Elastic properties of graphene flakes: Boundary effects and lattice vibrations

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(Received 23 March 2010; revised manuscript received 4 October 2010; published 30 November 2010)

We present a phenomenological theory together with explicit calculations of the electronic ground-state energy, the surface contribution, and the elastic constants (“Lamé parameters,” i.e., Poisson ratio, Young’s modulus) of graphene flakes on the level of the density-functional theory employing different standard functionals. We observe that the Lamé parameters in small flakes can differ from the bulk values by 30% for hydrogenated zigzag edges. The change results from the edge of the flake that compresses the interior. When including the vibrational zero-point motion, we detect a decrease in the bending rigidity, \( \kappa \), by \(-26\%\). The vibrational frequencies flow with growing \( N \) due to the release of the edge-induced compression. We calculate the corresponding Grüneisen parameters and find good agreement with previous authors.

DOI: 10.1103/PhysRevB.82.195445 PACS number(s): 81.05.ue, 62.20.D−, 62.25.—g, 63.22.Rc

I. INTRODUCTION

Since its fabrication has become technologically feasible,1 graphene has been in the focus of frontier research.2–4 One of its most celebrated properties is its massless low-energy excitations5,6 (“Dirac fermions”), which emanate from the symmetries of the honeycomb lattice. The electronic properties of graphene flakes are quite different from bulk graphene due to the finite size and the presence of edges.7,8 In particular, calculations suggest that the zigzag edges of graphene nanoribbons (quasi-one-dimensional) have two flat bands at the Fermi energy9,10 that introduce magnetism.11–18 Recent theoretical studies on zigzag-edged graphene flakes also confirm a tendency toward edge magnetism.17–20 Thus this gives an added motivation for fabricating graphene-based nanostructures,21–26 The fabrication of such structures with well-defined edges still poses a considerable technological challenge. Therefore, only very few experiments with structures exhibiting zigzag edges have been reported.27–29 A detailed investigation of the edge physics still needs to be done.

An increased interest in the elastic properties of graphene has developed recently.30–45 This is for instance, because experiments suggest that graphene samples exhibit a corrugated structure36–46 (“ripples”) even at relatively low temperatures. Their origin is thought to be due to residual elastic strain produced by the experimental preparation technique.47 Another motivation comes from exploring the feasibility of strain engineering the electronic band structure48 (“pseudo-magnetic” fields).

Also for elastic properties, edge effects can be highly relevant. Hence studies of flake elastic properties are interesting in their own right. Namely, there is an intimate relation between the electronic structure and the atomic geometry of graphene. For example, the electronic spectrum of a certain class of armchair graphene nanoribbons is reported to acquire a spectral gap due to an edge-induced lattice dimerization along the transport direction.13

In our study we investigate the ground-state energy, the elastic properties, and the phonon spectrum of \( N \times N \) graphene sheets (“flakes”) as displayed in Fig. 1 using the density-functional theory (DFT). We show that the different chemical nature of C-C bonds at the hydrogenated edge as compared to the bulk leads to a nearly homogenous isotropic compression, i.e., strain. As a consequence, the average C-C distance in a 3 \( \times \) 3 flake is reduced by a substantial amount, 0.3%; for comparison, strain as achieved in typical pressure experiments does not usually exceed values \( \sim 1\% \).34,49,50

The presence of the surface-induced strain leaves various traces in the flakes’ interior observables. (a) The flakes elastic constants, i.e., the Lamé parameters, are enhanced as compared to the bulk case. For isotropic strain in smallest flakes (3 \( \times \) 3), the (inverse) compressibility \( \mu + \lambda \) [for a precise definition see below, Eq. (2)] increases by 30%; for shear forces the increase is even bigger, almost a factor of 2. (b) Under bond compression the interatomic forces typically increase so that even the short-wavelength vibrations, in particular, the optical phonons, exhibit a “blueshift” of their frequencies with decreasing flake sizes. This “flow” can be seen in the variation in the Raman spectra with strain37,49,51–54 and can be described in the standard manner by Grüneisen parameters. The values that we find here of Grüneisen parameters agree reasonably well with previous reports.49,52,55

Even though one might suspect, that our topics have already been dealt with extensively in the literature,34–48 a detailed investigation of the elastic properties of nanoflakes is yet to be done; this refers, in particular, to an analysis of edge and finite-size effects of hydrogenated zigzag flakes which we perform in this work.

