

Rippling of graphene

R. C. THOMPSON-FLAGG, M. J. B. MOURA and M. MARDER^(a)

Center for Nonlinear Dynamics and Department of Physics, The University of Texas at Austin - Austin, TX, USA

received 4 November 2008; accepted in final form 9 February 2009
published online 10 March 2009

PACS 62.20.mq – Buckling
PACS 63.22.Dc – Free films
PACS 68.35.Ct – Interface structure and roughness

Abstract – We show that ripples observed in free-standing graphene sheets can be explained as a consequence of adsorbed OH molecules sitting on random sites. The adsorbates cause the bonds between carbon atoms to lengthen slightly. Static buckles then result from a mechanism like the one that leads to buckling of leaves. Buckles caused by roughly 20% coverage of adsorbates are consistent with experimental observations.

Copyright © EPLA, 2009

Introduction. – Meyer *et al.* [1] found that free-standing graphene sheets display spontaneous ripples. The ripples are of order 2–20 Å high and 20–200 Å wide. The sheets in which they appear are only one atom thick, and extend for around 5000 Å through vacuum between metal struts that support them. Other groups have since created free-standing graphene as well [2–4].

Fasolino, Los, and Katsnelson [5] and Abedpour *et al.* [6] studied the possibility that the ripples are due to thermal fluctuations. It seems unlikely to us that this mechanism explains the observations. According to Abraham and Nelson [7], the root-mean-square fluctuations of a thin sheet are

$$\langle h^2 \rangle \approx \frac{k_B T}{2\pi} \int_{L^{-1}}^{a^{-1}} \frac{q dq}{q^4 \kappa_R(q)} \sim L^2 \zeta, \quad (1)$$

where T is the temperature (the experiments are performed at room temperature), a is the lattice constant, $L \sim 5000$ Å is the length of the sheet, and $\kappa_R(q)$ is the renormalized bending stiffness. Anharmonic couplings were shown to stabilize the sheet and reduce the (roughness) exponent ζ from 1 to 0.59 [8]. The numerical computations of thermal fluctuations in graphene by Fasolino *et al.*, which account for all these effects, find wavelengths of 80 Å, but amplitudes of $\sqrt{\langle h^2 \rangle} \sim 0.7$ Å, which are 3 to 30 times smaller than the experiments.

A more vexing problem is created by the natural oscillation frequencies of the ripples. The kinetic and bending energy of a thin sheet are approximately [9]

$$E = \int d^2r \left[\frac{1}{2} \rho \dot{h}^2 + \frac{\kappa}{2} (\nabla^2 h)^2 \right], \quad (2)$$

where ρ is the mass per area. Thus, thermally excited ripples of wave number k should be oscillating at a frequency ω given by

$$\omega^2 = \frac{\kappa}{\rho} k^4. \quad (3)$$

Fasolino *et al.* find that $\kappa \sim 1$ eV is appropriate for wavelength on the order of 200 Å at room temperature. The oscillation frequency comes out to be of order 10^{10} Hz, while for waves of 50 Å the frequency is higher, 10^{11} Hz. These time scales are slow compared with electron dynamics, and thermal oscillations of graphene could affect transport properties [5,6,10]. However, diffraction through such a rapidly oscillating membrane should be sensitive only to the time average of the density-density correlation function, and that should be completely periodic on time scales much longer than 10^{-10} s, producing sharp Bragg peaks. However, the analysis of Meyer *et al.* obtains agreement with the broadened peaks they observed by assuming that the graphene has static ripples. Thus, the assumption that the observed wrinkling in the graphene layers is purely due to thermal fluctuations seems unlikely, and we decided to search for a mechanism that could produce ripples in the ground state.

