Strain dependence of the heat transport properties of graphene nanoribbons

Pei Shan Emmeline Yeo1,2, Kian Ping Loh1 and Chee Kwan Gan2,3

1 Department of Chemistry, National University of Singapore, 3 Science Drive 3, 117543, Singapore
2 Institute of High Performance Computing, Agency for Science, Technology and Research, 1 Fusionopolis Way, #16-16 Connexis, 138632, Singapore
E-mail: ganck@ihpc.a-star.edu.sg
Received 26 July 2012, in final form 19 October 2012
Published 13 November 2012
Online at stacks.iop.org/Nano/23/495702

Abstract
Using a combination of accurate density-functional theory and a nonequilibrium Green’s function method, we calculate the ballistic thermal conductance characteristics of tensile-strained armchair (AGNR) and zigzag (ZGNR) edge graphene nanoribbons, with widths between 3 and 50 Å. The optimized lateral lattice constants for AGNRs of different widths display a three-family behavior when the ribbons are grouped according to \( N \) modulo 3, where \( N \) represents the number of carbon atoms across the width of the ribbon. Two lowest-frequency out-of-plane acoustic modes play a decisive role in increasing the thermal conductance of AGNR-\( N \) at low temperatures. At high temperatures the effect of tensile strain is to reduce the thermal conductance of AGNR-N and ZGNR-N. These results could be explained by the changes in force constants in the in-plane and out-of-plane directions with the application of strain. This fundamental atomistic understanding of the heat transport in graphene nanoribbons paves a way to effect changes in their thermal properties via strain at various temperatures.

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

1. Introduction
Recently, there has been a surge in research activity on heat transport through nanostructures, as evidenced by the emergence of a few review papers [1–3]. There are many reasons for this change. The first is related to heat management in nanoelectronic circuits [4], since the miniaturization of electronic devices demands efficient dissipation of heat. The second is related to the utilization of the thermoelectric effect [5] to harness heat in nanostructures that may help in alleviating the worldwide energy problem. Graphene and its derivatives such as graphene nanoribbons (GNRs) are among the most promising materials in these respects. Various experimental values for the heat conductivity of graphene have been reported, e.g., 4840–5300 W m\(^{-1}\) K\(^{-1}\) [6], 600–630 W m\(^{-1}\) K\(^{-1}\) [7] and 1400–2500 W m\(^{-1}\) K\(^{-1}\) [8]. This points to the fact that high heat conductivity is expected for graphene (in stark contrast to, e.g., the heat conductivity of Ag which is only ~430 W m\(^{-1}\) K\(^{-1}\) at room temperature). The high thermal conductance of graphene has made it very popular for use as a filler in thermal interface materials [3]. For example, the heat conductivity of epoxy resins was improved by 30 times upon addition of 25 vol% graphene additive [9], and the heat conductivity was improved by 2.6 times when 2 wt% of graphene was added to polystyrene [10].

Graphene could also be potentially used as a thermoelectric material to generate thermoelectric power [3]. The efficiency of thermoelectric materials can be quantified using the thermoelectric figure of merit \( ZT = S^2 G_e T / (\sigma_{el} + \sigma_{ph}) \), where \( S \) is the Seebeck coefficient (also known as the thermopower), \( G_e \) is the electronic conductance, \( T \) is the temperature and \( \sigma_{el} (\sigma_{ph}) \) is the electronic (thermal) conductance. Graphene has a superior [11] electronic conductance \( G_e \), and a large [12] theoretical value of \( S \sim 30 \, \text{mV K}^{-1} \). Even though the experimental [13] values of \( S \) for graphene are more modest (40–80 \( \mu \text{V K}^{-1} \)) compared to those for inorganic [5, 14] thermoelectric materials (150–850 \( \mu \text{V K}^{-1} \)), graphene might...
still qualify as a good thermoelectric material if its high value of \((\sigma_{el} + \sigma_{ph})\) could be suppressed. Although graphene is a semi-metal, its heat conduction is dominated by \(\sigma_{ph}\) and not by \(\sigma_{el}\) due to the strong sp\(^2\)-hybridization that efficiently transmits heat through lattice vibrations [15]. Various ways have been proposed to increase the phonon scattering centers in graphene, e.g., by increasing the disorder at graphene edges [16], by introducing isotopes in graphene [17] and by creating vacancy defects in graphene [18]. GNRs with vacancy defects have been predicted to have a ZT of up to 0.25 [19].

