First-Principles-Based Interatomic Potential for SI and Its Thermal Conductivity

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ABSTRACT

Based on first-principles density-functional calculations, we have developed and tested a force-field for silicon, which can be used for molecular dynamics simulations and the calculation of its thermal properties. This force field uses the exact Taylor expansion of the total energy about the equilibrium positions up to 4th order. In this sense, it becomes systematically exact for small enough displacements, and can reproduce the thermodynamic properties of Si with high fidelity. Having the harmonic force constants, one can easily calculate the phonon spectrum of this system. The cubic force constants, on the other hand, will allow us to compute phonon lifetimes and scattering rates. Results on equilibrium Green-Kubo molecular dynamics simulations of thermal conductivity as well as an alternative calculation of the latter based on the relaxation-time approximation will be reported. The accuracy and ease of computation of the lattice thermal conductivity using these methods will be compared. This approach paves the way for the construction of accurate bulk interatomic potentials database, from which lattice dynamics and thermal properties can be calculated and used in larger scale simulation methods such as Monte Carlo.

1 Introduction

Classical molecular dynamics (MD) simulations use either semi-empirical potentials such as Stillinger-Weber (SW) [1], Abell-Tersoff-Brenner [2] or other type of force fields where the potential energy is an analytical function of the atomic positions, or first-principles potentials calculated typically using density-functional methods. The former are fast to compute but suffer from inaccuracies, while the latter are accurate but time-consuming to compute. Due to recent interest in thermal transport in semiconductor materials having attractive thermoelectric properties for energy conversion, and the topic of thermal management in general, there have been many calculations of the lattice thermal conductivity of materials using the Green-Kubo (GK) formula. This formula relates the thermal conductivity, through the use of the fluctuation-dissipation theorem, to the time-integral of the heat current autocorrelation function. The latter is calculated from a MD simulation, and the ensemble average is usually replaced by a time average. Semi empirical potentials such as SW are usually used to perform the MD simulation for a system such as Si. As the thermal conductivity of a perfect crystal is mainly due to anharmonic three-phonon processes, directly related to the third-derivatives of the potential energy with respect to atomic displacements, and the latter is generally not fitted or considered in the design of the semi-empirical potential, there is really no good reason to expect an accurate value for the thermal conductivity calculated from a GK-MD simulation. In the case of Si, when using the SW potential, however, for some magical reason [3], relatively good agreement is found between the experiment and the simulation results, even for a relatively small supercell [4–7]. In a similar work, using the EDIP potential, Pascual-Gutierrez et al. [8] also find thermal conductivity of bulk Si from MD in good agreement with experiments. In a subsequent work [9], the same group computed the thermal conductivity using the lattice dynamics (LD)
theory based on the same EDIP potential, similar to the work of Broido et al [10]. Calculations of the thermal conductivity by the latter, based on the solution of Boltzmann transport equation have shown that the thermal conductivity of Si using the SW potential is about 4-times larger than the experiment, while using the Tersoff or EIDP potentials are twice larger than the experimental values [10]. There is a discrepancy between the work of Broido et al. and that of Pascual-Gutierrez et al. Both used LD theory based on the same EDIP potential, but their obtained thermal conductivities disagree! The reason for this is unclear to us. Broido et al., later, used the density-functional perturbation theory (DFPT) formalism in order to calculate the phonon scattering rates from first-principles DFT calculations. They then used the same approach to solve Boltzmann equation, and were able to successfully reproduce the thermal conductivity of bulk Si [11].

One of us has recently developed a methodology to extract second, third and fourth derivatives of the potential energy from first-principles calculations [12], and showed that the phonon dispersion relation in Si can be well-reproduced. In this paper, we pursue this work further and use these derivatives to construct a force field in order to explore the results from MD simulations and perturbation calculation to calculate the thermal conductivity of bulk Si.