Mechanism for rippling. – Experience with mechanics of thin sheets led us to wonder if graphene might be rippling in a fashion similar to leaves and torn plastic [11–13]. In leaves and torn plastic, buckling results from a change in metric. For graphene, this mechanism can lead to buckling if for some reason the equilibrium distance between carbon atoms changes at some but not all parts of the sheet. To investigate this idea, we used the Modified

^(a)E-mail: marder@mail.utexas.edu

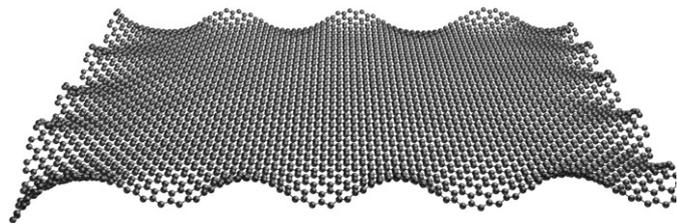


Fig. 1: Ripples in graphene produced by edge effects alone in graphene sheet simulated by MEAM, $100 \text{ \AA} \times 100 \text{ \AA}$.

Embedded Atom Method (MEAM) [14,15] potential, with parameters of Lee and Lee [16]. MEAM is a semi-empirical interatomic potential, based on density functional theory (it considers the superimposition of atomic density). Our implementation of this potential has been tested extensively in simulations of cracks in silicon [17] and shock waves in tin [18]. MEAM has previously been employed to describe graphene [16]. We remark that in an effort to better model the experimental conditions, all the simulations in this work are of finite-sized graphene sheets, in contrast to the work of Fasolino *et al.* and Abedpour *et al.*, which relies on periodic boundary conditions.

To find the bending stiffness we applied a similar method to ref. [19]. We constructed graphene cylinders of various radii and plotted energy per area *vs.* $1/R^2$. The energy per area of a thin elastic cylinder is $E = \kappa/2R^2$. We extract a modulus $\kappa = 1.77 \text{ eV}$ from these data, which is higher than the value of 1.1 eV employed by Fasolino *et al.* [5] and the experimental value of 1.2 eV found by Nicklow *et al.* [20] although of the same order of magnitude. To the extent the MEAM potential overstates the bending energy of graphene, it will tend to underestimate the scale of ripples.

A first possibility we checked is that under-coordinated carbon atoms at the edge of the sheet might create ripples at the edge that propagate all the way into the interior of the samples. Figure 1 shows a system $100 \text{ \AA} \times 100 \text{ \AA}$ in size. The edges are free, and the system is initially entirely flat, except that atoms are randomly displaced from initial conditions by around 10^{-2} \AA . Then the system is allowed to relax toward a minimum energy state through damped molecular dynamics.

Edge effects do indeed create ripples, and they are of the right size, around 30 \AA in width and 10 \AA in height. However, the ripples occur only at the edge of the system, and the amplitude decays to zero on the scale of 3.2 \AA (fig. 2). Thus, edge effects alone cannot explain the presence of ripples throughout a sample of size 5000 \AA .

Similar results to fig. 1 were also obtained independently by one of the authors, Moura, along with MacDonald, using Tersoff's potential [21], by Lu along with Huang [22], using Brenner's potential [23], and by Shenoy *et al.*, using an AIREBO potential [24].

In correspondence with A. Geim, we learned that OH molecules could be expected to be adsorbed on the surface

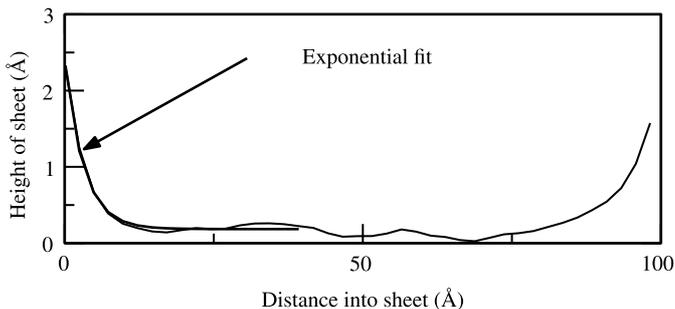


Fig. 2: Slice through system shown in fig. 1 showing that the ripples decay with a characteristic distance of about 3 \AA away from the edge of the graphene sheet.