II. GROUND-STATE ENERGY OF HOMOGENOUS, PLANAR FLAKES

Quite generally, the total energy of a graphene flake such as the one depicted in Fig. 1 is a sum of local contributions. In principle, these may be thought of as contributions per bond or per atom. The latter perspective has been worked out in the Appendix. Here, we will focus on a representation in terms of bond energies valid for flakes with a homogenous C-C distance, \( d \).
accordingly, the in approximating the binding energy of the corner groups C-C-CH edge group is close to 2\(A\) The flake coordinates are given with respect to a planar ref-
ten corner atoms, \(N\) instance, located C-C bonds with energy associated binding energy contributions, where \(N\) includes corrections of internal bonds, that also includes corrections of internal bonds, that measures the translation of each \(d\), and angles. In this formulation the elastic energy is simplified in the following sense. In general, the boundary shape of a given flake, e.g., as depicted in Fig. 1 does not of a given flake, e.g., as depicted in Fig. 1 does not share the hexagonal symmetry of the honeycomb lattice. For this reason, in flakes with a fully relaxed atomic structure bond lengths and bond angles are not strictly all the same. Our DFT calculations indicate, however, that such distortions, though clearly detectable, give only small corrections to those phenomenological parameters that we are mostly interested in.

The continuum theory of two-dimensional membranes has been devised for an inhomogeneous flake with neighboring bonds exhibiting slowly (in space) varying bond distances, \(d(r)\), and angles. In this formulation the elastic energy is represented by the functional:\(^{59}\)

\[
E = \frac{\kappa}{2} \int_A d^2 r (\nabla^2 h)^2 + \frac{\mu + \lambda}{2} \int_A d^2 r (u_{xx} + u_{yy})^2 + \frac{\mu}{2} \int_A d^2 r \left[ 4u_{xx}^2 + (u_{xx} - u_{yy})^2 \right].
\]

(2)

The flake coordinates are given with respect to a planar reference state with area \(A\), that lives in the \(r=(x,y)\) plane; accordingly, the in-plane coordinates constitute the displacement vector, \(\mathbf{u}(x,y)\), that measures the translation of each membrane point \((x,y)\) with respect to the reference state. The out-of-plane distortions define the height field \(h(x,y)\); for the planar case \(h=0\). \(\mathbf{u}\) and \(h\) together constitute the strain tensor \((i,j=x,y)\),

\[
\mathbf{u}_{ij} = \frac{1}{2} \left[ \partial_i u_j + \partial_j u_i + \partial_i h \partial_j h + \cdots \right],
\]

(3)

where (nonlinear) higher order gradient terms have been neglected. It is clear that the form of \(u_{ij}\) depicted in Eq. (3) is a symmetric construction with respect to the spatial derivatives of \(u\) ensuring, e.g., invariance under in-plane rotations. Such infinitesimal rotations correspond to \(u \propto (x,y)\) and hence the strain must be invariant under such displacements \(u\).

The total elastic energy Eq. (2) is a sum over contributions which resemble local oscillators in the membrane plane. The first term is proportionate to the curvature \(\nabla^2 h\) and introduces the bending rigidity \(\kappa\). It describes the energy cost for bending the membrane without changing the bond lengths or in-plane bond angles.\(^{60}\) The Lamé parameters, \(\lambda\) and \(\mu\), appearing in the second and third terms of Eq. (2) describe the in-plane rigidity.

For homogenous, planar membranes the elastic theory Eq. (2) may be considered as a continuum approximation to Eq. (1) which does not make explicit reference to boundary terms. Edges are accounted for only in the boundary conditions and (possibly) in a dependency of the Lamé parameters on the position with respect to the edge. Usually not included in Eq. (2) is the fact that this spatial dependency supports long-range terms, \(-1/\text{flake size}\). They modify the Lamé parameters appearing in Eq. (2) even inside the flake’s interior.

**Phenomenological parameters**

1. **Isotropic strain**

In order to illustrate the cooperative effect between surface and bulk, we consider an expansion of Eq. (1) in terms of the variable \(e=(d-d_0)/d_0\); \(e\) quantifies the strain inside the flake. The bulk energy per bond has an expansion,

\[
\psi = \Psi_0 + \frac{1}{2} \Psi_2 e^2 + \frac{1}{6} \Psi_3 e^3 + \frac{1}{24} \Psi_4 e^4 + \cdots,
\]

(4)

where the bulk bond length \(d_0\) is to be determined at \(N_{c,e} \rightarrow \infty\). The surface energy may also be expanded about a minimum bond length, \(d_0^s\), but, in general, \(d_0^s \neq d_0\). After all, in the limit \(N_{c,e} \rightarrow \infty\), just the first term in Eq. (1) contributes to the energy per area and therefore \(d_0\) needs to minimize \(\Psi\), only. Hence, we introduce the relative deviation of surface and bulk optimal bond lengths, \(\delta=(d_0-d_0^s)/d_0\), so that we have an expansion

\[
\psi = \psi_0 + \frac{1}{2} \psi_2 (e + \delta)^2 + \frac{1}{6} \psi_3 (e + \delta)^3 + \frac{1}{24} \psi_4 (e + \delta)^4 \cdots
\]

\[
= \psi_0 + \psi_1 e + \frac{1}{2} \psi_2 e^2 + \frac{1}{6} \psi_3 e^3 + \cdots,
\]

(5)

where the coefficients in the second line are defined in terms of the expansion the line before. The elastic properties of the flake are determined by the expansion parameters \(\Psi_2,3,4, \psi_1,2,3\).

