# Thermal Conductivity of Isolated and Interacting Carbon Nanotubes: Comparing Results from Molecular Dynamics and the Boltzmann Transport Equation

Davide Donadio* and Giulia Galli

*Department of Chemistry, University of California at Davis, One Shields Avenue, Davis, California 95616, USA*

(Received 12 September 2007; published 20 December 2007)

We investigate the thermal conductivity of single-wall carbon nanotubes (SWCNT) either isolated or in contact with external media by using equilibrium molecular dynamics and the Boltzmann transport equation. We show that, contrary to existing controversies, both methods yield a finite value of the thermal conductivity for infinitely long tubes, as opposed to the case of 1D, momentum-conserving systems. Acoustic and flexure modes with mean free paths of the order of a few microns are identified as major contributors to the high value of SWCNT conductivity. We also find that the interaction with an external medium may substantially decrease the lifetime of the low-frequency vibrations, reducing the thermal conductivity by up to 2 orders of magnitude.

DOI: 10.1103/PhysRevLett.99.255502 PACS numbers: 61.46.Fg, 63.22.+m, 66.70.+f, 81.07.De

Thermal energy transport in quasi-one-dimensional materials has recently attracted widespread attention [1], as nanotubes and nanowires display transport properties very different from their bulk counterparts, which make them appealing for several applications ranging from thermoelectric power generation, where low thermal conductivity is desirable, to heat dissipation, requiring high thermal conductivity. Single-wall carbon nanotubes (SWCNT) are known to have an unusually high thermal conductivity ($k$) [2–4], partly related to the peculiar propagation of phonons in a low dimensional medium [5]. Important theoretical efforts to understand heat conduction in nanotubes have recently been reported, either by using the Boltzmann transport equation (BTE) [5,6] or by utilizing molecular dynamics (MD) techniques [7–11]. However, these investigations have often provided contradictory results regarding the basic heat conduction mechanism in CNTs and the values of ballistic lengths, as well as for the importance of quantum effects and the dependence of $k$ on the length of the tube. For example, while with the BTE approach Mingo and Broido [6] predicted $k$ of an infinitely long SWCNT to be finite, very recent MD simulations [9,10] point at a divergence of $k$ with length similar to 1D momentum-conserving systems [12]. In addition, measurements are most often carried out either for tubes interacting with each other in a bundle or for tubes in contact with external viscous media or substrates [2,3]; in most instances calculations have instead been carried out for isolated systems, except for a very recent study [13].

In this Letter, we resolve the existing controversy on calculations of the thermal conductivity of SWCNTs, and we show that MD yields results in excellent agreement with the BTE approach [6] for isolated tubes. In spite of their low dimensionality, CNTs cannot be treated as ideal, momentum-conserving, 1D systems. Our calculations of phonon density of states and lifetimes show that a large number of vibrational modes contribute to $k$; however, acoustic and flexure modes, with mean free paths of a few $\mu$m, represent the major contribution. The interaction with an external medium may reduce the lifetime of these modes by up to 2 orders of magnitude and, correspondingly, the value of the thermal conductivity.

We first discuss the case of isolated nanotubes. We employed equilibrium MD simulations to compute the thermal conductivity and the vibrational properties of a representative SWCNT in vacuum and in a viscous medium [14]. $k$ was computed directly using the Green-Kubo method [15] and its value compared to that obtained from the BTE, based on the phonon dispersion and lifetimes computed at finite temperature.

