

Chapter 2

Background

2.1 2D Materials

Since the initial isolation of graphene there have been many successful attempts to observe 2D allotropes of other materials such as boron nitride and MoS_2 . As the layers of atoms in these materials are bound weakly to one another through van der Waals interaction it is possible to easily isolate and study them in their own right. Whilst all of these materials form two-dimensional films, and in many cases have similar atomic structures, they exhibit a wide range of behaviours. This wide range of behaviours allow atomic devices to be constructed that are only a few nm thick, here we study the basic properties of the three main vdW solids studied in this thesis; graphene, h-BN and MoS_2 .

2.1.1 Graphene

Graphene is a two-dimensional hexagonal structure, formed from the combinations of the s and $p_{x,y}$ orbitals to form a hybrid σ bond between three other carbon atoms leaving the p_z or π orbitals out of plane. It is these out of plane orbitals that form a basis for the electronic and chemical behaviour of graphene. An illustration of these bonds and the stacking structure of graphene is shown in Fig. 2.1.

2.1.1.1 Mechanical Properties

The Young's modulus E of graphene has been determined theoretically [1–4] and found experimentally [5, 6] to have a value of approximately 1 TPa. There have been other studies that have found the Young's modulus of graphene to be less than the widely accepted value of 1 TPa [7]. However the value presented for E from that case is inferred by fitting experimental data to the expected behaviour of a doubly-clamped beam, where the assumptions made may present a significant source of error.

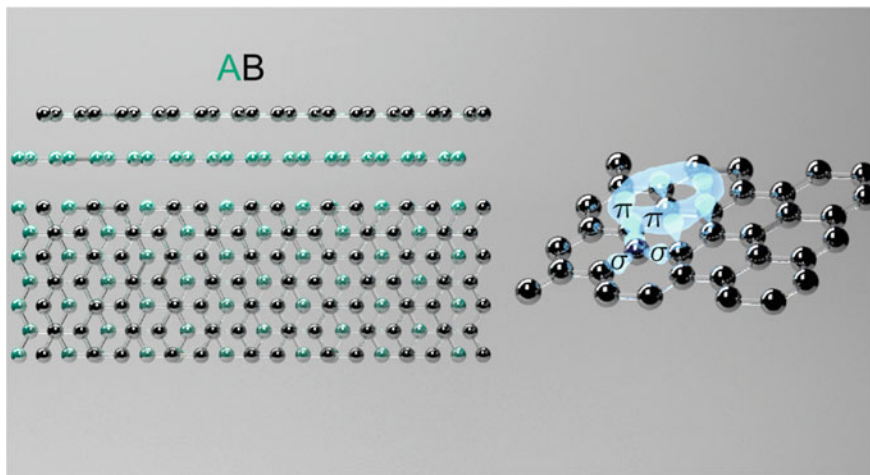


Fig. 2.1 The atomic and stacking structure of graphene where the preferred stacking is AB. The nature of the bonds in graphene is also shown where the hybrid in-plane σ bonds provide the strength of graphene and the π bonds allow for its great electrical conductivity. We show the bottom layer as light green and the top layer as black to more easily discern the stacking structure

The Young's modulus of a material, that is its stiffness in the elastic limit, is only one way of characterising its mechanical properties. To understand at what point a material begins plastic deformation one must consider the yield strength. For graphene this has been estimated [8] to be between 80–90 GPa. Beyond the yield strength is the ultimate tensile strength, which is the maximum stress the material can sustain before failure. The ultimate tensile strength for graphene has been calculated to be approximately 120 GPa for a perfect monolayer [8, 9], this translates into roughly 10% of the Young's modulus and is one of the highest ever observed.

2.1.1.2 Optical Properties

Monolayer graphene has been found to absorb 2.3% of red light [10] and 2.6% of green light [11], a surprisingly high absorbance for a material which is only one atom thick. The difference in these figures was expected to be due to some experimental uncertainty as the absorbance of graphene depends only on the fine structure constant, i.e. how light interacts with electrons [10]. By increasing the number of graphene layers one adds 2–3% of to the optical absorption each time. The absorption coefficient has also been found to change depending on the intensity of light incident on graphene. This effect is known as saturable absorption. The threshold for saturable absorption has been measured experimentally and calculated theoretically where a wide range of values have been found. In some experimental studies of monolayer and multilayer graphene the threshold was found to be as low as 0.53 MW cm^{-2} [12] for 100 fs pulses and as high as $250 \pm 80 \text{ MW cm}^{-2}$ [13]. Taking

the minimum value of 0.53 MW cm^{-2} for a spot size of $\approx 1 \text{ }\mu\text{m}$ diameter we see that this translates to a threshold laser power of $P_{th} = 5.3 \text{ mW}$, above any values of laser power incident on graphene used in our experiments by a factor of approximately 8, therefore saturation is not expected to be an issue. The refractive index for graphene is independent of the wavelength in the visible range, we therefore quote the value for $\lambda = 635 \text{ nm}$ ($\text{RI} = 2.73 - 1.35i$ [14]) as this is the laser wavelength used in this study. Graphite has also been found to exhibit optical birefringence, that is, a difference in the refractive indices in the in-plane and out-of-plane directions [15].

2.1.1.3 Electrical Properties

Graphene is known to be a semi-metal [16], that is the valence and conduction bands touch with no overlap. This point of zero overlap is called the Dirac point and at this point in k -space we see a wealth of interesting and useful physical phenomena. The density of states at the Dirac point is 0 therefore for pristine graphene where there are no sources of doping the Fermi level will sit in this zero density of states region and the conductivity will be extremely low. In practice this is not the case as there is always some source of doping whether it is intentional, e.g. through a back-gate voltage, or accidental, e.g. by interaction with the substrate and any electrostatic charge present. For this reason in our experiments we model graphene as a metal. It should also be noted that due to the linear dispersion relation electrons and holes in monolayer graphene behave as massless Fermions at the Dirac point thus greatly increasing the electron/hole mobility.

2.1.2 Hexagonal Boron Nitride (h-BN)

Boron nitride has many allotropes just like carbon, including a two-dimensional layered structure similar to graphene called hexagonal boron nitride (h-BN). In this hexagonal formation each nitrogen atom is bonded to 3 other boron atoms and vice versa. However, as with graphene these bonds are purely covalent and the boron-nitrogen bonds form a partly covalent, partly ionic bond [17]. The bond lengths have been measured to be $1.421 \text{ \AA}$ in graphene and $1.446 \text{ \AA}$ in h-BN [18], a difference of approximately 1.7%. This slight discrepancy between the two lattice constants is what leads to the Moiré pattern formation when graphene is aligned on a h-BN substrate, a topic which is discussed in more detail in succeeding sections and 4.2. The most stable form of h-BN is believed to be the AA' [19] stacking which means that each boron has a nitrogen above and below it as can be seen in Fig. 2.2.

