Nanotechnology 26 (2015) 045707 (7pp)

# Soliton instability and fold formation in laterally compressed graphene

## Amauri Libério de Lima<sup>1</sup>, Lucas A M Müssnich<sup>2</sup>, Taíse M Manhabosco<sup>1</sup>, Hélio Chacham<sup>3</sup>, Ronaldo J C Batista<sup>1</sup> and Alan Barros de Oliveira<sup>1</sup>

<sup>1</sup>Departamento de Física, Universidade Federal de Ouro Preto, Ouro Preto, MG, 35400-000, Brazil

<sup>2</sup> Departamento de Física-Matemática, Universidade de São Paulo, São Paulo, SP, 05314-970, Brazil

<sup>3</sup> Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, MG, 30123-970, Brazil

E-mail: deoliveira.alanbarros@gmail.com

Received 24 September 2014, revised 1 December 2014 Accepted for publication 2 December 2014 Published 8 January 2015



#### Abstract

We investigate—through simulations and analytical calculations—the consequences of uniaxial lateral compression applied to the upper layer of multilayer graphene. The simulations of compressed graphene show that strains larger than 2.8% induce soliton-like deformations that further develop into large, mobile folds. Such folds were indeed experimentally observed in graphene and other solid lubricants two-dimensional (2D) materials. Interestingly, in the soliton-fold regime, the shear stress decreases with the strain *s*, initially as  $s^{-2/3}$  and rapidly going to zero. Such instability is consistent with the recently observed negative dynamic compressibility of 2D materials. We also predict that the curvatures of the soliton-folds are given by  $r_c = \delta \sqrt{\beta/2\alpha}$ , where  $1 \le \delta \le 2$ , and  $\beta$  and  $\alpha$  are respectively related to the layer bending modulus and to the interlayer binding energy of the material. This finding might allow experimental estimates of the  $\beta/\alpha$  ratio of 2D materials from fold morphology.

Keywords: graphene, structure, 2D materials

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Graphene has gained much attention from the scientific community since its discovery because of its unique features. For example, it has been considered as a possible building block for circuit components due to its particular electronic properties. Ideally, deposited graphene should be perfectly flat. However, although graphene has one of the highest known Young's modulus, it has a small bending modulus [1]. In real applications, graphene sheets commonly present ripples and folds [2-5], which may change their electronic structure. For example, theoretical studies suggest that folded graphene under external magnetic fields act as an interferometer: it suffers the interference due to the interplay between gauge fields created by the fold and the external fields in the region of the fold [6]. Zheng *et al* have shown that the calculated Young's modulus, tensile strength, and fracture strain of folded graphene are comparable to those of graphene, while the compressive strength and strain are much higher than those of planar graphene [7].

Folds have been observed in several conditions and in a variety of forms. For example, they were seen in the top layers of graphite [8, 9] whereas edge folds in suspended graphene have been reported as well [10–14]. Yu and collaborators were able to obtain the structural information of wrinkles, such as hight and width, by gold deposition on its vicinity [15]. Yet, by concomitantly applying compressive and shear stresses through an atomic force microscopy tip upon few layer graphene, Barboza and collaborators obtained structures which appear to be single- and multi-folded graphene [16]. Multiply folded graphene—termed grafold by Kim and coworkers [17]—were indeed confirmed to exist and, not surprisingly, its novel electronic structure can be quite different in comparison to flat graphene [17–19].

Theoretical models suggest that folds in graphene can change its chemical affinity, since curvatures induce deformations in the  $\sigma$ -bonds of the lattice. Such out-of-plane deformed bonds could transfer charges to  $\pi$ -orbitals, which induce localized dipole moments in the graphene surface [20]. This property could lead to localized selective functionalization of atoms and molecules. For example, Tozzini and collaborators have shown that storage (through adsorption) and release of hydrogen can, in principle, be obtained by exploiting and controlling the corrugation of individual layers of graphene [21]. Storage of molecules can also be achieved by wrapping chemical species into graphene folds as sandwiches [17, 22, 23].

