Effect of Stone–Wales defects on the thermal conductivity of graphene

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Abstract

The problem of phonon scattering by strain fields caused by Stone–Wales (SW) defects in graphene is studied in the framework of the deformation potential approach. An explicit form of the phonon mean free path due to phonon-SW scattering is obtained within the Born approximation. The mean free path demonstrates a specific \( q \)-dependence varying as \( q^{-3} \) at low wavevectors and taking a constant value at large \( q \). The thermal conductivity of graphene nanoribbons (GNRs) is calculated with the three-phonon umklapp, SW and rough edge scatterings taken into account. A pronounced decrease of the thermal conductivity due to SW defects is found at low temperatures whereas at room temperatures and above the phonon–phonon umklapp scattering becomes dominant. A comparison with the case of vacancy defects shows that they play more important role in the reduction of the thermal conductivity in GNRs over a wide temperature range.

Keywords: graphene, thermal conductivity, stone-wales defects

(Some figures may appear in colour only in the online journal)
all main scatterers. In particular, this gives a possibility to compare the role of SW and vacancy scattering. We consider the canonical SW defects consisting of two pairs of five and seven-membered rings forming a rhomboid structure (see figure 1). Actually, this is nothing else than a 5-7-5-7 disclination quadrupole or, more precisely, the wedge disclination quadrupole (WDQ). The disclination lines with Frank vectors $\mathbf{\Omega} = \pm \mathbf{\Omega}_1 \mathbf{e}_1$ are oriented along the $z$-axis with coordinates $(\pm L/2 + \delta, L/2 \pm \delta)$ in the positive $xy$ half plane and $(\mp L/2 - \delta, -L/2 \mp \delta)$ in the negative one. Generally, we consider a rhombus which is transformed into the square for $\delta = 0$. The axes of the rotation of each disclination are not shifted relative to the disclination lines. Otherwise, extra dislocations would be present.

With this understanding, one can describe the SW-phonon scattering in terms of the deformation potential theory. This approach was successful in the description of the phonon scattering by disclination dipoles in dielectric materials [9, 10] and, more recently, by grain boundaries in graphene [11]. Namely, a phonon mean free path due to WDQ strain fields can be calculated within the deformation potential approach supposing the deformations are dilatations [12]. In this case, an effective perturbation energy reads

$$U(\mathbf{r}) = \hbar \omega_\lambda(q) \gamma_\lambda \text{Tr} E_\mathbf{q}(\mathbf{r}),$$

where $\hbar \omega_\lambda(q)$ is the phonon energy with wavevector $\mathbf{q}$, $\text{Tr} E_\mathbf{q}(\mathbf{r})$ is the trace of the strain tensor caused by the static WDQ, $\gamma_\lambda$ is the Grüneisen constant for a given phonon branch $\lambda$. At chosen in figure 1 geometry, the strain matrix for WDQ is known (see, e.g. [13]) and $U(\mathbf{r})$ takes the following form:

$$U(\mathbf{r}) = \frac{1}{2} \left[ \ln \left( \frac{x - L/2}{x + L/2} \right)^2 + \left( \frac{y - L/2}{y + L/2} \right)^2 + \ln \left( \frac{x + L/2}{x - L/2} \right)^2 + \left( \frac{y + L/2}{y - L/2} \right)^2 \right].$$

where $A = \hbar \omega_\lambda(q) \nu \gamma_\lambda(1 - 2\sigma)/(1 - \sigma)$, $\nu = \Omega/2\pi$, $\sigma$ is the Poisson constant, $L_1 = L + 2\delta, L_2 = L - 2\delta$. The phonon mean free path is given by

$$l^{-1}_{\text{sw}} = n_{\text{sw}} \int_0^{2\pi} (1 - \cos \theta) R(\theta) d\theta$$

with $R(\theta)$ being the effective differential scattering radius, $\theta$ the scattering angle, and $n_{\text{sw}}$ the areal density of WDQ. Within the Born approximation $R(\theta)$ is written as

$$R(\theta) = \frac{q S}{2\pi \hbar^2 v_\lambda} \left| \langle \mathbf{q}|U(\mathbf{r})|\mathbf{q}'\rangle \right|^2,$$

