Mapping nanoscale dynamic properties of suspended and supported multi-layer graphene membranes via contact resonance and ultrasonic scanning probe microscopies

Marta Mucientes1,4, Robert McNair2, Adrian Peasey2, Shouqi Shao2, Joshua Wengraf2, Kunal Lulla1, Benjamin J Robinson1,3 and Oleg Kolosov1,3,4

1 Physics Department, Lancaster University, Lancaster LA1 4YB, United Kingdom
2 Graphene Now/NANO CDT, School of Physics and Astronomy, The University of Manchester, Manchester M13 9PL, United Kingdom
3 Materials Science Institute, Lancaster University, Lancaster LA1 4YW, United Kingdom
4 E-mail: m.sanjuanmucientes@lancaster.ac.uk and o.kolosov@lancaster.ac.uk

Received 19 March 2020, revised 1 June 2020
Accepted for publication 18 June 2020
Published 17 July 2020

Abstract
Graphene’s (GR) remarkable mechanical and electrical properties—such as its Young’s modulus, low mass per unit area, natural atomic flatness and electrical conductance—would make it an ideal material for micro and nanoelectromechanical systems (MEMS and NEMS). However, the difficulty of attaching GR to supports, coupled with naturally occurring internal defects in a few layer GR can significantly adversely affect the performance of such devices. Here, we have used a combined contact resonance atomic force microscopy (CR-AFM) and ultrasonic force microscopy (UFM) approach to characterise and map with nanoscale spatial resolution GR membrane properties inaccessible to most conventional scanning probe characterisation techniques. Using a multi-layer GR plate (membrane) suspended over a round hole, we show that this combined approach allows access to the mechanical properties, internal structure and attachment geometry of the membrane providing information about both the supported and suspended regions of the system. We show that UFM allows the precise geometrical position of the supported membrane-substrate contact to be located and provides an indication of the local variation of its quality in the contact areas. At the same time, we show that by mapping the position sensitive frequency and phase response of CR-AFM response, one can reliably quantify the membrane stiffness, and image the defects in the suspended area of the membrane. The phase and amplitude of experimental CR-AFM measurements show excellent agreement with an analytical model accounting for the resonance of the combined CR-AFM probe-membrane system. The combination of UFM and CR-AFM provide a beneficial combination for the investigation of few-layer NEMS systems based on two dimensional materials.

Supplementary material for this article is available online

Keywords: nanomaterials, 2D materials, nanomechanics, SPM, ultrasonic force microscopy, NEMS

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

Graphene (GR) and other two-dimensional materials (2DM’s) have drawn extensive interests thanks to their remarkable structures and exceptional mechanical, electrical, thermal and optical properties. GR in particular holds significant potential for micro and nanoelectromechanical systems (MEMS and NEMS) applications, transparent and flexible electrodes, optical modulators and nanomechanical resonators operating in classical and quantum regimes [1–5]. However, there are several major challenges for such devices; particularly important for NEMS applications, is the quality of the 2DM-substrate contact, effects of inhomogeneous in-plane stresses [6] and, for the few-layer and heterostructured 2DM’s, interlayer defects. To investigate and mitigate these, one needs matching nanoscale characterisation methods, with the ability to map nanomechanical properties, sensitivity to the stresses in the suspended areas, and the capability to evaluate the quality of the interfacial contact. While commercially available atomic force microscopy (AFM) [7–11] and optical detection methods [12] have been commonly used to study suspended 2DM’s, the material-substrate interaction and nanomechanical mapping across the whole NEMS structure remains challenging with limited reports in this area [13–15]. One promising technique is contact resonance AFM (CR-AFM) which has been shown to be able to detect subsurface holes under the 2DM’s membrane [16–18] and to measure the local stiffness of the structure [18, 19]. At the same time, these studies indicated that the observed shape of the 2DM structure and recorded amplitudes varied significantly depending on the CR-AFM operation frequency, requiring independent methods to determine the geometry of such 2DM’s ‘nano-drums’. Here we combine AFM with ultrasonic excitation, ultrasonic force microscopy (UFM), and a phase sensitive variable frequency CR-AFM, to effectively observe the quality of the interface of the ‘supported’ graphene and the substrate, to obtain nanomechanical maps of the suspended GR nanodrum structures and to provide quantitative comparison of the nanomechanical images and theoretical models.

2. Experimental details

The multi-layer graphene (MLG) nanodrums were produced via transfer of mechanically exfoliated MLG on top of a Si/SiO₂ substrate with 300 nm thermal oxide on the top. The substrate was pre-patterned with circular holes with a diameter of 1.9 μm etched to the depth of 150 nm in SiO₂ layer via optical lithography and CHF₃/Ar reactive ion etching (see supplementary materials, SM, for the details). For the GR exfoliation [20], we used Gel-Pak® PF-4X film (0.5 mm thickness), with the resulting flakes transferred directly to the substrate. The substrate was treated in 98% Ar/2% O₂ plasma (PlasmaPrep2, Gala Instruments) for 10 min immediately prior to the transfer, to remove organic contamination and increase the adhesion of the graphene to the substrate.

