An all-optical blister test on suspended graphene

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Abstract

We report a comprehensive micro-Raman study of a pressurized suspended graphene membrane that hermetically seals a circular pit, etched in a Si/SiO$_2$ substrate. Placing the sample under a uniform pressure load results in bulging of the graphene membrane and subsequent softening of the main Raman features, due to tensile strain. In such a microcavity, the intensity of the Raman features depends very sensitively on the distance between the graphene membrane and the Si substrate, which acts as the bottom mirror of the cavity. Thus, a spatially resolved analysis of the intensity of the G and 2D mode features as a function of the pressure load permits a direct reconstruction of the blister profile. An average strain is then deduced at each pressure. This allows a determination of the Grüneisen parameters of 1.8 ± 0.2 and 2.4 ± 0.2 for the Raman G and 2D modes, respectively. The measured blister height is proportional to the cubic root of the pressure load, as predicted theoretically. The validation of this scaling provides a direct and accurate determination the Young’s modulus of graphene with a purely optical, hence contactless and minimally invasive approach. We find a Young’s modulus of (1.05 ± 0.10) TPa for monolayer graphene, in perfect match with previous nano-indentation measurements. This all-optical methodology opens avenues for pressure sensing using graphene and could readily be adapted to other emerging two-dimensional materials.

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I. INTRODUCTION

Two-dimensional crystals [1], being just one or a few atoms thick and having lateral dimensions ranging from micrometers up to macroscopic scales, are a new class of solid state membranes. Among these systems, graphene has attracted considerable interest, due to its unique electronic band structure [2], as well as its outstanding materials properties. In particular, graphene is endowed with exceptional mechanical properties, such as a large Young’s modulus and intrinsic strength [3], ultrastrong adhesion [4] and impermeability to standard gases [5]. Owing to the great electrical controllability of graphene [6], suspended graphene membranes can conveniently be integrated into nano-electromechanical resonators [7, 8]. In addition, graphene interacts strongly with optical radiation [9]. However, being atomically thin, a single layer of graphene is quasi-transparent over the infrared and visible ranges [10, 11]. This allows optical readout of mechanical resonances [5, 7, 12] and opens new perspectives for optomechanical studies [13].

It was also recently demonstrated that the impermeability and ultrastrong adhesion of graphene make it possible to form blisters (or balloons), by applying a pressure difference between both sides of a suspended graphene membrane [5]. Such systems are highly promising for molecular sieving applications [14]. In practice, bulging of the atomically thin membrane can be quantitatively investigated using atomic force microscopy (AFM) [4, 5] or nano-indentation [3], in what is known as a blister (or bulge) test [15]. In addition, the resulting strain field in the bulged graphene membrane may be probed optically, through frequency shifts of the main Raman scattering features [16–19]. A quantitative analysis requires, however, knowledge of the Grüneisen parameters, whose determination is challenging in pressurized suspended graphene membranes.

Here, we show that micro-Raman scattering alone not only permits to investigate strain-induced phonon softening in pressurized graphene membranes, but also readily provides the blister topography, resulting in a comprehensive, all-optical blister test. The height profile of a pressurized graphene blister is determined from the analysis of the integrated intensity of the main (G and 2D) Raman scattering features of graphene. This allows a direct determination of the tensile strain. The softening of the Raman features is then examined under known tensile strain, as a function of the pressure load. The Grüneisen parameters for the G and 2D mode features and, importantly, the Young’s modulus of graphene are then
obtained only by optical means. This novel approach is contactless and can thus be applied in a large variety of experimental conditions. It will serve as a guide for further optical and opto-mechanical studies on graphene and related systems.

II. EXPERIMENTAL METHODS

For an accurate blister test, high quality, impermeable and defect free graphene is mandatory. We therefore prepared our graphene samples by mechanical exfoliation of natural graphite. This material is known to well suited to investigate the intrinsic properties of graphene. Graphene layers were deposited over circular pits, etched in a Si/SiO$_2$ substrate by optical lithography and a subsequent reactive ion etching, as in ref. [20]. No silicon oxide was left within the pits. The graphene layers are tightly clamped around the border of the pit by van der Waals forces, resulting in a hermetically sealed membrane. The typical pit radius is $a \approx 4 \mu m$ and the pit depth $h_0$ was measured with a profilometer. In the following, we will present results obtained for a sample with $h_0 = (395 \pm 10)$ nm. Similar results were obtained on two other samples with different pit depths (see Supplemental Material).

