

“NanoMechanics: Elasticity and Friction in Nano-Objects”

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1. Introduction

Nanosheets, nanotubes, nanowires, and nanoparticles are gaining a large interest in the scientific community for their exciting properties, and they hold the potential to become building blocks in integrated nano-electronic and photonic circuits, nano-sensors, batteries electrodes, energy harvesting nano-systems, and nano-electro-mechanical systems (NEMS). While several experiments and theoretical calculations have revealed exciting novel phenomena in these nanostructures, many scientific and technological questions remain open. A fundamental objective guiding the study of nanoscale materials is to understanding what are the new rules governing nanoscale properties and at what extent well-known physical macroscopic laws still apply in the nano-world.

The vision of this DoE research program is to understand the mechanical properties of nanoscale materials by exploring new experimental methods and theoretical models at the boundaries between continuum mechanics and atomistic models, with the overarching goal of defining the basic laws of mechanics at the nanoscale.

The group of the PI has developed in the last years several studies on the mechanical properties of Carbon nanotubes and oxide nanobelts, more recently the PI and her collaborators have focused their attention on the properties of two-dimensional (2D) materials, such as graphene and MoS₂, which are a few-atomic-layer thick films with strong in-plane bonds and weak interactions between the layers. A large scientific and technological effort is underway to understand and control the properties of 2D materials because of their potential technological and energy applications. The most studied 2D material is graphene, existing as a single layer of graphite or a few-layer thick epitaxial graphene film. Graphene possesses a large in-plane Young's modulus as well as high intrinsic carrier mobility and high in-plane thermal conductivity. Besides graphene, also 2D films of graphene oxide (GO), hexagonal Boron Nitride (h-BN) and transition metal dichalcogenides such as MoS₂ exhibit unique and excellent properties and hold great promise for nanotechnology applications. One of the main characteristics of 2D materials is the high anisotropy between the in-plane and perpendicular-to-the-plane properties. For example, in graphite due to the strong covalent bonds between atoms in the plane, and the weak Van der Waals interlayer interaction, the in-plane Young's modulus is $E_{//} = 1$ TPa, while the interlayer perpendicular-to-the-plane Young's modulus is only $E_{\perp} = 36$ GPa. The in-plane Young's modulus of exfoliated graphene and MoS₂ has been widely studied in bending experiments where a film is suspended on trenches or holes, and a nano tip is used to bend the suspended film with deformations of tens and hundreds of nanometers. On the other hand, very little is known about the elasticity perpendicular to the planes, hereafter called perpendicular or interlayer elasticity, of 2D materials composed of very few atomic layers.

In summer 2015, the PI and her collaborators reported the first, at the best of our knowledge, investigation of the perpendicular elasticity of a-few-layer-thick 2D films. These investigations are an experimental challenge because they require to perform indentations on supported—as opposed to suspended—2D films where the indentation should remain smaller than the films interlayer distance, i.e., less than a few Angstroms. Nevertheless, the perpendicular elasticity is particularly important since it is related to the thermal, electronic, tribological, and optical properties of 2D films. The perpendicular elasticity is related to the structure and chemistry of the layers, the presence of stacking and intrinsic defects, and intercalation, which is a critical process for doping and tuning mechanical and electronic properties in 2D films. Mapping the interlayer elastic coupling in 2D films is therefore an important technological and scientific advancement.

The proposed experimental characterization of 2D materials was carried out in the laboratory of the PI by means of **atomic force microscopy (AFM)** based methods, and **confocal Raman microscopy coupled with AFM**. The experimental investigations were coupled with theoretical calculations developed by **Erio Tosatti (ICTP and SISSA) and Angelo Bongiorno (GeorgiaTech and College of Staten Island, and CUNY High Performance Computing Center) for classical molecular dynamics and *ab initio* calculations of friction forces, and perpendicular elasticity.** Finite elements and semi-analytical calculations were developed in the PI's group. The samples of epitaxial graphene were grown in the lab of **Prof. Walt de Heer** at the Georgia Institute of Technology.

2. Work under the DoE support

Under this DoE grant, which includes three funding rounds in the period 2007-2015, the PI has published 6 Book Chapters and 34 articles. During the this funding round, the PI has published in prestigious journals including three articles in *Nature Materials*, two articles in *Nature Nanotechnology*, one article in *Science* and two articles in *Nature Communications*. All these publications are included in the main Bibliography list. Furthermore, the work of the PI has been recognized with prestigious invitations at international meetings and boards, and with the honor to be elected Fellow of the APS “*For atomic force microscopy studies of nanoscale friction, liquid structure and nanotube elasticity, and the invention of thermochemical nanolithography*”.

Highlights of DoE research:

- * New Atomic Force Microscopy (AFM) method (modulated nanoindentation MoNI) to perform the first sub-Å-resolution indentation measurements of the perpendicular-to-the-plane elasticity of 2D materials and radial elasticity of nanotubes.
- * Discover of friction anisotropy in supported Nanotubes.
- * New understanding of the oxidation process and new preparation method of epitaxial graphene oxide films with improved properties.
- * New understanding of the perpendicular elasticity of a few-layers thick graphene and graphene oxide films, and the role of intercalated water.
- * Demonstration that experimental sub-interlayer distance indentations in 2D films can be accurately reproduced by the Hertz contact mechanics model for isotropic materials if using as Young's modulus the perpendicular modulus of the transversely isotropic layered material.

- * Demonstration of the thermochemical nanolithography method for controlled nanoscale complex patterning of surfaces.
- * New method for measuring with nanoscale resolution the thermal conductivity of materials in the direction perpendicular to the planes.
- * New measurements of the elasticity of short DNA molecules with RNA defective inclusions.
- * New understanding of the dissipative forces at liquid-solid interfaces as a function of the liquid-solid interaction.

Below here, we describe in detail some of the main scientific results.

2.1 Sliding on a Nanotube: Interplay of Friction, Deformations and Structure

The PI and her collaborators have initiated a study of the frictional properties of individual CNTs using a nano-size atomic force microscope tip sliding on individual CNTs lying on a substrate. The PI *et al.* found **a larger friction coefficient when the tip is sliding perpendicular to the CNT axis, as compared to sliding along the tube axis** (see Fig. 1). This behavior is explained by a deformation, similar to a **lateral swaying (or a “hindered rolling”) of the tube during the transverse sliding, which produces additional friction dissipation**. This soft deformation mode is absent, or partially absent, when the tip slides along the CNT axis, thus, for the longitudinal sliding the friction force arises mostly from sliding the hard nano-contact between the tip and the tube. The AFM tip can slide along the tube axis, namely longitudinal sliding, or alternatively perpendicularly to the NT axis, namely transverse sliding. We call **the ratio between transverse and longitudinal friction per unit area, friction anisotropy**.

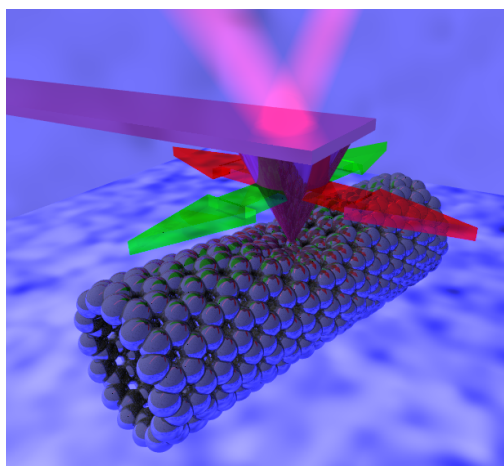


Figure 1. Cartoon of the friction experiments in the transverse (red) and longitudinal (green) direction.