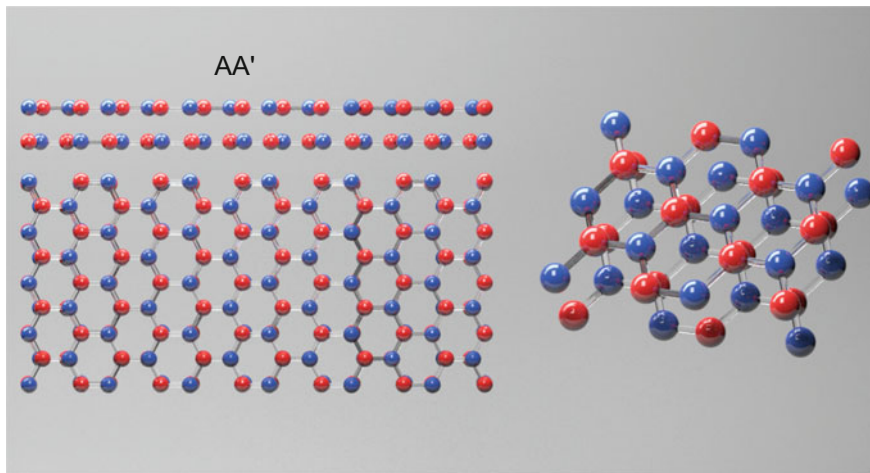


Fig. 2.2 The atomic and stacking structure of h-BN. Here we show the most stable stacking structure, AA', where a boron atom sits directly on a nitrogen atom and vice versa

2.1.2.1 Mechanical Properties

Being of a similar structure to graphene, hexagonal boron nitride also exhibits high mechanical stiffness. The values found for the in-plane elastic modulus of h-BN are 716 GPa [8] and 811 GPa [20], comparable to that of graphene. The Poisson ratio for h-BN was also found to be similar to that of graphene ($\nu_{h-BN} = 0.18$ [21] and $\nu_{gr} = 0.194$ [22]). We also quote the yield strength and ultimate tensile strength for monolayer h-BN as 70–85 GPa (estimate) [8] and 88–120 GPa [8, 23] respectively.

Whilst there is much focus on the high in-plane stiffness of graphene and h-BN it is also worth mentioning the out-of-plane elastic properties. The out-of-plane elastic constants will play a role when the sample is much thicker than a monolayer and beam bending becomes the dominating behaviour, not membrane behaviour (i.e. stretching). The out of plane elastic modulus E_3 for h-BN, again similar to that of graphene, is calculated as $E_3 = 38$ GPa [21].

2.1.2.2 Electrical Properties

Whilst graphene is a direct zero-gap semiconductor or semi-metal, h-BN has a large, indirect band-gap of 5.955 eV for indirect excitons and 6.08 eV for single particles [24]. Therefore under most experimental conditions h-BN will be electrically insulating. This insulating behaviour has made h-BN an attractive substrate, encapsulating and dielectric material for graphene and other 2D-material based devices [25–27].

2.1.2.3 Optical Properties

Whilst there is not a wealth of literature on the refractive index of h-BN perpendicular to the plane, we report several values for n in the visible range, unless otherwise stated, of approximately 2.2 [28], 1.91–2.05 ($\lambda = 110 - 550 \mu\text{m}$) [29], 1.22 [30] and 1.85 [31]. The imaginary part of the refractive index or extinction coefficient k approaches 0 in all of the above studies. Like graphene, h-BN also exhibits some degree of birefringence where the refractive index parallel to the layers: between 2.00–2.16 ($\lambda = 110 - 550 \mu\text{m}$) [29]. In addition to this the refractive index was calculated theoretically in the visible range [30] and was found to vary from 1.22 to approximately 1.5 between the out of plane and in-plane indices.

2.1.3 Molybdenum Disulphide MoS_2

Molybdenum disulphide is a part of the family of van der Waals solids like graphene and h-BN and, like graphene and h-BN, has long been used as a solid lubricant because of these weak interlayer vdW bonds [32]. Whilst MoS_2 belongs to the family of vdW solids it also belongs to another sub-group called the transition metal dichalcogenides (TMD's) which take the format of TX_2 where T is a transition metal and X is either sulphur, selenium or tellurium. The TMD's are different in that the atoms are not arranged in a purely two-dimensional plane, as a result there are different possible arrangements of the atoms. For MoS_2 there are a number of phases, however we consider two called $1T$ and $2H$ MoS_2 , seen in Fig. 2.3. The two exhibit different electrical properties with $1T$ being metallic and $2H$ being a direct-gap semiconductor in monolayer form [33]. The phase of MoS_2 that we shall refer to in the rest of this thesis is the semiconducting phase, $2H$.

2.1.3.1 Mechanical Properties

The in-plane elastic modulus of MoS_2 has been measured experimentally at a value of 330 ± 70 GPa [34], 270 ± 100 [35], 210 GPa [36] and calculated theoretically at a range of values from 128.75 GPa [37]. Values reported for the ultimate tensile strength have been given as an average of 23 GPa or approximately 10% [35]. No data on the yield strength was found in the literature.

Whilst MoS_2 has a relatively high in-plane stiffness, although not as high as graphene or h-BN, it also has a much higher out of plane stiffness than either graphene or h-BN, measured at a value of approximately 160 GPa [21]. This is roughly 4 times higher than that of graphene or h-BN and may be due to a higher vdW bonding strength between the layers.

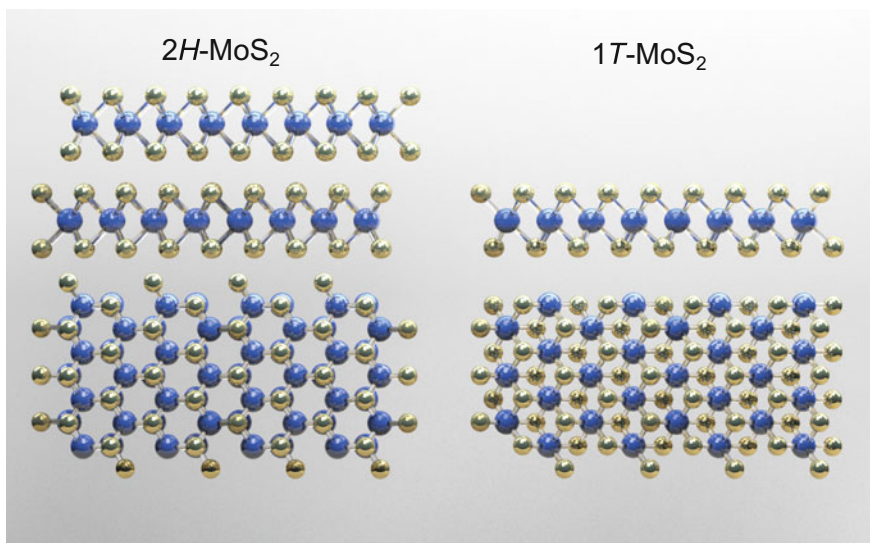


Fig. 2.3 The structures of $2H$ and $1T$ MoS_2 . The stacking of $2H$ MoS_2 is such that Mo atoms sit only directly above S atoms and vice versa. The stacking of $1T$ has a simple AA stacking so each layer is directly above and below other layers

2.1.3.2 Electrical Properties

As mentioned in previous sections $2H$ - MoS_2 is a direct band-gap semiconductor as a monolayer but transitions to an indirect gap semiconductor for thicknesses greater than this. The band-gap in the monolayer regime is approximately 1.8 eV [38] and for bulk MoS_2 the indirect band-gap is 1.29 eV [39].

