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THE DISPARATE THERMAL CONDUCTIVITY OF CARBON NANOTUBES AND DIAMOND NANOWIRES STUDIED BY ATOMISTIC SIMULATION

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Molecular dynamics simulations were used to calculate the thermal conductivity of carbon nanotubes and diamond nanowires with atomic interactions modeled by the Brenner potential. The dependence of thermal conductivity on length, temperature, and temperature "boundary" condition was investigated. Lengths from 50 nm to 1 μm were simulated at a temperature of 290 K, and additional simulations were performed at 100 K and 400 K, for the 100 nm length. Thermal conductivity was found to be significantly suppressed for the shorter lengths. Two different artificial thermostats were used to impose the temperature difference: one rescaled velocities (the Berendsen thermostat), the other assigned velocities sampled from the appropriate Boltzmann distribution to randomly selected atoms for each numerical time step (the Andersen thermostat). Thus, the Berendsen thermostat amplifies existing atomic motions, while the Andersen thermostat, in a sense, disrupts the atomic motions. Nevertheless, results were very similar. All simulations were run for at least 200,000 time steps of 1 fsec each.

INTRODUCTION

The thermal characteristics of carbon nanotubes [1] will be important for designing systems that might incorporate them. Applications in microelectronics are under intense investigation. As with any small electronics, the thermal properties of nanotubes are expected to be important. This study investigates the dependence of thermal conductivity on length and temperature for a (10,10) "armchair" nanotube [1]. See Harris [2] for a complete discussion of the structure of nanotubes [1]. Although thermal transport at these scales can be quite different than at macroscales, we follow the common practice of couching the discussion in the language of continuum heat transfer, particularly in our use of thermal conductivity in describing energy transport properties.

Our thermal conductivity results are compared with values that have been deduced in experiments and simulations performed using different methods of deducing the thermal conductivity. The longitudinal thermal conductivities of nanotubes have recently been measured. At $T = 300$ K, Shi [3] found $\lambda = 3000$ W/mK for a multi-walled nanotube and $\lambda = 1200$ W/mK for a 150 nm diameter multi-walled nanotube bundle. Hone et al. [4] estimated the thermal conductivity of single-walled nanotubes, based on the measured thermal conductivity of a crystaline rope of single-walled nanotubes, to be in the range of $\lambda = 1750$ to 5800 W/mK. Using a quasi-nonequilibrium molecular dynamics formulation with periodic boundary conditions and an area of approximately 29×10^{-19} m^2, Berber et al. [5] predicted $\lambda = 6600$ W/mK; using an equilibrium technique with the Green-Kubo relation to compute λ, Che et al. [6] found $\lambda \approx 2980$ W/mK, using an area of approximately 4.3×10^{-19} m^2, also for a single-walled nanotube. The values for thermal conductivity obtained in this study were somewhat lower, which is likely due to the current method of artificially imposing a temperature gradient, although it is not clear which method best corresponds to any particular physical configuration.

One of the difficulties that arises in simulating nanotubes comes from the fact that nanotubes are known to have phonon mean free paths on the order of microns [3]. Thus, we anticipate that the computations of long nanotubes with large numbers of atoms are required, in order to obtain a size independent thermal conductivity. Naturally occuring defects, such as voids or isotopes, have been shown to reduce thermal conductivity in shorter tubes [6], but only idealized defect free nanotubes are considered in the present study.

All predictions suggest that isolated defect free nanotubes have high thermal conductivity, which is expected, given their "clean" structure. For comparison, simulations of a diamond nanowire have been performed in an attempt to illuminate the differences in the phonon processes in these quasi-one-dimensional nanostructures. The structure of the diamond nanowire, with its relatively irregular surface, is expected to scatter the phonons and inhibit the transmission of heat, which previously has been investigated in silicon nanowires [7].

COMPUTATIONAL METHOD

The Brenner parameterization [8] of a Tersoff [9] bond-order potential was used as an empirical model for the atomic interactions. This potential has been used in the past for thermal conductivity calculations [6, 10], as well as for investigations into various other properties [11] of carbon nanotubes. There are several variants of the Brenner potential in the literature. The parameters we used are defined and tabulated in the Appendix. The equation of motion was integrated in time with the velocity Verlet algorithm [12], which has excellent energy conservation.