Very recently, the PI and her collaborators have shown **how structural defects, surface chemistry and possibly chirality can couple the transverse and longitudinal sliding, modulating nanotubes frictional properties**. Specifically, the PI *et al.* studied the frictional properties of supported multiwalled CNTs produced by Arc Discharge (AD), and Chemical Vapor Deposition (CVD), as well as chemically functionalized CVD (FCVD) CNTs, see the results as reported in Fig. 2. A **Raman Spectroscopy microscope** (see **Figure in the facilities document, purchased in part with DoE funds**) was used to study the amount of structural defects in the NTs. The measurements were performed on the NTs solutions. In the future (see next sections) we plan to investigate by Raman individual NTs in situ with AFM mechanical measurements. It resulted that FCVD NTs are very rich of defects, CVD NTs slightly less, and AD NTs have a negligible amount of defects (see inset in Fig. 2). **The friction anisotropy was found to decrease in the presence of defects (see Fig. 2)**. Isolated very high values of friction anisotropy, up to 14, for AD CNTs with no defects have been attributed to non-chiral CNTs. This anisotropy becomes less than 6 for CVD CNTs with defects and further reduced to less than 2 for FCVD CNTs with more defects and surface functionalization.

Furthermore, the PI *et al.* have developed a simple analytical model to compute the amount of “coupling” α , between the transverse and longitudinal sliding, the “intrinsic” hard contact sliding shear strength, σ^{int} , and the soft “hindered rolling” shear strength, σ^{HR} . The constitutive equations of the model are the following:

$$\begin{aligned}\sigma_L &= \sigma^{\text{int}} + \alpha \cdot \sigma^{\text{HR}} & \sigma_L &= \sigma^{\text{int}} + \alpha \cdot \sigma^{\text{HR}} \\ \sigma_T &= \sigma^{\text{int}} + (1 - \alpha) \cdot \sigma^{\text{HR}} & \sigma_T &= \sigma^{\text{int}} + (1 - \alpha) \cdot \sigma^{\text{HR}}\end{aligned}$$

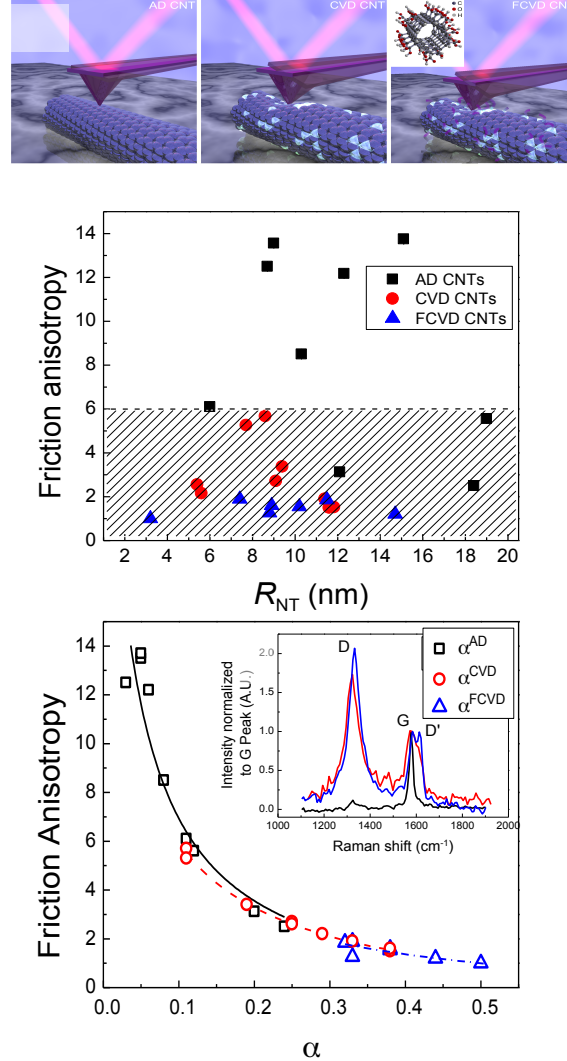


Figure 2. Top. Cartoon of the three types of NT investigated by the PI: AD NT, CVD NT, and Functionalized CVD NT. **Center.** Friction anisotropy vs NT radius, and **(Bottom)** vs. coupling coefficient α . In the inset Raman Spectra of AD, CVD, and FCVD nanotubes.

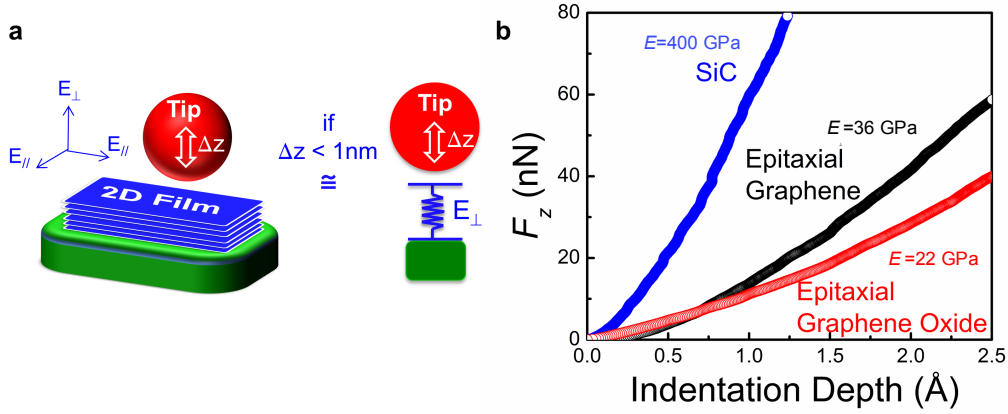


Fig. 3: (a) Schematics of inter-layer elasticity experiment – a hard AFM tip indenting 2D films. (b) Experimental MoNI indentation curves in graphene and graphene oxide with sub-Å resolution.

2.2 Perpendicular Elasticity in graphene and graphene oxide films

This work was part of a 3-year-long effort in the PI laboratory to investigate the mechanical and structural properties of functional graphene and graphene oxide. Graphene oxide (GO) holds great promise for a variety of applications, including supercapacitors, optical devices, and mechanical actuators. GO is a complex nonstoichiometric and hygroscopic material, and understanding and controlling its mechanical and physical chemical properties are matter of intense research. The overall goal in the PI's lab was to understand the mechanical and chemical interaction between the oxidized graphitic layers as a function of the degree of oxidation, type of oxygen chemical groups, and intercalated water.

