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Highly strained graphene samples of varying thickness and comparison of their behaviour

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Abstract
Mechanically straining graphene opens the possibility to exploit new properties linked to the stressed lattice of this two-dimensional material. In particular, theoretical analyses have forecast that straining graphene by more than 10% is a requirement for many novel applications that have not yet been experimentally demonstrated. Recently, we reported having achieved 12.5% strain in a trilayer graphene sample (3LG) in a controlled, reversible and non-destructive way. In this paper, we explore our method by straining samples of varying thicknesses and comparing their behavior, where strains of 14% and 11% were achieved for monolayer and four-layer graphene (4LG), respectively. For the analysis, optical tracking and the correspondent Raman spectra were taken. While doing so, we observed slippage between two layers in a bilayer sample of which one layer was clamped on one side only. The obtained results when stretching different samples to extreme strains demonstrated the exceptional elasticity of graphene, which might be essential for practical applications. Hysteretic effects observed in the partially clamped layer hints at small energy losses during slippage. This may shed new light on the superlubricity property of graphene that has been reported in the literature.

Keywords: graphene, extreme strains, tensile MEMS, clamping, mechanical stress, slippage

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of graphene [1], this two-dimensional (2D) material has represented a rapidly increasing ‘star on the horizon’ of material science and nanotechnology [2] because of its unique properties. As a result, scientists have been trying to explore novel opportunities in various fields. Theoretical work has predicted that straining graphene by more than 10% is a prerequisite for many expected applications [3–9]. These include, for example, using graphene as an active and reversible hydrogen storage medium [3, 4], engineering bandgaps [10] in graphene for nano-electronics [6] and optical devices [11], or generating synthetic electromagnetic fields [5]. A full list of the predicted applications of graphene under more than 10% strain can be found in the supplementary data. However, none of these applications have been experimentally demonstrated to their full extend so far, since achieving significant strains in a controlled way has represented a considerable challenge. Previous experimental efforts to strain graphene [7–9, 12–17] demonstrated maximum values of ~4.5% [7, 8, 16, 18], which were still restraining the intended applications. We have recently reported a controlled, reversible and nondestructive way to generate uniaxial...
extreme (>10%) strains in graphene using a microfabricated tensile device [19]. There, we reached a strain of 12.5% on a trilayer graphene (3LG) sample. In this study, we explore our method by straining samples of varying thicknesses and comparing their behavior, where strains of 14% and 11% were achieved for monolayer and four-layer graphene (4LG), respectively. While doing so, we observed slippage between two layers in a bilayer sample of which one layer was clamped on one side only.

The tensile device, briefly, consisted of two suspended beams that were aligned to and movable along a single axis (figure 1(a)). One of the beams could be actively pulled using a thermal in-plane microactuator (TIM), while the other was fixed to calibrated springs, which allowed force measurements. Both beams were then bridged by graphene, as shown in figures 1(b), (c). The graphene was stressed when the TIM was actuated, creating a tensile pulling effect. In most of the previously reported experiments, graphene was placed as a fully suspended membrane, ready to be strained [8, 9, 12, 15]. It has been observed that it slipped away from the surface when the van der Waals adhesion is overcome by the tensile force [9]. Consequently, proper clamping would dramatically increase the chances of achieving higher strains. Therefore, to prevent graphene from slipping away, it was clamped using epoxy patches locally deposited along the two edges of the graphene [19]. To accurately dispense the epoxy, we used a previously developed femtopipette (figure 1(d)) [20, 21]. During stretching, optical images and Raman spectra were taken.

2. Materials and methods

2.1. Graphene transferring

The transfer of graphene, based on previous work [22], was performed using mechanically exfoliated ribbons of different thicknesses. When the flake of interest was found, the oxidised Si-chip, onto which the flakes were originally transferred from adhesive tape, was dipped into a solution of cellulose acetate butyrate in ethyl acetate, which had a ∼30 mg mL⁻¹ ratio. After dipping, the substrate was removed from the solution and the solvent was allowed to evaporate under ambient conditions. After that, the chip was dipped into water under a ∼30 degree angle, allowing the water to enter...
through the interface formed between the hydrophobic polymer and the hydrophilic oxide. Due to the differences in surface energies, the polymer came off the substrate, peeling the graphene along with it. This was caused by hydrophobic interactions. When the polymer was floating on the water, a micromanipulator was used to hold it while the MEMS device (placed at the bottom of the beaker filled with water) was becoming aligned relative to the position of the graphene. Once they were aligned, the water was pumped out of the beaker, decreasing the distance between the polymer/graphene and the chip. Once in contact, the polymer was left until it dried out and finally dissolved to release the graphene.

