Band structure engineering of graphene by strain: First-principles calculations

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We have investigated the electronic structure of graphene under different planar strain distributions using the first-principles pseudopotential plane-wave method and the tight-binding approach. We found that graphene with a symmetrical strain distribution is always a zero band-gap semiconductor and its pseudogap decreases linearly with the strain strength in the elastic regime. However, asymmetrical strain distributions in graphene result in opening of band gaps at the Fermi level. For the graphene with a strain distribution parallel to C-C bonds, its band gap continuously increases to its maximum width of 0.486 eV as the strain increases up to 12.2%. For the graphene with a strain distribution perpendicular to C-C bonds, its band gap continuously increases only to its maximum width of 0.170 eV as the strain increases up to 7.3%. The anisotropic nature of graphene is also reflected by different Poisson ratios under large strains in different directions. We found that the Poisson ratio approaches to a constant of 0.1732 under small strains but decreases differently under large strains along different directions.

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Graphene, a single-layer graphite sheet, is a zero band-gap semiconductor. Since obtained successfully in 2004, it has attracted tremendous interests of theoretical and experimental studies. Graphene has unique electronic properties arising from its hexagonal honeycomb lattice structure, which makes electrons in graphene behave as massless relativistic fermions that satisfy the Dirac equation. The quantum Hall effect has been observed in graphene. Studies have also shown that spin-orbital coupling exists in graphene and the quantum spin Hall effect may occur at ultralow temperature. These and other unusual electronic properties of graphene make it a promising material for building electronic devices. Nevertheless, absence of band gap in graphene sets limitations on its practical applications. It is of crucial importance to find methods to effectively tune the electronic transport properties of graphene along different directions.

The Poisson ratio approaches to a constant of 0.1732 under small strains but decreases differently under large strains along different directions.
dispersion of a graphene system with lattice constant changes. explain the change of the pseudogap as the lattice constant the 2 zero, indicating that the system becomes metallic. From Fig. changes greatly and the DOS at the Fermi level is larger than larger than 0.3209 nm, the shape of the band structure near the Fermi level. However, as the lattice constant is conduction and valence of the graphene systems with lattice constants varying from 0.2009 to 0.3159 nm are still determined by the 2 atom, indicating that the C-C bond weakens gradually as increasing the lattice constant and eventually breaks down.

Figure 2(a) also shows that when the lattice constant is less than 0.3209 nm, band crossing occurs at the K point of the conduction and valence π bands. There is no band gap near the Fermi level. However, as the lattice constant is larger than 0.3209 nm, the shape of the band structure changes greatly and the DOS at the Fermi level is larger than zero, indicating that the system becomes metallic. From Fig. 2(a), we find that there exist two DOS peaks around the Fermi level, which form a pseudogap for the graphene system with a lattice constant less than 0.3209 nm. Figure 2(b) shows that the width of the pseudogap linearly decreases as the lattice constant increases.

It is well known that in graphene the sp² hybridization of the 2s, 2pₓ, and 2pᵧ orbitals of carbon atoms create lateral σ bonds, and the remaining 2pᵧ orbitals form the π bands. Our detailed calculations show that the states near the Fermi level of the graphene systems with lattice constants varying from 0.2009 to 0.3159 nm are still determined by the 2pᵧ orbitals. Thus, we can use the TB approximation of the π orbitals to explain the change of the pseudogap as the lattice constant changes.

In the framework of the TB approximation, the energy dispersion¹² of a graphene system with lattice constant α is described by

\[ E(\vec{k}) = \varepsilon_{2p} \pm \gamma f(\vec{k}), \]

with \( f(\vec{k}) = \sqrt{1 + 4 \cos \frac{\pi k_x}{a} \cos \frac{\pi k_y}{b} + 4 \cos^2 \frac{k_y}{2} \} \) and \( \gamma = \langle \varphi_\alpha(\vec{r} - \vec{R}_A) | H | \varphi_\alpha(\vec{r} - \vec{R}_A - \vec{R}_i) \rangle \) (i = 1, 2, 3). Here, γ is the hopping integral, \( \varepsilon_{2p} \) is the energy of the C-2pₓ orbitals (a constant), and \( \varphi_A \) and \( \varphi_B \) are the C-2pₓ orbitals of the two C atoms at positions \( \vec{R}_A \) and \( \vec{R}_B \) in the primitive cell as shown in Fig. 1. The band-gap width is given by

\[ E_{\text{gap}} = 2|\gamma f(\vec{k})|. \]  