As a characterisation tool, we make use of micro-Raman scattering spectroscopy [21, 22], which is highly sensitive to the number of layers, disorder [23, 24], doping, and, importantly, to strain [17–19, 25–32]. Since suspended graphene is immune to substrate-induced doping [20, 33] and minimally sensitive to atmospheric doping [34], these samples allow to directly investigate strain-induced changes in the Raman spectrum of graphene, without spurious contributions from a residual charge carrier density [35]. Here, micro-Raman measurements were performed in a backscattering geometry, with a home-built setup, using a 20× objective (NA = 0.45) and a 532 nm, diffraction limited laser spot. The objective is mounted onto a piezoelectric stage allowing spatially resolved Raman studies. The collected Raman scattered light was dispersed onto a charged-coupled device array by a single-pass optical spectrometer, with a spectral resolution better than 2 cm$^{-1}$. The laser beam was linearly polarized and the laser power was maintained at 0.7 mW, in order to avoid laser induced local heating and subsequent thermally induced spectral shifts or lineshape changes of the Raman features [36]. Suspended graphene monolayers were unambiguously identified from the characteristic lineshape of their Raman 2D mode feature [33], and their undoped character was systematically confirmed from a detailed spatially resolved Raman study [20].
FIG. 1: (Color online) Formation of a pressurized graphene blister. a) Sketch of a suspended graphene membrane at pressure equilibrium (upper part) and under a uniform pressure load (lower part). An optical image of a suspended graphene monolayer sealing a cylindrical pit with a radius $a \approx 4 \, \mu m$ is shown in the center left part of a). b) Micro-Raman spectra recorded at the center of the graphene membrane at different values of $\Delta p = p_{\text{int}} - p_{\text{ext}}$.

The relative integrated intensity of the defect related D-mode to that of the G-mode was less than 1 % on the samples investigated here. In order to form graphene blisters, the samples were held in a vacuum chamber equipped with a quartz window for optical access. The external pressure $p_{\text{ext}}$ is smoothly varied from $\approx 10^{-2} \, \text{Pa}$ to atmospheric pressure $(100 \pm 2) \, \text{kPa}$. Considering the bulging of the graphene membrane, we estimated, using the ideal gas law, that the corresponding pressure load $\Delta p = p_{\text{int}} - p_{\text{ext}}$, i.e., the difference between pressures inside and outside the blister, varied between $(0 \pm 2) \, \text{kPa}$ and $(74 \pm 5) \, \text{kPa}$, respectively. More details on the determination of $\Delta p$ are given in the Supplemental Material. Importantly, the highest $\Delta p$ achieved here is more than one order of magnitude below the threshold, at which delamination occurs [4]. Consequently, we will consider a constant blister radius throughout the manuscript.

Figure 1 shows a scheme of our experimental approach. The volume of the cylindrical pit is $V_0$, $V_B$ denotes the volume of the blister, and $N$ is the number of trapped air molecules. We note $h(r) \ll a$, the vertical displacement of the graphene layer and $h_{\text{tot}}(r)$, the total distance...
between graphene and the underlying Si substrate, at a distance \( r \) from the center of the blister. The maximum deflection \( h(0) \) is denoted \( h_{\text{max}} \). Considering our sample geometry, we estimate an upper bound for the maximum angle between the substrate and the bulged graphene of \( \approx 0.1 \text{ rad} \). Therefore, we will assume that the laser beam always impinges on the graphene membrane at quasi-normal incidence.

Over long timescales, on the order of several hours, graphene blisters tend to deflate, essentially due to slow diffusion of air molecules through the Si/SiO\(_2\) substrate \[4, 5\]. In order to verify whether the leak rate had to be considered, Raman measurements were performed on suspended graphene membranes at \( p_{\text{ext}} = p_{\text{int}} = 100 \text{ kPa} \) before pumping out the vacuum chamber and again at \( p_{\text{ext}} = 100 \text{ kPa} \), after a series of measurements as a function of \( p_{\text{ext}} \), starting from \( p_{\text{ext}} \approx 10^{-2} \text{ Pa} \). No significant changes of the Raman frequencies, and of the integrated intensity of the Raman features were observed. This demonstrates that the leak rate of our pressurized membrane could be neglected over the duration of a measurement run. Consequently, a constant \( N \) was assumed in the analysis described below. Data performed on longer timescales, revealing evidence for a finite leak rate, are shown in the Supplemental Material.

