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Molecular dynamics study of phonon transport in graphyne nanotubes

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ABSTRACT

We determine the thermal conductivities of α, β, and γ graphyne nanotubes (GNTs) as well as of carbon nanotubes (CNTs) using molecular dynamics simulations and the Green-Kubo relationship over the temperature range 50–400 K. We find that GNTs demonstrate considerably lower thermal conductivity than CNTs with the same diameter and length. Among α, β, and γ-GNTs, γ-GNT has the highest thermal conductivity at all temperatures. By comparing the phonon transport properties of GNTs with CNTs, we find that as the fraction of acetylene bonds in the atomic network increases, the population of high-energy optical phonons increases. This enhances phonon-phonon scattering, and reduces the mean free path, adversely affecting the thermal conductivity of GNTs relative to CNTs. Also reducing the thermal conductivity of GNTs relative to CNTs is the considerably lower acoustic phonon group velocities for the former as well as the lower volumetric heat capacity of GNTs. Optical phonons in α-GNT are high in energy (0.26 eV) with a high population number, making them more energetic than the electronic direct band gap and significantly more energetic than the thermal energy at room temperature. Therefore, we suggest α-GNT as a potential candidate for phonovoltaic energy conversion applications.

1. Introduction

Recently, there has been increasing interest in studying the thermal properties of materials, driven by both industrial demand and the desire for better fundamental understanding of conductivity mechanisms. In particular, heat dissipation in nanoscale electronic devices has necessitated a search for new heat conducting materials for future progress in electronics [1–3]. Another major body of research is the search for high figure-of-merit thermoelectric materials [4,5], and materials for novel energy conversion techniques, such as thermophotovoltaic [6,7], thermal bandgap [8], and phonovoltaic [9], which further motivates the study of thermal and electronic transport.

Carbon-based materials, with their multitude of allotropes, offer unique thermal and electronic properties which are of interest in electronics and thermoelectric applications [10,11]. Among these allotropes, graphene in the form of both two-dimensional sheets and carbon nanotubes has demonstrated an extremely large intrinsic thermal conductivity. Numerous empirical studies have been carried out to evaluate the temperature-dependent thermal conductivity of carbon nanotubes, which depends strongly on nanotube length, diameter and chirality [12]. Some experimental studies have reported thermal conductivities of 3000–3500 W m^{-1} K^{-1} for individual single (SWNT) and multiwall carbon nanotubes (MWNTs) [13–15], which exceeds that of diamond at room temperature. Li. et al. have reported an experimental value of 2400 W m^{-1} K^{-1} for a SWNT with 1.8 nm diameter and 20.5 μm length [16]. Ref [12] lists experimental measurements of thermal conductivities for SWNTs at room temperature ranging from 300 to 13350 W m^{-1} K^{-1} depending on nanotube length, diameter and measurement method.

In addition to experimental studies, molecular dynamics simulations are nowadays used to determine the thermal transport properties of carbon-based materials. Classical MD simulations do not include the electronic contributions to thermal conductivity. However, since the phonon contribution to the thermal conductivity of carbon nanotubes is dominant at all temperatures [17–20], neglecting the electronic effect can be justified. In addition, MD

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simulations provide atomistic information, which can be used for detailed analysis of spectral dependence of phonon transport in materials [21], and to determine the dominant modes of heat transfer at each condition. Numerous such studies using different classical MD techniques including those based on the Green-Kubo relationship [18,22,23], as well as non-equilibrium MD (NEMD) [24–26], reverse NEMD (RNEMD) [27–29], and homogenous NEMD (HNEMD) [30,31] simulations have been carried out to determine the thermal conductivity of carbon nanotubes and other carbon based materials.

Overall, the temperature dependence of thermal conductivity in CNTs is divided into two regimes with a peak in thermal conductivity occurring at around 300 K [22,32]. In the high temperature regime, the thermal conductivity decreases with increasing temperature due to Umklapp scattering. In the low temperature regime, Umklapp scattering is suppressed and inelastic phonon scattering occurs mostly due to fixed system boundaries. Therefore, the phonon relaxation time remains constant, and thermal conductivity demonstrates the same temperature dependence as heat capacity, which is a monotonic increase with temperature.

