Lattice Thermal Conductivity in SiC Nanotubes, Nanowires and Nanofilaments: A Molecular Dynamics Study

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This paper presents results of a non-equilibrium Molecular Dynamics approach to determine the lattice thermal conductivity of nanowires, nanotubes, and nanofilaments of silicon carbide. The nanostructures are modeled with the classical potential proposed in J. Appl. Phys. 101, 103515 (2007). These nanostructures display very low lattice thermal conductivity, about 50 times smaller than bulk SiC. Among the studied nanostructures, the 3C [100] nanowires have the highest thermal conductivity, and the (5, 5) nanotubes display the lowest. Dependence on temperature of the lattice thermal conductivity exhibits an inverse power relationship only for nanowires 3C [100], 2H [110] and the (4, 0), (2, 2) nanotubes. All other structures have thermal conductivities decreasing more gently as a function of increasing temperature, except for nanowires 3C and nanotubes (5, 5) where the thermal conductivity is almost constant as a function of temperature.

Keywords: Thermal Conductivity, Non-Equilibrium Molecular Dynamics, Silicon Carbide, SiC Nanowires, SiC Nanotubes, SiC Nanofilaments.

1. INTRODUCTION

Nanostructures began to emerge in the mid-1980s as building blocks useful to assemble larger materials and design special macromolecular constructs with novel mechanical and thermal characteristics. Today, nanodevices have emerged as fundamental for achieving improved mechanical, thermal, and electronic controls. Among other properties, the thermal conductivity of the device may be critical to the control function and the stability of the macro-system itself.1 One postulated application of nanodevices is to act as heat conduits/sinks or field emitting units.2 An important question is to whether these nanodevices are good or bad heat conductors and at the same time they remain stable at operational temperatures. Silicon carbide (SiC) is a broadly used material in nanoelectronics and has proven to sustain a variety of stable nanostructures.2,4 SiC nanotubes and nanowires have been fabricated experimentally,2,4 and a multitude of hollow fullerene-like clusters have been predicted which could be useful in building nanodevices.5

Carbon and silicon are both group-IV elements that exhibit sp2 and sp3 bonds. These bonds cause bulk SiC to be among the hardest materials and to be well suited for devices being operated in extreme environments.5 In fact, bulk SiC has a wide band gap,6 high thermal conductivity,7 and is resistant to various forms of radiation.8 It has been postulated that the use of SiC in nanostructures and nanodevices should exhibit equivalent characteristics.3 Although experimental advances are seen every day, it is still difficult to perform measurements of thermal properties at the nanometer scale. Therefore, computational simulations are useful for adding understanding of properties and mechanisms in systems at the nano-scale. A number of non-equilibrium molecular dynamics (NEMD) studies for the determination of thermal properties in non-homogeneous systems have been published.9–15 For example, NEMD was used for obtaining the lattice thermal conductivity by simulating the directional heat flow perpendicular to infinite thin films in one-, two-, or three-dimensional Lennard-Jones (LJ) systems.9,11,16 However, little has been investigated for thermal characteristics of SiC nanostructures, although a good number of atomistic simulations addressing thermal properties of SiC are available.17–22
of energetic stability and mechanical deformations of SiC nanowires and nanotubes\textsuperscript{23-25} have been put forward using the Tersoff potential.\textsuperscript{26} Electronic structure studies of SiC nanocages, nanotubes, and nanowires have been published, both within density functional theory\textsuperscript{27} and tight binding\textsuperscript{28} approaches. Studies of thermal conductivity of SiC nano-guides using the Tersoff potential have predicted a strong degradation of the thermal conduction ability.\textsuperscript{29} A study of thermal transport in SiC nanotubes within the Green-Kubo approach for calculating the thermal conductivity has been put forward.\textsuperscript{30} However, this approach is adequate for homogeneous, isotropic systems, which is not the case in nanotubes.

