Mechanisms governing phonon scattering by topological defects in graphene nanoribbons

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Abstract
Understanding phonon scattering by topological defects in graphene is of particular interest for thermal management in graphene-based devices. We present a study that quantifies the roles of the different mechanisms governing defect phonon scattering by comparing the effects of ten different defect structures using molecular dynamics. Our results show that phonon scattering is mainly influenced by mass density difference, with general trends governed by the defect formation energy and typical softening behaviors in the phonon density of state. The phonon scattering cross-section is found to be far larger than that geometrically occupied by the defects. We also show that the lattice thermal conductivity can be reduced by a factor of up to ~30 in the presence of the grain boundaries formed by these defects.

Keywords: thermal transport, graphene, defect, phonon scattering

(Some figures may appear in colour only in the online journal)

1. Introduction

Accurate heat flow manipulation is a fundamental challenge for many graphene-based devices, including electronic devices and nanoelectromechanical systems (NEMS) [1, 2]. Recent experiments showed that the existence of topological defects [3–5] exhibits a significant influence on the thermal transport properties of graphene [6–14], and they are thus a possible means to control graphene’s thermal conduction through nanostucturing [3–5, 15]. For instance, Haskins et al proposed to control graphene’s thermal and electrical transport by introducing vacancy and Stone–Wales (SW) defects into graphene nanoribbons (GNRs) [16]. Ng et al reported that SW defects can decrease graphene’s thermal conductivity by more than 50% [17]. The results of Tan and co-workers showed that the SW defect effect on thermal conduction in armchair-oriented GNRs is stronger than that in zigzag-oriented GNRs [18]. Hao et al further studied the dependence of thermal conductivity upon the SW defect concentration [19].

Although the above results are revealing, most recent studies have been confined to one or two types of typical lattice defect, such as the SW, and there has not been a comprehensive comparison between the different types of defect; consequently, our understanding of the fundamental mechanisms governing phonon scattering by graphene topological defects remains fragmented. On the other hand, the structures of graphene lattice defects may vary considerably...
For instance, experimentalists have shown evidence for C-8 rings in graphene\cite{21}. The existence of thermally stable point vacancies in graphene was also reported by a high-resolution transmission electron microscopy study\cite{3}. The conditions for these defects are not yet clear, despite their potential importance for graphene’s electronic and thermal transport properties.

2. Method

It is crucial to understand the conditions that lead to different types of lattice defects and the correlation between the defects’ physical properties and graphene thermal conductivity. Here we search for possible atomistic configurations of lattice defects synthesized via different annealing processes, and calculate their influence on the graphene lattice thermal conductivity using molecular dynamics. In our simulations, defects are inserted into GNRs by either removing atoms or rotating neighboring C–C bonds in the honeycomb lattice, as shown in figure 1. Molecular dynamics (MD) are then performed to find the stable atomistic configurations of the defective GNRs\cite{22–24}. We use the free boundary condition in three orthogonal directions. The system is relaxed at different temperatures for 0.5 ns with zero pressure using a Nosé–Hoover thermostat, before a stabilized configuration can be recorded. The inter-atomic potential used in our MD is the adaptive intermolecular reactive empirical bond-order hydrocarbon (AIREBO) model, in which the total inter-atomic energy is a collection of that of the individual bonds\cite{25}. Many-body effects are explicitly included by introducing a bond-order function, in which the influences of the bond angle, bond conjugation and atomic dihedral angle are taken into account. This approach showed accuracy in describing the interactions between \(sp^2\) carbon atoms in our previous studies\cite{22, 23}.