Our implementation of the Brenner potential was verified by computing the fracture stress and strain of a (10,10) nanotube and comparing it to the reported results of Belytschko et al. [13]; agreement was within 15%.
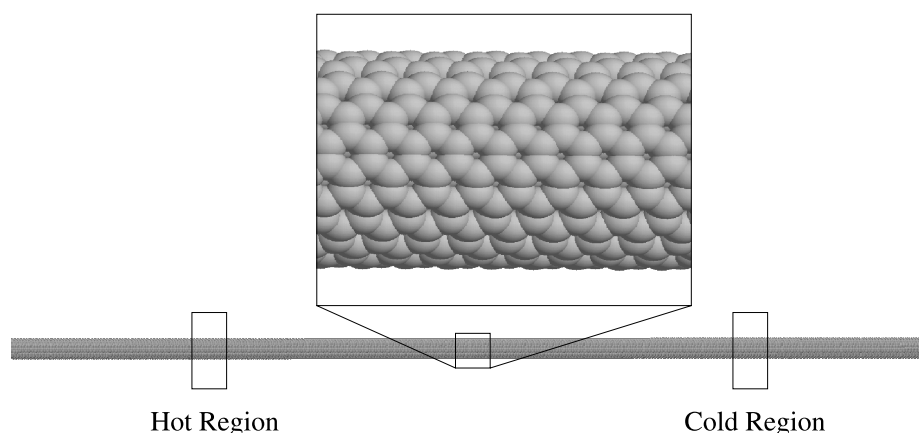
The initial atom positions were estimated based on the documented structure of carbon nanotubes and diamond and changed only slightly after the simulation began. However, only a slight change in length was needed to buckle the longer tubes simulated, so non-periodic test cases with stress free axial boundaries were run in order to identify

the stress free lengths of the tubes, as dictated by the Brenner potential. For the diamond nanowires, the atoms were initialized with positions corresponding to bulk diamond, but arrangement quickly relaxed at the free surface. Similar axial relaxation procedures were followed to remove net axial stresses. In both cases, initial velocities were random in both direction and magnitude (uniformly distributed with a maximum absolute value of 1000 m/s). Then, the nanotube or nanowire was slowly cooled with velocity rescaling, and a temperature gradient was applied, as discussed below.
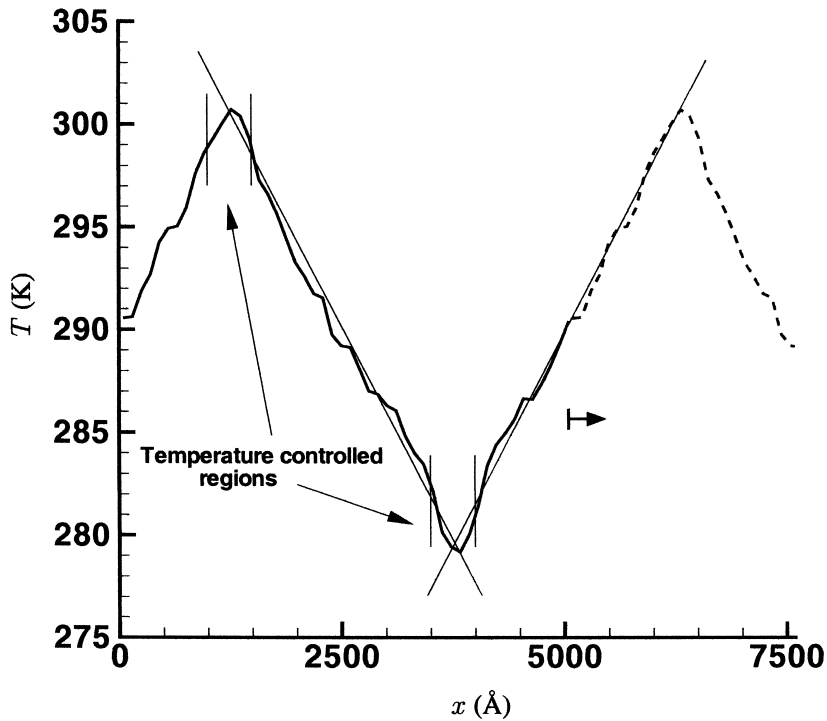
The algorithm was implemented in parallel by logically dividing the nanotube lengthwise across the individual processors of the computer. Computation time significantly outweighed inter-processor communication time, so the runtimes scaled nearly perfectly with the number of processors. The simulations reported were run on parallel platforms using 2 to 120 processors.