Graphene and other two-dimensional materials are characterized by strong covalent in-plane bonds and weak interactions between the layers. Their in-plane elasticity has been widely studied in bending experiments where a suspended film is deformed substantially; however, little is known about the films' elastic modulus perpendicular to the planes, as the measurement of the out-of-plane elasticity of supported 2D films requires indentation depths smaller than the films' interlayer distance. The PI and her collaborators have **invented an unconventional atomic force microscopy (AFM) based method, modulated nanoindentation (MoNI), allowing for sub-Å-resolution indentations to measure the elasticity of 2D films in the direction perpendicular to the layers, for a number of layers as small as two.** These indentation data, combined with semi-analytical models and density functional theory were then used to study the perpendicular elasticity of a few-layers thick epitaxial graphene, epitaxial graphene oxide, and conventional graphene oxide films at varying ambient humidity. These studies highlight how the interlayer elastic coupling in graphene and graphene oxide films is affected by the films chemistry, structure, water intercalation, and number of layers. Interestingly, the perpendicular Young's modulus of graphene oxide increases by increasing the amount of water trapped in between the layers until a full monolayer is produced. Then, when the second water layer is forming the modulus decreases. Finally, the **PI and collaborators showed that when using sub-interlayer distance indentations in 2D films, the AFM indentation curves are very sensitive to the elastic modulus perpendicular to the layers, $E_{\perp}$, and almost independent of the value of the in-plane Young's modulus, $E_{\parallel}$** (see Fig. 3). As a consequence, the indentation force curves can be fitted with a simple modified Hertz model as if the film is an isotropic material, where the Young's modulus of the film is indeed the perpendicular modulus $E_{\perp}$. This work is therefore offering a new experimental and theoretical framework to investigate the interlayer elastic coupling in 2D films. These investigations were focused on highly oriented pyrolytic graphite

(HOPG), 4H-SiC, regular graphene oxide (GO) films deposited with the conventional Hummers' method on Silicon, epitaxial graphene (EG) films grown on a SiC substrate, and **epitaxial graphene oxide (EGO) films grown with a method invented by the PI and collaborators by direct oxidation of EG films on SiC using a milder Hummers' method** which avoids graphene exfoliation and dispersion in solution.

Modulated NanoIndentation of 2D Materials

During a typical MoNI experiment, an AFM tip, which is vertically oscillated at a fixed frequency with a ~ 0.1 Å amplitude, applies an increasing pressure to a 2D film surface, in the z -direction perpendicular to the film surface (see Fig. 4). The oscillations are applied and controlled by a lock-in amplifier, while a constant normal force F_z between the tip and the 2D film is maintained constant by the feedback loop of the AFM. By working with a constant force, any thermal drift is avoided. Furthermore, using a lock-in detection system together with a differential measurement allows us to measure very shallow indentations, usually $< 1-3$ Å, with a resolution of 0.1 Å. Indeed,

instead of measuring directly the normal force as a function of the indentation, z_{indent} , we measure the slope of force vs. indentation curves at each constant normal force, namely $k_{\text{cont}}(F_z)$ (see Fig. 4). **Force vs. indentation curves are then obtained by integrating the measured $dF_z/dz_{\text{indent}} = k_{\text{cont}}(F_z)$:**

$$z_{\text{indent}}(F_z) = \int_0^{F_z} \frac{dF_z}{k_{\text{cont}}(F_z)} \quad (1)$$

This experimental set-up is therefore uniquely suited to investigate the perpendicular elastic modulus of 2D films, which are only a few layers thick. We notice that the lower limit of the integral in Eq. (1) is zero only when there are no adhesion forces. In case of an adhesive contact, the lower limit is the pull-off force, F_{po} , defined as the negative load at which the AFM tip loses the contact with the sample and can be easily determined experimentally. Furthermore, for SiC and the 2D materials investigated here, when the load is equal to F_{po} the contact area is indeed zero and $z_{\text{indent}}(F_{po}) = 0$. The curve $k_{\text{cont}}(F_z)$ — which is proportional to the contact radius and the squared root of the indentation depth — drops to zero when the load reaches F_{po} . We underline that while the F_z vs. z_{indent} curves could in principle be shifted along the z_{indent} -axis in very soft and adhesive materials depending on the value of $z_{\text{indent}}(F_{po})$, the shape of these curves does not depend on the type of adhesive contact. We also notice that in the experiments the pull-

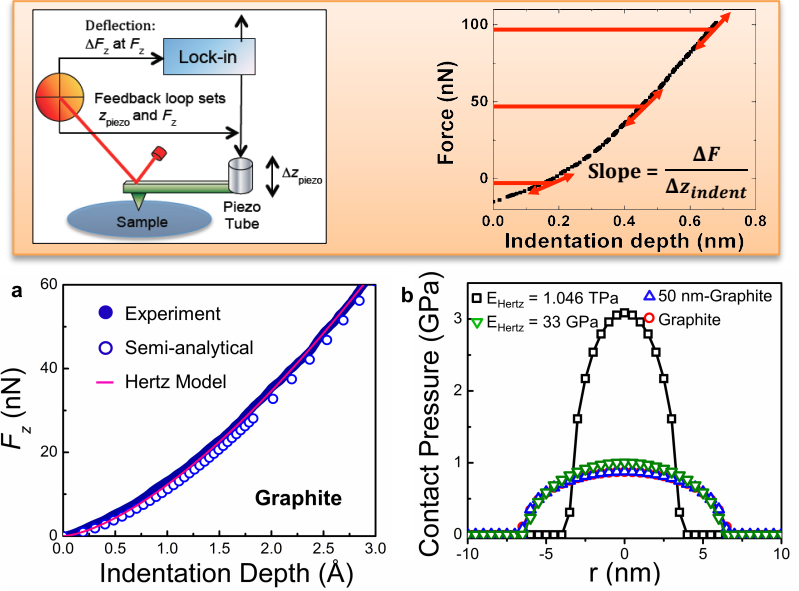


Fig. 4: Modulated Nanoindentation (MoNI). Top: Left, schematics of MoNI and right, MoNI measurement of the slope of an indentation curve. Bottom: **a**, experimentally measured indentation curves in HOPG (full circles), semi-analytical model simulations of indentation in Graphite (open circles), and Hertzian fitting (continuum line) of the indentation curves on HOPG. **b**, corresponding calculated contact pressures.

off force can change significantly from curve to curve, however ΔF_z remains consistent. This shift in the absolute value of the normal force is due to humidity and the drifting of the laser position on the photo-detector during the different individual experiments (we took hundreds of curves for each sample and condition). However, the clear determination of the pull-off force during each indentation experiment allows to always determine the corrected “absolute” normal load as $F_z = (F_z - F_{po})$, and to compare different curves independently of the laser position shifting and presence of adhesion forces. We remark that for the materials investigated here we can account for the adhesion force by simply adding to the load the pull-off force. This adhesive contact mechanics model is called the DMT model and it describes well stiff materials and small tip radii. Figure 1b shows the measured (and offset-corrected) F_z vs. z_{indent} at ambient humidity for different 2D films, namely epitaxial graphene and epitaxial graphene oxide. We remark that both EG and EGO in Fig. 1b are 10-layer thick. In Fig. 1b, it is also reported the force vs. indentation curve for a single crystal of Silicon Carbide, the substrate over which EG and EGO are grown. The indentation curves, all performed with the same AFM tip, clearly indicate a larger stiffness for 10-layer EG than 10-layer EGO. As expected from previous studies, SiC shows a very large stiffness. 4H-SiC has a hexagonal crystal structure, however its elastic behavior is very isotropic and therefore a simple Hertzian offset-corrected contact model can be used to extract from the force vs. indentation curves the Young’s modulus of the material. For the configuration of a sphere (the AFM tip) pressing on a flat surface of an isotropic half-space with a normal force F_z the Hertz model gives:

$$F_z = \frac{4}{3} E^* (R)^{1/2} z_{indent}^{3/2} \quad (2)$$

where $E^* = \left(\frac{1 - (\nu_{Hertz}^{sample})^2}{E_{Hertz}^{sample}} + \frac{1 - (\nu_{Hertz}^{tip})^2}{E_{Hertz}^{tip}} \right)$ with $\nu_{Hertz}^{sample,tip}$ and $E_{Hertz}^{sample,tip}$ being the Poisson’s ratio and