2.1.3.3 Optical Properties

Experimental studies into the value of the refractive index n and the extinction coefficients k of thin MoS_2 have shown that n varies between 5–7 over the visible range whereas the extinction coefficient k varies between 0–3, being higher at shorter wavelength and approaching 0 for red light [40]. Therefore to model the optical properties of MoS_2 the refractive index will need to be considered as wavelength dependent.

2.1.4 Optical Visibility of 2D Materials

Whilst only an atom or a few atoms thick, the class of 2D materials are surprisingly easy to identify with optical microscopy, even with the naked eye for large flakes. One

trick to increase the optical contrast of these atomic layers is through using a specific thickness of substrate on which the flake is to be placed. By selecting a thickness of SiO₂ on top of Si such that the conditions for interference of the incoming light are affected most by the additional path length provided by the 2D material, the optical contrast can be maximised.

There have been several studies on the affects of substrate on the optical visibility of graphene and other 2D materials, varying in complexity [40–44]. The simplest treatment that describes the visibility of graphene and other 2D materials on an Si/SiO₂ substrate is through analysing the Fresnel interference from a beam of light incident on the graphene and normal to the surface. This approach was first performed by H. Anders [45]. The Fresnel interference approach assumes light incident normal to the plane so that light reflected will be along the same path.

The equation produced by H. Anders [45] is shown below to give the portion of light reflected from an SiO₂/Si substrate

$$r_{SiO_2} e^{i\epsilon_{SiO_2}} = \frac{r_4 + r_3 e^{-i\Delta_2}}{1 + r_4 r_3 e^{-i\Delta_2}} \quad (2.1)$$

Where $r_4 = (n_0 - n_2)/(n_0 + n_2)$ is the relative refraction constant between air (n_0) and SiO₂ (n_2). Here r_3 is the relative refraction between the SiO₂ and the silicon beneath. The symbol $\Delta_n = 4\pi n_n d_n / \lambda$ represents the additional path the beam takes passing through a medium with refractive index n_n and back. Here λ is the wavelength of light used and d_n is the thickness of the medium.

To calculate the portion of reflected light for the case of SiO₂ on Si, as Eq. 2.1, with the addition of a thin layer of additional material, such as graphene or other 2D material, the equation becomes rather more complex. However through a clever technique devised by both [46, 47], seemingly independently, one can use the case of a 3 layer system such as Eq. 2.1 to deduce the case for a 4-layer system. Whilst this derivation is rather long we quote the result also presented in [45]

$$r_{gr} e^{i\epsilon_{gr}} = \frac{r_1 + r_2 e^{-i\Delta_1} + r_3 e^{-i(\Delta_1 + \Delta_2)} - r_1 r_2 r_3 e^{-i\Delta_2}}{1 + r_1 r_2 e^{-i\Delta_1} + r_2 r_3 e^{-i\Delta_2} + r_1 r_3 e^{-i(\Delta_2 + \Delta_1)}}. \quad (2.2)$$

Where r_1 and r_2 are the reflection coefficients for the air/graphene and graphene/SiO₂ interfaces respectively. To calculate the contrast C we use Eqs. 2.1 and 2.2 in the following way similar to [44]

$$C = \frac{|r_{SiO_2} e^{i\epsilon_{SiO_2}}|^2 - |r_{gr} e^{i\epsilon_{gr}}|^2}{|r_{SiO_2} e^{i\epsilon_{SiO_2}}|^2} \quad (2.3)$$

By plotting Eq. 2.3 for varying λ and oxide thickness d_2 we obtain the results shown in Fig. 2.4.

We see that for oxide thicknesses of approximately 90 and 290 nm the contrast is largest in the green wavelength region. Therefore we pick 290 nm oxide thicknesses

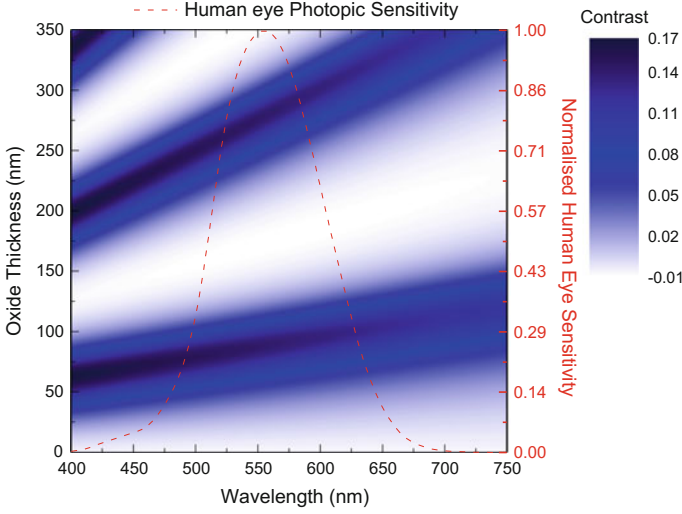


Fig. 2.4 The optical contrast of graphene on an Si/SiO₂ substrate as a function of the incident wavelength of light and the oxide thickness. The optical contrast is not seen to increase above 18%. On top of this plot we show the typical photopic sensitivity of the human eye in well-lit conditions which was taken from CIE (International Commission on Illumination) $V_M(\lambda)$ [48, 49] with the corresponding y-axis shown in red

throughout this thesis due to their commercial availability. For the implementation of Eqs. 2.1 and 2.2 we use the wavelength dependant refractive indices for Si and SiO₂, the refractive index of graphene is not dependant on wavelength and only depends on the fine structure constant, for this we use a refractive index of $2.73-1.35i$ [14]. Including the extinction coefficient for graphene and silicon ensures that we account for any absorption of the materials.

2.2 Nanoelectromechanical Systems (NEMS) from Graphene and Other 2D Materials

In this section we discuss some of the NEMS fabricated from graphene and other 2D materials in literature. We focus exclusively on the literature around resonator-type devices studying both the operating characteristics of such devices and the techniques used in understanding them (Fig. 2.5).