Given the relevance of graphene folds, it is important to understand the physics behind the folding process. Bending orientation, defects, and contamination are probably relevant to such a process [24-29]. In this work we investigate through molecular dynamics and theoretical calculations-the consequences of uniaxial lateral compression applied to the upper layer of multilayer graphene. At low strains, the cancellation of nonlinear and dispersive effects in graphene gives rise to a pulse that maintain its shape while traveling at constant speed. We have found that such solitons evolve into mobile folds with increasing strains. Our results include the derivation of curvature radii of some of the main structures formed during compression in terms of interlayer binding and bending energies,  $\alpha$  and  $\beta$ , respectively. Our results can be applied to any solid lubricant, such as molybdenum disulphide and hexagonal boron nitride.

This work goes as follows. In section 2, we describe the molecular dynamics methodology and the main fold structures that result from the simulations. In section 3, we develop analytical models for the fold structures. Section 4, analyzes the simulation results and compares them with the analytical models. In section 5, we present our conclusions.

### 2. Molecular dynamics: methodology and fold structures

Molecular dynamics techniques were used as implemented in the package LAMMPS [30]. Carbon atoms were modeled classically using the adaptive intermolecular reactive empirical bond order (AIREBO) potential for the C–C interaction [31]. Our system is composed of two graphene layers, each containing 1600 atoms. The bottom layer was kept 'frozen' during all simulations, i.e., the resultant force on every atom of this layer was set to zero. Both ends of the top layer were also maintained frozen: the resultant forces acting upon 32 atoms of each extrema were kept at zero in all simulations. The periodic boundary condition was used in the y direction, while directions x and z were finite. The dimensions of the layers were 207.0 and 18.1 Å in the x and y directions, respectively. The equilibrium distance between layers was found to be around 3.4 Å.

Simulations were performed in the canonical ensemble. The Nosé–Hoover thermostat [32, 33] as implemented by Shinoda and collaborators [34] was used in order to keep the temperature T = 10 K. The timestep used was 0.001 ps.

Compressive strain in the upper layer was imposed along the x direction by moving one of its frozen edges towards the other edge at constant velocity v = dx/dt = 0.1Å/ps in the x direction. By increasing the strain, different structures are formed in the upper layer. Here, we focus on



**Figure 1.** Projection of the graphene bilayer into the *xz* plane obtained through simulations. (a) The moment immediately before the soliton formation at strain s = 2.8% (see section 4 for the definition of the strain). (b) The soliton structure and (c) the structure we termed as the *standing fold*, which appear at s = 27.5%. (d) The structure which appears at approximately s = 28%. We named it as the *standing collapsed fold*.

those shown in figure 1. In figure 1(a) it is possible to see the *xz* projection of the upper layer in the moment immediately before a soliton-like structure appears. The soliton is shown in figure 1(b). By further increasing *s*, two distinct structures appear in sequence. The first is the *standing fold*, shown in figure 1(c). The second is the *standing collapsed fold*, as seen in figure 1(d). For studying such structures, we developed theoretical models which are detailed in the next section.

#### 3. Analytical model

Our model consists of a continuum two-dimensional (2D) material, ideally deposited on a substrate that is parallel to the *xy* plane. Wrinkles may appear parallel to the *y* direction, such that the local height *z* is a function of *x* only. The 2D material is incompressible but can be bent, with a bending modulus  $\beta$  defined such that the curvature energy per unit length, for a given curvature radius *r*, is given by  $\epsilon_b = \beta/r^2$ . We also consider that the binding energy per unit area between the 2D material and the substrate is given by  $\epsilon_a = \alpha$ . In this sense, we considered the zero energy when the 2D material lies deposited on the substrate. The energy cost to bend the material is  $\epsilon_b \ell_b$ , where  $\ell_b$  is the portion of the material which is curved, while the energy to detach the material from the substrate is  $\epsilon_a \ell_a$ , with the corresponding detached length  $\ell_a$ .

#### 3.1. The soliton structure

Let us first consider the soliton-like structure shown in figure 1(b). We model this structure with three circle segments, as shown in figure 2. Considering the continuum model described above, the formation energy per unit length



**Figure 2.** Model for the soliton formation.  $r_1$  and  $r_2$  correspond to the top and basis radii, respectively, along with its corresponding angles,  $\theta_1$  and  $\theta_2$ .

