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Molecular dynamics simulations of thermal conductivity of carbon nanotubes: Resolving the effects of computational parameters

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ABSTRACT

Predicting thermal conductivity, k, of carbon nanotubes (CNTs) has been the focus of many molecular dynamics (MD) simulation studies reported in the literature. The values of k obtained in these studies exhibit a large, up to an order of magnitude, variability that is commonly attributed to the variations in the computational setups adopted in different studies. The sensitivity of the computational results to the choice of individual parameters of the simulation setups, however, has not been systematically investigated and is often overlooked when the predicted values of k are compared across the literature. Here we present the results of several series of simulations specifically designed to evaluate the effects of common computational parameters of non-equilibrium MD (NEMD), such as the type of boundary conditions, size and location of heat bath regions, definition of the CNT length, and the choice of interatomic potential, on the computational predictions. The length dependence of thermal conductivity is found to exhibit a gradual transition from a strong increase of k with CNT length for nanotubes that are shorter than ~200 nm to a much weaker dependence for longer CNTs, reflecting the transition from ballistic to diffusive-ballistic heat transport regimes. The effect of increasing length of thermal bath regions is found to be nearly indistinguishable from the effect of increasing length of the unperturbed region between the bath regions, suggesting that the value of k is defined by the total length of the CNT (including the length of the heat bath regions) in NEMD simulations employing uni-directional heat flux. The choice of interatomic potential is shown to be responsible for an up to fourfold variability in predictions of k for otherwise identical simulation conditions. Overall, the results of this study help elucidate the cause of quantitative discrepancies across published data and provide recommendations on the choice of simulation setups that may improve the consistency of the computational predictions.

1. Introduction

The exceptionally high thermal conductivity of carbon nanotubes (CNTs) revealed in experiments [1–8] and computational studies [9–29] has put forward CNTs as promising structural elements for heat management applications and has motivated active exploration of the physical mechanisms responsible for the thermal transport in CNTs. Under conditions when systematic experimental investigation of the dependence of thermal conductivity on the geometrical and structural parameters of CNTs (length, diameter, chirality, curvature, presence of defects) and external conditions (temperature, thermal contact resistance, interactions with other CNTs and/or substrate) is hampered by technical challenges related to the small size of the individual nanotubes and their propensity to form bundles and aggregate into intertwined structures, atomistic molecular dynamics (MD) simulations present an attractive alternative. Indeed, atomistic simulations allow for complete control over the size and structure of the CNTs and have been used in investigations of the dependence of the thermal conductivity on CNT length [12–15,18,20–24,26,28–34], diameter [11–13,18,22–24,26–29,33,35], elastic deformation [25,36–38], buckling [39–41], as well as presence of isotope dopants [18,20,24,33], crystal defects [10,20,33], or chemisorbed molecules [14].

In spite of the ability of MD simulations to fully control the simulated environment and to provide detailed atomic-level information on the mechanisms responsible for the heat transfer in CNTs, the values of thermal conductivity, k, predicted in different MD simulations exhibit surprisingly large divergence even when the simulated system is nominally the same. For example, a sample of MD results obtained for single-walled CNTs of chirality (10,10) at ~300 K is listed in Table 1. The values of k exhibit variability by more than an order of magnitude, casting doubt on the ability

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Table 1
A sample of values of CNT thermal conductivity predicted in MD studies reported in the literature. All values are for (10,10) single-walled CNTs at ~300 K. The system length is defined as the total length of the computational system used in the simulations. The nomenclature for the names of the interatomic potentials is explained in the text.

Reference	k (W m^{-1} K^{-1})	System length (nm)	Potential	Method	Boundary conditions
Lukes and Zhong [21]	~20–160	5–40	Brenner-II + LJ	EMD	Periodic and non-periodic
Grujicic et al. [16]	~173–179	~2.5–40	AIREBO	EMD	Periodic
Pan [35]	243	~29.4	Brenner-II	NEMD	Periodic
Xu and Buehler [36]	301	49.26	AIREBO	NEMD	Periodic
Wei et al. [37]	302	49.26	AIREBO	NEMD	Periodic
Che et al. [10]	~240–305	~2.5–40	Brenner	EMD	Periodic
Padgett and Brenner [14]	~35–350	~10–310	Brenner-II	NEMD	Periodic
Thomas et al. [26]	~300–365	200–1000	Brenner-II	NEMD	Non-periodic
Maruyama [12]	~275–390	6–404	Brenner	NEMD	Non-periodic
Shiomi and Maruyama [23,42]	~130–475	~14–425	Simplified Brenner	NEMD	Non-periodic
Feng et al. [33]	~50–590	6.52–34.77	Brenner-II	NEMD	Non-periodic
Bi et al. [20]	~400–600	2.5–25	Tersoff	EMD	Periodic
Cao and Qu [28]	1580	4800	Optimized Tersoff	NEMD	Periodic
Ren et al. [25]	~1430	~60	AIREBO	NEMD	Non-periodic
Berber et al. [9]	~6600	~2.5	Tersoff	HNEMD	Periodic

of MD simulations to provide a reliable quantitative estimate of the thermal conductivity. It is important, therefore, to understand the reasons for the data variability across the published studies and, in particular, to evaluate the contributions of two fundamentally different factors: true variation of the intrinsic CNT conductivity due to the variation of length of the CNTs used in the simulations, and variation of k due to variability of computational procedures and interatomic potentials employed in different simulations.

