Anisotropic Failure of sp^2 -Hybrid Bonds in Graphene Sheets

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ABSTRACT: A combined atomic force microscopy and theoretical study reveals preferred fracture directions in the topmost graphene sheets of mechanically exfoliated graphite. Fractures in the basal plane of single-crystal grains are found to depend on applied stress direction and crystallographic orientation. Interatomic bonds that are aligned with the applied stress direction exhibit the largest resistance against fracture. The findings are modeled through an angle-dependent failure of sp^2 hybrid bonds which results from a larger interatomic energy dispersion of sheared C–C bonds.

I. INTRODUCTION

Many solids exhibit preferential fracture directions when subjected to external loads. It is a feature that relies on defect density and symmetry of atomic bond structure¹. Lamellar materials, however, have special mechanical responses usually at variance with continuum fracture models. One striking example is graphene, which shows a marked insensitiveness of failure strength to density, location, chemistry, and size of atomic defects^{2,4,6,39}.

The fracture mechanics of graphene is nowadays of great interest for the fabrication of nanoscale single-crystal nanoribbons, as they are considered key to development of many future electronic devices^{5,7,8}. This is due to their unique electronic properties conferred by the reduced width and atomic structure at edges. In particular, it has been shown that graphene edges with a certain degree of electron-hole symmetry near the Fermi level support quantum-confined electronic states relevant for anisotropic electron and spin transport^{9–14}.

Currently, a considerable effort is engaged to develop versatile techniques for the fabrication of graphene nanostructures with controlled edge orientations^{15,16}. Nanoparticle cutting^{17,18}, chemical ripping^{19,20}, Joule heating²¹, electron etching^{22,23}, or diamond nanotomy²⁴ are found very promising for graphene edge engineering. At the atomic scale, however, the problem boils down to how local factors impact the stability of individual atomic bonds subjected to a mechanical stress²⁵. This is a fundamental and technologically relevant issue which is far from being understood in a simple and intuitive manner. The fracture mechanics of graphene layers has been studied in relation with, elastic^{26–29} and inelastic^{30–32} bending properties, inherent presence of defects^{2,27,33}, and adhesive substrates^{34,35,45}. There are

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also studies predicting that armchair^{36–38,41} and zigzag^{22,23} crystal axes are preferred fracture directions. However, due to local topological changes and experimental conditions, an atomistic view of the failure of sp²-bond in graphene layers still deserves consideration.

Here, we first experimentally show that the mechanical exfoliation of graphite surface causes a strong anisotropic failure of the C–C bonds of the topmost graphene sheets. Then, by using density functional theory (DFT), we estimate the initial stretching characteristics of individual bonds when pulling in different directions. By combining the DFT results with a semiempirical description of interatomic interactions which includes entropic effects, we show through a simple model that stretching an individual bond along its axis translates in the largest resistance against rupture. We conclude that the nature of *sp*² covalent bonds and the robust 120° angles of the hexagonal lattice make atomic-scale shear forces very efficient to induce preferential linear fractures.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

The (0001) surface of highly oriented pyrolytic graphite (HOPG) was exfoliated by the scotch-tape method. The surface morphology was imaged by atomic force microscopy (AFM) operating in contact mode at pressures below 10^{−4} mbar, and occasionally by scanning tunneling microscopy. The AFM deflection signal was acquired simultaneously with topographic data while scanning along the cantilever axis. The integral gain of the feedback loop and the scanning speed were kept at low values to enable detection of cantilever buckling in deflection channel. AFM probes with normal spring constants of the order of 0.01 N/m were used. We employed normal forces of few nN. The crystalline structure of the graphite was analyzed by X-ray diffraction using 2 θ - and ϕ -scans with a Rigaku SmartLab diffractometer equipped with a Cu source and a Ge (220 × 2) crystal (45 kV, 200 mA, 0.154056 nm). The density functional theory (DFT) calculations were performed in order to determine the initial stretching properties of the C–C bonds by using the plane wave electronic structure package called Quantum-ESPRESSO, as described in detail in⁴². We used the results obtained by DFT into a semiempiric model able to explain the experimental observations.