This work addresses the determination of the lattice thermal conductivity of four types of SiC nanowires, and a variety of nanotubes with zigzag and armchair chiralities and different diameters. The approach is based on NEMD employing a potential proposed in Ref. [20]. The work builds on our previous NEMD implementation\textsuperscript{19} in which we examined thermal properties of thin films due to interfaces between two different LJ films. Additionally, nanowires and nanotubes stable configurations obtained in previous work\textsuperscript{28} are used as starting points for the atomistic simulations. This paper is organized as follows: Section 2 describes the combination of equilibrium molecular dynamics (MD) and NEMD approaches used for the numerical determination of the lattice thermal conductivity. Section 3 addresses the determination of the lattice thermal conductivity in the different nanostructures and presents our results for nanowires, nanotubes and nanofilaments. The summary in Section 4 concludes this paper.

\section{MOLECULAR DYNAMICS APPROACH: EQUILIBRIUM AND NON-EQUILIBRIUM}

To simulate the interaction between atoms in SiC, the model potential proposed by Vashishta, et al is used throughout.\textsuperscript{20,21} This model potential includes two-body charge multipole interactions as well as three body terms describing the covalent bond bending/stretching with a version of the Stillinger-Weber potential.\textsuperscript{31} Thus, the total potential of the system is given by

\begin{equation}
U = \sum_{i<j} U^{(2)}(r_{ij}) + \sum_{i<j<k} U^{(3)}(r_{ij}, r_{ik})
\end{equation}

Here, $n$ is the total number of atoms, $U^{(2)}$ is the 2-body term given by

\begin{equation}
U^{(2)}(r_{ij}) = \frac{H_{ij}}{r_{ij}} + \frac{Z_i Z_j}{r_{ij}} e^{-r_{ij}/\alpha} - \frac{D_{ij}}{2r_{ij}^2} e^{-r_{ij}/\delta} - \frac{W_{ij}}{r_{ij}}
\end{equation}

where $r_{ij}$ is the distance between atoms $i$ and $j$, $H_{ij}$ is the strength of the steric repulsion of 23.67291 eVÅ for Si–Si, 447.09026 eVÅ for Si–C, and 471.74538 eVÅ for C–C interactions, $Z_i$ is the effective charge of $+1.201$ e for Si and $-1.201$ for C, $D_{ij}$ is the strength of the charge-dipole attraction of 2.1636 eVÅ$^3$ for Si–Si, 1.0818 eVÅ$^3$ for Si–C, and zero for C–C interactions, $W_{ij}$ is the van der Waals strength of zero for Si–Si and C–C, and 61.4694 eVÅ$^6$ for Si–C interactions, $\eta_j$ is the exponent of the steric repulsion term of 7 for Si–Si and C–C, and 9 for Si–C interactions, $\lambda$ and $\xi$ are screening lengths of 5.0 Å and 3.0 Å, respectively.

The 3-body term $U^{(3)}$ in Eq. (1) is given by

\begin{equation}
U^{(3)}(r_{ij}, r_{ik}) = R^{(3)}(r_{ij}, r_{ik}) P^{(3)}(\Theta_{ijk})
\end{equation}

where $R^{(3)}$ is the bond-stretching interaction and $P^{(3)}$ is the bond bending potential. The contribution $R^{(3)}$ is defined as

\begin{equation}
R^{(3)}(r_{ij}, r_{ik}) = B_{ijk} \exp \left( -\gamma \frac{r_{ij} - r_0}{r_{ij} - r_0} - \gamma \frac{r_{ik} - r_0}{r_{ik} - r_0} \right) \delta(r)
\end{equation}

where, $B_{ijk}$ is the interaction strength of 9.003 eV, $\gamma$ is a unit conversion of 1 Å, and $\delta(r)$ is a step function cutting the force when distances between the $i-j$ or $j-k$ atoms are larger than 7.35 Å. The bond bending potential is defined as

\begin{equation}
P^{(3)}(\Theta_{ijk}) = \frac{(\cos(\Theta_{ijk}) - \cos(\Theta))^2}{1 + C_{ijk} (\cos(\Theta_{ijk}) - \cos(\Theta))^2}
\end{equation}

where $\Theta_{ijk}$ is the bond angle between $j-i-k$ atoms, $\Theta$ is the reference angle of 109.47$^\circ$ and $C_{ijk} = 5.0$. Even though the interior angles in a hexagon are 120$^\circ$, the 109.47$^\circ$ is the relaxed angle for a Si–C–Si or C–Si–C bonds.\textsuperscript{19-21}