Che et al. [14] suggest that a classical description of the mechanics should suffice for computing the phonon contribution to thermal conductivity. An estimate using the Wiedemann-Franz law and measurements of electrical conductivity [2] suggests that electron contributions constitute, at most, a small percent of the overall thermal conductivity, even for metallic nanotubes.

The temperature was controlled in separate hot and cold regions to maintain a temperature difference of 20 K. This configuration is shown in Figure 1. Such a large temperature gradient is necessary to converge statistics in reasonable amounts of time in atomistic simulations. Each temperature controlled region was 10% of the nanotube's or nanowire's length. The thermostats and the dependence of the results on their selection is discussed in the next section. The heat flux was calculated directly (and exactly) from the changes in kinetic energy brought about by the thermostats. Since the kinetic energy before and after the application of the thermostats is known, the difference can be taken and divided by the timestep length, which gives the net heat flux. An examination of the temperature profiles was used to determine when the simulations had reached a statistically stationary state. The temperature profile shown in Figure 2 is the average

Hot Region   Cold Region

Figure 1. Periodic simulation setup.

Figure 2. Temperature profile in temperature controlled periodic single-walled nanotube. Straight solid lines are visual fits, and – – – – shows the periodic extension.

for a 500 nm long (10,10) nanotube after 10^6 time steps. Convergence tests showed that least-squares linear fits of the temperature profile did not change significantly after 200,000 time steps.

The values for thermal conductivity are obtained by:

$$\lambda = \frac{\dot{Q}}{A\dfrac{dT}{dx}}, \tag{1}$$

where $\dot{Q}$ is the heat flux, A is the cross-sectional area, and dT/dx is the average temperature gradient. The area was calculated as the area of a circle with circumference defined by the centers of the atoms around the nanotube. This area was chosen for its simplicity and ease of comparison to the diamond nanowire with similar diameter. Had different cross-sections been used for each, comparisons between their thermal conductivities may have been misleading. The nanowires simulated had the same cross sectional area as the nanotubes (14.5×10^{-19} m^2), even though the nanotube is hollow. Che et al. [6] used a 1 Å thick ring for the area in the thermal conductivity calculations. This smaller area results in a higher value for thermal conductivity. Thus, our numbers may appear to be lower than expected. However, modifying their values to accomodate the difference in

area, the thermal conductivity becomes ~ 880 W/mK for a 40 nm nanotube. As we shall see, this is still somewhat higher than the values obtained in this study.

The temperature gradient was determined by a least-squares linear fit of the data in the middle third of the nanotube or nanowire length. This value did not change significantly after 200,000 time steps.

THERMOSTATS

Two different thermostats were used to fix the temperature in the controlled regions. The first is a Berendsen [15] thermostat, which rescales the velocities by χ each timestep, where:

$$\chi = \left[1 + \frac{\Delta t}{\tau} \left(\frac{T_{\mathrm{tar}}}{T} - 1 \right) \right]^{\frac{1}{2}}. \tag{2}$$

The target temperature is T_{tar}, and the instantaneous local temperature obtained from the atomic kinetic energy equation is T. The relaxation time τ, which sets the strength of the thermostat, was 10^{-13} sec and was chosen to be as weak as possible, while still being able to maintain the required temperature gradient in the 50 nm (shortest) tube. It was hoped that the largest possible value of τ would minimize the thermostat's interference with the phonon behavior. The 50 nm tube was used for these thermostat strength tests, because of the lengths simulated it required the highest thermostat strength to hold the temperature gradient.