At any finite value of \(N_{c,e}\), optimization must also include the boundary (i.e., surface) terms and therefore the optimal value of \(e, e_N\), is nonvanishing in this case; specifically,
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FIG. 2. (Color online) Bulk (Ψ), surface (edge, ψ), and corner (ψr) energy per carbon bond in the graphene flakes, calculated with density-functional theory (BP86 functional). Data based on the evaluation of three sets of flake sizes ranging from |N| = 3, . . . , 9, and a five-parameter fit to Eqs. (1) and (11) per d values. (a0 = 0.529 Å.)

In order to calculate the feedback of this shift into the elastic parameters, we expand F in the vicinity of its minimum, εN, to the fourth order in −εN. Recalling that this corresponds to a strain u(x) = εx, we can compare the result with Eq. (2) and thus find to leading order in Nc/Ni

$$\mu + \lambda = \frac{1}{4} \left( \psi_2 + \frac{N_c}{N_i} \psi_2 \right) + \frac{1}{4} \left( \psi_3 + \frac{N_c}{N_i} \psi_3 \psi_2 + \psi_4 \right).$$

The first term on the rhs of expression (7) simply accounts for the separate, additive contributions of bulk and surface (i.e., edge) energies. The edge contribution, that appears here, could formally be accounted for in a generalized version of Eq. (2) where one adds a boundary term. Similarly, by allowing for a dependency of the Lamé parameters on strain itself, one could also include additive anharmonic effects, second bracket first two terms. In either case, the phenomenological parameters that enter the conventional elastic theories of the continuum are the same for each flake size and shape. Adapting these parameters to each flake geometry separately is not foreseen in this framework.

The interesting pieces in εN are the terms, which mix the surface and bulk parameters: Ψ2εN = ψ0Ψ2 + ε/12 (Ψ3 + Nc/Ni ψ3 + Ψ4εN). The “cooperative” effect between boundary induced strain and bulk anharmonicities. It is due to them, that the flake elastic parameters need to be adjusted in principle for every geometry separately.

2. Shear strain

An analogous analysis as for the isotropic strain also applies to shear forces. The expansion is even in the shear strain u = (0, ε, x)

$$\Psi_N = \frac{\psi_0 N_c \psi_1}{\Psi_2 N_i} \frac{\psi_2 N_c}{\Psi_2 N_i},$$

$$\psi = \psi_0 + \frac{1}{2} \psi_2 \epsilon^2 + \frac{1}{24} \psi_4 \epsilon^4 + \cdots,$$

$$\mu = \psi_2 \psi_0 + \frac{1}{12} \psi_4 (\psi_4 + \psi_3).$$

Here, the surface and bulk energies give strictly additive contributions, and a cooperative effect does not emerge.

III. DENSITY-FUNCTIONAL CALCULATIONS

A. Method

In Fig. 1 we display the geometry of the N×N-graphene flake that is employed in our calculations: Nc = (N−1)(3N−1) and Nc = 8(N−1). Electronic structure calculations have been performed for a given atomic configuration (C-C distance, flake geometry, etc.) on the basis of the density-functional theory as implemented in the quantum chemistry package TURBOMOLE.61 We are comparing GGA functionals [BP86 (Refs. 62 and 63) and PBE (Refs. 64 and 65)] with a hybrid functional [B3LYP (Ref. 66)] and use a minimal basis set [SVP (Ref. 67)]. Specifically, we are working at zero temperature and approximate the ground-state energy, Eq. (1), by the DFT estimate for the total binding energy of the flake

$$F_{\text{el}}(N,d) = E_{\text{el}}(N,d) - E_{\text{free}}(N)$$

with
TABLE II. Bulk-energy coefficients as defined in Eq. (4). These coefficients are extracted from fitting Eq. (4) to the data in Fig. 2, upper panel.

|       | $-\Psi_0$  | $1/2\Psi_2$ | $1/6\Psi_3$ |
|-------|------------|-------------|-------------|
| BP86  | 5.223 ± 0.001 | 46.301 ± 0.082 | 128.3 ± 2   |
| B3LYP | 5.008 ± 0.001 | 47.7 ± 0.4    | 154 ± 32    |
| PBE   | 5.373 ± 0.004 | 45.57 ± 0.43  | 187 ± 25    |

\[ E_{\text{free}}(N) = N_{\text{H}}E_{\text{H}} + N_{\text{C}}E_{\text{C}}, \]  

where $E_{\text{H/C}}$ denote the DFT energies of a free charge neutral hydrogen/carbon atom and $N_{\text{H/C}}$ denotes the number of hydrogen/carbon atoms in the flake.

