Stability and gap opening in graphene under combined shear and uniaxial strains

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(Dated: Submitted to Physical Review on November 29, 2013: es2013nov29_613)

Using density-functional perturbation theory, we study the vibrational and electronic properties of graphene under combined shear and uniaxial strain. Shear strain of any value causes rippling instabilities with strain-dependent direction and wavelength, while for combined strain graphene remains stable and exhibits a fairly substantial semiconductor-like gap at small strain. Generally, the tendency to rippling is enhanced by shear and contrasted by armchair strain; shear seems unable to open a substantial gap by itself at small strains, but the shear symmetry lowering enables the armchair component of the combined strain to do so. The larger-than-usual strain-induced shifts of the split component the $G$ optical phonon line may be used as strain diagnostic tool.

PACS numbers: 63.22.Rc,61.48.Gh,73.22.Pr,64.70.K-

I. INTRODUCTION

Ideal free-standing and unstrained graphene is, strictly speaking, an abstraction. Real graphene is invariably subjected to strain, either intentional or unintentional, as it gets manipulated, deposited on a substrate, and attached to, or suspended from nanostructured devices.

Importantly, a general strain may happen to destroy the Dirac-cone band dispersion near the Fermi energy, and to trigger vibrational instabilities of the graphene sheet, such as long-wavelength rippling. Previous work has suggested that uniaxial strains does not cause either a gap opening or rippling. Apparently, shear stresses have been much less studied in this context. A recent work applying combined strains to graphene modeled with empirical potentials indicates that shear strain reduces drastically the graphene stability region in strain space, and specifically that the last “stability island” for large shear occurs for a combination of large armchair and shear strains.

In this paper, we consider the effects of shear strain, by itself and in combination with “armchair” uniaxial strain, on the vibrational stability of graphene from an ab initio point of view. We find that shear makes graphene unstable against a fairly short-wavelength rippling with direction depending on strain intensity, whereas graphene remains stable under a not too large combined strain; the results are consistent with a previous empirical-interatomic-potentials study. Further, we find that the Dirac-cone band structure is destroyed by strain, with a sizable gap of order 0.2 eV opening for small combined strains, whereas the shear-induced gap is small.

II. METHOD

Our ab initio calculations are done within local-density-functional perturbation theory using the QUANTUM ESPRESSO code and a plane-wave basis with principal cutoff 37 Ryd and charge cutoff 450 Ryd were used. For each strain state we fully relaxed the internal coordinates in the primitive cell of graphene until all force components were below 0.5 meV/Å. We then perform the phonon calculation on the relaxed structure. This is the standard procedure in the search for instabilities in high symmetry phases of, e.g., ferroelectric perovskites. After extensive testing, we settled on a $k$ integration mesh of $16 \times 16 \times 1$ for both energy selfconsistency and phonon calculations, with a cold smearing of 0.03 Ryd. Such a rather fine mesh is found to be necessary (and sufficient) to describe the much slower decay of the interatomic force constants in graphene compared to e.g. diamond. Indeed, coarser meshes tend to produce spurious instabilities in unperturbed graphene.

Our choice of the graphene primitive vectors is

$$a_1 = \frac{1}{2} a \hat{x} + \frac{\sqrt{3}}{2} a \hat{y}, \quad a_2 = -\frac{1}{2} a \hat{x} + \frac{\sqrt{3}}{2} a \hat{y},$$

(1)

with $a=2.448$ Å. We apply shear strain and a combination of shear and uniaxial “armchair” tension by multiplying the primitive vectors by the matrix

$$S = 1 + \left( \begin{array}{cc} \zeta_1 & \zeta_2 \\ \zeta_1 & \zeta_2 \end{array} \right)$$

(2)

whereby pure shear is obtained for $\zeta_2=0$. The shear and armchair strains in standard usage (e.g. Ref.3) are then $\epsilon_{xy}=2\zeta_1$ and $\epsilon_{yy}=\zeta_2$. Beside pure shear, we consider combined strains in the vicinity of $\epsilon_{xy}=\epsilon_{yy}$ (see below). Strain states are labeled by $(\epsilon_{xy},\epsilon_{yy})$ with strains expressed as percentage; for example $\epsilon_{xy}=0.02$, $\epsilon_{yy}=0.03$ is labeled (2,3).