### III. STRAIN-INDUCED PHONON SOFTENING

Raman spectra were recorded at the center of the membrane for \( \Delta p = 0 \text{ kPa} \) and \( \Delta p = 74 \text{ kPa} \), as shown in Figure 1b. At pressure equilibrium, the Raman G mode feature (fit to a single Lorentzian) is centered at \( \omega_G = 1578.8 \text{ cm}^{-1} \), with a full width at half maximum (FWHM) of \( \Gamma_G = (15 \pm 0.5) \text{ cm}^{-1} \), characteristic of an undoped sample \[20\]. Its integrated intensity is denoted \( I_G \). We note that \( \Gamma_G \) remains at \( (15 \pm 0.5) \text{ cm}^{-1} \) over the suspended membrane at each value of \( \Delta p \). This value confirms that doping from the surrounding air molecules can be neglected and that suspended graphene membranes allow investigations of strain without parasitic effects from unintentional doping. The 2D mode feature shows an asymmetric lineshape, as typically observed on suspended graphene, and is fit to a modified double Lorentzian profile, as in ref. \[33\]. The lower energy feature has much higher integrated intensity and its peak frequency coincides with the peak frequency of the 2D mode feature. The spectral shift between the low and the high energy features (\( \approx 15 \text{ cm}^{-1} \)), as well as their integrated intensity ratio (\( \approx 3 \)) are also constant over the
suspended part, irrespective of $\Delta p$. Hence, we use the position of the low-energy 2D mode subfeature as the peak frequency, denoted $\omega_{2D}$, and the sum of the integrated intensities of both subfeatures is referred to as $I_{2D}$. The fact that values of $\omega_G = 1578.8$ cm$^{-1}$ and $\omega_{2D} = 2660.0$ cm$^{-1}$ are slightly lower than expected for pristine graphene is attributed to an initial built-in strain of less than 0.1%, in accordance with our previous studies \[35\]. Very similar results to those described below were also obtained on suspended samples, on which no significant built-in strain was observed (see Supplemental Material). This suggests that prestrain has no major effect on bulging under uniform pressure load, which is consistent with the negligible bending rigidity of graphene \[3, 15\].

When placing the sample under high vacuum (see red curve in Figure 1b), both the G and 2D mode features soften (by 15 cm$^{-1}$ and 33 cm$^{-1}$ at the center of the membrane, respectively) but retain their peak shapes and show comparable values of $I_G$ and $I_{2D}$. A spectrum taken at an intermediate $\Delta p = 30$ kPa is also shown. Interestingly, it reveals a striking decrease of $I_G$, by one order of magnitude, and of $I_{2D}$ by a factor of only $\approx 4$, compared to the measurement at $\Delta p = 0$ kPa. These variations are key in our analysis and will be discussed later in the manuscript. We first concentrate on the Raman shifts and their dependence on $\Delta p$ and on $r$.

Figure 2 displays two-dimensional maps, of $\omega_G$ (a) and $\omega_{2D}$ (b), recorded at $\Delta p = 74$ kPa on the sample shown in Figure 1b. The pressurized suspended region exhibits centrosymmetric distributions of $\omega_G$ and $\omega_{2D}$ with minimum values much smaller than on the supported region. Indeed, a few microns away from the pit, the pressure-induced strain is relaxed, and homogeneous distributions of $\omega_G = (1581 \pm 1)$ cm$^{-1}$, $\omega_{2D} = (2661 \pm 2)$ cm$^{-1}$ and of $\Gamma_G = 9.5 \pm 0.5$ cm$^{-1}$ are observed on supported graphene. The latter value suggests that this region is slightly doped, by $\approx 2 \times 10^{12}$ cm$^{-2}$, while the values of $\omega_G$ and $\omega_{2D}$ are consistent with a built-in tensile strain comparable to the one observed on the suspended region at $\Delta p = 0$ kPa \[20, 29, 35\].

