A Bond-order Theory on the Phonon Scattering by Vacancies in Two-dimensional Materials

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We theoretically investigate the phonon scattering by vacancies, including the impacts of missing mass and linkages \( \tau_{A}^{-1} \) and the variation of the force constant of bonds associated with vacancies \( \tau_{A}^{-1} \) by the bond-order-length-strength correlation mechanism. We find that in bulk crystals, the phonon scattering rate due to change of force constant \( \tau_{A}^{-1} \) is about three orders of magnitude lower than that due to missing mass and linkages \( \tau_{V}^{-1} \). In contrast to the negligible \( \tau_{V}^{-1} \) in bulk materials, \( \tau_{A}^{-1} \) in two-dimensional materials can be 3–10 folds larger than \( \tau_{V}^{-1} \). Incorporating this phonon scattering mechanism to the Boltzmann transport equation derives that the thermal conductivity of vacancy defective graphene is severely reduced even for very low vacancy density. High-frequency phonon contribution to thermal conductivity reduces substantially. Our findings are helpful not only to understand the severe suppression of thermal conductivity by vacancies, but also to manipulate thermal conductivity in two-dimensional materials by phononic engineering.
**Results**

**Bond-order theory for phonon-vacancy scattering.** Perturbation theory in terms of the missing mass and the missing linkages deals with the scattering of phonons by vacancy defects in crystals:

\[
\tau^{-1} = x \left( \frac{AM}{M} \right)^2 \frac{\pi}{2} \left( \frac{E_z}{G} \right) \omega^2 g(\omega)
\]

where \( x \) is the density of vacancies, \( G \) is the number of atoms in the crystal, \( g(\omega) \) is the phonon density of states (DOS). For vacancy defect, the effective value of \( \frac{AM}{M} \) is \( \frac{M_d}{M} - 2 \), where \( M \) is the average mass per atom, \( M_0 \) is the mass of the missing atom, and the term \( -2 \) accounts for the potential energy of the missing linkages, or twice the potential energy per atom.

One important fact that has been overlooked in previous modeling is that bond under-coordinated atoms becomes shorter and stronger. Bond shortening and strengthening not only raises the local density of charge, mass and energy but also deepens the local potential, providing perturbation to the local potential. This under-coordination effect raises the local energy density, or the elastic potential, providing perturbation to the local potential. This under-coordination effect raises the local energy density, or the elastic potential, providing perturbation to the local potential. For two-dimensional materials, that is, graphene, the rate of phonon scattering by atoms of different force constant is given as:

\[
\tau_A^{-1} = x \left( \frac{\delta k}{k} \right)^2 4\pi \frac{\omega^2 g(\omega)}{G}
\]

where \( x \) is the density of imperfections, \( k \) is the force constant, and \( \delta k \) is the change of force constant.

According to Eq. (2) and Eq. (3), we can get

\[
\frac{k_{z-1}^{-1}}{k_z} = \frac{E_{z-1}d_z^2}{E_zd_z^{-1}} = (Cz-1)^{-(m+2)}
\]

\[
= \left\{ \frac{1 + \exp[(12-z)/(8z)]}{1 + \exp[(13-z)/(8z-8)]} \right\}^{-(m+2)}
\]

where \( k_{z-1} \) is the force constant of under-coordinated atoms near the vacancies whose CN is \( z-1 \), and \( k_z \) is the force constant of atom whose CN is \( z \). Therefore, according to Eq. (4) and Eq. (5), the scattering rate of phonons by the under-coordinated atoms near the vacancies is derived as:

\[
\tau_A^{-1} = \chi_A \left( k_{z-1}^{-1} - 1 \right)^2 \frac{4\pi \omega^2 g(\omega)}{G}
\]

\[
= 4\pi \chi \left\{ \left[ \frac{1 + \exp[(12-z)/(8z)]}{1 + \exp[(13-z)/(8z-8)]} \right]^{-m+2} \right\} \frac{\omega^2 g(\omega)}{G}
\]

where \( \chi_A \) is the density of under-coordinated atoms, and \( x \) is the density of single vacancy. \( m \) is a key parameter that represents the nature of the bond.

