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Thermoelectric properties of graphene nanoribbons, junctions and superlattices

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Abstract
Using model interaction Hamiltonians for both electrons and phonons and Green’s function formalism for ballistic transport, we have studied the thermal conductance and the thermoelectric properties of graphene nanoribbons (GNR), GNR junctions and periodic superlattices. Among our findings we have established the role that interfaces play in determining the thermoelectric response of GNR systems both across single junctions and in periodic superlattices. In general, increasing the number of interfaces in a single GNR system increases the peak $ZT$ values that are thus maximized in a periodic superlattice. Moreover, we proved that the thermoelectric behavior is largely controlled by the width of the narrower component of the junction. Finally, we have demonstrated that chevron-type GNRs recently synthesized should display superior thermoelectric properties.

(Some figures in this article are in colour only in the electronic version)

Since their discovery in 2004 [1–3], the transport properties of graphene and graphene-derived nanostructures have been of great interest because of the potential uses of these systems in nanoelectronic devices [4–9]. However, only relatively recently have researchers begun to study the thermal properties of these systems, both for a better understanding of thermal management in devices [10] and for thermoelectric applications [11–14]. In particular, the thermoelectric properties of a single ideal armchair edge GNR (AGNR) have been studied in [15], and in [16] enhanced thermoelectric figure of merit $ZT$ values have been reported when disorder is introduced on the edges of zigzag GNRs (ZGNR), demonstrating the possibility of engineering thermoelectric properties of GNRs by changing the atomic configuration of the ribbon’s edge. Thermal conductance studies of GNR junction structures have only appeared in the literature very recently [17]. To explore these aspects further we have investigated the thermoelectric behavior of a broad range of GNR interfaces and superlattice structures using model interaction Hamiltonians for both electrons and phonons and Green’s function formalism for ballistic transport in combination with the Landauer formalism [18–21].

Typical structures we have considered are summarized in figure 1. Following a common convention, we index both ideal ZGNRs and AGNRs by the number of dimers, $N$, in a single unit cell. Semi-infinite junctions are formed by extending both ends infinitely to the left and right, while superlattices are formed by repeating the structure periodically in the longitudinal direction. The number of hexagons across the longitudinal direction of a single superlattice structure is denoted by index $m$. Here we only consider junctions in whom both ends are of the same edge type, hence a ZGNR junction means both ends are of zigzag type and an AGNR junction means both ends are of armchair edges.

The electronic transport properties are modeled by a widely used nearest-neighbor $\pi$-orbital tight binding
Figure 1. Two examples of GNR junctions: (a) 4-2 ZGNR and (b) 9-3 AGNR. The two ideal GNRs that comprise the junctions are indexed according to the number of $C$ dimers present in the unit cell (indicated by a dashed line in the figure).

While the thermal transport is modeled by a fourth-nearest-neighbor force constant (4-NNFC) model [22, 23]. To validate this model, we have compared the results of a test structure with first-principles calculations carried out using the quantum-ESPRESSO software package [24]5. Figure 2 shows the phonon dispersion relations (left panel) along with the transmission coefficients (right panel) for an ideal 4-ZGNR. The results of the 4-NNFC model (black lines) are in good agreement with the first-principles results (red lines). These results are also in good agreement with a recent study [14] where a model potential was used to construct the force constant tensor of the system. Similarly to this latter study, our calculations demonstrate that the phononic contributions to the thermal conductance, $\kappa_{ph}$, exhibit a proportionality behavior with respect to the width for ribbons wider than 2 nm, and that ZGNRs have larger $\kappa_{ph}$ than AGNRs of similar widths.