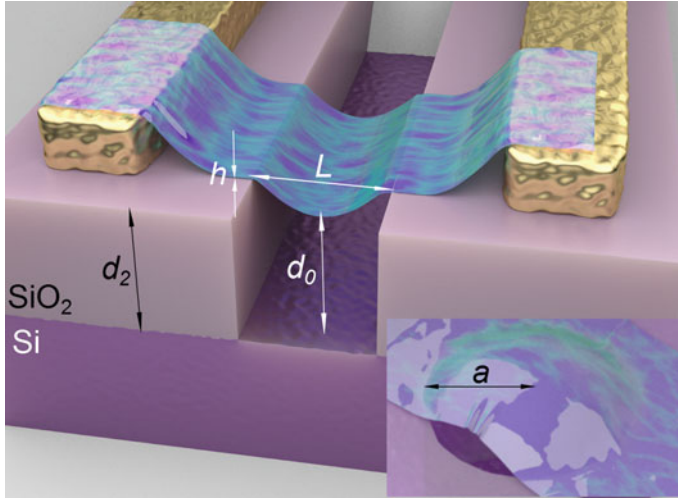


Fig. 2.5 The variables used in the characterisation of both a beam-like resonator and a drum-resonator (shown inset). Where L is the length of the suspended region, h the material thickness, d_2 the oxide layer thickness, d_0 the gap between the 2D material and the substrate and a the radius of a drum-type resonator

2.2.1 Electrostatic Actuation of Graphene Resonator Devices

Throughout this work we are primarily interested in developing methods to study the behaviour of NEMS resonators based on 2D materials. To do this we need to be able to, with a good degree of accuracy, ascertain properties of the resonators such as amplitude, resonant frequency and the effects of damping on the resonators. To be able to do this we give a theoretical basis with which one can compare any experimental results for validation.

To understand firstly the amplitude response of a resonator we start with the case of a doubly-clamped beam. The formula for the deflection at the centre of such a system is given below

$$\delta = \frac{\eta L^4}{384EI} \quad (2.4)$$

Where η is the force per unit length, L the length of the beam, E the Young's modulus and $I = wh^3/12$ is the area moment of inertia with respect to the direction in which the beam is suspended, w and h are the width and thickness of the beam. The electrostatic distributed load, η , can be approximated by considering the case of a parallel plate capacitor [50] and taking the derivative with respect to the distance between the plates

$$\eta = \frac{F}{L} = \frac{1}{2L} \frac{\partial C}{\partial z} V^2 \quad (2.5)$$

Where combining Eqs. 2.4 and 2.5 we obtain the following formula for the amplitude of vibration of a doubly clamped beam subjected to a uniform electrostatic load

$$\delta = \frac{\epsilon_0 \epsilon_r L^4 V^2}{32 E h^3 d_2^2} \quad (2.6)$$

Where ϵ_r is the relative permittivity of the material between the beam and the back-gate and d_2 is the distance between the beam and the back-gate (modelled as the oxide layer thickness). The approximation of the distance between the graphene and the back-gate being equal to the oxide thickness d_2 is valid for thick materials however for much thinner material, such as a monolayer, it is important to incorporate the sagging into the trench of the monolayer which was found to be as much as 100 nm. To obtain an approximation of the amplitudes we implement Eq. 2.6 for the specific case shown in Fig. 2.6.

Figure 2.6 shows the peak amplitude of the resonator type devices detailed. To understand how this matches with the proposed methods of measuring the electrostatic actuation with an AFM, we quote the typical noise floor for vertical measurements of around 10 pm.

While we also wish to map the amplitude response of resonator type devices we also wish to understand how the resonant frequency behaves. For this we use the following formula to approximate the resonant frequency of a doubly-clamped beam given by [50]

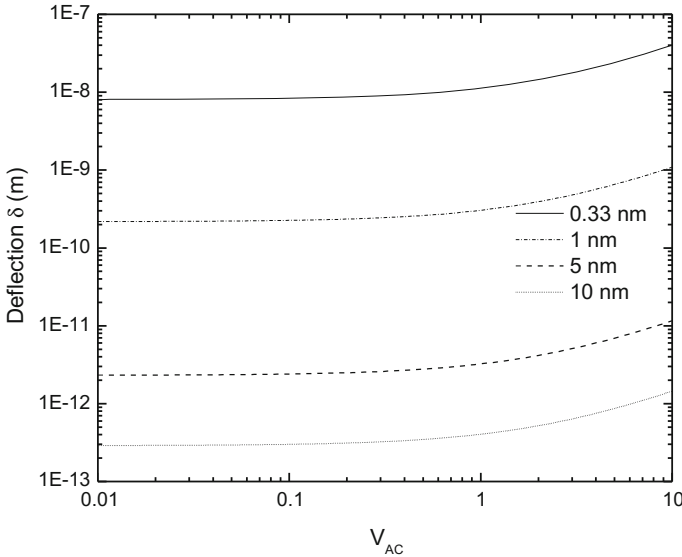


Fig. 2.6 The amplitude at the centre of the resonator for varying thicknesses of graphene ($E = 1.153$ TPa [22]) shown as a function of the applied V_{AC} voltage where the following resonator values are used: $L = 300$ nm, $\epsilon_r = 1$, $V_{DC} = 5$ V, $d_2 = 290$ nm

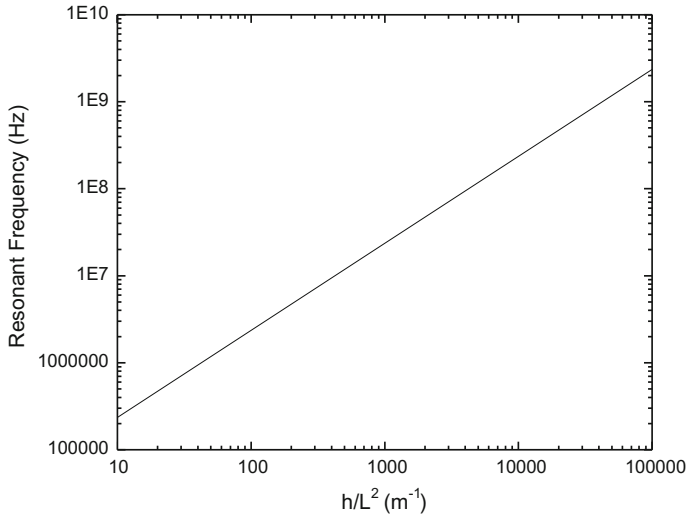


Fig. 2.7 The resonance frequency for a doubly clamped beam of graphene/MLG ($E = 1.153$ TPa [22], $\rho = 2200$ kg/m³ [52]) as a function of h/L^2 assuming no tension

$$f_0 = \left(\kappa \left(\frac{E}{\rho} \right)^{1/2} \frac{h}{L^2} \right)^2 + A^2 0.57 \frac{\Gamma}{\rho L^2 w h} \quad (2.7)$$

Where κ is the clamping coefficient and is shown to be 1.03 for a beam clamped on both ends [51] and Γ is the tension present in the beam. We then plot the resonant frequency of such a system as a function of h/L^2 (assuming $\Gamma = 0$) shown in Fig. 2.7.

The Eq. 2.7, holds for materials where bending is the primary mechanism. This is not always the case as for thin materials and devices driven at high amplitude membrane behaviour may become more dominant i.e. stretching (Fig. 2.8).

