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VIBRATIONAL CONTRIBUTION TO THERMAL CONDUCTIVITY OF SILICON NEAR SOLID-LIQUID TRANSITION

Christopher H. Baker[*]
Nanoscale Energy Transport Laboratory
University of Virginia
Charlottesville, Virginia, 22904
chb2fd@virginia.edu

Chengping Wu
Computational Materials Group
University of Virginia
Charlottesville, Virginia, 22904
cw5xj@virginia.edu

Richard N. Salaway
Computational Materials Group
University of Virginia
Charlottesville, Virginia, 22904
rns7a@virginia.edu

Leonid V. Zhigilei
Computational Materials Group
University of Virginia
Charlottesville, Virginia, 22904
lz2n@virginia.edu

Pamela M. Norris
Nanoscale Energy Transport Laboratory
University of Virginia
Charlottesville, Virginia, 22904
pamela@virginia.edu

ABSTRACT

Although thermal transport in silicon is dominated by phonons in the solid state, electrons also participate as the system approaches, and exceeds, its melting point. Thus, the contribution from both phonons and electrons must be considered in any model for the thermal conductivity, k, of silicon near the melting point. In this paper, equilibrium molecular dynamics simulations measure the vibration mediated thermal conductivity in Stillinger-Weber silicon at temperatures ranging from 1400 to 2000 K – encompassing the solid-liquid phase transition. Non-equilibrium molecular dynamics is also employed as a confirmatory study. The electron contribution may then be estimated by comparing these results to experimental measurements of k. The resulting relationship may provide a guide for the modeling of heat transport under conditions realized in high temperature applications, such as laser irradiation or rapid thermal processing of silicon substrates.

NOMENCLATURE

k thermal conductivity

k_B Boltzmann's constant

L length of non-equilibrium domain

q heat flux

$\vec{S}$ heat current

t time

τ correlation time

T temperature

V volume

EMD   equilibrium molecular dynamics

HCACF   heat current autocorrelation function

MD   molecular dynamics

NEMD   non-equilibrium molecular dynamics

TTM   two temperature model

Subscripts:

μ, ν vector components

t_f time limit of data to be autocorrelated

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[*]Address all correspondence to this author.

INTRODUCTION

In the rapidly evolving world of materials microfabrication, theoretical understanding of the processes involved is crucial due to the sensitivity of microstructured systems to input parameters. The present study is motivated by modeling femtosecond laser irradiation on a Au film-Si substrate system, which will be relevant to the area of semiconductor science and engineering. Knowledge of the electronic contribution to thermal conductivity of (liquid) Si will make this modeling possible using a computational model combining the two temperature model (TTM) [1–5] and the molecular dynamics (MD) method. The thermal conductivity of silicon has been experimentally measured in the high-temperature regime [6, 7]. Even though it is known that both phonons, a quantum of lattice vibration, and electron-hole pairs contribute to this high temperature thermal conductivity, especially above temperatures of 1000 K, it is difficult to differentiate one contribution from the other experimentally [6, 8]. Note that the term "phonon" implies a crystalline arrangement of atoms. Although the vibrational motion of atoms in a liquid is not due to phonons *per se*, this term will be used for the remainder of the paper to refer to non-electron mediated heat transfer in the liquid state.

The issue of distinguishing the effects of phonons and electrons, especially above the melting point of $\sim$1690 K, can be resolved by MD simulation, a popular technique for simulating phonon mediated nanoscale thermal conductivity. In this method, atoms are treated as classical point masses that interact via an interatomic potential. The system is then evolved according to Newton's equation of motion. In comparison to analytical techniques, MD makes no assumptions concerning phonon transport after the interatomic potential is defined. Thus, MD includes all anharmonic effects, a feature especially important for high temperature systems where larger atomic displacements lead to more anharmonicity.

By comparing the phonon contribution to thermal conductivity in MD to experimental results, the contributions of electrons can be determined and used in the combined TTM-MD model for the description of heat transfer in liquid silicon. Such a model assigns different temperatures to the phonon and electron systems and models them in parallel with a certain coupling constant [1–5]. TTM-MD methods for laser interaction with metals developed by the Computational Materials Group at the University of Virginia [1, 9, 10] can be extended to laser-metal-silicon systems.