The lattice thermal conductivity of defective GNRs is calculated by non-equilibrium molecular dynamics (NEMD), in which a temperature difference is imposed between the two fixed edges of a suspended GNR. The temperature gradient \(\Delta T\), as well as the heat current \(J\), are recorded in an analogous way to the typical experimental setup for measuring thermal conductivity, which is defined by Fourier’s law, \(\kappa = J/l\Delta T w t\), where \(l\) and \(w\) stand respectively for the length and width of thermal conduction part, and a value of 0.335 nm is assigned to \(t\) as the inter-planar spacing of graphite stacking. Our NEMD simulations consist of three steps: a Berendsen thermostat is used to help the system reach equilibrium at room temperature in the first simulation phase; the temperature in the heat source and sink is then controlled to reach the settled values (320 and 280 K respectively); and the GNR center progressively reaches a steady state in \(10^6\) simulation steps. The measured quantities are averaged over the third step of a further \(10^6\) steps. Note that we do not fix the
ribbon in the direction normal to the graphene plane to get closer to real graphene; the ribbon geometry is thus not perfectly flat, but has some distortion to the third dimension. One to five randomly placed defects per GNR are considered in the calculation with the zigzag edge geometry along the direction of the heat flow.

3. Results and discussion

Since graphene grows through very high temperature in its typical synthesis process, we simulate several different structures of defective graphene at 1000 K and 2000 K before cooling down to room temperature. The ribbon width is set large enough (20 nm) to reduce the edge effects. Our results show that most point vacancies are relatively stable at about 1000 K (figures 1(a)–(g)), while reform to other more stable structures at above 2000 K. This is consistent with the high-resolution transmission electronic microscopy observation reported by Hashimoto and co-worker [3]. Figures 1(h)–(j) also show that the well-known SW defects are indeed the most energetically favorable structures formed by the bond rotation, in agreement with the previous suggestions of Meyer and co-workers [4]. Furthermore, the 5–8–5 carbon ring defect structures formed through the reconstruction of di-vacancy (figures 1(b)–(d)) are also consistent with those previously reported [26]. We note that this structure exhibits a significant distortion to the direction normal to the graphene plane. Since hybridization of the π orbital is supposed to be markedly modified by such large lattice distortions, important changes to the electronic properties can be expected [27]. This effect will be particularly important in multi-layered graphene, due to modified van der Waals interactions and the possibility of spontaneously formed covalent bonds with neighboring layers via thermal fluctuation [28].

Physically speaking, there should be three major dependences for phonon scattering by lattice defects: (1) the local bonding energy/force change; (2) the mass difference caused by replacing or removing atoms; and (3) the defective cross-section area or width normal to the heat flow. We first plot the lattice thermal conductivity as a function of the atomic bonding energy density (ρ) in figure 2, in which an inverse proportionality can be clearly seen. We find that the group of defects formed by bond rotation exhibit a different dependence than the defects formed by point vacancies. This suggests that the mass density difference plays an important role along with the local energy change, while the effect of the cross-section area is not as significant as the above-mentioned mechanisms. No significant difference is found between the defect structures annealed at two different temperatures. The e1, g1, j1 (or e2, g2, j2) defects are found to reduce thermal conductivity the most, far beyond the limit of typical SW defects.

To further understand the defect effect on phonon transport, we compute the phonon density of state (PDOS) for each type of the above-mentioned defects as shown in figure 3. It can be seen that, compared with pristine graphene, the phonon spectra of defective graphene structures show a trend to shift towards higher frequencies. We note that defect-related spatially localized modes can be excited thermally or optically depending on their intrinsic frequency. This could lead to the localization of phonons, i.e. so-called phonon trapping [29]. The phonon modes around 18 THz and 55 THz are broadened when the lattice defects are introduced. These indicate typical phonon softening behavior. We note that PDOS shifts towards higher frequencies are commonly observed for strained systems [30]. The physical basis for this phenomenon was provided in previous studies: as the atomic bonds become shorter and stiffer around the defects region, this causes the corresponding vibrational modes to shift to higher frequencies [31]. The broadening of the PDOS peaks originates from the structural disorder from defects, which leads to a reduction of the phonon lifetime of the corresponding modes. Therefore, the mean free path of these modes as well as their contributions to the total thermal conductivity decrease [32–36].

