RAPID COMMUNICATIONS

PHYSICAL REVIEW B **77**, 041403(R) (2008)

Exchange-induced charge inhomogeneities in rippled neutral graphene

L. Brey[1] and J. J. Palacios[1,2]

[1]*Instituto de Ciencia de Materiales de Madrid (CSIC), Cantoblanco 28049, Spain*

[2]*Departamento de Física Aplicada, Universidad de Alicante, San Vicente del Raspeig, E-03690 Alicante Spain*

(Received 29 November 2007; published 4 January 2008)

A mechanism that induces charge density variations in corrugated graphene is proposed. Here it is shown how the interplay between lattice deformations and exchange interactions can induce charge separation, i.e., puddles of electrons and holes, for realistic deformation values of the graphene sheet. The induced charge density lies in the range of $10^{11}-10^{12}$ cm^{-2}, which is compatible with recent measurements.

DOI: 10.1103/PhysRevB.77.041403 PACS number(s): 73.21.−b, 73.20.Hb, 73.22.−f

The ability to isolate and manipulate graphene—single layers of carbon atoms packed in a honeycomb lattice—has opened and boosted the experimental study of the properties of two-dimensional (2D) massless Dirac fermions.[1–3] The existence of a strictly 2D crystal structure is puzzling in itself, as, according to theory and experiments, perfect 2D crystals cannot exist in a free state.[4–6]

Recently, transmission electron microscopy experiments[7] have resolved that suspended graphene sheets are not perfectly flat but exhibit microscopic roughness or ripples such that the surface normal varies by several degrees and the out-of-plane deformation can reach 1 nm. This deformation corresponds to a rather large strain, 1%, but is sustainable without plastic deformations or generation of defects.[7] Also, layers placed on SiO$_2$ seem to follow the corrugation of the substrate.[8,9] The height and width of these ripples are consistent with models which allow the carbon ions to form different types of bonds.[10]

Recent single-electron transistor-based experiments[11] have evidenced the existence of electron and hole puddles of densities $\sim 10^{10}-10^{11}$ cm^{-2} in the vicinity of the neutrality point. The existence of these puddles could be simply related to the presence of a disorder potential induced by the substrate.[12,13] An alternative to this explanation bears on the existence of ripples which leads to a modulation of the hopping amplitudes between carbon atoms. This modulation affects the electronic structure in a twofold manner. First, the modulation induces an effective magnetic field which changes locally the density of states, but does not separate charge.[14] In this respect it has been argued in Ref. 15 that a one-dimensional deformation of the graphene sheet will form zero-energy Landau levels corresponding to an effective magnetic field of tens of teslas. This will increase the compressibility of the system and eventually would induce electronic phase separation. Second, second-neighbor hopping changes can induce a potential on the carriers which does separate charge.[14] An additional source of change in the local density of states has been suggested to come from local Fermi velocity changes induced by the curvature associated to the ripples.[16] This effect induces charge inhomogeneities in doped graphene, but in the presence of electron-hole symmetry, cannot explain the existence of electron-hole puddles in undoped graphene.

In this paper we propose that because of the dependence of the exchange energy on the density of carbon atoms, the strain modulation produced by the ripples induces a charge modulation in undoped graphene. In order to emphasize and highlight the effect of the exchange on the charge inhomogeneity we have disregarded in this work the dependence of the hopping parameter on next-neighbor distance. This is a justified assumption as in graphene a variation of the hopping amplitude can be described by means of a fictitious vector potential which, in general, does not induce significant changes in the density of states.[14] In other words, the degeneracy of the Landau levels and their contribution to the compressibility[15] will be strongly suppressed if a randomly curved graphene sheet[7,10] is considered.

In the following we first point out how the existence of ripples in the graphene surface creates a modulation of the distance between first-neighbor carbon atoms. Then, within the Hartree-Fock approximation, we obtain the total energy of the system as a function of the distance between first-neighbor atoms, d, and of the extra charge per carbon atom, δ. Finally, we show that a long-wavelength modulation of the lattice parameter in the graphene sheet can induce a charge density modulation in undoped graphene.

