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The effects of computational time parameter in the thermal conductivity of single-walled carbon nanotubes by molecular dynamics simulation

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ABSTRACT

In this work was investigated the thermal conductivity λ of single-walled carbon nanotube (SWCNT), using the different empirical potentials: Tersoff, REBO and AIREBO. The Green-Kubo's equation was used to calculate λ through the Equilibrium Molecular Dynamics (EMD). The results were compared with SWCNT thermal conductivity reported in the literature using different methods and potentials. Through this investigation was possible to elucidate one possible reason for the huge difference of results for the SWCNT thermal conductivity reported in the literature. It has been shown that, for all the empirical potentials tested, the λ convergence was achieved when an appropriate choice of equilibrium time and simulation time was made. No significant change in λ was observed when different empirical potentials were used with adequate computational time parameters.

1. Introduction

Due to the extraordinary thermal properties of the carbon nanotubes (CNTs) [1,2] an intense investigation of this material has been occurring since its discovery by Iijima [3]. Looking for an increasing understanding of CNT thermal transport mechanisms, several researchers have used molecular dynamics (MD) techniques to collect information about the thermal properties of these materials [4–6]. Two approaches have been used for the simulations: the Equilibrium Molecular Dynamics (EMD), based on the Green-Kubo relations [6,7], or the reverse Nonequilibrium Molecular Dynamics (NEMD) [8], based on the Fourier law.

Using the EMD method, it is possible to find a great difference in the nanotube thermal conductivity values, for the longitudinal direction, when different empirical potentials were used [9–11]. To clarify, the Tersoff potential was created in 1988 by Tersoff [12,13]. This empirical interatomic potential is used to calculate the structural and energetic properties of covalent carbon bonds. The Brenner potential was developed by Brenner in 1990 [14]. It was modified from the Tersoff potential with the objective of studying different carbon structures, such as diamonds grown by chemical vapor deposition and carbon nanotubes [15]. It was named Reactive Empirical Bond-order Model (REBO). In 2000, Stuart et al. [16], developed the Adaptive Intermolecular Reactive Empirical Bond-order potential (AIREBO), by modifying the Brenner potential. For this, a description of the torsional interactions for rotation and an adapted treatment of the van der Waals interactions was added that was not present in the formalism of the Brenner potential. It consists of three terms:

$$E = \frac{1}{2}\sum_{I}\sum_{j\neq i}\left[E_{ij}^{REBO} + E_{ij}^{LJ} + \sum_{k\neq i,j}\sum_{l\neq i,j,k} E_{kijl}^{TORSION}\right] \quad (1)$$

where E_{ij}^{REBO} is the REBO potential, E_{ij}^{LJ} is the long-range interactions term and $E_{kijl}^{TORSION}$ represents dihedral angle preferences and was not considered in this work.

In this work, the thermal conductivity of SWNT was investigated using the molecular dynamics technique, using the EMD method. The Tersoff, REBO and AIREBO interatomic potentials were used. A systematic study of the time intervals used as parameters of computer simulation was done, which were: equilibrium time (t_{equil}) and simulation time (t_{simul}). From this study, we investigated the range in which these time parameters do not significantly affect the simulated values of the thermal conductivity for different potentials.

2. Computational method

It was used the single-walled carbon nanotube (10, 10), with 440 atoms, with the height and width of 1.5 nm (Fig. 1a) and longitudinal length of 2.7 nm (Fig. 1b), inserted inside a box of volume equal to 6.075 nm^3, as described in Fig. 1a. The potentials used were Tersoff, REBO and AIREBO, under periodic boundary conditions and implemented in the Large-scale Atomic/Molecular Massively Parallel

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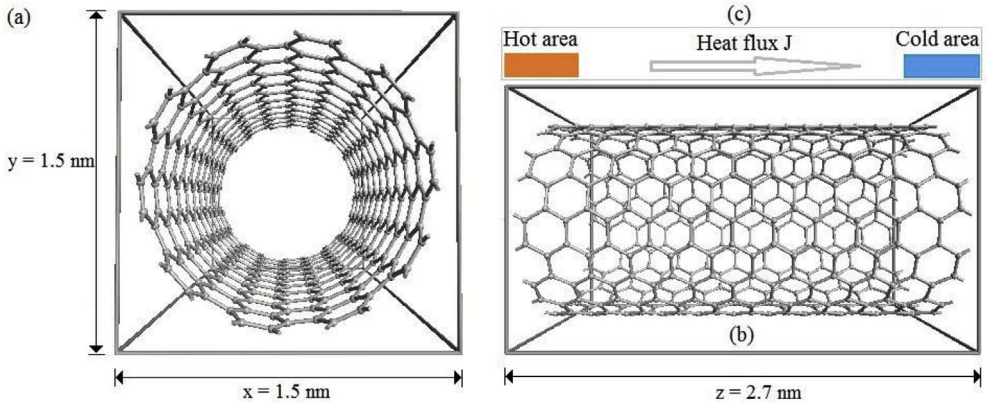

Fig. 1. Schematics of SWNT nanotube (a) top and (b) side faces. (c) Model of the heat flux direction used in the EMD simulation.