Young’s moduli of respectively the investigated sample and the AFM tip, while R is the AFM tip radius. For the silicon tip used in the MoNI measurements, $E_{Hertz}^{tip} = 169$ GPa and $\nu_{Hertz}^{tip} = 0.27$. The elastic modulus can therefore be obtained by using the relationship (2) to fit the experimental measurements of F_z vs. z_{indent} , as shown in Fig. 1b for a quasi-isotropic sample such as SiC. Indeed, the fitting procedure gives $E_{Hertz}^{SiC} = 400$ GPa, for a tip radius $R = 114$ nm, which is in excellent agreement with literature. Similar experiments have also been performed on other standard samples such as ZnO single crystals to insure the ability of MoNI to obtain reliable results.

The Contact Mechanics Problem when Indenting Transversally Isotropic Layered Materials

The Hertz relationship in (2) is in principle not well suited to model the contact mechanics between an AFM spherical tip and an anisotropic material such as graphite and other 2D materials since the Hertz model was originally only valid for isotropic half spaces. However, when studying the indentation of 2D films with extremely small indentation depths interesting new potential applications of the Hertz model can be found. To address this topic we have developed a back-of-the-envelope calculation of the in-plane and perpendicular-to-the-plane

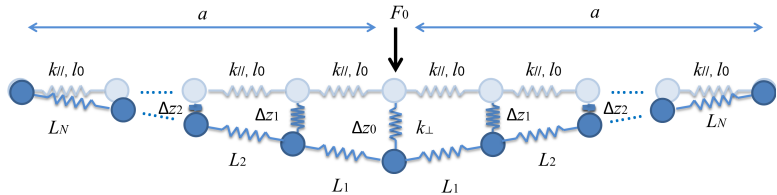


Fig. 5: Scheme for a simple calculation of the perpendicular and parallel distribution of the point indentation force.

stress distribution in a layered material when indenting the material perpendicular to the planes. The layered material can be regarded as a system of springs, as shown in Fig. 5. The perpendicular spring constant $k_{\perp}$ represents the inter-layer interaction (i.e. the van der Waals interaction) while the in-plane spring constant $k_{\parallel}$ represents the in-plane inter-atom interaction (i.e. covalence bonding). Also, $k_{\perp} / k_{\parallel} \sim E_{\perp} / E_{\parallel}$. The equilibrium lengths for the two types of springs ($k_{\perp}$ and $k_{\parallel}$) are the inter-layer distance d_0 and the length of the in-plane covalent bond l_0 , respectively. When a normal force F_0 is applied to the surface by a spherical tip, the number $2N$ of the “involved” $k_{\parallel}$ springs is simply given by a/l_0 , where a is the contact radius. After indentation, the length of the n^{th} in-plane spring becomes L_n . The compression of the n^{th} perpendicular spring is Δz_n . Thus, the elongation of the n^{th} in-plane spring Δl_n satisfies: $L_n^2 = l_0^2 + \Delta l_n^2$. If the tip radius is 100 nm and $\Delta z_0 = 0.3$ nm, the contact radius is about $a = 6$ nm (obtained from Hertz model). Then $\Delta z_0 \ll a, \Delta l_n \ll L_n$ and we can calculate the stress distribution among the two types of springs (in plane and perpendicular springs) given by the forces $F_{\perp}$ and $F_{\parallel}$, respectively, and the z-projection of $F_{\parallel}$. Setting $F_{\perp} + F_{\parallel,z} = F_0$ as the basic constraint. We obtain:

$$\frac{F_{\perp}}{F_{\parallel,z}} = \frac{\Delta z_0 \times k_{\perp} \times N}{2k_{\parallel} \times \frac{\Delta z_0}{N} \times \frac{\Delta z_0}{a} \times \frac{\Delta z_0}{a}} = \frac{k_{\perp}}{2k_{\parallel}} \cdot \frac{N^2 a^2}{\Delta z_0^2} \quad (3)$$

If we use graphite as an example, then $N = a/2l_0 = 6 \text{ nm}/0.15 \text{ nm} = 40$ where l_0 is the length of sp^2 bond. Δz_0 is ~ 0.3 nm or less. So $(Na/\Delta z_0)^2 = 0.64 \times 10^6$. For graphite $k_{\perp} / k_{\parallel} = E_{\perp} / E_{\parallel} = 36/1000 = 0.036$, which is very small. However the product of the two, still makes $F_{\perp} / F_{\parallel,z} = 10^4 \gg 1$. This means that since $F_{\perp} + F_{\parallel,z} = F_0$, we can approximate $F_{\perp} = F_0$, i.e., the contribution to the normal indenting force is almost exclusively supported by the perpendicular springs, and it is independent of the in-plane bonds. In other words, the normal force F_0 is mainly carried by the inter-layers interactions rather than the in-plane bonds. Therefore, if we fit the indentation curves for a 2D layered material with the isotropic Hertz model, the Young’s modulus obtained from the fit is almost equal to $E_{\perp}$. Notice that this simple analysis is valid only when $\Delta z_0 \sim 0.3$ nm, on the other hand we did not use any approximation for the values of the moduli $E_{\perp}$ and $E_{\parallel}$. From these calculations it appears clear that the key parameter controlling sub-nm indentations is the ratio $a^2/l_0 z_{\text{indent}}$, where a is the contact radius, and l_0 is the length of an sp^2 bond. For example, when indenting graphite with an AFM tip with $z_{\text{indent}} < 0.3$ nm, this simple model shows that we are sensing only $E_{\perp}$.

