Thermal conductivities of two-dimensional graphitic carbon nitrides by molecule dynamics simulation

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ABSTRACT

Two-dimensional (2D) graphitic carbon nitrides (2D GCNs) are a rising class of 2D polymeric materials. Compared with graphene, they have many attractive merits, such as their great semi-conductivity and photo-catalyticity. Despite much progress in studying their various properties, their thermal properties have been given little attention. In this work, thermal conductivities of three kinds of 2D GCNs, heptazine-based g-C_3N_4 (HEP), triazine-based g-C_3N_4 (TRI), and 2D polyaniline g-C_3N (PANI), were computationally investigated by non-equilibrium molecule dynamics (NEMD) simulations based on both Tersoff and ReaxFF potentials, which offer comprehensive understanding of their thermal properties. It was found that the PANI was predicted to show extrapolated bulk thermal conductivities of 810 W/(m·K) and 461.9 W/(m·K) by the Tersoff and ReaxFF potentials, respectively. The HEP and TRI have much lower bulk thermal conductivities, ranging from 14.1 to 119 W/(m·K). Nevertheless, they are still much higher than those of traditional polymers. The ReaxFF potential also shows that carbon–nitrogen bonds are stiffer than those modeled by the Tersoff potential, resulting in higher phonon harmonicity, and longer phonon mean free paths.

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1. Introduction

Increasing the thermal conductivity of polymers is highly desired due to their advantages of light weight, low cost, corrosion resistant, and easy manufacturability as heat management materials [1,2]. It was revealed that when made into low dimensional forms, polymers exhibit greatly enhanced thermal conductivities compared with their bulk counterparts. For instance, 1D polymers, which can be made by stretching single polymer chains, show high thermal conductivities. Henry and Chen demonstrated that the thermal conductivity of single polyethylene chains exceeds 100 W/(m·K) [3]. Liu and Yang show that the single extended polymer chains have 1–2 orders of magnitude higher thermal conductivity than their bulk counterparts [4]. Shen et al. reported the thermal conductivity of ultra-drawn polyethylene nanofibers to be as high as ~104 W/(m·K) [5]. These largely enhanced thermal conductivities were attributed to the highly aligned atoms, which would greatly decrease phonon scattering. For the same reason, one can expect that when the polymer chains or networks are confined to 2D atomic thickness, the 2D polymers would also show a similarly high thermal conductance. For example, graphene with one

dimension restricted to a few atomic thicknesses can be regarded as a natural 2D polymer [6]. It has shown ultra-high thermal conductivity of up to 5300 W/(m·K) [7–9], even higher than that of the diamond [10]. In addition, it has provided a platform for studying physics of thermal conduction in other 2D materials. Intensive research has been conducted to experimentally measure [7–11] or theoretically predict the thermal conductivity of graphene [12–17], targeting the utilization of graphene in future heat management devices.

Besides graphene, other kinds of synthetic 2D polymers have attracted much interest due to their excellent properties [6,18,19]. These materials outperform graphene in aspects of band-gap opening for the application in electronics [20], low cost for mass production [21], better dispersion in solvents [22], and better interfacial properties when making polymer composites [23]. Among them, the 2D graphitic carbon nitrides (GCNs) [24–28] are one class of 2D polymers made by polymerization of organic precursors such as heptazine and triazine. They have high 2D atomic crystallinity and inherent semi-conductivity. The s-heptazine (HEP) and s-triazine (TRI) based 2D GCNs are 2D structures containing atomic vacancies (Fig. 1a–b) [27], while 2D polyaniline (PANI) has a non-defective planar structure (Fig. 1c) [28]. Although these materials have been widely explored as promising candidates for fluorescence sensors [29], osmosis

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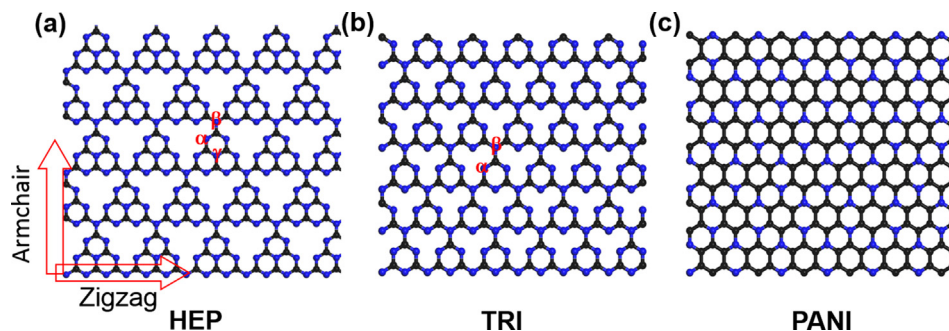
Fig. 1. Atomic structures of (a) heptazine-based g-C_3N_4 (HEP) (b) triazine-based g-C_3N_4 (TRI) and (c) 2D polyaniline g-C_3N (PANI). The atoms are colored by black for carbon and blue for nitrogen.

membranes [30], and catalytic devices [31,32], their potentials in thermal management are rarely explored.

