Mechanical properties of freely suspended semiconducting graphene-like layers based on MoS$_2$

Andres Castellanos-Gomez$^{1,2*}$, Menno Poot$^{1,4}$, Gary A Steele$^1$, Herre SJ van der Zant$^1$, Nicolás Agraït$^{2,3}$ and Gabino Rubio-Bollinger$^2$

Abstract
We fabricate freely suspended nanosheets of molybdenum disulphide (MoS$_2$) which are characterized by quantitative optical microscopy and high-resolution friction force microscopy. We study the elastic deformation of freely suspended nanosheets of MoS$_2$ using an atomic force microscope. The Young’s modulus and the initial pre-tension of the nanosheets are determined by performing a nanoscopic version of a bending test experiment. MoS$_2$ sheets show high elasticity and an extremely high Young’s modulus (0.30 TPa, 50% larger than steel). These results make them a potential alternative to graphene in applications requiring flexible semiconductor materials.

PACS, 73.61.Le, other inorganic semiconductors, 68.65.Ac, multilayers, 62.20.de, elastic moduli, 81.40.Jj, elasticity and anelasticity, stress-strain relations.

Keywords: Molybdenum disulfide nanosheets, Freely suspended, Mechanical properties, Atomically thin crystal, Mechanical exfoliation

Background
The application of graphene in semiconducting devices is hindered by its lack of a bandgap. Up to now, two different strategies have been employed to fabricate semiconducting two-dimensional crystals: opening a bandgap in graphene [1-3] or using another two-dimensional crystal with a large intrinsic bandgap [4]. Atomically thin molybdenum disulphide (MoS$_2$), a semiconducting transition metal dichalcogenide, has recently attracted a lot of attention due to its large intrinsic bandgap of 1.8 eV and high mobility $\mu > 200$ cm$^2$ V$^{-1}$ s$^{-1}$ [5,6]. In fact, MoS$_2$ has been employed to fabricate field-effect transistors with high on/off ratios [5], chemical sensors [7] and logic gates among other things [8]. Nevertheless, the study of the mechanical properties of this nanomaterial (which will dictate its applicability in flexible electronic applications) has just begun [9,10]. In a previous work, we studied the mechanical properties of freely suspended MoS$_2$ nanosheets using a bending test experiment performed with the tip of an atomic force microscope (AFM) [10].

Here, we perform a more detailed characterization of the fabricated nanosheets by quantitative optical microscopy and high-resolution friction force microscopy, and we extend the study of the mechanical properties to a larger number of MoS$_2$ nanosheets (with thicknesses in the range of 5 to 25 layers) to improve the robustness of our statistical analysis. We present force versus deformation curves measured not only by pushing the nanosheets (as usual) but also by pulling them, demonstrating that for moderate deformations pushing and pulling the nanosheets are equivalent. These measurements allow for the simultaneous determination of the Young’s modulus ($E$) and the initial pre-tension ($T_o$) of these MoS$_2$ nanosheets.

Methods
Although atomically thin MoS$_2$ crystals can be fabricated by scotch-tape-based micromechanical cleavage [11], this procedure can leave traces of adhesive. Thus, it is preferable to use an all-dry technique based on poly (dimethyl)siloxane stamps which have been successfully employed to
fabricate ultra-clean atomically thin crystals of graphene [12], graphene nanoribbons [13], NbSe2, MoS2 [14], and muscovite mica [15]. In order to fabricate freely suspended atomically thin MoS2 flakes, the cleaved flakes are transferred to a pre-patterned oxidized silicon wafer [16] with circular holes 1.1 μm in diameter and 200-nm deep.

After fabrication, an optical microscope (Nikon eclipse LV100, Nikon Instruments Inc., Melville, NY, USA) is used to identify MoS2 flakes at first glance. In fact, ultra-thin MoS2 flakes deposited onto a silicon wafer with a 285-nm-thick SiO2 capping layer can be easily identified by optical microscopy. Figure 1a shows a chart of the expected color of MoS2 flakes with different thicknesses when they are laying on the surface or covering a hole. The expected color has been calculated with a Fresnel law-based model, employing the refractive index of MoS2 in [14] and the response of the camera as indicated in [17]. The topography of selected flakes is then studied by contact mode atomic force microscopy to avoid possible artifacts in the flake thickness measurements [18]. Figure 1b, c is an optical micrograph and a contact mode AFM topography, respectively, of an 8-layer-thick MoS2 flake deposited onto a 285-nm SiO2/Si pre-patterned substrate.

