Effect of Confined Fluid Interaction on the Thermal Transport in Carbon Nanotubes

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ABSTRACT
Carbon nanotubes (CNTs) are one of the most commonly used engineering materials. The axial thermal conductivity of CNTs were found to be exceptionally high, which makes them one of the favourable candidates for the next generation thermal management devices. Previous works have indicated that the presence of confined fluid molecules inside the CNT lead to a reduction in the thermal conductivity of the CNT. In the present study, we investigate the effect of confined liquid flow through CNTs on the thermal transport of CNTs. Spectral energy density method is used to predict the phonon properties and lifetimes of the CNT. The phonon mode lifetimes were found to be greater under flow compared to filled condition for smaller diameter CNTs. But the flow does not seem to modify signifcantly the phonon mode lifetimes of larger diameter CNTs. These variations in the thermal transport properties of CNT is explained using the changes occuring in the physical behavior of the confined fluid as the tube diameter changes.

1. INTRODUCTION

In 1965, Gordon Moore predicted that the number of components that could be incorporated per integrated circuit would increase exponentially over time [1]. The number of components per chip has doubled every two years since 1970. This historical trend is referred to as the Moore's Law. As a consequence of this trend, the dimensions of electronic and mechanical devices shrinked to a few nanometers. This miniaturization was further accelerated in the last decade with the advent of advanced micro and nano-scale fabrication techniques like Molecular Beam Epitaxy and Chemical Vapour Deposition [2]. As a result of this extreme miniaturization and the resulting rise in the density of electronic components in devices, heat dissipation from integrated circuits has seen a steady increase. Without sophisticated cooling techniques, the microchips in todays microelectronic devices would melt [3]. Moreover, during the fabrication of microelectronic devices, the ability to measure, predict, and control thermal behavior during processing has always been a strict requirement [4, 5]. To maintain and improve device performance and reliability, heat generated in these devices must be efficiently dissipated, which requires very high thermal conductivity of the device components [3]. Thus, modeling and design of these devices aimed at better thermal properties is of great importance. Carbon Nanotubes (CNT) posses a unique combination of mechanical and transport properties that make them useful in nanoscale engineering systems. Moreover, CNTs can be metallic or semiconducting depending on their chirality and diameter. Thus, CNT-based composites are being tested as lightweight thermal management materials.

The experimental measurement of thermal conductivity becomes quite difficult for nanometer scale devices, particularly for real devices with complex geometries [6]. Consequently, theoretical and computational methods are preferred for predicting the thermal properties of nanoscale materials and devices [4]. Thermal conduction of a bulk material is determined by material type and atomic structure [4]. For example, thermal transport in metals is dominated by electrons. The corresponding electron thermal conductivity is usually approximated by the Wiedemann-Franz law. The contribution of phonons,

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which are coherent vibrations of atoms about their equilibrium lattice sites, is very small. In semiconductors, as the electrical conductivity decreases, phonons play an increasingly important role in thermal transport and the contribution of phonons becomes comparable to that of electrons [7]. In electrical insulators, electron transport is absent and phonons dominate thermal conduction [8]. Consequently, phonon transport studies are important in studying the mechanisms of thermal conduction in semiconductive nanostructures.

At low temperatures, harmonic or third order anharmonic lattice dynamics calculations can be used to predict the phonon properties of periodic systems. But for systems with nonperiodic interactions at realistic temperatures, lattice dynamics calculations cannot capture effects of phonon scattering and interaction with non-bonded molecules [9]. Classical Molecular Dynamics simulations, on the other hand, can be used to capture the fully temperature-dependent anharmonicity and also the interactions with non-bonded molecules [10]. Molecular Dynamics (MD) is a powerful simulation tool to compute the motion of molecules in model physical systems [11, 12]. The essence of the MD method is to solve Newton's equation of motion for a set of fictitious atoms, whose positions and velocities are stored in a computer, and which are assumed to interact via a model interatomic anharmonic potential. Any numerical solution of the continuous equations of motion will involve using small discrete time steps, with a method (the algorithm) to generate the atomic positions and velocities at a given time step from the positions and velocities of the previous time steps. The MD method will then be able to generate the trajectory of the collection of atoms over a period of time that is long enough to be able to analyse with adequate accuracy.