To simulate the experimental electron diffraction patterns,[7] it is needed to assume a ratio $L/h \approx 10$ between the lateral size of the ripples, L, and the out-of-plane displacement h (see Fig. 1). A prudent estimate for the typical lateral size of the crumpling has been estimated to be between 2 and 20 nm.[7] In our calculation we consider the following out-of-phase modulation:

$$z(\mathbf{R}_i) = h[\sin(GR_{x,i}) + \sin(GR_{y,i})], \tag{1}$$

where $G = 2\pi/L$ and the vectors $\mathbf{R}_i$ are the position of the carbon atoms in a perfectly flat graphene sheet. The average

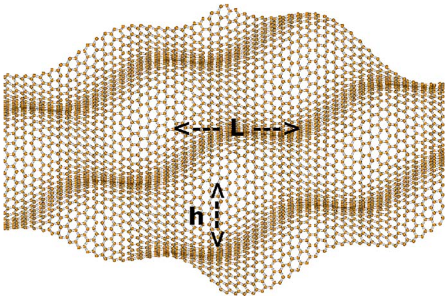

FIG. 1. (Color online) Schematic view of graphene with periodic ripples. L denotes the lateral extent of the ripples and h the out-of-plane displacements of the carbon atoms.

distance between an atom and its three first neighbors depends on the position of the considered atom and is given by

$$d(\mathbf{R}_i) \simeq \tilde{d}\left(1+\frac{h^2G^2}{8}[\cos(2GR_{x,i})+\cos(2GR_{y,i})]\right), \tag{2}$$

$\tilde{d}=d_0(1+h^2G^2/4)$ being the average distance between carbon atoms in the presence of the ripple and d_0 the equilibrium distance between the C atoms in flat graphene. Expression (2) indicates that a modulation in the out-of-plane position of the carbon atoms implies a modulation in the average distance between them.

The electronic active states of graphene are the bands formed by the carbon p_z orbitals which are ordered in a honeycomb lattice (triangular lattice with two atoms per unit cell). The band structure is accurately described by means of a first-neighbor tight-binding Hamiltonian with a unique hopping parameter t. Because of the bipartite character of the honeycomb lattice, the Hamiltonian in reciprocal space is represented by a 2×2 matrix. In undoped graphene there is one electron per carbon atom and the conduction and valence bands touch at two nonequivalent points of the Brillouin zone, which are called Dirac points.

For wave vectors near the Dirac points the electronic structure can be described by a Dirac Hamiltonian of the form

$$H_{kin}=\hbar v_F \mathbf{k}\cdot\boldsymbol{\sigma}, \tag{3}$$

where σ are the Pauli matrices, $\mathbf{k}$ is the electron momentum measured with respect the Dirac point, and the Fermi velocity only depends on the hopping energy t and the next-neighbor distance d_0,

$$\hbar v_F=\frac{3}{2}td_0. \tag{4}$$

The eigenvalues and eigenvectors of Hamiltonian Eq. (3) are

$$\varepsilon_{\pm}(\mathbf{k})=\pm\hbar v_F|\mathbf{k}| \qquad \psi_{\pm}(\mathbf{k})=\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{2}}\begin{pmatrix}1\\ \pm e^{i\theta_{\mathbf{k}}}\end{pmatrix}, \tag{5}$$

where $\theta_{\mathbf{k}}=\arctan k_x/k_y$.

The use of the continuum Dirac Hamiltonian for describing the properties of graphene requires the introduction of a maximum value of momenta, k_c, which is chosen to keep the number of states in the Brillouin zone fixed, i.e., $g_d\pi k_c^2=(2\pi)^2/S_0$. Here $g_d=2$ is the Dirac points degeneracy and $S_0=3\sqrt{3}d_0^2/2$ is the unit cell area.

When doping graphene with electrons or holes the extra carriers form a Fermi sea with Fermi wave vector $k_F=\sqrt{4\pi|n|/(g_dg_s)}$, where n is the 2D density of added charge and $g_s=2$ is the spin degeneracy. The kinetic energy of the system per carbon atom is given by

$$E_{kin}(\delta)=S_0\frac{\hbar}{3\pi}v_F(-k_c^3+k_F^3)=-t\left(\frac{\pi}{6\sqrt{3}}\right)^{1/2}[2^{3/2}-|\delta|^{3/2}], \tag{6}$$

where δ is the extra charge per carbon atom with respect the intrinsic situation. Note that due to the linear dispersion of the bands, when we discard the variation of t on distance, the kinetic energy per carbon atom does not depend on the distance between atoms. From the expression of the kinetic energy, Eq. (6), there is always a kinetic energy cost associated with modulating the charge in undoped graphene.

