Phononic thermal transport along graphene grain boundaries

Zhen Tong, Alessandro Pecchia, ChiYung Yam, Traian Dumitrica, and Thomas Frauenheim

1 Shenzhen JL Computational Science and Applied Research Institute, Shenzhen 518131, China.
2 CNR-ISMN, Via Salaria km 29.300, Monterotondo 00017, Rome, Italy
3 Beijing Computational Science Research Center, Beijing 100193, China
4 Department of Mechanical Engineering, University of Minnesota, Minnesota 55455, United States of America
5 Bremen Center for Computational Materials Science, University of Bremen, Bremen 2835, Germany

We reveal that phononic thermal transport in graphene is not immune to grain boundaries (GBs) aligned along the direction of the temperature gradient. Non-equilibrium molecular dynamics simulations uncover a large reductions in the phononic thermal conductivity ($\kappa_p$) along linear ultra-narrow GBs comprising periodically-repeating pentagon-heptagon dislocations. Green’s function calculations and spectral energy density analysis indicate that $\kappa_p$ is the complex manifestation of the periodic strain field, which behaves as a reflective diffraction grating with both diffuse and specular phonon reflections, and represents a source of anharmonic phonon-phonon scattering. Our findings provide new insights into the integrity of the phononic thermal transport in GB graphene.

Next generation of high-performance electronics and sensors require materials with high thermal conductivity able to spread effectively the high density of Joule heat generation along and across various thin films and substrates [1, 2]. Two-dimensional materials like graphene [3] are very attractive for these applications as they are relatively immune to detrimental size effects on basal-plane thermal conductivity. This is because the highly anisotropic phonon group velocity reduces the impact of scattering by the top and bottom surfaces [4, 5]. Nevertheless, thermal transport is significantly impacted [6] by the defects occurring during synthesis. In this respect, the widely-used chemical vapor deposition (CVD) [7] unavoidably produces grain boundaries (GBs). As domains nucleate randomly on substrates, their CVD growth and coalesce result in formation of GBs [8–11].

GBs are imagined as periodic arrays of dislocations [12]. In graphene, GBs are strings of pentagon-heptagon (5-7) edge dislocations [9, 13–15] and their organization can give rise to diverse GB shapes. While in general the thermal gradient can have an arbitrary orientation with respect to the GB line [16, 17], only transport across GBs is perceived to significantly impact $\kappa_p$. Green’s function (GF) calculations [18, 19] obtained that heat transmission across the GB can be significantly influenced by the GB structure, size, and shape. Non-equilibrium molecular dynamics (NEMD) simulations [20–22] revealed a discontinuity in the temperature ($T$) profile across GBs and that higher dislocation densities lead to lower $\kappa_p$.

In this Letter, we reveal that thermal transport is not immune to GBs oriented along the thermal gradient. By way of NEMD simulations with LAMMPS [23], we report $\kappa_p$ reduction along GBs with various 5-7 dislocation densities and length scales $L$ covering ballistic and diffusive transport, in systems of up to 59,0512 carbon (C) atoms treated with the optimized Tersoff potential [24]. To gain a clear understanding, we also conducted GF calculations of phononic transmission and conductance, and spectral energy density (SED) calculations to quantify phonon relaxation times. The uncovered $\kappa_p$ behavior with a non-monotonic dependence on 5-7 defect density is unaccounted for by the classical Klemens theory [6].