B. Results and discussion

1. Isotropic strain

A sequence of DFT calculations has been performed for $N=3,\dots,9$ and different values of the C-C distance, $d$. For each distance, $N_e(N,d)$ has been calculated. In order to extract the expansion coefficients of Eq. (1), $\Psi(d), \phi(d), \varphi(d), \delta(d), \psi(d), \theta(d)$, we have performed five-parameter fits on sets of raw DFT data. These fits were applied to three data sets consisting of $\{N\}=3,\ldots,7, \{N\}=3,\ldots,8,$ and $\{N\}=3,\ldots,9$. The results for the surface, bulk, and corner energy have been displayed in Fig. 2. The scatter between the fitting parameters belonging to different data sets is relatively small, which illustrates the stability of the fit.

The lattice constant of bulk graphene is estimated from the minimum position of $\Psi(d)$ Fig. 2, upper panel as $d_0 = 2.706\text{Å}$, where $a_0 = 0.529\text{ Å}$ denotes the Bohr radius. Comparing this position to the minimum of the edge (surface) energy, Fig. 2, center panel, $d_0 = 2.694\text{Å}$, we find $\delta = 0.44\%$. This indicates clearly the compression of the C-C bond length near the edge. The shift of the minimum position to lower values becomes even more pronounced near the corners, i.e., in $\varphi(d)$, see Fig. 2, lower panel.

To obtain also the other phenomenological parameters, a second (polynomial) fit of the traces $\Psi(d), \phi(d)$, Fig. 2, according to Eqs. (4) and (5) has been performed; all fitting parameters are summarized in Tables I–III.

When fitting the raw data to get $\Psi, \phi, \psi$ the terms in $1/N_{\text{el}}$ could not be neglected for the system sizes that we considered. The corresponding amplitudes are displayed in Fig. 3. Unlike it was the case with the previous data, Fig. 2, the amplitudes $\delta^{\text{pl}}$ of the $1/N_{\text{el}}$ corrections still exhibit a considerable variation with increasing system size, which is due to even order terms that have been neglected in the expansion $1/\ln N$. Interestingly, while the magnitude of $\delta^{\text{pl}}(\varepsilon)$ is still shifting the slope and perhaps also the sign of the two functions have converged, already. Under this assumption we may conclude that both amplitudes flow closer to zero values when $\varepsilon$ increases. This behavior is compatible with the simple expectation that the main effect incorporated in the $1/N_{\text{el}}$ corrections is the discreteness of the flake’s electronic spectrum with level spacings $\Delta_{\text{el}}$ for bulk and surface modes. With increasing $\varepsilon$ the bandwidth decreases and so do $\Delta_{\text{el}}$ and $\delta^{\text{pl}}$.

In the Appendix we have repeated this analysis for a representation of the free energy as a sum of atomic contributions, Eq. (A1). The results are equivalent, of course, but the detailed comparison of the results based on our phenomenological theory with earlier findings for bulk systems, which we have relegated there, is simplified in this way. In a nutshell, our extrapolation scheme recovers the known values for the surface free energy (per Angstrom) and the edge stress with excellent accuracy, see Table VII and below Eq. (A4).

2. Shear strain

A largely analogous method as was adopted for the isotropic strain has also been applied for shear forces. In this case, the convergence of the DFT calculations turned out to be considerably more difficult so that the investigated system sizes range from $\{N\}=3,\ldots,7,$ only. From our fitting procedure we could determine the response of the bulk energy and surface energy to the shear strain, $\varepsilon_{\text{el}}$, as shown in Fig. 4. The parameters entering Eqs. (8) and (9) can be extracted and are listed in Table IV.
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TABLE V. Comparison of C-C bond distance in bulk graphene, elastic constants, Poisson ratio [\(\nu=\lambda/(2\mu+\lambda)\)], and Young’s modulus \([Y=2(\mu+\lambda)(1-\nu)/A_{\text{ring}}]\) as extracted from Figs. 5–7, respectively, by extrapolating the values in bulk limit \((N\to\infty)\) with previous works. Data are shown for three different functionals we used in DFT calculation. The area of a benzene ring is estimated as \(A_{\text{ring}}=3\sqrt{3}d_{\text{0}}^2/2\).

|         | \(d_{\text{0}}\) (Å) | \(\mu_{\text{el}}+\lambda_{\text{el}}\) (eV) | \(\mu_{\text{el}}\) (eV) | \(\nu\)     | \(Y\) (N/m) |
|---------|----------------------|------------------------------------------|-----------------------|-----------|------------|
| BP86    | 1.432 ± 0.001        | 70.715 ± 0.011                         | 50.95 ± 0.01          | 0.162     | 356.23     |
| B3LYP   | 1.427 ± 0.001        | 71.21 ± 0.12                           |                       |           |            |
| PBE     | 1.431 ± 0.002        | 69.027 ± 0.012                         |                       |           |            |
| Prev. calc. | 1.42 (Refs. 37 and 70) | 66.571 (Ref. 37)                  | 49.45 (Ref. 37)       | 0.173     | 307 (Ref. 41) |
|         | 1.41 (Ref. 43)       |                                          |                       |           |            |
|         | 1.45 (Ref. 71)       |                                          |                       |           |            |
| Expt. (Graphene) | 1.421 (Ref. 74) |                                      |                       | 0.165     | 371 (Ref. 76) |
|         | 1.422 (Ref. 76)      |                                          |                       |           |            |
| Expt. (Graphite) | 1.421 (Ref. 74) |                                      |                       | 0.165     | 371 (Ref. 76) |