The UFM and CR-AFM measurement setup was implemented by modifying a commercial AFM (MultiMode with Nanoscope-VIII controller, Bruker, Santa Barbara, USA). In both modes the out-of-plane vibration of the sample was realised by attaching it to a high frequency piezoelectric transducer (PI, Germany) via crystalline salol [21], with the transducer excited by a 33220A function generator (Keysight, USA) (figure 1(a)). The resulting cantilever deflection signal was acquired using a custom-made signal access box with low noise high frequency signal buffers. In CR-AFM mode, the amplitude and phase of the AFM cantilever deflection at the excitation frequency in the range 10–100 kHz was detected by the lock-in amplifier (SRS-830, Stanford Research Systems, USA). In the UFM mode, the sample vibration was excited at the carrier frequency fₜₚₜ in the range 4–5 MHz and is amplitude modulated using a triangular waveform at frequencies fₘₐₜ between 1 and 5 kHz. In this mode, the lock-in amplifier was detecting the amplitude of the deflection at the modulation frequency fₘₐₜ. As previously reported [21], the UFM signal at the modulation frequency is the result of nonlinear force-vs-distance dependence of the force interaction between the probe tip and the sample, reflecting the local stiffness of the material under the AFM tip. In a qualitative explanation, stiffer areas of the sample have a higher slope of force-vs-distance dependence, resulting in a more efficient ‘rectification’ of the HF signal and hence a higher UFM signal. More detailed quantitative explanation of UFM sensitivity is given in [22]. With the range of effective Young’s moduli ranging from 5 to 80 GPa (see e.g. table II in [21]), one would expect that UFM will be fully sensitive to the graphene layers on the substrate [23].

In both modes, a commercial contact AFM probe (ContAl-G, Budget Sensors) cantilever with the nominal 10 nm tip radius of curvature was used. The spring constant of the cantilever was measured using ‘Sader method’ [24] to provide k₀ = 0.184 N m⁻¹, matching the data obtained by the thermal calibration method implemented by the AFM manufacturer (Bruker). In CR-AFM mode, the cantilever is brought into contact with the stiff material (SiO₂/Si substrate) resulting in an increase in the free cantilever resonance frequency of f₀ = 13 kHz to contact resonance frequency f_cₐₜ = 64.6 kHz (in the contact with the substrate in the absence of lateral scanning). In order to find this contact resonance frequency we performed frequency sweeps obtaining the maximum amplitude of the oscillatory deflection signal.

3. Results and discussion

Both UFM and CR-AFM use dynamic approaches for mapping the mechanical properties of the GR membrane; hence, the first question is, what membrane properties are measured? First, we estimate the resonance frequencies of mechanical resonators based on suspended MLG flakes; these depend on GR Young’s Modulus, Eₛ; Poisson’s ratio, νₛ; density, ρₛ; pretension, T, as well as the flake thickness, t, and the radius of the suspended area, R. For the resonators made by graphene monolayer the tension usually dominates as their bending rigidity is insignificant comparing with one produced by the

---

4 Authors to whom any correspondence should be addressed.
Figure 1. (a) Schematics of experimental setup for UFM and CR-AFM measurements, inset—SEM image of the hole in SiO2/Si substrate defined by optical lithography. (b) 3D rendering of contact AFM topography and (c) UFM nanomechanical image of the multilayer GR flake of 12 nm thickness over the hole in the substrate ($f_{UFM} = 4.2$ MHz). Scale bars 1.5 µm.

Figure 2. (a) AFM topography and (b) UFM map of the 12 nm thick MLG flake on the substrate with the hole (arrow) with $R = 940$ nm. (d, e, g, h, j, k) Set of the CR-AFM amplitude and phase maps of the same area (d)–(e) at 30.8 kHz, (g)–(h) 57.0 kHz, and (j)–(k) 66.6 kHz. Greek letters show different features of the structure: $\alpha$—supported GR membrane, $\beta$, $\beta'$—suspended membrane areas above the hole, $\gamma$, $\gamma'$—delaminated or weakly supported areas, $\delta$, $\delta'$—areas of contrast potentially linked with the subsurface defects in the membrane, (c, f, i, l) schematics of the nanomechanical features observed in the CR-AFM and UFM: (c) simplified diagramme of the interaction of dynamic AFM and the sample, (f) expected nanomechanical contrast in the $\alpha$, $\beta$ and $\beta'$ areas around the hole, $H$ and $L$ denoting high and low stiffness, respectively, (l) schematics of the nanomechanical features observed in the CR-AFM and UFM: (c) simplified diagramme of the interaction of dynamic AFM and the sample, (f) expected nanomechanical contrast in the $\alpha$, $\beta$ and $\beta'$ areas around the hole, $H$ and $L$ denoting high and low stiffness, respectively, (l) diagram explaining expected amplitude and phase of CR-AFM response in the area of high ($H$) and low ($L$) stiffness in supported and suspended areas, respectively, detailed description in the text.
tension [6, 7, 12]. However, for the resonator based on thicker MLG flakes, the minimal resonance frequency at zero tension is determined by the circular plate behaviour, with tension further increasing this frequency. For the plate the fundamental resonance frequency is given by the equation [25]

\[
f_p = \frac{10.21}{4\pi} \sqrt{\frac{E_s}{3\rho_s(1 - \nu_s^2)}} \frac{t}{R^2}
\]

