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Thermal conductivities of graphyne nanotubes from atomistic simulations

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ABSTRACT

Thermal conductivities (TCs) of graphyne-*n* nanotubes (GNT-*n*) are investigated by reverse non-equilibrium molecular dynamics simulations. Dependences of the generation number *n*, diameter *d*, and length *L* on TCs of GNT-*n* are derived with scaling relations and explained from the analysis of phonon density of states. Simulation results reveal that with the increase of the generation number *n*, TC decreases and scales as $\lambda \sim n^{-0.57}$. The diameter *d* has a weak impact on TC and a universal scaling law of $\lambda \sim d^{0.03}$ at $d > 5$ nm is derived for all GNT-*n*. With the increase of the length, the scaling relation between TC and *L* has a crossover. After the crossover, the scaling exponents are 0.16, 0.07, 0.05, 0.04, 0.03 for $n = 1$–5, respectively, which are much smaller than the scaling exponent of 0.48 for the carbon nanotube (CNT). TC values of GNT-*n* are estimated to be 92.4, 43.6, 30.4, 27.4, 23.0 W/(m K) for $n = 1$–5, respectively, at $L = 2.6$ μm by extrapolation, which are two orders of magnitude smaller than 2820.6 W/(m K) of the CNT with the same length. This implies the graphyne-*n* nanotubes may be more promising thermoelectric materials than the CNT.

1. Introduction

Thermoelectric materials (TEMs) that can make the conversion between thermal and electrical energies have garnered increasing attention due to their potential technical applications and are expected to play an important role in meeting the energy challenge. To evaluate the conversion efficiency of TEMs, the figure of merit, $ZT \sim S^2\sigma/\lambda$ is defined, where σ is the electronic conductivity, λ the thermal conductivity and S the Seebeck coefficient which is the intrinsic property of the material [1]. Therefore, to improve the performance of TEMs, the key is to increase σ and decrease λ.

Graphene as a new 2D material has been of great interest in theory and experiment because of its unique mechanical, thermal and electronic properties since its discovery in 2004 [2]. Graphene has fascinating electronic properties, but due to its also superhigh thermal conductivity, graphene cannot be an efficient TEM and its *ZT* value was reported to be as low as 0.01 [3]. Graphyne, proposed by Baughman et al. in 1987 [4], a new type of 2D carbon allotropes including both *sp* and sp^2 hybridized states, has recently been a hot spot with the upsurge of graphene research. By adjusting the number of acetylenic linkages between the nearest-neighbouring carbon hexagons, a family of graphyne labelled as graphyne-*n* where *n* is the generation number can be formed (see Fig. 1). Structural stability of the graphyne-*n* was confirmed in the previous theoretical study in which the binding energies of graphyne-*n* sheets were comparable to those of graphite and C_{60} according to the calculations with linear combination of atomic orbitals method [5]. Similar to rolling up graphene sheets to form carbon nanotubes, graphyne sheets can also be rolled up to form graphyne nanotubes (GNT-*n*)[6,7]. Analogous to CNTs, there are also armchair, zigzag, and other chiral GNT-*n*.

Some of these graphyne-*n* sheets had been reported not only to have the similar mechanical and chemical properties with graphene [5,8–10], but also to possess similar or even more amazing electronic properties than graphene due to the presence of two self-doped nonequivalent distorted Dirac cones and the directional anisotropic conductivity [11]. More importantly, the recent studies illustrated that the phonon-contributed thermal conductivity of graphyne is much lower than the thermal conductivities of graphene and carbon nanotubes resulting from the insertion of acetylenic linkages [12,13]. Wang et al. [14,15] have calculated the *ZT* values of graphyne and graphyne nanotube to be 0.157 and 0.83, respectively, by using the density functional theory (DFT) calculations combined with the non-equilibrium Green's function

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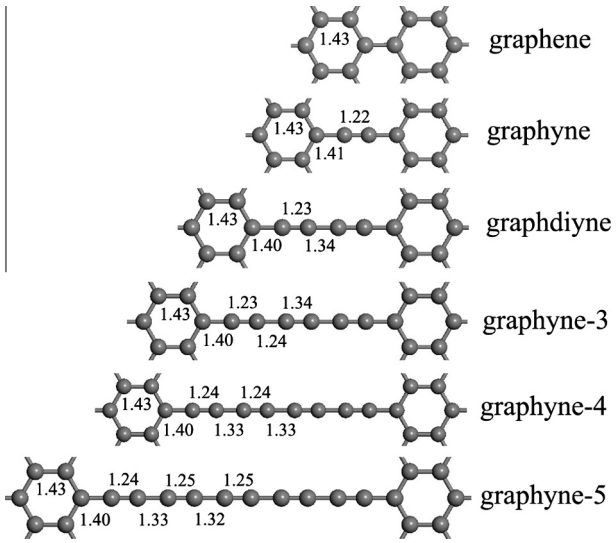

Fig. 1. Assignation for bonds of graphene and graphyne-*n* with *n* acetylenic linkages.

formalism, both of which are much higher than those of graphene and carbon nanotubes. Sevinçli et al. [16] calculated the *ZT* values of graphyne to be 0.17 at room temperature through DFT calculations and transmission spectrum analyses. For the graphyne nanoribbon, Ouyang et al. [17] and Zhou et al. [18] found higher *ZT* values of 0.25 and 0.27, respectively, based on the DFT calculation and Green's function method. These investigations suggest that graphyne-*n* or graphyne-*n* nanotubes may be a promising TEM applied in the energy conversion. Although only the graphdiyne (graphyne-2) [19,20] and its nanotube array [20] are successfully synthesized in experiment recently, the breakthrough of synthesizing other graphyne-*n* sheets and GNT-*n* is believed to come soon.

