Molecular dynamics simulation of temperature profile in partially hydrogenated graphene and graphene with grain boundary

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ABSTRACT

Temperature profile in graphene, graphene with grain boundary and vacancy defects and hydrogenated graphene with different percentage of H-atoms are determined using molecular dynamics simulation. We also obtained the temperature profile in a graphene nanoribbon containing two types of grain boundaries with different misorientation angles, $\theta = 21.8°$ and $\theta = 32.2°$. We found that a temperature gap appears in the temperature profile of a graphene nanoribbon with a grain boundary at the middle. Moreover, we found that the temperature profile in the partially hydrogenated graphene varies with the percentage of hydrogens, i.e. the C:H ratio. Our results show that a grain boundary line in the graphene sheet can change the thermal transport through the system which might be useful for controlling thermal flow in nanostructured graphene.

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1. Introduction

Graphene is a crystalline allotrope of carbon with two dimensional honeycomb lattice structure and sp^2 in-plane covalent bonds [1,2], which gained considerable attention in recent decade due to its exceptional physical properties [3–8]. Thermal properties of graphene are particularly interesting because it has the largest thermal conductivity among other materials, i.e. of about $1000\,W\,m^{-1}\,K^{-1}$. Therefore, graphene is a candidate for applications of thermal transport and heat management in nanoelectronic devices [9].

Faugeras et al. used local laser excitation and temperature readout from the intensity ratio of Stokes to anti-Stokes Raman scattering signals in order to study the temperature distribution in graphene [10]. They found a radial distribution for the temperature profile and reported thermal conductivity of graphene to be about $630\,W\,m^{-1}\,K^{-1}$. On the other hand several theoretical works on the thermal conductivity and thermal transport in graphene and hydrogenated graphene [11,12] confirm high thermal conductivity in the carbon based nano-structures (for a review on thermal conductivity of graphene see [13] and references therein). One of the proposed applications of thermal conductivity of graphene is

to create a driving force with a temperature gradient in order to move objects [14,15].

On the other hand hydrocarbons, i.e. $(CH)_n$, are the simplest organic structures made of merely carbon and hydrogen atoms [16] which have different thermal conductivity than pristine graphene [17]. The latter is due to the sp^3 bond formation in the hydrogenated graphene. Experimentally, it has been shown that hydrogenated graphene is obtained reversibly starting from a pristine graphene layer [18]. It is also a material of high interest due to its potential applications in nanoelectronics [19]. We recently found that fully hydrogenated graphene is an un-rippled system in contrast to graphene [20] and has a lower melting temperature than graphene [21]. "In the presence of F/H adatoms the C-bonds in graphene transit from sp^2 to sp^3 hybridization, which turn the conjugated, graphitic C—C bonds into single C—C bonds. This re-hybridization turns the lattice structure into an angstrom scale out-of-plane buckled shaped membrane known commonly as chair configuration." Moreover, graphene with various kinds of defects has been extensively investigated in the past few years [22], e.g. the buckling of graphene nano-ribbons with a grain boundary were studied using atomistic simulations with free and supported boundary conditions [23]. It was found that graphene with vacancy defects is a less stiff material as compared to perfect graphene [24].

In this study, using state of the art molecular dynamics simulations, we obtain the radial profile of temperature in perfect graphene, graphene with vacancy defects and graphene with grain boundary. We present an analytical model which gives

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good agreement with our MD results for pristine graphene and hydrogenated graphene. We show that the temperature profile in graphene is strongly affected by the presence of randomly distributed vacancy defects, grain boundaries but slightly varies with the number of hydrogens. We also study the temperature profile along a graphene nanoribbons containing a grain boundary. We found that the well known linear temperature gradient along a system with a grain boundary is divided into two lines which are separated by a temperature gap.

The paper is organized as the following. In Section 2 we present our model. In Section 3 we review the used molecular dynamics simulation method. In Section 4 the radial temperature profile is and corresponding results are presented. Finally we summarize the paper in Section 5.

2. The model

The partially hydrogenated systems are generated by removing randomly H atoms form both sides of graphane. The presence of two high-symmetry directions in graphene, armchair and zigzag, and any (local) misorientation angle close to 0 or 60 can be considered as small-angle grain boundary along these two directions, respectively. The large-angle grain-boundary, LAGBI, LAGBII, which are characterized by $\theta = 21.8°$ and $\theta = 32°$ has already been suggested in the literature [25]. In fact the two kind of grain boundaries, i.e. LAGBI and LAGBII are typical interfaces between domains of graphene with different crystallographic orientation. Mutual orientations of the two crystalline domains are described by the misorientation angle which for LAGBI is $\theta = 21.8°$ and for LAGBII is $\theta = 32.2°$ [26]. Top view of the pristine graphene, graphane (chair like configuration of fully hydrogenated graphene), graphene with grain boundary line which are named LAGBI and LAGBII are shown in Fig. 1(a)–(d), respectively. Two typical systems with 20% and 80% hydrogens are shown in Fig. 1(e)–(f).