Additionally, high resolution contact mode AFM measurements can provide lattice resolution even in the suspended region of the MoS2 flakes which demonstrates the very clean nature of our fabrication technique. Figure 1d, e shows two lateral force maps (friction images) obtained in the suspended and the supported parts of the MoS2 flake shown in Figure 1c. The atomic resolution can be better resolved in the suspended region of the MoS2 flake (Figure 1d), while in the supported part, the frictional force image mainly follows parallel stripes (Figure 1e). We have employed a two-dimensional Tomlinson model [19] to simulate the frictional force image measured in the supported part of the nanolayer (see inset in Figure 1e), finding a remarkable qualitative agreement. Interestingly, by reducing a 25% in the depth of the surface potential employed in the simulation the calculated friction force image qualitatively matches the one measured in the supported part of the MoS2 nanomembrane (Figure 1d). This difference in the frictional force image can be due to a slight modification of the MoS2 lattice induced by the pretension of the suspended part of the sheet. However, a detailed analysis of the tension dependence of frictional force images and their interpretation, although interesting, is beyond the scope of this work.

Results and discussion

Once the suspended nanosheet under study is identified and characterized, we measure its elastic mechanical properties using the AFM tip to apply a load cycle in the center of the suspended region of the nanosheet while its deformation is measured, as shown in the inset of Figure 2a. When the tip and sample are in contact, the elastic deformation of the nanosheet (δ), the deflection of the AFM cantilever (Δz_{c}), and the displacement of the scanning piezotube of the AFM (Δz_{piezo}) are related by the following equation:

\[ \delta = \Delta z_{\text{piezo}} - \Delta z_{c} \] (1)

The force applied is related to the cantilever deflection as \( F = k_{c} \Delta z_{c} \), where \( k_{c} \) is the spring constant of the cantilever (\( k_{c} = 0.75 \pm 0.20 \text{ N/m} \) [20]).
with \( v \) the Poisson’s ratio (\( v = 0.125, [22] \)), \( t \) the thickness, and \( R \) the radius of the nanosheet. As the effective spring constant depends on both the Young’s modulus and the pre-tension constant, one cannot separately determine these values just from the slope of a \( F(\delta) \) trace. To independently determine \( E \) and \( T \), however, one can use the thickness dependence of the effective spring constant. Indeed, according to Equation 2, the first term (which accounts for the bending rigidity of the layer) strongly depends on the sheet thickness, while the second one (which accounts for the initial pre-tension) is thickness independent. Fitting the measured \( k_{\text{eff}} \) versus thickness to Equation 2, one can determine \( E \) and \( T \). Figure 2b shows the measured \( k_{\text{eff}} \) as a function of the thickness of 31 different MoS\(_2\) layers and the fit to the experimental data using the following:

\[ E = 0.30 \pm 0.10 \text{ TPa} \quad \text{and} \quad T = 0.15 \pm 0.15 \text{ N/m} \quad (3) \]

This Young’s modulus value is extremely high, only one third lower than exfoliated graphene (one of the stiffest materials on earth with \( E = 0.8 \) to 1.0 TPa) [23,24] and comparable to other 2D crystals such as graphene oxide (0.2 TPa) [25] or hexagonal boron nitride (0.25 TPa) [26]. It is also remarkable that the \( E \) value is restrained between 0.2 and 0.4 TPa, indicating a high homogeneity of the MoS\(_2\) flakes, which is much smaller than the one observed for graphene (0.02 to 3 TPa) [27] or graphene oxide (0.08 to 0.7 TPa) [25]. The high Young’s modulus of the ultrathin MoS\(_2\) flakes (\( E = 0.30 \pm 0.10 \) TPa compared to the bulk value \( E_{\text{bulk}} = 0.24 \) TPa [28]) can be explained by a low presence of stacking faults. Indeed, the thinner the nanosheet the lower the presence of stacking faults, allowing the study of the intrinsic mechanical properties of the material.

