Edge currents and nanopore arrays in zigzag and chiral graphene nanoribbons as a route toward high-$ZT$ thermoelectrics

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We analyze electronic and phononic quantum transport in zigzag or chiral graphene nanoribbons (GNRs) perforated with an array of nanopores. Since local charge current profiles in these GNRs are peaked around their edges, drilling nanopores in their interior does not affect edge charge currents while drastically reducing the phonon heat current in sufficiently long wires. The combination of these two effects can yield highly efficient thermoelectric devices with maximum figure of merit $ZT \approx 5$, at both liquid nitrogen and room temperature, achieved in long zigzag GNRs with nanopores of variable diameter and spacing between them. Our analysis is based on the nonequilibrium Green’s function formalism combined with the $\pi$-orbital tight-binding Hamiltonian including up to third-nearest-neighbor hopping for an electronic subsystem, or with an empirical fifth-nearest-neighbor force-constant (5NNFC) model for a phononic subsystem. Additionally, we demonstrate that different empirical FC models typically overestimate the phonon conductance when compared to first-principles results.

The recent explosion of research on graphene—a one-atom-thick allotrope of carbon—has been largely focused on its unique electronic structure and transport properties governed by a two-dimensional honeycomb lattice of carbon atoms. Very recently, the exploration of its thermal and thermoelectric properties has been initiated by measuring the thermopower and phonon thermal conductivity of large-area graphene. The measured values of $S \approx 100 \, \mu V/K$ near the Dirac point (DP), as well as the room-temperature $K_{ph} \approx 4000 \, W/mK$ (averaged over values obtained using different samples and experimental techniques) which outperforms virtually all other known materials, point out that large-area graphene is not suitable for thermoelectric applications.

Thermoelectrics transforms temperature gradients into electric voltage and vice versa. Although a plethora of other known materials, point out that large-area graphene is not suitable for thermoelectric applications.

The total thermal conductance has contributions from both electrons $\kappa_{el}$ and phonons $\kappa_{ph}$. The devices with $ZT > 1$ are regarded as good thermoelectrics, but values of $ZT > 3$ are required for thermoelectric devices to compete in efficiency with conventional power generators and refrigerators. Finding thermoelectrics with $ZT \approx 2$–3 that are stable over a broad temperature range and with low parasitic losses is presently considered as a realistic goal.

Thus, a number of proposals have been put forth to evade the problem of high lattice thermal conductivity of large-area graphene that could open a pathway for its thermoelectric application. For example, large-area graphene could reach $ZT \approx 0.3$ if perforated by the so-called antidot lattice that is tailored to impede phonon propagation. Switching to quasi-one-dimensional graphene nanoribbons (GNRs) makes further enhancement of $ZT$ possible, where it has been predicted that long (~1 $\mu$m) GNRs with zigzag edges and disorder introduced around the edges by removing carbon atoms could reach $ZT \approx 4$ at room temperature. Another route is to engineer structural defects in GNRs that can block phonons while retaining quasiballistic electronic transport.

However, it is more advantageous to search for high-$ZT$ devices among nanowires with well-defined edges since edge or surface disorder can significantly affect electronic conductance. For example, the experiments on etched GNRs with rough edges find Coulomb blockade effects (not taken into account in Ref. 6) and a transport gap that is much larger than the band gap.

In this Rapid Communication, we exploit the peculiar electronic transport properties of GNRs with zigzag (ZGNR) or chiral (CGNR) edges, as illustrated in Fig. 1, where the local charge current density carried by quasiparticles sufficiently close to the DP is peaked around the nanoribbon edges, as demonstrated in Figs. 2(b) and 2(d). Thus, drilling nanopores in the ZGNR or CGNR interior will not substantially modify such “edge currents.” This is confirmed in Fig. 2 by using spatial profiles of the bond currents, as well as by the transmission function in Figs. 3(a) and 3(c), which is reduced from $T_{0}(E) = 3$ in infinite homogeneous GNRs to $T_{0}(E) \approx 2$ around the DP for both ZGNR and CGNR with an array of nanopores. Furthermore, $T_{0}(E)$ around the DP does not change as one increases the length of GNRs because “edge currents” propagate quasiballistically.