(1)

For MLG flake with the dimensions presented in figures 1 and 2, the fundamental resonance frequency is \(f_p \sim 138 \text{ MHz}\). This is several orders or magnitude higher than the frequencies of both CR-AFM (10–100 kHz) and UFM (4–5 MHz), used in our experiments, and therefore we can consider the GR membrane as a spring, neglecting its mass, allowing to use the formalism reported elsewhere [26–28] to describe the dynamics of the cantilever terminated with the spring. As we see later in the theoretical analysis section, the cantilever-sample system can be modelled as a cantilever supported at the free end by a spring, with respective \(k_s\) and \(k_c\) cantilever and sample stiffness, \(k_c = \frac{dF}{dz}\) where \(F\) is the force experienced by the cantilever and \(z\) is the deflection of the plate from the equilibrium measured at the point of contact [29, 30]. Therefore, as a good approximation, we can consider that both UFM and CR-AFM are measuring a local stiffness of the membrane. With UFM being essentially an off-resonance method known to monotonously map the stiffness to the amplitude to the signal [21], the CR-AFM due to its resonance nature [21] provides more complicated response that we first investigate experimentally and then theoretically analyse comparing these studies.

The combination of AFM and high frequency excitation increases the sensitivity of the measurement setup to the mechanical properties compared to the standard force-distance spectroscopy and its option Peak Force TM. These allowed mapping of the entire sample area, with true nanoscale spatial resolution and, in the case of UFM, eliminating friction [31] therefore providing a non-destructive approach especially valuable when the supported sample is investigated. Figures 1(b), (c) shows a typical topography and UFM images of the GR flake spanning the hole in the Si/SiO2 substrate (inset in figure 1(a)), with the UFM image showing a well-defined hole in the supported area. Figure 2 compares topography, UFM and CR-AFM modes for this flake. CR-AFM uses the resonance frequency of the cantilever in contact with the sample while scanning across the sample, to quantify the sample contact stiffness, \(k_s\) using analytical approaches described elsewhere [26, 32]. In both methods the \(k_s\) is probed by the AFM cantilever that can be in the minimal approximation represented as a spring \(k_c\) and effective mass \(m^*\) as schematically illustrated in the figure 2(c) with changes in \(k_s\) affecting the measured amplitude (UFM) or a frequency dependent response (CR-AFM). The detailed analysis of this measurement in application to the GR flake is presented in the theoretical part of this section. Figure 2(a) shows the topography of the test sample with the 12 nm MLG flake deposited over the hole. In the topography image, the hole \(\beta\) is barely observed as the smooth depression on the surface of MLG (arrow). The UFM nanomechanical image figure 2(b) clearly delineates the boundary of the hole corresponding to the edge between the lower stiffness (denoted by L in the figure 2(f)) suspended region \(\beta\) and supported area \(\alpha\) of higher stiffness (H, figure 2(f)) enabling high precision measurements of the geometry of the membrane boundary (radius \(R = 940 \pm 5\) nm in this structure). UFM also reveals neighbouring defects \(\gamma\) and \(\gamma'\) that show in the topography image as bulges of variable height, resulting in the weaker MLG—substrate interaction and interfacial defects and reducing contact stiffness (darker contrast in figure 2(b)), with the similar contrast to delaminations reported elsewhere [33]. It is interesting to note that the defects that has the internal particle show in UFM with the bright (higher stiffness) area inside the defect (\(\gamma'\)) while defects without such particle (\(\gamma\)) have uniform low stiffness, as schematically illustrated in the figure 2(i). While UFM has superior contrast to the high stiffness (supported) areas of GR nanostructures, it is not sensitive to the variations of the contact stiffness within the suspended membrane area, which in this case is below the UFM sensitivity range of \(10^5\) to \(10^7\) N m\(^{-1}\) [22, 34]. It should be noted, though, that for 2D membranes of smaller dimensions and/or larger thickness, the UFM may become directly sensitive to the properties of the suspended areas as well as seen from the \(\psi\) and \(\gamma'\). In the case of our nanostructure, to map and quantify its stiffness, we used CR-AFM that provided an excellent mechanical contrast in the suspended areas. Figure 2 panels (d, e, g, h, j, k) shows a set of the CR-AFM amplitude and phase images obtained by detection of amplitude and phase of the cantilever deflection at the different sample excitation frequencies \(f_{\text{CR}}\) [35]. For reference, the topography and UFM image of the same area are provided in the panels (a) and (b). While CR-AFM demonstrates excellent contrast to the suspended area of the membrane and to the supported areas of the MLG, one can see that both the contrast, shape, and dimensions of the membrane are varied significantly depending on the frequency used.