2.2.2 Damping Mechanisms Present in 2D NEMS

The first and most obvious damping mechanism present in not only graphene and 2D NEMS but all MEMS is damping due to the air in the ambient environment. Firstly, and while not strictly a damping mechanism, it was observed that if a resonator is deposited over a hole in the substrate under ambient conditions and then studied in vacuum, an increase in the resonant frequency is seen. This has been observed experimentally [53] where the excess pressure of the air in turn induces tension on the beam resulting in an upwards shift in the resonant frequency. In the same study Lee et al. distinguish between two damping mechanisms. The first regime, for the devices used in the study [53], is for pressures over approximately 60 Torr. This damping

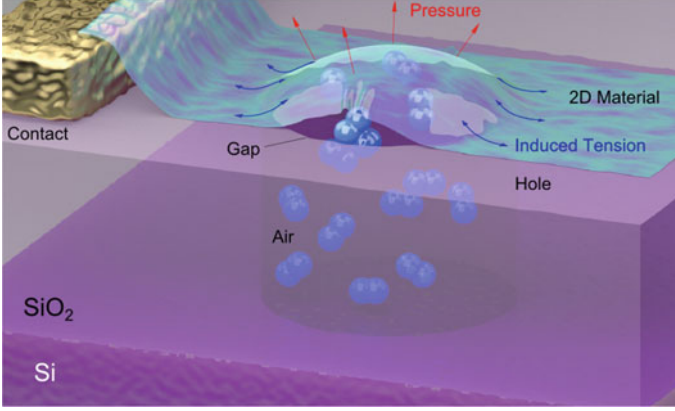


Fig. 2.8 Illustration of some of the mechanisms present when depositing a device over a hole and operating under vacuum. If the device is fabricated under atmospheric pressure then this pressure will act to increase the tension in the suspended material at low outside pressure. This is seen as an increase in the resonant frequency. Additionally we show that devices with small gaps allow air to enter or escape the otherwise covered hole as described in the main text

regime is called free molecule flow (FMF) damping and the Q -factor, a measure of how quickly a particular resonance can dissipate energy, has a characteristic $1/p$ dependence as can be seen below [54]

$$Q_{FMF} = \frac{\rho h \omega_0}{4} \left(\frac{\pi R T}{2m} \right)^{1/2} \frac{1}{p} \quad (2.8)$$

Where ρ is the density, R is the gas constant $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, T temperature, m the mass of the air molecule, h the thickness of the beam and ω_0 the angular resonant frequency of the device. The physical mechanism for FMF damping is through the collision between the resonator and the molecules present in the atmosphere.

Whilst not strictly a damping mechanism it was also reported that on devices where there was a partial covering of the hole to make an incomplete drum there was an additional tension present in the device [53]. This scenario only occurred where the mean-free path (MFP) of the air was larger than the opening in the partially covered drum, thereby not allowing air molecules to enter the cavity at a rate that could be seen over the course of the experiment. Upon an increase in pressure and thus decrease in MFP the pressure was able to equilibrate, removing any tension in the beam caused by the pressure difference.

A topic discussed in the context of traditional beam-like resonators is the effect of viscous damping [55–57]. One figure of merit to understand whether viscous damping has a significant effect on a device's performance is through the Knudsen number given below

$$Kn = \frac{\lambda_{MFP}}{l} = \frac{k_B T}{\sqrt{2} \pi \ell^2 p l} \quad (2.9)$$

Where ι is the air molecule diameter and l the characteristic length of the device. Various values for the value of Kn at which viscous damping becomes important have been given: $Kn < 0.1$ [56] and $Kn < 0.01$ [58].

There are several other damping effects which are special to the case of graphene resonators. One of the main effects observed is the effect of the van der Waals forces on the morphology of the resonator devices. It has been proposed [59, 60] that graphene and similar carbon nanotubes can effectively adhere to the side walls of the trench etched into the substrate through vdW forces giving an induced tension in the device and therefore an increase in the resonant frequency.

2.2.3 *Beam-Membrane Mechanical Transition in 2D Materials*

In the study of resonator type devices there are, broadly, two regimes of mechanical behaviour which are exhibited by devices. The first of these two regimes is beam bending which is associated with compression along one surface and extension along the opposite, i.e. a bending moment is set up. This mechanism depends on a wide range of the mechanical properties of the material such as shear modulus G and out-of-plane elastic modulus E_3 amongst others. The second mechanism is membrane behaviour whereby stretching in-plane of the material contributes to the overall response of the system. For graphene, with an extremely high in-plane elastic modulus but a relatively low out-of-plane stiffness we expect membrane behaviour to dominate, especially for relatively thin samples. To understand whether we expect beam or membrane behaviour to dominate the stiffness characteristics of our resonators we employ the parameter Π shown in Eq. 2.10 [61]. This equation describes the behaviour of a material suspended over a hole.

$$\Pi = [12(1 - \nu^2)]^{3/2} \left(\frac{Fa^2}{Eh^4} \right) \quad (2.10)$$

where ν is the Poisson ratio, E the elastic modulus, F the applied load, a the radius of the suspended material and h the film thickness. We implement Eq. 2.10 and use the values Π given [61] to determine the various regimes.

The graph in Fig. 2.9 shows that for low loads the graphene resonator will be in the plate regime however for higher loads applied to the centre we see a departure from plate behaviour to that of a beam/membrane.

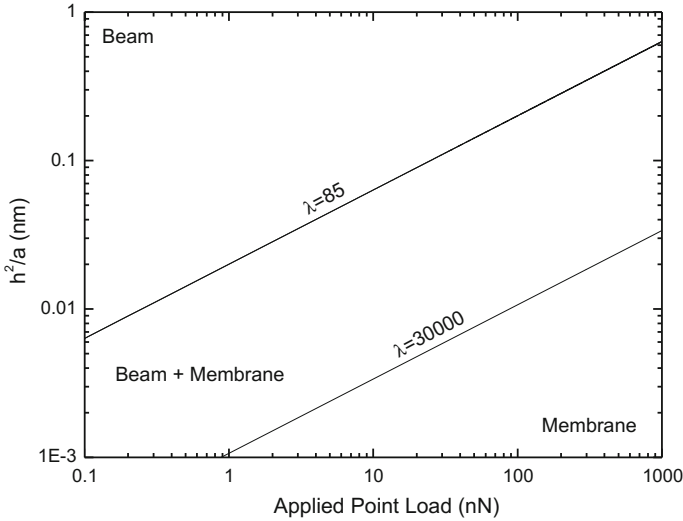


Fig. 2.9 We show the three main regions of behaviour for a graphene resonator: beam, membrane and a mixture of the two. The regions shown hold for a circular arrangement of suspended graphene/MLG ($E = 1.15$ TPa, $\nu = 0.194$) clamped at the edges with an applied load at the centre

2.2.4 Characterisation of NEMS Based on 2D Materials

2.2.4.1 Optical Readout Techniques

For typical graphene resonators suspended over either a trench or a hole etched into an SiO_2 substrate it is possible to use a simple setup where two lasers are used, one for the actuation, another for detection. The laser light incident on the sample, as discussed in earlier sections, undergoes interference when reflected from the underlying Si/SiO_2 , where the total intensity of the light output depends on the position of the suspended graphene or 2D material. This is a setup adopted in various studies of graphene NEMS [50, 59, 62–64] and MoS_2 NEMS [26, 53, 65]. The only study to explicitly state the sensitivity of the measurement system found values in the range of 30.2–243.1 $\text{fm/Hz}^{1/2}$ [26], these values depended greatly on the devices themselves. For the study [26] a He-Ne laser ($\lambda = 632.8$ nm) was incident on the MoS_2 resonator.