For the study of individual phonons using MD we need to consider the Fourier components of the atomic trajectory obtained from MD. Dove et al. has developed a method for obtaining normal-mode coordinates from the atomic trajectory [10]. This method can directly give the dispersion relations. But, the calculations become tedious for systems with multiple atom unit cells. Thomas et al. has recently derived a technique for predicting phonon dispersion relations and lifetimes from their normalmode coordinates using the spectral energy density (SED) [13]. The phonon dispersion relations can be obtained from SED profile with some assistance from harmonic lattice dynamics calculations. k_z can then be obtained from phonon properties (calculated from the dispersion relation) by combining the Boltzmann transport equation under the relaxation-time approximation with the Fourier law to give

$$k_z = \sum_k \sum_v c_{ph} v_{g,z}^2 \tau \tag{1}$$

where C_{ph} is the phonon specific heat, $v_{g,z}$ is the axial group velocity, and τ is the phonon lifetime.

The present study makes use of the SED analysis technique developed by Thomas et al. [13] to examine the phonon lifetimes of Single-Walled Carbon Nanotubes (SWCNTs) under three different conditions - empty CNT, filled CNT and CNT with flow. A CNT can be assumed to be produced by curling a graphene sheet into a hollow cylinder. They can be characterized by a wrapping vector C_h as

$$C_h = na_1 + ma_2 \tag{2}$$

where a1 and a2 are graphene lattice basis vectors and the indices (n, m) are positive integers with $n \geq m \geq 0$. Based on the direction of wrapping of the graphene sheet, CNTs can be characterized into armchair (n = m), zig-zag (m = 0) and chiral (n > m > 0). All the simulations were carried out for armchair SWCNTs with n values of 8, 12, and 16 represented as (8, 8), (12, 12) and (16, 16). The results indicate that inducing a flow to water molecules inside (8, 8) CNT increases the phonon lifetimes of the acoustic modes, thus increasing the thermal conductivity of (8, 8) CNT. The flow do not seem to affect the thermal conductivity in the case of (12, 12) and (16, 16) CNTs.

2. SIMULATION MODELS

All the simulations were carried out using LAMMPS open source libraries [14]. The various simulation systems used in the present study are explained below.

2.1. Empty CNT

The simulation box consists of 50 CNT unit cells along the z-axis with 32, 48 and 64 atoms in the unit cell for (8,8), (12,12) and (16,16) nanotube respectively. The C-C interaction was modelled using 2nd generation Reactive Empirical Bond Order (REBO) potential [15]. Periodic Boundary Conditions were imposed along the axial direction. The nanotube was first equilibrated for 1 ns with 0.5 fs timestep. The temperature was fixed at 300K using the Nose-Hoover Thermostat during the equilibration. After equilibration, the velocity data of carbon atoms were collected every 5 fs for 1 ns under NVE (constant mass, volume, and energy) MD simulation.

2.2. Filled CNT

The simulation box in this case consists of 50 unit cells along the z-axis for nanotube filled with water molecules. The density of water molecules was kept at 1 gm/cm3. The C-C interaction was modelled using 2nd generation Reactive Empirical Bond Order (REBO) potential. Water molecules were modelled using the TIP3P potential [16]. The C-O interactions were modelled using Lennard-Jones potential. The parameters used for LJ Potential was taken from the work of Hummer et al. [17]. The simulation box was equillibriated at 300K for 1 ns with a timestep of 0.5 fs. Velocity data of the carbon atoms were collected every 5 fs during the 1 ns production run.

2.3. CNT with flow

The simulation box and the interaction model in this case is the same as for filled CNT. The system was first equilibrated under NVT ensemble at 300 K for 1 ns with a timestep of 0.5 fs. A Poissuelle flow is induced inside the nanotube by adding a small force to all the water molecules along the positive z-direction. The temperature of water molecules were maintained at 300 K using Nos`e-Hoover thermostat. Atoms in the nanotube were integrated using NVE ensemble and velocity data was collected every 5 fs for 1 ns.

3. METHODS

Thomas et al. has derived a straightforward technique to predict the phonon properties and lifetimes from atomic velocities using the spectral energy density (SED) analysis technique [13]. The SED can be calculated from the atomic velocity using

$$\phi(\kappa,\omega)=\frac{1}{4\pi\tau_0 N_T}\sum_{\alpha}\sum_{b}^{B} m_b\left|\int_0^{\tau_0}\sum_{n_{x,y,z}}^{N_T}\dot{u}_\alpha\left(n_{x,y,z},b;t\right)\times\exp\left[\,i\kappa\, r\left(n_{x,y,z},0\right)-i\omega t\right]dt\right|^2 \tag{3}$$

where τ_0 is the total time of integration (= 1 ns), N_T is the total number of unit cells, $u_\alpha\left(n_{x,y,z},b;t\right)$ is the velocity in the α direction of atom b (of mass m_b) inside the unit cell $n_{x,y,z}$, $r(n_{x,y,z};\,0)$ is the equilibrium atom positions.