In Figure 2c, we further compare the G and 2D mode frequencies at $\Delta p = 0$ kPa and $\Delta p = 74$ kPa along a line cut through the center. For both data sets, the measured G mode frequencies converge very near the border of the pit (at $\approx 4$ $\mu$m from the center), whereas for $\omega_{2D}$ the convergence is observed at $\approx 5.5$ $\mu$m from the center of the pit. We attribute this difference to the subtle interplay between the evolution of $\omega_G$ and $\omega_{2D}$, due to strain relaxation at the edges of the pit, and the presence of residual doping on the supported part.
FIG. 2: (Color online) Strain-induced phonon softening. a-b) Spatially resolved Raman maps of the G and 2D mode frequencies recorded on the sample shown in Figure 1a, under a uniform pressure load of $\Delta p = 74$ kPa. The step size is 250 nm. The upper left part of the sample contains a supported bilayer region, where, as expected, $\omega_{2D}$ upshifts significantly. The border of the pit is represented by gray dashed circles. c) Line scans of the frequencies of the G (black squares) and 2D (red circles) mode features, recorded at $\Delta p = 0$ kPa (filled symbols) and $\Delta p = 74$ kPa (open symbols), with a step size of 100 nm. d) Correlation between $\omega_G$ and $\omega_{2D}$ plotted for each pressure difference at four different values of $r$, ranging from $r = 0$ µm to $r = 3$ µm. The solid line is a linear fit with a slope $\partial \omega_{2D}/\partial \omega_G = 2.2$. e) $\partial \omega_{2D}/\partial \omega_G$ as a function of $r$, the distance from the blister center.

These effects will be discussed in details elsewhere, since we are interested in studying pure strain on suspended graphene.

To further unveil phonon softening induced by tensile strain, we now investigate the correlation between $\omega_{2D}$ and $\omega_G$ as a function of $\Delta p$ and the position on the graphene membrane. For this purpose, we record Raman line scans with a step size of 500 nm for
19 different values of $\Delta p$ ranging from 74 kPa down to 0 kPa. In Figure 2d we show the correlation between $\omega_{2D}$ and $\omega_G$ recorded with varying $\Delta p$, at the center of the pressurized membrane, and at $r = 1 \mu m$, $2 \mu m$ and $3 \mu m$ from the center.

At $\Delta p = 74$ kPa, $\omega_G$ ($\omega_{2D}$) shifts down to $1563.8 \text{ cm}^{-1}$ ($2627.2 \text{ cm}^{-1}$) at the center, whereas $\omega_G$ ($\omega_{2D}$) is $1567.7 \text{ cm}^{-1}$ ($2636.0 \text{ cm}^{-1}$) at $3 \mu m$ away from the center. As shown in Figure 2b, when varying $\Delta p$, the correlation between $\omega_{2D}$ and $\omega_G$ is linear, with a slope of $\frac{\partial \omega_{2D}}{\partial \omega_G} = 2.2 \pm 0.1$, irrespective of the position on the suspended graphene blister, within a distance of $3 \mu m$ from the center.

Given the membrane geometry, strain is essentially biaxial in the pressurized blister [17]. Still, there may be a dominant radial, hence uniaxial, contribution when approaching the edges of the pit [18]. In our measurements, we have observed a splitting of the G mode feature below 500 nm from the border, which may arise from uniaxial strain [25, 26]. However, the resulting G mode lineshape is independent on the polarisation of the incoming and scattered photons (see Supplemental Material). The apparent bimodal G-mode feature is thus attributed to a superposition of the Raman responses of the supported and suspended regions, due to the finite size of the laser spot ($\approx 1 \mu m$ in diameter), as it has been observed by J-U. Lee et al. [18]. This suggests that contributions from uniaxial strain cannot be unambiguously resolved in the present study. Nevertheless, uniaxial or quasi-uniaxial strain presumably results in the smaller phonon softening that is observed when approaching the edges of the pressurized membrane, compared to the larger downshifts measured near the center, which arise from biaxial strain. We believe that the levels of strain achieved here are presumably too small to result in a sizable splitting of the Raman features near the edges of the graphene blister.

IV. RECONSTRUCTION OF THE BLISTER TOPOGRAPHY

We now address the strong variations of the Raman scattering intensity observed when varying $\Delta p$. Since the Si surface at the bottom of the pit acts as a semi-reflecting mirror for visible photons, we expect the intensities of the Raman G and 2D mode features to depend sensitively on the height of the graphene blister, due to interference effects [37, 38]. Indeed, interference rings appear clearly on the Raman maps of $I_G$ and $I_{2D}/I_G$ recorded at $\Delta p = 74$ kPa (see Figure 3a and b). This demonstrates that $I_G$ and $I_{2D}$ vary significantly
over the pressurized membrane, and not in the same manner. Conversely, as shown in the line scans of the Raman scattering intensities (see Figure 3c), $I_G$ and $I_{2D}$ are nearly constant over the suspended area at $\Delta p = 0$ kPa, which is consistent with a nearly flat suspended membrane at pressure equilibrium.