It is interesting to see how an interface affects $\kappa_{ph}$ in semi-infinite junctions. In figure 3 we plotted the phononic contribution to thermal conductance as a function of temperature for several ideal GNRs and semi-infinite junctions that can be composed with them. In general, the thermal conductance of the junction is always smaller than the smallest of the conductances of the components. For instance, at room temperature, the thermal conductance of the 12-6 AGNR junction is only 68% of the conductance of the 6-AGNR, the narrower of the two. Similarly, $\kappa_{ph}$ in 6-3 AGNR, 8-4 ZGNR and 4-2 ZGNR is only 66%, 77% and 72% of the $\kappa_{ph}$ of the narrower component.

The thermoelectric properties of GNRs and GNR junctions can be computed by combining both electronic transport and phononic transport to obtain the thermoelectric figure of merit:

$$ZT = \frac{S^2GT}{(\kappa_{el} + \kappa_{ph})}$$

where $G$ is the electronic conductance, $S$ is Seebeck’s coefficient, $T$ is the temperature, and $\kappa_{el}$ and $\kappa_{ph}$ are the electronic conductance and phonon conductance, respectively.

5 See also www.quantum-espresso.org. Technical details of the calculation are as follows: $12 \times 1 \times 1$ Monkhorst-Pack grid for Brillouin zone integration, 70 Ryd energy cutoff for the plane wave basis expansion, local density approximation for the exchange and correlation and norm-conserving pseudopotentials. A vacuum region of 14 Å separates the periodic images of the nanoribbon in a supercell geometry.
and phononic contribution to the total thermal conductance, respectively [15].

In our calculations we have considered only GNRs and GNR junctions and superlattices with unsaturated edges in the tight binding approximation for the electronic structure. Although edge effects (saturation, magnetic states, etc) will influence electronic and thermal conductance and hence the thermoelectric properties on these systems, we are confining our investigation to simple model interaction Hamiltonians for both electrons and phonons and leaving higher-order effects to future investigations. In the simple π-orbital tight binding approximation, all ZGNRs and 1/3 of AGNRs are metallic, while only 2/3 of AGNRs possess an energy gap [25].

Metallic systems are not good thermoelectric materials since their free electrons quench thermoelectric properties. Our results for ideal semiconducting AGNRs show that the thermoelectric figure of merit, ZT, exhibits peaks at the subband edges (in agreement with the results of [15]) and the peak positions move towards the center of the energy gap, as the ribbon widths are increased. Similar to the inverse proportionality behavior of the energy band gap of ideal AGNRs with respect to width, we have also identified an approximate inverse proportionality behavior of these peak ZT values with respect to the widths of the GNRs, as displayed in figure 4.

Semi-infinite ZGNR junctions do not exhibit any significant thermoelectric figure of merit values because they are metallic. However, if we increase the number of interfaces in the region between semi-infinite leads, we observe a substantial enhancement of ZT. Figure 5 shows ZT for several 4-2 ZGNR semi-infinite junctions with different numbers of interfaces between the leads: the trend in figure 5 shows a transition from metal to insulator simply by adding more interfaces to the central region, a precursor of the behavior observed in GNR superlattices.

On the other hand, most of the semi-infinite AGNR junctions are intrinsically insulating, provided that one end of the junction is insulating. The calculations for the 9-3 AGNR semi-infinite junction as in figure 1(b) give a peak ZT value of 0.2355 at room temperature. It is important to note that, in such small junctions, the geometry of the bonding itself has a great influence on the ZT value. By making the interface less symmetric (i.e. moving the narrower ribbon (3-AGNR) more towards the edge of the junction) we observe a drop of one order of magnitude in the ZT value, a demonstration of the strong geometrical dependence of the thermoelectric behavior in these extremely small GNR junctions. However, if we increase the widths of the GNRs comprising this interface by three times (27-9 AGNR) we obtain a ZT ≈ 0.05, irrespective of the bonding geometry, indicating that the strong geometrical dependence disappears for larger structures.