The frequencies and the lifetimes of phonon modes are determined from position of the peak and the linewidth on the SED curve. The SED for a particular mode is a highly peaked function as shown in Fig. 3. The peaks are centered at values of κ and ω at which phonon modes exist. The shape of the frequency spread for each mode can be fit to a Lorentzian function

$$\phi(\kappa_z,\omega)=\frac{I}{1+\left[\left(\omega-\omega_c\right)/\gamma\right]^2} \tag{4}$$

where I is the peak magnitude, ω_c is the frequency at peak center, and γ is the half-width at half-maximum. The phonon mode lifetime can then be obtained using

$$\tau = \frac{1}{2\gamma} \tag{5}$$

For each wave vector mode, frequency dependent SED plot will include 96, 144, 192 peaks for (8,8), (12,12) and (16,16) SWCNT respectively. Each peak was fitted with a Lorentzian function using the Levenberg-Marquardt algorithm [18]. Thomas et al. has shown that the 4 acoustic phonon modes in (8,8) CNT contribute nearly 50% of its thermal conductivity [13]. Thus, in the present work, we try to study the change in phonon lifetimes for only the four lowest frequency acoustic modes. The SED analysis was carried out using a selfwritten code. Fitting of SED peaks to Lorentzian function was done using Fityk software [18].

4. RESULTS AND DISCUSSIONS

In this section, the results corresponding to MD simulation studies on the changes in thermal transport of CNTs while interacting with water will be analysed. Each data point corresponds to an average value taken from five independent simulations with different initial conditions. Figure 3 shows the variation of SED with frequency for the four acoustic modes in (8, 8) CNT along kz = 0. The figure clearly shows a shift in frequencies of the phonon modes and also, the linewidths (half-width at half-maximum) appears to have broadened in the presence of water molecules. The increased linewidth and the consequent reduction in phonon mode lifetimes for (8, 8) CNT filled with water molecules has already been predicted by Thomas et al. [13]. Figures 1 and 2 show the SED profile for the empty and water-filled (8,8) CNT respectively. The SED profile for water-filled CNT appears to be a bit more smeared compared to empty CNT due to the increased linewidths of the Lorentzian profiles. These observations clearly indicate that the interaction between the carbon atoms and the water molecules have considerable influence on the phonon transport in the CNT. The water molecules are found to scatter the low frequency phonons of the CNT.

Table 4.1 lists the frequencies of the acoustic modes for each case of (8, 8) CNT and their corresponding mode lifetimes inside the bracket. Clearly, the lifetimes are greater under flow compared to filled condition. This maybe due to the reduction in carbon-oxygen interaction time in the case of