![Figure 3](image)

**FIG. 3:** (Color online) Influence of the pressure load on the Raman scattering intensity. Maps of (a) the integrated intensity of the G mode feature $I_G$ and (b) of $I_{2D}/I_G$, the ratio of the integrated intensities of the 2D and G mode features recorded on the sample shown in Figure 1a, under a uniform pressure load of $\Delta p = 74$ kPa. The step size is 250 nm. The border of the pit is represented by gray dashed circles. c) Line scans of $I_G$ (black squares) and $I_{2D}$ (red circles), recorded at $\Delta p = 74$ kPa (filled symbols) and $\Delta p = 74$ kPa (open symbols), with a stepsize of 100 nm.

The evolution of $I_G$ and $I_{2D}$ as a function of $\Delta p$ at $r = 0$ µm are represented in Figure 4b. The ratio between the maximal and minimal value of $I_G$ ($I_{2D}$) reaches $\approx 13$ ($\approx 6$), and these two quantities are not proportional to each other. The Raman enhancement factor in the
The graphene – air – silicon layered system can be calculated using a simple analytical model, using the tabulated dielectric constants of Si and bulk graphite, as introduced by Yoon et al. Since we have used a relatively low numerical aperture objective (NA = 0.45), we have assumed that the normal incidence approximation was valid in the vicinity of the graphene blister. The key point of this model is that the measured Raman scattering intensity depends not only on the total intensity of the laser beam (at wavelength $\lambda_{\text{laser}}$) at the location of the graphene membrane, but also on the total intensity of the backscattered Raman G and 2D mode photons at wavelengths $\lambda_{2D} > \lambda_G > \lambda_{\text{laser}}$. Both quantities are strongly dependent on $h_{\text{tot}}$ (see Figure 1). Consequently $I_G$ and $I_{2D}$ are expected to exhibit distinct and non-periodic evolutions as a function of $h_{\text{tot}}$. Thus, from the measured Raman intensities, it is possible to deduce $h_{\text{tot}}(r)$, and finally the blister height $h(r) = h_{\text{tot}}(r) - h_0$.

The Raman enhancement factors for the G and 2D Raman modes, computed using the analytical model of Yoon et al. are shown in Figure 4b as a function of $h_{\text{tot}}$, for $\lambda_{\text{laser}} = 532$ nm. We note that although the values of $h_{\text{tot}}$ corresponding to maxima and minima of the enhancement factors are essentially determined by the wavelengths of the laser and Raman scattered photons, the contrast between the maximal and minimal enhancement factors depends sensitively on materials parameters, such as the wavelength dependent dielectric constants of Si and graphene. This contrast may also be affected by experimental factors, such as local corrugation on the Si surface, as well as slight deviations from the normal incidence approximation, arising from the numerical aperture of the microscope objective or occurring near the edges of the pressurized membrane. Consequently, the calculated enhancement factors have been renormalized with respect to the experimentally measured maxima and minima of $I_G$ and $I_{2D}$. In practice, this renormalisation has a minor impact of the determination of $h_{\text{tot}}(r)$.

Let us emphasize that in principle, a simple measurement of the back reflected laser intensity could be employed to deduce $h_{\text{tot}}(r)$ [37, 38]. However, due to the quasi transparency of single layer graphene, the maximum contrast expected in a reflectivity measurement is at most on the order of $\approx 15\%$ for a graphene monolayer [37], while we obtain a contrast of more than one order of magnitude on $I_G$. In addition, Raman measurements also provide quantitative information on the strain field in the graphene blister, as discussed above.

We now compare the data in Figure 4a and Figure 4b. The experimental evolution of $I_G$ and $I_{2D}$ as a function of $\Delta p$ (Figure 4a) qualitatively resembles the calculated Raman
FIG. 4: (Color online) Determination of the blister height from the Raman scattering intensity. a) Evolution of the integrated intensities of the G and 2D mode features measured at the center of the sample shown in Figure 1a, as a function of the pressure load $\Delta p$. b) Calculated Raman enhancement factors. c) Raman G mode intensity $I_G$ and d) blister height $h(r)$, deduced from the data in c), as a function of the distance from the blister center $r$ and the pressure load $\Delta p$.