2 Methods

We construct the potential energy for the MD simulation as a Taylor expansion up to fourth order in the atomic displacement $u_i$ of atom $i$ about its equilibrium position:

$$V = V_0 + \sum_i \Pi_i u_i + \frac{1}{2!} \sum_{ij} \Phi_{ij} u_i u_j$$

$$+ \frac{1}{3!} \sum_{ijk} \Psi_{ijk} u_i u_j u_k + \frac{1}{4!} \sum_{ijkl} \chi_{ijkl} u_i u_j u_k u_l$$

$$= \sum_i (e_i - \frac{1}{2} m_i v_i^2)$$

The last equation defines the on-site energy $e_i$ and if the displacements $u_i$ are around the equilibrium position, $\Pi_i = 0$. Such coefficients in the expansion must satisfy certain symmetry constraints: namely invariance under interchange of the coefficients, translational and rotational invariance, and invariance under symmetry operations of the crystal. The details of the needed constraints and how they are imposed can be found in our previous work [12].

A set of force-displacement data are calculated using first-principles DFT methods. In this work, we have used the Quantum-Espresso package [13] in order to perform such calculations for Si atoms in a $2 \times 2 \times 2$ supercell of 64 atoms. The set of force-displacements data along with the symmetry constraints form an over-complete linear set of equations needed to determine the potential derivatives, also called the force constants. We use the local density approximation (LDA) of Perdew and Zunger [14] with a cutoff energy of 40 Ryd and 10 k-points in the irreducible Brillouin zone of the cubic supercell. The range of different ranks of force constants can be chosen by the user. We have set the range of harmonic forces constants (FCs) to 5 nearest neighbor shells, and that of the cubic and quartic force constants to the first neighbor shell only. This results in 17, 5 and 4 independent harmonic, cubic and quartic FCs respectively. The corresponding number of terms in the Taylor expansion of the potential energy are, however, equal to 1500, 1146 and 7980 respectively. This is why the ranges were restricted to 5, 1 and 1 nearest neighbor shells in order to limit the computational time to a reasonable amount. Note that despite the large number of terms to be computed, arithmetic operations are only limited to additions and multiplications.

Using the harmonic FCs, we can obtain the phonon spectrum. As can be seen in Fig.1 the speeds of sound and most of the features are reproduced with very good accuracy. In order to reproduce the flat feature in the TA modes near the X point, one must go well beyond the fifth neighbor. The anharmonicity can be characterized by the Gruneisen parameters (GP). The force constant GP is defined as $\gamma_\lambda = -d \ln \phi / 2d \ln V$ where $V$ is the volume and $\phi$ a given force constant as the ones appearing in eq. (2). The mode GP is defined as: $\gamma_\lambda = -d \ln k_{\lambda \alpha} / d \ln V$ where $k_{\lambda \alpha}$ is the phonon frequency evaluated at the point $K$ and band index $\lambda$. It can be calculated analytically as a function of the cubic coefficients by projecting on the normal mode basis. Thus it can give a good indication of the strength of the cubic interactions. In Fig.1 we have also compared the GP coming from the first neighbor cubic FC model to the experiment. The optical and LA modes are in good agreement, but the TA modes are overestimated near the X and L points. This can lead to a higher scattering rate of the TA modes if one considers the simplified Klemens formula:

$$\frac{1}{\kappa_{\lambda \alpha}^{\text{Klemens}}} = \gamma_\lambda \frac{2k_B T}{M v_{\lambda \alpha}^2} \frac{\alpha_{\lambda \alpha}^2}{\alpha_{\lambda \alpha}^\text{suit}}$$

Thus it is expected that our model might slightly underestimate the thermal conductivity.

In the following we follow two paths to compute the thermal conductivity. The first is to use the Green-Kubo formula, by using the results from a MD simulation:

$$\kappa^{\alpha \beta} = \frac{1}{V k_B T^2} \int_0^\infty dt < J^\alpha(0) J^\beta(t) >$$

where it can be shown that the heat current $J(t)$ is given by:
The forces and currents are calculated according to eqs. (6), (7) and (5).

\[ J^\alpha = \sum_{ij} R_{ij}^\alpha (v_i - \frac{\partial e_i}{\partial u_j}) \]  

\[ F_i = -\sum_j \Phi_{ij} u_j - \frac{1}{2} \sum_{jk} \Psi_{ijk} u_j u_k - \frac{1}{6} \sum_{kl} \chi_{ijkl} u_j u_k u_l \]  

\[ \frac{\partial e_i}{\partial u_j} = \frac{u_i}{2} \Phi_{ij} + \frac{u_i}{3} \sum_k \Psi_{ijk} u_k + \frac{u_i}{8} \sum_{kl} \chi_{ijkl} u_k u_l \]  

In the above, \( R_{ij} \) is the vector separating the equilibrium positions of atoms \( i \) and \( j \). Typically a supercell is constructed with periodic boundary conditions, and a MD simulation is performed over a long enough time steps in order to reach thermal equilibrium, followed by a long \((N,V,E)\) simulation in order to collect data on \( J \) for later statistical processing, i.e., time and ensemble averaging of its autocorrelation. The forces and currents are calculated according to eqs. (6), (7) and (5).