(along y) of such a soliton is given by

$$\epsilon = 2\alpha \left( r_1 \theta_1 + r_2 \theta_2 \right) + 2\beta \left( \frac{\theta_1}{r_1} + \frac{\theta_2}{r_2} \right). \tag{1}$$

As a result of the soliton formation, the 2D material will have an apparent reduction in length, along *x*, of magnitude  $\mu$ . From figure 2,  $\mu$  is given by

$$\mu = 2(r_1\theta_1 + r_2\theta_2) - 2(r_1\sin\theta_1 + r_2\sin\theta_2).$$
(2)

If we consider small angles  $\theta_1$  and  $\theta_2$ , we can approximate equation (2) as

$$\mu \approx \frac{r_1 \theta_1^3}{3} + \frac{r_2 \theta_2^3}{3}.$$
 (3)

Defining variables  $q_i \equiv 2\beta \theta_i / r_i$  and  $t_i \equiv 2\alpha r_i \theta_i$ , with i = 1, 2, equations (1) and (3) can be rewritten as

$$\epsilon = t_1 + t_2 + q_1 + q_2 \tag{4}$$

and

$$\mu = \frac{1}{24\alpha^2 \beta} \Big( q_1 t_1^2 + q_2 t_2^2 \Big). \tag{5}$$

The profile of the soliton can be found by minimizing its energy, equation (4), with  $\mu = \text{ constant.}$  We find

$$t_1 = t_2 = \left(24\alpha^2\beta\mu\right)^{1/3}$$
 and  $q_1 = q_2 = \frac{1}{2}t_1$ . (6)

Equations (6) lead to

$$r_1 = r_2 = \sqrt{2} \sqrt{\frac{\beta}{\alpha}} \tag{7}$$

$$\theta_1(\mu) = \theta_2(\mu) = \left(\frac{3}{2}\sqrt{\frac{\alpha}{2\beta}}\right)^{1/3} \mu^{1/3}$$
(8)

$$\epsilon(\mu) = 3\left(24\alpha^2\beta\right)^{1/3}\mu^{1/3} \tag{9}$$



**Figure 3.** Model for the *standing fold* structure. It has a top part modeled as a semi-circle with radius  $R_1$  connected to the basis (quarter circles with radius  $R_2$ ) by straight lines with length *h*.

$$l(\mu) = 4 \left(\frac{3\beta}{\alpha}\right)^{1/3} \mu^{1/3}.$$
 (10)

From equations (7)–(10) we see that the soliton radii  $r_1$ and  $r_2$  are independent of  $\mu$  (and thus must be strain independent), whereas the angles  $\theta_1$  and  $\theta_2$  scale with  $\mu^{1/3}$ . This interesting behavior suggests that for  $\mu \to 0$ , the soliton localizes and disappears without 'flattening'. Another interesting behavior is that of the tension f (force per unit length) necessary to maintain the soliton at a given  $\mu$ . From equation (9), we obtain

$$f(\mu) = -d\epsilon/d\mu = K\mu^{-2/3},$$
(11)

with  $K = -(24\alpha^2\beta)^{1/3}$ . That is, the magnitude of *f* reduces with increasing soliton size, and tends to infinity as the soliton disappears.

#### 3.2. The standing fold structure

For larger values of compressive strain, the soliton structure evolves to the pattern shown in figure 1(c), and schematically shown in figure 3. We model this structure as follows. The profile of the top part is composed by a semi-circle with radius  $R_1$ . A stem is formed by two straight lines with length h, and the basis is formed by quarter circles with radii  $R_2$ . The formation energy of such a structure is given by

$$E = \left[\pi \left(R_1 + R_2\right) + 2h\right] \alpha + \beta \pi \left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$
 (12)

The net length to form this structure can be written as

$$\mu = (\pi - 2)(R_1 + R_2) + 2h.$$
(13)

Equations (12) and (13) reduce to

$$E = \alpha \Big[ \mu + 2 \big( R_1 + R \big) \Big] + \beta \pi \bigg( \frac{1}{R_1} + \frac{1}{R_2} \bigg).$$
(14)

After minimizing equation (14) with respect to  $R_1$  and  $R_2$  with  $\mu$  constant, one obtains

$$R_1 = R_2 = \sqrt{\frac{\pi}{2}} \sqrt{\frac{\beta}{\alpha}}.$$
 (15)



**Figure 4.** The proposed model for the *standing collapsed fold*. The top and the basis are arcs of a circle with radii  $R_1$  and  $R_2$ , respectively.