We calculated the ZT values for a series of AGNR and ZGNR superlattice junctions with a superlattice periodicity m = 4. Here the thermoelectric figure of merit ZT peaks are still observed in the vicinity of subband edges of the superlattice electronic band structure. However, the electronic subbands are greatly altered compared with ideal GNRs because of the periodic interfaces present in the systems. In table 1 we list the three highest ZT peak values for a variety of superlattices. We report only the peak values of ZT and their corresponding chemical potentials μ in the range 0–2.0 eV relative to the reference energy. From these data we can see that peak ZT values of these systems are largely determined by the index of the smaller GNR in the superlattice. An increase in the width of the smaller end decreases the ZT values. The highest ZT values observed are in AGNR superlattice junctions with the narrowest small end widths. For example, the highest ZT peak value of 24-3 AGNR is 0.6005 at a chemical potential μ = 1.728 eV. We have summarized these data in figure 6, where we plotted the highest peak ZT values of a series of AGNR and ZGNR superlattices varying both their small end widths and the width ratios. Table 1 and figure 6 support the conclusion that the thermoelectric performance of the GNR superlattices is largely dominated by the behavior of the narrower component. However, there

![Figure 4](image1.png)

**Figure 4.** Tight binding energy gap (black, circles) and peak ZT (red, squares) as a function of width in ideal AGNRs with indexes $N = 3, 4, 6, 7, 9, 10, 12, 13, 15, 16, 18, 19$. Room temperature ($T = 300$ K) $ZT$ values are presented in this figure (and elsewhere in the paper).

![Figure 5](image2.png)

**Figure 5.** Thermoelectric figure of merit ZT values of 4-2 ZGNR semi-infinite junctions with 5 (solid), 7 (dashed), 9 (dotted) and 11 (dashed–dotted) interfaces in the conductor region. The zero in the chemical potential is chosen as the center of the energy gap.
Figure 6. Highest $ZT$ peaks for AGNR and ZGNR superlattice junctions: (upper panel) AGNR superlattice junctions with the narrow end fixed at $3$-AGNR, $6$-AGNR and $9$-AGNR, respectively; (lower panel) ZGNR superlattice junctions with narrow end fixed at $2$-ZGNR, $4$-ZGNR and $8$-ZGNR, respectively.

is no general rule on how to determine at which chemical potential the highest peak is achieved even in junctions with the same small ends. In fact, the change of width ratios changes the electronic subband structure of the superlattice, and thus the $ZT$ peak values, which are determined by the interplay between electronic conductance, Seebeck’s coefficient and total thermal conductance.

Finally, we have investigated thermal transport and thermoelectric properties of chevron-type GNRs as recently synthesized with an atomically precise bottom-up approach using surface-assisted coupling of molecular precursors into linear polyphenylenes and their subsequent cyclodehydrogeneration [26]. In figure 7, we show the thermal conductance of the chevron-type GNR with periodicity $1.7$ nm and a pure armchair edge structure, as reported in [26] (see the inset of figure 7). The thermal conductance of an ideal (straight) $9$-AGNR, which is of the same width as the chevron-type GNR, is plotted for comparison. At room temperature, the thermal conductance of the chevron-type AGNR is reduced to $36\%$ of that of its straight counterpart. This reduction is very significant since a lowered thermal conductance associated with good electronic conductance is a necessary condition for enhanced thermoelectric properties. In comparison, in a $6$-$3$ AGNR semi-infinite junction (see figure 3) the reduction in conductance induced by the interface was only $34\%$ of the original value for the narrower end. Figure 8 shows the electronic transmission and $ZT$ for the same chevron-type GNR. There are two high peaks at $\mu = 1.21$ and $1.35$ eV (at two of the subband edges) where $ZT = 0.63$, one the largest value among all the structures considered in the current study. In comparison, its straight counterpart, $9$-AGNR, has a peak $ZT$ value of only $0.145$. It is clear that chevron-type GNRs demonstrate a great potential for optimal design of graphene nanostructures with superior thermoelectric properties.