The second method consists in solving the Boltzmann equation. The simplest approach is to use the relaxation time approximation (RTA), which leads to the following well-known expression for the thermal conductivity:

\[ \kappa = \frac{1}{3} \sum_{k\lambda} \tau_{k\lambda} \hbar \omega_{k\lambda} \frac{\partial n_{k\lambda}}{\partial T} \]  

The relaxation time \( \tau_{k\lambda} \) in this expression represents the time after which a phonon in mode \( k\lambda \) reaches equilibrium on the average, and depends on the scattering processes involved. In a pure bulk sample, the only source of phonon scattering is anharmonicity dominated usually by three-phonon processes. Using perturbation theory or the well-known Fermi Golden rule (FGR), one can derive the expression of the relaxation time as a function of the cubic force constants [16].

\[
\frac{1}{\tau_{k\lambda}} = \frac{\pi}{\hbar^2} \sum_{1,2} |V(k,1,2)|^2 \left[ (1 + n_1 + n_2) \right. \\
\left. \times \delta(\omega_{k\lambda} - \omega_1 - \omega_2) + 2(n_1 - n_2) \delta(\omega_{k\lambda} + \omega_1 - \omega_2) \right]
\]  

Here, \( n_i \) are the equilibrium Bode-Einstein distribution functions, and \( V \) is the cubic anharmonic force constants in the normal mode representation as detailed for instance in [16].

### 3 Results and Discussion

The computation of the thermal conductivity using the RTA is to some extent more straightforward than the use of GK-MD. The former involves a double summation in the first Brillouin zone and has very little systematic error in it, whereas the MD simulations require an ensemble averaging process with a relatively large error bar, not to mention the much longer CPU time needed to run the MD simulations.

There are large fluctuations in the integrated autocorrelation if only one initial condition is considered. We thus average the autocorrelation over 27 initial conditions for the 10x10x10 supercell. Since from each MD run one can really extract three autocorrelation functions \( \kappa_{xx}, \kappa_{xy}, \) and \( \kappa_{zz} \), and use all three in the averaging process, the average can be considered to be over 81 different initial conditions.

The error bars are determined by the large fluctuations in the integrated autocorrelations divided by the square root of the number of ensembles. The error bar due to the time average is usually much smaller if MD simulations are run for a long enough time.

The results for two different supercell sizes of 7 and 10 are summarized in table 3 as compared with the experimental data of Slack et al. [17] at 600 K. One can notice an underestimation...
of the experimental data, which is reduced as the supercell size is increased.

<table>
<thead>
<tr>
<th>Supercell size</th>
<th>Present work</th>
<th>experiment</th>
</tr>
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<tbody>
<tr>
<td>7x7x7</td>
<td>37 ± 10</td>
<td>64 ± 3</td>
</tr>
<tr>
<td>10x10x10</td>
<td>43 ± 12</td>
<td>64 ± 3</td>
</tr>
</tbody>
</table>

There are a few competing effects which can explain this discrepancy: the most important one is size effect. The results, as can be seen, depend on the size of the simulation cell which can only accommodate a discrete number of modes of largest wavelength \( L \), \( L \) being the length of the simulation supercell. This imposes a lower cutoff in the momenta contributing to \( \kappa \), and since the dominant relaxation time is that of acoustic modes, proportional to \( 1/\omega^2 \), at small momenta or frequencies, this size effect should lead to an underestimation of the thermal conductivity. Similarly, the larger value of the Gruneisen parameter for the acoustic modes in our model will produce a smaller relaxation time (see the Klemens formula in Eq. 3). The following effects will lead to an overestimation of the thermal conductivity: in the classical MD simulations, the number of modes is the high-temperature limit of the Bose-Einstein distribution, \( k_B T/\hbar \omega_{\lambda} \), which is larger than the quantum distribution. This leads to a heat capacity per mode of nearly \( k_B \) and therefore an overestimate of the true heat capacity. In a finite size cell, the allowed frequencies are quantized and energy conservation after a 3-phonon process can never be exactly satisfied, this will lead to an effectively longer lifetime for phonons, and thus to also an overestimate of \( \kappa \). It is not easy to quantify these errors except for those due to the phonon occupation numbers. It is therefore possible that there is some cancellation, and using the SW potential in the MD simulations, one gets a thermal conductivity in pretty good agreement (to within 30%) with experiments [4, 5] whereas Broido et al. [10] have shown, by solving Boltzmann equation beyond the RTA, that \( \kappa_{\text{SW}} \geq \approx 4 \kappa_{\text{experiment}} \). Recently Sellan et al. [7] investigated size effects in GK-MD simulations and associated this previous error, which leads to a good agreement with experiments, with a small supercell size, and recovered the prediction of Broido et al [10].