Classical MD simulations of a periodically replicated SWCNT have been performed using the Tersoff bond order potential [16]. The nanotubes have been thermalized to 300 K for 200 ps [17] and the length of the cell was optimized so as to yield zero axial stress. The heat flux along the axis of the tube was then recorded every 2 fs in eight microcanonical runs up to 80 ns long, with statistically independent initial conditions. The thermal conductivity was obtained from the time integral of the autocorrelation function of the heat flux [18]. It is noteworthy that not only very long simulation times are necessary to obtain converged values of $k$, but it is also important to average the results over statistically independent runs due to the poor ergodicity of the system. The use of nonequilibrium MD (NEMD) techniques would in principle allow for faster convergence [19]; however, their application has several drawbacks. In general, finite size and boundary effects are serious concerns in nonhomogeneous NEMD simulations; in addition, 1D systems do not obey Fourier's law [20]; thus, $k$ may not be calculated directly from the temperature gradient, though it is still a well-defined quantity in terms of heat currents [12,20]. As for homogeneous NEMD methods, the formation of solitons makes these techniques inefficient for the calculation of $k$

 

in 1D and quasi-1D systems [21]. Although heat transport in CNTs turned out to be different from that of ideal 1D models, the use of NEMD simulations does not appear to be appropriate, as it would add technical uncertainties to already existing theoretical controversies [22].

We modeled an infinitely long SWCNT by using periodically repeated supercells; however, supercells of different lengths ($L$) were considered, with $L$ ranging from 0.5 to 200 nm, to investigate the convergence properties of $k$ as a function of phonon wavelength and lifetime sampling. In qualitative agreement with the BTE prediction, our MD results converge to $k \sim 7000$ W/m K for $L > 20$ nm (Fig. 1). This value is larger than the one reported in Ref. [6] where a different force field was adopted to model phonon dispersion curves and density of states, and the calculation of the lifetimes contained approximations; we expect the Tersoff potential adopted here to overestimate the thermal conductivity in carbon systems, although without affecting the general picture of heat transport. In addition, as discussed below, the use of classical (in our MD) and quantum phonon distributions (in Ref. [6]) may be responsible for the present, quantitative discrepancy with Ref. [6]. Our simulations show that the transport properties of SWCNTs differ significantly from those of momentum-conserving 1D models, where $k$ diverges as $k(l) = l^{\alpha}$, with $l$ being the length of the 1D chain [12,23]. We note that our findings disagree with those of previous MD simulations [9], which may have been affected by ergodicity issues and by a poor sampling of the phase space. In our simulation, as the tube lengths are increased, several flexure modes in the low-frequency region of the power spectrum appear. If these modes and their lifetimes are not properly described, converged values of the conductivity are not attained.

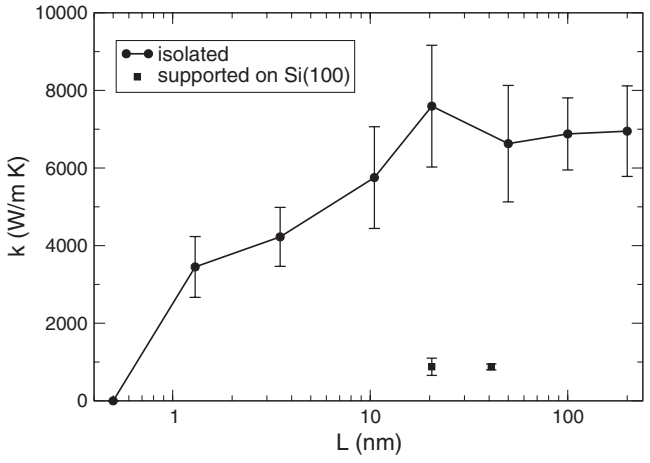


FIG. 1. Thermal conductivity of a periodically replicated (10, 0) SWCNT as a function of the supercell length ($L$). Convergence is achieved for $L > 20$ nm; however, a rather large uncertainty on $k$ remains, due to the strongly harmonic character of the phonons of the nanotube. The two square dots indicate the values of $k$ for a (10, 0) SWCNT deposited on a Si(100) $2 \times 1$ substrate.

In order to gain a better understanding of the contributions of various vibrational modes to the value of the thermal conductivity, we also computed $k$ by using the BTE approach. First, we tested the ability of the chosen classical model to reproduce the vibrational properties of SWCNT, and, in particular, the quadratic dispersion relation exhibited by "flexure modes." The inset of Fig. 2 shows the dispersion curves computed both at zero temperature, with the frozen phonon method, and at room temperature, in the low-frequency region. The dispersion curves display qualitatively good agreement with density functional calculations [24] and with lattice dynamics calculations with enforced symmetry rules [25]. The correct degeneracy and dispersion relation ($\nu \propto q^2$) for the long-wavelength flexure modes are reproduced, and the effect of finite temperature is negligible.

