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Thermal conductivity for single-walled carbon nanotubes from Einstein relation in molecular dynamics

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ABSTRACT

Equilibrium molecular dynamics based Einstein relation with an appropriate definition for integrated heat current (i.e., with modified energy moment) are combined to quantify the thermal conductivity of individual single-walled carbon nanotubes, armchair, zigzag and chiral tubes. The thermal conductivity has been investigated as a function of three parameters, tube radius, length and chirality at and near room temperature with Brenner potential model. Thermal conductivity is found to have unusually high value and varies with radius, length and chirality of tubes. Also the thermal conductivity at temperature range from 50 to 100 K is found to have a maximum value. For 12.1 nm tube length, the thermal conductivity has converging trend which its value dependents on the tube radius and chirality. Tubes with large radius have lower values of thermal conductivity. Furthermore, the results show that armchair tubes have large values of the thermal conductivity comparing with zigzag and chiral tubes. It seems possible to uncover carbon nanotubes thermal properties based on measurements having heat dependence by adding another methods for calculations.

1. Introduction

The study of the heat conduction in single-walled carbon nanotubes (SWNTs) is very important. The unique physical properties and potential applications of carbon nanotubes (CNTs) have been well documented since their discovery, using both theory and experiment [1–6]. The electronic properties of singled-walled carbon nanotubes (SWNT) are largely dependent on the atomic structures of individual CNTs, which can be accurately defined using the tube diameter $d=\frac{a}{\pi}\sqrt{n^2+nm+m^2}$ and helical angle u $\theta=\tan^{-1}(\frac{\sqrt{3}m}{2n+m})$ [7]. The indices (n,m) of single-walled carbon nanotubes are crucially important for the electronic properties of the nanotubes. Tubes for which $n-m=3i$, with i an integer, are metallic; all other are semiconductors. Both the semiconductors and metallic types of nanotubes may be of use for nanoscale electronic devices. CNTs have bright prospects for applications: they can be used to fabricate field emission devices, tips for scanning probe microscopy instruments, and constituents of nanoelectronics devices [8–11]. The thermal properties of CNTs, such as thermal conductivity, have been proposed as attractive for thermal transport management in ultra large-integration chips due to high heat flow along the axis of CNTs [12–15]. This new class of one dimensional carbon could have a thermal conductivity equal to or greater than that of diamond and graphite [16]. Berber et al. [17] predicted CNTs to have an unusually high thermal conductivity associated with a large phonon mean free path by virtue of the molecular dynamics simulations.

There are mainly two approaches to study theoretically the thermal conduction phenomena of nanoscale materials: first approach is a macroscopic method using continuum models and kinetic theories, such as Boltzmann transport equation [18,19]. A second approach is a fundamental microscopic method based on the first principles atomistic simulations or quantum mechanics models. This approach is particularly useful for nanoscale devices where the experimental determination of the thermal conductivity is quite challenging. In this approach, various methods are proposed to model the physical system and calculate the thermal conductivity. These methods include equilibrium and no equilibrium molecular dynamics (MD) simulation. These methods study the physical system from scratch and make little empirical assumptions.

Two main components are contributed in the thermal conductivity: (a) an electronic component and (b) a lattice component. In the present paper, only the lattice contribution to thermal conductivity of carbon nanotubes is considered using atomistic simulations. The electronic contribution to thermal conductivity is very small and can be neglected in materials with relatively large band gaps. As far as the carbon nanotubes are concerned, the size of their band gap is found to be dependent on their chirality (screw symmetry) as well as on their diameter and length. Many

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theoretical studies were done for thermal conductivity of carbon nanotubes based on Green–Kubo expression [19] that relates this quantity to the integral over time t of the heat flux autocorrelation function [17,20]. The results were an unusually high thermal conductivity for isolated (10,10) nanotubes at room temperature and at $T=100$ K the the thermal conductivity has a maximum value [17]. The effect of the chirality, radius and length of carbon nanotubes can also affect the lattice contribution to the thermal conductivity and actually there are a lot of theoretical and experimental studies focused on thermal conductivity of SWNTs [21–27]. The thermal conductivity for an isolated SWNT is not a well defined quantity, since the cross section of the heat conduction can be chosen in various ways. In the present work, we consider tube as a solid cylinder with circle cross section area equal to $\pi d^2/4$. Of course, the values of the thermal conductivity change with consider a hollow cylinder with cross section area equal to $do/2$, where δ is the thickness of the wall equal to 0.34 nm. But still the behavior of the thermal conductivity of SWNTs does not depend on value of cross section area. Therefore, there are different values of thermal conductivity with different definitions of the cross section area. Our main goal of this study is how the thermal conductivity varies with tube parameters, radius, length and the chirality, as well as to obtain its value. Three types of SWNTs, armchair, zigzag and chiral tubes are investigated over a temperature range 50–400 K.