In figure 2 we compare three sets of the CR-AFM phase and amplitude response for the excitation frequency around the tip-substrate contact resonance frequency \(f_{\text{CR} - \text{R}} = 64.6\) kHz. A CR-AFM image at \(f_{\text{CR}} = 66.6\) kHz (figures 2(d), (e)) shows the hole (\(\beta\)) as a uniformly dark area surrounded by the bright (high amplitude) substrate (\(\gamma\)), as would be expected as frequency corresponds to the resonance of the cantilever-tip in contact with the substrate. The hole is similar to the UFM image in size, whereas the phase is presented as a concentric bright halo around the darker hole. The amplitude images are generally similar to ones reported by Ma et al [16] including the area of the delaminations \(\gamma\) and \(\gamma'\) as they affect the resonance conditions, whereas phase images that show variations similar to the UFM image, although with opposite contrast, require more detailed analysis. At lower frequency \(f_{\text{CR}} = 57.0\) kHz (figures 2(g), (h)) both amplitude and phase CR-AFM clearly shows the similar donut-shaped hole, with lower stiffness of the GR membrane in the suspended areas \(\beta\), suggesting lower resonance frequency, that explains the generally brighter contrast of these areas at the lower excitation frequency as indicated in figure 2(f). Surprisingly, the apparent diameter of the hole is now reduced with a clear \(\beta'\) segment (bright in the amplitude and dark in the phase image)
Figure 3. Plot of the CR-AFM response as the function of the position \( r \) across the hole (horizontal axis, \( r \)) and frequency (vertical axis, \( f_{dr} \)) with (a) amplitude \( A \) as the function of \( A(r, f_{dr}) \) and (b) \( \phi(r, f_{dr}) \) phase profile at driving frequency \( f_{dr} \) changing from 50 to 69 kHz in 1 kHz steps.

![Figure 3](image-url)

Figure 4. Resonant frequency for the CR-AFM \( f_{CR} \) for the first contact resonance mode \( (n = 1) \) as a function of the cantilever-sample stiffness ration \( k_c/k_s \).

![Figure 4](image-url)

Running at 45° across the hole. Given absence of the linked topographical features on the surface of the membrane, that is likely to be attributed to the change of the membrane thickness at the back side of the membrane in the \( \beta' \) area. Interesting that amplitude CR-AFM image in the figure 2(d) indicates a faint line across the hole coinciding with the \( \beta-\beta' \) boundary. Finally, the \( f_{dr} = 30.8 \) kHz amplitude image (figure 2(j)) shows the hole as a donut-shaped bright area with a darker central area (\( \beta \)), whereas the phase image (figure 2(k)) has practically no contrast to the hole. At the same time, both amplitude and phase images clearly show the internal structure of the membrane (\( \delta, \delta' \)) not visualised in the topography, UFM or CR-AFM at other frequencies. Given the shape of the features and the absence of the contrast in the topographical image (sensitive to the surface features) and in UFM (that would be most sensitive to sample—interface contact) these might be interpreted as internal cracks or extra planes in the MLG flake which induces a change in the stiffness of this particular area, possibly accounting for shear forces contribution to the CR-AFM signal. Overall, while the rich contrast obtained in CR-AFM for such GR nanostructure is outstanding, and the ability to observe subsurface features corresponds to the one reported by the variable frequency AFM imaging of cellulose fibres [36], the strong qualitative and quantitative dependence of the contrast on the excitation frequency requires more detailed experimental studies and matching analysis to help with the interpretation of the CR-AFM data.

In order to consistently analyse the frequency dependent response of CR-AFM, we obtained a set of 1D scans—profiles along the single line shown in figure 2(b), while changing the frequency in 1 kHz steps from 50 to 69 kHz that includes the reference, \( f_{CR} \), (stiff sample). By continuing acquisition of the amplitude and phase signal, we collected the 2D amplitude and phase—vs position/frequency graphs, correspondingly, \( A(r, f_{dr}) \) and \( A(\phi, f_{dr}) \), as shown in figure 3 where the horizontal axis is the position of the probe across the hole, \( r \), and vertical—the driving frequency \( f_{dr} \), whereas the brightness corresponds to the amplitude or phase of the CR-AFM.

