The Disparate Thermal Conductivity of Carbon Nanotubes and Diamond Nanowires Studied by Atomistic Simulation

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Abstract

Nonequilibrium molecular dynamics simulations were used to calculate the thermal conductivity of carbon nanotubes and diamond nanowires. Atomic interactions were modeled by the Brenner potential. The dependence of thermal conductivity on length, temperature, and temperature "boundary" condition were investigated. Lengths from 50nm to 1μm were simulated at temperatures of 100K, 290K, and 400K. Thermal conductivity was found to decrease significantly with shorter lengths. Two different thermostats were used to set the temperature difference: one rescaled velocities (Berendsen thermostat), the other picked a few atoms at random every timestep and gave them a velocity sampled from the appropriate Boltzmann distribution (Andersen thermostat). The Andersen thermostat resulted in slightly higher values for thermal conductivity. All simulations were run for at least 100,000 timesteps of 1fsec each.

Introduction

The thermal characteristics of carbon nanotubes[1] will be important for designing systems that incorporate them. This study investigates the dependence of thermal conductivity on length and temperature for a (10,10) armchair nanotube. We also discuss the sensitivity of the results to how the energy is added and removed. Results are compared with both experimental values[2,3] and simulations performed using different methods,[4,5] which suggest high thermal conductivity. 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. Single walled carbon nanotubes have a naturally "clean" structure and it is believed that this results in excellent transmission of phonons, resulting in an extremely high thermal conductivity. The structure of the diamond nanowire, with its relatively irregular surface, is expected to scatter the phonons and inhibit the transmission of heat, which has been investigated previously in silicon nanowires.[6]

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 150nm diameter nanotube bundle. Hone *et al.*[2] 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 5800W/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.*[4] predicted $\lambda = 6600$W/mK; using an equilibrium technique with the Green-Kubo relation to compute λ, Che *et al.*[5] found $\lambda \approx 2980$ W/mK using an area of approximately 4.3×10^{-19}m^2, also for a single-walled nanotube.

One of the difficulties that arises in simulating nanotubes is that nanotubes are expected to have long phonon mean free paths, on the order of microns.[3] Thus computations of long nanotubes with large numbers of atoms are expected to be necessary 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.[5]

Computational Method

The Brenner hydrocarbon potential[7] was used to model the atomic interactions. This potential has been used in the past for thermal conductivity calculations,[5,8] as well as for investigations into various other properties[9] of carbon nanotubes. The initial atom positions were determined based on the known structure of carbon nanotubes and diamond. In these simulations, a (10,10) armchair nanotube was used. Initial velocities were random in both direction and magnitude (uniformly distributed with a maximum absolute value of 1000m/s). A velocity Verlet algorithm was used to advance the solution in time.

The algorithm was implemented in parallel. Computation time dominated communication time and the code scaled nearly perfectly with number of processors. It has been run on parallel plat-

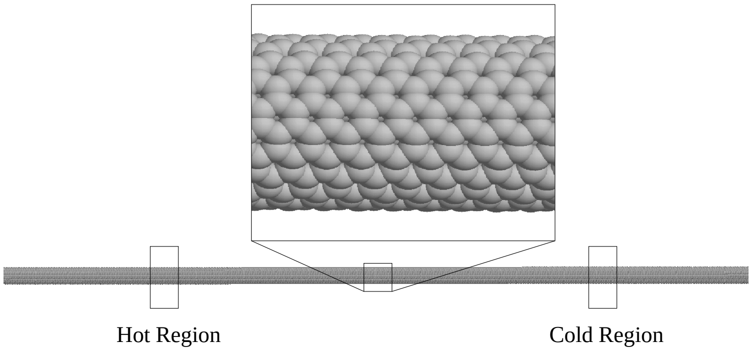

Figure 1: Periodic simulation setup.

forms using anywhere from 2 to 120 processors.

Che *et al.*[10] suggest that a classical description of the mechanics should suffice for computing the thermal conductivity. Estimates using the Wiedemann-Franz law and measurements of electrical conductivity[11] suggest that electron contributions to thermal conductivity are negligible compared to total thermal conductivity, even for metallic nanotubes. In this study, a nonequilibrium approach was used to calculate the thermal conductivity. The temperature was controlled in separate hot and cold regions in order to maintain a temperature difference of 20K. This configuration is shown in figure 1. The width of each temperature controlled region was 10% of tube length. The tube was periodic. Dependence on the thermostats used is discussed in the next section. The heat flux was calculated from the changes in kinetic energy brought about by the thermostats. Once the simulation has reached steady state, the time average of this value becomes statistically station-

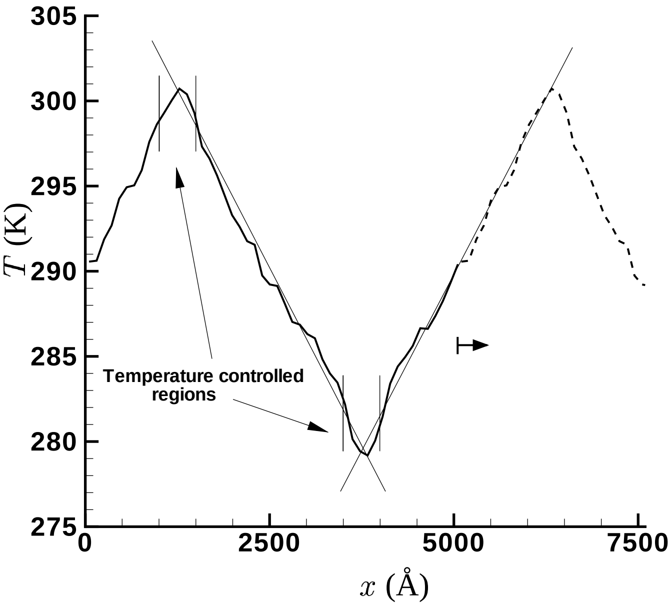

Figure 2: Temperature profile in temperature controlled periodic single-walled nanotube: straight solid lines are visual fits, and ---- shows the periodic extension.

ary and the temperature profile becomes smooth. The temperature profile shown in figure 2 is the average for a 500nm long (10,10) nanotube after 10^6 timesteps.