There have also been various theoretical analysis of the optical detection of metallized NEMS [66] where near-field effects are considered, showing a shot-noise limited detection down to 7 $\text{fm/Hz}^{1/2}$ with the use of a Michelson interferometer. Near-field effects become dominant where the width of the resonator beam is of the order of the wavelength of light and diffraction around the edges of the beam plays a non-negligible role.

In other studies that use near-field effects for the optical detection of graphene NEMS [67], sensitivities of 260 $\text{fm/Hz}^{1/2}$ have been reported. In this study evanes-

cent waves, which couple to a graphene resonator, are measured by placing a glass microsphere in close proximity to the device whilst laser light passes nearby. The resolution of this system was found to be limited by the Q factor of the microsphere used, with large room for improvement reported.

Optical readout techniques predominantly make use of a laser as the primary sensing method. This has issues in that lasers provide noise in both the amplitude of the output beam and also the phase. There is also mode-hopping where temperature changes can result in quick variations in the wavelength. With optical interferometers there can also be a great deal of noise associated with the drift of one arm with respect to the other.

Another issue that is considered in studies [26, 50] is the heating of the device due to the focused laser beam incident on it. For this it has been shown that for laser powers of <0.6 mW ($\lambda = 632.8$ nm) there was negligible heating of isolated MoS₂ resonators [26]. The effect of the laser heating is however thought to be greatly dependent on both the flake thickness and also whether the flake is contacted electronically as this will provide a cooling channel.

2.2.4.2 SPM Based Measurements of Resonator-Type Devices

One of the primary downsides for the techniques of optical and electrical readout is that one is limited in the lateral resolution with which one can probe the characteristics of the devices. With optical techniques one is held back by the diffraction limited laser spot size, meaning that devices much smaller than the wavelength will be subjected to near-field effects along with a greatly diminished signal. For the electrical readout one can sense the actuation of extremely small devices but again a lateral resolution is not available. To combat this limit of resolution for both optical and electrical techniques, attention has been turned to the use of scanning probe microscopy. With a lateral resolution of a few nm, depending on tip size, one should be able to probe the spatial properties and functions of even the smallest NEMS.

The direct application of SPM to high-frequency graphene resonators was performed by Garcia-Sanchez et al. [68]. In this particular study a contact mode cantilever is scanned across the surface of the resonator-type devices. During the scanning the graphene is actuated via external electrodes at high frequency. As the resonant frequency of the contact mode cantilever is typically of the order of 10 kHz, much lower than the resonant frequency of the graphene NEMS, the cantilever becomes inertially stiffened and is not sensitive to the individual vibrations. To overcome this Garcia-Sanchez et al. apply a sinusoidal modulation signal to the resonator at a much lower frequency. It is then possible to extract the amplitude of this envelope signal and thus the amplitude of the resonator. One additional trick used in this study is to tune the modulation frequency to that of the contact resonance of the cantilever, with the idea that the increase in amplitude will provide a much greater signal. One downside to this approach may lie in the use of the cantilever's contact resonance. If the Q -factor is high then any change in the contact resonant frequency, through a change in the sample stiffness, will result in a shift-along the resonance curve and a

sharp decrease in the measured amplitude which would not be representative of the sample motion.

One additional drawback to this technique is the difficulty of implementation, as NEMS often require operation in a vacuum, preferably at low temperature to obtain the best performance characteristics. This is difficult for all but the most sophisticated AFM systems. However despite this Garcia-Sanchez et al. managed to image graphene NEMS in ambient conditions and extract high-resolution maps for the vibrational amplitude of the devices studied. From this they were able to deduce different eigen modes of the resonator beams as well as uncover that the amplitude distribution was highly irregular and depended greatly on the local stresses within the beam. It was also found that a new set of eigen modes where the amplitude was greatest at the edges of the device, rather than the centre, were present. Whilst this method is able to measure the high frequency amplitude maps of graphene NEMS it is not possible to measure the high frequency time-dependant phenomena which would be necessary for measuring the response time of such devices.

In another study by Rivas et al. [69] an atomic force microscope is used to map the amplitude response of traditional tuning forks manufactured from LiNbO_3 with resonant frequencies in the 50–60 kHz range. In this particular study the AFM was operated in contact mode with cantilevers with a high resonant frequency 70–300 kHz, higher than that of the MEMS devices studied. In this case there is no need for any modulation techniques to overcome the high-frequency detection barrier so the case is rather more simple. In this study the effect of the cantilever on the resonant amplitude of the device was studied, with loads of up to $1.5 \mu\text{N}$ applied to the surface of the MEMS device. Only small changes in the amplitude response were seen. It should be noted that the dynamic stiffness of the piezoelectric tuning fork used in this case is comparable to that of the cantilever so the effects should be minimal. This is not the case as with previous studies using graphene based NEMS and MEMS [68] where the inertia of the graphene NEMS is negligible compared to that of the tip and is much more likely to be affected by its presence.

2.2.4.3 Electrical Readout Techniques

NEMS are designed to be used in conventional Si wafer processing techniques for integration into electronic circuits. For this reason it is important to understand how one can measure the behaviour of such devices electronically. To measure the response of the system electronically the suspended graphene resonator is used to form a capacitor with the back-gate electrode whereby the capacitance varies as the graphene vibrates. To do this there are usually two RF signals applied to the sample which differ by Δf . This plays on the fact that the conductance of graphene changes at high frequency so effectively acts as a non-linear mixer which will allow one to detect the properties of the system at the much lower frequency Δf [70–72].

One problem with the electrical readout technique is that it becomes extremely difficult to quantify, for example the amplitude of vibration, as the rate of change of the conductance as a function of the gate voltage must be known. The cut-off

frequency for such a system is rather higher than those of current optical or AFM techniques due to the nature of the down-mixing of the frequencies and is limited to approximately 1 GHz in current setups [72]. The limiting factor in such a case comes from the capacitance between the gold contacts and the underlying silicon.

2.3 Investigating Sample Electrical and Mechanical Properties with SPM

Throughout this work we use extensively a variety of scanning probe methods (SPM) therefore we shall introduce some of the less commonly used techniques. The three techniques we are introducing are mainly involved in the mechanical characterisation of materials and devices, each has its merits and drawbacks.