where $S$ is a projected area, $v_\lambda$ is the sound velocity, and the bar denotes an averaging procedure over $\alpha$ which defines an angle between the scattering vector $\mathbf{q} - \mathbf{q}'$ and the $x$-axis. Finally, we obtain the following exact expression:

$$l^{-1}_{\text{sw}} = 4q^2 n_{\text{sw}} B^2 (2L^2 (J^2_0(qL) + J^2_1(qL)) - J_0(qL) J_1(qL) \nu qL)$$

$$- \sum_{n=1}^{2} L_q^2 (J^2_n(\sqrt{2} qL_n) + J^2_1(\sqrt{2} qL_n)) - J_0(\sqrt{2} qL_n) J_1(\sqrt{2} qL_n)),$$

where $J_i(z)$ is the Bessel function of the $i$th kind, $B = \gamma_\lambda(1 - 2\sigma)/(1 - \sigma)$, $n_{\text{sw}}$ is the areal density of WDQ, $L = \sqrt{L_1^2 + 4\delta^2}$. In graphene lattice with flat SW defect the parameter $\delta$ is small, so that almost quadratic WDQ is realized (see figure 1). For this reason, we restrict our further consideration to the case $\delta = 0$.

The total phonon mean free path including the most important scatterers reads

$$l^{-1}_{\text{tot}} = l_0 + l^{-1}_{\text{sw}} + l^{-1}_{\text{pd}} + l^{-1}_{\text{ph-ph}},$$

where $l_0$, $l_{\text{pd}}$ and $l_{\text{ph-ph}}$ come from the phonon-rough boundary, phonon-point defect (PD) and phonon-phonon scattering, respectively. Explicitly,
The phonon-PD mean free path takes the form

$$l_{0}^{-1} = \frac{1}{d} \frac{1-p}{1+p}$$

where \(d\) is the graphene layer size and \(p\) is the specularity parameter that can be chosen to be momentum-independent [7]. The parameter set used is: \(\gamma_{LA} = 2.0, \Gamma = 0.001, L = 2.5 \, \text{Å}, n_{sw} = 2.0 \times 10^{22} \, \text{cm}^{-2}, \nu = 0.16, \sigma = 0.165\).

The total thermal conductivity includes all possible scatterers and dominant phonon branches. We take into account the most important acoustic phonon branches: transverse (TA), longitudinal (LA), and out-of-plane (ZA). Explicitly, one gets (see, e.g. [7])

$$\kappa(T) = \frac{1}{4\pi k_B T \gamma_{\text{eff}}} \sum_{\lambda} \int_{0}^{\infty} \left( \frac{h \omega_{\lambda}(q)}{\nu_{\lambda}(q)} \right)^{2} \kappa_{\text{tot},\lambda}(q,T) \omega_{\lambda}(q) \gamma_{\text{eff}}(q) \left( \omega_{\lambda}(q) / (\hbar k_B T) - 1 \right) d\omega_{\lambda}(q),$$

where summation is performed over phonon polarization branches with the dispersion relations \(\omega_{\lambda}(q) = \sqrt{\nu_{\lambda}(q)} q B_{\lambda}\) for \(\lambda = \text{LA}, \text{TA}, \text{ZA}\), and \(\nu_{\lambda}(q) = q^{2}/2m\) for \(\lambda = \text{ZA} \) (\(m\) is an effective parameter), \(k_B\) is the Boltzmann constant, \(\kappa_{\text{tot},\lambda}(q,T)\) is the phonon mean free path given by equation (6), \(h_{\text{eff}}\) is the effective graphene layer thickness.

Figure 3 shows the calculated thermal conductivity in a 5 \(\mu\)m wide ribbon with vacancies of different concentrations. We use the parameter set typical for graphene and the values of adjustable constants of phonon–phonon umklapp scattering are taken from a fit to the results of [8] at \(\Gamma = 10^{-4}\) \((n_{pd} \approx 2 \times 10^{11} \, \text{cm}^{-2})\) which, in turn, are in good agreement with experimental data [16, 17]. As is seen, at low vacancy concentrations the umklapp scattering dominates at room temperatures which agrees with conclusions in [8]. At higher concentrations the contribution from vacancy scattering markedly increases, however, the umklapp processes are still of importance. This qualitatively agrees with the results of MD simulations and an analysis made in [7]. Notice that for pristine GNs the calculated curve has a false bump in the temperature range of 50–90 K. This follows from the fact that the phenomenological expression (9) for umklapp scattering is not universal and gives good fits in the restricted temperature range. For example, for CdTe the correct region was found to be 0.05\(\Theta < T < 2\Theta\) [14].