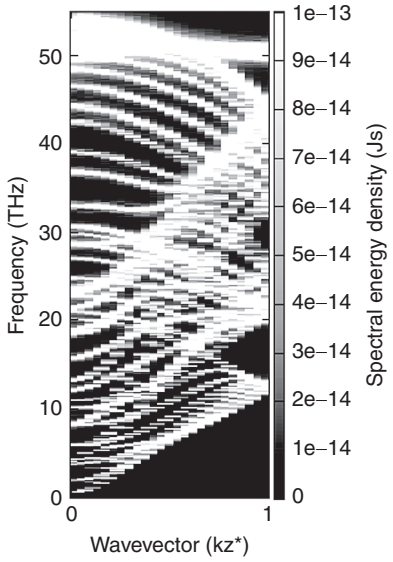

Figure 1. SED Profile for Empty (8, 8) CNT

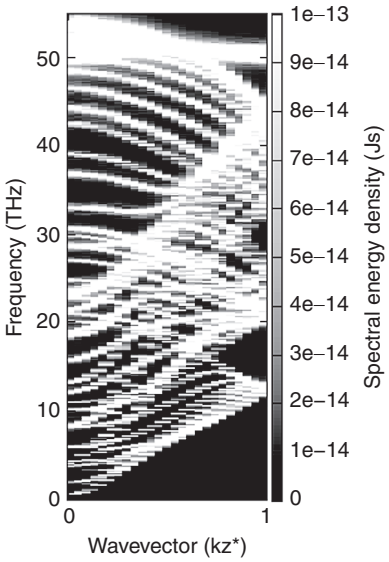

Figure 2. SED profile for filled (8, 8) CNT

Table 1. Phonon Mode Frequencies in THz (Lifetimes in ps) for (8,8) Cnt

	Empty	Filled	With flow
1st	0.773 (500)	0.872 (11.58)	0.854 (25)
2nd	2.139 (524.1)	2.427 (4.7)	2.411 (6)
3rd	3.955 (56.6)	4.183 (61.8)	4.186 (114.5)
4th	4.217 (88.2)	4.353 (6.4)	4.353 (13.12)

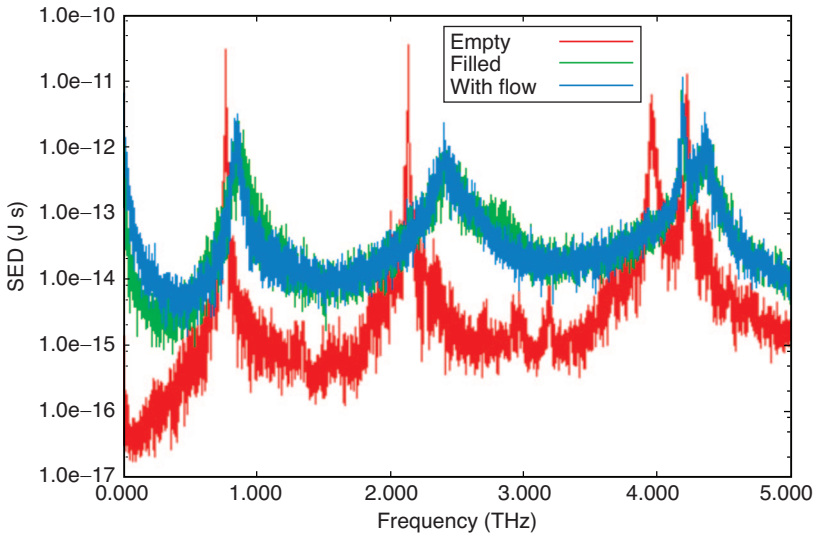

Figure 3. Frequency dependent SED plot (along $K_z = 0$) showing the four acoustic modes for (8,8) CNT

Table 2. Phonon Mode Frequencies in THz (Lifetimes in ps) for (12,12) Cnt

	Empty	Filled	With flow
1st	0.358 (1086.9)	0.464 (6.9)	0.457 (6.9)
2nd	1.005 (363.1)	1.138 (2.1)	1.112 (3)
3rd	1.892 (89.8)	2.011 (1.3)	2.017 (1.8)
4th	2.776 (285.7)	2.764 (87.26)	2.767 (66)

Table 3. Phonon Mode Frequencies in THz (Lifetimes in ps) for (16,16) Cnt

	Empty	Filled	With flow
1st	0.204 (297.6)	0.243 (7.0)	0.235 (4.64)
2nd	0.575 (92.3)	0.637 (2.8)	0.658 (2)
3rd	1.095 (373.1)	1.107 (2.0)	1.125 (2.5)
4th	1.756 (87.7)	2.066 (85.7)	2.067 (74.9)

water flowing through the CNT. This leads to differences in the phonon scattering behavior. Tables 4.2 and 4.3 show the frequencies and mode lifetimes for (12, 12) and (16,16) CNTs respectively. The phonon lifetimes are not significantly different for water-filled CNT compared to CNT with flow. This can be attributed to the difference in the physical behavior of confined fluid as the tube diameter changes. In the case of small CNTs (diameter < 1 nm) we have entropy stabilised, vapor-like phase of water, for medium-sized (diameter between 1 nm and 1.2 nm) we have enthalpy stabilised icelike phase of water and bulk like liquid for tubes larger than 1.4 nm [19]. This indicates that in smaller CNTs the rotational entropy of water molecules is very high. Under flow conditions, the pressure drop applied influences the rotational motion of the molecules leading to changes in the interaction between the CNT and water molecules. This causes the observed variation in phonon transport for smaller diameter CNTs. But in the case of larger diamter CNTs the bulk like motion dominates. Due to the presence of hydrogen bonding network similar to bulk water in such tubes the fluid-wall interaction is comparitively reduced and application of pressure drop does not influence the fluid-wall interaction further. Hence, significant variation is absent between both flilled and liquid flow cases in larger nanotubes.

