

# Adhesion and dynamic nanotribology of graphene in polar and non-polar liquid environments studied with ultrasonic force microscopy

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## ABSTRACT

We report the characterisation of exfoliated few layer graphene (FLG) flakes using a range of scanning probe techniques. We have examined FLG and its substrate material, SiO<sub>2</sub>, in air, polar liquid (water) and non-polar liquid (dodecane) environments. We present analysis of absolute adhesion and relative friction between SPM probe and FLG and examination of surface and subsurface nanoscale structure. Adhesion is greater in ambient conditions, due to water meniscus formation at the probe-sample interface, than continuum liquid coverage. Friction shows negligible velocity dependence and is consistently lower for FLG than SiO<sub>2</sub>. The presence and dynamics of sub-surface delaminations and surface point defects are observed at a range of quantified normal forces (0 – 75 nN).

**Keywords:** graphene, SPM, nanotribology, nanomechanics, underliquid.

## 1 INTRODUCTION

Graphene is a one-atom-thick planar sheets of sp<sup>2</sup>-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. It has demonstrated remarkable physical properties including high values of electron mobility, transparency, Young's modulus, thermal conductivity and a high specific surface to mass ratio.<sup>1</sup> But to exploit these properties for incorporation into devices such as supercapacitors, rechargeable batteries, fuel cells and sensors it is essential to understand the changes in graphene's properties resulting from its local environment.

Graphene has been extensively studied in vacuum and dry air environments, but little experimental work has been performed on graphene in liquids. The understanding of the modification of the interaction of supported graphene due to different liquid environments is essential for the development of real graphene based devices e.g. rechargeable batteries, supercapacitors and displays.

## 2 EXPERIMENTAL DETAILS

### 2.1 Sample preparation

Contact mode Atomic Force Microscopy (AFM) and Ultrasonic force microscopy (UFM)<sup>2</sup> have been used for the characterisation of the morphological and nanotribological

changes of exfoliated few layer graphene (FLG) on planar silicon dioxide substrate. These measurements were performed in ambient laboratory atmosphere, immersed in ultra-pure water (Millipore, Direct Q3 UV purification system) and immersed in dodecane (Sigma Aldrich, used with no further purification).

Graphene samples were prepared via exfoliation from large area graphite flakes. Initial layer separation was achieved using the well-established 'scotch tape' method.<sup>3</sup> Sample splitting was performed up to ten times before transfer to a gel film piece (Gel-Pak, USA) in order to eliminate contamination due to chemical adhesives. To preserve surface integrity, final stage exfoliation is postponed until the substrate silicon dioxide substrate, previously cleaned in piranha solution (3:1 concentrated H<sub>2</sub>SO<sub>4</sub> to 30% H<sub>2</sub>O<sub>2</sub>), was processed using a plasma cleaner (2% O<sub>2</sub>, Ar). Immediately, final exfoliation is performed and the freshly cleaved graphene is transferred to the functionalised substrate. The sample was mounted on a 4 MHz piezoceramic disc (PI instruments), covered by a glass cover slip, using Phenyl salicylate heated to 45 °C prior to re-crystallisation.

Estimations of FLG flake presence, size and thickness were made using optical microscopy. Appropriate samples were transferred to the AFM/UFM setup, a Multimode Nanoscope III (Bruker-Veeco-DI). It was necessary to use silicon AFM probes with no back coating (Contact-G, Budget Sensors) as the signal from the coated probes is adversely affected by damage to the aluminium from rapid reaction upon contact with aqueous environment.

### 2.2 Ultrasonic Force Microscopy

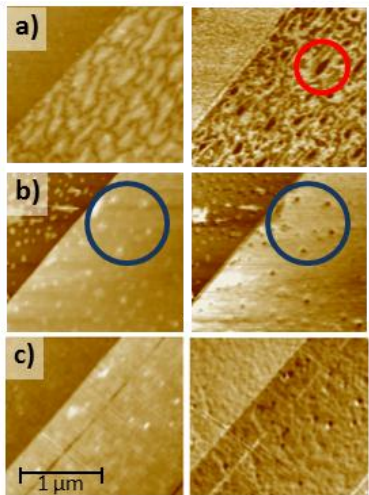
UFM is a modification of standard contact mode AFM with the addition of an amplitude modulated (using gated saw-tooth shape at the 1.7 kHz frequency) MHz frequency oscillation of the substrate via the mounting piezoceramic. The applied oscillations produces a sample displacement of the order of a few angstroms whilst being well above the frequency of the AFM cantilever resonance. Whilst tapping mode AFM is commonly employed in order to minimise damage to ultrathin samples such as graphene during imaging it is limited in the information that it can provide about the surface-environment interface. The periodic breaking of tip-sample contact, during a lateral scan, inherent in UFM effectively eliminates friction and hence the surface damage which would usually be caused by contact mode at higher set forces<sup>4</sup>. The ability of UFM to

detect sub-surface features of both stiff and compliant materials has been reported and is used here to investigate the changes in graphene-substrate interfaces in different environmental conditions.

