International Journal of Heat and Mass Transfer 85 (2015) 880–889

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

# On the origin of abnormal phonon transport of graphyne

Yuhang Jing [a,*], Ming Hu [b,c,*], Yufei Gao [d], Licheng Guo [a], Yi Sun [a]

[a] *Department of Astronautical Science and Mechanics, Harbin Institute of Technology, Harbin 150001, China*
[b] *Institute of Mineral Engineering, Division of Materials Science and Engineering, Faculty of Georesources and Materials Engineering, Rheinisch-Westfaelische Technische Hochschule (RWTH Aachen University), 52064 Aachen, Germany*
[c] *Aachen Institute for Advanced Study in Computational Engineering Science (AICES), RWTH Aachen University, 52062 Aachen, Germany*
[d] *School of Architecture & Civil Engineering, Shenyang University of Technology, Shenyang 110870, China*

A R T I C L E I N F O

*Article history:*
Received 21 September 2014
Received in revised form 5 January 2015
Accepted 17 February 2015

*Keywords:*
Graphyne
Phonon transport
Two-dimensional material
Molecular dynamics

A B S T R A C T

Graphyne, a two-dimensional planar carbon allotrope and consisting of *sp* and $sp^2$ carbon atoms, receives great attention in a wide community of scientists and engineers beyond graphene. Herewith we investigate the thermal transport property of graphyne and graphyne nanoribbons by performing nonequilibrium molecular dynamics simulation. Our simulations reveal abnormal thermal transport in graphyne that exhibits a low thermal conductivity (as low as 8 W/mK at room temperature), which is two to three orders of magnitude lower as compared to graphene. Detailed lattice dynamic calculations and phonon polarization analysis suggest that, the intrinsically low thermal conductivity of graphyne originates from the localization and the domination of the low frequency in-plan longitudinal modes to the acetylenic linkages and the large lattice vibration mismatch between the linkages and the hexagonal rings, which induces inefficient energy transfer between the soft phonon modes in the linkages and the stiffer vibrational modes in the hexagonal rings. We also illustrated an intriguing width dependent thermal conductivity of graphyne nanoribbons, which is fundamentally different from that of graphene nanoribbons and stems from the surface dominated phonon modes presented in the graphyne edge. Our simulations provide a detailed physical picture of thermal transport in graphyne and could offer useful guidance for engineering the thermal transport properties of graphyne for applications of graphyne related devices such as thermoelectrics.

## 1. Introduction

Carbon-based nanostructures, e.g. one-dimensional carbon nanotube and two-dimensional graphene, have attracted tremendous interests due to their extraordinary mechanical [1,2], thermal [3,4], and electronic properties [5,6]. Many emerging applications of carbon-based nanostructures in nanodevices have already been reported in literature [7,8]. Graphyne, a two-dimensional carbon allotrope like graphene and consisting of planar carbon sheets containing both *sp* and $sp^2$ carbon atoms, has been investigated theoretically since 1980s [9]. Another two-dimensional carbon allotrope – graphdiyne – was proposed by Haley, Brand, and Pak [10], which belongs to the same family as graphyne. At the same time, experimental work on synthesizing both graphyne and graphdiyne structures has been conducted [11,12] and thin film of graphdiyne [13] have been successfully fabricated. Thereafter, studies on the electronic properties of graphyne and its related structures including graphyne-based nanotubes [14–16], took off rapidly [17–19]. Both theoretical and experimental studies have shown that graphdiyne is naturally semiconductor [13,20], which make it very promising in the future nanoelectronics application. Recently, Malko et al. [21] found that the electronic properties of graphyne are much superior to that of graphene, due to its directional anisotropy and its nonequivalent Dirac points. In this line, studies on the mechanical properties of graphyne and its family have also been performed. It was demonstrated that, unlike graphene, the mechanical properties of graphyne depend strongly on the direction of the applied loading [22]. Recently, using molecular dynamics simulations, it was found that the presence of the acetylene links in the graphyne structure plays very important role in the Young's modulus, fracture stress, and fracture strain of the graphyne [23–25].

In addition to the electronic and mechanical properties, thermal transport properties of graphyne are also of great interest for

---

* Corresponding authors at: Institute of Mineral Engineering, Division of Materials Science and Engineering, Faculty of Georesources and Materials Engineering, Rheinisch-Westfaelische Technische Hochschule (RWTH Aachen University), 52064 Aachen, Germany (M. Hu).

*E-mail addresses:* jingyh@hit.edu.cn (Y. Jing), hum@ghi.rwth-aachen.de (M. Hu).

http://dx.doi.org/10.1016/j.ijheatmasstransfer.2015.02.050
0017-9310/© 2015 Elsevier Ltd. All rights reserved.

fundamental physics and potential applications. However, little theoretical work on the thermal transport properties of graphyne and the related structures have been reported [26–28]. Very recently, the thermal conductivity of four different graphyne, namely $\alpha$, $\beta$, $\gamma$, and 6, 6, 12-graphenes, was investigated using reverse non-equilibrium molecular dynamics simulations [28]. It was found that the presence of the acetylenic linkages in the graphyne can cause a significant reduction in the thermal conductivity because of the associated low atom density in the structures and weak single bonds in the acetylenic linkages. Here, we focus on the graphyne with identical and isotropic carbyne-like chains and variable length and width. The electronic and mechanical properties of graphyne and its family has been found to be associated with the number of acetylenic linkages in their structures [24,25,29,30]. However, the deterministic effect of number of acetylenic linkages on the thermal transport properties of graphyne is not understood yet.