The length dependence of thermal conductivity of CNTs is commonly observed in MD simulations performed for nanotubes with length up to hundreds of nanometers [10,12,14–18,21–24,26,28,29,33]. There are two main reasons for this behavior. First, when the sample length is less than or comparable to the phonon mean free path, phonons are capable of traveling ballistically through the sample without being impeded by phonon–phonon scattering. As the sample length increases, the effective length of this ballistic transport increases, which increases overall thermal transport and results in higher conductivity values. Second, the longest available phonon wavelength that can exist in a CNT is dictated by the sample length. Thus, as the sample length increases, the maximum allowable phonon wavelength increases. The additional long-wavelength phonons offer effective channels for thermal transport and can make a substantial contribution to the thermal conductivity [21,28]. The CNT length that corresponds to the transition from the ballistic conduction regime, where the thermal conductivity increases with CNT length, to the diffusive regime, where the thermal conductivity approaches a constant value, is temperature dependent as the phonon mean free path decreases with increasing temperature. A recent review of room temperature experimental measurements performed for CNTs with length exceeding 0.5 μm [43] suggests the diffusive regime of the heat transfer. At the same time, the results of MD simulations performed for CNTs with lengths of 10s to 100s of nm typically exhibit a pronounced increase of k with increasing CNT length, that is characteristic of the ballistic and transitional diffusive-ballistic phonon transport [12,14,15,18,21–24,26,28,33]. The length dependences predicted in different MD studies, however, vary widely for the same (10,10) CNT, with the transition to the diffusive regime (saturation of k) predicted for as short CNTs as 10 nm in some of the investigations [10,15–17,29], while no saturation is observed for CNTs with length exceeding 1 μm in other studies [23,28]. In order to reconcile the diverging results on the CNT length dependence, the sensitivity of the predictions of MD simulations to the interatomic potential and computational procedures used in the calculations of thermal conductivity has to be systematically evaluated.

The interatomic potential that defines the interaction forces between atoms in the simulated system is a key ingredient of any MD model. The choice of interatomic potential has direct effect on any quantitative prediction of MD simulations, including prediction of the value of thermal conductivity. A sample of results obtained with interatomic potentials commonly used in simulations of CNTs are listed in Table 1. Note that some of the potentials have been modified and different versions and generations of the same potential are concurrently used by different research groups. As a result, there can even be confusion as to the exact version of potential indicated by name in a published work.

For clarity, the following nomenclature convention is defined in this paper. The Tersoff potential is the early bond order potential that has the original functional form and parameterization defined by Tersoff in 1988 [44,45]. The Brenner potential is the potential developed by Brenner in 1990 [46]. Stuart and colleagues modified the Brenner potential, added a description of torsional interactions for rotation about single bonds and developed an adaptive treatment of non-bonded van der Waals interactions within the bond order formalism of the Brenner potential. This potential, described by Stuart et al. in 2000 [47] is referred to as adaptive intermolecular reactive bond order (AIREBO) potential. In 2002, Brenner et al. made changes to the functional form and parameterization of the original Brenner potential to improve the accuracy of the description of hydrocarbon molecules and various properties of diamond [48]. We refer to this second-generation Brenner potential as Brenner-II. A description of van der Waals interactions through simple addition of the Lennard–Jones (LJ) potential to the Tersoff, Brenner, and Brenner-II potentials has also been used in simulations that do not involve formation/dissociation of chemical bonds and do not require adaptive treatment of the intermolecular interactions [21,32,49]. These potentials can be denoted as Tersoff + LJ, Brenner + LJ, and Brenner-II + LJ, and a set of parameters ϵ and σ of the Lennard–Jones potential should be provided to define the combined potentials. New sets of parameters for the Tersoff and Brenner potentials, optimized for the description of phonon thermal transport in carbon nanotubes and graphene, were recently suggested by Lindsay and Broido [50]. We refer to these potentials as optimized Tersoff and optimized Brenner in this paper. Finally, Yamaguchi and Maruyama [51] used a simplified version of the original Brenner potential, in which the conjugate-compensation term is eliminated to facilitate the formation of poly-cyclic structures in simulations of fullerene formation process. This implementation was used by Shiomi and Maruyama [23] in simulations of thermal conductivity of CNTs and is referred to as simplified Brenner in this paper.

Another factor that may be responsible for the inconsistency of the computational predictions is the variability of the methods employed for the calculation of thermal conductivity in MD