Evidently, with a proper definition of \(\Gamma\), the results shown in figure 3 are also valid for isotope scattering (see [8]).
more accurate study of this problem has been recently presented in [18] within the Callaway’s theory in its full form (normal processes are included). The authors [18] found a qualitatively similar behavior of the thermal conductivity and made a conclusion that the isotopic effect on the conductivity is significant in the low-temperature range 50–300 K.

The calculated thermal conductivity in the presence of SW defects is shown in figure 4. As is seen, there is a similar decrease within a wide temperature range though SW defects have less impact on the thermal conductivity in comparison to vacancies with the same concentrations. Qualitatively, this conclusion agrees with the results of MD calculations. However, at room temperature the reduction in the thermal conductivity due to SW defects is found to be markedly smaller because of the dominant influence of phonon–phonon umklapp scattering. A possible healing of the graphene monovacancies [19, 20] and the SW defects [21] can additionally reduce the corresponding contributions to the thermal conductivity via decreasing the defect densities, especially at high temperatures. Notice that a crucial parameter for phonon-SW scattering is a size of the quadrupole: the more size the more reduction in the thermal conductivity takes place.

We have compared the role of SW and vacancy defects in figure 5. As is seen, the SW-induced contribution is less pronounced in comparison to monatomic vacancies of the same concentration. The maximum difference occurs in the region near the thermal conductivity peak (∼ 120 K). At low temperatures the phonon-rough boundary scattering prevails while at high temperatures the umklapp three-phonon processes are essential. Notice that our analysis confirms the conclusions in [8] concerning the role of different phonon branches. Like in [8] for both SW and vacancy defects the TA mode has the largest contribution to the thermal conductivity at room temperature whereas the ZA mode is stronger at low temperatures (below the peak).

In conclusion, within the Born approximation we have obtained the exact analytical result for the mean free path due to phonon-SW scattering. This allows us to calculate the corresponding contribution to the thermal conductivity in a wide temperature range and compare it to other scattering mechanisms. The results demonstrate that SW defects markedly decrease the thermal conductivity below 250 K. At higher temperatures, the role of three-phonon umklapp scattering becomes dominant. The comparison with vacancy defects shows that the influence of point impurities being qualitatively similar is more pronounced in the same temperature range at equal concentrations. The reason is clearly seen in figure 2: the mean three path $l_{sw}$ resembles $l_{pd}$ at low wavevectors whereas at high $q$ the role of phonon-SW scattering diminishes.

Our consideration gives a possibility to analyse heat conduction in graphene nanoribbons with various widths, edge roughness and SW defect concentrations. In this paper, we have restricted our analysis to the case when Young’s modulus does not depend on the concentration of defects. Notice, however, that a recent study in [22] shows that the in-plane Young’s modulus increases with increasing defect density up to almost twice the initial value for vacancy content of 0.2%. It is not clear whether something similar can be observed in a graphene lattice with SW defects, which also can be introduced by ion or electron beam irradiation [23]. In that case, the mean free paths due to both the SW and three-phonon umklapp scattering would be markedly influenced.

We have used a rather simple phenomenological single-mode relaxation time approach with the smallest possible set of parameters. The more careful analysis requires inclusion of the three-phonon normal processes, for example, as it has been done in [18] within the Callaway’s theory. Another interesting problem concerns the role of the ripples in graphene. We have considered the flat graphene flake. A wavy shape will induce a local symmetry breaking of graphene lattice. As a result, the phonon symmetry selection rule will be broken [24]. This, in turn, leads to the interaction between different phonon branches and, in particular, to the damping of the ZA mode. Thus, the wavy shape should lead to a reduction in the thermal conductivity. This effect is likely to be not significant for small flakes, but should be noticeable when the flake size increases. The detailed study of this problem still remains open. In our case, the explicit form of a wavy graphene shape
should be described in the presence of SW defects, which even complicates the analysis.

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