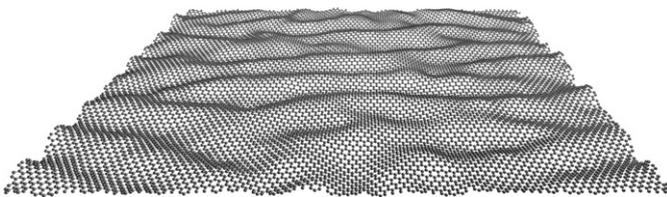


Fig. 3: Ripples in graphene produced by 20% coverage of OH, $200 \text{ \AA} \times 200 \text{ \AA}$ system.

of the graphene sheet. Other molecules such as water and hydrogen may also be present [25–27]. Details of the molecule are not likely to be critical, and we discuss OH in order to have a specific example. The density of the adsorbates is not known, so we have treated it as a free parameter, and considered the effects of randomly placing OH molecules on graphene. According to Xu *et al.* [28], attaching an OH molecule to a carbon surface has the consequence of increasing the length of two adjoining C-C bonds by around 10% (see their fig. 2, LOD + OH). Rather than directly simulating the interactions of graphene with OH, we simply chose carbon atoms randomly from the lattice, and increased the equilibrium length to two randomly chosen neighbors by this amount. This corresponds to a small-scale change in the metric of the sheet. For the bonds we wished to stretch, the MEAM parameter R_c was increased to 1.48 \AA from 1.42 \AA . This value was chosen because if used for the entire crystal, it produces an equilibrium lattice parameter close to what Xu *et al.* find for the C-C bonds stretched by OH. The energy associated with the OH attachment is 0.17 eV . Here as in the clean-sheet case, we apply a perturbation to the initially flat sheet with free edges and allow it to relax toward a minimum energy configuration.

As shown in fig. 3, with a 20% concentration of OH adsorbates, graphene develops ripples whose wavelength and amplitude are comparable to those seen in experiment. The peak-to-peak amplitude of ripples is around six times greater than the rms amplitude, so by 40% concentration, the ripples have a peak-to-peak amplitude of around 10 \AA (see fig. 4). It is not possible to deduce the OH concentration from these computations because