2.3.1 *Cantilever Dynamics*

To understand how the behaviour of the cantilever changes in response to particular outside influences such as tip-surface interaction, especially at higher frequencies, it is necessary to use a continuum model. For this we typically use the Euler-Bernoulli beam theory. To determine the dynamic properties of a beam using this model will employ the time-dependant model given below

$$\frac{\partial^2}{\partial x^2} \left(EI \frac{\partial^2 w}{\partial x^2} \right) = -\mu \frac{\partial^2 w}{\partial t^2} + q(x) \quad (2.11)$$

Where E is the Young's modulus, I the second moment of area, $w(x, t)$ denotes the displacement of the beam at position x along the beam, $q(x)$ denotes the distributed load on the cantilever and μ is the mass per unit length.

One particular mechanism that is of interest is the contact-resonance of a cantilever, this is the shift in resonant frequency upon contact or intermittent-contact with the sample. By studying the response of the cantilever to varying levels of tip-surface interaction it was found that higher forces translate to an increase in the resonant frequency of the cantilever [73]. In the same study it was found that higher resonant frequencies of the cantilever are much less sensitive to the tip-surface interaction, i.e. the force applied.

2.3.2 Mechanical Techniques

2.3.2.1 Force Modulation Microscopy (FMM)

Force modulation microscopy is performed whilst the AFM tip is in constant contact with the surface [74]. Then either the tip or the sample is vibrated at a frequency of typically 2–3 kHz. The reason for this frequency range is two-fold. Firstly the motion of the cantilever must be fast enough such that the feedback of the AFM is too slow to try and compensate; secondly the frequency should be lower than the contact resonance of the cantilever, this is so that the response to the material stiffness is unaffected by the cantilever resonance dynamics.

As FMM relies on the cantilever to cause an indentation to or flexing of the sample, the sensitivity of the system is limited to a range of stiffness' close to that of the cantilever. It is therefore only useful for relatively compliant samples. To extract quantitative data from FMM one can use a simplified two-spring model, where one spring is the cantilever with stiffness k_c and the other the sample with stiffness k_s , to derive an expression as seen in Eq. 2.12

$$k_s = k_c \frac{V_s}{V_h - V_s} \quad (2.12)$$

Where V_h and V_s are the FMM signals on a hard surface and the area of interest respectively. It is suggested that V_h be taken on a surface that is significantly stiffer than the cantilever such as the substrate itself in order to obtain the most accurate results.

2.3.2.2 Ultrasonic Force Microscopy (UFM)

Where FMM is unable to provide the stiffness sensitivity required, usually for stiffer samples, we use ultrasonic force microscopy as its high frequency nature allows the imaging of much stiffer materials. Ultrasonic force microscopy was invented by Kolosov and Yamanaka [75] and is an adaptation of scanning acoustic microscopy [76]. UFM allows one to probe the tip-surface interaction and therefore is affected by such properties as tip-sample adhesion and the sample stiffness. The implementation of UFM involves the application of high frequency vibrations typically 2–100 MHz [77] and is implemented by oscillating the sample or the tip (called waveguide UFM [77, 78]) with a piezoelectric transducer.

As is demonstrated in Fig. 2.10 the vibration frequency applied to the piezo is on the order of MHz whilst we apply an envelope function with a frequency of a few kHz typically. The purpose of this is to vary the piezo amplitude to find the point at which the non-linearity is reached, the additional deflection produced by the non-linear region is then present in the deflection of the cantilever at the modulation frequency.

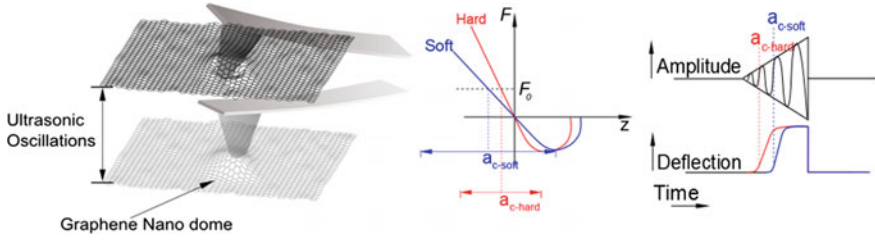


Fig. 2.10 Operation of UFM shown where ultrasonic vibrations cause the force on the cantilever to vary according to the van der Waals interaction. Softer materials require a larger vibration amplitude as shown in the difference in a_{c-soft} and a_{c-hard} . The piezo amplitude is modulated with a triangular waveform, seen on the right hand side allowing the location of the amplitude at which the ultrasonic deflection occurs to be found. This appears as a sudden increase in the deflection of the cantilever at the modulation frequency, something that is relatively easy to detect

As UFM works at frequencies much higher than the typical resonance of a contact mode cantilever, the tip does not have time to react to the vibrations applied to it. Therefore the cantilever can be thought of as being inertially stiffened. Using a point mass attached to a spring approximation, the effective spring constant of the cantilever is given by $k_c^* = m\omega^2$, which for a frequency of 4 MHz gives a stiffness of $k_c^* \approx 10,000$ N/m. This increased stiffness effectively causes the tip to indent into the sample. One may think that this would cause damage to anything but the most robust materials however during the modulation cycle contact is broken between the sample and the tip periodically thousands of times. This removes any torsional forces on the cantilever and greatly reduces the damage done to the sample.

On a final note ultrasonic force microscopy can be thought of as a near-field technique as the wavelength of the elastic waves in the sample is at best, $\lambda \approx 500$ μm , clearly too large to map nanoscale structures.

Whilst UFM has the capability to discern between areas of high stiffness it is, due to difficulties with establishing contact area, difficult to quantify these results. Dinelli et al. proposed a method by which the effective contact stiffness S_{eff} can be inferred [79]

$$S_{eff}(F) = \frac{F_2 - F_1}{a_2 - a_1} \quad (2.13)$$

Where F denotes the static force applied by the tip to the sample and a represents the amplitude at which the jump-in or additional ultrasonic deflection occurs. Subscripts 1 and 2 denote the values at two different static forces applied by the AFM tip to the surface. The image in Fig. 2.11 shows the UFM signal as a function of sample vibration amplitude.