III. RESULTS AND DISCUSSIONS

A schematic of the mechanical exfoliation process is presented in Fig. 1. The HOPG sample depicted as a top view in the inset is a 5 × 5 mm² block which was fixed on a sample holder (not shown). The exfoliation was performed at different azimuthal angles (ϕ) by keeping the sample oriented in the same position. After each exfoliation the sample was placed in the AFM microscope in the same position in order to allow a direct comparison of the resulting atomic steps in the images. A side view of the exfoliation process is shown in the inset for a $\phi = 0^\circ$. A typical surface morphology obtained after an exfoliation at 0° is shown in Fig. 1(a). The surface presents various atomic steps which, as observed, are preferentially aligned along the vertical axis. A similar surface morphology was found at different

macroscopic zones at the sample surface. More than half of the atomic steps have heights corresponding to a single atomic layer. To quantify the in-plane orientation of the steps, we used the first derivative of the topographic signal which significantly highlights the atomic steps, as seen in Fig. 1(b). In the derivative image, ascending/descending steps appear as bright/dark lines, respectively. The advantage of performing a derivative of the topographic image is that the 2D Fast-Fourier Transform (FFT) is then able to better reveal the steps orientation. This is because for the derivative image, the steps generate a 90° rotated FFT spectral feature, as can be observed in Fig. 1(c). Moreover, the width of the FFT spectral signal also reflects the angular distribution of the orientation of the steps.

The results shown in Fig. 1, are compared with those obtained for $\phi = 30^\circ$, 60° and 90° exfoliation directions in Fig. 2. In each case, the orientation of the steps is found to closely follow the exfoliation direction, *i.e.* the angle ϕ . This can be directly seen in the topographic images [top row (a) to (d)] and confirmed by the FFT images [middle row (e) to (h)]. The angular orientation of the steps, and to some extent they distribution, can also be deduced from the bottom row [(i) to (l)] of Fig. 2, where profiles performed along a concentric circle - as exemplified in Fig. 2(e)

FIG. 1: (a) AFM topographic image acquired after an exfoliation at $\phi = 0^\circ$. (b) First-derivative image of the topographic signal from (a), showing enhanced contrast at the step-edges. (c) FFT image corresponding to the derivative image from (b). The insets are macroscopic schematics of the exfoliation process with respect to the HOPG sample.

- are shown. The 90° direction, the one perpendicular to the exfoliation direction, is indicated by white arrows in the FFT images from (e) to (h). A quick inspection of the corresponding FFT profiles [(i) to (l)] clearly reveal that FFT signal indeed presents peaks which are very close to $\phi + 90^\circ$ with respect to the exfoliation direction. The widths of the peaks are rather broad, but in all these cases hardly exceed 15° at full-width half maximum. This value, which reflects the distribution in the failure direction depends in turn on the lateral size of the topographic image, as discussed below in relation with the larger AFM image presented in Fig. 6. Anyway, the experiments presented in Fig. 2 quantitatively demonstrate that the orientation of the steps, which mirror the failure directions of the topmost graphene layers, does not deviate much from the exfoliation direction. This is a intriguing result clearly speaking in favor of a grained structure isotropically distributed in the surface plane.

FIG. 2: (a - d) AFM topographic images revealing the surface morphologies after various exfoliation directions. The arrows indicate the ϕ angles of the exfoliation. (e - h) FFT images corresponding to the first-derivative (not shown) of the topographic images. The arrows show the $\phi + 90^\circ$ direction relevant for FFT signal formation (green color). The arrowed circle in (e) shows the location where the FFT amplitude profiles were measured. The location is the same in (f - h). (i - l) Amplitude profiles corresponding to the four exfoliation directions, showing peaked amplitude signals at $\phi + 90^\circ$.