Simulation (LAMMPS) molecular dynamics program [17]. LAMMPS does not have a graphical user interface (GUI), so Nanolab virtual was used as GUI [18]. All simulations were performed using the EMD method, with heat flow according to the model of Fig. 1c, and fixed step time t_{step} = 0.4 fs The use of a step time of 0.4 fs allows to equilibrate and relax the temperature more slowly avoiding abrupt temperature fluctuations throughout the simulation and maintaining the equilibrium of the system during the simulation. The simulation was performed varying the equilibrium time of the system from 4 ps to 2000 ps, using canonical ensemble (*NVT* ensemble), and after this process the simulation time of the thermal conductivity was set to t_{simul} = 1600 ps for all other simulations. In this study, the focus was the determination of the thermal conductivity λ in the direction of the tube length (axial z-direction). The thermal conductivity λ_z is represented by

$$\lambda_Z = \frac{1}{k_B T^2 V}\int_0^\infty J_z(t)\cdot J_Z(0)dt \tag{2}$$

where k_B is the Boltzmann constant and V and T are the system's volume and absolute temperature, respectively. V is defined the volume of the simulation box of the SWNT, Fig. 1b.

The heat flux $J_z(t)$ is in the z-direction and can be obtained by

$$J_z(t) = \sum_i v_{z,i}E_i + \sum_i z_i\frac{dE_i}{dt} \tag{3}$$

where z, v_z and E are the atomic coordinate, velocity and total energy, respectively.

3. Results and discussion

The thermal conductivity of the SWNT (10, 10) was investigated for the Tersoff and REBO potentials, as a function of equilibrium time, t_{equil}, as shown in Fig. 2. The equilibrium time ranged from 4 ps to 2000 ps, keeping the t_{simul} parameter constant at 1600 ps. The mean value of the simulated thermal conductivity of the SWNT was obtained from Fig. 2, considering the last three values of the equilibrium time tested. The values converged to 140 W/m·K for the Tersoff potential and 141 W/m·K for the REBO potential. At the equilibrium time of 4 ps, the simulation temperature was not constant for the Tersoff potential and the thermal conductivity presented a value that reached 316 W/m·K.

Based on Fig. 2, it can be concluded that using a suitable simulation time, the equilibrium time plays a supporting role in the thermal conductivity results. For the REBO potential, the thermal conductivity remained practically constant for the range of equilibrium times tested, proving to be a very stable potential for simulations of the SWNT thermal conductivity. For the Tersoff potential an equilibrium time greater than 1200 ps is necessary to obtain a more reliable result. For the Tersoff potential, there was a large oscillation of the thermal conductivity up to 1200 ps. Only for an equilibrium time greater than

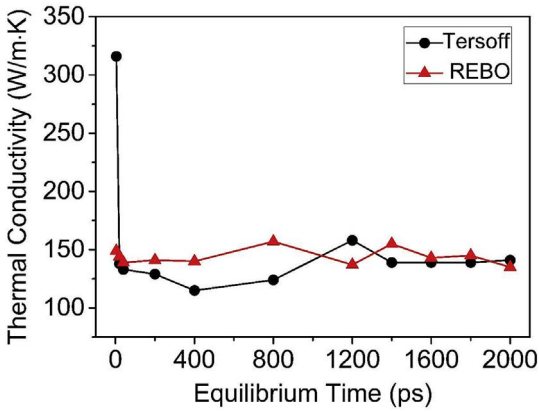

Fig. 2. Dependence of the simulated thermal conductivity as a function of the equilibrium time for the Tersoff and REBO interatomic potentials. t_{simul} = 1600 ps.

1200 ps a constant value seems to have been obtained.

The behavior of the thermal conductivity as a function of the simulation time, t_{simul}, was investigated and the results obtained from the simulation are presented in Fig. 3. A system equilibrium time of 1600 ps was used for the two potentials tested (Fig. 3a). It was observed that only with simulation time intervals above 600 ps the thermal conductivity was stable for both potential. For small values of the equilibrium time, according to Fig. 3b, there is a fluctuation in the value obtained for the thermal conductivity during the simulation. In Fig. 3c is presented a comparison of the simulation made with the AIREBO potential with the other potentials. It was observed that the use of the AIREBO potential in the simulation led to the achievement of a thermal conductivity of 152 W/m·K, a value close to those found for the Tersoff and REBO.

In order to allow a better comparison of the results obtained for the simulated SWNT thermal conductivity, we present in Table 1, the simulated λ value for four pair of the t_{equil} and t_{simul} parameter. These values were obtained from Figs. 2 and 3. As can be observed in Table 1, when the simulation time is 40 ps, the simulations result in very different values for the two potentials tested, regardless of the t_{equil} value. This would lead to the conclusion that the value obtained for the thermal conductivity could depend on the potential used. Meanwhile, when t_{simul} is increased to 1600 ps, the λ values obtained using REBO or Tersoff potentials converge to a very close value. For the t_{equil} parameter, the dependency with the t_{simul} parameter must be considered. As discussed earlier, for lower equilibrium times it is possible to observe an oscillation of the λ simulated values, even though t_{simul} is as high as 1600 ps (Tersoff Fig. 2). In view of these discussions, it can be said that an appropriate choice of the t_{simul} and t_{equil} parameters would allow to obtain very close simulated values of thermal conductivity, regardless