The nanopore arrays have been explored before in bulk thermoelectric materials. Furthermore, their fabrication in graphene has been pursued recently by a variety of experimental techniques. Since they break homogeneity of the nanowire, they can substantially impede the propagation of phonons in sufficiently long GNRs. This is corroborated by our results for the phonon transmission function in Figs. 4(a) and 4(c) and the corresponding lattice thermal conductance in Figs. 4(b) and 4(d). The ZGNR and CGNR length is chosen as $L \gtrsim 1.2 \, \mu$m, which is close to the limit beyond which a further increase of $L$ does not reduce $\kappa_{ph}$ significantly. The number of nanopores hosted by GNRs of these lengths is 300.
FIG. 1. (Color online) Schematic view of (a) 20-ZGNR (composed of 20 zigzag chains) and (b) (8,1)-CGNR with a chiral angle $\theta = 5.8^\circ$. The size of the nanopores, assumed to be drilled in the GNR interior away from its zigzag or chiral edges, and the distance between them is illustrated by plotting two repeated supercells of each GNR. The length of these GNRs in the actual calculations is set to $L \simeq 1.2$ $\mu$m, which supports 300 nanopores.

Combining these two effects, we obtain maximum $ZT \simeq 4$ at $T = 77$ K and $ZT \simeq 2$ at $T = 300$ K in Fig. 5(a) for the case of 20-ZGNR, whose identical nanopores are arranged in a periodic array. The values of $ZT$ for (8,1)-CGNR with a periodic array of nanopores are lower, as shown in Fig. 5(c).

In realistic GNR-based devices, it may be challenging to control the pore arrangement to a high precision as assumed in Fig. 1. Therefore, in Figs. 5(b) and 5(d) we assume that the pore diameter $D$ is a uniform random variable, such as $D \in [9 d_{AB}, 15 d_{AB}]$ for pores in 20-ZGNR or $D \in [3 d_{AB}, 7 d_{AB}]$ for pores in (8,1)-CGNR, as well as that the position of

FIG. 2. (Color online) Spatial profiles of local charge currents in (a) 20-ZGNR and (c) (8,1)-CGNR with nanopores for electronic transport close ($E_F = -0.43$ eV) to the DP. The corresponding current profiles over the transverse cross section of nanoribbons are shown in (b) and (d) for both infinite homogeneous GNRs and GNRs with nanopores. Note that the sum of bond currents (Ref. 15) $J_{nm}/V$, which describe charge flow from site $n$ to site $m$ of the honeycomb lattice if hopping $t_{nm} \neq 0$ is nonzero between the two sites, gives the conductance $G = I/V$ ($I$ is the total current in the leads and $V \to 0$ is small bias voltage driving the linear-response transport).

FIG. 3. (Color online) The zero-bias electronic transmission $T_{el}(E)$ for (a) infinite homogeneous 20-ZGNR or finite length 20-ZGNR with a periodic array of identical nanopores shown in Fig. 1(a), and (c) infinite homogeneous (8,1)-CGNR or finite length (8,1)-CGNR with a periodic array of identical nanopores shown in Fig. 1(b). (b) and (d) show the thermopower at two different temperatures corresponding to finite length 20-ZGNR with nanopores in (a) or finite length (8,1)-CGNR with nanopores in (c), respectively.

FIG. 4. (Color online) (a) The phonon transmission function $T_{ph}(\omega)$ and (b) the corresponding phonon thermal conductance $\kappa_{ph}$ for an infinite homogeneous 20-ZGNR or 20-ZGNR with a periodic array of identical nanopores shown in Fig. 1(a). (c) The phonon transmission function and (d) the corresponding phonon thermal conductance $\kappa_{ph}$ for an infinite homogeneous (8,1)-CGNR or (8,1)-CGNR with a periodic array of identical nanopores shown in Fig. 1(b).
the nanopores is shifted randomly by $\Delta x \in [-2 d_{AB}, 2 d_{AB}]$ in 20-ZGNR or $\Delta x \in [-0.5 d_{AB}, 0.5 d_{AB}]$ in (8,1)-CGNR, where $d_{AB} \approx 0.142$ nm is the C-C bond length. This yields a maximum value of $ZT \approx 5$ in our study, at both $T = 77$ and $300$ K, as shown in Fig. 5(b).