A. Role of grains

In order to reinforce the results described above, we conducted an XRD study by performing 2θ (out-of-plane), and ϕ (in-plane) scans. The 2θ spectra show characteristic spectral lines for graphite, which consist in narrow peaks corresponding to the high-symmetry (hkl) crystal planes of the hexagonal structure [Fig. 3(a)]. Note that 2θ scans are only a proof of the good crystal-structure of grains, but they are not informing much about the grain orientation. The orientation of the grains, in general and importantly, the orientation of armchair and zigzag axes of the grains within the surface plane in particular, are only revealed by XRD ϕ -scans. Such scans consist in measuring the intensity of (hkl) peaks while rotating the sample in the surface plane, typically by 360° . If all grains are oriented in the same way (single crystal case), a ϕ -scan would present a pronounced wavy shape, reflecting the hexagonal structure of the HOPG. This behavior would be even more pronounced if higher order planes are measured. As shown in Fig. 3(b), for the (002), (011), and (016) planes, the amplitude of all peaks are invariant when changing the ϕ angle. This is a clear indication that the grains are isotropically oriented within the sample plane, explaining therefore why the surface morphology at large scales is rather independent on the exfoliation direction.

FIG. 3: (a) X-ray diffraction (XRD) patterns of the three first (hkl) planes of the hexagonal HOPG sample, as revealed by a 2θ symmetrical scan. (b) X-ray diffracted intensity acquired for the symmetrical (002), and asymmetrical (011), and (016) planes of the graphite crystal structure when rotating the sample in the plane by 360° .

B. Atomic resolution: armchair *vs.* zig-zag

Figure 4 shows an example of scanning tunneling microscopy (STM) image of the exfoliated HOPG surface. The image unveils single- (SL) and double- (DL) layer step edges oriented along an AC axis. The atomic resolution seen in the inset is a typical hexagonal atomic structure measured by STM. At variance with the real honeycomb lattice of graphene, the image displays a hexagonal structure containing an additional feature in the center of each hexagon defined for instance by the dark spots. This is a known consequence of the ABAB stacking order in the normal direction to the surface plane, as detailed in⁴². An easy way of identifying the crystal orientation is by performing a 2D FFT analysis of the atomically resolved image. As seen in the inset, such an analyze reveals an orientation of the steps (failure directions) along an AC axis. Note that due to the hexagonal structure there are three AC axes in the plane of a graphene layer. As a consequence, we conclude that it is the one which is the closest to the exfoliation direction which predominantly fails, although a complete statistical study along the full length of the steps is hampered by the small scale images needed to obtain the atomic resolution. Importantly, the presence of grain boundaries or other defects are found to strongly affect the step orientations. Such defects are known to induce additional deformation fields^{39,40}, which can then interfere with the exfoliation-induced stress, aspects discussed in

FIG. 4: (a) STM image used for the identification of failure direction with respect to atomic lattice. (b) Height profile corresponding to the horizontal dashed line from (a). The profile reveals step heights associated to single-layer SL and double-layer DL steps. The location where the atomically-resolved image from the inset was acquired is marked by a white square. All atomic steps (layers) belonging to the same crystal grain were identified with the same orientation. A grain boundary crossing almost horizontally through the image can be seen in the upper part of the image from (a).

the next section.

C. Grains and large-scale imaging

Figure 5 shows how a combined topographic and deflection imaging reveals fracture properties of single-crystal graphite grains. In this example, the topography discloses several subsurface dislocations, but also, a triangular vacancy island in the topmost graphite layer. The vacancy is about 3 Å deep, value corresponding to a single graphite layer [Fig. 5(c)]. The angle between the two fractured vacancy edges reflects the two sets of high-symmetry directions of the honeycomb in-plane graphite lattice [$3 \times$ zig-zag (ZZ) and $3 \times$ armchair (AC)], rotated to each other by 30° [Fig. 5(d)]. This characteristic indicates that the preferred failure directions are not only the AC, but also to some extent and ZZ crystal axes.