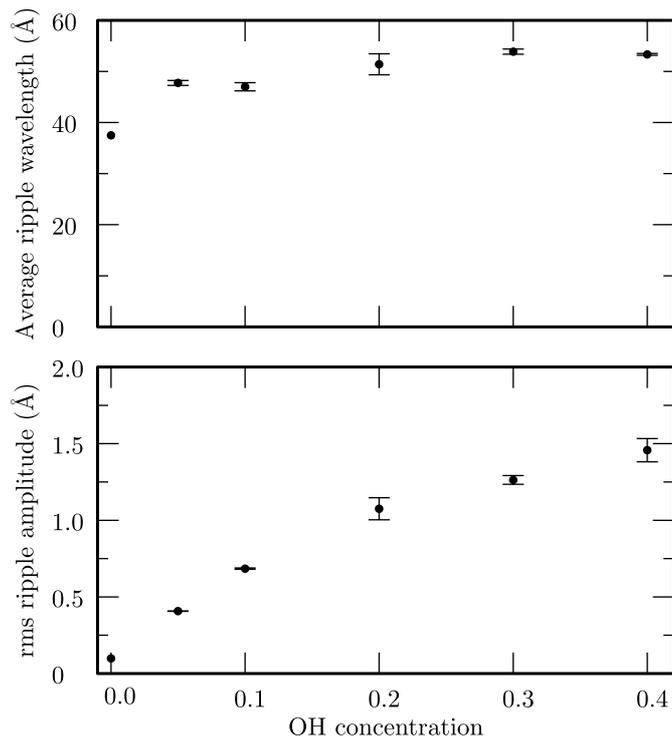


Fig. 4: Wavelength and amplitude of buckles in $200 \text{ \AA} \times 200 \text{ \AA}$ sheets as a function of OH concentration. The wavelength changes rather little with concentration, while rms amplitude increases. Amplitudes of the rippled peaks are around six times larger than the rms amplitude; peak-to-peak amplitude at 40% OH concentration is around 10 \AA . Wavelength and rms amplitude were computed for free-standing sheets after excluding 20 \AA of material at the edge of the sample. Wavelength was computed by decomposing the sheet into a series of line scans, taking the one-dimensional Fourier transform of them in turn, finding the average wave vector \bar{k} for each line weighted by the amplitude of the Fourier transform, computing $\lambda = 2\pi/\bar{k}$ and finally averaging λ over all the line scans. Error bars represent standard errors after averaging over three independent trials per concentration.

both experimental and computational uncertainties are too large at this point to permit it.

Conclusions. – The experimental creation of a free-standing two-dimensional crystal has spurred some discussion of the Mermin-Wagner [29,30] theorem, according to which a truly two-dimensional crystal does not exist except at zero temperature. We do not believe that the Mermin-Wagner theorem is very significant here. What this theorem says is that when a two-dimensional crystal remains completely planar, it will undergo rotations at large distances that cause a breakdown of long-range order. In the case of graphene at room temperature, the scale l on which this happens can be estimated from the expression

$$l \sim a \exp[Ga^2/k_B T], \quad (4)$$

where a is a lattice spacing and G is the shear modulus of graphene. Since the bulk shear modulus $\mu \approx G/a$ of

graphite is 440 GPa [31], and the lattice spacing is greater than $a \gtrsim 1 \text{ \AA}$, one has $l > 10^{30} \text{ m}$. So the angular rotation of the crystal on the scale of microns should be irrelevant. The mechanism on which we have focused is of a completely different sort, and depends upon small changes in carbon-carbon bond lengths that lead to buckling out of plane. Whether this mechanism is in fact responsible for the buckles might be determined by experiments on adsorbate-free surfaces conducted in high vacuum.

However, it is worth noting that since Meyer *et al.*'s experiment [1] the understanding of the experimental significance of the presence of adsorbates in graphene has increased. Many graphene samples now pass through a heat treatment before being used for measurements. In the experiment of Ishigami *et al.* [32], performed on graphene on top of a silicon dioxide substrate, the authors were able to distinguish between the rippling of the graphene sheet and that of the substrate, and found that by heating and cleaning their samples they observe fewer impurities and smaller ripples, which is in agreement with the mechanism we have suggested.

We thank A. MACDONALD for pointing this problem out to us, A. GEIM for correspondence concerning the possible mechanism for buckling, Fulbright and CAPES for scholarship funding and the National Science Foundation for funding through DMR 0701373.

REFERENCES

- [1] MEYER J. C., GEIM A. K., KATSNELSON M. I., NOVOSELOV K. S., BOOTH T. J. and ROTH S., *Nature*, **446** (2007) 60.
- [2] GARCIA-SANCHEZ D., VAN DER ZANDE A. M., PAULO A. S., LASSAGNE B., MCEUEN P. L. and BACHTOLD A., *Nano Lett.*, **8** (2008) 1399.
- [3] BOLOTIN K. I., SIKES K. J., JIANG Z., KLIMA M., FUDENBERG G., HONE J., KIM P. and STORMER H. L., *Solid State Commun.*, **146** (2008) 351.
- [4] BOLOTIN K. I., SIKES K. J., HONE J., STORMER H. L. and KIM P., *Temperature dependent transport in suspended graphene*, arXiv:0805.1830 (2008).
- [5] FASOLINO A., LOS J. H. and KATSNELSON M. I., *Nat. Mater.*, **6** (2007) 858.
- [6] ABEDPOUR N., NEEK-AMAL M., ASGARI R., SHAHBAZI F., NAFARI N. and TABAR M. R. R., *Phys. Rev. B*, **76** (2007) 195407.
- [7] ABRAHAM F. F. and NELSON. D. R., *J. Phys. (Paris)*, **51** (1990) 2653.
- [8] LE DOUSSAL P. and RADZIHOVSKY L., *Phys. Rev. Lett.*, **69** (1992) 1209.
- [9] LANDAU L. D. and LIFSHITZ E. M., *Theory of Elasticity*, 3rd edition (Pergamon Press, Oxford) 1986.
- [10] KIM EUN-AH and CASTRO NETO A. H., *EPL*, **84** (2008) 57007.
- [11] SHARON E., ROMAN B., MARDER M., SHIN G.-S. and SWINNEY H. L., *Nature*, **419** (2002) 579.