The BTE approach was previously compared with MD simulations for bulk models, such as a Lennard-Jones fcc crystal [26,27] and bulk silicon [28], but no such comparison is available for nanostructures. In the single mode relaxation time (SMRT) approximation [27] the BTE approach yields a simple expression where the contribution to $k$ of each phonon mode $i$ with momentum $\mathbf{q}$ is [28]

$$k_i(\mathbf{q}) = C_i(\mathbf{q}) v_i^2(\mathbf{q}) \tau_i^{\mathrm{ph}}(\mathbf{q}), \tag{1}$$

where $v_i(\mathbf{q})$ and $\tau_i^{\mathrm{ph}}(\mathbf{q})$ are the group velocities and the lifetimes, respectively. $C_i(\mathbf{q})$ is the specific heat per unit volume of each vibrational state. Using the Bose-Einstein statistics $C_i(\mathbf{q})$ is

$$C_i^{\mathrm{QM}}(\mathbf{q}) = \frac{1}{V} k_b x^2 \frac{e^x}{(e^x - 1)^2}, \tag{2}$$

with $x = \hbar\omega_i(\mathbf{q})/k_b T$, and $\omega_i(\mathbf{q})$ being the phonon frequency; $k_b$ is the Boltzmann constant and $T$ the tempera-

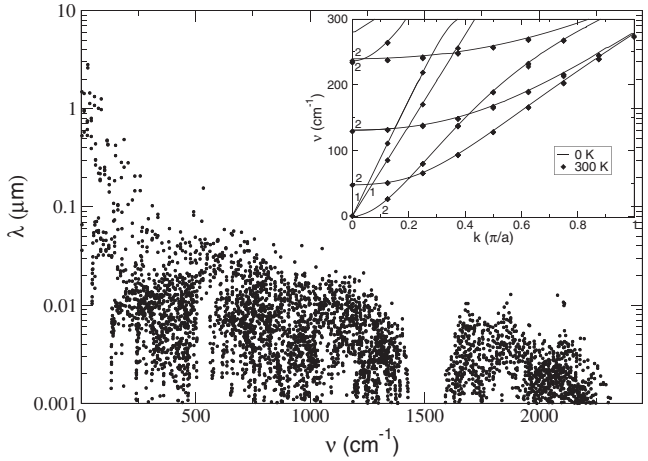


FIG. 2. Phonon mean free path computed from the correlation function of the eigenmodes of a (10, 0) SWCNT in a 20 nm long supercell, and dispersion curves at zero (lines) and room temperature (dots) of the low-frequency modes (inset). The numbers on the dispersion curves indicate their degeneracy.

ture. To compare directly to the classical MD results, we will also consider the classical specific heat of the phonons, $C_i^{\mathrm{CL}}(\mathbf{q}) = k_b$. The total thermal conductivity is then $k = \sum_i \sum_q k_i(\mathbf{q})$, where, if a supercell large enough is considered, the phonon dispersion can be neglected and the sum reduced to the $\Gamma$ point only. The group velocities have been obtained by finite differences from the phonon dispersion curves around the $\Gamma$ point, while the lifetime $\tau_i^{\mathrm{ph}}$ of every mode $i$ was obtained from the integral of the autocorrelation function of eigenmode energies, computed over a microcanonical MD trajectory 2.5 ns long (see Refs. [26,27] for details). Lifetimes were computed for 20 nm supercells (1880 atoms), so as to ensure converged results. Relaxation times are determined by anharmonic interactions (scattering) between phonon modes. At variance with the BTE approach used in Ref. [6], the method used here does not involve approximations or assumptions on the order of the anharmonicity to be considered. In the SWCNT the low-frequency modes exhibit very weak anharmonicity; thus, phonon modes with very long (up to 200 ps) and relatively long lifetimes ($\tau^{\mathrm{ph}} \sim 10$ ps) are found for frequencies up to 700 $\mathrm{cm}^{-1}$. From the computed lifetimes, we obtain phonon propagation lengths $\lambda_i = v_i \tau_i^{\mathrm{ph}}$, from which we can estimate the ballistic thermal length: this is few $\mu$m [5]. This result is consistent with experiments that found ballistic heat transfer in a 2.76 $\mu$m long CNT [3]. The phonon propagation lengths computed by MD are displayed in Fig. 2, which shows that several low-frequency modes have $\lambda \sim 1$ $\mu$m.