Experimental demonstrations of the excellent heat properties of graphene and GNRs have stimulated a great deal of theoretical work [20–28]. It is known that the application of strain to graphene induces changes to the electronic structure [29], resistance [30], Raman spectra [31] and thermal conductivity [32]. For GNRs, different theoretical approaches have been used to study the heat properties of both unstrained and strained GNRs. Thus far, molecular dynamics (MD) studies have concluded that both compressive and tensile strains are detrimental to the heat conductivity of graphene [32] or GNRs [24, 25, 33]. Wei et al [25] and Gunawardana et al [33] concluded that the conductivity of armchair edge GNRs is more sensitive toward strain than their zigzag edge counterparts. Guo et al [24] used a slightly different approach to that used in [25], which resulted in slightly different but essentially similar predictions. We note that the MD method is well suited for the investigation of heat conduction in the diffusive regime and at high temperatures. However, in the ballistic regime and at low temperatures intricate quantum-mechanical effects come into play [28]. Since the phonon mean free path in graphene is \(\sim 775 \text{ nm}\) at room temperature [4], the heat conduction is ballistic for small-scale graphene nanodevices. The phonon mean free path is reduced to \(\sim 20 \text{ nm}\) in the presence of edge disorders [34, 35]. Zhai et al [36] addressed the thermal conductance of GNRs using a ballistic nonequilibrium Green's function (NEGF) approach [37–39]. They extracted the force constants of strained graphene via the elasticity theory and applied them to study strained GNRs. They concluded that thermal conductance is enhanced with tensile (compressive) strain corresponds to \(\varepsilon > 0\) (\(\varepsilon < 0\)). We note that the large 19% strain applied in [36] might put the applicability of the elasticity theory in the high strain regime to a severe test.

In this work, we investigate the thermal conductance characteristics of strained GNRs by using a combination of (1) density-functional theory (DFT) that accurately treats the atomic and electronic structures of sub-nanometer width GNRs, and (2) the NEGF method that has been extensively used to study the heat [37, 39] and electron [40] transport through nanostructures. Our results may shed light on how the heat conductivity of graphene–polymer composites could be affected under loading, and the possibility of using strain to tune the thermal conductance of GNRs to improve their ZT values.

2. Models and methodology

In this work, we calculate the thermal conductance of zigzag (ZGNR-N) and armchair (AGNR-N) edge graphene nanoribbons (AGNR-N), as shown in figure 1(a), using a combination of first-principles density-functional calculations and the ballistic nonequilibrium Green’s function (NEGF) method [37–39, 41]. The uniaxial strain imposed on the GNRs is described by the strain parameter \(\varepsilon = (\ell - \ell_0)/\ell_0\), where \(\ell (\ell_0)\) is the length (relaxed length) of the ribbon along the edges. A tensile (compressive) strain corresponds to \(\varepsilon > 0\) (\(\varepsilon < 0\)). We note that the GNR edges have compressive edge stresses [42] that might cause the GNRs to buckle [43, 44], which would lead to a decrease of thermal conductance [32, 24, 25] due to increased phonon–phonon scattering. A proper treatment of buckled GNRs using DFT involves many atoms in a supercell and this demands extensive computing resources. Therefore we limit this work to studying the effects of tensile strain on flat GNRs. The thermal conductance \(\sigma (T, \varepsilon)\) at temperature \(T\)
and strain $\varepsilon$ is calculated from the Landauer expression

$$\sigma(T, \varepsilon) = \int_0^\infty dv \hbar v \theta(v) \frac{\partial n_B(v, T)}{\partial T},$$

(1)

or equivalently [45]

$$\sigma(T, \varepsilon) = \frac{\hbar^2}{kT^2} \int_0^\infty dv \hbar v^2 \theta(v) \frac{e^{\hbar v/kT}}{(e^{\hbar v/kT} - 1)^2},$$