- [12] SHARON E., MARDER M. and SWINNEY H. L., *Am. Sci.*, **92** (2004) 254.
- [13] MARDER M., DEEGAN R. D. and SHARON E., *Phys. Today*, **60**, issue No. 2 (2007) 33.
- [14] BASKES M. I., *Phys. Rev. B*, **46** (1992) 2727.
- [15] BASKES M. I., ANGELO J. E. and BISSON C. L., *Model. Simul. Mater. Sci. Eng.*, **2** (1994) 505.
- [16] LEE B. J. and LEE J. W., *Calphad*, **29** (2005) 7.
- [17] HOLLAND D. and MARDER M., *Adv. Mater.*, **11** (1999) 793.
- [18] LANE J. M. D. and MARDER M., *Numerical method for shock front Hugoniot states*, in *Proceedings of Shock Compression of Condensed Matter-2005*, edited by FURNISH M. D., ELECT M., RUSSELL T. P. and WHITE C. T., Vol. **845** (American Institute of Physics) 2006, pp. 331–334.
- [19] TERSOFF J., *Phys. Rev. B*, **46** (1992) 15546.
- [20] NICKLOW R., WAKABAYASHI N. and SMITH H. G., *Phys. Rev. B*, **5** (1972) 4951.
- [21] TERSOFF J., *Phys. Rev. Lett.*, **61** (1988) 2879.
- [22] LU Q. and HUANG R., private communication.
- [23] BRENNER D. W., *Phys. Rev. B*, **42** (1990) 9458.
- [24] SHENOY V. B., REDDY C. D., RAMASUBRAMANIAM A. and ZHANG Y. W., *Phys. Rev. Lett.*, **101** (2008) 245501.
- [25] ECHTERMAYER T. J., LEMME M. C., BAUS M., SZAFRANEK B. N., GEIM A. K. and KURZ H., *A graphene-based electrochemical switch*, arXiv:0712.2026 (2007).
- [26] HALUKA M., OBERGFELL D., MEYER J. C., SCALIA G., ULBRICHT G., KRAUSS B., CHAE D. H., LOHMANN T., LEBERT M., KAEMPGEN M., HULMAN M., SMET J., ROTH S. and VON KLITZING K., *Phys. Status Solidi (b)*, **244** (2007) 4143.
- [27] MOSER J., VERDAGUER A., JIMENEZ D., BARREIRO A. and BACHTOLD A., *Appl. Phys. Lett.*, **92** (2008) 123507/1.
- [28] XU S. C., IRLE S., MUSAEV D. G. and LIN. M. C., *J. Phys. Chem. C*, **111** (2007) 1355.
- [29] MERMIN N. D. and WAGNER H., *Phys. Rev. Lett.*, **17** (1966) 1133.
- [30] MERMIN N. D., *Phys. Rev.*, **176** (1968) 250.
- [31] POPOV V. N., DOREN V. E. V. and BALKANSKI M., *Phys. Rev. B*, **61** (2000) 3078.
- [32] ISHIGAMI M., CHEN J. H., FUHRER M. S. and WILLIAMS E. D., *Nano Lett.*, **7** (2007) 1643.