The second type of thermostat used is due to Andersen [16]. It works by stochastically coupling the system to a constant temperature bath. For each timestep, each atom has a $\nu \Delta t$ probability of "colliding" with a particle in the constant temperature bath. If an atom is selected for such a virtual collision, it is given a random velocity, selected from the Boltzmann distribution for the desired temperature. ν was chosen to be 0.01 for these simulations. This value was arrived at in a similar manner as the relaxation parameter for the Berendsen thermostat. Again, it was desired to have as weak a thermostat as possible, while still being able to maintain the applied temperature.

Both the Andersen and Berendsen thermostats are artificial. Neither attempts to model any particular physical mechanism of exchanging energy with the system. Thus, these two, which have very different characteristics, were selected to provide a measure of how sensitive our results might be to the details of the thermostats used. We compared their thermal conductivity predictions for a 100 nm nanotube and nanowire with a mean temperature of 300 K. The results are shown in Table 1. The Andersen thermostat gives different values for thermal conductivity than the Berendsen does, but the results do not seem to be highly sensitive to our choice of thermostat. Subsequent results all use the Berendsen thermostat.

Table 1. Dependence of thermal conductivity on thermostat

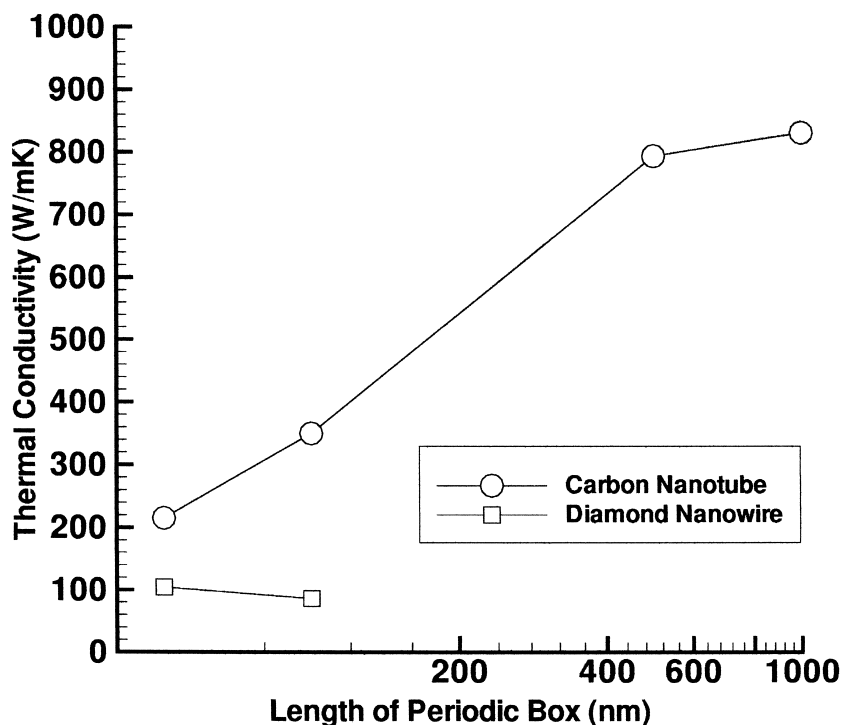| Simulation	Berendsen	Andersen
Carbon nanotube	350 W/mK	457 W/mK
Diamond nanowire	238 W/mK	134 W/mK

Table 2. Dependence of thermal conductivity on length

		50 nm	100 nm	500 nm	1000 nm
Present	(10,10) nanotube	215 W/mK	350 W/mK	794 W/mK	831 W/mK
	Diamond nanowire	104 W/mK	86 W/mK		
	Che et al. [6]	[†]880 W/mK			
	Berber et al. [5]		[‡]6600 W/mK for length < 10 nm		
	Experiment [4]		1750–5800 W/mK for length ∼ 1 μm		

[†]Tube length was 40 nm. Number adjusted to match our definition of A.
[‡] Area based on estimated packing structure. No adjustments attempted.