For all MD simulations elongated SiC tubes, filaments, and wires are laid along the $X$-axis. No periodic boundary conditions are used. Our initial configurations are nanowires obtained from cuts of the 3C and 2H crystalline polytypes, and nanotubes with either armchair or zigzag chirality. These initial configurations are consistent with optimized and stable geometries optimized under the tight-binding approximation.\textsuperscript{28} The alternation of Si and C atoms in these systems is such that bonds of around 1.9 Å,\textsuperscript{20,21,27,28} are the dominant majority.

The first stage of our simulations is the determination of wires and tubes stability under the model potential. This is achieved by equilibrating with constant energy MD the open-end wire or tube systems at various temperatures. Runs to equilibrate the systems are performed for about a half million time steps of $\Delta t = 0.3 \times 10^{-15}$ sec.

The NEMD stage is achieved through a setup consisting of a simulated thermostat attached at each end of the elongated tube or wire that has been equilibrated at a desired temperature. As depicted in Figure 1, each thermostat is a continuation of the tube or wire containing about 100–150 atoms that are kept at a constant temperature. One thermostat is kept at relatively high temperature and the other thermostat is kept at lower temperature such that a temperature gradient would develop across the tube.
or wire. The thermal baths are sized such that their length along the X-axis is greater than 7.35 Å, the cutoff radius of the 2-body part of the model potential. Atoms in each thermal bath are kept at a desired constant temperature by scaling their velocities at every time step. On the outside ends of the bath, three-to-four planes of atoms are kept fixed in position to prevent deformations of the cross sections of the nanostructures. Atoms in the region between the two thermal baths move according to iso-energy MD and data are collected only on these central atoms (typically 320 to 384 atoms).

When a temperature drop exists between the two thermal baths, a thermal energy flow is established along the elongated tube or wire and the system is neither in thermal equilibrium nor in a steady state. However, after about 200 picoseconds the system reaches the steady state and the thermal energy current is roughly constant along the length of the nanosystem. This NEMD arrangement has been adopted in other lattice thermal conductivity calculations. However, in our case there are no periodic boundary conditions in any direction as in such works.

3. LATTICE THERMAL CONDUCTIVITY OF SiC NANOSTRUCTURES

Because a temperature gradient sets in once the system reaches a steady state, the Fourier law of heat conduction is applicable, such that:

\[ \vec{J} = -\kappa \vec{V} T \]  

where \( \vec{J} \) is the heat current per unit volume and \( \kappa \) is the lattice thermal conductivity. Atomistic inspection of \( \vec{J} \) is obtained from:

\[ \vec{J} = \frac{1}{V} \sum_{i=1}^{n} E_i \vec{v}_i + \frac{1}{2V} \sum_{i=1}^{n} \sum_{j=i+1}^{n} (\vec{v}_i \cdot \vec{F}_{ij}) \vec{r}_{ij} \]  

where \( E_i \) is the total energy of each atom, \( \vec{v}_i \) is the velocity of each atom, \( \vec{F}_{ij} \) and \( r_{ij} \) are the forces and interatomic distance vectors between each pair of atoms, and \( V \) is the volume.