*Assuming graphene thickness 0.335 nm.

contributions of the surface (\(\phi_2\) term) and the surface-induced bulk compression (\(\Psi_{\mu\nu}\) term) diminish. A nonvanishing value of \(\Psi_{3}/12\) for the slope will remain however even in the bulk limit.

B. Shear strain

Following the same strategy as we did before with Fig. 6, we plot in Fig. 7 the excess energy \(\Delta E_{\text{ex}}\) induced by pure shear strain, \(u(x)=\varepsilon_{\text{x}}(0,x)\). Again, the plot emphasizes the curvature in this quantity, \(\mu_{\text{el}}\), and how it evolves with the flake size. Since \(\Delta E_{\text{ex}}\) is even in the shear strain, only positive values of \(\varepsilon_{\text{x}}\) are given. Also, for the same reason anharmonic terms exist only in the quartic order so that the displayed data traces have zero slope. Similar to the previous case of isotropic strain, we also witness here a very strong dependency of the elastic constant on the flake size. In fact, for shear strain it reaches almost 70% for the small system sizes that we are considering.

C. Buckling-induced strain

We present results from an additional DFT study, where we investigate the transverse stiffness of the graphene flake that gives rise to the elastic parameter \(k\). To this end we employ the following strategy. Each flake has a center pair or center ring of carbon atoms, see Figs. 1 and 8. To create a transverse probing field \(h(r)\), we lift the center atoms by the distance \(h_0\) over the reference plane. After this, the atomic

![FIG. 7. (Color online) Estimate for Lamé parameter \(\mu_{\text{el}}\) determined from the excess energy \(\Delta E\) per unit cell under pure shear strain with strength \(\varepsilon_{\text{x}}\). (Procedure similar to previous Fig. 6.) Left panel: dependency of curvature \(\Delta E_{\text{ex}}(\varepsilon_{\text{x}})\) on the linear flake size \(N\). Due to mirror symmetries of the unit cell, linear corrections do not appear for the shear parameter \(\mu_{\text{el}}\). Right: extrapolating the curvature into the bulk limit.](image1)

![FIG. 8. Buckling flakes of \(N=5\) and \(6\) with different central configurations of carbon atoms. The atomic configuration of C atoms is relaxed under the constraint that the center atoms remain at a given height \(h_0\) above the ground plane while edge atoms (H and C) remain sitting within this plane \((h=0)\).](image2)
structure of the flake is relaxed under the constraint that the set of edge atoms (H atoms and edge C atoms) can move only within the reference plane; edge atoms cannot shift in h direction.\(^6\) In this way, a flake is equipped with a single ripple while at the same time the associated strain field \(\mathbf{u}(\mathbf{x})\) remains negligibly small. In order to estimate the integrated curvature we numerically compute the bivariate function which interpolates the scattered data values \([h(\mathbf{r}) \text{ field}]\) at any predefined smooth mesh. We then use this interpolated function to perform the second-order numerical derivative at any arbitrary precision.

Figure 9 displays how the excess energy \(\Delta E_h\) associated with the ripple grows with the integrated integrated curvature,

\[
I_h = \frac{1}{2} \int d^2r [\Delta h(\mathbf{r})]^2.
\]

The increase is linear, as expected from Eq. (2) with a slope that is only weakly dependent on the flake size, see inset Fig. 9. This implies that nonlinearities remain small as long as the ratio of the ripples amplitude and wavelength, \(h_0/L\), does not exceed \(\sim 5\%\). The bending rigidity thus found is \(\kappa_{el} = 1.24\ \text{eV}\) which is well consistent with the value 1.1 eV obtained by Fasolino et al.\(^{30}\)

Notice that there is a significant scattering of almost 20% in earlier theoretical estimates for \(\kappa\) and derived quantities, see Table 2 in Ref. 78. Discrepancies appear because different theoretical techniques are being employed, e.g., empirical potentials\(^{32}\) and density-functional theory but also because of modeling artifacts. For example, extracting \(\kappa\) from the elastic energy of carbon nanotubes (radius \(R\)) requires a very careful extrapolation in \(1/R\). If subleading terms are ignored, there is a pronounced tendency for overestimation, e.g., \(\kappa = 1.46\ \text{eV}\) in Ref. 72. These authors used nanotubes with smaller tube radius, hence bigger curvature, where nonlinear effects become important. We can check the bending rigidity using the same curvature in Fig. 9 (inset) as reported in Ref. 72 and find a reasonable agreement with their value.