LENGTH DEPENDENCE

Simulation of (10,10) nanotubes with lengths from 50 nm to 1 μm show a strong dependence of thermal conductivity on length. Diamond simulations require significantly more computing power and have thus only been simulated up to 100 nm in length so far. The mean temperature was 300 K, with a ΔT of 20 K. Results are shown in Table 2, and plotted in Figure 3. As the periodic box gets longer, becoming a larger fraction of the

Figure 3. Nanotube thermal conductivity versus length.

Table 3. Dependence of thermal conductivity on mean temperature

Simulation	100 K	290 K	400 K
Carbon nanotube	590 W/mK	350 W/mK	294 W/mK
Diamond nanowire	238 W/mK	86 W/mK	

phonon mean free path, the thermal conductivity is less affected by its size. The thermal conductivity becomes less sensitive to the length for the longer tubes. Table 2 also shows results from experiments and other simulations. We believe that our lower values are due to the the temperature boundary conditions applied, which, acting over only a short section of the tube, can not excite the full phonon spectrum and will disrupt the energy carrying phonons.

TEMPERATURE DEPENDENCE

Simulations were performed at three different mean temperatures, yet keeping $\Delta T = 20$ K and a periodic box length of 100 nm. The thermal conductivity values obtained are shown in Table 3. Both the nanotube and diamond showed higher thermal conductivity at lower temperature, though the effect is more subtle than was expected for the nanotube. Berber et al. [5] found a six fold increase in thermal conductivity, when going from room temperature down to 100 K. This behavior was explained by the fact that the phonon mean free path gets smaller at the higher temperatures, due to Umklapp processes. This results in a lower thermal conductivity. It is believed that the low temperature dependence shown here may be an indication of size effects, since the dependency found is much less than for bulk materials. This is currently being investigated. The diamond wire, however, is more sensitive to temperature. Unfortunately, it seems unstable to surface diffusion at the higher temperatures, even for the short times of these simulations. The nanowire breaks apart before any reasonable value for the thermal conductivity can be obtained.

CONCLUSION

The thermal conductivity of a (10,10) nanotube has been calculated, using molecular dynamics simulations. Results varied from 215 W/mK, for a 50 nm periodic box length, to 831 W/mK, for a 1 μm box. The higher value is within the range of values obtained in recent experiments [3, 4]. Simulations also showed that the significantly different means of imposing a temperature gradient on the tube had a small effect on the thermal conductivity calculations, with the Berendsen [15] thermostat giving a slightly lower value for the nanotube thermal conductivity than the Andersen [16] thermostat, and vice versa for the nanowire. The simulated nanowires had a much lower thermal conductivity than the nanotubes, presumably due to scattering at their relatively irregular surfaces. Both the diamond and nanotube showed decreasing thermal conductivity with increasing temperature.

Table 4. Parameters used for potential energy equations

Parameter	Value
R_e	1.39 Å
D	6.0 eV
β	2.1 Å^{-1}
S	1.22
δ	0.5
R_1	1.7 Å
R_2	2.0 Å
a_0	0.00020813
c_0	330
d_0	3.5

APPENDIX

The specific values of the parameters we used in the Brenner potential, as defined in the potential formulation below, are tabulated in Table 4.

$$E_i = \sum_{j(\neq i)} \left[f(r_{ij})A(r_{ij}) - B_{ij}f(r_{ij})C(r_{ij}) \right] \tag{3}$$

$$f(r_{ij}) = \frac{1}{2} \left[1 + \cos\left(\pi \frac{r_{ij} - R_1}{R_2 - R_1} \right) \right] \qquad R_1 \leq r_{ij} \leq R_2 \tag{4}$$

$$A(r_{ij}) = \frac{D}{S-1} \exp\left(-\beta\sqrt{2S}\left(r_{ij} - R_e \right) \right) \tag{5}$$

$$C(r_{ij}) = \frac{DS}{S-1} \exp\left(-\beta\sqrt{2/S}\left(r_{ij} - R_e \right) \right) \tag{6}$$

$$B_{ij} = \left[1 + \sum_{k(\neq i,j)} G(\theta_{ijk})f(r_{ik}) \right]^{-\delta} \tag{7}$$

$$G(\theta_{ijk}) = a_0 \left[1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + \left(1 + \cos\theta_{ijk} \right)^2} \right]. \tag{8}$$

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