In this work, we investigate the phonon transport of graphyne using nonequilibrium molecular dynamics (NEMD) simulations. The effects of number of acetylenic linkages, length, and nanoribbon width on the thermal conductivity are explicitly considered. In Section 2, we briefly describe the model structure and the methodology used for the simulation. In Section 3, we report the lattice thermal conductivity of graphyne, evidencing the abnormal heat conduction of graphyne. The salient feature of the extremely low thermal conductivity of graphyne as compared with graphene is identified and the governing mechanism is explained in terms of the vibrational mismatch between the acetylenic carbon (*sp*) and the graphene carbon ($sp^2$). We consolidate the underlying phonon transport mechanism by quantitatively determining the relative contributions from different regions of the graphyne structure to the overall lattice thermal conductivity and by performing polarization analysis as well. We also identified the mechanism for the abnormal width dependence of thermal conductivity of graphyne nanoribbon. In Section 4, we present a summary and conclusion.

## 2. Model structure and simulation methodology

In this paper, we investigate the thermal conductivity of graphyne-*n* structures in both armchair and zigzag direction. A representative graphyne structure is shown in Fig. 1. We define “*n*” in graphyne-*n* as a graphyne structure in which there are *n*-acetylenic linkages (corresponding to $2 \times n$ carbon atoms) between the nearest-neighboring carbon hexagons. In all MD simulations performed herein, the adaptive intermolecular reactive empirical bond order (AIREBO) potential derived from the second-generation Brenner potential [31,32] is used to describe the interactions between C and C atoms, C and H atoms, and H and H atoms. The AIREBO potential is widely used in MD simulation of graphene and provides better representations of the lattice dynamics and phonon thermal transport in graphene with optimized parameters [27,32]. The parameters we adopted for the C–H systems in this paper are also usually used for computing the thermal conductivity of other similar atomic systems, such as graphene nanoribbons [33], carbon nanotubes [34,35].

All MD simulations are performed using LAMMPS package [36]. The Velocity–Verlet algorithm is employed to integrate the equations of motion with a timestep of 0.55 fs. All molecular systems were equilibrated at a constant pressure of 1 atm and a temperature of 300 K using *NPT* (constant number of particles, pressure, and temperature) for 100 ps. The temperature is controlled by employing the Nosé–Hoover thermostat [37]. After the *NPT* relaxation, we continued to relax the system with an *NVE* (constant volume and no thermostat) ensemble for 100 ps. During this stage, we monitored the total energy and temperature of the whole system. We found that the total energy conserved very well and the temperature remained constant with small fluctuations around 300 K, which meant that the system had reached the equilibrium state.

Following equilibration, the thermal conductivity of the graphyne structures is computed using nonequilibrium molecular dynamics. The constant heat flux is imposed by the Muller-Plathe method [38]. The outmost two unit cells of graphyne on both ends are defined as “hot slab” and “cold slab”, respectively. The coldest atoms in the “hot slab” and the hottest atoms in the “cold slab” are selected and their kinetic energies are exchanged every several hundred time steps to a few thousand time steps, depending on the thermal conductivity of the structure. This operation will induce a constant heat flux in the system and also a temperature gradient along the heat flux direction after running some time. The thermal conductivity is finally calculated by the Fourier’s law

$$\kappa = -\frac{J_L}{\partial T/\partial z}, \tag{1}$$

where $J_L$ is the averaged heat flux and $\partial T/\partial z$ is the temperature gradient determined from the linear fitting to the temperature profile. It is worth pointing out that, when we output the temperature profile, we divided the system into slices, each containing at least 400 atoms, which is enough to gain reliable temperature gradient when averaged over a long simulation runs. Each temperature profile is averaged over 100 ps. Once the steady state is reached, which typically takes about 3 ns depending on the system, we run additional 5 ns to collect data for obtaining the heat flux (by linear

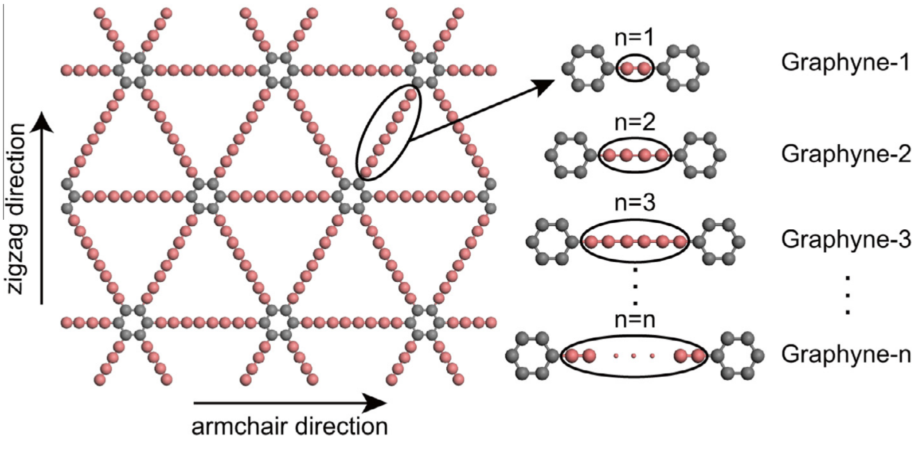

**Fig. 1.** Schematic of graphyne-*n* structure with the definition of *n*. Zigzag and armchair direction are denoted by arrows.