#### 3.3. The standing collapsed fold structure

By further increasing the strain, the next type of structure observed for compressed graphene is schematically shown in figure 4. It corresponds to the structure shown in figure 1(d) obtained through simulations. We call this structure a *standing collapsed fold*. We modeled such a structure as an arc of circle of radius  $\mathcal{R}_1$ , forming the top of the structure, which is connected to the basis by arcs of circle of radius  $\mathcal{R}_2$ .  $g_1(\mathcal{R}_1, \phi) = \mathcal{R}_1 \phi$  and  $g_2(\mathcal{R}_2, \psi) = \mathcal{R}_2 \psi$  are the functions that define the head and the basis curves in polar coordinates, respectively.  $g_1$  and  $g_2$  intercept each other at the point P. In this sense,  $g_1(\mathcal{R}_1, \phi = \gamma) = g_2(\mathcal{R}_2, \psi = \theta)$ . Since  $\gamma = \pi/2 - \theta$ , we find that

$$\theta = \frac{\mathcal{R}_1 \pi}{2(\mathcal{R}_1 + \mathcal{R}_2)}.$$
(16)

The formation energy is given by

$$\mathcal{E} = (\pi + 2\theta) \left[ \left( \mathcal{R}_1 + \mathcal{R}_2 \right) \alpha + \left( \frac{1}{\mathcal{R}_1} + \frac{1}{\mathcal{R}_2} \right) \beta \right]. \quad (17)$$

The variable  $\theta$  can be eliminated from equation (17) with the help of equation (16). Thus, the energy reduces to

$$\mathcal{E} = \alpha \pi \left( 2\mathcal{R}_1 + \mathcal{R}_2 \right) + \beta \pi \left( \frac{1}{\mathcal{R}_1} + \frac{2}{\mathcal{R}_2} \right).$$
(18)

By minimizing with respect to  $\mathcal{R}_1$  and  $\mathcal{R}_2$ , i.e., performing  $\partial \mathcal{E} / \partial R_1 = 0$  and  $\partial \mathcal{E} / \partial R_2 = 0$ , one finds

$$\mathcal{R}_1 = \frac{\sqrt{2}}{2} \sqrt{\frac{\beta}{\alpha}} \quad \text{and} \quad \mathcal{R}_2 = \sqrt{2} \sqrt{\frac{\beta}{\alpha}}.$$
 (19)

It is possible to calculate the length of the rope,  $\mathcal{L}$ , detached from the substrate as a function of  $\alpha$  and  $\beta$ . By



**Figure 5.** Tension in the upper graphene layer as a function of the induced strain *s*. At *s* = 0, the tensile force upon the graphene layer is zero. By increasing *s*, the graphene behaves as an elastic medium until the soliton formation at *s* = 2.8%. At this point, internal forces are released, causing the discontinuity seen in the figure. For *s* > 2.8 the curve decays as  $s^{-2/3}$  which is explained by our theoretical model (see section 3). Arrows (a)–(d) correspond to the instants where the structures seen in figure 1 appear.

simple inspection of figure 4, we see that

$$\mathcal{L} = (\pi + 2\theta) \big( \mathcal{R}_1 + \mathcal{R}_2 \big). \tag{20}$$

Once  $\mathcal{R}_2 = 2\mathcal{R}_1$ , equation (16) gives  $\theta = \pi/6$ . This result, along with equations (19) and (20), gives

$$\mathcal{L} = 2\sqrt{2}\,\pi\sqrt{\frac{\beta}{\alpha}}\,.\tag{21}$$

Another important result we can derive from this model is the minimum distance between the base arcs d. From figure 4, we find that

$$d = 2\left[\left(\mathcal{R}_1 + \mathcal{R}_2\right)\cos\theta - \mathcal{R}_2\right]$$
$$= \frac{\sqrt{2}}{2}\left(3\sqrt{3} - 4\right)\sqrt{\frac{\beta}{\alpha}},$$
(22)

where we have used equation (19) and  $\theta = \pi/6$ .

#### 4. Simulation results

We define the compressive strain in the upper layer as  $s(t) = vt/L_x$ , where  $L_x$  is the dimension of the layer in the x direction and t is the time. In this sense, the strain is zero at the initial time, t = 0, and it is at maximum (s = 100 %) when  $vt = L_x$ .

In order to characterize the structures shown in figure 1, namely, the soliton, the *standing fold* and the *standing collapsed fold*, we calculated the tension versus the compressive strain in the upper layer. The tension was calculated as  $P_{xx}L_y$ , where  $P_{xx}$  is the virial contribution for the component of the stress tensor in the x direction, and  $L_y$  is the dimension of the



**Figure 6.** Dots: the soliton as obtained in our simulations. Continuous curve: result from the soliton model (equations (7) and (8)).