As we can see, the apparent ‘diameter’ of the hole as seen by the CR-AFM is varied from the largest at \( f_{dr} < f_{CR} \) to significantly reduced at lower driving frequencies (\( f_{dr} < f_{CR} \)). Also, the second maximum (arrow in the figure 3(a)) that would create a ‘ring’ in the x-y image, appeared in the amplitude CR-AFM at the frequencies \( f_{dr} < f_{CR} \). These phenomena can be qualitatively explained by the changing of contact stiffness of the tip-membrane contact that is the lowest in the centre and the largest at the periphery approaching ‘infinite’ stiffness for the supported MLG layer. It is known that the resonance frequency of the cantilever-tip in contact with the membrane decreases with the decrease of its stiffness [26, 32]. Therefore the condition for the resonance for the decreased driving frequency \( f_{CR} \) are satisfied in the more central area of the membrane away from its border, resulting in the smaller diameter of the membrane, creating a bright ring at the position where the resonance occurs. In order to better understand and quantify our observations, we have used the analytical and modelling approach described below.

The equation of the dynamic deflection of the cantilever is given as

$$\frac{\partial^2 z}{\partial t^2} + \frac{E_c}{12\rho_c} \frac{\partial^4 z}{\partial x^4} = 0$$

where \( E_c \) is the Young’s Modulus,
\( \rho_c \) is the density, \( h \) is the thickness of the cantilever and \( x-z \) are the coordinates according the sketch in the figure 1(a). With density and Young’s modulus of Si known, the length of the cantilever can be easily determined, by the optical microscope image, allowing to use Sader method providing cantilever stiffness \( k_s = 0.184 \pm 0.008 \text{ N m}^{-1} \) that allows us to estimate the thickness of the cantilever \( h = 5.86 \times 10^{-7} \text{ m} \). We can then calculate the resonance frequency of the cantilever in the contact with the samples of varied sample stiffness \( k_s \) (see SM section SM3 for the derivation of this dependence). By substituting the values for the free cantilever, \( k_s \rightarrow 0 \), and experimentally obtained resonance frequency: \( f_0 = 13.8 \text{ kHz} \) and the experimentally obtained CR-AFM frequency for the Si/SiO2 substrate that can be presented as infinitely stiff for the fundamental mode of the contact resonance [26], \( k_s \rightarrow \infty \), in the substrate area of \( f_{CR} = 64.6 \text{ kHz} \), we obtain the CR-AFM response curve in figure 4. This curve 4 relates the resonant frequency of the cantilever with the ratio between the stiffness of the cantilever and the sample (\( k_s/k_s \)). We used high precision measurements of contact stiffness using a force modulation approach. It uses a ratio of the low frequency (2.7 kHz) quasi-static response of AFM in supported and suspended areas as described elsewhere [11]. Using this, we found that the stiffness of the sample in the centre of the membrane to be \( k_s = 2.15 \pm 0.008 \text{ N m}^{-1} \). By substituting this value in the equations in the SM section SM3 (graphically represented in figure 4), we expect the resonance in the centre of the membrane to be around 45 kHz that corresponds well to the images in figure 2, showing a brighter contrast of the membrane central area.

In the case of a circular plate, the stiffness of the sample probed by the AFM tip depends on the distance from the centre of the plate to the contact point, as well as on the boundary conditions at the edge of the MLG flake. It is useful to estimate the possibility of shear stresses occurring during the CR-AFM measurement affecting the measurements and hence, data interpretation. We therefore calculated the maximal shear stresses in the MLG plate using final elements analysis (see SI section 4 and figure S1 available online at stacks.iop.org/NANO/31/415702/mmedia)). We found that the maximal shear stress in all directions was below \( 1.5 \times 10^7 \text{ N m}^{-2} \) for the typical maximal force applied to the AFM tip of 50 nN. These values are an order of magnitude smaller than typical shear strength between GR layers required for the sliding of \( 1.5-1.8 \times 10^8 \text{ N m}^{-2} \) [37, 38]. Given that the modulation of the shear stress is at most 10% of the permanent shear stress, we conclude that interlayer sliding should not occur in the oscillatory AFM measurements confirming considerations elsewhere [7, 8, 39].

For the circular plate the two typical boundary conditions are: (a) simply supported at the single circular line around the hole rim resulting in no bending moment applied to the plate at the edges (figure 5(a)) and (b) — clamped when the edges of the plate are forced to be kept parallel to edges of the substrate surface (figure 5(b)). In the first case, the distribution of the stiffness as a function of radius \( r \) from the centre of the plate is given by [40]

\[
k_s(r) = \frac{1}{H(r)c_0a^3}
\]

where \( a \) is the radius of the plate and \( H(r) \), \( b_0 \) and \( c_0 \) expressed as

\[
H(r) = \frac{1}{\pi Da^2} \frac{2(1 + \nu_s)}{9(5 + \nu_s)} \left( r^2 - b_0a^2 + c_0a^3 \right);
\]

\[
b_0 = \frac{3(2 + \nu_s)}{2(1 + \nu_s)} c_0 = \frac{4 + \nu_s}{2(1 + \nu_s)}
\]

with the bending stiffness \( D \) defined as \( D = \frac{E_c \pi}{12(1-\nu_s)^2} \).