A temperature gradient is introduced in the radial direction by increasing the temperature of a small region (hot spot) in the center of the system, see Fig. 2(a). Such a model simulates the experimental set-up of Ref. [10]. For graphene nanoribbons we apply a temperature gradient along the longitudinal direction by keeping the two ends at different temperatures.

3. Computational methods

Here we give details about our molecular dynamics simulations. All molecular dynamics simulations were performed using the Large-Scale Atomic/Molecular Massively Parallel Simulator package (LAMMPS) [33]. The simulated sample is a square sheet of graphene with length 35 nm in zig-zag and arm chair direction. In order to apply a temperature gradient we keep the temperature of the central atoms (a circle with 476 atoms) to $T_H = 310$ K and the outer circle to $T_C = 290$ K. To calculate the middle region temperature we divided our sample into several rings (which are shown by different colors in Fig. 2(a)). We used Tersoff potential [28] to model the interaction between carbon atoms in graphene and AIREBO potential [29,30] to describe the interaction between C—C and C—H atoms in partially hydrogenated graphene and graphane. The temperature of the hot and the cold spots are controlled by Nose Hoover thermostat [31,32] using an NVT ensemble. In order to find steady state condition we perform 100 ps simulation. During equilibration the middle rings are simulated by an NVE ensemble. Moreover, to prevent non-desired crumpling at the edges the other atoms beyond the outer circle shown in Fig. 2(a) are fixed. Because the two hot and cold regions are hold at different temperatures, a steady heat flux flows from the innermost circle to the outermost

ring. The temperature of the middle rings is calculated in each time step and averaged over 1.22 ns.

4. Radial temperature profile

At some initial time, say $t = 0$, a nonuniform temperature profile $T(r, t)$ is applied to graphene. This temperature profile generates a local heat current $J(r, t)$. Due to energy conservation and basic thermodynamics (continuity equation) one can write

$$q(r, t) = c_a(T) \frac{\partial T(r, t)}{\partial t} = -\nabla \cdot \vec{J}, \tag{1}$$

where c_a is the specific heat per unit area. Using Fourier's law for the steady state the latter equation can be written in a time independent form and yields the radial temperature distribution in the graphene sheet by solving the following radial differential equation

$$\kappa \nabla^2 T(r) + q(r) = 0, \tag{2}$$

where $q(r) \propto P \exp(-|\vec{r} - \vec{r_0}|^2 / \sigma^2)$ is the heat source which causes heat flow into the system (it can be generated by light absorption from a laser beam with power P focused around $\vec{r_0}$) and κ is the thermal conductivity of the system (in practice σ corresponds to the estimated radius of the laser spot on the sample). The solution of Eq. (1) is a logarithmic function

$$T \approx T_0 - \frac{\alpha}{2} \ln\left(\frac{r}{r_0}\right) - \frac{\alpha\gamma}{4}, \tag{3}$$

where T_0 is the central region temperature, $\alpha = (P/(\pi\kappa d))$ and $\gamma = 0.5772$ is the Euler's constant with 'd' the thickness of membrane [10]. In order to numerically analyze our results, we use a simplified version of Eq. (3) by introducing two fitting parameters A and T_1:

$$T \approx T_1 - A\ln(r), \tag{4}$$

where T_1 is linearly proportional to the temperature in the central region and 'A' is determined by thermal conductivity, the total absorbed laser power for given laser spot region and the edge temperature.

4.1. Graphene

By applying a temperature gradient of about 20 K between the two hot and cold spots of the system, and after reaching steady state, we calculated the radial distribution of temperature (see Fig. 3). In Fig. 3 we show two typical MD simulations results (symbols) and corresponding fits (solid curve and solid line) for the systems depicted in Fig. 2, i.e. perfect graphene and graphene with 2% vacancy defects. We found that the temperature profile for LAGBI and LAGBII are close to each other and to the one with 2% vacancy defect. There is an obvious difference in the temperature profile between defected graphene (linear fit) and perfect graphene (logarithmic fit). It is seen that the radial temperature profile in the defected graphene does not follow the above theoretical model. Therefore using Eq. (4) is only valid for perfect graphene without any kind of defects such as vacancies and grain boundaries. Since Eq. (4) is based on a continuum model we conclude that a continuum model is not applicable for the heat transfer in defected graphene. The fitting parameters for different studied systems are listed in Table 1.

4.2. Graphane and partially hydrogenated graphene

We also studied the temperature profile in graphane and partially hydrogenated graphene with different C:H ratio. Using 'A' as a fitting parameter in Eq. (4), we found that the radial temperature profile obeys the above mentioned continuum model