Because \( f(\vec{k}) \) is always zero at the K point of the Brillouin zone, the band-gap width keeps zero at the Fermi level for any values of the lattice constant. We found that the pseudogap is determined by the M point in the band structure where \( f(\vec{k}) = 1 \). As a result, the pseudogap width is given by \( \Delta_{\text{pseudogap}} = 2|\gamma| \), namely, linearly dependent on the hopping
Asymmetrical strain distributions in graphene result in different results. To study the graphene system with asymmetrical strain distribution parallel to C-C bonds, we used a deformed primitive cell with a fixed value of \( L_x \). The value of \( L_x \) was obtained as the system reaches its lowest total energy during structural relaxation. The deformed primitive cell with the given parameter \( L_x \) and the optimal parameter \( L_y \) was then used to calculate the electronic structure. The graphene systems with \( L_y \) varying from 0.2146 to 0.2496 nm were studied. Figure 3(a) shows the band structure, projected density of states (PDOS), and ELF of the asymmetrically deformed graphene systems with \( L_y=0.2146, 0.2256, 0.2396, \) and 0.2496 nm. The changes of \( L_y \) and the band-gap width are illustrated in Figs. 3(b) and 3(c), respectively. Figure 3(b) shows that \( L_y \) is linearly dependent on \( L_x \), as \( L_x \) is between 0.2136 (without deformation) and 0.2296 nm, indicating that the deformation is elastic. When \( L_y \) is larger than 0.2296 nm, \( L_x \) continues to decrease with a nonlinear decay behavior. A remarkable difference of the band structure for a graphene system with an asymmetrical strain distribution is that the symmetry breaking results in band-gap opening at the Fermi level. Figure 3(c) shows that the width of the band gap increases with \( L_y \) in the regime of \( L_y<0.2396 \) nm and then decreases for \( L_y>0.2396 \) nm. For 0.2136 nm < \( L_y < 0.2396 \) nm, both the valence-band maximum and the conduction-band minimum locate at \( K \) and \( R \) points, indicating that the system has a direct band gap. For \( L_y = 0.2396 \) nm, the conduction-band minimum locates at \( K \) point and the valence-band maximum locates at the left side of \( K \) point, indicating that the band gap is indirect. For 0.2396 nm < \( L_y = 0.2496 \) nm, both the valence-band maximum and the conduction-band minimum locate at the left side of \( K \) point and the band gaps become direct again.

The ELFs in Fig. 3(a) show that the shape of the high ELF regions elongates along the direction of \( L_y \), while being kept almost unchanged along the \( L_x \) direction. This indicates that the C-C bonds become weaker along the \( L_y \) direction while remaining strong along the \( L_x \) direction.

The PDOS in Fig. 3(a) shows that the states near the Fermi level are contributed mainly by the 2\( p_z \) orbitals. Thus, the \( \pi \)-orbital TB approximation is applicable to the system. We found that the energy dispersion of a graphene system with the above asymmetrical strain distribution is given by

\[
E_{\pm}(k) = E_{2p} \mp |\omega|,
\]

with

\[
\omega = \gamma_1 e^{i \vec{k} \cdot \vec{R}_A} + \gamma_2 e^{i \vec{k} \cdot \vec{R}_B} + \gamma_3 e^{i \vec{k} \cdot \vec{R}_C},
\]

\[
\vec{R}_1 = \vec{R}_B - \vec{R}_A \quad (i = 1, 2, 3),
\]

\[
\gamma_1 = \langle \varphi_A | H | \varphi_B (\vec{r} - \vec{R}_B) \rangle \quad (i = 1, 2),
\]

\[
\gamma_2 = \langle \varphi_A | H | \varphi_B (\vec{r} - \vec{R}_B) \rangle.
\]

Here \( \vec{R}_A \) and \( \vec{R}_B \) are the positions of \( C \) atoms marked in Fig. 1(c). Equation (3) gives the band gap,

\[
E_{gap} = 2|\omega|.
\]

Because of the symmetry breaking, the hopping integral \( \gamma_1 \) is not equal to hopping integral \( \gamma_2 \). Our analysis to the function \( \omega \) shows that the band gap can have nonzero values if \( \gamma_1 \) is not equal to \( \gamma_2 \). We found that the first-principles result of the band-gap width can be nicely given by Eq. (4) after choosing appropriate values of \( \gamma_1 \) and \( \gamma_2 \). Figure 4 shows the band structures of the graphene system with \( L_y = 0.2296 \) nm calculated by the first-principles method (curves), and by Eq. (4) (symbols) using \( \gamma_1 = -2.491 \) eV and \( \gamma_2 = -2.03 \) eV. Apparently, two different methods give almost the same result in the energy region close to the Fermi level, showing the existence of a band gap of 0.22 eV. This confirms that it is the symmetry breaking that opens band gap at the Fermi level.