The values for thermal conductivity are obtained by

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

where $\dot{Q}$ is the heat flux, A is the cross-sectional area, and dT/dx is the average temperature gradient. The nanowires simulated had the same cross sectional area as the nanotubes ($14.5 \times$

10^{-19}m^2 measured to the centers of the surface atoms), which were taken as solid for computing this area. Che *et al.*[5] used a 1 Å thick ring for the area in the thermal conductivity calculations. This smaller area results in the high value for thermal conductivity they report. Rescaling their values to accomodate the difference in area, the thermal conductivity becomes ~ 880W/mK for a 40nm nanotube, which is closer to but still higher than our value of 606W/mK for a slightly longer 50nm nanotube.

Thermostats

Two different thermostats were used to control temperature. The first is a Berendsen[12] thermostat, which rescales the velocities by χ each timestep, where

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

The target temperature is $T_{\rm tar}$ and the instantaneous local temperature 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 a 50nm tube.

The second type of thermostat used is due to Andersen.[13] It works by stochastically coupling the system to a constant temperature bath. Each timestep, each atom has a $\nu\Delta t$ probability of “colliding” with a particle in this bath. If an atom is selected for collision, it is given a random

Simulation	Berendsen	Andersen
Carbon Nanotube	1248 W/mK	1390 W/mK
Diamond Nanowire	378 W/mK	533 W/mK

Table 1: Dependence of thermal conductivity on thermostat.

velocity drawn from the Boltzmann distribution for the desired temperature. ν was chosen to be 0.01 for these simulations.

For both thermostats, a 100 nm length was used, with a mean temperature of 300K. The results are shown in table 1. The Andersen thermostat gives slightly higher 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.

Length Dependence

Simulation of (10,10) nanotubes with lengths from 50nm to 1μm show a strong dependence of thermal conductivity on length. (Diamond simulations require significantly more computing power and have thus only been simulated up to 100nm in length so far.) The mean temperature was 300K with a ΔT of 20K. Results are shown in table 2, and the values for the nanotube are plotted in figure 3. The table also shows results from experiments and other simulations.

		50 nm	100 nm	500 nm	1000 nm
Present	(10,10) Nanotube	606 W/mK	1248 W/mK	3241 W/mK	3650 W/mK
	Diamond Nanowire	299 W/mK	378 W/mK		
Che *et al.*[5]		†880 W/mK			
Berber *et al.*[4]		‡6600W/mK for length < 10nm.			
Experiment[2]		1750-5800W/mK for length $\sim 1\mu$m			

† Simulation length was 40 nm and a 1 Å ring was used for cross-sectional area.
The value shown has been adjusted for the different area used.

‡ It is not clear what area was used in the calculation. The original value is shown.

Table 2: Dependence of thermal conductivity on length.

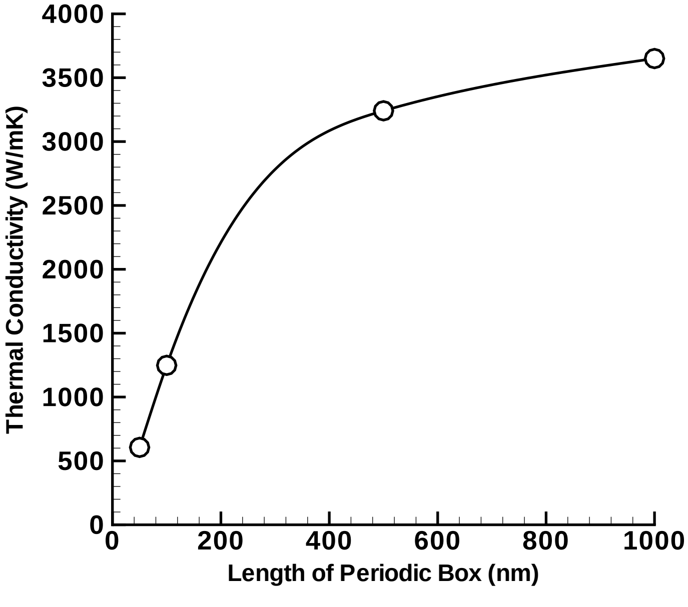

Figure 3: Nanotube thermal conductivity versus length.

Simulation	100 K	290 K	400 K
Carbon Nanotube	1300 W/mK	1248 W/mK	1174 W/mK
Diamond Nanowire	539 W/mK	378 W/mK	

Table 3: Dependence of thermal conductivity on mean temperature.

Temperature Dependence

Simulations were performed at three different mean temperatures, but keeping $\Delta T = 20$K and a periodic box length of 100nm. 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.*[4] found a six fold increase in thermal conductivity when going from room temperature down to 100K. 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.

Conclusion

The thermal conductivity of a (10,10) nanotube has been calculated using nonequilibrium molecular dynamics simulations. Results varied from 606W/mK for a 50nm periodic box length to

3650W/mK for a 1μm box. This is within the range of values obtained in recent experiments.[2,3] Simulations also showed that the type of thermostat has a small effect on the thermal conductivity calculations for Berendsen[12]and Andersen[13] thermostats, with the latter giving slightly higher values. Similar simulations were also performed for a diamond nanowire and these showed a reduced thermal conductivity in comparison to the nanotube. Both the diamond and nanotube showed decreasing thermal conductivity with increasing temperature.

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