In order to further assess this point, we show in Fig. 6 a large-scale AFM image presenting the surface morphology after an exfoliation at $\phi = 0^\circ$. The orientations of the steps are revealed by the 2D-FFT from the inset. The main FFT oval-like feature is given by the vertical step edges aligned along an AC axis, while the smaller feature rotated clockwise by 30°, is built by the fewer ZZ step-edges. As also mentioned above, beside the directional failure direction,

FIG. 5: Topographic (a) and deflection (b) image of a graphite surface after an exfoliation from left to right. A single-crystal grain is observed as a dark contrast in deflection image. (c) Profile along black line in (a). (d) Sketch of graphene crystal structure [not rotated to correspond to in-plane crystal structure from (a) and (b)] revealing the two sets of high-symmetry directions [armchair (AC) and zigzag (ZZ)].

FIG. 6: (a) Large-scale AFM image ($6 \times 6 \mu\text{m}^2$) showing a directional failure of topmost graphite layers after an exfoliation from bottom to top. The image is the first derivative of the topographic (height) signal. White arrows show examples of grain boundaries inducing reorientation or cessation of step edges. The first one is a direct measure of lattice mismatch between adjacent grains. Circles indicate typical fracture morphologies. Inset: 2D-FFT map of height image from (a) revealing step-edge orientations and their distributions. The curved arrow corresponds to FFT profile from (b). (b) FFT profile along the curved arrow from inset. (c - e) AFM images ($500 \times 500 \text{ nm}^2$) showing surface morphologies for three single-crystal grain orientations depicted at the bottom of each image. Red segments indicate the atomic bonds which are expected to break in order to produce the respective morphologies.

the FFT also informs about the distribution of the orientation of the steps [peak widths in Fig. 6(b)], which, in this case, is mainly induced by crystal grains [see for instance white arrows in Fig. 6(a)]. In such large AFM images, it is possible to identify three characteristic surface morphologies which are shown in Fig. 6 (c - e). Therefore, we can conclude that grains with an AC direction matching the exfoliation direction display long linear fractures evidenced

FIG. 7: (a) Schematic view of molecular orbitals building σ and π bonds between two carbon atoms. (b) Zoom on the graphene slab⁴² used in DFT calculations showing two stretching configurations. (c) Summary from (b) depicting the force direction with respect to a C–C bond axis. (d) Energy difference per bond found by DFT for the two stretching directions. Note that the two curves cross at the equilibrium distance. Full lines are Morse fits (Eq. 1). Dashed lines correspond to calculated gradients of Morse fitted curves.

as bunches of parallel atomic steps in the AFM images [Fig. 6(d)]. Also, triangular fractures appear to originate from grains that have neither a ZZ, nor an AC axis aligned with the exfoliation direction [Fig. 6(c), also seen for instance in the upper right corner of Fig 1(a).]. Conversely, grains presenting a ZZ axis oriented with the exfoliation direction produce large flat areas without any fractures in the surface layers [Fig. 6(e)].

The exfoliation is a macroscopic process where only the equilibrium final state of the surface morphology can be measured. How an exfoliation as the one described in Fig. 1 (which is the standard procedure used for graphite) translates in force fields at microscopical levels cannot be directly accessed. It is nevertheless expected that the macroscopic forces induce both in-plane and out-of-plane local stretching force components. The rather weak van der Waals interlayer interactions may also play a role by temporarily permitting lifts of layers before the final breaking of the bonds. This process can strongly be impacted by the local environment which may include atomic scale defects, interlayer pinning sites, dislocations, grain boundaries, or other structural inhomogeneities of relevance for the initiation of rupture and for the subsequent propagation. As a consequence, the exact local stress direction is difficult to predict. In the literature, there are some studies which consider the fracture modes of the continuous mechanics in relation with few-layers or single graphene failure. It is worth noting that, in general, tearing of a non-lamellar material