**Figure 7.** Dots: the *standing fold* structure, as obtained in the simulations (also seen in figure 1(c)). Continuous curves: curvature radii as obtained from the analytical model, see equation (15) and relation (24).

simulation box in the ity direction.  $P_{xx}$  is given by

$$P_{xx} = \frac{1}{V} \sum_{i=1}^{N} x^{i} f_{x}^{i}, \qquad (23)$$

where *V* is the volume of the simulation box, *N* is the number of particles,  $x^i$  is the coordinate *x* of particle *i*, and  $f_x$  is the component of the resultant force acting on particle *i* in the *x* direction.

Our tension versus strain results are summarized in figure 5. Arrows (a)–(d) indicate the instants where the structures shown in figure 1 appear. In the first stages of compression, the layer behaves elastically, with linear response to the applied strain. The straight, continuous line corresponds to a linear fitting through the data whose angular coefficient was found to be 0.21 N m<sup>-1</sup>. After reaching a maximum tension  $\tau$  value, at s = 2.8%, the soliton appears, releasing internal forces, which explains the discontinuity in the stress–strain curve. Further increasing *s*, the tension decays towards zero with a  $s^{-2/3}$  dependence. Such a dependence is explained by our analytical model,



**Figure 8.** Dots: *collapsed standing fold* structure, also seen in figure 1(d). Countinuous curve: analytical model; see equations (19) and (24).

equation (11). The fitting for s > 2.8% (dashed line) was made by using a function in the form  $\tau = \kappa s^{-2/3}$ , where  $\kappa = 0.003$  N m<sup>-1</sup>.

We have also compared predictions of our theoretical models with the results from the simulations. Figures 6-8 show the structures seen in figures 1(b)-(d), respectively, superimposed with continuous curves that correspond to curvatures as obtained by our models.

The results from the models depend on the interlayer binding energy and the bending modulus of the graphene ( $\alpha$ and  $\beta$ , respectively), always in the form  $\sqrt{\beta/\alpha}$ , which turned out to be an *intrinsic length scale*. There have been several attempts to determine the graphite binding energy, both experimentally [35–37] and theoretically [38–42]. To the best of our knowledge, the most recent, direct graphite binding energy measurement is given by Liu *et al*, who have obtained  $\alpha = 31$  meV/atom [43]. For the graphene bending modulus, the most direct measurement is due to Barboza and collaborators [1] who have found  $\beta = 1.64$  eVÅ<sup>2</sup>/atom. Thus, the *intrinsic length scale* seen in our models is given by

$$\sqrt{\beta/\alpha} = 7.0 \text{ Å.} \tag{24}$$

The soliton model (figure 2) predicts that the radii of both basis and top must be the same. We have found such curvature radii  $r_1 = r_2 = 9.9$  Å (see equation (7)). In order to compare the model and simulation results, we have used equation (8) with  $\mu = 3.0$  Å (estimated from simulations) for drawing the soliton as predicted by our model. This leads to  $\theta = 44^\circ$ . The resulting curve is seen in figure 6 as a line, while the circles mark the position of carbon atoms, obtained by simulations.

Figure 7 shows the *standing fold* structure as obtained by simulations. This structure is seen when the strain *s* is around 27.5% (see figure 5). We have modeled such a structure as having circumference arcs in the top (with radius  $R_1$ ) and in the basis (radius  $R_2$ ) (see figure 3). Top and basis are connected by straight lines with length *h*. We obtained  $R_1 = R_2 = 8.8$  Å (see equation (15)). Figure 7 shows the model



**Figure 9.** Height of the fold structures, relative to the unstrained upper layer, versus the induced strain. The black curve refers to simulations with increasing strain, and red curve refers to simulations with decreasing strain. The *standing collapsed fold* is formed at s = 28% in the increasing strain simulation, but it persists for strains up to s = 13.4% in the decreasing strain simulation, evidencing a hysteresis effect.

predictions (lines) along with simulations results (circles). We see that in spite of the model's simplicity, it gives reasonable results compared to simulations without the need of any information from it other than the bending modulus and the binding energy values. Therefore, such models can be used to make predictions on the fold geometry of other solid lubricants and vice-versa, that is, to predict the value of the ratio  $\beta/\alpha$  based purely on fold geometry.