The primitive cell and Brillouin zone for graphene under shear and combined strain is shown in Fig. Shear lowers the symmetry of graphene to the $C_{2h}$ point group (and $2/m$ space group). The six equivalent $K$ points where the Dirac cone is located in pristine graphene become now three pairs of inequivalent points $K$, $K'$, and $K''$ under strain. The lattice vectors both rotate clockwise under shear (rate $8'/\%$, i.e. about 1° at 7%); under combined stress $a_1$ rotates counterclockwise (rate $5'30''/\%$) and $a_2$ clockwise (rate $22'16''/\%$).
III. RESULTS

A. Vibrational stability

The phonon dispersion for unperturbed graphene (not shown) is in good agreement with previous calculations. Under all the shear strains investigated, the phonon dispersion exhibits imaginary frequencies near zone center, signaling long-wavelength vibrational instabilities. This can be seen in the dispersion, shown in Fig. 2 for shear 3%, which is quite typical of all strains investigated, as well as, more clearly, in a contour map of the unstable frequencies in Fig. 3 left panel. The wavevector of the largest (in modulus) unstable frequency directly provides the wavelength and direction of the “rippling” distortion pattern that will freeze-in into the graphene lattice upon condensation of the unstable modes. Its wavelength decreases with shear, namely 17.3, 15.4, 12.6, 10.6 Å for shear 3%, 5, 7, 10 %, and the normal to the rippling wavefront backs away counterclockwise from the shear axis (the bisector of the direct lattice vectors) for increasing strain, towards an angle of 45° from the axis.

For combined shear and armchair-tensile strain, at strains below about 10% there appears to be no instability. The quartic dispersion $\omega^2 \approx q^4$ of the flexural ZA mode[9][10] acquires a quadratic term that tends to increase with strain amplitude. As can be seen for the typical case of the (3,3) strain in Fig. 4, the dispersion is significantly anisotropic. At 10% combined strain, a marginal instability appears, as can be seen in Fig. 3 right panel. We tend to believe this instability to be real, despite its small energy content and the very limited phase space in which it happens. The wavelength in this case is 45-50 Å, and the angle is much larger than for pure shear, i.e. 160° from the horizontal zig-zag chain direction (Fig. 4) at zero strain.

A previous search for rippling by ab initio methods under uniaxial strain produced negative results[2]. A work on combined strain[3] using empirical potentials suggests (Fig. 3 of Ref.[3]) that shear strain reduces the graphene stability region in strain space. Our results are in general agreement with this conclusion. In particular, instability ensues at any pure shear strain; further, our largest calculated strain of 10%, where we barely glimpsed an incipient instability, is indeed at the border of stability as predicted in Ref.[3]. From our calculations we infer the qualitative phase diagram for stability drawn in Fig.[5] which in this region looks similar to the relevant section of Fig. 3 of Ref.[3]. It is appropriate to note that vibrational instability is predicted to set in abruptly at $\epsilon_{yy}$ around 20% according to both empirical and ab initio calculations. A qualitative conclusion is that shear is strongly destabilizing for graphene, while blending in a measure of uniaxial tension re-establishes stability in a vast region of strain space. In passing, we note that for symmetry reasons to be discussed below the gap-opening region in the phase diagram would be all of Fig.[5] except
FIG. 4. Phonon dispersion for combined-strain state (3,3). No instability is present.

the $\epsilon_{yy}$ axis.

Another interesting byproduct of our combined-strain calculations is the strain derivative of the energies of the optical “$G$” lines resulting from the strain splitting of the optical phonon. For uniaxial strain, these slopes were measured\textsuperscript{[12]} by Raman scattering, and found to be $-10.8$ and $-31.7$ cm\textsuperscript{-1}/%. As shown in Fig. 6, obtained by additional calculations at small combined strains, both lines shift linearly. The strain derivatives we obtain are $-16.0$ cm\textsuperscript{-1}/% for the $G^+$ line and $-39.8$ cm\textsuperscript{-1}/% for the $G^-$ line. These values are significantly larger than for uniaxial strains, and could be useful as a diagnostic indicator of the presence of shear in uniaxially strained samples.