usually results in mode-III stress at a crack tip. In contrast, for a graphene layer, tearing was found to promote a large out-of-plane bending at the crack tip, due to a large in-plane to out-of-plane stiffness ratio, inducing a crack-tip mode mixity^{41,43–45}. Moreover, using reactive force field (ReaxFF) analyses, Huang *et al.*⁴³ found, by evaluating the virial stress components at the crack tip of a teared graphene, that the dominant fracture mode is mode-I. This is the mode which involves in-plane force components and again is of importance for the case of graphite due to the fact that van der Waals interlayer interactions allow a bending of the layers in the direction normal to the surface. Following these studies, we consider that at single-bond level at the crack tip the in-plane strain components (mode-I and -II) are likely of relevance for graphene failure.

To address the stretching characteristics at the atomic scale along different crystal directions, we performed DFT calculations while stretching a graphene layer in two orthogonal directions, as shown by arrows in Fig. 7 (b)(also see Sup. Mat.). Briefly, all bonds crossed by the green and red lines are allowed to change when the slab is stretched. This allows us to compute the energy gained upon stretching the lattice in a direction parallel (// case) or at an angle (sheared case) with respect to an individual bond axis, as depicted in Fig. 7 (c) (see bonds crossed by red and green lines). Figure 7 (d) shows the variation of energy difference between stretched and stress-free configurations, as well as the resulted energy gradients (forces). The largest force needed to stretch the bonds at the same strain is in // case. This result is consistent with the larger modulus found along AC direction by AIREBO simulations⁴⁶.

D. Numerical simulations

To provide a simple model for the anisotropic fractures of C–C bonds observed experimentally, we intentionally choose a crude energy functional described by a Morse interaction potential obtained by fitting the DFT results:

$$V(r) = V_0\{[1 - e^{\beta(r-r_0)}]^2 - 1\}, \quad (1)$$

where $V_0 = 5.6311 \times 10^{-19}$ J is the C–C binding energy, r is the C–C bond length, and $r_0 = 1.39$ Å is the equilibrium bond length. The parameter β defines the shape and width of the potential well, and is related to the gradient of the curves shown in Fig. 7(d). For the // case, we found $\beta_{//} = -1.77$ Å⁻¹, a value close to what is known from literature⁴⁷. Importantly, for sheared configuration, we found $\beta_{sheared} = -1.48$ Å⁻¹, value corresponding to a gradient difference of 17%. The fact that $\beta_{//}$ is larger has a crucial importance when stretching the bonds. This is because β characterizes the variation of the bond energy as a function of interatomic distance. As for any linear or nonlinear spring-like behavior the stiffness terms provide the force magnitude needed to deform the spring. For the bond configurations treated in our case the stiffness, quantified therefore by the β values, is larger for the parallel case, an effect which comes from the overlapping of electronic states within the hybrid sigma bonds. We therefore are not treating a complete angular dependence of the interaction potentials as a function of distance because the structural symmetry of the crystal lattice permits addressing first the two limit cases of parallel and 30° sheared configurations, but also

because a full angular description would involve more elaborated calculations.

Figure 8 (a) shows the variation of the total interaction potential for shear case when applying F_c ($T = 0$ K) and $F_{T \neq 0}$, where $F_c > F_{T \neq 0}$. In this example, $F_{T \neq 0}$ is set to 3.12 nN, value corresponding to bond failure at 295 K (see Table 1). Generally speaking, a pulling force progressively distorts the interatomic potentials in such a way that for large enough displacements the local potential minimum responsible for covalent bonding disappears. Figure 8(b) shows the situation (thick lines) when a "sheared" bond breaks, while a "//" bond is still protected by a finite potential barrier ΔV . At $T \neq 0$ K, however, individual bonds can break well before $\Delta V = 0$ [Fig. 8(c)]. According to thermal activation theories^{48–50}, the lifetime τ of a stretched bond can be written as a function of stretching force F , temperature T , and vibration frequency of the bond atoms $1/\tau_0$:

$$\frac{1}{\tau}(\tilde{V}, T) = \frac{1}{\tau_0} \exp \left[\frac{(F_c - F)^{3/2}}{\tilde{\beta} k_B T} \right]^{-1}, \quad (2)$$

where we used: $\Delta V = [(F_c - F)^{3/2}]/\tilde{\beta}$ as the instantaneous potential barrier depending on F , $\tilde{\beta}$ as a parameter defining the shape of the total interaction potential close to the critical point, and F_c the critical force at $T = 0$ K. Writing ΔV in this way accounts for the fact that a bond failure preferentially occurs close to the critical point, where the remaining barrier is small [Fig. 8(d)]. This is similar to atomic scale friction^{51,52}, or other phenomena described by a transition rate^{53,54,56}. It is important to observe that according to Eq. 2, thermal effects are only relevant for strain rates lower than $r_c - r_0/(\tau_0 r_0)$, with r_c the critical displacement needed for bond failure at $T = 0$ K. In other words, thermal effects are increasingly important as the vibration period τ_0 is smaller than the time t_c needed to reach r_c . Taking a typical exfoliation strain rate of 24×10^{-5} ps^{-149,57}, the time t_c to stretch a bond from its equilibrium distance to r_c , which for instance corresponds to a displacement of 0.47 Å for the shear configuration in Fig. 8, is 2 ns. This value is 10⁵ times larger than the longitudinal or transverse vibration period t_{ph} of graphene atoms, which both are of the order of 20 fs⁵⁸. Moreover, phonon periods along Γ - M and Γ - K - M high-symmetry directions, *i.e.* ZZ and AC axes, are quite close, remaining of the order of several fs^{58,59}. We therefore conclude that at typical exfoliation speeds encountered in lab experiments thermal effects isotropically contribute to the bonds failure in graphite. The fact that the graphite basal layers break anisotropically can then entirely be explained by the larger dispersion of interatomic interaction potentials for sheared cases as compared with // configurations.

It is possible to get r_c and F_c for the two configurations, as exemplified in Fig. 8 (a,b) for the red curves. At finite temperature a thermally activated bond failure over the potential energy barrier ΔV leads to $F < F_c$, and the probability $W(t)$ that such an event occurs at time t is given by the standard rate equation $W'(t) = \tau^{-1}W(t)$, where $W'(t)$ is the first derivative of the probability as a function of time. Solving this equation and imposing the condition for the maximum probability $d^2W/dF^2 = 0$ lead to the relation between the applied force F and temperature T . The complete description of these expressions has been done on different occasions, including for flux admittance in

FIG. 8: (a) Shear interatomic potentials before [$V(r)$ line] and after (dashed and solid lines) applying external forces. Used parameters: $F_{T \neq 0} = 3.12$ nN, value corresponding to the failure force at 295 K (see text), and, $F_c = 4.17$ nN which represents the failure force at 0 K, i.e. $\Delta V = 0$. (b) Evolution of total interaction potential in both shear (reddish lines) and // (green lines) cases in the proximity of equilibrium distance for increasing values of external forces. The thick red/green curves show the particular case of applying $F = 4.17$ nN (black line is $-Fr$) leading to $\Delta V = 0$ for shear case (absence of a local minimum), and a finite, yet high, ΔV for // case. (c) Total interaction potentials for // and shear cases when applying $F = 3.12$ nN, leading to failure in shear configuration. The thick lines from (b) are shown for comparison. Note that all $-|F| r$ lines intersect zero at the equilibrium distance. (d) Variations of the barrier height ΔV as a function of external force F obtained by simulations (dots), and calculated, as described in text, with the expression $[(F_c - F)^{3/2}]/\tilde{\beta}$ (lines). A good agreement can be seen for low ΔV values.