The NEMD setup is presented in Fig. 1(a). Two-unit
cells at each end were kept fixed throughout simulation and ten other neighboring unit cells were designated as “hot” and “cold” baths maintained at the temperatures $T_h=310 \text{ K}$ and $T_c=290 \text{ K}$, respectively. At steady-state, the heat flux $\dot{Q}$ was calculated as the difference of the rate of the kinetic energy extraction from the two reservoirs $\dot{Q} = 0.5<Q_h-Q_c>$, where $Q_h$ and $Q_c$ are the instantaneous heat currents flowing into and away from the “hot” and “cold” baths. The angular brackets indicate a statistical average taken after the steady state was reached. Graphene edges [25] can significantly impact thermal transport [16]. The application of periodic boundary conditions along $y$ eliminates the lateral edges and allows for the simulation of the thermal transport perpendicular to a single GB line and along antiparallel GB lines (i.e., the 5-7 defect lines run parallel to each other but with opposite directionality) separated by the lateral periodicity $W$. Therefore, differences in calculated $T$ profiles, Fig. 1(b), can be attributed solely to GBs.

The NEMD calculations of Fig. 1(b) at $L = 400 \text{ nm}$ and $W = 15.5 \text{ nm}$ reveal a stark difference in the $T$ profiles across and along the considered GBs, which comprises aligned 5-7 defects separated by one hexagonal ring. In agreement with Azizi et al. [22], there is a sharp temperature drop $\Delta T = 2.2 \text{ K}$, corresponding to a thermal resistance $\Delta T/\dot{q}$ of 0.035 K m$^2$/GW across this GB. Here $\dot{q}$ is $\dot{Q}$ per cross-sectional area (defined here based on the 0.33 nm thickness of graphene [26, 27]). Nevertheless, along the GB line, the $T$ profile is smooth and resembles the one obtained for the pristine graphene. By thermal symmetry, the GB lines oriented along the heat flow are adiabatic lines. If heat transfer was purely one-dimensional, then $\kappa_p$ would hardly be impacted along GBs. Nevertheless, the extracted $\kappa_p = -\dot{q}(dT/dx)$, reveal a nearly 50% reduction (633.2 W/mK vs. 1,259.4 W/mK) demonstrating that through the two-dimensionality of the heat transport $\kappa_p$ is significantly impacted even by such linear ultra-narrow GBs.

We have checked the robustness of our result by extensive NEMD, see Fig. S2(b), which considered symmetric tilt GB systems with similar widths $W$ but different $L$ and spread out linear arrangements of the 5-7 defects, which decrease the tilt angles $\theta$ [28] formed by the crystallographic directions of the neighboring domains, Fig. 2(a). Additionally, a 5-7 pair introduces local off-plane

![FIG. 2: (a) The top and side views of 6 considered GBs with different $\theta$. (b) Bird’s eye view along two GB lines.](image)

![FIG. 3: NEMD computed (a) $\kappa_p$ vs. $L$ at 300 K in graphene and along GBs with different $\theta$. (b) $\kappa_p$ vs. $\theta$ for different $L$. The inset shows the 5-7 density vs. $\theta$.](image)
elevations [29] as a way of reliving the strain stored in the dislocation core. The resulting “bumpy” landscape with a rather blazed profile is visible in Fig. 2(b) for the $\theta=4.41^\circ$ GB. On the same figure, it can be also seen that the C-C bond extension and compression deformations are strongly localized around the 5-7 cores. The off-plane displacement are opposite in neighboring GB lines, such stable ripple structures are formed. As shown in the side views of Fig. 2(a), the ripples acquire significant amplitudes of 15±1.5 Å. Only for $\theta=21.78^\circ$, the closeness of the 5-7 cores inhibits their off-plane displacements reducing the ripple amplitude to only 4.17 Å. For this case, the C-C bond deformations are continuous along the GB line, Fig. 2(b). Overall, in all of the rippled structures of Fig. 2 found by energy minimizations, the C-C bonds away from the GB lines are undeformed; the axial prestrain is also very small; it varies monotonically with $\theta$, from -0.2 % ($\theta=4.41^\circ$) to 0.1 % ($\theta=21.78^\circ$), see Fig. S1(b).