The contribution of the different phonon modes to $k$ can be appreciated from Fig. 3, where $\sum_i k_i$ is represented; $k_i$ is from Eq. (1), using either the classical or the quantum phonon specific heat. The low-frequency modes ($\nu <$ 700 $\mathrm{cm}^{-1}$) account for most of the thermal conductivity. The classical and quantum contributions to $k$ are substantially different for $\nu < 700$ $\mathrm{cm}^{-1}$, and the contribution of the phonon modes with frequency larger than 1200 $\mathrm{cm}^{-1}$ becomes negligible when using the Bose-Einstein distribution. The value of $k$ obtained using $C^{\mathrm{Cl}}$ (6660 W/m K) is in very good agreement with the one computed directly from the MD simulations. It differs by $\sim$1300 W/m K, i.e., by more than 20% from the value obtained using the Bose-Einstein distribution. The quantum correction puts our results in better quantitative agreement with the calculations of Mingo and Broido [6].

We now turn to the case of SWCNT interacting with a viscous medium. To this aim, we model different viscosities by performing Langevin dynamics [29] with different values of the friction coefficient $\gamma$. In hydrodynamics $\gamma$ is related to the viscosity of a fluid $\eta$ and to an effective diameter of the particle $a$ by $\gamma = 6\pi\eta a/m$. Note that $\gamma$ can be expressed in terms of a relaxation time as $\gamma = \tau^{-1}$. In a microscopic picture, $\tau$ is related to the frequency of impacts between the particles and the viscous medium. In Fig. 4 the effect of different $\tau$ on the thermal conductivity

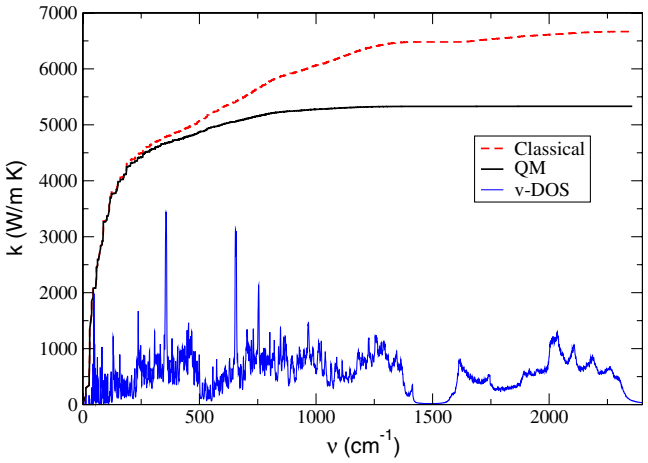


FIG. 3 (color online). Thermal conductivity ($k$) computed by the BTE [Eq. (1)] using the phonon group velocities and lifetime computed by MD. The value of $k$ is shown as a function of the phonon frequencies included in the sum of Eq. (1) (the spectrum is shown on the $x$ axis), when using quantum (Bose-Einstein) (solid/black line) and classical (dashed/red line) occupation. The BTE with classic occupation of the vibrational states yields $k$ well within the error bar of the corresponding equilibrium MD simulation (see Fig. 1).

