



5

The elasticity and strength of graphene

Nicola M. Pugno

Laboratory of Bio-inspired Nanomechanics “ Giuseppe Maria Pungo
Department of Structural Engineering and Geotechnics, Politecnico di Torino
Corso Duca degli Abruzzi 24, 10129 Torino, Italy, National Institute of Nuclear
Physics (INFN) National Laboratories of Frascati, Via E. Fermi 40, 00044 Frascati
Italy, National Institute of Metrological Research (INRIM), Strada delle Cacce 91,
10135, Torino, Italy.

An explosion of interest in the fabrication and characterization of graphene sheets is currently taking place¹⁻⁴, due to their predicted fascinating mechanical (and electrical) properties and thanks to recently available new nanotechnological tools. The paper by Lee, Wei, Kysar and Hone⁵, is a benchmark in the field. These Authors measured, by atomic force nanoindentation, the elastic properties and the ideal strength of free-standing monolayer graphene sheets.

The material constitutive law was assumed to be isotropic non-linear elastic, in the form of $\sigma = E\varepsilon + D\varepsilon^2$,

Where σ is the stress, ε is the strain, E is the Young modulus and D is the third-order elastic modulus. They measured values of $E = 1.0 \pm 0.1$ TPa and $D = -2.0 \pm 0.4$ TPa. While a one terapascal Young's modulus was expected and consistent with the abundant data in the literature, the measurement of D reveals new insights regarding the non-linear elastic behaviour of graphene. In order to check the plausibility of their computed value, we may note that a simple model⁶ predicts $D = -E^2 a^3 \alpha / k_B$, where α is the (linear) expansion coefficient, k_B is the Boltzmann's constant and a is here the C-C bond length (in graphene). Roughly considering the modulus of the thermal expansion coefficient of the order of 10^{-5}K^{-1} one would deduce $D = -2.1$ TPa.

The non-linear elasticity affected only the small region of the graphene around the point where the load was applied and not the cubic force-load displacement curve (as imposed by the large displacements involved in the stretching). Accordingly, under the atomic force tip a stress/strain concentration took place, numerically computed by the Authors⁵, from which the material strength was derived. Even if the precision of an intrinsic strength measurement based on the stress-concentration concept of the continuum (which ignores energy release rate and quantization) is questionable, leading towards stress-intensifications to obvious strength overestimations, a value of $\sigma_{\text{int}} = 130 \pm 10$ GPa was deduced following this approach. The predicted huge strength suggests to have measured the ideal material intrinsic strength, expected to be of the order of one tenth of the Young's modulus. Weibull moduli one order of magnitude larger than those that we observed in carbon nanotubes^{7,8} showed a more deterministic failure and seem to confirm the observation of the ideal strength.

The membranes were analyzed by Scanning Tunneling Microscopy (STM), confirming the absence of defects over an area of hundreds of square nanometers, a size comparable to that of the highly stressed zone developed under the nanoindenter tip. Since the stress-concentration rapidly decays by increasing the distance from the point where the load is applied, moderate defects placed far from the contact zone could not prevail, as observed. However, defects are thermodynamically unavoidable. At the thermal equilibrium, the vacancy fraction, $f = n/N$, where n is the number of vacancies and N is the total number of atoms, is estimated to be $f \approx e^{-W/(k_B T)}$ where $W \approx 7 \text{eV}$ is the energy to remove one carbon atom and T is the absolute temperature at which the carbon is assembled. Considering a maximum value of $T \approx 4000$ K leads to $f \approx 1.5 \times 10^{-9}$, thus to a maximum number $N \approx 6.5 \times 10^8$ of atoms in which less than one vacancy is expected⁹. This corresponds to a defect-free maximum surface area of the order of one square micrometer, thus

again compatible with the Authors' observation. Even if atomistic defects are tediously and not easily observable by STM investigation and the defect density is usually imposed by the fabrication process rather than by the thermodynamic limit, our argument agrees with the Authors' observations.

Thanks to their huge elasticity, strength and peculiar planar topology graphene sheets are expected to play a key role in the next Material Science.

References

1. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I. V. Grigorieva, A.A. Firsov, Electric field effect in atomically thin carbon films, *Science* 2004, 306, 666–669.
2. C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A.N. Marchenkov, E.H. Conrad, P.N. First, W.A. de Heer, Electronic confinement and coherence in patterned epitaxial graphene, *Science* 2006, 312, 1191–1196.
3. S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, Graphene-based composite materials, *Nature* 2006, 442, 282–285.
4. D.A. Dikin, S. Stankovich, E. J. Zimney, R.D. Piner, G.H.B. Dommett, G. Evmenenko, S.T. Nguyen, R.S. Ruoff, Preparation and characterization of graphene oxide paper, *Nature* 2007, 448, 457–460.
5. C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Science* 321, 385–388.
6. N. Pugno, F. Marino, A. Carpinteri, Towards a periodic table for the nanomechanical properties of element, *Int. J. of Solids and Structures* 2006, 43, 5647–5657.
7. N. Pugno, R. Ruoff, Nanoscale Weibull Statistics *J. of Applied Physics* (2006), 99, 024301/1-4.
8. N. Pugno, R. Ruoff, Nanoscale Weibull Statistics for nanodibers and nanotubes. *J. Of Aerospace Engineering* (2007), 20, 97-101
9. N. Πυγνο, Τη ρολε οφ δεφεχτσ ιν τηε δεσιγν οφ τηε σπαχε ελεπωατορ χαβλε: φρομ νανοτυβε το μεγατυβε, *Αχτα Ματεριαλια* 2007, 55, 5269–5279.