superconducting loops⁶⁰, magnetization switching^{54,61,62}, breaking nanocontacts⁵⁵, nucleation processes^{56,63}, sliding friction and adhesion^{51,64–68}, or generically in⁵³. Here, the relationship between the force F and temperature T , can be written as:

$$F(\tilde{V}, \dot{\epsilon}, T) = F_c - [\tilde{\beta} k_B T \ln(\dot{\epsilon}^*(t))]^{2/3}, \quad (3)$$

where $\dot{\epsilon}^*(t)$ is the reduced strain rate corresponding to the ratio between the critical strain rate – at which thermal effects are not any more relevant – and the strain rate resulting from exfoliation. Hence, $\dot{\epsilon}^*(t)$ is also given by t_c/t_{ph} , resulting, as outlined above, in 10^5 . Note that as long as $t_c \gg t_{ph}$ the logarithm has only a limited impact on F values. Instead, $\tilde{\beta}$ and $k_B T$ are key parameters for failure force F at finite temperatures. With a Taylor expansion

TABLE I: Parameters resulting from numerical simulations, and failure force values F at $T = 295$ K obtained from Eq. 3.

	$\delta r_c [\text{\AA}]$	$F_c [\text{nN}]$	$V_{x_c}''' [\text{J/m}^3]$	$\tilde{\beta} [\text{N}^{3/2}/\text{J}]$	$F [\text{nN}]$
shear	0.47	4.17	-1.8×10^{12}	7.14×10^5	3.12
//	0.39	5.01	-3.1×10^{12}	9.43×10^5	3.74

near the critical point r_c , the local shape of the total potential can be calculated as $\tilde{\beta} = [3/(4\sqrt{2})]\sqrt{-V_{r_c}'''}$, where V_{r_c}''' is the third derivative of $V(r)$ at r_c . Table I summarizes our findings for shear and // configurations. F values at $T = 295$ K are both $\approx 26\%$ smaller than at 0 K. Additionally, although r_c is larger in shear configuration the failure forces are smaller as compared with // case. This, again, is a consequence of the larger spatial dispersion of shear interaction potential [Fig. 7 (d)]. The failure force in // configuration is thus about 17% larger than in shear case. This value is expected to vary with the angular difference between the two configurations – here being set to 30° . Going back to Fig. 6, it is therefore important to remark that sheared configurations can arise along many crystal axis, depending mainly on the grain orientation with respect to the exfoliation direction. In Fig. 6(c), it is seen that ZZ and AC directions are equally preferred as long as the involved bonds are sheared at equivalent angles. This finding can be extended into a systematic description of failure as a function of angular difference between a grain axis and a stretching force. From a theoretical point of view this can be done by carefully resolving the problem of fracture mode mixity and initial fracture notch as done for instance in⁴³. Experimentally, such a study is hampered by inherent structural defects^{2,39}, changes of grains orientation, and/or invasion of environmental molecules⁴³.

IV. CONCLUSION

In conclusion, we revealed that an exfoliation process induces a strong anisotropic failure in the basal plane of single-crystal graphite grains, generating atomic steps aligned in specific directions with respect to the local lattice. The atomic steps are preponderantly found along armchair and zig-zag directions, demonstrating preferences for fracture of some C–C interatomic bonds over others. By combining density functional theory calculations with numerical atomistic simulations we provide a very simple model for understanding anisotropic failure effects of graphene sheets. The model allows an easy and intuitive description of the mechanical resistance of the sp^2 C–C bonds which is likely relevant for the local failure mechanics of graphene sheets during the exfoliation of graphite. For scales exceeding the grain sizes, defects such as grain boundaries are experimentally found to either stop or reorient the fracture directions depending on crystal orientations of adjacent grains.

SUPPORTING INFORMATION:

Additional details about the numerical calculations and imaging of the atomic lattice are supplied as supporting

information.

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Figure 1: TOC graphic