A better insight of the contact pressure distribution as a function of the material elastic constants can be obtained using simulations with semi-analytical methods (SAM), which have proven their efficiency in describing the contact mechanics of anisotropic materials. Here, we used SAM to simulate the force vs. indentation curves in graphite. We use graphite elastic constants found in literature, and we model the indentation of an AFM silicon tip ($R = 100$ nm) in a graphite sample deposited on SiC. We use this configuration because the 2D materials studied here have been deposited either on SiC (epitaxial graphene and epitaxial graphene oxide) or Si (conventional graphene oxide). **Figure 2a shows the results from the SAM simulations on graphite along with the experimental curves obtained by MoNI on a bulk sample of highly oriented pyrolytic graphite.** In Fig. 4a, the SAM simulated curve agrees extremely well with the experiments on HOPG, it is important to note that in the SAM simulations for graphite we use, according to literature, as in-plane Young’s modulus $E_{\parallel} = 1.046$ TPa, and as z-axis (perpendicular to the planes) Young’s modulus $E_{\perp} = (36.4 \pm 1)$ GPa, more details are given in the Methods

part. Very interestingly, when the Hertz model in (2) is applied to fit the experimental indentation curves measured on graphite, as if graphite was an isotropic material, the result of the fitting procedure gives as the single isotropic modulus $E_{Hertz}^{HOPG} = (33 \pm 3)$ GPa, for $R = 100$ nm like the AFM tip radius. The Hertz model fitting curve is also reported in Fig. 2a to show the perfect agreement with experiments and SAM simulations. The Hertz model is therefore able with a simple fitting procedure to obtain a value of Young's modulus which is equal, within an error of 10%, to the most accepted value for the perpendicular-to-the-plane Young's modulus of graphite, i.e. $E_{\perp} = 36$ GPa.

Intercalated water and perpendicular elasticity in Graphene Oxide

MoNI experiments have been performed to measure the perpendicular elasticity of epitaxial GO films grown with the new method developed by the PI group and GO films produced with the conventional exfoliation/filtration/deposition method. In ambient humidity it was obtained: $E_{\perp} = (35 \pm 10)$ GPa (for conventional GO), $E_{\perp} = (36 \pm 3)$ GPa (for 10-layer EG), $E_{\perp} = (33 \pm 3)$ GPa (for HOPG), and $E_{\perp} = (23 \pm 4)$ GPa (for EGO). The perpendicular elastic modulus is larger in 10-layer EG films than in HOPG, this difference is probably related to the absence of defects in 10-layer EG compared to HOPG. 10-layer epitaxial graphene oxide is much softer than 10-layer epitaxial graphene, this result can be explained by the increase of the interlayer distance d , in EGO compared to EG, precisely from $d = 3.4$ Å to $d = 9.3$ Å as observed in the X-ray diffraction spectroscopy measurements. To understand the origin of the large interlayer perpendicular elasticity in conventional GO compared to epitaxial graphene oxide, we have performed density functional theory (DFT) calculations on the elasticity of GO with a different amount of intercalated water. We have then compared these calculations with MoNI experiments on GO and EGO

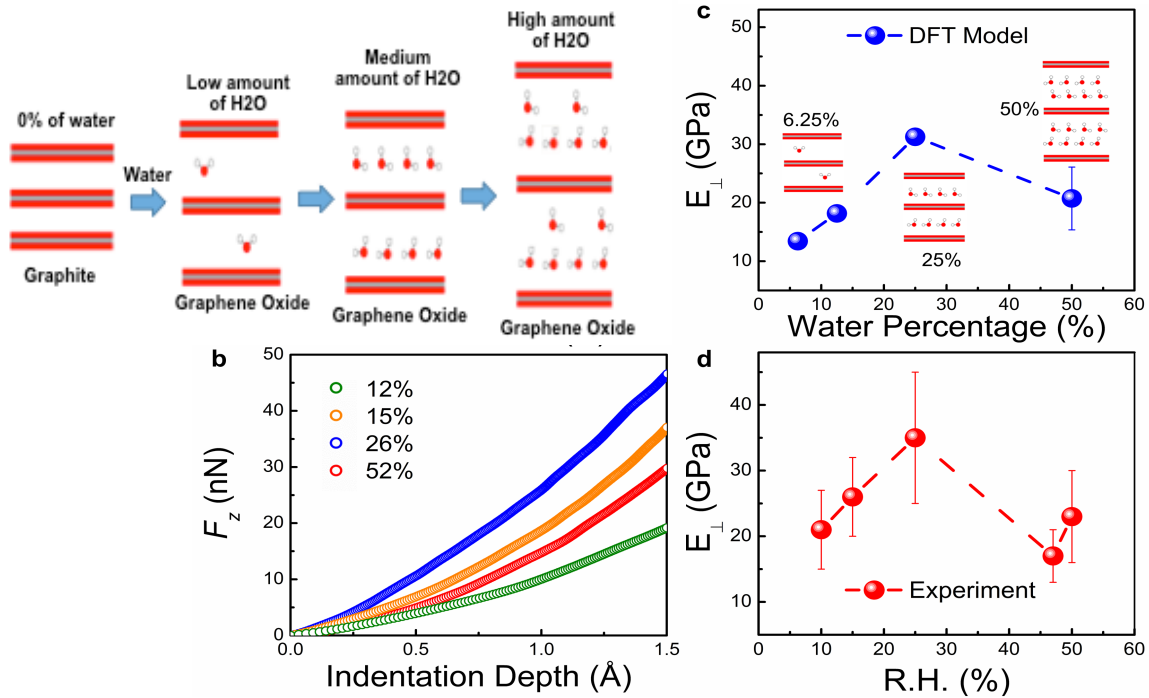


Fig. 6: **a**, Cartoon showing how water molecules fill the interlayer spacing. **b**, experimental F_z vs. indentation curves at different relative humidity in conventional GO. **c-d**, Experimental and DFT results of $E_{\perp}$ of GO as a function of water content and relative humidity. Each experimental point of $E_{\perp}$ is an average value on more than 30 measurements.

performed at different ambient humidity. DFT calculations have been performed in Bongiorno's laboratory on model structures of graphene oxide³⁶. Figure 6(b) presents the experimental MoNI results on conventional GO at different relative humidity (R.H.). Figures 6(c) and (d) show the resulting $E_{\perp}$ as a function of intercalated water percentage compared to carbon (for DFT calculations) and relative humidity (for MoNI experiments), respectively. The agreement between experiments and DFT calculations is striking. DFT calculations and experiments show that $E_{\perp}$ increases with the amount of intercalated H₂O molecules (and relative humidity), reaching a maximum value of about 31 GPa at 25% of H₂O, and 35 GPa at R.H. = 25%, for the DFT calculations and indentation experiments, respectively. The perpendicular elastic modulus then decreases down to 20 GPa at 50% of water, and 23 GPa at 50% relative humidity, for the DFT calculations and indentation experiments, respectively. DFT calculations show that the interlayer distance and perpendicular Young's modulus in GO change abruptly between the case of dry layers and a multilayer film including small amount of H₂O (<6%), while more gradual variations of these physical properties are obtained for increasing the water content between 6.25% and 25% (Fig. 6c). In particular, $E_{\perp}$ drops from about 35 GPa (close to EG) in dry films to about 11-14 GPa when the layered structure includes 6.25% of H₂O. This behavior can be understood by considering that when the amount of water is only a few percentages of the Carbon amount, H₂O molecules swell the graphene structure increasing the interlayer distance from 3.4 Å to about 6.2 Å, but leaving the interlayer space mainly empty and therefore producing a soft structure with a low perpendicular elastic modulus. This interlayer modulus increases with increasing amount of water, which fills the interlayer space without changing too much the interlayer distance. However, at 25% of water, H₂O molecules have completely filled a water layer in between the layers, and this situation corresponds with the maximum in perpendicular elastic modulus. Above 25% of water, the perpendicular elastic modulus decreases because a second water layer starts to form in between the layers further swelling and softening GO. A different behavior is experimentally observed in conventional EGO, which is not a porous structure and water intercalation is minimal and independent of humidity. For this reason we find that $E_{\perp}$ in EGO remains constant ~ 22 GPa for all RH. On the other hand, conventional GO is porous³ and intercalated water can change depending on the humidity, therefore in agreement with DFT calculations we observe a maximum in conventional GO when varying the RH.