enhancement factors (Figure 4b). In particular, at $\Delta p = 0$ kPa, $h_0 = (395 \pm 10)$ nm, $I_G$ and $I_{2D}$ are close to their maximum values, which are reached at a finite $\Delta p \approx 1$ kPa. This
evolution is very consistent with the calculated enhancement factors, which predict maxima at \( h_{\text{tot}} = 416 \text{ nm} \) (\( h_{\text{tot}} = 426 \text{ nm} \)) for \( I_{G} (I_{2D}) \). Similarly, \( I_{G} \) and \( I_{2D} \) reach local minima at \( \Delta p \approx 14 \text{ kPa} \), corresponding to \( h_{\text{tot}} \approx 550 \text{ nm} \) and rise again towards another local maximum at higher \( \Delta p \), which would correspond to \( h_{\text{tot}} = 692 \text{ nm} \) (\( h_{\text{tot}} = 712 \text{ nm} \)) for \( I_{G} (I_{2D}) \). This readily allows us to estimate that the maximum height \( h_{\text{max}} = h_{\text{tot}}(0) - h_{0} \) of the graphene blister, attained at \( \Delta p = 74 \text{ kPa} \), is close to 270 nm. Interestingly, the evolution of \( I_{2D} \) vs. \( \Delta p \) also reveals a slight bump in the range 15 kPa – 45 kPa, with a secondary maximum around \( \Delta p \approx 30 \text{ kPa} \). This feature also appears clearly in the theoretical calculation of the enhancement factor of the 2D mode near \( h_{\text{tot}} \approx 580 \text{ nm} \) (i.e., \( h \approx 185 \text{ nm} \)). Conversely, no secondary maximum is expected, nor observed for \( I_{G} \) in the height range investigated here. This observation further validates our experimental approach for the determination of the blister profile.

**FIG. 5:** (Color online) Reconstruction of the blister topography. a) Reconstructed three-dimensional image of the pressurized blister topography at \( \Delta p = 74 \text{ kPa} \). b) Blister height profile recorded at various values of \( \Delta p \). The error bars in Figure 5b take into account the fact that it is not possible to give an accurate value of the height when the Raman intensity is approaching a local minimum (see Figure 4b). The dashed lines are guides to the eye.
As an example, contour plots of $I_G$ and of the corresponding blister height are presented as a function of $\Delta p$ and $r$. Similar data for $I_{2D}$ and for another sample are shown in the Supplemental Material. We find that the heights deduced from $I_G$ and $I_{2D}$, respectively, are very similar (see also Figure 7). We are now able to investigate the blister topography in more details. In Figure 5a, we show a three-dimensional image of the pressurized blister, reconstructed from the Raman map of $I_G$ shown in Figure 3a, using the approach described above. Cross sections at different values of $\Delta p$ are shown in Figure 5b. When approaching the border of the circular pit, the measured Raman intensities may be affected by contributions from the neighboring supported graphene. Therefore, the blister profile was linearly interpolated between $r = 3 \mu m$ and $r = 4.1 \mu m$, where $h = h_0$.

V. DETERMINATION OF THE GRÜNEISEN PARAMETERS

Having determined the blister topography, we can now estimate an average tensile strain induced by the uniform pressure load $\epsilon_p = L/2a - 1$, where $L$ is the length of the cross section of the pressurized graphene blister (see Figure 5b). We find that $\epsilon_p$ reaches values of up to $(0.33 \pm 0.07) \%$.

We can now correlate $\epsilon_p$ to the Raman frequencies $\omega_G$ and $\omega_{2D}$ measured at the center of the blister, as it is shown in Figure 6. Over the range $\epsilon_p = 0 \% - 0.33 \%$, we observe roughly linear scalings with slopes $\partial \omega_G / \partial \epsilon_p = (-47 \pm 5) \text{cm}^{-1}/\% \text{strain}$ and $\partial \omega_{2D} / \partial \epsilon_p = (-101 \pm 10) \text{cm}^{-1}/\% \text{strain}$, respectively. Nevertheless, in the limit of small deflections, a precise determination of $\epsilon_p$ remains challenging. Therefore, in the following, we will consider the range $\epsilon_p = 0.1 \% - 0.33 \%$, for which, $\epsilon_p$ can be estimated with sufficient accuracy. Within this range, we find slightly larger slopes of $\partial \omega_G / \partial \epsilon_p = (-57 \pm 5) \text{cm}^{-1}/\% \text{strain}$ and $\partial \omega_{2D} / \partial \epsilon_p = (-128 \pm 10) \text{cm}^{-1}/\% \text{strain}$, respectively. This allows us to estimate the Grüneisen parameters of the G and 2D modes under biaxial strain, as $\gamma_G = \frac{1}{2\omega_G^0} \frac{\partial \omega_G}{\partial \epsilon_p} = 1.8 \pm 0.2$ and $\gamma_{2D} = \frac{1}{2\omega_{2D}^0} \frac{\partial \omega_{2D}}{\partial \epsilon_p} = 2.4 \pm 0.2$, respectively, where $\omega_G^0$ and $\omega_{2D}^0$ are the G and 2D mode frequencies in pristine graphene.
FIG. 6: (Color online) Determination of the Grüneisen parameters. Evolution of the G mode (a) and 2D mode (b) frequencies measured at the center of the sample shown in Figure 1a, as a function of the tensile strain $\epsilon_p$ induced by the uniform pressure load. The straight lines are linear fits.