**The unusual vacancy effects on phonon scattering in 2D materials.** The ratio of \( \tau_A^{-1} \) to \( \tau_V^{-1} \) in the case of different \( m \) and different coordination number is shown in Fig. 2. For bulk materials whose effective atomic CN is always 12 in the BOLS correlation mechanism, \( \tau_A^{-1} \) is three orders of magnitude less than \( \tau_V^{-1} \), so the scattering of phonons by the under-coordinated atoms near the vacancies is negligible in bulk materials. The ratio \( \tau_A^{-1}/\tau_V^{-1} \) increases quickly with decreasing the coordination number. For two-dimensional materials with \( z = 3 \), such as silicene, hexagonal Boron Nitride, graphene and MoS2, \( \tau_A^{-1} \) is 3- to 10-fold larger than \( \tau_V^{-1} \), therefore the scattering of phonons by the under-coordinated atoms near the vacancies must be taken into account, and the total scattering rate of phonons by the imperfections should be \( \tau_V^{-1} + \tau_A^{-1} \).

Moreover, the ratio \( \tau_A^{-1}/\tau_V^{-1} \) increases with the parameter \( m \) increases. For carbon-based 2D materials, that is, graphene, \( m \) is
Vacancy effects on phonon scattering in graphene flakes. It is an important phononic engineering technique to modulate the thermal transport by phonons with different range of frequency. Next using graphene flake as an example, we discuss the impacts of vacancies on phonon scattering rate and thermal conductivity contributed from phonons with different frequency. The Matthiessen’s rule which assumes that different scattering mechanisms are independent is adopted, so the total phonon scattering rate is given as:

\[
\tau_1^{-1} = \tau_A^{-1} + \tau_B^{-1} + \tau_{\lambda A}^{-1} + \tau_{\lambda B}^{-1}
\]

The Umklapp phonon-phonon scattering rate \(\tau_{U,\lambda}^{-1}\) and the phonon-boundary scattering rate \(\tau_{B,\lambda}^{-1}\) are given as:

\[
\tau_{U,\lambda}^{-1} = \frac{\gamma_\lambda k_B T \omega^2}{4\pi^2 v_{\lambda D,\lambda}^2}
\]

\[
\tau_{B,\lambda}^{-1} = \frac{v_{\lambda,\lambda} 1 - P}{W 1 + P}
\]

where \(M\) is the mass of a graphene unit cell, \(\gamma_\lambda\) is the Grüneissen parameter, \(W\) is the width of graphene ribbon, \(v_{\lambda,\lambda}\) is the component of the phonon velocity in branch \(\lambda\) perpendicular to the longitudinal direction of graphene ribbon, and \(P\) is the specularity parameter, which is defined as the probability of phonon’s specular reflection at the lateral boundaries. In order to fit the experimental thermal conductivity value of pristine graphene, we set the specular parameter as 0.8, and the width of graphene flake as 5 \(\mu\)m, which are consistent with Ref. 40 and Ref. 41. As the major concern of the present work are the mechanism of phonon scattering by vacancies and the reduction of thermal conductivity by vacancies, the values of specular parameter and flake width are fixed. The Grüneissen parameters for acoustic branches originate from the results of first-principles calculations in Ref. 42. Based on the linear dispersion for in-plane branches and quadratic dispersion for out-of-plane branch (see Eq. 16 in the section of Methods), the function for phonon DOS of graphene is:

\[
\tau_1^{-1} = \frac{S \omega}{2 \pi v_\perp^2} \left\{ \begin{array}{l}
\lambda = LA, TA \\
\frac{S}{4 \pi x} \\
\lambda = ZA
\end{array} \right.
\]

Therefore according to Eq. (1), the rate of phonon scattering by single vacancies is given as:

\[
\tau_{V,\lambda}^{-1} = \left\{ \begin{array}{l}
2.25x\Omega \frac{\omega^3}{v_\perp^2} \\
1.125x\Omega \frac{\omega^2}{x} \\
\lambda = LA, TA \\
\lambda = ZA
\end{array} \right.
\]

where \(x\) is the density of vacancies, and \(\Omega\) is the primitive cell area of graphene.