Figure 3(a) demonstrates that the differences between $\kappa_p$ in pristine ($\theta=0$) [30, 31] and along GBs with different $\theta$ remain significant at different $L$. In the pristine case, the initial linear increase of $\kappa_p$ ($L<100$ nm) is a signature of pure ballistic behavior, while the subsequent lowering of the rate of increase in $\kappa_p$ at $L \sim 100$ nm signals that the thermal transport enters into a diffusive regime. $\kappa_p$ is expected to increase in a logarithmically divergent manner at much larger than the average phonon mean free path ($\sim 775$ nm at $T = 300$ K) [30, 31]. Along GBs, $\kappa_p$ initially increases with a smaller slope than in the pristine case. At larger $L$, $\kappa_p$ becomes convergent at $L \sim 400$ nm when the diffusive regime sets in. At the largest considered $L=1 \mu$m, the $\kappa_p$ reduction is of ~60% or larger with respect to the pristine case. While the dislocation density increases with $\theta$, $\kappa_p$ displays non-monotonic variations, which are more pronounced for $L > 100$ nm, Fig. 3(b): $\kappa_p$ decreases from $\theta=4.41^\circ$ up to $\theta=13.18^\circ$ but presents an anomalous enhancement at $\theta=21.78^\circ$, where the 5-7 density is largest.

To gain insight into the mechanism of $\kappa_p$ reduction, we have pursued complementary GF investigations. As in NEMD, we have partitioned the system into “hot” bath, device region, and “cold” bath, Fig. 1(a), such as the GB lines extend in all regions. The dynamical matrix $D$ was computed using the same optimized Tersoff potential [24] with a finite difference scheme of the atomic forces, not accounting for finite temperature phonon softening effects owing to anharmonicity. We computed the ballistic transport for $\theta=4.41^\circ$, $13.18^\circ$ and $21.78^\circ$ and compared them to the pristine graphene. The conductance $g$ is evaluated within the Landauer approach in terms of the transmission coefficient, $t_p(\omega)$, [32]

$$g = \frac{\hbar^2}{2\pi k_B T^2} \int \omega^2 \frac{e^\frac{e\hbar\omega}{k_BT}}{(e^\frac{e\hbar\omega}{k_BT} - 1)^2} t_p(\omega) d\omega,$$

where $k_B$ and $\hbar = \hbar/2\pi$ are the Boltzmann and the Planck constants, respectively. $t_p(\omega)$, in turn, is computed [33] based on $D$, as $t_p = T[G^\prime G^\ast \Sigma + \Sigma^\ast G^\prime T]$. The retarded GF is given by $G^\prime(\omega) = [\omega^2 - D - \Sigma^\ast - \Sigma]^{-1}$ and $\Sigma$ are the broadening functions, $\Gamma_L/R = i[\Sigma_L/R - \Sigma^\ast_L/R]$, for the “hot” and “cold” contacts.

At $L = 10$ nm considered here, transport is coherent and influenced by the elastic scattering onto the GBs. Plots of $t_p(\omega)$ at different $\theta$ are shown in Fig. 4(a). Consistent with NEMD, $t_p$ in pristine graphene is higher than in GBs and yields a higher $g$ value, Fig. 4(b). The conductance is ballistic as reflected in the integer values of $t_p$, depending on the number of phonon states at each $\omega$. Surprisingly, the $t_p(\omega)$ reduction by GBs is inversely proportional to the 5-7 density (i.e., $t_p$ is largest for $\theta=21.78^\circ$ and smallest for $\theta=4.41^\circ$). This dependence uncovers the strain field periodicity effect, which operates as a diffraction grating onto the traveling phonons. Through elastic scattering on the strain around the 5-7 cores, reflective diffraction spectra of various orders take place. One one hand, for $\theta=21.78^\circ$, strain is continuous along the GB line, Fig. 2(b). Diffraction is dominated by the zero-order, which is associated with a specular reflection and larger group velocity. On the other hand, for $\theta=4.41^\circ$ GB which has lowest $g$, the 5-7 defects are ~3.2 nm apart. Destructive interferences introduce stronger phonon localization, which is associated to diffuse reflections and manifests into important thermal resistivity contributions. These important higher diffraction orders
are not considered by Klemens [6, 34]. This situation reminds of the $\kappa_p$ reduction along central screw dislocations located in nanowires [35, 36], an effect also not captured by the classical theory [6]. By introducing periodic nanoscale grooves onto the nanowire surface [37], $\kappa_p$ could be further reduced through localization of the phonons that were specularly reflected by the dislocation core.