Thermal conductivity of graphyne sheets [13] and electronic properties of graphyne nanotubes [6,7] have been studied in theory, while to the best of our knowledge, thermal conductivities of graphyne nanotubes and their dependences on the generation number, tube diameter and length are still lacking. Here we present the TC studies of GNT-*n* by reverse non-equilibrium molecular dynamics (RNEMD) [21] simulations. The scaling relations between the TC and the generation number, length and diameter of GNT-*n* will be investigated and the comparison of their TCs with the TC of the CNT will be addressed in detail.

The subsequent text is organized as follows. The second section introduces the model of GNT-*n* and the simulation method. The third section discusses dependences of the generation number, the diameter and length on TCs of GNT-*n* and the last section is the conclusions.

2. Model and method

2.1. Model of graphyne nanotubes

Fig. 2 shows the graphyne structure and three representative chiral vectors. The unit cell of the graphyne can be defined by two vectors $\mathbf{a}_1 = a\,\mathbf{x}$ and $\mathbf{a}_2 = a/2(\mathbf{x} + \sqrt{3}\mathbf{y})$, where $\mathbf{x}, \mathbf{y}$ are the unit direction vectors, a is the optimized lattice length and a = 6.90, 9.46, 11.94, 14.61 and 17.19 Å for graphyne-*n* with n = 1–5, respectively. The optimized lattice length, the internal coordinates of carbon atoms and the bond lengths shown in Fig. 1 for each graphyne-*n* are from our previous density functional theory (DFT) calculations with PBE exchange–correlation functional [22]. A graphyne nanotube can be generated by rolling up the graphyne sheet along the chiral vector $\mathbf{C_h} = p\mathbf{a}_1 + q\mathbf{a}_2$, where p and q are the indices of the GNT. Similar to the CNT, the nomenclature (p,q) can also be applied to denote the chirality of the GNT. It is worth noting that (p,p) and $(p,0)$ represent zigzag and armchair GNT-*n* [5], respectively, which are contrary to the definitions of zigzag and armchair CNTs. In the present work, we only focus on zigzag and armchair single-walled GNT-*n*.

2.2. Reverse non-equilibrium molecular dynamics (RNEMD) simulations

The RNEMD method was proposed in Ref. [21] and implemented in LAMMPS [23] software package. The heat source is placed at the middle of the tube and a heat sink is attached to each end of the tube. Periodic boundary conditions are used along the axial direction. A schematic of the simulation model used in the present work is shown in Fig. 3(a). A temperature gradient will be generated symmetrically along the tube axis from the heat source zone to the heat sink zone as shown in Fig. 3(b) by exchanging the velocities of atoms between the hottest atom in the heat sink zone and the coldest atom in the heat source zone. A heat flux is also generated and is counter to the energy transfer resulting from the unphysical velocity exchange. The TC of GNT-*n* then can be calculated from the heat flux and the temperature gradient along the tube using the well-known Fourier's law,

$$\lambda = \frac{J}{2A\partial T/\partial z}$$

where J is the heat flux, $\partial T/\partial z$ the temperature gradient and A the cross-section area of the GNT-*n*. We follow the standard practice to treat the GNT as a hollow tube of diameter d and a wall thickness of 0.142 nm, just as the same as the length of sp^2 C–C bond in graphene [24,25]. The factor 2 in the denominator accounts for the periodicity of the system.

All the simulations were performed at 300 K with a time step of 0.5 fs. The interaction among carbon atoms is described by the second-generation REBO (REBO-II) potential [26] which has been widely adopted to investigate the mechanical and thermal properties of carbon-based nanomaterials including carbon nanotubes and graphene [27–30]. Before beginning the RNEMD simulation, each GNT-*n* was simulated first in the NS_zT ensemble for 3 ns with zero strain in the z dimension and the x, y directions held as a constant and then in the NVE ensemble for another 3 ns to ensure the GNT is thermo-mechanically equilibrated. During the NS_zT simulation, the Nosé-Hoover thermostat and barostat were used with a temperature relaxation time of 0.5 ps and a pressure relaxation time of 1.0 ps. After equilibrium, five different initial configurations were created and used to perform the RNEMD simulation for the uncertainty estimate of the TC data. Each RNEMD simulation is performed for 5–9 ns depending on the size of the simulation system. During the RNEMD simulation, the system temperature is found to be fairly constant around 300 K with a fluctuation of less than 1.0 K. The temperature gradient along the heat flow direction is obtained by averaging over the final 3 ns RNEMD simulation data.

3. Results and discussions

3.1. Generation number dependence of the thermal conductivity

Under the simulation conditions described above, TCs of CNT and GNT-*n* (n = 1–5) with approximately equal diameter (~3.9 nm) and length (~21.0 nm) are calculated and displayed in the Table 1. The variation of the TC with the generation number