As shown in Fig. 1(a), the CN of carbon atoms in graphene is 3. There are 3 under-coordinated atoms whose CN is 2 near the single vacancy. Based on BOLS theory, the bond between the under-coordinated atoms becomes shorter and stronger. Girit et al. discovered that breaking a C–C bond of the 2-coordinated carbon atoms near the monolayer-GNR vacancy required 7.50 eV per bond, that was 32% higher than the energy (5.67 eV/bond) required for breaking one bond between 3-coordinated carbon atoms in the interior of a suspended graphene sheet. The mechanical strength of graphene increases with the density of defects (the reconstructed 5- and 7-atom rings forming the grain boundaries), because of the particular strength of the ring bonds and their elongation dynamics. These findings provide evidence for the BOLS prediction of the shorter and stronger bonds at vacancies. According to Eq. (5), the ratio of force constant of the 2-coordinated carbon atoms near the vacancy to that of the 3-coordinated carbon atoms is 2.03, and according to Eq. (6), the rate of phonon scattering by the 2-coordinated carbon atoms near the single vacancies is given as:

\[
\tau_{A,\lambda}^{-1} = \left\{ \begin{array}{l}
6.36x\Omega \frac{\omega^3}{v_\perp^2} \\
3.18x\Omega \frac{\omega^2}{x} \\
\lambda = LA, TA \\
\lambda = ZA
\end{array} \right.
\]

From Eq. (12) and Eq. (11), we know that the phonon scattering by the under-coordinated atoms near the vacancy dominates over that by the vacancy in graphene.

In the pristine graphene sheet, the Umklapp phonon-phonon scattering is dominant at room temperature, but in the defective graphene, the situation is quite different. Fig. 3 presents the frequency-dependent scattering rate of LA phonons for all kinds of
mechanisms in the single vacancy defective graphene. The vacancy density is 1%. For the ultra-low frequency phonons, the boundary scattering is dominant. However, for $\omega > 2.5$ Trad/s, the scattering by the under-coordinated carbon atoms dominates over other mechanisms. The situation is similar for other branches. However, this most important scattering mechanism is neglected in previous theoretical model on phonon scattering by vacancies.

Vacancy effects on thermal conductivity in graphene flakes. Many researches presented that the thermal conductivity of graphene could be remarkably reduced by point defects, such as isotope and vacancy. The vacancy effect on the thermal conductivity is more remarkable than that of isotope. By molecular dynamics simulations, Haskins et al. found that even for a very low vacancy concentration 0.1%, a 81% reduction of thermal conductivity of graphene was achieved. Although Klemens’s model agrees well with the theoretical calculations, the severe suppression of thermal conductivity of graphene by vacancies is much over the prediction of Klemens’s theory. Incorporating phonon scattering by the under-coordinated atoms near the vacancies to the linearized phonon Boltzmann transport equation within relaxation time approximation (see in the section of Methods), we calculate the relative thermal conductivity ($k/k_0$) of defective graphene (single vacancies and double vacancies) as a function of defect density at room temperature, which is shown in Fig. 4. $k_0$ (the thermal conductivity of pristine graphene) calculated by this work, 3750 W/mK, is coherent with various experimental measurements and theoretical calculations. The dash line is the calculation results from Klemens’s model from Ref. 26, in which the phonon scattering by the 2-coordinated carbon atoms near the single vacancy, as shown in Fig. 1(b). According to Eq. (6), the rate of phonon scattering by the 2-coordinated carbon atoms near the double vacancies at the same defect density $x$ is given as,

$$\tau_{A,1}^{-1} = \begin{cases} 4.24x\Omega \frac{\omega^3}{\lambda}, & \lambda = LA,TA \\ 2.12x\Omega \frac{\omega^3}{\lambda}, & \lambda = ZA \end{cases}$$

where the defect density $x$ is defined as the number of defected atoms divided by the total atom number in pristine graphene. The rate of phonon scattering by the 2-coordinated carbon atoms near the single vacancies is as 1.5 times as that near the double vacancies at the same defect density. Therefore, the single vacancy defective graphene possesses the lower thermal conductivity than the double vacancy defective one. For example, for graphene flakes with 0.1% defected atoms, for single vacancy defective graphene, $k/k_0$ is 0.19, while for double vacancy defective graphene, $k/k_0$ is 0.23. Thus under the same defected atom density, single-vacancy can result in larger reduction in thermal conductivity with respect to double-vacancy defects. This explains the phenomenon observed by molecular dynamics simulations.
In summary, we find a new phonon scattering mechanism which is the scattering by the under-coordinated atoms near the vacancies. This mechanism origins from the increase of force constant of bonds associated with vacancies. The scattering of phonons by the under-coordinated atoms near the vacancies is negligible in bulk materials. However, because of the low coordination number, this mechanism has dominant effect on the phonon transport in two-dimensional vacancy defective materials. This finding is helpful not only to understand the severe suppression of thermal conductivity by vacancies, but also to apply phononic engineering to manipulate thermal conductivity in two-dimensional materials.