2.2. Clamping the graphene

The clamping of graphene was also based on our previous work [19]. To start with, an epoxy resin was mixed with an amine-containing curing agent. For this experiment, the 353ND epoxy (EpoTek technology) was used, consisting of bisphenol F. A small volume of the freshly mixed epoxy was accurately dispensed on the edges of the graphene using a femtopipette previously developed in our group [20, 21]. To further control the positioning of the femtopipette, it was mounted with 4 degrees of freedom on a robot used for nanomanipulation. The robot, with the femtopipette mounted on the edge of its actuated arm, was placed underneath an optical microscope and remotely controlled.

2.3. Raman analysis

The experimental setup comprised a Horiba Labram HR Raman spectroscope and a probe station. The excitation source was a 532 nm laser with a power below 0.1 mW on the graphene sample to avoid laser-induced local heating. A 50x objective lens (numerical aperture 0.75) was used to focus the laser to a spot size of around 1 μm. The device containing the
clamped graphene was positioned under the laser spot of the Raman such that the TIM could be simultaneously actuated using two probe needles. A digital voltage source, Hameg HMP2020, heated the TIM with a power sweep from 0 W to 2.4 W.

3. Results and discussion

3.1. Stretching graphene of varying thicknesses

We started analyzing a bilayer sample by optical tracking, from which we extracted the original length of the flake, $L_0 = 9.7 \mu m$. At a maximum applied force of 330 $\mu$N, and based on visual displacement of the beams, the stretched flake showed an elongation of $\Delta L = 1.37 \mu m$, denoting an achieved strain of $\varepsilon = $ 14% (figure 2(a)). The optical images showed the gradual appearance of an edge after reaching $\varepsilon = 8.7\%$, suggesting that only one of the monolayers was properly clamped on both sides, and that slippage between both monolayers occurred upon straining. We confirmed this by observing the in situ shifts of the graphene’s Raman spectra caused by increasing strain. It is well known that when probing the edge of graphene via Raman, the presence of the D-band is observed [23]. In our case, we noticed the initial appearance of that band while applying a force of $\sim 200 \mu$N (figure 2(b)), corresponding to the same strain where we observed the initial appearance of the edge during optical tracking. As the edge displaced and became more visible for the laser, the D-band showed increasing intensity with a maximum at 1356.9 cm$^{-1}$. Similarly, this was reversible, as the band gradually disappeared when returning to the relaxed state. Consequently, only the fully clamped monolayer experienced maximum strain in this experiment, while the other slipped and experienced a smaller strain. At this point, we can only speculate about the possible scenarios of why the complete clamping of the bilayer might have failed. One possibility is that one of the monolayers was shorter, preventing it from reaching both shuttles to be fully clamped. Alternatively, the glue might not have covered both edges of such a layer. We do not believe that the observed slippage is indicative for a fundamental failure of clamping bilayer graphene with our method.

From the Raman spectra, the G and 2D bands were individually analyzed. Initially the G-band was located at 1583.8 cm$^{-1}$, but displayed continuous redshift, resulting in 1579.2 cm$^{-1}$ for $\varepsilon = 14\%$ (figure 3(a)). The complete evolution of the G-band, which can be found in figure 2 of the supplementary data, showed partial splitting and rise of
different peaks. Previously, it was demonstrated that, when strained at \( \varepsilon = 0.5\% \), the G-band of graphene splits into \( G^+ \) and \( G^- \) [24]. The individual G-band of each monolayer reacted separately because of their different strain values. When relaxed, the G-band of our bilayer showed two Lorentzian fits with maxima at 1583.8 cm\(^{-1} \) and 1589.3 cm\(^{-1} \) (figure 3(b)). The increase in strain was coupled to redshifts of both Lorentzians, eventual splitting, broadening, and dropping in intensity. At \( \varepsilon = 0.5\% \), the G-band of the fully clamped monolayer divided into \( G^- \) at 1575.9 ± 0.3 cm\(^{-1} \) and \( G^+ \) at 1580.9 ± 0.2 cm\(^{-1} \), as confirmed by a third Lorentzian (supplementary Data figure 2(d)). This suggested initial redshifts for the \( G^- \) and \( G^+ \) sub-bands of \(-15.9\% \) and \(-6.1\% \), respectively, which agrees with earlier findings [25]. At \( \varepsilon = 8.7\% \), a fourth Lorentzian appeared, denoting the G-band splitting of the partially clamped monolayer (supplementary Data figure 2(i)). The G-band shape in figure 3(c) indicates an overlap of both monolayer’s individual bands at their maximum experienced strain. The fully clamped monolayer showed its maxima at 1562.4 ± 0.3 cm\(^{-1} \) and 1592.2 ± 0.2 cm\(^{-1} \), while the partially clamped at 1579.2 ± 0.4 cm\(^{-1} \) and 1597.3 ± 0.2 cm\(^{-1} \). When analyzing the 2D band (figure 3(d)), we noticed that strain caused the appearance of an additional band, which we attribute to the individual 2D bands of each monolayer. At \( \varepsilon = 14\% \), the spectra depicted two bands with redshifts of \(-58.9\% \) (partially clamped monolayer) and \(-372.4\% \) (fully clamped monolayer) with respect to the original 2D band, located at 2726.6 cm\(^{-1} \). From these observations, we extracted a redshift of \(-26.6\% \) for the 2D band, in agreement with a previously reported redshift for the same band [26], which represented an experienced \( \varepsilon = 2.21\% \) for the partially clamped monolayer.

