Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

How controlled rippling of graphene via irradiation and applied strain can modify its mechanical properties: a nanoindentation simulation study*

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S1. Calculation of mechanical properties from nanoindentation simulations

During the current study, the load-displacement curves were fitted to equation 2 in the article:

$$F(\delta) = \pi\, \sigma_0^{2D}\, \delta + q^3/a^2\, E_{2D}\, \delta^3 \qquad \text{(S1)}$$

by means of the least-square method. Figure S1 shows an example of some of the curves obtained from the nanoindentation simulations for the case of the sample under different strains before irradiation. In the equation above δ is the deflection, σ_0^{2D} is the membrane pre-tension, E_{2D} is the two-dimensional Young's modulus, *a* is the radius of the membrane and *q* is a correction factor for a Poisson's ratio (ν) other than one third and it takes the form of $q \sim 1.0491 - 0.1462\nu - 0.15827\nu^2$. See Komaragiri et al[1] for details on the determination of the *q* function. As a result the E2D values derived turned out to be around 30% below the average value reported in the experimental literature[2].

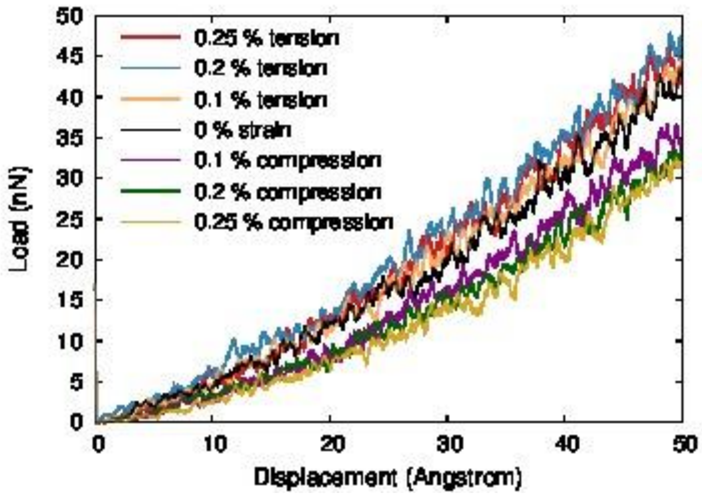

Figure S1: Load versus displacement obtained from nanoindentation simulations for different applied strains, as compared to no strain before irradiation.

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In a recent MD study[3] the increase in stiffness in defective graphene was investigated. Referring to Fig. 1.b of this reference, while the authors report on a simulation derived E2D value close to experimental values, they also show a clear size dependence of E2D with the drumhead radius, with a monotonic decrease of E2D with increasing drumhead size. An extrapolation of that tendency matches the E2D values presented in the current paper.

There are other reasons that are worth pointing out as potential causes of the relatively low E2D value systematically found. These are:

- Penetration-rate effects: While experiments are typically performed in a load-controlled quasi-static procedure, MD simulations are typically performed in a displacement-controlled dynamic way, at a penetration-rate that is orders of magnitude higher than in nanoindentation experiments. This can induce undesired dynamic behavior into the graphene flake altering its E2D value.
- Effect of intrinsic ripples: As mentioned in the main article, recent molecular dynamics simulations have shown that intrinsic ripples of graphene affect its elasticity, resulting in softening of this material[4]. The results available in the reference are derived from simulations of uniaxial tests, not nanoindentation. Still they allow for the supposition that similar effects can be taking place during nanoindentation tests. The distribution of ripples given by the interatomic potential used in this work might not be accurate enough, giving rise to this discrepancy.
- Temperature effects: Due to its 2D nature, graphene is highly sensitive to temperature. This not only affects the length of the C-C bonds but also has a significant effect on rippling. As the bonds get longer, the only possibility to accommodate the expansion with fixed boundaries is by increasing existing ripples or even producing new ones, whose effect into E2D is not only far from understood but also the subject of the current paper.
- Size Limitations on the fitting equation: This point has already been raised by Tan et al. APL 2013[5]. The authors have shown that graphene has different responses to the indentation depending on the magnitude of the deflection. In a so-called small deflection rate, the indenter has barely a point contact with graphene, and the point load model is applicable, as it was done in the current paper. However if the indenter is relatively large, the size effect of the indenter is evident in the large deflection range, and the sphere load model should be used. While precaution was taken to perform the current study within the applicability of the point load model, this is another potential source of uncertainty in the determination of E2D.
- Penetration-rate limitations on the fitting equation: Under the non-linear Föppl membrane theory, a circular elastic membrane with clamped boundary conditions and a point load in its center is considered to deflect as shown by the dashed lines in Fig.S2.