VI. DETERMINATION OF THE YOUNG’S MODULUS OF GRAPHENE

We now consider the evolution of $h_{\text{max}}$, the height measured at the center of the blister, as a function of $\Delta p$. As demonstrated by Hencky in 1915 [40, 41], the third power of deflection of a thin circular plate with negligible bending stiffness, i.e., a membrane, is expected to be proportional to $\Delta p$:

$$\Delta p = \frac{K(\nu)Et}{a^4} h_{\text{max}}^3, \quad (1)$$

where $E$ is the Young’s modulus, $t$ is the thickness of the membrane ($t = 0.335$ nm for monolayer graphene), and $K(\nu)$ is a constant that depends on the Poisson ratio of the membrane. In addition, the volume of the blister $V_B$ writes:

$$V_B = C(\nu)\pi a^2 h_{\text{max}}, \quad (2)$$

where $C(\nu)$ is another constant that is directly related to $K(\nu)$ [40, 41]. Similarly to the determination of $\epsilon_p$, we also estimated $V_B$ for each value of $\Delta p$ (i.e., of $h$). This allowed
us to estimate an average $C(\nu) = 0.52 \pm 0.02$ (see Supplemental Material). This value is very close to those previously suggested for monolayer graphene, using $\nu \approx 0.16$, the value of bulk graphite $[4, 5]$. In these conditions, one expects $K(\nu) \approx 3$ $[4, 5, 40, 41]$. 

In Figure 7, we show the relationship between $h_{\text{max}}^3$ and $\Delta p$. Both curves follow very similar linear scalings through the origin, in excellent agreement with Eq. 1. Using $K = 3.09$ $[4, 5]$ and $a = (4.1 \pm 0.1) \mu$m, we determine the Young’s modulus of monolayer graphene as $E = (1.05 \pm 0.1)$ TPa.

![Graph showing the relationship between $h_{\text{max}}^3$ and $\Delta p$.](image)

**FIG. 7:** (Color online) Determination of the Young’s modulus of graphene. Third power of the height of the graphene blister, $h_{\text{max}}$, measured at its center as a function of the pressure load. Data obtained from the measurement of the G (2D) mode integrated intensity are shown with black squares (red circles). The straight lines is a linear fit, which allows to deduce a Young’s modulus of $E = (1.05 \pm 0.1)$ TPa.

### VII. DISCUSSION

A summary of our experimental results and a brief survey of relevant literature values are presented in Table I. Let us first consider the slope $\partial \omega_{2D}/\partial \omega_G$. Our value of $2.2 \pm 0.1$ is in good agreement with recent studies by Zabel et al. $[17]$ on a graphene bubble and by J-U. Lee et al. $[18]$ on suspended graphene. Interestingly, we demonstrate, for the first time, that the slope $\partial \omega_{2D}/\partial \omega_G$ is the same at the center of a pressurized blister, where strain is biaxial, and near its edges, where shear deformation ($i.e.,$ a uniaxial strain component) is present. We conclude that the value $\partial \omega_{2D}/\partial \omega_G = 2.2 \pm 0.1$, which also has been proposed by J-E. Lee
et al. [29] for thermally annealed, supported graphene, seems to be universal for graphene, in the limit of moderate strains below 1%. As reported, larger uniaxial strains induce shear deformation and subsequent splittings of the Raman features, which strongly depend upon the polarisation of the incoming and scattered phonons relative to the crystal orientation [19, 25, 26, 30–32]. This complicates the determination of $\partial \omega_{2D}/\partial \omega_G$ and consequently of the Gr"uneisen parameters.