The interaction between both monolayers as a function of strain is shown in figure 4(a). During straining, the weak inter-layer interaction enables the mechanism of slippage due to the presence of delocalized \( \pi \) electrons in the adjacent layers [27]. In our case, an estimated slipped distance of 1.19 \( \mu m \) was observed. This propensity for sliding also means that the local stacking of monolayer sheets can be disrupted. Similarly, we believe that the effect of tensile strain in the graphene causes a shift in the carbon-bonding configuration from sp\(^2\) towards more sp\(^3\), hence an increased interaction occurs between layers. However, our data is currently not detailed enough to reach this conclusion. The strain difference between the monolayers, \( \Delta \varepsilon \), should be linked to the change in the interaction potential between the two layers, as well as the location of the atoms (figure 4(b)). Moreover, the reversibility of the mechanism was analyzed. The sample was controllably strained to its maximum strain and brought back to a relaxed state, and no changes in the spectra of the fully clamped monolayer were observed. Such a reversible and fast recovery property demonstrated the exceptional elasticity of graphene, which might be crucial for practical applications.

Figure 4. Slippage analysis between monolayers under extreme strain and stiffness comparison with multilayer. (a) We observed non-linear interaction between straining layers. (b) The strain difference between the monolayers, \( \Delta \varepsilon \), is linked to the change in the interaction potential between both layers, as well as the location of the atoms. (c) When analyzing system reversibility, no changes in the spectra of the fully clamped monolayer were observed. However, when focusing on the partially clamped monolayer, a small hysteresis was observed in the spectra. The narrow hysteresis (or friction) loop implies a small amount of energy was lost as the slippage occurred when bringing the sample back to a relaxed state. (d) The force required to strain a monolayer to \( \varepsilon = 14\% \) was 330 \( \mu N \), however, such force would only induce a \( \varepsilon = 7.5\% \) on a 4LG sample, denoting the higher stiffness of the latter.
However, when focusing on the partially clamped monolayer, a small hysteresis was observed in the spectra, likely due to interlayer slippage. Figure 4(c) shows the obtained hysteresis loop, also referred to as the friction loop. The narrow loop implies a small amount of lost energy as the slippage occurred when bringing the sample back to a relaxed state. This corroborates the high lubricity of graphene that has been previously measured [28]. Similarly, earlier studies showed that ultra-low friction between is indeed caused by the incommensurate contact between the graphite layers [29]. Additionally, such controlled and reversible slippage resembled the experiments performed by Cumings et al [30], where the core tubes of multiwalled carbon nanotubes were telescoped outward, realizing low-friction.

To further exploit the behavior of highly stressed graphene, we repeated the experiments on a four-layer (4LG) sample. The confirmation of the number of layers is shown in figure 3 of the supplementary data. As expected, a smaller force was required to stretch the monolayer in comparison to the 4LG, as the latter was stiffer (figure 4(d)). For comparison, using a force of nearly 350 μN was enough to strain the monolayer by 14%, while the same force resulted in only 7.5% for the 4LG.

The optical tracking of the 4LG (figure 5(a)) revealed a maximum achieved strain of ε = 11%. However, the Raman analysis showed different behavior in comparison with a highly strained monolayer. In 4LG, splitting the bands did not occur, and their redshift was much smaller. Its G-band redshifted from 1578.2 cm\(^{-1}\) to 1577.6 cm\(^{-1}\), representing an average shift of \(-0.05\) cm\(^{-1}\)/% (figure 5(b)). Similarly, its 2D band shifted from 2733.1 cm\(^{-1}\) to 2731.2 cm\(^{-1}\), which represented an average shift of \(-0.17\) cm\(^{-1}\)/% (figure 5(c)).

