Effects of Strain on Electronic Properties of Graphene

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We present first-principles calculations of electronic properties of graphene under uniaxial and isotropic strains, respectively. The semi-metallic nature is shown to persist up to a very large uniaxial strain of 30% except a very narrow strain range where a tiny energy gap opens. As the uniaxial strain increases along a certain direction, the Fermi velocity parallel to it decreases quickly and vanishes eventually, whereas the Fermi velocity perpendicular to it increases by as much as 25%. Thus, the low energy properties with small uniaxial strains can be described by the generalized Weyl’s equation while massless and massive electrons coexist with large ones. The work function is also predicted to increase substantially as both the uniaxial and isotropic strain increases. Hence, the homogeneous strain in graphene can be regarded as the effective electronic scalar potential.

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Mechanical strain often gives rise to surprising effects on electronic properties of carbon nanomaterials1–5. It can turn the metallic nanotube into semiconductor and vice versa.6 Along with the uniquely strong mechanical properties of the sp2- and sp3- bonded carbon materials7,8, the interplays between mechanical and electronic properties may be useful in various applications.9 A recent successful isolation of a new carbon allotrope9, graphene, offers a new opportunity to explore such interesting electromechanical properties in two dimensions.

At low energies, graphene at equilibrium has two linear energy bands that intersect each other at the high symmetric points, K and $K'$, of the first Brillouin zone (BZ) and are isotropic with respect to the points.2 Without strains, the density of states vanishes linearly at the Fermi energy ($E_F$) or the Dirac point ($E_D$), exhibiting a semi-metallic nature. Thus, charge carriers are well described by the Dirac’s equation for a (2+1)D free massless fermion.2 Electron states here have another quantum number called a pseudospin which is either parallel or antiparallel to the wavevector of the electron and is of central importance to various novel phenomena.2–13. Mechanical strains can introduce new environments in studying such novel physics of graphene.

In this Rapid Communication, we show that no sizable energy gap opens in uniaxially strained graphene and the variation in energy bands strongly depends on the direction of uniaxial strains. We also predict that the work function increases substantially as both the uniaxial and isotropic strain increases. When an uniaxial strain less than 26.2% is applied along the zigzag chain direction, the semi-metallicity is sustained. Beyond that, the system develops a small energy gap up to 45.5 meV at a strain of 26.5% and then close its gap quickly due to the downshift of the $\sigma^*$ band to the $E_F$. This differs from conclusions of the previous literatures14–21. With uniaxial strain along the armchair chain direction, no energy gap develops. Under uniaxial strain, the group velocities at the $E_F$ are shown to be strong functions of the wavevectors so that the low energy properties with small uniaxial strains can be described by the generalized Weyl’s equation13,22–27. With large uniaxial strains, quasiparticles become massive along the strain direction while ones in the perpendicular direction are still massless.

Computations were carried out using the pseudopotential density functional method with a plane-wave basis set.29 The exchange-correlation interactions were treated within the Perdew-Berke-Enzelhof generalized gradient approximation. The cutoff energy for expansion of wavefunctions and potentials was 400 eV and the Monkhorst-Pack k-point grid of 12 × 12 × 1 is used for the atomic relaxation and of 60 × 60 × 1 for electronic structure calculations. The atomic relaxation was carried out until the change in the total energy per one unit cell was smaller than 0.1 meV. The layer-to-layer distance between adjacent graphene in the supercells is 15.0 Å.

Here, we consider graphene only under uniaxial and isotropic strains, respectively. For comparison, the electronic structures of graphene under uniaxial strains along the two special directions are investigated. The effects of uniaxial strain along arbitrary directions and those of isotropic strains will also be discussed later. Following previous conventions,29 the uniaxial strain along the zig-
zab chain direction [x-axis in Fig. 1(a)] in the honeycomb lattice is denoted by the Z-strain and one perpendicular to this (y-axis) by the A-strain. From the fully relaxed atomic geometries, the calculated Poisson’s ratios for graphene as functions of the magnitude and direction of strains agree with the previous calculations.22

We find that if the magnitude of strain is less than 26.2%, no gap opens with the Z-strain. Graphene with the A-strain also has no energy gap up to a magnitude of 30%. As shown in the energy contour from first-principles calculations, the $E_D$’s coincide with the high symmetric $K$ and $K'$ (or $R$) points of the first BZ without strains (Fig. 1(c)). With the A-strain, the $E_D$’s are away from the symmetric points and the two adjacent $E_D$’s along the $k_y = 0$ line repel each other as the strain increases (Figs. 1(d) and (f)), agreeing with previous calculations.23 Contrary to the cases with the A-strain, the two adjacent $E_D$’s with the Z-strain approach each other (Figs. 1(e) and (g)) and merge together eventually at strain of 26.2%.