| Method | $\frac{\partial \omega_{2D}}{\partial \omega_G}$ | $\gamma_G$ | $\gamma_{2D}$ | $E$ (TPa) |
|--------|---------------------------------|------------|--------------|--------|
| This work | Raman | 2.2 ± 0.1 | 1.8 ± 0.2 | 2.4 ± 0.2 | 1.05 ± 0.1 |
| Graphene bubble [17] | Raman + AFM | 2.45 ± 0.3 | 1.8 ± 0.2 | 2.6 ± 0.1 | – |
| Suspended graphene [18] | Raman + simulation | 2.2 ± 0.2 | – | – | 2.4 ± 0.4 |
| Pristine graphene [25, 22, 43] | First principles | – | 1.8 – 2.0 | 2.7 (ref. [25]) | – |
| Suspended graphene [3] | Nano-indentation | – | – | – | 1.0 ± 0.1 |
| Pristine graphene [44, 45] | Molecular dynamics | – | – | – | 1.0 ± 0.1 |

TABLE I: Comparison of our results with other works. Ratio of the shift rate of the 2D mode to that of the G mode under biaxial tensile strain, Gr"uneisen parameters for the G and 2D mode features and Young’s modulus of graphene determined in the present study. Our all-optical measurements are compared with experimental and theoretical values reported in the literature.

Under biaxial strain, the Gr"uneisen parameters are determined more reliably, since these are simply proportional to $\partial \omega_{2D}/\partial \omega_G$. The main challenge is then to determine the amount of strain with accuracy. Remarkably, our all-optical determination of $\epsilon_p$, $\gamma_G$ and $\gamma_{2D}$ agrees well with an estimation based on combined AFM and Raman measurements on a graphene bubble on a Si/SiO$_2$ substrate [17]. We also find a good agreement with theoretical predictions [25, 42, 43]. Interestingly, we demonstrated that a direct determination of $\epsilon_p$ from the integrated intensity of the Raman features can be performed in situ, as a function of $\Delta p$. Similar studies would be much more challenging using AFM. In any event, we note that precise determinations of the Gr"uneisen parameters of graphene remain difficult, since these typically combine a local Raman measurement with an estimation of the amount of strain that is averaged over a much larger area. This may, in part, explain the relatively large spread in the reported experimental values of $\gamma_G$ and $\gamma_{2D}$ reported in the literature.
Finally, our measurement of the Young’s modulus of graphene matches the value of bulk graphite and is in excellent agreement with values obtained using scanning probe techniques, such as nano-indentation [3] and AFM [4], as well as with molecular dynamics simulations [44, 45]. Here, the Young’s modulus is determined with accuracy using a simple, all-optical and minimally invasive approach. We note, that J-U. Lee et al. have recently proposed a significantly larger value of $E$ (see Table I and ref. [18]). The latter estimate was obtained from a comparison of Raman scattering measurements with finite elements simulations [18]. We believe that this discrepancy is due to the fact that $\epsilon_p$ has been qualitatively estimated using previously reported Raman measurements on uniaxially strained supported graphene [31]. This further highlights the interest of our approach, which allows a combined study of the topography and of the vibrational properties of suspended graphene, from a consistent set of measurements.

VIII. CONCLUSION

Using micro-Raman scattering spectroscopy, we have performed a constant $N$ blister test on a suspended graphene membrane under a uniform pressure load. By analysing the frequencies and the integrated intensities of the main Raman features of graphene, we have reconstructed the blister topography, and deduced the Grüneisen parameters and the Young’s modulus. Our analysis reveals that the intensity of the Raman features of a suspended graphene membrane can vary by one order of magnitude for pressure changes of only a few kPa. Considering Eq. 1, the relative change in blister height will be particularly strong close to pressure equilibrium, i.e., for $\Delta p \approx 0$ kPa. This suggests that typical fluctuations of the atmospheric pressure, as low as 1 kPa, could be sensed with accuracy, using graphene-based barometers. Our all-optical approach can be directly generalized to other two-dimensional materials, such as transition metal dichalcogenides [12]. It could also be implemented for all-optical adhesion studies, under larger pressure loads [4], as well as for optical studies on two-dimensional electromechanical systems [39].
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Supplemental Material

Details on the determination of the pressure load, determination of the blister height from the analysis of the intensity of the 2D mode feature, dependence of our results on the laser focusing conditions, polarization resolved Raman measurements, data measured on other samples, measurements on a concave blister.

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