For the non-equilibrium analysis, the data collection section of each wire or tube shown in Figure 1 is subdivided in slices along its length. Each slice contains typically 40 to 48-atoms. The purpose of these sub-regions is the ability to average properties locally within each slice. Simulations are started for the equilibrated configuration of all systems. Once the temperature difference between the two thermostats is established, there is a transient time in which the average thermal current (Eq. (7)) in each slice is not constant. Similarly, during this transient time, the temperature profile across the length of the system (built from local averages in each slice) is not linear. However, once the steady state of thermal energy conduction is reached, then the thermal current is approximately the same in all slices, and the temperature profile is remarkably linear. A typical case is shown in Figure 2 illustrating both temperature and thermal current profiles across the length of a 3C nanowire at an average temperature of \( \sim 300 \) K. Points in this figure correspond to averages for each slice over 6 ps after the steady state is reached. As a result of the different dynamics between the atoms in the thermostat and the atoms in the active central region where data are taken, a few planes of atoms adjacent to the thermal baths were not considered for reporting of results in the sections to follow. A similar consideration has been adopted in the literature by several authors.

With this geometrical setup, the heat current components perpendicular to the energy flow should be negligible. Indeed, that is the case in our calculation where the perpendicular flow is around 1% of the flow along the length of the nanostructure. Additionally, it is confirmed that the longer data are averaged, the smaller the perpendicular flow becomes. The temperature difference between the two thermal baths is chosen to be large with respect to the temperature fluctuations but small enough to reproduce attainable laboratory situations. In our simulations the cold bath temperature is about 40% of the hot bath temperature. This choice is similar to that employed in other works. Both \( \vec{J} \) and \( T \) are calculated within the NEMD approach described in the previous section and then the lattice thermal conductivity \( \kappa \) is obtained from Eq. (6). The objective

Fig. 1. Computational setup for the non-equilibrium molecular dynamics simulations.

Fig. 2. Temperature and heat current across the device. (a) Temperature profile. Error bars identify standard deviations (s.d.). (b) Heat current at an average temperature of \( \sim 300 \) K.
is to find $\kappa$ at five temperatures: 150 K, 300 K, 500 K, 750 K, and 1000 K.

3.1. Nanowires

Nanowire configurations are obtained by carving the zinc-blende 3C and the wurzite 2H crystalline polytypes of SiC along the [100], [111] and [001], [110] directions, respectively. These elongated cuts have been demonstrated to be stable\(^{28}\) and are shown in Figure 3. During the MD equilibration process these four nanowires are extremely stable throughout the runs at all temperatures in the range 150 K–1000 K. Indeed, these wires kept their structure up to temperatures of 1000 K. The equilibrium MD average potential energies per SiC pair, extrapolated to zero temperature, have values of $-11.75$ eV, $-11.46$ eV for 3C [100], [111] and $-11.98$ eV, $-11.43$ eV for 2H [100], [110] nanowires. These results match qualitatively the tight binding energies per SiC pair of $-11.7$ eV, $-11.0$ eV for 3C [100], [111], and $-11.6$ eV, $-10.3$ eV for 2H [001], [110] nanowires calculated in Ref. [28].

The MD equilibrated configurations of these four nanowires were taken as initial configurations for the NEMD calculation of the lattice thermal conductivity $\kappa$. The results of $\kappa$ as a function of temperature are shown in Figure 4. The 3C [100] nanowire has the highest thermal conductivity, which is expected since this is the most stable wire among those studied here. The almost constant $\kappa$ obtained for 2H [001] and 3C [111] wires are close to predictions in Ref. [29]. Although the 3C [100] and 2H [110] wires, present the expected $T^{-1}$ power law decrease as a function of temperature, our results predict thermal conductivities two orders of magnitude lower than in bulk SiC measurements.\(^{7,18}\) In conclusion, nanowires are poor heat conductors, a property that can be used in a variety of nanodevices.