Similar behavior exists in the graphene system with asym-
metrical strain distribution perpendicular to C-C bonds. In these systems, \( L_x \) was given by a value between 0.1243 and 0.1353 nm, and the value of \( L_y \) was obtained when the system reaches its lowest total energy during the structural optimization. The band structure, PDOS, and ELF for the systems with \( L_x \) of 0.1283, 0.1303, 0.1323, and 0.1343 nm are shown in Fig. 5(a). Changes of \( L_y \) and band gaps induced by different values of \( L_y \) are illustrated in Figs. 5(b) and 5(c), respectively. Figure 5(b) shows that the response of \( L_y \) is linear and thus elastic in the range of 0.1233 nm < \( L_y \) < 0.1323 nm, where 0.1233 corresponds to the standard graphene without deformation. For \( L_y \) > 0.1323 nm, \( L_y \) continues to decrease but deviates from the linear behavior. Figure 5(c) shows that in the elastic region with \( L_y \) < 0.1323 nm, the band-gap width increases as \( L_y \) increases, whereas it decreases in the inelastic region with \( L_y \) > 0.1323 nm. For 0.1233 nm < \( L_y \) < 0.1323 nm, both the valence-band maximum and the conduction-band minimum locate at \( K \) and \( R \) points, indicating that the system has a direct band gap. For \( L_y \) = 0.1323 nm, the conduction-band minimum locates at \( R \) point and the valence-band maximum locates at the right side of \( R \) point, indicating that the band gap is indirect. When \( L_y \) is in the inelastic region, both the valence-band maximum and the conduction-band minimum locate at the right side of \( R \) point, and thus the band gap becomes direct again.

The PDOS in Fig. 5(a) shows that the states around the Fermi level are mainly contributed by the 2\( p_z \) orbitals of carbon atoms. Using the same TB approach as described in Eq. (3), we found that the band-gap width obtained by the first-principles method can be nicely reproduced by the TB model as well. This further confirms that symmetry breaking in graphene leads to band-gap opening at the Fermi level.

In summary, the electronic properties of graphene systems with different types of strain distributions have been studied by the \textit{ab initio} calculations and the TB approach. Our results show that the nature of the band structure of graphene depends on its lattice symmetry. With a symmetrical strain distribution, the graphene does not open a band gap at the Fermi level. In this case, one finds zero density of states at the Fermi level and its pseudogap decreases linearly as the strain increases. Asymmetrical strain distributions in graphene open band gaps at the Fermi level. For the strain distribution parallel to C-C bonds, the band gap increases from 0 to 0.486 eV as the strain increases to 13.1% before it decreases under large deformation. For the strain distribution perpendicular to C-C bonds, the band gap increases from 0 to 0.170 eV as the strain increases to 4.91% before decreasing. Clearly, the strain distribution parallel to C-C bonds induces larger band gaps compared with the strain distribution perpendicular to C-C bonds.