FIG. 5. Schematic phase diagram for vibrational stability. Triangles are calculated strains.

B. Band structure and gap opening

While phonons are dramatically affected by shear, the electronic structure changes moderately. For any of the strains we consider, the appearance of a gap at the conical intersections at the K points of the Brillouin zone is guaranteed by symmetry. Shear strain lowers the symmetry of graphene to the space group 2/m; hence the little group of any $k$ point in the Brillouin zone can be at most the point group $C_{2h}$, which has only one-dimensional irreducible representations. This implies that band degeneracies are not protected by symmetry anywhere in the Brillouin zone. It is unclear a priori how large the gap will be under a particular kind of strain, especially at small strain values, but there will be one.

FIG. 6. Position of strain-split optical-phonon lines vs combined strain.

In Fig. 6 we show a typical portion of the band structure for the (3,3) combined and (3,0) shear strains. For combined strain, a large gap appears clearly even on this scale. For strains in this vicinity, the minimum gaps clus-
ter around 0.2 eV, and appear in the immediate neighborhood of the former K points. In the case of shear, the gap is not quite unambiguous on this scale. Indeed, we find that pure shears as large as (18,0) must be applied to obtain gaps of order 0.1 eV, i.e. comparable to those at small combined strain. Even then, the gap remains considerably smaller than those obtained previously, possibly due to the effects of atomic relaxations (not allowed in Ref.1) and to the incipient density-functional gap underestimate. In any event, accidental gap closures do not seem to occur under shear strain. The strain derivatives of the gaps are in the whereabouts of 5 meV/% for shear, and 50-100 meV/% of armchair strain at non-zero shear.

To show that a gap is present at small shear, we zoom in onto two representative, formerly Dirac-like points at (3,0) strain in Fig.8. In the right panel a sizable curvature is visible at the band edges, so this is obviously a bona fide gap. On the left, this is less obvious, because no curvature is visible yet at this magnification. But even on this scale, we can assert that this gap is real noting that the portion of the lower band to the left of the gap point is not on the same straight line as the portion of the upper band to its right (dotted lines), and the same for lower right vs upper left (solid lines): these band sectors cannot therefore lay on a cone generatrix, i.e. the conic intersection has broken up.

The density of states (DOS) confirms these conclusions. At strain (3,3), the DOS has a clearly 2D-like onset at the gap edges, and there is no sign of the small-slope linear DOS of the conic points. For the small gap cases, such as at (3,0), the situation is quite similar: the gap being so small, the DOS steps below and above the gap almost coalesce, giving the impression of a continuous flat DOS on a wide energy scale.

The general conclusion about gaps is thus that shear enables their opening, though it opens only very small gaps by itself, and needs the support of the armchair strain to increase them. This step-like shape of the DOS, with a rapid ramp-up into the conduction band and smallish density, may well be interesting for thermoelectricity, whose figure of merit is

\[ Z \propto \frac{1}{n} \left( \frac{\partial n}{\partial E} \right)^2 \]

under rather general conditions. Of course, doping difficulties may prevent applying this insight to graphene other than in a field-effect context.

![Image of the band structure at strain (3,0) near the formerly Dirac-like points K' and K' (taken as wavevector zero). Energy zero is gap center.](image)

![Image of the density of states (DOS) of graphene in the strain state (3,3).](image)

### IV. SUMMARY

In summary, ab initio phonon calculations indicate that graphene is stable against rippling instabilities for combined armchair-shear strains, whereas shear strains cause instability. Our stability diagram agrees with previous estimates based on empirical potentials. The electronic structure exhibits a gap at all investigated strain, as expected based on symmetry. The gap is very small under small shears (order 0.01 eV at 3%), and it is amplified by armchair strain in the combined strain case, whereby the typical value is 0.2 eV around (3,3) strain.

To obtain a comparable gap by pure shear one should crank up the shear to over 20%. We reported the strain derivatives of the strain-split components of the G line, which turn out to be are 25 to 45% larger than under uniaxial strain, and could be useful as diagnostic measure of shear strain.

Work supported in part by the MIUR-PRIN 2010 project Oxide, Fondazione Banco di Sardegna and CINECA grants.

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