5. CONCLUSIONS

In the present work, phonon mode lifetimes of CNTs of different diameters in 3 different cases - i) empty, ii) filled with water, and iii) water flowing through - were studied by postprocessing the trajectory output of MD. The results indicate that flow of water inside CNT affects its phonon modes and thus its thermal conductivity in the case of (8, 8) CNT. But, the flow does not seem to modify significantly the phonon mode lifetimes of (12, 12) and (16, 16) CNT. These variations in the thermal transport properties of CNT was explained using the changes occuring in the physical behavior of the confined fluid as the tube diameter changes. Future works can investigate the effect of different flow velocities and even for different molecules on the phonon mode lifetimes of CNTs.

REFERENCES

[1] Moore, G., *Cramming more components onto integrated circuits*. Electronics Magazine, 1965, 38(8).

[2] Pradeep, T., *NANO: The Essentials-Understanding Nanoscience and Nanotechnology*, Tata McGraw-Hill, 1965, New Delhi.

[3] Sobhan, C. B., and Peterson, G. P., *Microscale and Nanoscale Heat Transfer: Fundamentals and Engineering Applications*, CRC Press, 2008, New York.

[4] Cahill, D. G., Ford, W. K., Goodson, K. E., Mahan, G. D., Majumdar, A., Maris, H. J., Merlin, R., and Phillpot, S. R., *Nanoscale thermal transport*, Journal of Applied Physics, 2003, 93, p. 793.

[5] Pop, E., and Goodson, K. E., *Thermal phenomena in nanoscale transistors*, ASME Journal of Electronic Packaging, 2006, 128, p. 102.

[6] Cahill, D. G., Goodson, K. E., and Majumdar, A., *Thermometry and thermal transport in micro/nanoscale solid-state devices and structures*, ASME Journal of Heat Transfer, 2002, 124, p. 223.

[7] Baillis, D., and Randrianalisoa, J., *Prediction of thermal conductivity of nanostructures: Influence of phonon dispersion approximation*, International Journal of Heat and Mass Transfer, 2009, 52 , p. 2516.

[8] Chung, J. D., McGaughey, A. J. H., and Kaviany, M., *Role of phonon dispersion in lattice thermal conductivity modeling,* Journal of Heat Transfer, 2004, 126 , p. 376.

[9] Srivastava, G. P., *The Physics of Phonons*, Adam Hilger, 1990, Bristol.

[10] Dove, M. T., *Introduction to Lattice Dynamics*, Cambridge University Press, 1993, Cambridge.

[11] Haile, J. M., *Molecular dynamics simulation. Elementary methods*, John Wiley & Sons, 1992, New York.

[12] Sadus, R. J., *Molecular simulation of fluids- Theory, Algorithms and Object-orientation*, Elsevier Science B V, 2002, Amsterdam.

[13] Thomas, J. A., Turney, J. E., Iutzi, R. M., Amon, C. H., and McGaughey, A. J. H., *Predicting phonon dispersion relations and lifetimes from the spectral energy density*, Phys. Rev. B, 2010, 81, p. 081411.

[14] Plimpton, S., *Fast parallel algorithms for short range molecular dynamics*, J Comp Phys, 1995, 117, p. 1.

[15] Brenner, D. W., Shenderova, O. A., Harrison, J. A., Stuart, S. J., Ni, B., and Sinnot, S. B., *A second-generation reactive empirical bond order (rebo) potential energy expression for hydrocarbons*, J. Phys: Condensed Matter, 2002, 14 , p. 783.

[16] Jorgensen, W. L., Chandrasekhar, J., Madura, J. D., Impey, R. W., and Klein, M. L., *Comparison of simple potential functions for simulating liquid water*, J. Chem. Phys., 1983, 729 , p. 926.

[17] Hummer, G., Rasaiah, J. C., and Noworyta, J. P., *Water conduction through the hydrophobic channel of a carbon nanotube*, Nature, 2001, 414, p. 188.

[18] Wojdyr, M., *Fityk: A general purpose peak-fitting program*, J. Applied Crystallography, 2010, 43, p. 1126.

[19] Pascal, T. A., Goddard,W. A., and Jung, Y., *Entropy and the driving force for the filling of cabon nanotubes with water*, PNAS, 2011, 108, p. 11794.