Finally, figure 8 shows the standing collapsed fold, which was modeled as having  $R_1$  for the top radius and  $R_2$  for the basis (as shown in figure 4). We concluded that the condition that minimizes the energy of the collapsed fold is  $R_2 = 2R_1$ , given by equations (19). Our findings are  $R_1 = 4.95$  Å and  $R_2 = 9.9$  Å. Note that the laterals of this structure tend to approach the bilayer distance (around 3.4 Å) for big strains as expected. The result from the model for such a distance is d = 5.9 Å (see equation (22)), which lies in the same order of magnitude. Since we have not considered the occurrence of a van der Waals interaction between layers, it is not surprising we have found a bigger value for such a distance than the expected value of ~3.4Å.

We have found from the *standing collapsed fold* model an expression for the length of the layer which is detached from the substrate as a function of  $\alpha$ , and  $\beta$ , in the moment it is formed (equation (21)). We estimate such a value from simulation as 84 Å, while equation (21) gives 62 Å.

In order to investigate the stability of the *standing collapsed fold* structure, we proceeded as follows. As stated in section 2, strain was induced in the x direction of the upper layer by moving one of its extremities towards the opposite one at constant velocity. After a certain maximum strain, we inverted the movement direction, keeping the velocity modulus, which continuously reduces the strain. During this 'forward backwards' process, we monitor the height of the structures in relation to the upper layer against the induced

strain. The results are summarized in figure 9. From this figure, we see all the stages approached in this work, namely, the soliton (see the jump at around s = 2.8% which characterizes its appearance) and its continuation until the *standing fold* takes place at around s = 27.5%. At s = 28%, we observe the transition from *standing fold* to *standing collapsed fold* with linear dependence between height and strain for s > 28%. When the direction of the movement is inverted, the *standing collapsed fold* becomes stable for strains below s = 28%. Indeed, the 'uncollapsing' transition occurs at s = 13.4%. Figure 9 has the characteristics of a hysteresis curve, in which the state of the system depends not only on the strain at a certain time, but also on its history.

#### 5. Conclusions

This work is an investigation-through molecular dynamics and analytical calculations-of a laterally compressed graphene monolayer atop uncompressed graphene (simulating an uncompressed graphite surface). Under compression, several structures appear in the top graphene layer. Three structures can be clearly identified: the soliton, the standing fold, and the standing collapsed fold structures. We propose models for each of these structures, and we have determined curvature radii for those structures in terms of  $\alpha$  and  $\beta$ , the interlayer binding and bending energies, respectively. Our models indicate that all structures have characteristic radii in terms of  $\sqrt{\beta/2\alpha}$ , as seen in equations (7), (15), and (19). This result is general and can be applied to other solid lubricants, such as MoS<sub>2</sub>, talc, and hexagonal boron nitride, for example, to estimate the ratio  $\beta/\alpha$  from fold morphology. We have also found that the standing collapsed fold shows bi-stability in relation to the strain s, depending on the path for achieving critical strains. Upon increasing strain, this structure appears at s = 28%. Once it appears, if the strain is decreased, the standing collapsed fold remains stable until s = 13.4%, showing a hysteresis behaviour.

#### Acknowledgments

We are grateful for financial support from the Brazilian science agencies CNPq, CAPES, and FAPEMIG. This work was also partially supported by the project INCT-Nanomateriais de Carbono.

#### References

- Barboza A P M, Chacham H and Neves B R A 2009 *Phys. Rev. Lett.* **102** 025501
- [2] de Parga A L V, Calleja F, Borca B, Passeggi M C G, Hinarejos J J, Guinea F and Miranda R 2008 *Phys. Rev. Lett.* 100 056807
- [3] N'Diaye A T, Bleikamp S, Feibelman P J and Michely T 2006 *Phys. Rev. Lett.* 97 215501
- [4] Lui C, Liu L, Mak K, Flynn G and Heinz T 2009 Nature (London) 462 339