2.3 Radial Elasticity of Nanotubes

Here, the PI and her collaborators have used **the AFM based modulated nano-indentation (MoNI) technique developed in the PI's group (Fig. 7)** to investigate the radial stiffness of individual nanotubes and with a wall thickness approximately equal to 0.5 times the external radius, R_{ext} , as obtained by the statistical TEM analysis. The radial deformation is here always measured during the unloading regime for indentations below 10% of R_{ext} to insure the probing of the local radial elasticity of the nanotubes. During a typical MoNI experiment, an AFM tip, which is vertically oscillated at a fixed frequency with sub-nanometer amplitudes, applies a localized radial pressure on NT lying on a Si substrate. The oscillations are applied to the AFM tip via a piezoelectric stage rigidly attached to the cantilever, and controlled by a Lock-in amplifier (Stanford Research Systems, SR830), while a constant normal force F between the tip and the NT is maintained by the feedback loop of the AFM (see Fig. 7). In order to remain in the linear elastic regime, the piezo-stage oscillations are chosen to be only 1.0 Å.

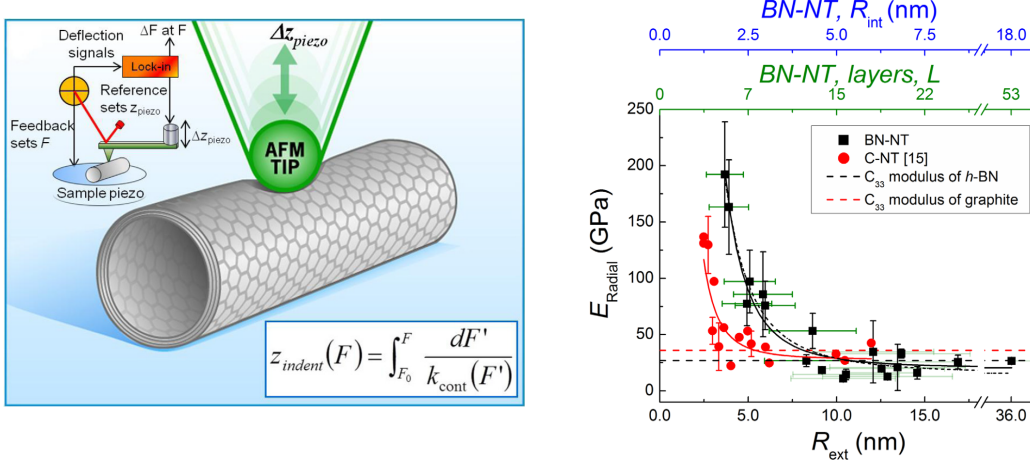


Figure 7. **Left.** Cartoon of the MoNI method. **Right.** Radial effective elastic modulus vs radius for BN and C- NTs.

During the indentation, the fixed piezo-stage oscillation amplitude Dz_{piezo} is equal to the sum of the cantilever bending and tip-nanotube normal deformation. Under such circumstances, the AFM cantilever and the tip-nanotube contact can be considered as two springs connected in series: the cantilever with stiffness k_{lev} and the tip-nanotube contact with stiffness k_{cont} . The force required to stretch these two springs in series with a total displacement Dz_{piezo} is equal to the normal force variation DF . This experimental configuration allows us to measure the total stiffness k_{tot} at each normal load F , fixed by the feedback loop of the AFM, from the following relation:

$$\frac{\Delta F}{\Delta z_{piezo}} = k_{tot}(F) = \left(\frac{1}{k_{lev}} + \frac{1}{k_{cont}} \right)^{-1} \quad (4)$$

Since k_{lev} is known, the measurement of $\Delta F/\Delta z_{piezo}$ at different normal loads F allow us to acquire the radial stiffness k_{cont} as a function of F . If the substrate deforms during indentation, an additional term, $1/k_{NT-substrate}$, needs to be added into equation (4) and the radial elasticity of BN-NTs shows up to a 20% increase (see Ref. and its Supplementary Material). Force vs. indentation curves are then extracted by integrating the equation $\Delta F/k_{cont}(F) = \Delta z_{indent}$. To extract the effective radial modulus from MoNI data, we calculate the AFM tip-NT contact area with the Hertz model adding the contribution of the adhesion force F_{Adh} , which can be determined directly from the experimental data. For the configuration of a sphere in contact with a cylinder with a normal force F that compresses them together, the Hertz model gives:

$$\frac{dF}{dz_{indent}} = k_{cont} = \beta \cdot \left(\frac{4}{3} E^* \right)^{2/3} \cdot (R \cdot (F + F_{Adh}))^{1/3} \quad (5)$$

where $\frac{1}{R} = \frac{1}{R_{tip}} + \frac{1}{2R_{ext}} \frac{1}{R} = \frac{1}{R_{tip}} + \frac{1}{2R_{NT}}$, $E^* = \left(\frac{1-\nu_{NT}^2}{E_{Radial}} + \frac{1-\nu_{tip}^2}{E_{tip}} \right)^{-1}$, F_{Adh} is the adhesion force between the

tip and the nanotube, $K = \frac{3}{4} \left(\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right)^{1/3} \cdot n_{NT,tip}$ and $E_{Radial,tip}$ are the Poisson's ratio and Young's moduli of respective materials. The parameter β takes into account the geometry of the tip-NT contact and more details about the exact calculation of β as a function of tip and NT radius are given

in the Supplementary Material of Ref. and in . To better gather an intuition on the meaning of equation (5), it is possible to calculate the elliptical contact area between the tip and the nanotube, and rewrite the relationship between the effective Young modulus and the contact stiffness as:

$$\frac{dF}{dz_{indent}} = k_{cont} = \gamma \cdot \sqrt{Area} \cdot E^* \text{ where } Area \text{ is the contact area, and } g \text{ is a numerical factor which is function}$$

of only R_{tip} and R_{NT} . The radial elastic modulus can thus be calculated using these equations from the experimental measurements of $k_{cont} = dF/dz$.

It was found that E_{Radial} of MW BN-NTs decreases with increasing R_{ext} and the number of layers, L , from about 192.2 ± 46.8 GPa for $R_{ext} = 3.7 \pm 0.1$ nm and $L = 5.4 \pm 1$, to a plateau value of 24 ± 11 GPa. These elastic moduli are larger than previously reported values for MW BN-NTs because of the small indentation and large number of wall layers in the BN-NTs studied in this letter. When probing thick tubes the ovalization process at small indentations as in our experiments is minimal, instead, the localized radial compression creates a dimple in the tube's top layers and the elasticity depends on the layer-layer interaction and layer curvature. Here, the PI *et al.* found indications of the key role of the morphology in determining the radial rigidity of MW BN-NTs, in particular they found that the external and internal radii, R_{ext} and R_{int} , may have a stronger influence on the radial modulus than the thickness of nanotube, t . Using an empirical relationship it was proposed that the radial modulus varies with the morphology of a nanotube as:

$$E_{Radial} = A \sqrt{t / (R_{ext}^2 (R_{int} - 0.34)^2)} + E_0, \text{ where } A \text{ and } E_0 \text{ are two constants.}$$

For the regime of morphology investigated here, it was found that $E_0 = 20.3 \pm 3.4$ GPa for the BN-NTs and $E_0 = 27.9 \pm 6.0$ GPa for C-NTs with similar morphology. These values are very close to the elastic constants along the C_{33} axis of the corresponding bulk materials, i.e., 27 GPa for hexagonal Boron Nitride (*h*-BN) and 36 GPa for Highly ordered pyrolytic graphite (HOPG), while the elastic modulus along the direction of C_{33} of these materials, namely E_{33} , is reported to be 36 GPa for *h*-BN and about 28-31 GPa for HOPG, respectively.