V. ZERO-POINT MOTION

In this chapter we extend our analysis of flake elastic properties and take also the zero-point motion of the atom cores into account, that constitute the hexagonal lattice. Now, the energy acquires a second term,

\[
F(N,d) = F_{el}(N,d) + F_{vib}(N,d)
\]

with

\[
F_{vib} = \frac{1}{2} \sum_p \hbar \omega_p(N,d)
\]

where \(\omega_p[N,d(N)]\) denotes the vibration energies in the absence of strain and \(d(N)\) the equilibrium bond length, see inset Fig. 5. Also \(\Delta F_{vib}\) can be expanded in terms of the slow elastic modes,

\[
\Delta F_{vib}[h,\mathbf{u}] = \frac{1}{2} \int_A d^2r \sum_{ij} \gamma_{ii}^p u_{ij}^p(\mathbf{r})
\]

with expansion parameters \(\gamma_{ii}, \gamma_a\) that represent averages of Grüneisen parameters over all vibrational modes. Specifically, we have in isotropic media

\[
\gamma_{ii} = \frac{1}{2} \sum_p \omega_p \Gamma_{ii}^p, \quad \gamma_a = \frac{1}{2} \sum_p \omega_p \Gamma_{ii}^p,
\]

where \(\Gamma_{ii}^p = \partial \ln \omega_p / \partial h_{ii}\) and \(\Gamma_{ii}^a = \partial \ln \omega_p / \partial \epsilon_{ii}\). In a two-dimensional sample\(^{79}\) with a mirror symmetry one expects \(\gamma_{ii} = \gamma_a = 0\); the change in phonon frequencies should be even in the shear strain, \(\epsilon_{ii}\). Combining Eq. (17) with an expansion of \(\Delta F_{el}\) in full analogy with Eq. (2) and after completing the square, we find

\[
\Delta F_{elvib}(N,d) = \frac{\kappa_{el} + \gamma_{ii}}{2} \int_A d^2r (\nabla^2 h)^2 + \frac{\mu_{el} + \lambda_{el}}{2} \int_A d^2r \left( u_{xx}^2 - u_{yy}^2 + u_{xy}^2 \right)
\]

For clarity, we have indicated in this expression the bare electronic coefficients (i.e., with frozen atomic cores) by \(\kappa_{el}, \mu_{el}, \lambda_{el}\). Likewise, the displacement field \(\mathbf{u}(\mathbf{x})\) is defined with respect to the optimum flake geometry-ignoring vibrational terms.

FIG. 9. (Color online) Estimating the Lamé parameter \(\kappa\) determined from the excess energy \(\Delta E\) of a bulging flake with maximum height at \(h_0\) over the unperturbed (flat) plane (see Fig. 8). Main panel: change in energy \(\Delta E\) with the integrated curvature \(I_h = [\int d^2r (\Delta h(r))^2]\) for different flake sizes \(N\). Inset: the ratio \(\kappa = \Delta E/I_h\) depend on \(N\) due to the effect of edge compression.
In this way we can observe two facts. (i) Vibrations modify the bare transverse stiffness $\kappa_{\|}$ in Eq. (19), $\kappa = \kappa_{\|} + \gamma_b$, (ii) Vibrations also affect interatomic distances. The effect can be understood as an effective strain, which stretches the bare C-C distances: $\gamma_b^{ii} / (\mu_{el} + \lambda_{el})$. (iii) The change in the C-C bond lengths eventually feeds back into all elastic coefficients. Therefore, in a more complete treatment of higher order terms also modifications in $\mu_{el}, \lambda_{el}$ would occur.

A. DFT calculations of the Grüneisen parameters

In order to estimate the Grüneisen parameters, $\gamma_b, \gamma_e$, we should calculate the vibrational spectrum of flakes with and without applied strain. To this end we adopt the following procedure. For every flake size, $N$, we find the atomic geometry with the optimal electronic energy, see, e.g., Fig. 1. This constitutes the set of freely relaxed “parent states.” The relaxation ensures the Hessian, that characterizes interatomic forces, to become a positive definite matrix.\(^{80}\)

In the present study we focus on the impact of phonons on the bulk elastic constants. There we may eliminate contributions of surface vibrations by assigning an infinite mass to the surface H and C atoms. Other than this, the calculation of vibrational modes and frequencies for the relaxed flake is a standard procedure.\(^{81,82}\)

Thereafter, each parent state thus obtained is used in order to create two new families. The first family is constructed to obtain $\gamma_b$. It derives by changing the bond length of edge C-C-pairs by a factor of $1+\varepsilon$ keeping all atoms still inside the base plane ($h=0$). For each value $\varepsilon$ the internal C atoms are relaxed and the vibrational spectrum together with the average strain field, $I_0(\varepsilon) = \int d\mathbf{r} (u_{x\varepsilon} + u_{y\varepsilon})$, are recalculated. In this process it is important to have edge atoms at infinite mass. This ensures that the flake energy is in a (constrained) minimum so that all frequencies are real.

