong direction, away from the quantum prediction and the location and magnitude of the maximum do not agree with the quantum results.

REFERENCES