of a (10, 0) SWCNT is shown. The SWCNT can be seen as made of spheres of diameter equal to the average bond distance $d = 1.4$ Å. Assuming that the particles of the medium cannot penetrate the nanotube, only about half the surface of every carbon atom is subject to collisions with the particles of the medium, then, to relate $\tau$ to $\eta$, we define $a = d/\sqrt{2} = 1$ Å. Within this assumption, the viscosity of air at room temperature and pressure corresponds to $\tau = 0.55$ ps and the one of acetone, a much less viscous liquid, corresponds to $\tau = 0.035$ ps. Langevin dynamics simulations have been performed for SWCNT in supercells

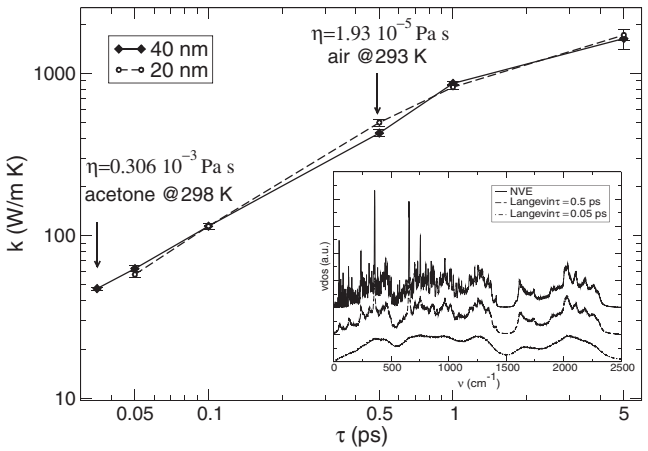


FIG. 4. Effect of the relaxation time $\tau$ of the Langevin thermostat on the thermal conductivity of a (10, 0) SWCNT and on its power spectrum (inset). The viscosity $\eta$ of two media (air and acetone) at the corresponding $\tau$ is shown (see text).

20 and 40 nm long, showing that $k$ is already well converged in the smaller cell. When short Langevin relaxation times, corresponding to the viscosity of liquids, are used, the thermal conductivity drops by 2 orders of magnitude, while a $\tau$ compatible with the viscosity of air at room conditions reduces $k$ by an order of magnitude. $k$ depends linearly on $\tau$, for $\tau$ smaller than 1 ps. To understand the effect of the Langevin viscosity on the vibrational properties of the SWCNT, we have computed the phonon lifetimes and the phonon density of state for different values of $\tau$ (inset of Fig. 4). The viscous drag smoothens the power spectrum of the isolated nanotube, without producing a shift of the frequencies and without changing the character of its normal modes. At 300 K the effect on the phonon lifetimes is instead more important; the long lifetime phonons of the isolated tube are reduced to values around that of the Langevin $\tau$. This explains the linear dependence of $k$ on $\tau$ up to a threshold value affecting only the propagation of the phonons with lifetimes longer than $\tau$.

We have also calculated the thermal conductivity of a SWCNT deposited on silicon: a more realistic case that may be of interest to nanoelectronic applications. The structure of nanotubes on such a surface has recently been investigated by first principle methods, and it was found that CNTs form a number of covalent bonds with the substrate that alter their electronic properties and may even induce a gap opening in metallic tubes [30]. Using the Tersoff potential [16] we modeled a (10, 0) SWCNT deposited on a Si(100) slab, 4 layers thick. The main axis of the SWCNT is in the (001) direction, and the atoms in the bottom layer of the silicon slab are frozen. Covalent bonds are formed between the SWCNT and the dimers of the reconstructed (100) Si surface. The thermalization and the production runs were performed in the same way as for the isolated nanotubes. At variance with the isolated tubes, no significant convergence problems were encountered. The interaction with the substrate substantially reduces the thermal conductivity to $k = 875 \pm 75$ W/m K. This is an upper-bound value, as it is computed using a classical phonon distribution.