In the rest of this Rapid Communication we explain the details of our models for electronic and phononic subsystems, which are coupled to the nonequilibrium Green’s function formalism (NEGF) to treat their elastic quantum transport. Early theoretical studies of ZGNR-based devices have utilized a simplistic tight-binding model (TBM) with a single $\pi$ orbital per site and nearest-neighbor hopping only, or its long-wavelength (continuum) approximation—the Dirac-Weyl Hamiltonian—which is valid close to the DP. However, both of these models predict that the transmission function of an infinite homogeneous ZGNR is $T_\text{el} = 1$ around the DP and that the current density profile is peaked in the middle of ZGNR (even though the local density of states reaches a maximum around the edges). This contradicts first-principles calculations, or TBM with up to third-nearest-neighbor hopping parameters fitted to such first-principles calculations, which predict $T_\text{el} \approx 3$ around the DP, as well as that the local current density is mostly confined to flow around the zigzag edges. It is worth mentioning that the majority of recent studies focused on the thermoelectric properties of ZGNRs with edge disorder or a finite length graphene antidot lattice have utilized the TBM with nearest-neighbor hopping, so that the possibility to exploit “edge currents” around zigzag or chiral edges for thermoelectric device applications has been overlooked.

Most importantly, recent experiments have confirmed the existence of “edge currents” in metallic ZGNRs by actually utilizing them to increase the heat dissipation around the edge defects and, thereby, rearranging the atomic structure locally until a sharply defined zigzag edge is achieved. Also, the very recent chemical synthesis of (8,1)-CGNRs via the carbon nanotube unzipping method has exhibited properties in subnanometer-resolved scanning tunneling microscopy and spectroscopy that can only be explained by the existence of smooth edges supporting edge quantum states (i.e., wave functions whose probability density is large around the edges). Although ZGNRs or CGNRs are insulating at very low temperatures due to one-dimensional spin-polarized edge states coupled across the width of the nanoribbon, such unusual magnetic ordering and the corresponding band gap is easily destroyed above $T > 10$ K.

We adopt the TBM with a single $\pi$-orbital per site,

$$\hat{H} = \sum_n \varepsilon_n c_n^\dagger c_n - \sum_{n,m} t_{nn}^{m} c_n^\dagger c_m + \varepsilon_0$$

(1)

to describe the electronic subsystem of 20-ZGNR and (8,1)-CGNR in Fig. 1. The operators $c_n$ ($c_n^\dagger$) create (annihilate) electrons in the $\pi$ orbital located on site $n$ of the honeycomb lattice whose lattice constant is $a \approx 0.246$ nm. For impurity-free GNRs assumed here, the on-site potential is set to zero $\varepsilon_n = 0$. We consider up to third-nearest-neighbor hopping parameters $t_{nn}^{0} = 2.7$ eV, $t_{nn}^{1} = t_{nn}^{2} = 0.2$ eV, and $t_{nn}^{3}$ eV—which describe the nearest-, next-nearest-, and next-next-nearest neighbor hopping, respectively. Since the honeycomb lattice of graphene is composed of two triangular sublattices $A$ and $B$, the parameters $t_{nn}^{0}$ and $t_{nn}^{1}$ describe intersublattice hopping, while $t_{nn}^{2}$ describes the intrasublattice hopping.

In realistic devices, the active region consisting of ZGNR or CGNR of finite length with nanopores will eventually need to be connected to metallic electrodes. However, since the GNR + nanopores devices we analyze are rather long, 86-210 nm, and screening takes place over a distance that is much shorter than the active region, it is justified to use semi-infinite homogeneous ZGNRs or CGNRs as leads for simplicity. In the elastic transport regime, where electron-phonon and phonon-phonon scattering can be neglected, independent electron and phonon transport quantities can be obtained from NEGF-based formulas, whose technical details can be found in Ref. 12. This methodology does not take into account the resistive umklapp phonon-phonon scattering which plays an important role in the interpretation of experiments on the room-temperature lattice thermal conductivity of large-area graphene. However, this effect, which is easy to describe using the Boltzmann equation but is very expensive computationally within the NEGF formalism, does not play an important role in GNRs depicted in Fig. 1 because their width is much smaller than the mean free path $\ell \approx 677$ nm due to phonon-phonon scattering in large-area graphene at room temperature.

The widely used methodology to compute $\kappa_{\text{ph}}$ of GNRs couples NEGF to empirical fourth-nearest-neighbor force-constant (4NNFC) or 5NNFC models. The parameters of the 4NNFC and 5NNFC models have been refined over the years to reproduce the newly acquired experimental data on the phonon dispersion of graphite, fit density functional theory (DFT) calculations for infinite graphene sheets, and satisfy the symmetry imposed conditions (such as rotational symmetry).
invariance\(^{25}\). However, direct application of these models to GNRs is not warranted since force constants on the edge carbon atoms will be modified when compared to those in their interior. While the resulting shift in the phonon density of states and the corresponding reduction of \(\kappa_{\text{ph}}\) are typically assumed to lead only to a minor improvement,\(^2\) here we explicitly compare \(\kappa_{\text{ph}}\) obtained from these models to first-principles calculations.