The exchange contribution to the total energy per carbon atom has the form[17–19]

$$E_{ex}=-\frac{g_sg_d}{4}S_0\sum_{s,s',\mathbf{k},\mathbf{q}}v(q)F_{s,s'}(\mathbf{k},\mathbf{k}+\mathbf{q})n_s(\mathbf{k})n_{s'}(\mathbf{k}+\mathbf{q}), \tag{7}$$

where s and s' is the band index (± 1), $v(q)=2\pi e^2/\epsilon q$ is the 2D Fourier transform of the Coulomb interaction, ϵ is the dielectric constant of the system, $n_s(\mathbf{k})$ is the Fermi occupation function of the state $\{s,\mathbf{k}\}$, and $F_{s,s'}(\mathbf{k},\mathbf{k}+\mathbf{q})$ is the square of the overlap between the wave functions $\psi_s(\mathbf{k})$ and $\psi_{s'}(\mathbf{k}+\mathbf{q})$,[20,21]

$$F_{s,s'}(\mathbf{k},\mathbf{k}+\mathbf{q})=\frac{1}{2}(1+ss'\cos\theta), \tag{8}$$

with θ the angle between the wave vectors $\mathbf{k}$ and $\mathbf{k}+\mathbf{q}$. For Coulomb interaction, the factor (8) makes the exchange interaction larger between states in the same band. In the expression (7) we have neglected the exchange energy between electrons belonging to different Dirac cones. This is appropriated in the long-wavelength approximation because the difference in momentum between states coming from different Dirac points is very large.

Following the notation of Ref. 17 the exchange energy per carbon atom can be written as

$$E_{ex}(d,\delta)=-\frac{1}{16\pi^2}\frac{e^2}{\epsilon d}\left(\frac{2\pi}{\sqrt{3}}\right)^{3/2} \times\left[2^{3/2}R_1(1)+|\delta|^{3/2}R_1(1)+\delta 2^{3/2}R_2\left(\sqrt{\frac{|\delta|}{2}}\right)\right] \tag{9}$$

where the functions $R_n(a)$ are defined in Ref. 17. In the limit of small extra charge one can approximate

$$R_1(1)\simeq 3.776,$$

$$R_2\left(\sqrt{\frac{|\delta|}{2}}\right)\simeq\frac{\pi}{3}\left[3+\sqrt{\frac{|\delta|}{2}}\ln\sqrt{\frac{|\delta|}{2}}+\cdots\right]. \tag{10}$$

In Eq. (9) the first term corresponds to the exchange energy of the full occupied valence band, the second term the exchange energy of the extra electrons or holes, and the last term the variation of the exchange energy because of the interaction between the extra carriers and the valence band electrons. Note that the last term in Eq. (9) changes sign with the electron on hole character of the extra carriers.

Expressions (6) and (9) have been obtained for a uniform system. For long-wavelength modulations of d and δ, the total energy per carbon atom can be written as

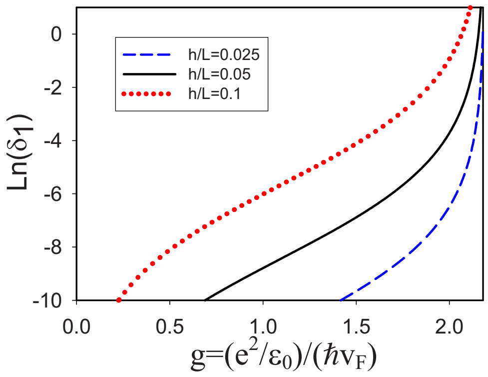

FIG. 2. (Color online) Amplitude of the charge modulation per carbon atom, δ_1, as a function of the coupling constant for different values of the ratio h/L.

$$E_T = \frac{1}{S}\int d\mathbf{r}[E_{kin}(\delta(\mathbf{r})) + E_{ex}(d(\mathbf{r}),\delta(\mathbf{r}))]. \qquad (11)$$

This equation couples a modulation of the first-neighbor distance between carbon atoms with a modulation of the electron density.