### 3 RESULTS AND DISCUSSION

#### 3.1 Surface and sub-surface imaging

Contact mode AFM has been extensively employed to study the surface properties of graphene but direct mapping of the graphene – substrate interface remains relatively poorly understood.<sup>5</sup> Many of the interactions occurring at this interface show little or no distinctive characteristics when studied using conventional scanning probe techniques. Ultrasonic force microscopy (UFM) is a technique by which both the surface and the subsurface properties of an ultrathin material may be mapped simultaneously with a resolution of a few nanometres, thus providing information about the material – air and material – substrate interfaces and crucially any co-dependency between the two.



**Figure 1: Contact mode topography (left) and UFM response (right) images of FLG and SiO<sub>2</sub> in a) air, b) water and c) dodecane environments. Sub-surface delamination (red circle) and point defects (blue circles) are highlighted.**

In addition to surface topology, using UFM we are able to image the graphene-substrate interface as a function of environment.<sup>6</sup> Delaminations, resulting from breaking of the solid-solid contact which suppresses the propagation of ultrasound, are clearly observed between the FLG and SiO<sub>2</sub> substrate in ambient conditions (red circle figure 1a). These delaminations, arising from the transfer of the exfoliated sample are profoundly modified when the sample is immersed in a liquid environment but return when the sample is allowed to completely dry suggesting that the emersion liquid, independent of polarity, propagates

underneath the flake and is displaced when the sample is returned to the dry environment. Hard point defects are observed in both surface topography and sub-surface ultrasound detection (blue circles, figure 1b). Similar defects are observed in both liquid environments but not in ambient conditions where their small height profile is obscured by the non-contact delaminations. It is unclear if these defects are contaminants arising from the exfoliation of the FLG or artefacts of the substrate surface.

#### 3.2 Adhesion

Adhesion of the AFM probe to the FLG and SiO<sub>2</sub> was measured using force spectroscopy, corrections arising from the change in refractive indices of the media, have been applied.

Medium	FLG-tip adhesion (nN)		SiO <sub>2</sub> -tip adhesion (nN)
Air	25.1 ± 0.3	>	21.3 ± 1.3
Water	9.7 ± 0.7	>	6.9 ± 0.5
Dodecane	1.9 ± 0.3	<	4.1 ± 0.1

**Table 1: Quantified sample-tip adhesion for FLG and SiO<sub>2</sub> in air, polar and non-polar environments measured at an approach/retraction rate of 0.1 Hz**

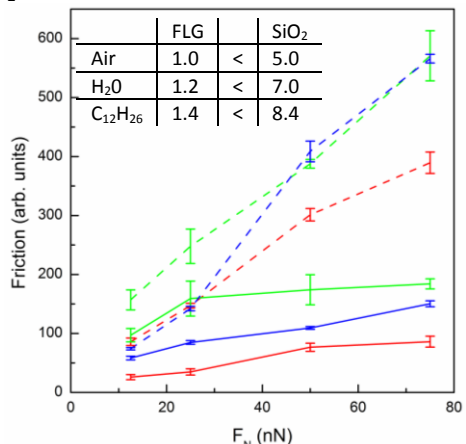
Adhesion, between an AFM tip and a substrate, is a composite term for the effect of numerous attractive forces, the most dominant for which are van der Waals, electrostatic and capillary.<sup>7</sup> Capillary forces dominate in ambient atmosphere due to the formation of a water meniscus between AFM tip and sample, hence the ‘air’ measurements demonstrate the strongest adhesion as not only does the tip-graphene attraction need to be overcome but also the breaking of the meniscus. This increase due to the pressure differential between the liquid within the meniscus and the external atmosphere is eliminated when a sample is immersed in a liquid environment and the adhesion can be considered a property of the sample-liquid-tip interface.

We can therefore compare the adhesion in two distinct ways, i) air vs water, where we observe the same surface forces but control the presence of the capillary effect and ii) water vs dodecane, where we eliminate the meniscus effect by completely immersing the system in liquid but compare the interaction of the graphene with a polar and non-polar liquid. Through elimination of the capillary effect and limiting the effectiveness of electrostatic interactions, whilst the van der Waals forces remain approximately the same for each surface, the adhesion is therefore a property of the surface energy of the liquid – the energy associated with formation of a new interface.