(2)

where $n_B(v, T) = \frac{1}{\exp(\hbar v/kT) - 1}$ is the Bose–Einstein distribution for frequency $v$ and temperature $T$. $\hbar$ ($k$) is the Planck (Boltzmann) constant. The key quantity is the transmission function $\theta(v)$ that may be calculated in general cases using the nonequilibrium Green’s function method [38] or by counting the number of phonon bands at frequency $v$ for quasi-one-dimensional periodic systems [45]. We have used the latter approach to get $\theta(v)$ due to its computational efficiency in treating the problem at hand. It is interesting to note that at low temperatures $T$, only the very low-frequency modes contribute to the thermal conductance. Therefore, $\theta(v \to 0) = N_m$ in equation (2) may be taken out of the integral sign and this leads to a quantization [46, 47] of the thermal conductance according to $\sigma(T, \varepsilon) = \frac{k^2T}{h} N_m \int_0^\infty dv \hbar v \omega^2 = N_m \frac{\pi^2k^2T}{3h}$. We perform density-functional theory (DFT) calculations using the SIESTA package [48]. The local-density approximation is used for the exchange–correlation functional. Double-$\xi$ basis sets and Troullier–Martins pseudopotentials are used for the C and H atoms. We use a vacuum separation of 15 Å in the $y$ and $z$ directions consistent with the convention adopted in figure 1(b). The mesh cutoff is 400 Ryd. The atomic positions are relaxed using the conjugate gradient algorithm with a force tolerance criterion of $10^{-3}$ eV Å$^{-1}$. As was demonstrated in [49, 52], spin-polarization effects are particularly important for ZGNRs. We therefore perform spin-polarized (non-spin-polarized) calculations for ZGNR-N (AGNR-N).

The phonon dispersion relations for GNRs are calculated using the supercell method [50–52]. To minimize interactions from the distant periodic images of an atom displaced from its equilibrium position, a supercell of nine primitive cells, which is sufficient for this purpose, is used [28]. We displace the $i$th atom in a primitive cell from its equilibrium position by $\pm \delta_{ia} = \pm 0.015$ Å and evaluate the forces acting on the $j$th atom in the supercell, $F_{ij}(\pm \delta_{ia})$, using the Hellmann–Feynman theorem. $\alpha$ and $\beta$ denote the Cartesian directions. We then use a central-difference scheme to evaluate the matrix elements of the force constant matrix $K$, where $K_{\alpha \beta} = \frac{\partial^2 E}{\partial \delta_{ia} \partial \delta_{ib}} = \frac{-2K_{ij}(\pm \delta_{ia}) - F_{ij}(\mp \delta_{ia})}{2\hbar\delta_{ia}}$. To reduce the number of static DFT calculations, we exploit the space group operations of AGNR-N and ZGNR-N so that only atoms in inequivalent positions are displaced. The forces [50] or interatomic force constants on the equivalent atoms are deduced from those of the inequivalent atoms. AGNR-N with $N = 2(p + 1)$ and $N = 2p + 1$ belong to the space groups 51 and 47, respectively, where $p \geq 1$ is a positive integer, while ZGNR-N with $N = 2p$ and $N = 2p + 1$ belong to the space groups 47 and 51, respectively. Unstrained (strained) graphene belongs to the space group 191 (65).

Figure 2. The approach of the optimized lateral lattice parameter $a_0$ for AGNR-N ($N = 4–41$) and ZGNR-N ($N = 2–25$) toward $a_0^\infty$, the optimized lattice parameter of graphene (denoted by a horizontal dashed line), as the width $W$ of the ribbon increases. A three-family behavior is observed for AGNR-N.