The mismatch of the Dirac points with the high symmetric BZ points can be easily understood by one-orbital tight-binding approximations.23 25 26 In the elastic regime under the Z-strain, the kinetic hopping integrals $(t)$ between the nearest neighbors will depend on its connecting vectors, $\delta_i$ $(i = 1, 2, 3)$ such that $t_1 = t_2 < t_2$ where $t_1 \equiv t(\delta_i)$ $(i = 1, 2, 3)$ (Fig. 1(a)). Under the A-strain, $t_1 = t_3 > t_2$. Considering the nearest-neighbor hoppings only, the Hamiltonian of graphene with $Z(A)$-strain can be written as $\mathcal{H} = -t_2 \sum_{k} \xi(k) c_{Ak}^{\dagger} c_{Bk} + c.c.$

where $\xi(k) = e^{i\mathbf{k} \cdot \mathbf{\delta}} (1 + 2 \tan\theta \cos(\kappa_{x} \alpha_{y}))$, $\eta \equiv t_1/t_2 = t_3/t_2$. $k = (k_\alpha, k_\nu)$ and $c_{A(B)k}$ is an annihilation operator for an electron with momentum $k$ on the sublattice $A(B)$. The resulting energy dispersion is given by $E_k = \pm t_2 |\xi(k)|$, $\eta < 1 (\eta > 1)$ for the $Z(A)$-strain. On the $k_y = 0$ line in the first BZ, the $x$-component of $K$-point is given by $k_x = \frac{\pi}{\sqrt{3}a} (1 + \frac{2}{\eta^2})$ whereas the Dirac point with strains, i.e., the zero energy solution, $\xi(k_D, 0) = 0$, is given by $k_D = \frac{\pi}{a_x} \cos^{-1}(\frac{1}{\eta})$. Hence, under the $A(Z)$-strain, $k_D \neq k_K$ as shown in Fig. 1.

We find that the energy splitting between the $\sigma$ and $\sigma^*$ bands at the $S$ point is reduced when the Z-strain increases (Fig. 2) and one at the $\Gamma$ point does with the A-strain (not shown here). The strain-induced small energy gap is eventually closed due to downshift of the $\sigma^*$ band at the Z-strain of 27% (Fig. 2). In very high strain regime, a single orbital tight-binding approximation fails to capture the downshift of $\sigma^*$-orbitals although it shows approximately similar variations of $\pi$-bands in the low and moderate strain regimes.23 It is noticeable that $\pi$ ($\pi^*$) electrons along $SR$ become massive but that those along $ST$ are still massless after the gap closure (Fig. 2). Anomalous area expansion, i.e., the negative Poisson’s ratio is found when the $\sigma^*$ band touches the $E_F$ at the Z-strain larger than 27% because the antibonding states are occupied (the unit cell area increases by 35% under the Z-strain of 30%). However, at this point, graphene may not be stable.21 22 Hereafter, we will consider graphene with strains less than 26.5%.22

As uniaxial strain increases, the group velocity at the $E_D$ increases or decreases substantially depending on the wavevectors (Fig. 3). We calculate the group velocities of electrons by differentiating the energy dispersion of conduction bands directly, i.e., $v_k = \frac{1}{\hbar} \frac{\partial E_k}{\partial k}$. The group velocity along the A-strain ($v_{AA}$ in Fig. 3) decreases as increasing strain while ones ($v_{A1}$ and $v_{A4}$) in direction perpendicular to strains increase. Up to the A-strain of 24%, $v_{AA}$ is reduced by almost 60% of the group velocity without strains ($v_0$) and $v_{A1}$ and $v_{A4}$ increase linearly by 25%. We also find that $v_A$ differs $v_{A4}$ (opposite direction to the former) as shown in Fig. 3(a). Along the specific direction 2 in insets of Fig. 3, $v_{A2} \simeq v_{22} \simeq v_0$. Under the Z-strain, the similar behav-
The group velocities \( (v_{\alpha}) \) of \( \pi \) and \( \pi^* \) electrons with the \( A \)-strain (a) and \( v_{Z2} \), with the \( Z \)-strain along the direction \( i (= 1, 2, 3, 4 \) in inset) in an unit of isotropic group velocity \( (v_0) \) without strain. The angle between the direction A2 and A3 in inset of (a) is 52° and one between Z2 and Z3 in (b) is 38°.