In case of MLG flake clamped in the edges (figure 5(b)), the reference [40] provides stiffness distribution governed by the following equation

\[
k_s(r) = \frac{16\pi Da^2}{(a^2 - r^2)^2}
\]

In the centre of the plate the stiffness is then expressed as \( k_s(r = 0) = 16\pi D/a^2 \). By substituting the parameters of the flake into the equation and using the in-plane Young’s modulus of graphene of 1 TPa [41], we obtain the calculated value of the stiffness in the centre of the plate of \( k_s = 5.94 \text{ N m}^{-1} \), that is more than twice the experimental one, \( k_s = 2.15 \pm 0.008 \text{ N m}^{-1} \) measured using the force modulation.
method explained above. At the same time, for the simply supported plate, the stiffness in the centre will be expressed as

\[ k_s(r = 0) = \frac{9\pi D(5 + \nu_s)}{2\varepsilon_0^2 \alpha^2 (1 + \nu_s)} \]  

resulting in calculated \( k_s(r = 0) = 2.35 \text{ N m}^{-1} \). We can therefore conclude that the simply supported model has better fit with the experimental results.

The equations (2) and (3) together with the relation presented in the figure 4 (with the corresponding equations in SI) allow to link the resonant frequency \( f_{CR} \) and the stiffness of the membrane with the spatial position (the radius from the centre where the probe is located) where the maximum amplitude is located. We can further extend this analysis by considering the amplitude and phase of a cantilever as driven damped simple harmonic oscillator with the resonance frequency calculated by the approach defined above. In this case, the amplitude \( A \) and phase \( \varphi \) of the response of the cantilever are expressed as

\n
Figure 6. (a) Modeling of the amplitude response \( A(r, f) \) of the CR-AFM as the function of the radius from the centre of the plate and the driving frequency \( f_d \) for the 50–69 kHz frequency range, (b) experimental CR-AFM data of the \( A(r, f) \) response for the same frequency range. (c), (d) comparison of the simulated and measured 1D profiles \( A(r) \) at the frequencies below and above contact resonance frequency for the solid contact. (e) Experimentally measured CR-AFM response in the area of the suspended MLG plate vs supported graphene, the frequency shift allows precisely determine the stiffness of the GR membrane in the particular point.
\[ A = \frac{A_0 [\omega_{CR}(r)]^2}{\sqrt{[\omega_{CR}(r)]^2 - \omega_0^2 + \frac{\omega_0^2}{Q} \omega_{dr}^2}}; \]

\[ \varphi = \tan^{-1} \frac{\omega_{CR}(r) \omega_{dr}}{\frac{1}{Q} \left( [\omega_{CR}(r)]^2 - \omega_0^2 \right)} \]  

(6)

where \( A_0 \) is the amplitude in the resonance, \( \omega_{CR}(r) = 2 \pi f_{CR}(r) \) is the circular resonance frequency of the cantilever in the contact that depends on the position \( r \), and \( \omega_{dr} = 2 \pi f_{dr} \) is the circular driving frequency, and \( Q \) is the quality factor of the cantilever in the contact. Using this formalism, we can now simulate the amplitude dependence of the CR-AFM \( A(cR_{dr}) \) that was presented in figure 3(a) and compare it to the experimental data. The results of this simulation are presented in figures 6(a), (b) and show an excellent agreement between the model and the experimental measurements. As one can see, at \( f_{dr} \) close to the frequency of contact resonance of the supported MLG \( f_{CR-R} \) (65 kHz, figure 6(d)) all suspended areas have low response, whereas at the frequency below \( f_{CR-R} \) (62 kHz, figure 6(c)) the resonance appears at the radius close to the rim—explaining the bright ring we observed in figure 2(g). Essentially, by comparing the resonance frequency of the supported and the suspended areas figure 6(e), the modelling presented in the figure 4, and calibrated cantilever stiffness, allows one to directly determine the ratio of MLG plate stiffness in this point to the cantilever stiffness \( k_c/k_s = 231 \) resulting at the membrane stiffness in this point of 42.7 \( \pm \) 0.2 N m\(^{-1}\). This figure also demonstrates that the amplitude in the supported area is higher than the one in the centre of the membrane at 66 kHz while becoming lower at excitation frequencies below 65 kHz cross-over frequency. It is useful to note that CR-AFM is well suited for mapping and quantitative measurements of stiffness of stiffer membranes, that becomes a valuable feature for smaller sub-\( \mu \)m dimensions MEMS structures of 2D\( ^{\prime} \)M’s. By using real-time mapping of the resonance frequency at each point of the sample during scan (similar to approach used in the piezo-force microscopy [42]) and analysis above, it is possible to produce high precision stiffness maps allowing direct interpretation of the internal structure in the multilayered and heterostructured 2D\( ^{\prime} \)M’s observed in figures 6(c)–(e).