3. Results and discussion

3.1. Optimized lattice parameters of GNRs

Since this work concerns the effect of the strain $\varepsilon = (\ell - \ell_0)/\ell_0$ on the thermal conductance, we first need to obtain the optimized length $\ell_0$ (see figure 1) of GNR-N for different $N$ (or, equivalently, width $W$). We obtain $\ell_0$ for each $N$ by performing atomic relaxation of GNRs with different ribbon lengths $\ell$ in the $x$ direction (see figure 1). The total energies of the relaxed structures are then fitted to a polynomial function to obtain the optimized ribbon length $\ell_0$. For ease of comparison between AGNR-N and ZGNR-N, the optimized lateral lattice parameter $a_0$ is calculated according to $a_0 = \frac{\ell_0}{\sqrt{3}}$ and $a_0 = \ell_0$ for AGNR-N and ZGNR-N respectively. From figure 2, we find that while $a_0$ for ZGNR-N monotonically increases toward $a_0^\infty = 2.471$ Å (the optimized lattice parameter of graphene) with increasing $W$, $a_0$ of AGNR-N monotonically decreases toward $a_0^\infty$, with an observation that AGNR-N exhibits a three-family behavior for $a_0$, i.e., the convergence of $a_0$ is systematic when the AGNR-N are grouped according to $N$ modulo 3. We note that other three-family behaviors for AGNR-N have also been found for the electronic bandgap [49], edge energy [42, 53] and LO/TO splitting [54]. The three-family behavior for $a_0$ of the AGNR-N ribbons may be understood using the concepts of aromaticity and resonance bond theory [55]. Wassmann et al argued that AGNRs can be classified into three different families depending on the number of equivalent Clar’s structures that can be constructed for each AGNR-N [53]. Clar’s structures must contain the maximum number of aromatic $\pi$-sextets that can be accommodated by the structure. In figure 3, we show examples of the equivalent Clar’s structure that can be constructed for AGNR-N belonging to the three different families, and the bond lengths for the optimized structures. For AGNR-N where $N = 3p$ and $p$ is an integer, only one Clar’s structure can
be constructed; for \(N = 3p + 1\), there are two equivalent Clar’s structures, and for \(N = 3p + 2\), more than two equivalent Clar’s structures can be constructed. Since the C–C resonance bond is shorter than the C–C single bond, the \(N = 3p\) structures will have longer bond lengths—which result in a larger \(\lambda_0\)—as compared to the \(N = 3p + 1\) and \(N = 3p + 2\) structures. In contrast, for ZGNR-\(N\) with unpaired spins at the edges, more than two equivalent Clar’s structures can be drawn for any \(N\). For width \(W \sim 50\) Å, the value of \(\lambda_0\) differs from that of the bulk graphene by less than 0.1\% (0.02\%) for AGNR-\(N\) (ZGNR-\(N\)).

**3.2. The thermal conductance of unstrained GNRs**

Using the optimized \(\ell_0\) and atomic coordinates for GNR-\(N\), we perform the phonon dispersion calculation (see figure 6 for typical results) and subsequently obtain the thermal conductance by the counting method [45]. Figure 4(a) shows the thermal conductance \(\sigma(T, \varepsilon)\) at \(T = 300\) K and \(\varepsilon = 0.00\) for GNRs as a function of \(W\). We find that ZGNR-\(N\) have higher conductances as compared to AGNR-\(N\) with comparable \(W\). This is due to the fact that the phonon dispersions of ZGNRs are more dispersive (a single phonon branch is more dispersive if it covers a larger frequency range) compared to those of AGNRs [28], thus increasing the thermal conductance through a change in the transmission function \(\theta(\nu)\). Since the dispersiveness is related to the gradient \(\partial \omega / \partial k\), which is the phonon velocity [46], we may also say that ZGNRs have higher phonon velocities than AGNRs, resulting in higher thermal conductance.

While bulk graphene is a fully \(\pi\)-resonant structure with equal C–C bond lengths between the C atoms, the presence of edges in the GNRs limits the extent of the \(\pi\)-resonance. Hence not all of the C–C bond lengths are equivalent, as explained in figure 3. Therefore, we expect the thermal conductance of GNRs to be different from bulk graphene due to this edge effect. In figure 4(b), we show the average transmission function \(\theta(\nu)\) for bulk graphene in the armchair and zigzag directions. The \(\sigma(300\) K, 0.00) for bulk graphene in the armchair (zigzag) direction is 0.18 nW K\(^{-1}\) (0.32 nW K\(^{-1}\)). As \(W \to \infty\), the edge effect of GNRs should converge to some finite value, and hence the conductance increase from AGNR-\((N - 1)\) to AGNR-\(N\) should approach the conductance value of bulk graphene in the armchair direction. The expected conductance slopes for AGNRs and ZGNRs are shown in figure 4(a). Table 1 shows that for the largest \(W\) values investigated in this study—AGNR-11 and ZGNR-7—the conductance slope for AGNR-11 is 34\% lower than that predicted for bulk graphene, whereas the slope is only 5\% lower for ZGNR-7. These discrepancies may be attributed to the strong edge effect on the narrow width ribbons that we have studied here. Even though we are unable to provide a quantitative measure of the edge effects, we are able to provide qualitative evidence of the edge effect. In figure 4(c), we show the phonon densities of states (DOSs) for AGNR-11.
Figure 5. The primitive cell of AGNR-3 (a) shows a large negative frequency of $\sim 100 \text{ cm}^{-1}$ in the phonon dispersion relations at the zone boundary (b). The relaxed structure (c) of the enlarged primitive cell AGNR-3, where the torsion angle between the two hexagon rings is $30^\circ$. (d) The phonon dispersion relation of the enlarged primitive cell of AGNR-3 shows no soft modes.