We found that the anisotropic nature of the band-gap opening of graphene under large strain is reflected by different Poisson ratios in different directions. Figure 6 illustrates the Poisson ratios \( \nu_x \) and \( \nu_y \) in the directions perpendicular to or parallel to C-C bonds; here the Poisson ratios were calculated directly using the definitions \( \nu_x = (\Delta L_x / L_x) / (\Delta L_y / L_y) \) and \( \nu_y = (\Delta L_y / L_y) / (\Delta L_x / L_x) \). Figure 6 shows that, under small strain (less than 2%), the Poisson ratios in the two directions take the same values, indicating that graphene is isotropic under small strain. Under even smaller strain less than 1.5%, we found that the Poisson ratios are a constant of 0.1732. However, in the regime of large strain (larger than 2%), the two Poisson ratios apparently follow two different decay behaviors, indicating that graphene is anisotropic under large deformation. We note that understanding the elastic properties of 2D graphene is not trivial due to the many-body interatomic interactions as well as the charge redistributions under finite deformations. Early studies suggested that the...
2D hexagonal symmetry of pure C lattice ensure its isotropic elastic properties and thus can be described by an isotropic shell model.\textsuperscript{18–20} The isotropic Poisson ratio under small deformations was found to be 0.149 by first-principles calculations,\textsuperscript{20} which is close to the constant value of 0.1732 we obtained under small strain. Recently, a finite deformation continuum theory was derived from classical interatomic potentials for the analysis of the elastic properties of 2D graphene and carbon nanotubes,\textsuperscript{21} which shows that only the infinitesimal elasticity tensor of 2D honeycomb lattices is isotropic, leading to a Poisson ratio of 0.412 on the basis of Brenner’s potential. The theory also pointed out that the elastic properties of graphene under finite deformations can be anisotropic. Molecular-dynamics simulations based on Brenner’s potential were performed for understanding the elastic properties of finite graphene sheets with finite deformation and the computed elastic constants of rectangular-shaped graphene sheets were found to conform to orthotropic material behavior.\textsuperscript{22} For the rectangular graphene sheet with only two edges constrained to be straight, the Poisson ratio is 0.416 and 0.465 for the strain distribution parallel to or perpendicular to C-C bonds, respectively. For the rectangular graphene sheet with four edges constrained to be straight, the Poisson ratio is 0.428 and 0.520 for the strain distribution parallel to or perpendicular to C-C bonds, respectively. Our first-principles results about the anisotropic behavior of the Poisson ratio for the graphene under large strain qualitatively agrees well with the trend observed in the molecular-dynamics study. We note that, because large strains induce significant changes of the band-gap structure and electron redistribution, the elasticity anisotropy of graphene is a quantum effect that cannot be elucidated completely by applying the classical theory of elasticity. This is why classical potentials can only give a Poisson ratio that is almost three times larger than the values obtained by the first-principles calculations.

In general, breaking the hexagonal symmetry is expected to modify the band structure of graphene.\textsuperscript{9,10} In previous studies, the symmetry breaking of graphene is introduced either by substrates or by cutting graphene to form ribbons. It has been demonstrated that the asymmetrical surface of SiC induced by the surface reconstruction opens band gaps in graphene.\textsuperscript{9} It has also been shown that breaking the symmetry of graphene by cutting it along different directions leads to graphene ribbons with very different electronic properties.\textsuperscript{23–25} The ribbons with zigzag edges obtained by cutting graphene along the direction perpendicular to C-C bonds are metals while those with armchair edges obtained by cutting graphene along the direction parallel to C-C bonds are semiconductors.\textsuperscript{23–25} In our situation, symmetry breaking is induced by the strain perpendicular or parallel to C-C bonds, which corresponds to the zigzag edge or the armchair directions, respectively. Therefore, our results about the anisotropic behaviors of the band structure and the Poisson ratio are in agreement with existing findings in graphene. The anisotropy can be understood by considering the consequences under large strains. The large strain parallel to C-C bonds leads to weakly coupled zigzag carbon chains while the large strain perpendicular to C-C chains results in weakly coupled carbon dimmers. It is understandable that the two different structures have different elastic properties. We note that despite the interest of graphite as basic building block of a variety of nanostructured materials, there is no complete and reliable data set of its elastic properties. The experimental difficulty comes from the lack of large single crystals while the computational efforts are limited by the two completely different types of interatomic bonding—exceptionally strong intralayer bonding and the weak van der Waals interlayer bonding. Experiments using pyrolytic graphite\textsuperscript{26} only observed the significant difference between the in-plane Poisson ratio (\(\nu=0.16\)) and the out-of-plane Poisson ratio (\(\nu=0.012\)) but failed in revealing the in-plane anisotropy due to the large amount of randomly oriented crystallites in the samples. Confirmation of the anisotropic nature of graphene requires further experimental studies using high-quality samples of crystalline graphene and graphite.

It was recently proposed that spin-orbital coupling in graphene also leads to gap opening.\textsuperscript{5–8} However, first-principles calculations\textsuperscript{8} showed that the gap induced by the spin-orbital coupling is very small: about 10\(^{-6}\) eV. Our study indicates that the band gap of graphene can be tuned in the order of 10\(^{-1}\) eV not only by the strength but also by the direction of the strain. Evidently, the strain distributions dominate the gap opening in graphene. Our findings are important for understanding and controlling the transport properties of graphene systems.

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