In summary, we have studied heat transport in a SWCNT and compared results from equilibrium classical MD and from BTE-SMRT. Contrary to previous claims, we found that both approaches yield finite values for the conductivity of infinitely long SWCNT, and our results confirm the BTE calculations reported in [5,6]. MD results are in quantitative agreement with those of the BTE when a classical statistics is used, and differ by $\sim$20% from those obtained using the Bose-Einstein statistics at $T \simeq 300$ K. Our estimated ballistic length, of the order of a few microns, is consistent with recent experiments at room temperature [3]. $k$ is significantly reduced by the interaction with external media: up to 2 orders of magnitude for a SWCNT in a viscous liquid medium, and by about 1 order of magnitude when the SWCNT is deposited on silicon. These reductions account for the difference of about 1 order of magnitude between the measured $k$ of isolated SWCNTs [3] and of crystalline ropes of SWCNTs [4], and stem from the decrease of the lifetime of acoustic and flexure long-wavelength modes, which provide the largest contribution to the thermal conductivity of isolated nanotubes.

We gratefully acknowledge support by the DARPA-PROM program under Grant No. W911NF-06-1-0175 and J. Grossman for useful discussions.

*ddonadio@ucdavis.edu

[1] S. Volz, *Microscale and Nanoscale Heat Transfer*, Topics in Applied Physics (Springer, New York, 2007), Vol. 107.
[2] P. Kim *et al.*, Phys. Rev. Lett. **87**, 215502 (2001).
[3] C. Yu *et al.*, Nano Lett. **5**, 1842 (2005).
[4] J. Hone *et al.*, Phys. Rev. B **59**, R2514 (1999).
[5] N. Mingo and D. A. Broido, Phys. Rev. Lett. **95**, 096105 (2005).
[6] N. Mingo and D. A. Broido, Nano Lett. **5**, 1221 (2005).
[7] S. Berber *et al.*, Phys. Rev. Lett. **84**, 4613 (2000).
[8] J. Che *et al.*, Nanotechnology **11**, 65 (2000).
[9] Z. Yao *et al.*, Phys. Rev. B **71**, 085417 (2005).
[10] G. Zhang and B. Li, J. Chem. Phys. **123**, 114714 (2005).
[11] J. R. Lukes and H. Zhong, J. Heat Transfer **129**, 705 (2007).
[12] O. Narayan and S. Ramaswamy, Phys. Rev. Lett. **89**, 200601 (2002).
[13] P. A. Greaney and J. C. Grossman, Phys. Rev. Lett. **98**, 125503 (2007).
[14] We considered a (10, 0) CNT with a diameter of 1 nm to compare with existing results, e.g., Refs. [5,6].
[15] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, New York, 2002), 2nd ed.
[16] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).
[17] G. Bussi *et al.*, J. Chem. Phys. **126**, 014101 (2007).
[18] To compare directly to the results of Ref. [5], the section of the (10, 0) SWCNT has been defined as $s = 2\pi R\delta$ with $R = 4$ Å being the radius of the SWCNT and $\delta = 3.35$ Å the layers' separation in graphite.
[19] D. J. Evans and G. P. Morris, *Statistical Mechanics of Non-equilibrium Liquids* (Academic, New York, 1990).
[20] K. Aoki and D. Kusnezov, Phys. Rev. Lett. **86**, 4029 (2001).
[21] F. Zhang *et al.*, Phys. Rev. E **64**, 021102 (2001).
[22] Soliton formation was presumably not observed in Ref. [7], because of the small supercell size ($L = 25$ Å) and the short simulation times (4 ps).
[23] S. Lepri *et al.*, Phys. Rev. E **68**, 067102 (2003).
[24] O. Dubay and G. Kresse, Phys. Rev. B **67**, 035401 (2003).
[25] S, Phys. Rev. B **70**, 075405 (2004).
[26] A. J. C. Ladd *et al.*, Phys. Rev. B **34**, 5058 (1986).
[27] A. J. H. McGaughey and M. Kaviany, Phys. Rev. B **69**, 094303 (2004).
[28] P. Chantrenne *et al.*, J. Appl. Phys. **97**, 104318 (2005).
[29] G. Bussi and M. Parrinello, Phys. Rev. E **75**, 056707 (2007).
[30] S. Berber and A. Oshiyama, Phys. Rev. Lett. **96**, 105505 (2006).