#### 3.3 Friction

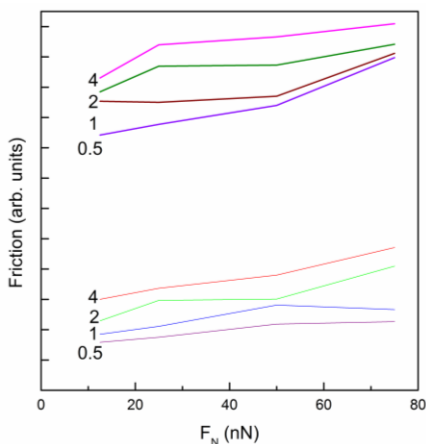
Friction is calculated from multiple positions across the sample, SiO<sub>2</sub> and FLG simultaneously, as the difference

between the forward and reverse traces of the torsion motion of the AFM cantilever in contact mode. Friction measurements were taken at multiple points across the sample at a range of quantified normal sources (0 -75 nN) and the resulting coefficients of friction were calculated. We note that in agreement with literature,<sup>8</sup> friction was observed to be lower for FLG than for SiO<sub>2</sub>, corresponding to the low nanoscale surface roughness of graphene against SiO<sub>2</sub>.



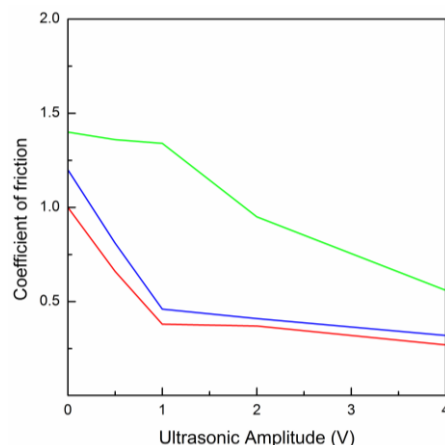
**Figure 2: Relative friction of FLG (solid lines) and SiO<sub>2</sub> (dashed) in air (red), water (blue) and dodecane (green). Insert. Coefficients of friction (slopes) of above**

Again, due to the potential of water meniscus formation we should consider the friction as occurring in two distinct regimes, in the presence of a water meniscus and in liquid immersion. Higher friction is observed for the non-polar dodecane lubricated system than for polar water. Despite the strongly hydrophobic nature of graphene we still report a lower coefficient of friction for water lubricated motion than that for dodecane.



**Figure 3: Variation of friction on FLG at applied load as measured at a range of scan rates (0.5, 1, 2 and 4 over an area of 3 μm) in continuum dodecane (top) and water (bottom)**

For both FLG and SiO<sub>2</sub>, we observe negligible change in each lubricants coefficient of friction, relative to the difference between the coefficients of different systems, as both a function of scan rate in the range 0.5-4Hz (figure 3) and ultrasonic amplitude in range 0.5-4V (figure 4).



**Figure 4: Change of coefficient of friction for FLG as a function of ultrasonic amplitude in air (red), water (blue) and dodecane (green).**

The change in coefficient due to ultrasound for water lubricated and ambient conditions show a closely related response, compared to the response of the dodecane lubricated system. Whilst the role of a tip induced meniscus in adhesion is clearly understood, the dynamical implications for friction are not.<sup>9</sup> We observe that a clear differentiation between friction as a function of load measured in ambient conditions and complete liquid layers.

Whilst it is generally accepted that the formation of a water meniscus affects the contact friction due to an additional force arising the energy loss associated with the meniscus movement along the with the sliding contact<sup>10</sup>, there is a great deal of disagreement over the precise nature of the role that the water meniscus plays.<sup>9-11</sup> The stability of the meniscus, during dynamic contact, is dependent on relative humidity, temperature, sliding velocity and surface roughness,<sup>12</sup> these factors combine to give a highly material sensitive dependence where by a dynamically stable water bridge may or may not form.<sup>11</sup> However, we conclude that during our scans, under ambient conditions, the water meniscus not only successfully forms but is also stable at a range of applied loads, scan rates and ultrasonic amplitudes

The lower value of the coefficient of friction in ambient rather than lubricated conditions, suggests that significantly more molecules are trapped between the rubbing surfaces. Therefore the Laplace pressure is sufficient to maintain the lubricant at the interface and the naturally occurring water meniscus in ambient conditions provides a more effective lubricant on FLG surfaces than a continuum layer of water.

## 4 CONCLUSIONS

We investigated the mechanical and interfacial properties of few layer graphene in ambient, polar and non-polar liquid environments. Using ultrasonic force microscopy we mapped the presence and change in subsurface delaminations and point defects. Subsurface analysis reveals that delaminations between the FLG and substrate SiO<sub>2</sub> are eliminated during emersion of the system in liquids but return when the sample is allowed to redry in ambient conditions.

Meniscus formation between the AFM tip and sample due to atmospheric moisture, results in the highest observed adhesion and lowest interfacial friction due to affinity of polar liquid with surfaces, even hydrophobic graphene coupled with stability arising from Laplace pressure. Lowest adhesion is observed for dodecane surfaces, corresponding to the lower surface energy associated with the interfacial creation. Friction, in all systems, is observed to be higher for SiO<sub>2</sub> than FLG as explained by nanoscale roughness and higher elastic moduli.

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