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Uncertainty quantification of thermal conductivities from equilibrium molecular dynamics simulations

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ABSTRACT

Equilibrium molecular dynamics (EMD) simulations along with the Green-Kubo formula have been widely used to calculate lattice thermal conductivities. Previous studies, however, focused primarily on the calculated thermal conductivities, with the uncertainty of the thermal conductivities remaining poorly understood. In this paper, we study the quantification of the uncertainty by using solid argon, silicon, and germanium as model material systems, and examine the origin of the observed uncertainty. We find that the uncertainty increases with the upper limit of the correlation time, $t_{\text{corre,UL}}$, and decreases with the total simulation time, t_{total}, whereas the velocity initialization seed, simulation domain size, temperature, and type of material have minimal effects. The relative uncertainties of the thermal conductivities, $\sigma_{k_x}/k_{x,\text{ave}}$, for solid argon, silicon, and germanium under different simulation conditions all follow a similar trend, which can be fit with a "universal" square-root relation, as $\sigma_{k_x}/k_{x,\text{ave}} = 2(t_{\text{total}}/t_{\text{corre,UL}})^{-0.5}$. We have also conducted statistical analysis of the EMD-predicted thermal conductivities and derived a formula that correlates the relative error bound (Q), confidence level (P), $t_{\text{corre,UL}}$, t_{total}, and number of independent simulations (N). We recommend choosing $t_{\text{corre,UL}}$ to be 5–10 times the effective phonon relaxation time, τ_{eff}, and choosing t_{total} and N based on the desired relative error bound and confidence level. This study provides new insights into understanding the uncertainty of EMD-predicted thermal conductivities. It also provides a guideline for running EMD simulations to achieve a desired relative error bound with a desired confidence level and for reporting EMD-predicted thermal conductivities.

1. Introduction

Equilibrium molecular dynamics (EMD) simulation along with the Green-Kubo formula is an effective way to calculate lattice thermal conductivities [1–9]. In this method, the thermal conductivity is related to the integration of the heat current autocorrelation function (HCACF), as [4]

$$k_{\alpha\beta} = \frac{V}{k_B T^2}\int_0^\infty \langle J_\alpha(0) J_\beta(t_{\text{corre}})\rangle \, \mathrm{d}t_{\text{corre}}, \tag{1}$$

where $k_{\alpha\beta}$ is the $\alpha\beta^{\text{th}}$ component of the thermal conductivity tensor, V is the volume of the material system, k_B is the Boltzmann constant, T is temperature, t_{corre} is the heat current autocorrelation time, and J_α is the α^{th} component of the full heat current vector $\mathbf{J}$, which is typically computed as [10]

$$\mathbf{J} = \frac{1}{V}\left(\sum_i \mathbf{v}_i \epsilon_i + \sum_i \mathbf{S}_i \cdot \mathbf{v}_i\right), \tag{2}$$

Here, $\mathbf{v}_i$, ϵ_i, and $\mathbf{S}_i$ are the velocity, energy, and stress of atom i. In LAMMPS, [10] a widely used, open-source molecular dynamics simulation package, the default heat current formula is based on Eq. (2) with the interatomic forces calculated from the per-atom stresses. Recently Fan et al. reported new heat current formulas for many-body potentials, but the different heat current formulas are shown to affect mainly low-dimensional materials [11]. In theory, the V, integration upper limit, and heat current autocorrelation time in Eq. (1) should all approach infinity to calculate the lattice thermal conductivity of bulk materials. In real practice, however, the V is chosen to be of a finite size based on some domain size effect studies, the integration is carried out up to a finite upper limit, which we define as the upper limit of the correlation time, $t_{\text{corre,UL}}$, and the heat current autocorrelation is calculated up to a finite duration, which we define as the total simulation time, t_{total}. As a result, Eq. (1) becomes

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$$k_{\alpha\beta} = \frac{V}{k_B T^2} \int_0^{t_{\text{corre,UL}}} \langle J_\alpha(0) J_\beta(t_{\text{corre}}) \rangle |_{t_{\text{total}}} \, \mathrm{d}t_{\text{corre}}. \quad (3)$$

Although this method has been widely used to calculate the lattice thermal conductivity of many material systems, previous studies focused primarily on the thermal conductivity values or the average values from multiple independent simulations, with the uncertainty of the predicted thermal conductivities remaining poorly understood, as seen from the very limited investigations on it so far [12–14]. On the other hand, it is a common practice to report both the values and uncertainties of the predicted thermal conductivities from EMD simulations. A typical way of doing it is to run each simulation for multiple times (usually 3–12) and then calculate the average value as the thermal conductivity and the standard deviation as the uncertainty (plotted as error bars). This practice, however, often lacks consistency (or a well-defined guideline) because the values and uncertainties could vary greatly depending on how the simulations are conducted. In addition, it was pointed out that the uncertainty of the thermal conductivity from EMD simulations is about 20%, [3] for which no explanation was provided. Furthermore, when thermal conductivities from EMD simulations are compared with those from other sources (*e.g.*, experiments or other simulation methods), it is often concluded that the agreement is good if the error bars overlap, but little is known about the information carried by the error bars.