**Conclusion**

We have studied the mechanical properties of ultrathin freely suspended MoS\(_2\) nanosheets with 5 to 25 layers thick. The mean Young’s modulus of these suspended nanosheets, \( E = 0.30 \pm 0.07 \) TPa, is extremely high, and they present low pre-strain and high strength, being able to stand elastic deformations of tens of nanometers elastically without breaking. In summary, the low pre-tension and high elasticity and Young’s modulus of these crystals make them attractive substitutes or alternatives for graphene in applications requiring flexible semiconductor materials.

**Abbreviations**

AFM: Atomic force microscope; MoS\(_2\): Molybdenum disulfide.

**Acknowledgements**

This work was supported by MICINN (Spain) through the programs MAT2008-01735, MAT2011-25046 and CONSOLIDER-INGENIO-2010.
Nanoscience Molecular’ CSD-2007-00101, Comunidad de Madrid through program Nanobimagnet S2009/MAT-1726, and the European Union (FP7) through the program RODIN.

Author details
1Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, Delft 2628, C.J. The Netherlands
2Department of Física de la Materia Condensada (C-III), Universidad Autónoma de Madrid, Campus de Cantoblanco, Madrid E-28049, Spain
3Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanocentro), Madrid E-28049, Spain
4Department of Engineering Science, Yale University, Becton 215, 15 Prospect St., New Haven, CT 06520, USA

Authors’ contributions
AC-G carried out the transfer and characterization of MoS2 nanolayers and the bending test measurements. MP fabricated the pre-patterned substrates. AC-G and GR-B participated in the design and coordination of the experiments and designed the manuscript layout. MP, GAS, HSJvdZ, and NA participated in the drafting of the manuscript and helped with the interpretation of the experiments. All authors read and approved the final manuscript.

Authors’ information
AC-G and MP are post-doctoral researchers at the Kavli Institute of Nanoscience at Delft University of Technology and at the Department of Engineering Science of Yale University, respectively. GAS and HSJvdZ are assistant professor and full professor, respectively, at the Kavli Institute of Nanoscience at Delft University of Technology. NA and GR-B are associate professor and full professor, respectively, at the Department of Condensed Matter at Universidad Autónoma de Madrid. NA is also an associated senior researcher at the Madrid Institute for Advanced Studies in Nanoscience (IMDEA-Nanoscience).

Competing interests
The authors declare that they have no competing interests.