Next, we show in Fig. 3 the calculated inverse lifetimes of the 3 acoustic and optical modes versus frequency at two different temperatures of 20 and 600 K.

When using the RTA from Eq. 7, the calculated thermal conductivity is shown in Fig. 4. The two curves correspond to the quantum and classical version. The latter is obtained from the same formula as the former, except that the Bose-Einstein occupation number in the lifetimes and heat capacity are replaced by their classical version, namely \( k_B T/\hbar \omega \) and \( k_B \) respectively. This is to quantify the errors due to using classical dynamics, and to provide a benchmark for comparison with classical GK-MD re-
sults. In the classical case, we can note an overestimation which is quite small beyond the Debye temperature. This is a combination of the larger heat capacity and a smaller lifetime in the classical case. At lower temperatures, the quantum calculation tends to zero due to the quantum heat capacity, while the classical results diverges as $1/T$.

The above calculation involves a summation in the first Brillouin zone, which is done numerically. For a mesh of kpoints equal to the number of primitive cells included in the MD supercell, one expects to obtain agreement between MD results and the classical version of Eq.7. And in fact, this agreement is observed at 600K where MD simulations were performed. Generally, a finer mesh of kpoints in the LD calculations is needed in order to capture the contribution of long wavelength phonons which have also a large mean free path. To obtain the converged value of thermal conductivity, we perform the k-summation for several k-mesh values of 7, 10, 14, and 18. We then extrapolate the obtained values to the infinite k-mesh by fitting $\kappa$ versus $1/k$=mesh with a straight line, and reading off the y-intercept. This final result is plotted versus T in Fig. 4.

4 Conclusions

Using first-principles calculations, we developed a classical force field which was used both in a molecular dynamics simulation and in the calculation of anharmonic phonon lifetimes. Both methods provided an estimate for the thermal conductivity of pure crystalline silicon. The slight underestimation in MD was traced back to the finite size of the cell thereby disallowing long wavelength phonons to participate in heat conduction. The LD calculations were extrapolated to infinite k-mesh points and were found to be in good agreement with experimental results of Glassbrenner and Slack [17]. Size effects were discussed and arguments were provided why previous estimations of $\kappa$ using MD with the Stillinger-Weber potential were accidentally in good agreement with experimental results. This potential has the advantage of being amenable to systematic improvement by including more neighbor shells if needed. The approach of using the FGR for the estimation of relaxation rates and the RTA or an improved approximation to $\kappa$ by solving the linearized Boltzmann equation, allows one to obtain a relatively accurate estimate of the thermal conductivity of an arbitrary bulk crystalline structure from a few force-displacement relations obtained using first-principles calculations, without any fitting parameters. This method paves the way for an accurate prediction of thermal conductivity of nanostructured or composite materials in a multiscale approach, which takes as input the relaxation times due to anharmonicity and defect scatterings.

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REFERENCES

[3] One reason for the success of the SW potential compared to others, can be attributed to its ability to reproduce a relatively correct Gruneisen parameter and thermal expansion coefficient. It is not clear to us whether or not this is accidental, as the way SW determined their parameters was not clarified in their paper. The properties of SW and Tersoff potential have been discussed by Porter, Justo and Yip in Jour. Appl. Phys. 82, 5381 (1997).
[13] Quantum Espresso is an electronic structure package based
on the density functional theory developed at SISSA. The methodology is detailed in: P. Giannozzi et al., JPCM 21, 395502 (2009).