In this study, we conduct a systematic study on quantifying the uncertainty of thermal conductivities from EMD simulations. We consider solid argon, silicon, and germanium as model material systems, and study the effects of the velocity initialization seed, simulation domain size, upper limit of the correlation time ($t_{\text{corre,UL}}$), total simulation time (t_{total}), temperature, and type of material. The results show that the uncertainty increases with $t_{\text{corre,UL}}$ and decreases with t_{total}, but the velocity initialization seed, simulation domain size, temperature, and type of material have minimal effects on the relative uncertainty. By analyzing the results of different materials under different simulation conditions, we have obtained a "universal" square-root relation for quantifying the relative uncertainty, σ_k/k_{ave}, as a function of $t_{\text{total}}/t_{\text{corre,UL}}$. We have also obtained a formula that correlates the relative error bound (Q), confidence level (P), $t_{\text{corre,UL}}$, t_{total}, and number of independent simulations (N). This paper is organized as follows. Section 2 details the method used in this study, particularly the EMD simulations. Section 3 presents some results and discussion on the uncertainty of the EMD-predicted thermal conductivities of solid argon, silicon, and germanium. It also reports some results on quantifying the general uncertainty of EMD-predicted thermal conductivities, choosing appropriate $t_{\text{corre,UL}}$ and t_{total} for EMD simulations to achieve a desired relative error bound with a desired confidence level, and reporting EMD-predicted thermal conductivities. Section 4 summarizes the main findings from this study.

2. Methodology

All the molecular dynamics simulations were conducted with the `LAMMPS` package [10]. The material systems of solid argon, silicon, and germanium all have a face-centered cubic (FCC) structure with nominal lattice constants (before the structures are relaxed) of 5.26, 5.43, and 5.66 Å, respectively. The interatomic interactions are characterized with the Lennard-Jones potential [15] for solid argon and the Tersoff potential [16] for silicon and germanium. We considered a domain size of $6 \times 6 \times 6$ unit cells (u.c.) for solid argon (except for the domain size effect studies) and $4 \times 4 \times 4$ u.c. for silicon and germanium. Periodic boundary conditions were applied in x, y, and z directions. The time steps were chosen as 4, 1, and 2 fs for solid argon, silicon, and germanium, respectively. Nosé-Hoover barostat and thermostat [17,18] were used to control the pressure and temperature of the material systems. In all simulations, the material systems were first equilibrated in an *NPT* (constant number of atoms, pressure, and temperature) ensemble before they were switched to an *NVE* (constant number of atoms, volume, and energy) ensemble for data production. The $t_{\text{corre,UL}}$ and t_{total} values were chosen such that the predicted average thermal conductivities converged. We varied the $t_{\text{corre,UL}}$ and t_{total} over a wide range to investigate their effects on the uncertainty of the predicted thermal conductivities. Each simulation was run for 100 times, which had independent initial velocity distributions. It is an inherent assumption in this study that 100 independent simulations provide a representative sample for the relevant statistical analysis. The thermal conductivities were calculated according to Eq. (3). Since each individual EMD simulation can provide three thermal conductivity values (for the x, y, and z directions), there are a total of 300 thermal conductivity values for each simulation condition. We report the average and standard deviation of the 300 values as the predicted thermal conductivity and its uncertainty, respectively. Because the three materials considered in this study are all isotropic in the x, y, and z directions, the 100 k_x, 100 k_y, and 100 k_z values for each simulation condition could be equivalently treated as 300 k_x values. As a results, the analysis in this study essentially corresponds to the thermal conductivity along a single direction. Alternatively, the thermal conductivities can be first averaged over the x, y, and z directions and then the average and standard deviation of the 100 values from the 100 simulations calculated as the predicted thermal conductivity and its uncertainty, respectively. The average from these two methods will be the same, but the standard deviation from the second method will be statistically $1/\sqrt{3}$ times that from the first method. Considering the second method is restricted to isotropic materials, we adopted the first method to make our analysis more general.

3. Results and discussion

In this section, we present the results for the three materials — solid argon, silicon, and germanium. For solid argon, we show the effects of the velocity initialization seed, simulation domain size, t_{total}, $t_{\text{corre,UL}}$, and temperature on the EMD-predicted thermal conductivity and its uncertainty. For silicon and germanium, we focus on the effects of the t_{total} and $t_{\text{corre,UL}}$. Based on the solid argon, silicon, and germanium results, we provide some consideration on quantifying of the general uncertainty of EMD-predicted thermal conductivities. We also show how to appropriately choose $t_{\text{corre,UL}}$, t_{total}, and N for EMD simulations so that the predicted average thermal conductivity achieves a desired relative error bound with a desired confidence level and how to report EMD-predicted thermal conductivities.

3.1. Solid argon

In EMD simulations, independent simulations are usually conducted to reduce the statistical error, which can be realized by assigning different velocity initialization seeds. In LAMMPS, the only requirement for a velocity initialization seed is that it be a positive integer [10]. To understand how the seeds affect the thermal conductivity predictions, we considered two schemes of assigning the seeds, namely, uniform and random seeds. The uniform seeds are described as 1000n, where n is the simulation ID (varying from 1 to 100), whereas the random seeds are random numbers (from 1000 to 100,000) generated with the `rand` function of `MATLAB`. In Fig. 1(a), we show some typical HCACF profiles for solid argon. It is seen that the normalized HCACF starts from one, decreases gradually to zero, and then fluctuates around zero. Typically the correlation time, $t_{\text{corre,UL}}$, should be long enough so that