Received: 19 December 2011 Accepted: 25 April 2012
Published: 25 April 2012

References
1. Chen Z, Lin Y, Rooks M, Avouris P. Graphene nano-ribbon electronics. Physica E 2007, 40:228-232.
2. Li X, Wang X, Zhang L, Lee S, Dai H. Chemically derived, ultrasmooth graphene nanoribbon semiconductors. Science 2008, 319:1229.
3. Castellanos-Gomez A, Woytzaszek M, Tombros N, van Wees BJ. Reversible hydrogenation and bandgap opening of graphene and graphite surfaces probed by scanning tunneling spectroscopy. Small 2012, 8:1607-1613.
4. Podzorov V, Gershenson ME, Kloc C, Zeis R, Bucher E. High-mobility field-effect transistors based on transition metal dichalcogenides. Appl Phys Lett 2004, 84:3301.
5. Radisavljevic B, Radenovic A, Brivio J, Giacometti V, Kis A. Single-layer MoS2 transistors. Nat Nanotechnol 2011, 6:147-150.
6. Korn T, Heydrich S, Hirmer M, Schmutzler J, Schüller C. Low-temperature photocarrier dynamics in monolayer MoS2. Appl Phys Lett 2011, 99:102109.
7. Li H, Yin Z, He Q, Huang X, Lu G. Fabrication of single- and multilayer MoS2 micro- and nanoflakes by mechanical exfoliation. Appl Phys Lett 2011, 99:233105.
8. Castellanos-Gomez A, Woytzaszek M, Tumbros N, van Wees BJ. Reversible hydrogenation and bandgap opening of graphene and graphite surfaces probed by scanning tunneling spectroscopy. Small 2012, 8:1607-1613.
9. Podzorov V, Gershenson ME, Kloc C, Zeis R, Bucher E. High-mobility field-effect transistors based on transition metal dichalcogenides. Appl Phys Lett 2004, 84:3301.
10. Radisavljevic B, Radenovic A, Brivio J, Giacometti V, Kis A. Single-layer MoS2 transistors. Nat Nanotechnol 2011, 6:147-150.
11. Korn T, Heydrich S, Hirmer M, Schmutzler J, Schüller C. Low-temperature photocarrier dynamics in monolayer MoS2. Appl Phys Lett 2011, 99:102109.
12. Li H, Yin Z, He Q, Huang X, Lu G. Fabrication of single- and multilayer MoS2 micro- and nanoflakes by mechanical exfoliation. Appl Phys Lett 2011, 99:233105.
13. Moreno-Moreno M, Castellanos-Gomez A, Rubio-Bollinger G, Gomez-Herrero J, Agrait N. Ultralong natural graphene nanoribbons and their electrical conductivity. Small 2009, 5:924-927.
14. Castellanos-Gomez A, Agrait N, Rubio-Bollinger G. Optical identification of atomically thin dichalcogenide crystals. Appl Phys Lett 2010, 96:213116.
15. Castellanos-Gomez A, Woytzaszek M, Tombros N, Agrait N, van Wees BJ, Rubio-Bollinger G. Atomically thin mica flakes and their application as ultrathin insulating substrates for graphene. Small 2011, 7:2491-2497.
16. Warkamp B, Poort M, van der Zant H. Bending-mode vibration of a suspended nanotube resonator. Nano Lett 2006, 6:2904-2908.
17. Henrie J, Kells S, Schultz S, Hawkins A. Electronic color charts for dielectric films on silicon. Opt Express 2004, 12:1464-1469.
18. Nemes-Ince P, Osv¡dh Z, Kamaraš K, Bird LP. Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy. Carbon 2008, 46:1435-1442.
19. Sasaki N, Kobayashi K, Tsukada M. Atomic-scale friction image of graphite in atomic-force microscopy. Phys Rev B 1996, 54:2138.
20. Sader JE, Chou JWM, Muhney P. Calibration of rectangular atomic force microscope cantilevers. Rev Sci Instrum 1999, 70:3967.
21. Landau L, Lifshitz E. Theory of Elasticity. 3rd edition. Stoneham: Butterworth-Heinemann, 1959.
22. Lovell M, Khonsari M, Masangoni R. A finite element analysis of the frictional forces between a cylindrical bearing element and MoS2 coated and uncoated surfaces. Wear 1996, 194:60-70.
23. Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. Science 2008, 321:385.
24. Li P, You Z, Haugstad G, Cui T. Graphene fixed-end beam arrays based on mechanical exfoliation. Appl Phys Lett 2011, 98:253105.
25. Gomez-Navarro C, Burghard M, Kern K. Elastic properties of chemically derived single graphene sheets. Nano Lett 2008, 8:2045-2049.
26. Song L, Li L, Lu H, Soroñkin PB, Jin C, Ni J, Kvasnin AG, Kvasnin DG, Lou J, Yakobson BI, Ayayan PM. Large scale growth and characterization of atomic hexagonal boron nitride layers. Nano Lett 2010, 10:3209-3215.
27. Poort M, van der Zant H. Nanomechanical properties of few-layer graphene membranes. Appl Phys Lett 2008, 92:063111.
28. Feldman J. Elastic constants of 2 H-MoS2 and 2 H-NbSe2 extracted from measured dispersion curves and linear compressibilities. J Phys Chem Solids 1976, 37:1141-1144.

Cite this article as: Castellanos-Gomez et al. Mechanical properties of freely suspended semiconducting graphene-like layers based on MoS2. Nanoscale Research Letters 2012 7:233.

doI:10.1186/1556-276X-7-233

Submit your manuscript to a SpringerOpen journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ➤ springeropen.com