The low energy properties of graphene with moderate strains as revealed by our first-principles calculations can be described well by the generalized Weyl’s equation. By expanding \( \xi(k) \) around \( (k_D, 0) \) up to the first order of small momentum \( q \), \( \xi(q) = \xi (k_D + q_x, q_y) \approx (-\eta^2 - 1)^{1/2} q_x^2 - i q_y q_y \). The resulting Hamiltonian can be written as \( H \equiv v_x \sigma_x q_x + v_y \sigma_y q_y \) where \( \sigma(x,y) \) are Pauli matrices. 

The density of states \( n(E) \) with \( D(E) \) is found to be

\[
q = \left( q_x^2 + q_y^2 \right)^{1/2} \quad \text{and} \quad \Phi(q) = \frac{v_0^*}{v_0} \frac{\cos \phi_q - 1}{\cos \phi_q + 1} \cos \frac{\phi_q}{\cos \phi_q + 1} \cos \frac{\phi_q}{\cos \phi_q + 1}.
\]

The strain-induced reductions in the averaged anisotropic group velocities \( \bar{v}_F^\alpha \) will increase the slope of \( D(E) \) as shown in Fig. 4. The \( D(E) \) changes significantly when \( \sigma^* \) band is near the \( E_F \) with the \( Z \)-strain (Fig. 4(b)). With the large \( Z \)-strain, the merging of two Dirac points signifies the van Hove singularities of the \( \pi \) and \( \pi^* \) bands (24\% case in Fig. 4(b)). When the gap opens with the \( Z \)-strain of 26.5\%, \( D(E < E_F) \sim \sqrt{D_{26.5}} \) and \( D(E > E_F) \) shows a steep enhancement due to the \( \sigma^* \) band.

The work function in uniaxially strained graphene is predicted to increase substantially as the strain increases (Fig. 5). The calculated work function of graphene without strain is 4.5 eV agreeing with the previous theoretical and experimental estimations. As the strain increases up to 12\%, the work function increases linearly by 0.3 eV regardless of the direction of strains as shown in Fig. 5. The work function rises up further to 5.2 eV as the \( A \)-strain reaches 26\%. However, with larger \( Z \)-strains, the work function saturates to 4.8 eV. Hence the variations in the work function can also char-

![FIG. 3: (color online) The group velocities \( (v_{\alpha}) \) of \( \pi \) and \( \pi^* \) electrons with the \( A \)-strain (a) and \( v_{Z2} \), with the \( Z \)-strain along the direction \( i (= 1, 2, 3, 4 \) in inset) in an unit of isotropic group velocity \( (v_0) \) without strain. The angle between the direction A2 and A3 in inset of (a) is 52° and one between Z2 and Z3 in (b) is 38°.](image)

![FIG. 4: (color online) Calculated density of states of graphene with (a) the \( A \)-strain and (b) \( Z \)-strain.](image)

![FIG. 5: (color online) Calculated work functions (\( \Phi \)) of graphene with the \( A \) and \( Z \)-strain.](image)
characterize the direction of the strain. Our calculated results indicate that the controlled charge transfer between gaseous molecules and graphene can be realized by straining graphene. We also anticipate that the strain affects the band lineup at the graphene-metal contact.

To study the effect of uniaxial strains in arbitrary directions, we study the band structure of graphene stretched along the direction rotated by 10.9° with respect to the x-axis in Fig. 1(a). We confirm that no energy gap opens up to a strain of 30% (not shown here). The work function also increases as strain increases. Our ab initio calculations conclude that no energy gap opens under uniaxial strain less than 26% along any arbitrary direction.

Finally, we calculate the variations of electronic properties of graphene under the isotropic strain (I-strain).