In undoped graphene a modulation $d(\mathbf{R})$ of the form described in Eq. (2) will produce, in the linear regime, a modulation of the electric charge of the form

$$\delta(\mathbf{R}) = \delta_1[\cos(2GR_{x,i}) + \cos(2GR_{y,i})], \qquad (12)$$

where the amplitude of the charge modulation, δ_1, is obtained by minimizing the total energy, Eq. (11). To lowest order, the charge amplitude δ_1 only depends on the ratio h/L and on a dimensionless coupling constant defined as

$$g = \frac{e^2/\epsilon_0}{\hbar v_F}. \qquad (13)$$

The constant g indicates the ratio between the Coulomb and the kinetic energy of the electron system.

For values larger than a critical coupling constant, $g_c \sim 2.18$, the total energy does not present a minimum as function of δ_1. This indicates that the system is unstable against more correlated phases, and therefore the lower-order calculation fails. This value of the coupling constant is considerably smaller than the critical value of g ($g \sim 5.3$) needed for the occurrence of instabilities towards highly correlated states in flat graphene.[17] For values of $g < 2.18$ the total energy presents a minimum and the electronic system reacts to the lattice deformation by modulating the charge according to Eq. (12). In Fig. 2 we plot the value of δ_1 that minimize the total energy as function of the coupling constant for different values of the ratio h/L.

The distance between carbon atoms in graphene and the hopping amplitude are quantities well established: $t \cong 2.5$ eV and $d_0 = 1.42$ Å. Therefore a realistic estimation of the coupling constant g only requires knowledge of the value of the dielectric constant. This should take account both the effect of the screening current in the substrate and the weak intrinsic screening in graphene.[22] We estimate that depending on whether the graphene sheet is freely suspended or it is placed on top of an insulator, the dielectric constant would take values in the range $3 < \epsilon < 4$. For these values of ϵ, the coupling constant takes values in the range $0.66 < g < 0.88$. For these values of g, we can see in Fig. 2 that the use of the lower-order coupling between h and δ_1 is appropriate.

For an intermediate coupling constant $g = 0.75$, we obtain $\delta_1 \simeq 9\left(\frac{h^2}{L^2}\right)^2$ which, for values of the ratio h/L in the range 0.05–0.1, implies values of δ_1 in the range 5.6×10^{-5}–0.9×10^{-4}. This corresponds to density modulations in the range 2.25×10^{11}–3.6×10^{12} cm^{-2}. From this estimate we conclude that a modulation of the out-of-plane position of the carbon atoms of amplitude $h \sim 1$–2 nm in a lateral size $L \sim 10$–20 nm induces a modulation in the charge density of the order of 10^{11} cm^{-2}. This magnitude of the charge modulation agrees with the density of charge in the electron-hole puddles observed by single-electron transistor-based experiments.[11] Interestingly, in suspended graphene the contribution of the substrate to the dielectric constant is practically suppressed. In this case the coupling constant becomes larger than in the case of graphene placed on a dielectric. Therefore we expect a higher-density modulation in suspended graphene than the observed in graphene on SiO$_2$.

It is also pertinent to estimate the importance of the Hartree repulsion on the values of the charge density modulation. The Hartree energy per carbon atom takes the form

$$E_H = \frac{S_0}{8\pi^2}\sum_{\mathbf{G}'}\frac{2\pi e^2}{\epsilon G'}n(\mathbf{G}')n(-\mathbf{G}') = \frac{1}{8\pi^2 3\sqrt{3}}\delta_1^2\frac{L}{d_0}\frac{e^2}{\epsilon d_0}. \qquad (14)$$

In the above expression $n(\mathbf{G}')$ is the $\mathbf{G}'$-component Fourier transform of the charge. For values of the dielectric constant and L we obtain that the Hartree energy is much smaller than the kinetic and exchange energy and the values obtained for the charge density modulation are practically unaffected by the Hartree repulsion.