Table 1. The deviation $\Delta \sigma$ of the thermal conductance of strained GNR from the corresponding strained graphene at $T = 300 \text{ K}$ for different strains $\varepsilon$, where $\Delta \sigma = (\sigma_{\text{AGNR-N}} - \sigma_{\text{ZGNR-N}} - \sigma_{\text{Graphene}}) / \sigma_{\text{Graphene}} \times 100\%$.

| $\varepsilon$ | AGNR-11 (%) | ZGNR-7 (%) |
|--------------|-------------|------------|
| 0.00         | $-34$       | $-5.2$     |
| 0.05         | $-28$       | $-6.6$     |
| 0.10         | $-40$       | $-7.1$     |

Figure 6. Phonon dispersion relations for (a) AGNR-5 and (b) ZGNR-3. Three different strain values of $\varepsilon = 0.00, 0.05$ and 0.10 are considered.

and AGNR-10*, which is sum of the DOS of AGNR-10 and the DOS of bulk graphene. We find that the edge effect is still rather strong in the GNRs since the DOS of AGNR-11 does not match well with AGNR-10*. Similarly the DOS of ZGNR-7 does not match well with ZGNR-6*. This in turn suggests why the conductance slopes do not agree for very narrow width ribbons. We point out the fact that ZGNRN-N has a better agreement in the conductance slope compared to AGNR-N is consistent with the observation that $a_0$ converges faster to $a_0'$ (the optimized lattice parameter of graphene) for ZGRN-N than for AGNR-N, as shown in figure 2.

It is found that, except for AGNR-3, all unstrained ZGNR-N and AGNR-N are stable when $l_0$ corresponds to $a_0'$ and $a_0' \sqrt{3}$, respectively, with a small adjustment according to figure 2. Figure 5(b) shows the phonon dispersion of AGNR-3 (more commonly known as polyphenylene) of a 10 atom primitive cell that possesses soft modes extending from the $\Gamma$ point to the zone boundary with a large negative frequency of $\sim 100 \text{ cm}^{-1}$. We create a new 20 atom supercell by combining two adjacent primitive cells along the $x$ direction, which causes the soft mode of the original supercell at the zone boundary to be folded to the $\Gamma$ point of the Brillouin zone of the enlarged supercell. We perform a phonon calculation for the 20 atom supercell and use the eigenvector of the lowest frequency (i.e., the eigenmode with imaginary frequency) to displace the atoms for a further atomic relaxation. We obtain the relaxed structure shown in figure 5(c), where a torsion angle of $30^\circ$ between alternate hexagon rings is observed. This is slightly smaller than the $40^\circ$ calculated by Brocorens et al using the Hartree–Fock AM1 method for terphenyl [56]. The enlarged supercell for AGNR-3 is indeed stable according to the phonon dispersion relation shown in figure 5(d), where no soft modes are observed. This unit cell has a lower total energy of 4 meV/atom compared to that of unstable, planar AGNR-3.
3.3. The effect of tensile strain on the thermal conductance of GNRs

Next we investigate the effect of tensile strain on the thermal conductance of GNRs. Two different strain values, \( \varepsilon = 0.05 \) and 0.10, have been applied to the GNRs. Similarly to section 3.2, we perform phonon calculations for AGNR-\( N \) and ZGNR-\( N \) before calculating the thermal conductance. Figure 6 shows the typical phonon dispersion relations for AGNR-5 and ZGNR-3. We see that while the highest-frequency \( C-H \) stretching modes of \( \sim 3200 \text{ cm}^{-1} \) are not affected by strain, all other high-frequency modes between \( \sim 1000 \) and 1600 \text{ cm}^{-1} are consistently reduced. On the other hand, the two lowest-frequency out-of-plane acoustic (ZA) modes increase in frequency as strain is applied. (In the case of graphene, Bonini \textit{et al} observed that the frequency of the out-of-plane mode increases as isotropic tensile strain is applied [57].) The changes to the eigenmode frequencies may be understood from the changes to the force constants as strain is applied, as shown in figure 7 (to simplify the analysis, we show only the \( xx \), \( yy \) and \( zz \) diagonal components). Tensile strain in AGNR-5 leads to substantial decrease in the in-plane force constants along the longitudinal \( (x) \) and transverse \( (y) \) directions due to the lengthened \( C-C \) bonds [58, 59]. The largest decreases in the force constants for AGNR-5 are \( -24\% \) and \(-10\%\) in the \( xx \) and \( yy \) directions, respectively. For ZGNR-3, the largest decreases are \( -42\% \) and \(-13\%\) in the \( xx \) and \( yy \) components, respectively. However, the force constants in the out-of-plane \( (z) \) direction have either increased slightly or remained the same, and this leads to the increase of the frequency of the out-of-plane modes. The largest increase in the force constants in the \( zz \) component is \( 6\% \) (\( 8\% \)) for AGNR-5 (ZGNR-3).