In order to determine $\gamma_b$ a second family has been constructed. It consists of the buckled flakes, Fig. 8, that we have studied in the previous section in order to extract $\kappa_{\|}$. Again, after assigning infinite mass to the edge atoms for each family member, the vibrational spectrum and the consecutive modification of the zero-point energy can be calculated.

B. Results and discussion

In Fig. 10 the change in the zero-point energy, $\Delta F_{\text{vib}}$, is plotted over the integrated strain fields. The Grüneisen parameters are given by the slope near zero strain; their numerical values are listed in Table VI. For a discussion of our results we first recall that the vibrational spectral density of states of the carbon sheet has a strong peak in the optical frequency regime, cf. Fig. 11, near 1600 cm$^{-1}$. It is the “G-peak,” that corresponds to an in-plane mode, where neighboring atoms vibrate in opposite direction as depicted in Fig. 12.
between the edge and bulk properties which are mediated via long-range elastic forces.

Specifically, we are able to disentangle bulk, surface and corner contributions to the energy together with the leading higher order corrections. The binding energy per surface (edge) bond (7.5 eV) is roughly 2 eV higher than the one for interior (bulk) bonds (5.2 eV); similarly, edge bonds have a tendency to be shorter than bulk ones. As a consequence, the flake’s interior undergoes a surface-induced compression which is the more pronounced the smaller the flake is. This compression manifests itself in the way in which various observables depend on the flake size, \( N \). For example, elastic constants (i.e., Lamé parameters) of small flakes can exceed their bulk limit (\( \mu + \lambda = 70 \) eV per ring, \( \mu = 51 \) eV per ring, \( \nu = 0.162 \)) by 30% (\( \mu + \lambda \)) or even by 70% (\( \mu \)). In comparison, the sheet (out-of-plane, buckling) stiffness, \( \kappa = 1.2 \) eV, is less sensitive to \( N \). Nonlinearities remain weak (less than 10% increase) as long as the ratio of out-of-plane amplitude and in-plane wavelength of buckling is below 5%. To highlight the importance of quantum effects on elasticity we have also calculated the vibrational spectrum of graphene flakes. Quantum corrections affect mostly the sheet stiffness, \( \kappa \), lowering it significantly, about 26% within our DFT framework.

Finally, based on these results we predict a pronounced shift of the Raman G- and D-peaks with decreasing flake size to higher values. It is a natural consequence of the edge-induced flake compression. The associated Grüneisen parameters are \( \gamma_D \approx 2.6 \) and \( \gamma_G \approx 2.2 \).

**ACKNOWLEDGMENTS**

We are grateful to A. Bagrets, M. van Setten, and V. Meded for helping us with the data visualization and also with the \textit{ab initio} calculation. We are thankful to J. Weissmüller for numerous discussions during this work. Also, we acknowledge support from the Landesgraduiertenförderung Baden-Württemberg and Center of Functional Nanostructures of the Deutsche Forschungsgemeinschaft, project 4.11.

**APPENDIX: COMPARISON**

In order to compare our results with previous authors here we perform a consistency check by evaluating the bond energies. We have a binding energy \( \Psi(d_b) = -5.22 \) eV for bulk carbon bonds. It translates into an energy per bulk C atom (cohesive energy) \( 3 \Psi(d_b)/2 \approx -8.06 \) eV which compares favorably well with an earlier estimate \( -7.9 \) eV.

For the edge energy we use the earlier definition,

\[
E_{\text{edge}} = \frac{1}{L} \left( E_{\text{tot}} - N_C E_C^b - \frac{N_H}{2} E_{H_2}^b \right),
\]

where \( N_C \) is the total number of carbon atoms and \( E_C^b \) denotes the energy of a carbon atom in bulk graphene. \( E_{H_2}^b = -31.496 \) eV is the energy of a hydrogen molecule and \( N_H \) is the total number of hydrogen atoms that terminate the graphene edge of total length \( L \). In order to estimate \( E_C^b \) we parameterize the total energy in full analogy with Eq. (1),
FIG. 13. (Color online) Bulk ($E_C^b$), surface ($E_C^s$), and corner ($E_C^c$) energy as extracted from Eq. (A2) using density-functional theory (PBE functional). Data based on the evaluation of flake sizes ranging from $|N|=4, \ldots, 8$ per $d$ values ($a_0=0.529$ Å). (□) denotes data from a three-parameter fit to first three terms of Eq. (A2) ignoring the correction terms. (○) and (○) are the data with four- and five-parameter fits of Eq. (A2) including the correction terms. The scattering between the data sets that include the finite-size correction terms is relatively small, which shows the stability of the fitting procedure.