In addition to the effect discussed in this work one should also consider the influence of the hopping dependence on lattice strain discussed in Refs. 14 and 15. Realistic estimates of the influence of second-neighbor hopping variations indicate that these are typically smaller than the one discussed here. In any case, both effects are compatible. Regarding the formation of Landau levels and their influence on the compressibility, we have verified numerically[23] that the density of states close to the neutrality point is not seriously affected by the effective magnetic fields when crumpled graphene with uncorrelated ripples is taken into consideration. This contrasts with the strong influence that periodic ripples exert on the density of states near the Dirac point.[15]

We notice that the exchange interaction between carriers produces a coupling between a modulation of the distance between first-neighbor atoms in graphene and a charge density modulation. This mechanism connects the presence of ripples in undoped graphene with the existence of electron-hole puddles of density up to 10^{12} cm^{-2}. These densities are of the same order than those observed recently in single-electron transistor measurements.[11] In suspended graphene the absence of substrate makes the exchange energy stronger and we predict that this increase will produce a higher modulation of the charge density.

We acknowledge useful discussions with F. Guinea, M. A. H. Vozmediano, A. Cortijo, and C. Tejedor. This work has been financially supported by MEC-Spain (Grants Nos. FIS2004-02356 and MAT2006-03741) and by Generalitat Valenciana (Grants Nos. ACOMP07/054 and GV05-152). This work has also been partly funded by FEDER funds.

---

[1] K. S. Novoselov, A. K. Geim, S. V. Mozorov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Gregorieva, and A. A. Firsov, Science **306**, 666 (2004).

[2] K. S. Novoselov, D. Jiang, T. Booth, V. Khotkevich, S. M. Morozov, and A. K. Geim, Nature (London) **438**, 197 (2005).

[3] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, Nature (London) **438**, 201 (2005).

[4] N. D. Mermin, Phys. Rev. **176**, 250 (1968).

[5] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1980), Pt. 1.

[6] K. S. Novoselov, A. K. Geim, S. V. Mozorov, D. Jiang, M. I. V. Gregorieva, S. V. Dubonos, and A. A. Firsov, Proc. Natl. Acad. Sci. U.S.A. **102**, 10451 (2005).

[7] J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J. Booth, and S. Roth, Nature (London) **446**, 60 (2007).

[8] E. Stolyarova, K. T. Rim, S. Tyu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hyberstein, and G. W. Flynn, Proc. Natl. Acad. Sci. U.S.A. **104**, 9209 (2007).

[9] M. Ishigami, J. H. Chen, W. G. Cullen, M. S. Fuhrer, and E. D. Williams, Nano Lett. **7**, 1643 (2007).

[10] A. Fasolino, J. H. Los, and M. I. Katsnelson, arXiv:0704.1793 (unpublished).

[11] J. Martin, N. Akerman, G. Ulbricht, T. Lohmann, J. H. Smet, K. von Klitzing, and A. Yacoby, arXiv:0705.2180 (unpublished).

[12] E. H. Hwang, S. Adam, and S. Das Sarma, Phys. Rev. Lett. **98**, 186806 (2007).

[13] B. I. Shklovskii, arXiv:0706.4425 (unpublished).

[14] A. Castro Neto and E. A. Kim, arXiv:cond-mat/0702562 (unpublished).

[15] F. Guinea, M. I. Katsnelson, and M. A. H. Vozmediano, arXiv:0707.0682 (unpublished).

[16] F. de Juan, A. Cortijo, and M. A. H. Vozmediano, Phys. Rev. B **76**, 165409 (2007).

[17] N. M. R. Peres, F. Guinea, and A. H. Castro Neto, Phys. Rev. B **72**, 174406 (2005).

[18] E. Hwang, B.-K. Hu, and S. Das Sarma, Phys. Rev. Lett. **99**, 226801 (2007).

[19] Y. Barlas, T. Pereg-Barnea, M. Polini, R. Asgari, and A. H. MacDonald, Phys. Rev. Lett. **98**, 236601 (2007).

[20] B. Wunsch, T. Stauber, F. Sols, and F. Guinea, New J. Phys. **8**, 318 (2006).

[21] L. Brey and H. A. Fertig, Phys. Rev. B **75**, 125434 (2007).

[22] J. Gonzalez, F. Guinea, and M. A. H. Vozmediano, Phys. Rev. B **59**, R2474 (1999).

[23] J. J. Palacios and L. Brey (unpublished).