2.4 Other Major Accomplishments: Nanoscale Thermal Conductivity

Over the last decade nanoscale thermal transport has been at the focus of widespread interest, partly driven by a number of technologically important applications. Nanoscale thermal transport also plays a critical role in the design of better thermal insulation and enhanced thermoelectric energy recovery. Under DoE support we demonstrated an alternate route to thermal conductivity imaging with nanoscale resolution. Our approach leverages on the unique properties of the nitrogen-vacancy (NV) centre in diamond, a spin-1 defect that can be individually initialized and readout with the aid of optical and microwave pulses. Thermal changes in the NV vicinity can be detected by monitoring the NV spin resonance frequency, which strongly depends on the system temperature. In our experiments we use a diamond-nanocrystal-hosted NV as a nanoscale probe attached to a sharp silicon tip. The latter is part of an atomic force microscope cantilever with an integrated heater, which can be used to warm the tip to a predefined temperature above ambient. We obtain an image of the sample thermal conductivity as we record the NV temperature drop upon contact with the substrate while scanning the tip on a material with sub-20 nm resolution. Further, we showed that the time response of our spin probe is fast, a consequence of the excellent thermal conductivity and minuscule mass of the diamond host.

2.5 Other Major Accomplishments: Thermochemical Nanolithography

The PI and her collaborators have demonstrated the ability of a hot nano-size probe to control with exquisite precision the properties of a material at the nanoscale. Properties such as magnetic dipoles orientation, presence of oxygen and other chemical groups can be controlled with 10-nm precision or below by thermochemical nanolithography (TCNL).

3. Publications during DoE Funding Period August 2006 - December 2015:

- Yang Gao, Si Zhou, Suenne Kim, Hsian-Chih Chiu, Daniel Nélias, Claire Berger, Walt de Heer, Laura Polloni, Roman Sordan, Angelo Bongiorno and Elisa Riedo, “Elastic coupling between layers in two-dimensional materials”, **Nature Materials** 14, 714–721 (2015), DOI: 10.1038/nmat4322
- E. Albisetti, D. Petti, M. Pancaldi, M. Madami, S. Tacchi, J. Curtis, W.P. King, A. Papp, G. Csaba, W.Porod, P. Vavassori, E. Riedo, R. Bertacco, “Nanopatterning reconfigurable magnetic landscapes via thermally assisted scanning probe lithography” **Nature Nanotechnology**, (2016)
- Abdelghani Laraoui, Halley Aycock-Rizzo, Yang Gao, Xi Lu, Elisa Riedo, Carlos Meriles, “Imaging thermal conductivity with nanoscale resolution using a scanning spin probe” **Nature Communications** 6, 8954, (2015) DOI:10.1038/ncomms9954
- Kyung Duk Koh, Hsiang-Chih Chiu, Elisa Riedo and Francesca Storici “Measuring the elasticity of ribonucleotide(s)-containing DNA molecules using AFM”, book chapter in *Methods in Molecular Biology with the topic of RNA nanotechnology*, Springer Protocols, (2015).
- Ricardo Garcia, Armin Knoll, and Elisa Riedo “Advanced Scanning Probe Lithography”, **Nature Nanotechnology**, 9, 577 (2014) DOI: 10.1038/NNANO.2014.157.
- Robert Szoszkiewicz and Elisa Riedo “Sliding Charges” *News & Views*, **Nature Materials**, 13, 666–668 (2014) DOI: 10.1038/nmat4020.
- Hsiang-Chih Chiu, Tai-De Li, Deborah Ortiz-Young, Elisa Riedo, “Nanorheology by atomic force microscopy “, **Review of Scientific Instruments**, 85 (12), 123707 (2014)
- Hsiang-Chih Chiu, Kyung Duk Koh, Marina Evich, Annie L. Lesiak, Markus W. Germann, Angelo Bongiorno, Elisa Riedo and Francesca Storici “How RNA intrusions change DNA structure and elastic properties”, **Nanoscale** 6 (17), 10009-10017 (2014) DOI: 10.1039/C4NR01794C.
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- Keith M. Carroll, Xi Lu, Suenne Kim, Yang Gao, Hoe-Joon Kim, Suhas Somnath, Laura Polloni,

Roman Sordan, William P. King, Jennifer E. Curtis, Elisa Riedo “Parallelization of Thermochemical Nanolithography”, **Nanoscale** 6 (3), 1299 – 1304, (2014).

- Deborah Ortiz-Young, Hsiang Chih Chiu, Suenne Kim, Kislon Voitchovsky and Elisa Riedo “The interplay between apparent viscosity and wettability in nanoconfined water”, **Nature Communications**, DOI: 10.1038/ncomms3482 (2013).
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- Suenne Kim, Si Zhou, Yike Hu, Muge Acik, Yves J. Chabal, Claire Berger, Walt de Heer, Angelo Bongiorno, and Elisa Riedo “Room Temperature Metastability of Multilayer Epitaxial Graphene Oxide”, **Nature Materials**, 11, 544, (2012).
- Marcel Lucas, and Elisa Riedo, Invited Review Article: “Combining scanning probe microscopy with optical spectroscopy for applications in biology and materials science”, **Rev. Sci. Instrum.** 83, 061101 (2012) (**Cover**).
- Hsian-Chih Chiu, Beate Ritz, Suenne Kim, Erio Tosatti, Christian Klinke, Elisa Riedo “Sliding on a Nanotube: Interplay of Friction, Deformations and Structure” **Adv. Mat.** 24, 2879 (2012) (**Cover**).
- Suenne Kim, Yaser Bastani, Haidong Lu, William P. King, Seth Marder, Kenneth H. Sandhage, Alexei Gruverman, Elisa Riedo, and Nazanin Bassiri-Gharb “Direct fabrication of arbitrary-shaped ferroelectric nanostructures on plastic, glass and silicon substrates”, **Adv. Mat.** 23, 3786–3790, (2011). (**Cover**)
- D. Wang, V. Kodali, J. Curtis, E. Riedo, “Nanofabrication of Functional Nanostructures by Thermochemical Nanolithography” book chapter in *Tip Based Nanofabrication: Fundamentals and Applications*, Springer (2011).
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- M. Lucas, Z. L. Wang, and E. Riedo, “Growth direction and morphology of ZnO nanobelts revealed by combining in situ atomic force microscopy and polarized Raman spectroscopy” **Phys. Rev. B** 81, 045415 (2010).