The effect of strain on the thermal conductance is shown in figure 8 for three representative temperatures, \( T = 50 \) (low temperature), 300 (intermediate temperature) and 500 K (high temperature). To directly compare the conductances of a strained GNR and an unstrained GNR we define the relative conductance as \( \sigma(T, \varepsilon) = \frac{\sigma(T, \varepsilon)}{\sigma(T, 0)} \). The results for \( \sigma(T, \varepsilon) \) are shown in figure 9.

We find that at a low temperature of \( T = 50 \text{ K} \), the thermal conductance is dominated by the low-frequency modes [28] since the derivative \( \partial \ln \sigma / \partial T \) diminishes rapidly with increasing \( v \). For AGNR-\( N \), the thermal conductance substantially increases when tensile strain is applied, where an increase of up to 20\% compared to the unstrained AGNR can be achieved. This increase in conductance is due to an increase in the frequencies of the two lowest-frequency acoustic phonon eigenmodes upon the application of strain, as was discussed in figure 6(a).

However, for ZGNR-\( N \) at \( T = 50 \text{ K} \), \( \sigma(T, \varepsilon) \) with \( \varepsilon = 0.05 \) and 0.10 does not increase, but remains fairly constant at 1, despite the fact that the lowest-frequency out-of-plane ZA modes also increase in frequency after strain is applied. This is because the two low-frequency out-of-plane ZA phonon eigenmodes of unstrained ZGNR-\( N \) are more dispersive than those of AGNR-\( N \) (e.g., the frequency at the zone boundary is \( 370 \text{ cm}^{-1} \) for ZGNR-3 versus \( 90 \text{ cm}^{-1} \) for AGNR-5, as shown in figure 6), even though the frequencies of the lowest two ZA phonon branches increase with strain. Hence we can understand that the increase of thermal conductance in AGNR-\( N \) is due to the presence of new low-frequency modes that are easily excited at a low temperature. For ZGNR-\( N \), a low temperature only excites the existing low-frequency modes because the new low-frequency modes (from the effect

![Figure 7](image-url)


![Figure 8](image-url)


![Figure 9](image-url)
Figure 8. Conductance plots for (a) AGNR-\(N (N = 4–11)\) and (b) ZGNR-\(N (N = 3–7)\) for \(\varepsilon = 0.00, 0.50\) and 0.10 and \(T = 50, 300\) and 500 K.

Figure 9. The relative conductance \(\sigma_r(T, \varepsilon)\) of AGNR-\(N (N = 4–11)\) and ZGNR-\(N (N = 3–7)\) of width \(W\) for (a) \(\varepsilon = 0.05\) and (b) \(\varepsilon = 0.10\) for \(T = 50, 300\) and 500 K.

Figure 10. Cross-over temperatures (see text) for (a) AGNR-\(N (N = 4–11)\) and (b) ZGNR-\(N (N = 3–7)\) at \(\varepsilon = 0.05\) and 0.10.

of strain) occur at much higher frequencies as compared to those of AGNR-\(N\), and therefore cannot be easily excited thermally. Our results at low temperature differ from those reported in [36] where essentially the same increase in thermal conductance occurs for both AGNR-\(N\) and ZGNR-\(N\). As the temperature increases, the higher-frequency modes start to contribute to the thermal conductance in addition to the lower-frequency ones. However, since the high-frequency modes are suppressed due to the smaller force constants caused by the lengthening of the strained bonds, there will be competition between the reduction in thermal conductance due to the high-frequency modes and the increase due to low-frequency modes. For AGNR-\(N\) at \(T = 300\) and 500 K, the former effect is stronger than the latter, especially at a larger strain value, and this explains the significant reduction of the thermal conductance as shown in figure 8(a) at progressively higher temperatures. However, for ZGNR-\(N\), the effects of high and low frequency almost cancel each other out, thus leading to a near-constant behavior of the thermal conductance. From table 1, we see that the edge effect is generally stronger for AGNRs than for ZGNRs even in the presence of strain.