Because the I-strain maintains all crystal symmetries of graphene, the electronic structures show no significant changes unlike uniaxially strained cases. The Fermi velocity decreases linearly to 86% of \( v_0 \) as the I-strain increases up to 10% (Fig. 6 (a)). The work function of the system also increases linearly up to 0.64 eV as the I-strain reaches 10% (Fig. 6(b)). From the calculation results, it is shown that the uniform strain induces effective vector\(^{22}\) and electric scalar potential in graphene.

In summary, from first-principles calculations, it is shown that strained graphene does not develop an energy gap and that the group velocities under uniaxial strain exhibit a strong anisotropy. We show that the generalized Weyl’s equation is an appropriate model for uniaxially strained graphene that incorporates all assessed properties that go beyond the simple tight-binding approximations. It is also shown that the work function of strained graphene increases substantially as strain increases.

Note added.—After submission, we became aware of related work on similar systems from other groups\(^{37,38}\).

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1 R. Heyd, A. Charlier and E. McRae, Phys. Rev. B 55, 6820 (1997).
2 L. Yang, M. P. Anantram, J. Han and J. P. Lu, Phys. Rev. B 60, 13874 (1999).
3 T. W. Tombler et al., Nature 405, 769 (2000).
4 L. Yang and J. Han, Phys. Rev. Lett. 85, 154 (2000).
5 E. D. Minot et al, Phys. Rev. Lett. 90 156401 (2003).
6 M.-F. Yu et al., Science 287, 637 (2000).
7 V. Sazonova et al., Nature 431, 284 (2004).
8 K. S. Novoselov et al., Science 306, 666 (2004).
9 A. H. Castro Neto et al, Rev. Mod. Phys. 81, 109 (2009).
10 K. S. Novoselov et al., Nature 438, 197 (2005).
11 Y. Zhang et al., Nature 438, 201 (2005).
12 C.-H. Park et al, Nano Lett. 8, 2920 (2008).
13 C.-H. Park et al, Phys. Rev. Lett. 101, 126804 (2008).
14 Z. H. Ni et al., ACS Nano 2, 2301 (2008).
15 K. S. Kim et al., Nature 457, 706 (2008).
16 T. M. G. Mohiuddin et al., Phys. Rev. B 79, 205433 (2009).
17 M. Huang et al., Proc. Nat. Acad. Sci. 106, 7304 (2009).
18 C. Lee et al., Science 321, 385 (2008).
19 M. L. Teague et al., Nano Lett. 9, 2542 (2009).
20 N. Ferralis, R. Mabouian and C. Carraro, Phys. Rev. Lett. 101, 156801 (2008).
21 R. Khare et al., Phys. Rev. B 75, 075412 (2007).
22 F. Liu, P. Ming and J. Li, Phys. Rev. B 76, 064120 (2007).
23 V. M. Pereira, A. H. Castro Neto and N. M. R. Peres, Phys. Rev. B 80, 045401 (2009).
24 M. Farjam and H. Rafii-Tabar, Phys. Rev. B 80, 167401 (2009).
25 Y. Hasegawa et al., Phys. Rev. B 74, 033413 (2006).
26 M. O. Goerbig et al., Phys. Rev. B 78, 045145 (2008).
27 A. Kobayashi et al., J. Phys. Soc. Jpn. 76,034711 (2007).
28 N. Tajima et al, Europhys. Lett. 80, 47002 (2007).
29 G. Kresse and J. Hafner, Phys. Rev. B 49, 14 251 (1994).
30 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
31 R. Lakes, Science 235, 1038 (1987).
32 D. Porezag et al, Phys. Rev. B 51, 12947 (1995).
33 V. M. Pereira and A. H. Castro Neto, Phys. Rev. Lett. 103, 046801 (2009).
34 M. M. Fogler, F. Guinea and M. I. Katsnelson, Phys. Rev. Lett. 101, 226804 (2008).
35 G. Giovannetti et al., Phys. Rev. Lett. 101, 026803 (2008).
36 C. Oshima and A. Nagashima, J. Phys. Condens. Mat. 9, 1 (1997).
37 M. Mohr et al., Phys. Rev. B 80, 205410 (2009).
38 F. M. D. Pellegrino et al., Phys. Rev. B 81, 035411 (2010).