The Stillinger-Weber potential [11] was selected for this study because its original formulation used properties near the melting point as the fitting criteria, it is one of the best silicon potentials for modeling thermal effects [12], and it is prevalent in the literature. Past studies have focused on silicon's structural and thermodynamic properties for the solid and liquid states [13–15]. Recent MD studies of silicon have compared and contrasted the equilibrium and non-equilibrium approach to the calculation of thermal conductivity with attention to size effects [12, 16]. In the present study, equilibrium and non-equilibrium molecular dynamics methods are employed to determine the phonon contribution to bulk thermal conductivity of silicon at temperatures between 1400 and 2000 K.

METHODS

Equilibrium molecular dynamics (EMD) has been shown to return the bulk thermal conductivity of silicon even when using small system sizes [12, 16, 17]. In this method, the fluctuation-dissipation theorem is invoked to determine the conductivity according to the Green-Kubo formalism [18].

$$k_{\mu\nu}(\tau) = \frac{1}{Vk_BT^2} \int_0^\tau \langle \vec{S}_\mu(\delta) * \vec{S}_\nu(0) \rangle d\delta \tag{1}$$

where $k_{\mu\nu}$ is the thermal conductivity tensor, V is the system volume, k_B is Boltzmann's constant, T is the temperature, τ is the correlation time, and δ is a dummy variable. The term appearing in brackets is the heat current autocorrelation function (HCACF), given by:

$$\langle \vec{S}_\mu(\tau) * \vec{S}_\nu(0) \rangle = \frac{1}{t_f - \tau} \int_0^{t_f - \tau} \vec{S}_\mu(t+\tau) * \vec{S}_\nu(t) * dt \tag{2}$$

In practice, the integral in Eqn. 2 becomes a summation due to the discrete nature of simulations. In essence, the Green-Kubo formalism uses the decay time of fluxes resulting from instantaneous temperature gradients to determine the thermal conductivity. The advantages of this technique are that the full thermal conductivity tensor can be obtained from one simulation, fewer than 10,000 atoms are needed to model bulk transport, and thus the simulations are quick. However, as evidenced in the following section, the results are often difficult to interpret due to random fluctuations of the HCACF. Also, this method cannot be used where both bulk and interface conductances are important since it will average these effects. These strengths and weaknesses are complementary to those of non-equilibrium molecular dynamics (NEMD): more easily interpreted results, but longer simulation times. Because none of the limitations of EMD are applicable for the simple system studied here, EMD is a suitable choice. However, a brief NEMD study is also employed to validate the results because of the difficulty in defining the converged value of the HCACF.

Non-equilibrium molecular dynamics uses Fourier's law,
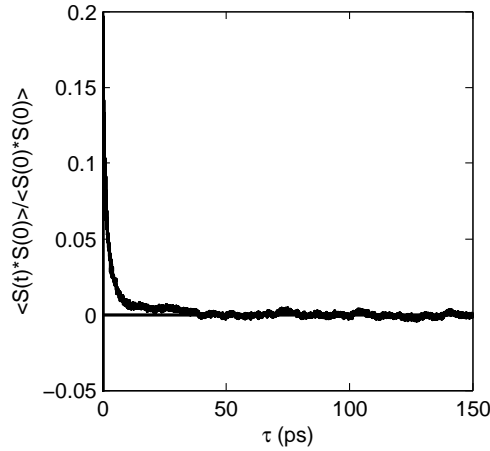
$$q = -k\frac{\Delta T}{L} \tag{3}$$

FIGURE 1. THE NORMALIZED HCACF AVERAGED OVER 10 SIM-ULATIONS AND PLOTTED AGAINST CORRELATION TIME FOR SOLID SILICON AT 1600 K. A CHARACTERISTIC REDUCTION TO ZERO IS SEEN BY $\tau = 40$ PS. THE HCACF THEN RANDOMLY FLUCTUATES ABOUT ZERO.

for a domain length of L, to calculate the thermal conductivity, k, where q and ΔT are the applied flux and resulting tempera-ture drop, respectively. Typically, the system is brought to the desired temperature, then a heat flux is applied by adding energy to the hot bath on one end and taking energy from the cold bath at the other end. After the system equilibrates, data are taken and the temperature gradient fit to obtain k. For any finite length do-main, especially for those smaller than the mean free path of the dominant heat carrying phonons, some phonons will travel bal-listically from one bath to the other. This decreases the thermal conductivity compared to the bulk value through the premature scattering of these phonons at the baths. In this study, because NEMD is being used only as validation, size effects are not ex-plicitly taken into consideration. For further information, Sellan *et al.* give an excellent account of size effects in NEMD simula-tions [16].