The ribbon geometry boundary filters part of the phonons in a specific frequency range, depending on the boundary dimensions and roughness [37], while the defects have different preferences for the selection of phonons to scatter, as shown in this work. When these two effects take place together, there must be combinations of them for efficient or invalid phonon scattering, with respect to the contributions to the total thermal conductivity from phonons of different frequencies.

To show a quantitative correlation between the defect concentration and the thermal conductivity, in figure 4 we plot the thermal conductivity ratio of the different defects as a function of the defect concentration. We see that κ/κ0 exhibits an exponential-like decay at increasing defect number, and this is in agreement with the results reported by Hao and co-workers [19]. Similar thermal conductivity variation trends with respect to defect concentration were also reported previously [38–40]. It should be mentioned that our simulations may not provide the accurate absolute value of the graphene thermal conductivity since the sample size is far smaller than the phonon mean free path in graphene [41].
The lattice defects can connect with each other to form line defects, which are widely distributed as grain boundaries in graphene synthesized through chemical vapor deposition. Given their importance, we extended our NEMD simulations on a narrow GNR with aligned 5-8-5 defects placed at the ribbon center. Our results in figure 5 show a sharp temperature decrease crossing the line defects, resulting in an extremely high thermal resistance \([42]\). The thermal conductivity was reduced by a factor of about 29.7. It should be mentioned that the model provided by \([43]\) is also interesting for smaller systems based on first-principles calculations. Due to the unavoidable quantum effects in small systems, they cannot be described correctly in classical molecular dynamics. We note that, theoretically speaking, the sharp jump in the temperature profile should be weakened if the ribbon becomes smaller, due to the corresponding

Figure 3. Phonon density of state for the lattice defects shown in figure 1 annealed at 2000 K.
decrease of the phonon mean free path \[35\]. However, this effect should not be significant in our case since the phonon mean free path is supposed to be much larger than the ribbon’s longitudinal dimension.

To illustrate the similarities and differences between the heat flow in graphene with defect phonon scattering and fluid flow passing an obstacle, in figure 6 we depict the thermal energy distribution in GNRs with three different lattice defects. We see that the thermal energy distribution at most parts of the GNR surface is modified with a surface area much larger than that geometrically occupied by the lattice defect. This is because phonons reflected by the defect collide further with phonons propagating in other directions, and finally form a large scattering pattern. In comparison, we see that the C-5-7-5-7-5-8-5 rings scatter the least with phonons (figure 6(b)), and give the most homogeneous heat distribution. With the highest energy and distortion to the third dimension, the C-5-8-5-7-4-7 rings exhibit the strongest phonon scattering, and generate a high-temperature spot (figure 6(a)). The phonon scattering surface from this defect is particularly large, with the thermal energy distribution modified markedly at more than half of the GNR surface. The C-7-5-5-7-5-8-5 rings exhibit the largest distorted surface area in figure 6(c), creating the broadest phonon scattering region near the heat source. We note that the distance between the edges and the defects could play an important role in changing the mean free path of phonons, which would further impact on the thermal conductivity \[44\].

4. Summary

By simulating phonon scattering in GNRs with ten different defect structures, we showed that the local formation energy gradient is the key to reducing the thermal conductivity, while the mass density difference also plays a leading role. Phonon density of state analyses show a typical phonon softening behavior induced by the topological defects. Our results also show that the lattice thermal conductivity can be reduced by a factor of up to \(~30\) in the presence of grain boundaries. The scattering pattern is found to be far larger than the space geometrically occupied by the defects. The existence of these lattice defects, including C-5, C-7, and C-8 rings, can also be expected to explain the experimentally measured thermal conductivities that are lower than the ballistic limit \[41, 45\], and may also suggest new avenues of graphene microscopy research for experiments.
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