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- D. B. Wang, S. Kim, W. D. Underwood, Lee, W. P. King, R. Marder, E. Riedo, “Direct Writing and characterization of PPV nanostructures”, **Appl. Phys. Lett.** 95, 233108 (2009).
- D. Wang, V. Kodali, W. D. Underwood, J. E. Jarvholm, T. Odaka, S. C. Jones, M. Rumi, Z. Dai, W. P. King, S. R. Marder, J. E. Curtis, and E. Riedo “Thermochemical nanolithography of multi-functional templates for assembling nano-objects” **Adv. Funct. Mat.** 19, 3696 (2009) (Cover Article).
- T.-D. Li, and E. Riedo “Nonlinear viscoelastic dynamics of nanoconfined wetting liquids”, **Phys. Rev. Lett.** 100, 106102 (2008) (Featured in the NSF News and other News Media).
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- D. B. Wang, M. Lucas, R. Szoszkiewicz, E. Riedo, T. Okada, S. C. Jones, S. R. Marder, Lee, W. P. King, “Local wettability modification by thermochemical nanolithography with write-read-overwrite capability”, **Appl. Phys. Lett.** 91, 243104 (2007) (Highlighted by Virtual Journal of Nanoscale Science & Technology).

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- S. Yoo, W. J. Potscavage Jr., B. Domercq, S.-H. Han, T.-D. Li, S. C. Jones, R. Szożkiewicz, D. Levi, E. Riedo, S. R. Marder, B. Kippelen, “Analysis of improved photovoltaic properties of pentacene/C60 organic solar cells: Effects of excitons blocking layer thickness and thermal annealing”, **Solid-State Electronics** 51, 1367 (2007).

Invited Talks at International Conferences:

- November 2015. NanoFab in NYC Workshop
- October 2015, Tribology Frontiers Conference, Denver
- September 2015, Active and Adaptive Materials Workshop, NYC
- September 2015, Mechanical Behavior of Materials Workshop
- February 2015, Nanoscience NY Workshop, NYC
- June 2014, 13th International Ceramics Conference, CIMTEC
- January 2014 – Workshop on “Thermal Lithography”, IBM Zurich
- November 2013 - Conference on Frontiers of Condensed Matter Physics, ICTP, Trieste
- October 2013: AVS 60th International Symposium and Exhibition, “Novel 2D Materials”
- August 2012: "Dynamics and Jamming in Complex Environments," ACS National Meeting in Philadelphia, PA
- August 2012: MRS Joint Meeting, XXI International Materials Research Congress, Cancun
- April 2012: Lorentz Center Workshop “Fundamentals of Friction and Lubrication” (Netherlands)
- February 2012: NSF Site Visit of GT MRSEC – co-PI Seminar
- September 2011: Joint ICTP-FANAS Conference on Trends in Nanotribology, International Center of Theoretical Physics (ICTP)
- June 2011: International Conference on Mechanical Behavior of Materials, ICM11, Villa Erba
- May 2011: South east Soft Materials Workshop, Georgia Institute of Technology
- September 2010: DOE/BES Mechanical Behavior and Radiation Effects of Materials Contractors' Meeting, Washington DC, (USA).
- June 2010: 8th International Workshop on Epitaxial Semiconductors on Patterned Substrates and Novel Index Surfaces Como (Italy)
- October 2009: “NanoComposite 2009” Lake Louise, Canada.
- August 2009: “Gordon Conference: Chemistry and Physics of Liquids”, Holderness School, Plymouth NH (USA).
- October 2008: “Conference on the Physics, Chemistry, and Biology of Water 2007”, Vermont (USA).
- June 2008: “Physics of Micro- and NanoFluids”, Lorentz Center, Leiden (NL).
- April 2008: “Behavior of Defects in Materials - Contractors Meeting 2008”, Warrenton, VA (USA).

- October 2007: “Conference on the Physics, Chemistry, and Biology of Water 2007”, Vermont (USA).
- October 2006: Workshop on “Frontiers of Scanning Probe Microscopy,” Purdue University, West Lafayette, Indiana, (USA).
- September 2006: 5th ESF-Nanotribology Workshop, Antalya (Turkey).
- March 2006: ACS National Meeting in Atlanta, Georgia (USA).
- Fall 2004: GT Materials Council Nano-materials Forum, (USA).
- June 2005: 4rd ESF-Nanotribology Workshop, Porcherolles (France).

Societal and policy impacts (last three years):

- “Method and equipment for magnetic nanopatterning of substrates” patent filed in the name of Politecnico di Milano and Georgia Tech Research Corporation
- United States Patent Application: Thermochemical Nanolithography Components, Systems, And Methods, Serial No.: 12/791,466, Issue Date: 18 June 2013, US 8,468,611
- May 2014, Women in Physics (WiP) at Georgia Tech, co-Founder.
- April 2014, Public Lecture for Prospective Undergraduates at Georgia Tech

APPENDIX 1

ELISA RIEDO, www.picoForceLab.org

Educational Background:

B.S., Physics, 1995, *Summa cum Laude*, University of Milano, Italy

Ph.D., Physics, 2000, University of Milano, Italy

Employment History:

2016 – present:	Professor of Nanoscience and Founding Member of the CUNY Advanced Science Research Center (ASRC), NYC (USA)
2016 – present:	Full Professor, Physics, City College of New York (USA)
2015:	Full Professor, School of Physics, Georgia Tech (USA)
July 2009 – 2014:	Associate Professor (with Tenure), School of Physics, Georgia Tech (USA)
2006 – present:	Adjunct Professor, School of Chemistry and Biochemistry, Georgia Tech (USA)
2003 – 2009:	Assistant Professor, School of Physics, Georgia Tech (USA)
1999 – 2003:	Post Doctoral Fellow, École Polytechnique Fédérale Lausanne (EPFL) (CH)
1998 – 1999:	Research Assistant, European Synchrotron Research Facility (ESRF) (France)
Feb – Jun 1998:	Research Assistant, TASC – INFN labs, Trieste (Italy)
June 1998:	Visiting Research Assistant, Forschungszentrum of Jülich (Germany)
1996 – 1998:	Research Assistant, CoreCom (Politecnico of Milan and Pirelli) (Italy)

Synergistic Activities (selected ones)

- 2013: Elected APS Fellow, Division of Condensed Matter Physics
 - Editorial Board Member for “*Scientific Reports*” Nature publishing Group (2012-present)
 - Member of the program committee for the 2014 AVS Symposium on Novel 2D Materials
 - May 2014, Women in Physics (WiP) at Georgia Tech, co-Founder.
 - Co-Organizer and Founder of the Workshop Series “Southeast Workshops on Soft Materials”, GeorgiaTech and Emory Campus. (2008 - present).
 - Member of the Editorial Board of “*Review of Scientific Instruments*” (2008-2010).
 - Co-Organizer and Chair of three *Focused Topics* of the Division of Materials Physics for the 2007, 2010, and 2015 March Meeting of the American Physical Society (APS).
 - Session Chair at the 2013 AVS Symposium on Novel 2D Materials.
 - Co-Organizer of the workshop *NanoFab in NYC*, November 2015
-