For these purposes, we apply the Einstein relation with energy moment formulation suggested by Kinaki et al. [28]. This method was also tested by Kinaki et al. [28] and they found that it produced a corrected thermal conductivity and overcomes some of the difficulties encountered when they calculated heat current for solid argon and silicon. Model potential is requires in our calculations and we are select the Brenner potential.

2. Computation of thermal conductivity using MD

In MD simulation, the classical position and momentum space trajectory of a system of particles are determined using interatomic forces (which are calculated from an appropriate potential-energy function), Newton's second law, equations of motion with the velocity Verlet algorithm are used to calculate the new positions and velocity and then the force on the atoms. The net flow of heat in such a system, given by the heat current vector **J** that indicates the magnitude and direction of the flow of heat in a system, fluctuates about zero at equilibrium. In an equilibrium system and in the Green–Kubo method, the thermal conductivity is related to how long it takes for these fluctuations to dissipate, and is given as [29]

$$\lambda = \frac{V}{K_B T^2}\int_0^{\infty} \langle J_f(t)\, J_f(0)\rangle dt \tag{1}$$

where K_B is the Boltzmann constant, V is the volume of the simulation cell, and $\langle J_f(t)J_f(0)\rangle$ is the heat flux autocorrelation function (HFACF). The heat flux for many-body potential is given by [29]

$$J_f(t) = \frac{1}{V}\frac{d}{dt}\sum_i r_i(t)e_i(t) = \frac{1}{V}\Big(\sum_i v_i(t)e_i(t) + \frac{1}{2}\sum_i\sum_j r_{ij}(f_{ij}^i v_i),\Big) \tag{2}$$

where e_i, $r_i(t)$ and $r_{ij}(t)$ are total energy, time-dependent coordinate of atom i and the nearest distance, respectively, and f_{ij} the interaction force on i atom due to j atom. The first term in Eq. (2) corresponds to the contributions of convection and the second term corresponds to conduction. In MD simulations, the total potential energy can be divided among atoms: the site energy $e_i(t)$ can be taken to be

$$e_i = \frac{1}{2}m_i v_i^2 + \frac{1}{2}\sum_j u(r_{ij}). \tag{3}$$

In the above equation, $u(r_{ij})$ is in fact a many-body potential [30,31]. First and second terms are the total kinetic and potential energy of atom i. It has been shown that the thermal conductivity of a crystal with a monatomic unit cell can be decomposed into contributions from short and long scale interactions for acoustic phonons by fitting the HFACF to a function of the form [15,32]:

$$\langle J_f(t)J_f(0)\rangle \equiv A_s\exp(-t/\tau_s) + A_l\exp(-t/\tau_l) \tag{4}$$

The A terms are constants, and the τ terms are time constants. Using Eqs.(1) and (4), we have

$$\lambda = \frac{V}{K_B T^2}(A_s\tau_s + A_l\tau_l) \tag{5}$$

The short-range component is associated with phonons with a mean free path less of their wavelength while the long-range component describes phonon with longer mean free paths. The short-range component and its associated time constant are independent of the temperature while the long-range component is temperature dependent and it accounts for majority of thermal conductivity.

The energy moment $R(t)$ and heat current, $J(t)$, which appears in Eq. (2) are

$$R(t) = \sum_i^N e_i(t)r_i(t) \tag{6}$$

The heat current, $J(t)$, is the time derivative of $R(t)$

$$J(t) = \frac{dR(t)}{dt}. \tag{7}$$

The thermal conductivity via Einstein relation as related to doubly integrated form of the expression is given

$$\lambda = \frac{1}{VK_B T^2}\lim_{t\to\infty}\frac{1}{t^2}[\langle R(t) - R(0)\rangle]^2 \tag{8}$$

Kinaci et al. [28] proposed an expression for energy moment, $R(t)$, and they separated it into potential R_p and kinetic R_k contributions. The modified form for the potential energy portion of R, R_p, is [28]

$$R_p = \sum_{i,j>i}\frac{u_{ij}}{2}(r_i + r_j) \tag{9}$$

The transfer of kinetic energy from atom i to all atoms that interact with it is mediated by power term $\vec{f}\,\bar{v}$. The kinetic portion then can be written as [28]

$$R_k = \sum_{i,j>i}(r_i\int_0^t f_{ij}^i v_i dt + \int_0^t f_{ij}^j v_j dt) \tag{10}$$

where f_{ij}^i represents the force on atom i due to j.

The kinetic part does not depend explicitly on the potential form and by simply rearranging the summation as [28]:

$$R_k = \sum_l r_l\int_0^t f_l v_l dt \tag{11}$$

where the summation over atoms that make up n-body interaction groups.

They found that this new formula of $R(t)$ gives a proper thermal conductivity and can be reduced numerically to give the exact value of $J(t)$.

The empirical interatomic interaction used in our calculation is Brenner-type of the bond order dependent potential [30–33]. The Brenner potential is widely used in modeling carbon based system such as diamond, graphite sheet, fullerenes and carbon nanotubes.