Since the thermal conductance of the GNRs displays a nonmonotonic behavior with temperature, it may be useful to discuss the ‘cross-over temperature’ of the GNRs, which is the temperature below (above) which the thermal conductance of a strained GNR is more (less) than that of the unstrained GNR. We show in figure 10 the cross-over temperatures of the strained GNRs, and note that they are close to room temperature. This shows that we may control the thermal conductance of strained GNRs within a reasonable range of temperatures.

Finally, we also investigate the relative conductance of a few GNRs at different strain values, the results of which are shown in figure 11. At low temperatures such as \(T = 50\) K, the thermal conductance of AGNR-\(N\) increases monotonically with increasing \(\varepsilon\), whereas it remains fairly constant for ZGNR-\(N\). At higher temperatures of \(T = 300\) and 500 K, \(\sigma_r(T, \varepsilon)\) for both AGNR-\(N\) and ZGNR-\(N\) decreases with increasing \(\varepsilon\), with AGNR-\(N\) showing a larger relative drop for the same amount of \(\varepsilon\). We find that the thermal conductance of AGNRs is more sensitive to tensile strain than that of ZGNRs at 300 K, which is consistent with the conclusions of Wei et al [25]. Zhai et al [36] predicted that with the application of \(\varepsilon = 0.19\) on GNRs of wide widths (~2.6 nm), the thermal conductances of strained GNRs should be higher than the corresponding unstrained ones even at 400 K. In the case of the narrow width GNRs studied in this paper, we show in figure 10 that the cross-over temperatures do not exceed
We attribute the discrepancy between our results and those obtained by Zhai et al to our assumptions that the out-of-plane elastic constants do not change with strain and that only nearest-neighbor force constants are used. Recently, significant progress has been made toward synthesizing GNRs of specific edge orientations [60]. Based on our results, the thermal conductance anisotropy between AGNRs and ZGNRs suggests selective use of ZGNRs as fillers in thermal interface materials because their thermal conductance is higher and less adversely affected by strain as compared to AGNRs. AGNRs, on the other hand, might act as a suitable thermoelectric material because of their inherent lower thermal conductance compared to ZGNRs, and their thermal conductance can be further lowered with the application of strain. However, the nonmonotonic variation of thermal conductance with respect to strain for the AGNRs means that straining the AGNRs to decrease their thermal conductance will only be effective above the cross-over temperature.

4. Conclusion

In conclusion, we have investigated the thermal conductance of AGNR-N and ZGNR-N as a function of tensile strain on GNRs with accurate density-functional theory calculations and the nonequilibrium Green’s function method. The lateral lattice constants of AGNR-N are found to follow a three-family behavior that depends on N. We found that tensile strain decreases the force constants in the in-plane directions of the GNRs, but slightly increases the force constants in the out-of-plane direction, which increase the two lowest-frequency out-of-plane acoustic modes. These modes play a decisive role in increasing the thermal conductance of AGNR-N at low temperatures, but not ZGNR-N. Hence, the fact that the phonon dispersions of ZGNR-N are more dispersive than those of AGNR-N of comparable widths results in two important outcomes: (1) unstrained ZGNR-N have higher thermal conductances compared to unstrained AGNR-N of comparable widths and (2) at low temperatures, the thermal conductance of strained ZGNR-N is less sensitive toward the effect of strain than that of AGNR-N. At high temperatures, the thermal conductances of strained ZGNR-N and AGNR-N decrease (relative to the unstrained ones) with strain due to the fact that the frequency of the high-frequency modes shifts down as a result of the weakening of the interatomic force constants in the in-plane direction. The use of state-of-the-art techniques such as density-functional theory and the nonequilibrium Green’s function method reveal intricate quantum-mechanical effects, which might be hard or impossible to capture with force-field type interactions. Finally, it might be interesting to study the role of out-of-plane modes in other strained single-layer systems such BN, MoS2 and WSe2.

Acknowledgments

The authors gratefully acknowledge useful discussions with Jian-Sheng Wang, Zhen Wah Tan and Jinghua Lan. We acknowledge the support of the A*STAR Computational Resource Center (A*CRC) of Singapore.

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