**Methods**

According to the linearized phonon Boltzmann transport equation within relaxation time approximation, the thermal conductivity in branch \( l \) of single layer graphene (SLG) in the y direction (the longitudinal direction of graphene ribbon) is derived as:

\[
\kappa_l = \frac{S}{(2\pi)^2} \int_0^{v_l} v^2 q^2 dq
\]  

where \( S \) is the area of the sample, \( v_l \) is the y component of the group-velocity vector in branch \( l \) (LA, TA and ZA), only acoustic branches are considered in this section, \( c_l \) is the averaged phonon relaxation time between successive scattering events, \( \tau \) is the wave vector, and \( c_l \) is the volumetric specific heat of each mode, which is given as:

\[
\kappa_l = \frac{2\pi k_B}{h} (\text{det} \mathbf{h}_l)^{1/2} \frac{v_l^2}{v_l^2 + \omega_l^2} \Omega_l
\]  

where \( \kappa_l \) is the Boltzmann constant, \( \delta = 0.335 \text{ nm} \) is the thickness of graphene, \( h \) is the reduced Planck constant, and \( T \) is the absolute temperature. In SLG, the LA and TA acoustic branches are linear, whereas the ZA branch shows a quadratic dependence of the frequency on the wave vector \( v_l \), so

\[
\omega_{l\Omega} = \left\{ \begin{array}{ll}
\frac{v_{l\Omega}}{\Omega} & \lambda = \text{LA, TA} \\
\frac{q_{l\Omega}}{\Omega} & \lambda = \text{ZA}
\end{array} \right.
\]

where \( \omega_{l\Omega} \) is the Debye frequency, which is given as

\[
\Omega_l = \frac{v_{l\Omega}}{k_B T} \frac{\Omega l}{4\pi v_{l\Omega}} \lambda = \text{LA, TA}
\]

where \( \Omega \) is the primitive cell area.

The total phonon scattering rate \( \tau^{-1} \) is the sum of \( \tau_{l1}^{-1}, \tau_{l2}^{-1}, \tau_{l3}^{-1} \), and \( \tau_{l4}^{-1} \), which are given as Eq. (1) - (8) respectively. For a flat graphene sheet lying in the x-y plane, the reflection symmetry requires that the Hamiltonian be invariant under \( z \rightarrow -z \). Seol et al. obtained a selection rule for three-phonon scattering, which requires that an even number of ZA phonons is involved in each process. This selection rule is adopted in our calculation.

The normalized accumulated thermal conductivity is defined as

\[
\tilde{\kappa}(\omega) = \frac{\kappa_{\text{LA}}(\omega) + \kappa_{\text{TA}}(\omega) + \kappa_{\text{ZA}}(\omega)}{\kappa_{\text{LA}} + \kappa_{\text{TA}} + \kappa_{\text{ZA}}}
\]

where \( \kappa_{\text{LA}}(\omega) \) is given as:

\[
\kappa_{\text{LA}}(\omega) = \left\{ \begin{array}{ll}
\frac{2\pi k_B}{h} (\text{det} \mathbf{h}_{\text{LA}})^{1/2} \frac{v_{\text{LA}}^2}{v_{\text{LA}}^2 + \omega_{\text{LA}}^2} \Omega_{\text{LA}} & \lambda = \text{LA, TA} \\
\frac{2\pi k_B}{h} (\text{det} \mathbf{h}_{\text{ZA}})^{1/2} \frac{v_{\text{ZA}}^2}{v_{\text{ZA}}^2 + \omega_{\text{ZA}}^2} \Omega_{\text{ZA}} & \lambda = \text{ZA}
\end{array} \right.
\]

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Acknowledgments
This work was financially supported by National Natural Science Foundation of China (NSFC) (Grant Nos. 11275163, 11274011, 11304264), and the Ministry of Education of China (Grant No. 20110001120133).

Author contributions
G.F.X. and G.Z. established the theoretical models and supervised the project, G.F.X. and Y.L.S. performed the calculations and data analysis, G.F.X. wrote the paper, G.Z. revised the paper. X.L.W., L.W.Y., H.P.X. and J.X.Z. discussed the results.

Additional information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Xie, G.F. et al. A Bond-order Theory on the Phonon Scattering by Vacancies in Two-dimensional Materials. Sci. Rep. 4, 5085; DOI:10.1038/srep05085 (2014).

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