### 3.2. Comparing behaviors of stretched graphene samples

The average shifts of both the G-band and the 2D band shown by the 4LG were much smaller than that of the monolayer. Nevertheless, they were very similar to that of the previously reported 3LG [19], suggesting a general behavior for highly stressed multilayer graphene (figures 6(a), (b)). As opposed to a monolayer where the G-band showed clear splitting due to strain, in the multilayer, splitting did not occur. Instead, the increase in strain was accompanied by a noticeable decrease.
in intensity and a smaller redshift. The 2D band of 4LG exhibited an average decrease of 4.8% in intensity per 1% strain, similar to that shown by the G-band of the monolayer. In the latter case, the average decrease in intensity was calculated to be 6% per 1% strain. On the other side, the G-band of the 4LG showed an average decrease of 1.26% in intensity per 1% strain, similar to the average decrease of the 2D band of a monolayer, which was measured to be 1.7% per 1% strain (figure 6(c)). In every case, these measurements were based on the maxima of the bands. Moreover, when the 4LG was strained from 0% to 11% and backwards, no hysteresis in the spectra were observed (figure 6(d)), corroborating the reversibility previously observed for monolayer graphene and the 3LG [19].

As observed in our earlier-reported results [19], it is due the C$_{3v}$ group symmetry of graphene that the applied tensile strain distinguishes between the strain felt by the three bonds of graphene (denoted as 1, 2 and 3 in figure 5(a)). We believe that the asymmetric response of the three bonds of C$_{3v}$ group symmetry gave rise to the behaviours reported here. The level of the strain and the strain energy of each C–C bond must differ with the relative direction between strain and crystal orientation. It is, therefore, not surprising that mechanical strain induces phonon-band splitting [31].

The bond order-length-strength (BOLS) correlation theory [31–34] helped us to once again calculate the individual elongations of the bonds in monolayer graphene. There are two extreme conditions defined by the angle $\theta=0^\circ$ or $\theta=30^\circ$, figure 5(a)). On one hand, when $\theta=0^\circ$, the strain is along bond 2, $\varepsilon_1=\varepsilon_3=\lambda\varepsilon_2<\varepsilon_2$, where $\lambda=0.31$ for the upper branch and $\lambda=1.0$ for the lower branch. This means that bonds 1 and 3 are elongated by 31% compared to bond 2 when strain is along that bond. If we use 0.142 nm as the length for C–C bond in graphene [31] under the relaxed state, it would mean that bond 2 reached a length of 0.161 nm for $\varepsilon=14\%$ achieved in our monolayer experiment, while bonds 1 and 3 reached 0.148 nm. Straining at $\theta=0^\circ$ should correspond to band splitting, which has been observed in monolayer graphene. On the other hand, when strain is perpendicular to bond 3, at $\theta=30^\circ$, the strain is $\varepsilon_1=\varepsilon_2>\varepsilon_3\sim 0$ and therefore there should be a branch retaining the original frequency as $\varepsilon_3\sim 0$. We believe that was the case in our 4LG, since no significant redshift for the 2D band was observed. Moreover, the diverse scattering paths (given by those three C–C bonds) for electrons and holes between the Dirac cones at the K and K’ points offer equal impact to the intensity of the 2D band. Therefore, if the symmetry is lost, a reduction of the intensity would be expected as a function of strain [35].

Figure 6. Comparison of behaviour between highly strained monolayer and multilayer. (a) The G band of multilayer graphene exhibited a very small Raman shift, as opposed to the monolayer, where the shift was more pronounced. Similarly, (b) the 2D band of the multilayer graphene remained almost static, while the monolayer displayed a noticeable shift. (c) The increase in strain was accompanied by a decrease in band intensity. In the case of a monolayer, an increase in strain resulted in a considerable decrease of intensity for the G-band and a minor decrease for the 2D band. In the case of the multilayer, however, the behaviour was the opposite. (d) Stretching the graphene from a relaxed state to a maximum strain and backwards resulted in the same Raman spectra, as shown by the absence of hysteresis, confirming the high elasticity of graphene.
4. Conclusions

By using Raman spectroscopy to analyze graphene [36], we demonstrated the behavior and main differences between highly strained monolayers and multilayers. The results confirmed the feasibility of using an in-plane tensile device to uniaxially stress graphene of varying thicknesses to extreme strains. As stated in our earlier results [19], the combination of the high-force output, long displacements, the high control provided by our MEMS device and the strong epoxy clamps were the main reasons for achieving high strains. The comparable results observed for 3LG and 4LG convinces us that the behavior of samples with a larger number of layers could be predicted. We expect such larger numbers to result in small redshifts for the 2D band and an overall decrease of intensity, as long as all the layers are being strained. However, working with thicker samples could make the clamping more difficult, as the glue might not reach every layer. This given the fact that all layers might not have free edges where the glue could bind. Nonetheless, we believe our results can provide a deeper understanding of graphene’s behavior as a function of strain and varying thickness. These results might open doors to novel applications in electronics, optical devices and hydrogen-storage technologies. In addition, the observed slippage behavior might be of high interest for further understanding of nanoscale friction and superlubricity, while providing insight for the design of novel lubricants.

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