In summary, the GF calculations obtained that the resistive contributions caused by the diffuse GB reflection scale inversely with the defect density. The $g$ reductions are seen also in the inset of Fig. 4(b), which shows $g_{GB}/g_{pristine}$ as a function of $T$, with $g_{GB}$ and $g_{pristine}$ being $g$ for a given GB and graphene pristine, respectively.

As transport advances into the diffusive regime, the decay of heat carrying phonons by inelastic scatterings becomes increasingly important. Recalling that in a phonon gas model, thermal conductivity is $\kappa_p = \sum \lambda c_\lambda v_\lambda^2 \tau_\lambda$, where $c_\lambda$, $v_\lambda$, and $\tau_\lambda$ are the specific heat capacity, phonon group velocity, and phonon relaxation time of phonon mode $\lambda$, respectively. Figure 5(a) shows $\tau_\lambda$, as calculated by SED scheme [35, 38] and room-temperature equilibrium MD runs. When compared to pristine graphene, GBs lead to significant $\tau_\lambda$ reductions. For the “bumpy” GBs, $\tau_\lambda$ decreases with the increase in defect density. This dependence is opposite to the one for the ballistic phonon transmission delineated above, and explains the crossover in $\kappa_p$ as transport advances into the diffusive regime. However, for $\theta = 21.78^\circ$ GB, where $t_p$ is largest compared to other GBs, we also find the largest $\tau_\lambda$ in Fig. 5(a). This concerted behavior explains the consistently larger $\kappa_p$ values for $\theta = 21.78^\circ$ GB with respect to the other considered GBs, Fig. 3(b). The key role of $\tau_\lambda$ is further supported in Fig. 5(b) by the lattice dynamics [39] computed $v_\lambda$, which is another key contributor to $\kappa_p$. While for some phonon modes $v_\lambda$ decreases in $\theta = 21.78^\circ$ GB, it remains unchanged for the acoustic phonon modes, which are playing a main role in thermal conduction. Therefore, the weaker phonon scattering in $\theta = 21.78^\circ$ GB (as reflected by the larger $\tau_\lambda$) and not an enhancement of $v_\lambda$ is the mechanism behind the anomalous $\kappa_p$ behavior. We associate the weaker anharmonic scattering presented in $\theta = 21.78^\circ$ GB to the flatter landscape along the GB line. The 5-7 off-plane distortions at the other GBs are enhancing anharmonic scattering as they locally couple the in-plane and out-of-plane degrees of freedom [19], which are otherwise decoupled [40].

In conclusion, we uncovered that through the two-dimensionality of the heat transfer, $\kappa_p$ along linear ultranarrow GBs is significantly affected. The explanation for the $\kappa_p$ reduction with the defect density goes beyond the simple phonon specular reflection accounted for by Klemens [6, 34]. $\kappa_p$ along GB with 21.78° is largest, which is opposed to the expected deterioration of thermal transport at larger dislocation density [19]. The $\kappa_p$ boost is caused by a diffraction grating effect of the GB strain field periodicity, which leads to a specular scatter-

![FIG. 5: MD calculated (a) phonon relaxation times and (b) phonon group velocity in pristine and GB graphene.](image-url)

**SUPPLEMENTARY MATERIAL**

Details on information of GBs, NEMD simulations, SED calculations, phonon transmission.

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* Electronic address: dtraian@umn.edu

† Electronic address: thomas.frauenheim@bccms.uni-bremen.de

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