To best of our knowledge, experimental measurement on the thermal conductivities of these 2D GCNs have yet been demonstrated. Prior to their demonstration, theoretical study on their thermal properties provides initial guidance for screening them as heat management materials. Among a variety of computational approaches, due to relatively low computational cost, molecule dynamics (MD) simulations serve as promising tools to predict the thermal conductivity of these 2D polymeric materials. In contrast to numerous amount of MD work on the thermal conductivity of graphene [16,17,33,34], MD studies on thermal and phonon properties of the 2D GCNs are limited. One possible reason is that the C-N interaction is seldom given in traditional empirical potentials. Mortazavi et al. studied the HEP and TRI by equilibrium MD (EMD) simulation, and their thermal conductivities were reported to be 3.5 W/(m·K) and 7.7 W/(m·K) [35], respectively. The PANI was also studied by Mortazavi et al. by non-equilibrium MD (NEMD) simulation [36]. A size-dependent thermal conductivity was observed. They found that as the length increased the thermal conductivity increased, with an extrapolated bulk thermal conductivity of ∼810–826 W/(m·K), which is even higher than that of the hexagonal boron nitride (h-BN) [37]. However, phonon properties that account for the thermal transport behaviors were not analyzed in these works, which resulted in a lack of insights when comparing their thermal conductivities with graphene. Moreover, in these works [35,36] Mortazavi et al. used the optimized Tersoff potential [38] to describe C-C interactions and adopted the potential developed by Matsunaga et al. [39] and Kınacı et al. [40] to describe the C-N interactions. Since parameters given by Kınacı et al. [40] were optimized for simulating interfaces of the graphene and boron nitride, the employed potential may induce inaccuracy when simulating 2D GCNs. The ReaxFF force fields [41–44] can avoid such inconsistence in modeling the C-N interactions in these 2D GCNs. These force fields were parameterized based on a large number of quantum mechanics calculations to characterize the atomic interactions under various conditions. The training set contains bond breaking and forming curves for all bonds, angles, and torsions [42]. The bonded and non-bonded forces are both included in the intramolecular potential energies. The bond order dependent energy terms are suitable to characterize the intramolecular interactions between organic elements, where multiple bonding states are possible (such as single, double and π bonds).

In previous work, we performed NEMD simulation for studying thermal conductivity of the graphene by the ReaxFF potentials [45]. Among them, the Reax-03 potential containing C-H-O-N elements was shown to be the best candidate for describing the out-of-plane (ZA + ZO) phonon modes in the graphene. It is worth noting that the ReaxFF potentials are also effective in calculating the thermal transport in other low dimensional materials such as

1D polymer [46], 2D boron [47], and metal dichalcogenides [48]. However, to the best of our knowledge, the ReaxFF potential has not been employed for studying the thermal properties of the 2D GCNs. Thus, to obtain a comprehensive understanding of the thermal conductivities of the 2D GCNs, in this work, we performed NEMD simulations on the HEP, TRI, and PANI by both Tersoff and ReaxFF potentials. The length-dependent thermal conductivities, as well as the phonon properties of these 2D GCNs were compared based on these potentials. Results demonstrate the distinctive thermal properties of these GCNs. The ReaxFF potential reproduces better lattice structures than the Tersoff potential. The thermal conductivities of the HEP and TRI predicted by the ReaxFF potential are higher than those by the Tersoff potential. This result is opposite to the case of the PANI. The mechanism of these distinctions is further analyzed by studying their phonon density of states and phonon dispersion relation.

2. Method

2.1. Calculation on structures of 2D GCNs

The 2D GCNs investigated in this work are shown in Fig. 1. It is shown that the HEP contains C_6N_7 core groups, with three of them enclosing a vacancy (Fig. 1a). There are three types of N atoms in the HEP, as marked α-N, β-N, and γ-N. The α-N is pyridinic and stays beside the vacancies. The β-N serves as the junction among three C_6N_7 core groups. The γ-N is in the center of a C_6N_7 core group. The TRI is made of C_3N_3 core groups, three of which enclose a vacancy that is smaller than that in the HEP. There are two types of N atoms in the TRI, as marked α-N and β-N in Fig. 1b. The α-N is pyridinic and stays beside the vacancies, and the β-N is at the junction of three C_3N_3 core groups. In the PANI (Fig. 1c), all N atoms are graphitic, resulting in only one type of C-N bond and one type of C-C bond. The HEP and TRI have thickness of 3.28 Å [49], and the PANI has a thickness of 3.20 Å [36]. All MD simulations were performed by the LAMMPS package [50]. The ReaxFF potential [41,42] and the Tersoff potential parameterized by Kınacı et al. [40] were used to describe the C-C and C-N interactions. The time step was set to 0.1 fs for all simulations. Periodic boundary conditions were applied in all Cartesian directions. The 2D films were placed at z = 0 planes, with at least 10 nm distance between two periodic images in the z direction to avoid image-image interference. Before the NEMD simulation on the thermal conductivity, we first carried out an equilibrium MD simulation to validate the structures of these 2D GCNs. In this step, a single layer of each type of materials with a dimension of 10 nm × 10 nm was built. The systems were relaxed at a constant pressure of 1 atm controlled by the Nosé-Hoover barostat in x, y directions. The volume in the z direction was fixed. The temperature was kept at 300 K. After