4. Conclusions

In summary, here we use the combination of the low and high frequency excitation dynamic force microscopy in the frequency range from 10 kHz to 5 MHz to investigate the details of the nanomechanical behaviour of the multilayer graphene plate suspended on the micromachined substrate. In particular, the high frequency UFM mapping allowed precise determination of the geometry of the suspended region even for the relatively thick plate, as well as observation of the faults at the MLG-substrate interface. By building an analytical model of the CR-AFM in application to the elastically deformed circular plate, we were able to perform absolute measurements of the mechanical stiffness of the 2DM nanostructure and to interpret the novel contrast phenomena specific to the 2DM’s.

The excellent agreement between the experimental and modelling data and high sensitivity of the method to the internal structure of MLG opens a great possibility to investigate multilayer heterostructures of 2D\( ^{\prime} \)M’s, and the 2DM—substrate interface.

Acknowledgments

Authors acknowledge the support of Manchester-Lancaster EPSRC Graphene Now!NANO CDT, Lancaster University QTC and Lancaster Materials Science Institute. O V K acknowledges support of EPSRC Grants Nos. EP/K023373/1 and EP/G06556X/1, EU Graphene Flagship (grant number 881603), UKRI Faraday Institution NEXGENNA project and Paul Instrument Fund PI170026, c/o The Royal Society.

ORCID IDs

Marta Mucientes https://orcid.org/0000-0002-3436-5628
Adrian Peasey https://orcid.org/0000-0002-8955-1081
Oleg Kolosov https://orcid.org/0000-0003-3278-9643

References

[1] Wang P, Gao W and Huang R 2016 Entropic effects of thermal rippling on van der Waals interactions between monolayer graphene and a rigid substrate J. Phys. D: Appl. Phys. 119 074305
[2] Walker M L Weatherup R S, Bell N A W, Hofmann S and Keyser U F 2015 Free-standing graphene membranes on glass nanopores for ionic current measurements Appl. Phys. Lett. 106 023119
[3] Liu Y and Chen X 2014 Mechanical properties of nanoporous graphene membrane J. Phys. D: Appl. Phys. 115 034303
[4] Young W C and Budynas R G 2002 Stress and Strain vol 7 (New York: McGraw-Hill)
[5] Poot M and van der Zant H S J 2012 Mechanical systems in the quantum regime Phys. Rep. Rev. Sect. Phys. Lett. 511 273–335
[6] Zande A M V D, Barton R A, Alden J S, Ruiz-Vargas C S, Whitney W S, Pham P H Q, Park J, Parpia J M, Craighead H G and McEuen P L 2010 Large-scale arrays of single-layer graphene resonators Nano Lett. 10 4869–73
[7] Poot M and van der Zant H S J 2008 Nanomechanical properties of few-layer graphene membranes Appl. Phys. Lett. 92
[8] Booth T J et al 2008 Macroscopic graphene membranes and their extraordinary stiffness Nano Lett. 8 2442–6
[9] Clark N, Oikonomou A and Vijayaraghavan A 2013 Ultrafast quantitative nanomechanical mapping of suspended graphene Phys. Status Solidi B 250 2672–7
[10] Khestanova E, Guinea F, Fumagalli L, Geim A K and Grigorieva I V 2016 Universal shape and pressure inside bubbles appearing in van der Waals heterostructures Nat. Commun. 7 12587
[11] Rollier A-S et al 2005 Tensile stress determination in silicon nitride membrane by AFM characterization TRANSDUCERS, The 13th Int. Conf. on Solid-State Sensors, Actuators and Microsystems Seoul, Korea
[12] Storch I R, De Alba R, Adiga V P, Abhilash T S, Barton R A, Craighead H G, Parpia J M and McEuen P L 2018 Young’s modulus and thermal expansion of tensioned graphene membranes Phys. Rev. B 98 085408
[13] Dinelli F, Pingue P, Kay N D and Kolosov O V 2017 Subsurface imaging of two-dimensional materials at the nanoscale Nanotechnology 28 085706

[14] Tu Q, Kim H S, Oweida T J, Parlak Z, Yingling Y G and Zauscher S 2017 Interfacial mechanical properties of graphene on self-assembled monolayers: experiments and simulations ACS Appl. Mater. Interfaces 9 10203–13

[15] Mazucco R, Robinson B J, Rabot C, Delamoreau A, Zenasni A, Dickinson J W, Boxall C and Kolosov O V 2015 Surface and interfacial interactions of multilayer graphitic structures with local environment Thin Solid Films 585 31–39

[16] Ma C, Wang W, Chen Y, Arnold W and Chu J 2019 Depth-sensing using AFM contact-resonance imaging and spectroscopy at the nanoscale J. Phys. D: Appl. Phys. 126 124302