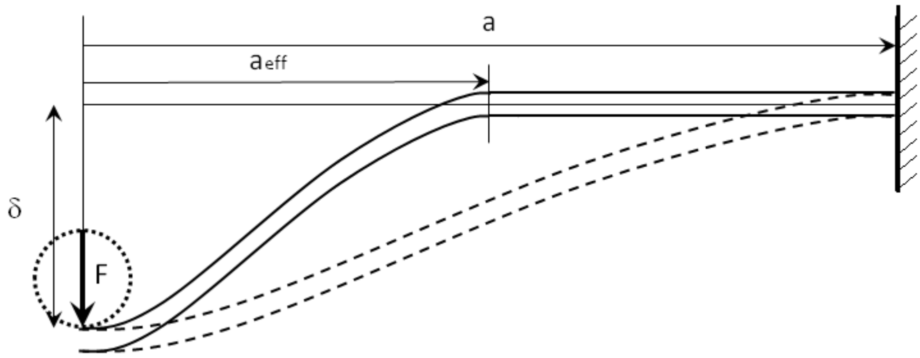

Figure S2: Schematic representation of the difference in the deflection pattern between the scheme used for the solution of the non-linear Föppl membrane theory of a circular membrane subjected to a static central point loading with clamped boundaries (dashed lines) and the deflection pattern produced by the dynamic indentation of the graphene flakes (solid lines). Within a first approximation, Eq. S1 can be used to model the dynamic indentation problem provided a is replaced by a_{eff}. Adapted from Komaragiri et al [1].

In experimental setups[2,6] the force-displacement curves are obtained by a quasi-static increase of the force and the membrane suffers a deflection very similar to the proposed deformation shown in dashed lines in Fig. S2. However, in displacement-controlled mode indentation, such as in the setup used in these simulations, the deformation of the membrane can deviate to the solid line deformation pattern of Fig.S2.

Hence the use of Eq. S1 without further analysis can lead to unrealistic results in the determination of E_{2D}. The key issue for its proper determination is the election of radius a. In the case of the classical non-linear Föppl membrane theory treatment, a takes the value of the membrane radius. However, inspection of Figure S2 suggests the use of smaller radius, here termed a_{eff}so that the deformation from the central point load to that radius does follow the deformation pattern from which the fitting equation was derived in ref. 1. Visual inspection of the deformation profiles of the entire set of simulations reveals that a_{eff} is in fact smaller than the drum head radius for the penetration depths inspected in this study. As a result, this is another potential cause for differences in the computed E2D value.

S2. Defects produced under irradiation

In Figure S3 the percentage of defects produced as a function of dose for two different strain conditions is represented: -0.2% (compressive) and 0.2% (tensile). Firstly, the number of defects produced increases linearly with dose, as expected, since there is no overlap of cascades for these low doses, and vacancy migration at this temperature is very slow. The number of monovacancies created is the same for both strains, however, there is a higher production of divacancies when a compressive strain is applied.

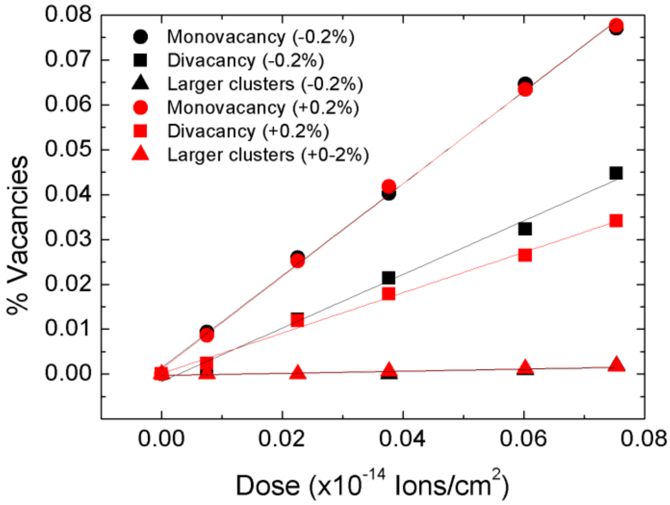

Figure S3: Percentage of vacancies created by the irradiation as a function of dose for two applied strains, -0.2% (compression) and 0.2% (tension). Monovacancies, divacancies and higher order clusters are shown for these two cases.

References

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