In summary, we have investigated the thermoelectric properties of a range of graphene nanoribbon structures. In particular, we have elucidated the role that interfaces play in determining the thermoelectric response of GNR systems both across single junctions and in periodic superlattices. In general, increasing the number of interfaces in a single GNR system increases the peak $ZT$ values, superlattice GNR nanostructures have enhanced thermoelectric performances and the thermoelectric behavior of GNR junctions is largely controlled by the width of the narrower component of the

<table>
<thead>
<tr>
<th>Superlattice junction type</th>
<th>First highest peak $ZT$ at ($\mu$ (eV))</th>
<th>Second highest peak $ZT$ at ($\mu$ (eV))</th>
<th>Third highest peak $ZT$ at ($\mu$ (eV))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$15$-$3$ AGNR</td>
<td>$0.5520$ (0.826)</td>
<td>$0.5516$ (1.030)</td>
<td>$0.3684$ (1.784)</td>
</tr>
<tr>
<td>$24$-$3$ AGNR</td>
<td>$0.6005$ (1.728)</td>
<td>$0.5700$ (1.362)</td>
<td>$0.5595$ (1.530)</td>
</tr>
<tr>
<td>$30$-$6$ AGNR</td>
<td>$0.3710$ (0.866)</td>
<td>$0.3631$ (0.664)</td>
<td>$0.3402$ (0.478)</td>
</tr>
<tr>
<td>$48$-$6$ AGNR</td>
<td>$0.4425$ (1.714)</td>
<td>$0.3876$ (1.090)</td>
<td>$0.3514$ (0.604)</td>
</tr>
<tr>
<td>$45$-$9$ AGNR</td>
<td>$0.2982$ (1.518)</td>
<td>$0.2183$ (0.700)</td>
<td>$0.2121$ (0.322)</td>
</tr>
<tr>
<td>$72$-$9$ AGNR</td>
<td>$0.3452$ (1.524)</td>
<td>$0.2212$ (1.230)</td>
<td>$0.2003$ (0.690)</td>
</tr>
<tr>
<td>$10$-$2$ ZGNR</td>
<td>$0.4495$ (1.044)</td>
<td>$0.4472$ (1.446)</td>
<td>$0.4451$ (1.668)</td>
</tr>
<tr>
<td>$16$-$2$ ZGNR</td>
<td>$0.4910$ (1.014)</td>
<td>$0.4456$ (1.794)</td>
<td>$0.2678$ (1.308)</td>
</tr>
<tr>
<td>$20$-$4$ ZGNR</td>
<td>$0.2708$ (1.946)</td>
<td>$0.2622$ (0.474)</td>
<td>$0.1684$ (1.808)</td>
</tr>
<tr>
<td>$32$-$4$ ZGNR</td>
<td>$0.3271$ (0.474)</td>
<td>$0.2142$ (1.858)</td>
<td>$0.0717$ (1.348)</td>
</tr>
<tr>
<td>$40$-$8$ ZGNR</td>
<td>$0.1505$ (0.114)</td>
<td>$0.0561$ (1.816)</td>
<td>$0.0535$ (1.672)</td>
</tr>
<tr>
<td>$64$-$8$ ZGNR</td>
<td>$0.1508$ (0.114)</td>
<td>$0.0255$ (0.838)</td>
<td>$0.0231$ (1.598)</td>
</tr>
</tbody>
</table>
interface. Finally, it is important to note that the emergence of precise bottom-up fabrication techniques of graphene nanoribbons is opening the way not only to the experimental confirmation of our theoretical predictions but also to the possibility of designing the geometrical parameters of GNRs for optimal thermoelectric performance. This has been demonstrated using a chevron-type GNR as a prototypical system.

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[10] Prashar R 2010 Science 328 185

Figure 8. Electronic transmission (black, dashed) and thermoelectric figure of merit (ZT) (red, solid) for a chevron-type GNR. The zero in the chemical potential is chosen as the center of the energy gap.