[17] Yip K, Cui T, Sun Y and Filliter T 2019 Investigating the detection limit of subsurface holes under graphite with atomic force acoustic microscopy Nanoscale 11 10961–7

[18] Ma C, Chen Y, Arnold W and Chu J 2017 Detection of subsurface cavity structures using contact-resonance atomic force microscopy J. Phys. D: Appl. Phys. 121 164301

[19] Wenting W, Wenhao Z and Yuhang C 2020 Enhancement of contact resonance AFM subsurface imaging by mass-attached cantilevers J. Phys. D: Appl. Phys. 53 215301

[20] Blake P, Hill E W, Castro Neto A H, Novoselov K S, Jiang D, Yang R, Booth T J and Geim A K 2007 Making graphene visible Appl. Phys. Lett. 91 063124–3

[21] Bosse J L, Tovee P D, Huey B D and Kolosov O V 2014 Physical mechanisms of megahertz vibrations and nonlinear detection in ultrasonic force and related microscopies J. Phys. D: Appl. Phys. 115 144304

[22] Dinelli F, Biswas S K, Briggs G A D and Kolosov O V 2000 Measurements of stiff-material compliance on the nanoscale using ultrasonic force microscopy Phys. Rev. B 61 13995–4006

[23] Robinson B J, Kay N D and Kolosov O V 2013 Nanoscale interfacial interactions of graphene with polar and nonpolar liquids Langmuir 29 7735–42

[24] Sader J E et al 2016 A virtual instrument to standardise the calibration of atomic force microscope cantilevers Rev. Sci. Instrum. 87 093711

[25] Castellanos-Gomez A, Singh V, van der Zant H S J and Steele G A 2015 Mechanics of freely-suspended ultrathin layered materials Ann. Phys. 527 27–44

[26] Yamanaka K and Nakano S 1996 Ultrasonic atomic force microscope with overtone excitation of cantilever Japan. J. Appl. Phys. 1 35 3787–92

[27] Hirsekorn S, Rabe U and Arnold W 1997 Theoretical description of the transfer of vibrations from a sample to the cantilever of an atomic force microscope Nanotechnology 8 57–66

[28] Wright O B and Nishiguchi N 1997 Vibrational dynamics of force microscopy: effect of tip dimensions Appl. Phys. Lett. 71 626–8

[29] Rossing T D and Fletcher N H 2004 Principles of Vibration and Sound 2nd edn (Berlin: Springer) p 330

[30] Sherchenkov A et al 2018 Crystallization mechanism and kinetic parameters in Ge2Sb2Te5 thin films for the phase change memory application Chalcogenide Lett. 15 45–54

[31] Dinelli F, Biswas S K, Briggs G A D and Kolosov O V 1997 Ultrasound induced lubricity in microscopic contact Appl. Phys. Lett. 71 1177–9

[32] Rabe U and Arnold W 1994 Acoustic microscopy by atomic force microscopy Appl. Phys. Lett. 64 1493–5

[33] Kay N D, Robinson B J, Fal’ko V I, Novoselov K S and Kolosov O V 2014 Electromechanical sensing of substrate charge hidden under atomic 2D crystals Nano Lett. 14 3400

[34] Kolosov O and Yamanaka K 1993 Nonlinear detection of ultrasonic vibrations in an atomic-force microscope Japan. J. Appl. Phys. 32 1095–5

[35] Yuya P A, Hurley D C and Turner J A 2008 Contact-resonance atomic force microscopy for viscoelasticity J. Phys. D: Appl. Phys. 104 074916

[36] Tetard L, Passian A and Thundat T 2010 New modes for subsurface atomic force microscopy through nanomechanical coupling Nat. Nanotechnol. 5 105–9

[37] Liu Z, Zhang S-M, Yang J-R, Liu J Z, Yang Y-L and Zheng Q-S 2012 Interlayer shear strength of single crystalline graphite Acta. Mech. Sin. 28 978–82

[38] Reguzzoni M, Fasolino A, Molinari E and Righi M C 2012 Friction by shear deformations in multilayer graphene J. Phys. Chem. C 116 21104–8

[39] Zandiatashbar A, Lee G-H, An S J, Lee S, Mathew N, Terrones M, Hayashi T, Picu C R, Hone J and Koratkar N 2014 Effect of defects on the intrinsic strength and stiffness of graphene Nat. Commun. 5 3186

[40] Young W C, Budynas R G and Sadegh A M 2002 Roark’s Formulas for Stress and Strain vol 7 (New York: McGraw-Hill)

[41] Lee C, Wei X, Kysar J W and Hone J 2008 Measurement of the elastic properties and intrinsic strength of monolayer graphene Science 321 385–8

[42] Jesse S, Maksymovych P and Kalinin S V 2008 Rapid multidimensional data acquisition in scanning probe microscopy applied to local polarization dynamics and voltage dependent contact mechanics Appl. Phys. Lett. 93 112903