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Effect of hydrogenation on graphene thermal transport

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ABSTRACT

We studied thermal conductivity of the three most stable hydrogenated graphene (graphane) conformers by means of non-equilibrium molecular dynamics. We estimated thermal conductivity for pristine graphene with sample length 2.1 (2.4) μm as large as $\kappa = 745.4 \pm 0.3$ and $819.1 \pm 0.3\ \mathrm{W\ m^{-1}\ K^{-1}}$ in the armchair and zigzag directions, respectively, in very good agreement with previous theoretical results based on the Boltzmann transport equation. In the case of the three graphane isomers we observed a dramatic κ reduction by at least one order of magnitude with respect to pristine graphene. We elucidated this reduction in terms of different phonon density of states and mean-free path distribution between graphene and graphane. The deterioration of thermal transport upon hydrogenation in graphene, could be proposed as a way to tune thermal transport in graphene for phononic applications such as thermal diodes.

1. Introduction

Thermal management is a critical issue in electronic industry for the designing of next generation integrated circuits. The performances of ultra-large scale integrated circuits are in fact critically affected by temperature. The raise of the interconnections number and the transistor size reduction increase thermal resistance making difficult to remove heat in integrated circuits. In this perspective graphene represents a promising material as a heat dissipator showing an unusually high thermal conductivity [1,2].

In the last few years several experimental results have been collected on the estimation of graphene thermal conductivity coefficient κ providing a wide range of values ranging between 600 and 5000 $\mathrm{W\ m^{-1}\ K^{-1}}$ [3–5]. These differences have been justified in terms of different sample qualities, grain sizes, thickness non uniformity, real temperature of the samples and strain distribution. Several experiments pointed out a tiny anisotropy in graphene thermal conduction with respect to the zigzag and armchair directions.

In order to predict the value of κ many theoretical approaches have been widely used to study thermal conductivity in pristine graphene, including Boltzmann transport equation [6], molecular dynamics [7,8], Green's functions approaches [9] and lattice dynamics [10,11]. In this work we focused in particular on molecular dynamics methodologies which accurately describe graphene phonon transport properties. Both equilibrium (EMD) [12] and non-equilibrium (NEMD) [13] methods have been implemented to study thermal properties of graphene. However also in this case there are large discrepancies in the resulting thermal conductivity values as due to the different numerical technicalities and/or model potentials. In particular, the graphene thermal conductivity has been predicted to range between 89 and 3000 $\mathrm{W\ m^{-1}\ K^{-1}}$ [14–16].

Both chemical and/or physical strategies have been proposed to tune graphene thermal transport, which could

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be useful in nanoscale engineering and heat management. For instance, by nanopatterning, a graphene sheet can be divided in stripe domains with different thermal conductivities, creating a sort of nano-guide causing heat to preferentially flow in one definite direction (thermal diode or thermal wire). In particular, graphene hydrogenation has been shown to be very effective on controlling thermal conductivity. In Ref. [14] theoretical NEMD calculations demonstrated that by randomly adding as few as 10% hydrogen atoms on top of pristine graphene causes a sharp drop of thermal conductivity.

Motivated by this scenario, as well as by the need to improve our basic understanding of thermal transport properties in 2D carbon sheets, we present here a through investigation addressed to thermal conductivity in hydrogenated graphene. Instead of a randomly decorated graphene lattice we considered ordered graphene decorations where H atoms are attached to each C atom with 1:1 ratio. This hydrogenated form of graphene is referred to as graphane [17]. It has been synthesized by cold hydrogen plasma exposure at low pressure [18]. Graphane exhibits very different transport and elastic properties with respect to pristine graphene [19,17]. In particular, graphane is characterized by a change in the carbon atoms hybridization from sp2 to sp3 which gives rise to a metal to insulator transition due to the opening of an energy gap as large as 3 eV.

Eight different graphane isomers have been identified so far, the most stable ones are three conformers referred to as chair (C-graphane), boat (B-graphane) or washboard (W-graphane) [17,19]. In C-graphane the hydrogens alternate on both sides of the carbon sheet, in B-graphane pairs of hydrogen atoms alternate along the armchair direction of the carbon sheet, finally in W-graphane double rows of hydrogens are aligned along the zigzag direction of the carbon sub-lattice and alternate on both sides of the carbon sheet. According to first principles calculations, C-graphane is the most energetically favorable conformer followed by W- and B-graphane [19,20].