$$E_{\text{tot}} = N_C^b E_C^b + N_C^s E_C^s + N_C^c E_C^c + N_H E_H + \frac{d^s}{N_C} + \frac{d^b}{N_C}$$

(A2)

with

$$N_C = N_C^b + N_C^s + N_C^c,$$

(A3)

where $N_C^b$ denotes the number of bulk carbon atoms (having only C atoms as nearest and next-nearest neighbors) with an associated energy $E_C^b$, $N_C^s$ denotes the number of edge carbon atoms with energy $E_C^s$, and $N_C^c$ is the number of corner carbon atoms with energy $E_C^c$ (CH groups with at least one more CH group as nearest neighbor; $N_C^c=10$ in our case), $d^s$ and $d^b$ are further expansion coefficients. $N_H=(N_C^c-4)/2+N_C^s$ is the total number of hydrogen atoms with energy per atom $E_H=-13.568$ eV in vacuum which is calculated separately. In order to estimate the bulk carbon energy we have performed a three-, four-, and five-parameter fit on the raw DFT data. The fit is stable against the number of fitting parameters with data set consisting of $N=4, \ldots, 8$, as shown in Fig. 13. Our estimate of the bulk energy $E_C^b$, edge energy $E_C^s$, and corner energy $E_C^c$ per carbon atom are listed in Table VII.

Finally, using these estimates we calculate the edge energy per unit length and its variation with homogenous, isotropic strain, $\varepsilon$, (Fig. 14). The result at zero strain, $0.114\pm0.001$ eV/Å, compares well with earlier works $0.106$ eV/Å.68,69 Furthermore, we extract the edge stress, $\tau_{\varepsilon}$, following the conventional definition,68

$$\tau_{\varepsilon} = \frac{dE_{\text{edge}}}{d\varepsilon}.$$  

(A4)

Our value, $\tau_{\varepsilon}=0.26$ eV/Å, is significantly enhanced compared to the values reported for uniaxial strain, $\tau_{\varepsilon}^{\mu\nu}=-0.01$ eV/Å,68,69 that have been obtained in a ribbon geometry. The lower sensitivity on homogenous uniaxial strain is not a surprise, since in that case a considerable part of the elastic energy cost for longitudinal stretching can be released by the transverse contraction. With homogenous isotropic strain the surface unit cell experiences stretching in all directions and there is no partially compensating relaxation process.

In order to understand the relative smallness of the edge energy, $E_{\text{edge}}$, of the hydrogen-terminated graphene flakes we rewrite Eq. (A1) after substituting $E_{\text{tot}}$ from Eq. (A2),

TABLE VII. Survey over the fitted total-energy parameters and edge energy as defined in Eqs. (A1) and (A2). Data extracted at zero strain, where the bulk C-C bond distance is minimum, $d_0=1.431$ Å (see Table I).

| Parameter | PBE functional | Prev. calc. |
|-----------|----------------|-------------|
| $E_C^b$ (eV) | $-1035.33\pm0.01$ | |
| $E_C^s$ (eV) | $-1036.25\pm0.02$ | |
| $E_C^c$ (eV) | $-1037.18\pm0.06$ | |
| $E_{\text{edge}}$ (eV/Å) | $0.114\pm0.001$ | $0.106^{ab}$ |

aReference 68.
bReference 69.
ELASTIC PROPERTIES OF GRAPHENE FLAKES:

\[ E_{\text{edge}} = \frac{N_C^e}{L} (E^e_C - E^b_C) + \frac{N_C^e}{L} (E^e_C - E^b_C) + \frac{1}{2} \frac{N^b_H}{L} \frac{E^b_H}{2} + \phi^e \]

\[ + \frac{L}{N_C^e} \]  

with

\[ L = \sqrt{3d^2 + 4d} + \frac{8d}{\sqrt{3}}, \]

where \( N_C^e \) denotes the total number of edge C atoms of a graphene flake and \( E^b_H = 2E_H - E_{1s} \approx 4.36 \text{ eV} \) is the binding energy of a hydrogen atom. Now, considering the limit \( L \to \infty \), Eq. (A5) reduces to

\[ \lim_{L \to \infty} E_{\text{edge}} = \frac{E^e_C - E^b_C + E^b_H/4}{\sqrt{3}d/2}. \]

Using the above-mentioned estimate, \( E^e_C - E^b_C \approx -0.92 \), we see that difference in bulk and edge binding energy is largely compensated by the additional binding energy averaged over two edge C atoms contributed by the \( H_2 \) molecule, \( E^b_H/4 \approx 1.09 \).

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Note that certain effects related to the thickness of the graphene sheet are left out in Eq. (2). For example, a linear displacement field \( h(r) = r \times a \) has no energy cost because the description assumes that such a conformation is equivalent to a rotation. However, this ignores that a rotation gives the orbital a new direction in space while the lifting up of atoms mediated by the attachment of contacts. Also this may produce gradient terms \( \nabla h \) in the functional Eq. (2).

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