3.2. Armchair Nanotubes

Simulations are done on nanotubes with armchair chirality, as shown in Figure 5. Four armchair nanotube diameters are considered: (2, 2), (3, 3), (4, 4), and (5, 5). When the MD equilibration process is done on these nanotubes, not all nanotubes maintain their initial shape. The armchair (2, 2) and (5, 5) nanotubes are structurally stable under the model potential and remain in a tubular shape throughout the simulation at all temperatures in the range 150–1000 K. However, the (3, 3) and (4, 4) nanotubes collapse into flatten structures which we refer to as nanofilaments F33 and F44. Moreover, these new structures remain stable and equilibrate well at the considered temperatures. Figure 5 shows the resulting stable nanofilament structures. The average potential energy per SiC pair extrapolated to zero temperature is $-11.4$ eV for both the (2, 2) and (5, 5) nanotubes and $-11.5$ eV, $-11.63$ eV for the collapsed (3, 3), (4, 4) tubes. The potential energies of both nanotubes are in qualitative agreement with the tight binding results of 10.0 eV, 10.5 eV\(^{28}\) and are close to those calculated with MD in Ref. [24]. In both the (2, 2) and (5, 5) single wall nanotubes, the carbon atoms are slightly pushed toward the outside of the tube surface and the
silicon atoms toward the inside. The puckering is about 0.1 Å and decreases as temperature increases.

The dependence of $\kappa$ with temperature for these armchair tubes and filaments is shown in Figure 6. The temperature dependence of $\kappa$ for tube (2, 2) follows a power law $\kappa \sim T^{-1}$. In contrast, tube (5, 5) presents an almost constant $\kappa$ as a function of temperature. This prediction is discrepant with results in Ref. [30] where the Green-Kubo (GK) approach was used. We note that the GK is appropriate for isotropic systems, and thus is not adequate for structures such as tubes. The power law relationship of $\kappa$ for the nanofilaments is $\kappa \sim T^{-0.65}$ indicating a more gentle decrease with increasing temperature. The fluctuations for these tube/filament systems are quite large, as is visually seen in Figure 6. For clarity, only the positive standard deviation (s.d.) is depicted in the figure.

### 3.3. Zigzag Nanotubes

The zigzag nanotube (4, 0) remains stable and equilibrated well in a configuration similar to the initial structure while nanotubes (6, 0), (8, 0), and (10, 0) collapsed into nanofilaments that acquired shapes different than those obtained from the armchair nanotubes. We refer to these nanofilaments as F60, F80, F100 as a way to identify their original nanotube configuration. The resulting zigzag filaments have a (4, 0) tube twinned on the side with other tubes. Figure 7 shows these resulting nanofilament structures, showing that cross sections of filaments F60 and F100 are comparable, namely a (4, 0) distorted tube twinned to hexagonal side tubes. On the other hand, filament F80, has intercalated a (2, 2) tube intermixing tubes with different chiralities. This effect is consistent with structural changes from hexagonal rings into rings of 5 or 7 atoms observed by other researchers in SiC armchair and zigzag nanotubes under thermal and mechanical stresses.\textsuperscript{12-19,23} The average potential energy per SiC pair at a zero temperature is $-11.4$ eV for the (4, 0) nanotube, which compares well with the tight binding energy of $-10.5$ eV.\textsuperscript{28} The extrapolated-to-zero-temperature potential energies of the nanofilaments F60, F80, F100 are $-11.6$, $-11.7$, and $-11.7$ eV indicating that these structures are very stable. The prediction is then than nanofilaments are structurally preferred under the potential model used in this work.

Figure 8 shows the dependence of $\kappa$ with temperature. The (4, 0) nanotube presents a gentle power law behavior as a function of temperature, $\kappa \sim T^{-0.5}$. The decrease in $\kappa$ due to increasing temperature in the three nanofilaments is quite comparable, smoother than the degradation occurring in the (4, 0) nanotubes, and behaving approximately as $T^{-0.65}$. By analyzing Figures 6 and 8, one concludes that $\kappa$ for all nanofilaments behave comparably as a function of temperature.

### 4. CONCLUSIONS

In this work we have analyzed the temperature dependence of the lattice thermal conductivity for a variety of SiC...
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