In contrast to the large variety of experimental and theoretical works on graphene thermal properties, few information are available on hydrogenated graphene. In particular, to the best of our knowledge, neither experimental nor theoretical works have been published on thermal conductivity of C-, B- and W-graphane, therefore, in this work we studied thermal conductivity of these isomers by means of “approach to equilibrium molecular dynamics” (AEMD) [21,22].

2. Method

AEMD is based on the Fourier heat-transport equation under given border and initial conditions [21,22]. By assuming periodic boundary conditions and a step-like initial temperature profile as shown in Fig. 1, the solution of the heat equation predicts the system evolution from the initial non-equilibrium condition toward uniform equilibrium with $T = (T_1 + T_2)/2$.

Fig. 2 shows the time evolution of the initial step-like temperature profile with $\Delta T(0) = 200$ K generated across a graphene sample with $L_z = 503.2$ nm; while the smooth lines represent the formal solutions of the Fourier equation, the noisy lines represent the direct MD calculation of the local temperature, during a microcanonical run. The local temperature $T(z,t)$ was calculated on a thin slab centered at z with thickness 20.1 nm. We remark that no educated guess nor approximation has been adopted for the MD simulations, during which the time evolution of the initial temperature profile is straightforwardly calculated on-the-flight. Therefore, the excellent agreement between the formal solution of the Fourier equation (full black lines) and the MD data stands for the validity of the former even in the nanoscale system here investigated.

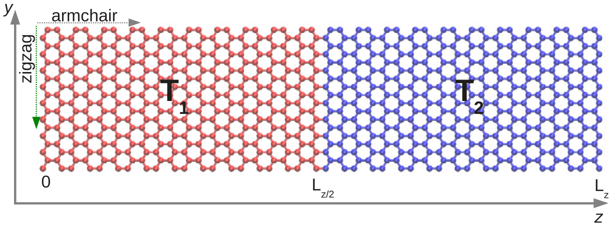

Fig. 1 – Stick and ball representation of a typical simulation cell: the left (right) region is initially set at temperature T_1 (T_2), with $T_1 > T_2$. (A colour version of this figure can be viewed online.)

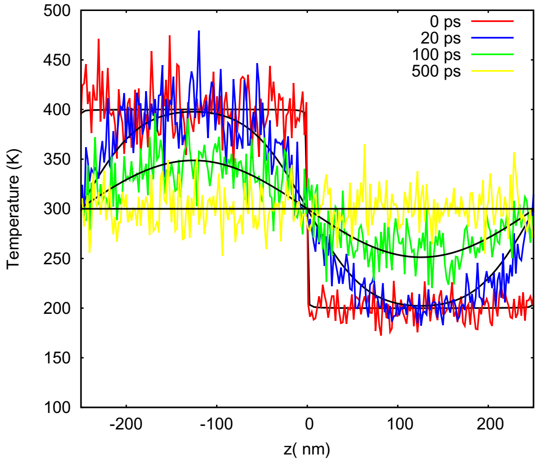

Fig. 2 – Time evolution of the temperature profile across a graphene sample with $L_z = 503.2$ nm and $L_y = 4.6$ nm as obtained by solving analytically the Fourier equation (smooth black lines) and by direct MD calculation of local temperature (noisy color lines). (A colour version of this figure can be viewed online.)

During the transient toward equilibrium the time-dependent difference $\Delta T(t)$ between the average temperature in the right and left regions is given by

$$\Delta T(t) = \sum_{n=1}^{\infty} C_n e^{-\alpha_n^2 \bar{\kappa} t} \tag{1}$$

where $\bar{\kappa}$ is thermal diffusivity, $\alpha_n = \frac{2\pi n}{L_z}$, L_z the length of the simulation cell and

$$C_n = 8(T_1 - T_2)[\cos(\alpha_n L_z/2) - 1]^2/\alpha_n^2 L_z^2 \tag{2}$$