EQUILIBRIUM MOLECULAR DYNAMICS

All simulations were carried out with LAMMPS (Large-scale Atomic/Molecular Massively Parallel Sim-ulator), maintained by Sandia National Laboratories (http://lammps.sandia.gov) [19]. For perfectly homogeneous, isotopically pure, defect free systems, a lack of nucleation sites requires superheating of the lattice in order to achieve a melted system. To ensure a liquid phase at 1700 K and above, the system's initial temperature was set to 3000 K, and then cooled to the desired temperature. For all MD simulations, a time step of 0.5 fs was used to ensure total energy conservation in simu-lations of both solid and liquid phases to within 0.01% of the
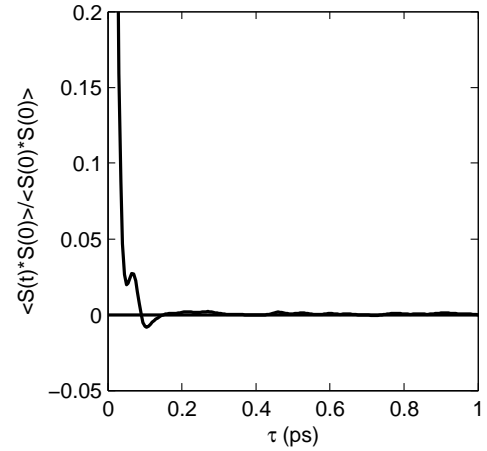

FIGURE 2. THE NORMALIZED HCACF AVERAGED OVER 10 SIM-ULATIONS AND PLOTTED AGAINST CORRELATION TIME FOR LIQUID SILICON AT 1700 K. THE FUNCTION DECAYS MUCH MORE RAPIDLY THAN FOR THE SOLID.
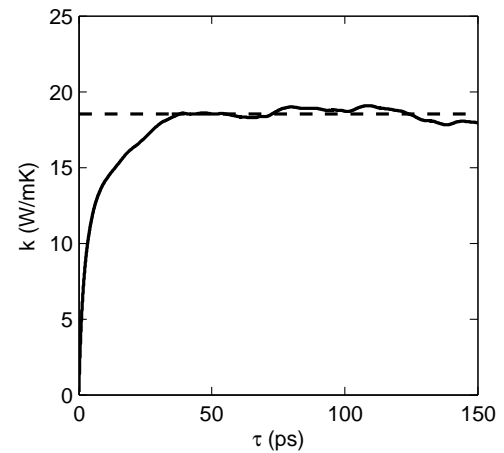

FIGURE 3. CONDUCTIVITY VERSUS INTEGRATION LIMIT IN EQN. 1 OF SOLID SILICON AT 1600 K DERIVED FROM FIG. 1. THE WAN-DERING IN THE HCACF LEADS TO AMBIGUITY IN THE CONDUCTIV-ITY. THE DOTTED LINE DENOTES A MEAN OF THE CONDUCTIVITY OVER A RANGE OF INTEGRATION TIMES. NOTE THAT THIS PLOT DEPICTS CONDUCTIVITY RESULTING FROM AN AVERAGED HCACF (FIG. 1); THE MEAN HERE IS NOT THE DATUM OF TABLE 1.

thermal energy. The pressure and temperature were controlled using a Nose-Hoover barostat and thermostat. The heat current was computed every 10 time steps over a period of 1.5 ns. The HCACF was then computed for correlation times, τ, up to 150 ps. Representative results for the normalized HCACF for the solid and liquid phases are plotted in Figs. 1 and 2. The HCACF shows a pronounced reduction to zero by 40 and 0.2 ps for solid and liquid, respectively. The shorter decay time of the liquid
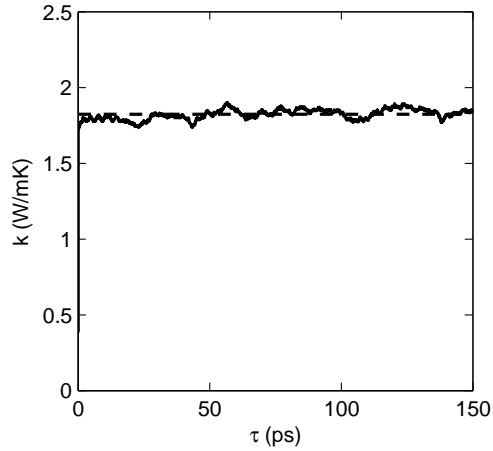
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FIGURE 4. Conductivity versus integration limit in Eqn. 1 of liquid silicon at 1700 K derived from Fig. 2.