- [5] Neto A C, Guinea F, Peres N, Novoselov K and Geim A 2009 *Rev. Mod. Phys.* 81 109
- [6] Rainis D, Taddei F, Polini M, León G, Guinea F and Fal'ko V I 2011 Phys. Rev. B 83 165403
- [7] Zheng Y, Wei N, Fan Z, Xu L and Huang Z 2011 Nanotechnology 22 405701
- [8] Hiura H, Ebbesen T W, Fujita J, Tanigaki K and Takada T 1994 Nature (London) 367 148
- [9] Roy H-V, Kallinger C and Sattler K 1998 Surf. Sci. 407 1
- [10] Meyer J C, Geim A K, Katsnelson M I, Novoselov K S, Booth T J and Roth S 2007 *Nature (London)* 446 60
- [11] Warner J H, Rümmeli M H, Gemming T, Büchner B and Briggs G A D 2009 Nano Lett. 9 102
- [12] Huang J Y, Ding F, Yakobson B I, Lu P, Qi L and Li J 2009 Proc. Natl. Acad. Sci. USA 106 10103
- [13] Liu Z, Suenaga K, Harris P J F and Iijima S 2009 Phys. Rev. Lett. 102 015501
- [14] Zhang J, Xiao J, Meng X, Monroe C, Huang Y and Zuo J-M 2010 Phys. Rev. Lett. 104 166805
- [15] Yu S U, Park B, Cho Y, Hyun S, Kim J K and Kim K S 2012 ACS Nano 8 8662
- [16] Barboza A P M, Chacham H, Oliveira C K, Fernandes T F D, Ferreira E H M, Archanjo B S, Batista R J C, de Oliveira A B and Neves B R A 2012 Nano Lett. 12 2313
- [17] Kim K, Lee Z, Malone B D, Chan K T, Alemán B, Regan W,
- Gannett W, Crommie M F, Cohen M L and Zettl A 2011 Phys. Rev. B 83 245433
- [18] Zhu W, Low T, Perebeinos V, Bol A A, Zhu Y, Yan H, Tersoff J and Avouris P 2012 Nano Lett. 12 3431
- [19] Xie Y, Chen Y, Wei X L and Zhong J 2012 Phys. Rev. B 86 195426
- [20] Feng J, Qi L, Huang J and Li J 2009 Phys. Rev. B 80 165407
- [21] Tozzini V and Pellegrini V 2011 J. Phys. Chem. C 115 25523
- [22] Yuk J M et al 2011 Nano Lett. 11 3290

- [23] Monthioux M and Flahaut E 2007 Mater. Sci. Eng. C 27 1096
- [24] Qi L, Huang J Y, Feng J and Li J 2010 Carbon 48 2354
- [25] Bunch J S 2011 Nat. Nanotechnology 6 331
  [26] Su N, Liu M and Liu F 2011 Nano Res. 4 1242
- [27] Pang A L J, Sorkin V, Zhang Y-W and Srolovitz D J 2012
- Phys. Lett. A 376 973
  [28] Catheline A 2012 Soft Matter 8 7882
- [29] Ortolani L, Cadelano E, Veronese G P, Boschi C D E, Snoeck E, Colombo L and Morandi V 2012 Nano Lett.
   12 5207
- [30] Plimpton S J 1995 Phys. J. Comp. 117 1
- [31] Stuart S J, Tutein A B and Harrison J A 2000 J. Chem. Phys. 112 6472
- [32] Nosé S 1984 J. Chem. Phys. 81 511
- [33] Hoover W G 1985 Phys. Rev. A 31 1695
- [34] Shinoda W, Shiga M and Mikami M 2004 Phys. Rev. B 69 134103
- [35] Girifalco L A and Lad R A 1956 J. Chem. Phys. 25 693
- [36] Benedict L X, Chopra N G, Cohen M L, Zettl A, Louie S G and Crespi V H 1998 Chem. Phys. Lett. 286 490
- [37] Zacharia R, Ulbricht H and Hertel T 2004 *Phys. Rev.* B 69 155406
- [38] Charlier J-C, Gonze X and Michenaud J-P 1995 *Europhys.* Lett. 29 43
- [39] Trickey S B, Müller-Plathe F, Diercksen G H F and Boettger J C 1992 Phys. Rev. B 45 4460
- [40] Rydberg H, Dion M, Jacobson N, Hyldgaard S E P, Simak S I, Langreth D C and Lundqvist B I 2003 Phys. Rev. Lett. 91 126402
- [41] DiVincenzo D P, Mele E J and Holzwarth N A W 1983 Phys. Rev. B 27 2458
- [42] Schabel M C and Martins J L 1992 Phys. Rev. B 46 7185
- [43] Liu Z, Liu J Z, Cheng Y, Li Z, Wang L and Zheng Q 2012 Phys. Rev. B 85 205418