We also include the Brenner empirical interatomic potential\(^{27}\) (EIP), which offers much faster numerics than full DFT methodology while being able to match the DFT results for some device geometries.\(^{5,12}\)

The first-principles extraction of the FC matrix \(\mathbf{K}\) is performed via the GPAW package,\(^{28}\) which is a real space electronic structure code based on the projector augmented wave method.\(^{29}\) The electronic wave functions are expanded in atomic orbitals with a double-zeta polarized (DZP) basis set, and Perdew-Burke-Ernzerhof (PBE) parametrization of the generalized gradient approximation for the exchange-correlation functional is used. The whole active region, composed of a segment of 8-ZGNR with or without a nanopore and a few layers of the semi-infinite 8-ZGNR leads, is first relaxed to a maximum force of 0.01 eV/Å per atom. Subsequently, we displace each atom \(I\) by \(Q_{Ia}\) in the direction \(\alpha = [x, y, z]\) to get the forces \(F_{J\beta}(Q_{Ia})\) on atom \(J \neq I\) in direction \(\beta\). The elements of the \(\mathbf{K}\) matrix are then computed from finite differences \(K_{I\alpha, J\beta} = [F_{J\beta}(Q_{Ia}) - F_{J\beta}(-Q_{Ia})]/2Q_{Ia}\). The intra-atomic elements are calculated by imposing momentum conservation, such that \(K_{I\alpha, J\beta} = -\Sigma_{J\beta I} K_{I\alpha, J\beta}\). In the case of the Brenner EIP-based calculation, we initially relax the active region and then compute the force constant between atom \(I\) in direction \(\alpha\) and atom \(J\) in direction \(\beta\) using the analytical derivatives \(K_{I\alpha, J\beta} = \partial U / (\partial R_{I\alpha} \partial R_{J\beta})\), where \(U\) is the total energy. These calculations are also performed using the GPAW package.\(^{28}\)

Since calculations based on 4NNFC and 5NNFC models do not include passivation of edge carbon atoms (or hydrogen, for Brenner EIP-based analysis). This approximation is further justified by the first-principles results of Ref. \(30\), where ZGNRs with and without hydrogen passivation exhibit virtually the same \(\kappa_{\text{ph}}\) due to the fact that the edge C-C bonds are only slightly perturbed in the presence of hydrogen.

A comparison of different \(\kappa_{\text{ph}}\) values, computed by coupling NEGF to four different FC matrices in Fig. 6, shows that all three empirical models overestimate the phonon thermal conductance of 8-ZGNR + nanopore, as our testbed system containing small number of C atoms, when compared to the first-principles result. In the case of an infinite homogeneous ZGNR, Brenner EIP and DFT calculations yield virtually the same \(\kappa_{\text{ph}}\) in Fig. 6, while 4NNFC and 5NNFC models lead to an overestimation of this quantity. While the first-principles calculations of \(\kappa_{\text{ph}}\) are too expensive to be applied to our \(L \simeq 1.2 \mu\text{m}\) GNRs (that are also wider than the 8-ZGNR example used in Fig. 6), a comparison of different methods applied to a testbed system in Fig. 6 demonstrates that actual \(ZT\) or the proposed ZGNR and CGNR devices will be even higher than the one computed in Fig. 5 using the 5NNFC model.

In conclusion, we predicted that ZGNRs and CGNRs perforated by an array of nanopores in their interior could serve as the building blocks of highly efficient thermoelectric devices. This is due to the fact that local charge current density is peaked around their edges, as demonstrated explicitly by Fig. 2 and confirmed experimentally,\(^{19}\) so that nanopores do not impede such “edge currents” while drastically reducing phonon conduction in sufficiently long ZGNRs or CGNRs. In the case of a periodic array of identical nanopores, we find that the largest \(ZT\) \(\simeq 4\) at \(T = 77\, \text{K}\) and \(ZT \simeq 2\) at \(T = 300\, \text{K}\) can be reached by using ZGNR-based devices. On the other hand, if the pore diameter takes a random value within some interval and the distance between the pores is varied, then we find the possibility of an even higher figure of merit which can reach \(ZT \simeq 5\) all both \(T = 77\) and \(300\, \text{K}\) in the case of ZGNR + nanopores devices.

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