Temperature (K)	k, EMD (W/mK)	k, expt. (W/mK) [7]
1400	24.03 ± 9.26	22.3
1500	25.20 ± 16.11	20.1
1600	18.55 ± 8.49	20.4
1700	1.82 ± 0.70	56.5
1800	1.92 ± 0.75	
1900	1.51 ± 0.33	
2000	1.78 ± 0.50	

phase is due to the increased scattering of "phonons" from the highly disorganized atomic structure. After the initial reduction to zero, the HCACF randomly fluctuates about, but does not converge to, zero, possibly due to artificial correlation of the heat current caused by unscattered phonon modes wrapping around the domain through the periodic boundaries [17, 20]. The result is that for longer correlation times, the integral does not converge to a definite value (Figs. 3 and 4). This phenomena extends to 150 ps, the limit of correlation time studied here. Therefore, the thermal conductivity is taken as the mean value resulting from 10 independent simulations. Each simulation's conductivity was calculated by taking the average value over times greater than the decay time. The uncertainty is taken from twice the standard deviation of these 10 samples; the results are given in Table 1. The thermal conductivity of the liquid is much less than that of the solid due to the much greater scattering of phonons.

NON-EQUILIBRIUM MOLECULAR DYNAMICS

Non-equilibrium molecular dynamics simulations of silicon at 1600 K (solid) and 1700 K (liquid) were executed to confirm the results of the EMD study. A domain length of 200.8 nm for the solid phase was chosen since it is comparable in length to the longest domain used in a previous study at 1000 K [12]. The liquid phase's length of 51.1 nm was selected by roughly quartering the solid phase's domain length. The much lower conductivity obtained by the equilibrium method, along with knowledge that the mean free path of phonons is very small in liquids, justifies the smaller domain size. The liquid phase was generated in the same manner as for EMD. The domain's cross sectional dimensions were 4 by 4 unit cells, and the domain was divided into one unit cell long bins along the direction of transport for the

purpose of temperature profiling. After the system reached the desired temperature, a flux of 2 GW/m^2 and 0.75 GW/m^2 was applied for the solid and liquid, respectively, and data were acquired every 10 steps for 5 ns. The fluxes were chosen from test runs to keep temperature differentials less than 20 K across the domain. The resulting steady state temperature profile was used to calculate the conductivity, k, according to Fourier's law. The NEMD simulations resulted in a conductivity of 13.14 W/mK for the solid phase at 1600 K and 1.27 W/mK for the liquid phase at 1700 K.

DISCUSSION AND SUMMARY

From the EMD results obtained here, it is possible to draw comparison to experimental results for high temperature silicon. Experiments have found that this material's thermal conductivity is approximately 22.3-20.4 W/mK over the range 1400 to 1600 K and 56.5 W/mK for liquid silicon at 1700 K [7]. The much larger value after melting is consistent with the onset of free electron dominated thermal transport. The EMD results of this study are of the same order of magnitude for the solid phase, ranging from 24.03 to 18.55 W/mK. This result is surprising considering the finding of Glassbrenner *et al.* that diffusion of electron-hole pairs accounts for approximately 30-40% of the thermal conductivity at the melting point [6, 8]. However, given the uncertainty of the EMD thermal conductivity and the use of the SW potential, which merely approximates the interatomic bonding, the simulations agree quite well with experiment. In the liquid phase, the vibrational contribution found through EMD drops precipitously to 1.82 W/mK at 1700 K, much smaller than the 56.5 W/mK of real liquid silicon. Thus for the liquid phase, free electrons dominate the thermal transport, with phonons contributing less than 4%.

It is important to understand the limitations of this comparison to experimental results. Stillinger-Weber silicon is but

a model of real silicon; trends in the data merely elucidate the magnitude of the underlying contributions of phonons and electrons, not their precise values. Furthermore, the large error bars inherent in EMD simulations must be considered. Although the system studied here was 100% ^{28}Si, whereas the natural composition has about 8% combined ^{29}Si and ^{30}Si, at such high temperatures, isotopic scattering is anticipated to have a minor role compared to phonon-phonon scattering.

The long domain length NEMD simulations show agreement with the EMD results. In fact, the results of 13.14 and 1.27 W/mK at 1600 K and 1700 K for NEMD are slightly smaller than 18.55 and 1.82 W/mK for EMD, a discrepancy consistent with considerations of domain size effects [16]. Thus the NEMD results corroborate the accuracy of the EMD results.

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