First suggested by Ref. [33], graphyne is a class of graphene allotropes which contains carbon triple bonds. Its atomic structure has three main symmetric types; α, β, γ graphyne (structures are shown in Fig. 1) with 33.3%, 28.6%, and 20.0% carbon triple bonds respectively. Similar to CNTs, graphyne nanotubes can be formed by rolling up the graphyne sheet into cylinders. The thermal transport properties of graphyne nanotubes (GNTs) have been far less investigated to date. A number of MD calculations have determined the thermal conductivity of graphyne sheets and nanostructures. For example, Zhang et al. [28] have performed NEMD simulations to determine the thermal conductivity of graphene and γ-graphyne sheets in the temperature range of 200–800 K. They showed that as the temperature increases the thermal conductivity decreases monotonically. They reported that the acetylenic bonds in γ-graphyne cause a significant reduction in thermal conductivity in comparison to graphene sheets, mainly due to the low atom density and weak C–C bonds in the graphyne structure. In addition, a strong directional anisotropy in the thermal conductivity of graphyne sheets was reported. Pan et al. [34] carried out NEMD simulations of γ-graphyne nanoribbons at various temperatures and reported a strong orientation dependence in thermal conductivity. They also found a higher value of thermal conductivity for armchair γ-graphyne nanoribbon than for the zigzag forms. This was attributed to more phonon transport channels and higher phonon group velocity in armchair γ-graphyne nanoribbon over the whole frequency range, relative to the other forms. It was also shown as the temperature rises from 200 K to 800 K, the thermal conductivity decreases [34]. Hu et al. [35] performed NEMD simulations on a perfect γ-graphyne nanotube (γ-GNT), and reported an extremely low thermal conductivity (below 10 W/m K at room temperature), which they attributed to the atomic structure of γ graphyne, which consists of weak acetylenic bonds and strong hexagonal (sp^2 C–C) bonds, which have a large vibrational mismatch. They indicated that, because of the large number of

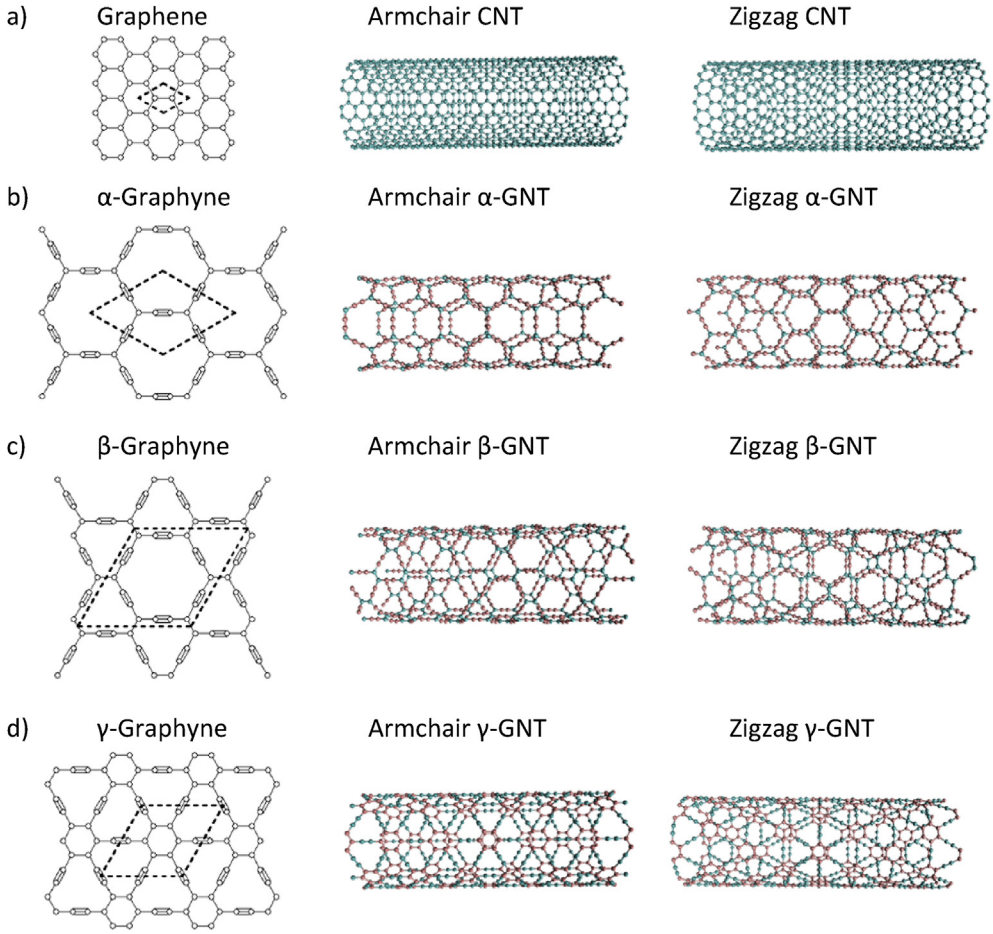

Fig. 1. Schematic representation of: (a) graphene sheet, armchair CNT, and zigzag CNT, (b) α-graphyne sheet, armchair α-GNT, zigzag α-GNT, (c) β-graphyne sheet, armchair β-GNT, zigzag β-GNT, (d) γ-graphyne sheet, armchair γ-GNT, zigzag γ-GNT. Unit cells are enclosed in dashed lines. (A colour version of this figure can be viewed online.)