The piezo amplitude at which the onset of the ultrasonic deflection occurs can be found through the use of an oscilloscope however it is necessary to be able to convert the applied voltage at the piezo into an amplitude, typically in nm. Whilst one can characterise the sample motion relatively easily using such techniques as laser interferometry it has been found that the piezo amplitude varies measurably over

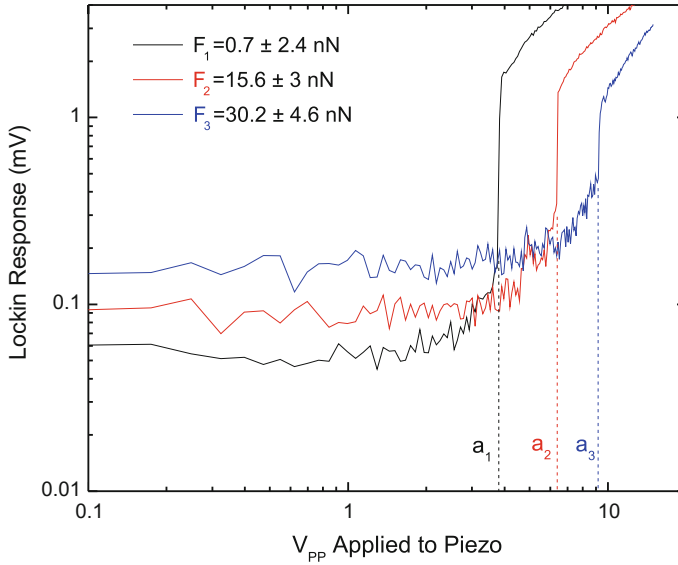


Fig. 2.11 The piezo amplitude at which the additional deflection is achieved is indicated by symbols $a_{1,2,3}$ which correspond to the three difference forces applied $F_{1,2,3}$

the scale of $100 \mu\text{m}$ on the sample [80], leading to possibly inaccurate results. To counteract this it was found that by increasing the amplitude of the sample vibrations to much higher than the jump-in amplitude the rate of increase of the piezo amplitude was equal to the increase in ultrasonic deflection [81]. From here the increase in the lockin amplifier response (given in r.m.s) can be converted to nm through the deflection sensitivity of the AFM/cantilever combined system. For a more detailed discussion on this see Sect. B.2 in the Appendix.

2.3.3 Electrical Techniques

Whilst mechanical SPM techniques are useful in ascertaining the properties of NEMS they can only provide us with one half of the story. The other half, how the NEMS interacts with its surroundings electrically, must be probed with additional SPM techniques. Here we discuss the basics behind the main techniques used for electrical characterisation.

2.3.3.1 Electrostatic Forces Acting on a Conductive Probe

When a bias is applied between two conductive materials an electrostatic charge builds up on both materials. The amount of charge that accumulates depends on the capacitance of the system and the bias applied. This build up of charge in turn causes an electrostatic force to act between the two pieces. Considering the specific case where we have two materials, one a conductive cantilever and another a silicon back gate, which can be considered conductive, we model the forces present by considering two identical parallel metallic plates given as

$$F = -\frac{\epsilon_0 V^2 A}{2(h_t + d_2)^2} \quad (2.14)$$

Where V is the DC bias between the plates, A is the surface area of the metallic plates and $h_t + d_2$ is the separation between the two plates given as the sum of the tip height and the oxide layer thickness.

Whilst the model of the conductive cantilever biased with a Si back-gate is similar to the above mentioned case it is not completely accurate. For the case of a conductive AFM probe, the cantilever itself is not perpendicular to the sample and therefore the end close to the tip will contribute more. In addition to this there are contributions to the total capacitance from the cone, tip apex and the cantilever holder. Therefore to accurately describe the behaviour of the system it is necessary to consider these contributions as is shown below [82] where F_{cl} was derived by [83]

$$F_{tip} = -\epsilon_0 \epsilon_r \pi R_t^2 V^2 \left(\frac{1 - \sin \theta}{d_2(d_2 + R_t(1 - \sin \theta))} \right) \quad (2.15)$$

$$F_{cone} = -\frac{\epsilon_0 \epsilon_r \pi V^2}{(\ln(\tan(\theta/2)))^2} \left(\ln \left(\frac{d_2 + h_t}{d_2 + R_t(1 - \sin \theta)} \right) + \left(d_2 + R_t - \frac{R_t}{\tan \theta} \right) \left(\frac{1}{d_2 + h_t} - \frac{1}{d_2 + R_t(1 - \sin \theta)} \right) \right) \quad (2.16)$$

$$F_{cl} = -\frac{\epsilon_0 w V^2}{2} \left(\left(\frac{\cos \beta}{\tan \beta} \right) \left(\frac{1}{(h_t + d_2) \cos \beta + L \sin \beta} - \frac{1}{(h_t + d_2) \cos \beta} \right) \right) \quad (2.17)$$

Where R_t is the tip radius, d_2 the separation between the tip and conducting plane given here as the oxide thickness, h_t the height of the tip/cone, θ the angle of the cone. The symbol β is the angle the cantilever makes to the surface, L and w are the length and the width of the cantilever.

From Fig. 2.12 we can see that for the case where the tip is positioned on an SiO₂/Si sample (300 nm oxide) the tip forces are extremely small and below the sensitivity of the system for even the most compliant of cantilevers. However the forces acting on the cone and the cantilever beam itself are detectable. If the sample is in contact with the insulating substrate then forces acting on the tip/cone only act to increase the force between the sample and the tip but will contribute little to the overall deflection of the cantilever.

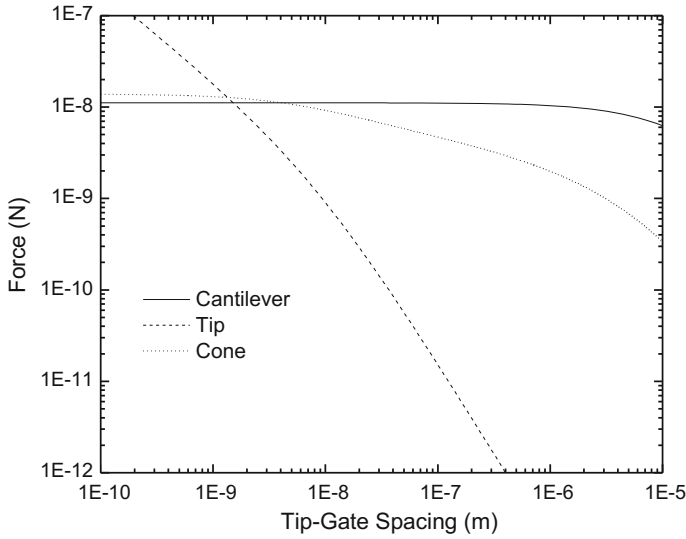


Fig. 2.12 The calculated forces acting on the tip, cone and cantilever as a function of the separation between the tip and the conducting sample. Values used are $R_t=10$ nm, $L = 500$ μ m, $w = 50$ μ m, $V = 15$ V, $\beta = 0.262$ rad, $\theta = 0.175$ rad and $h_t = 15$ μ m

2.3.3.2 Electrostatic Force Microscopy

Electrostatic force microscopy is a term given to the family of scanning probe methods which detect properties of materials such as charge density, work function and surface potential with nanoscale resolution. The basic operating principle of the family of EFM techniques is to apply an AC+DC bias between the conductive probe and the sample. The principles of which are illustrated in Fig. 2.13 where by a conductive AFM probe is scanned over a sample with a varying local electrostatic environment, such as trapped charges. The charges will act on the conductive cantilever electrostatically, this is felt as an increase in the vibration amplitude. By using a feedback loop we are able to apply a DC voltage to counteract this.

To understand the principles behind EFM and how DC voltages and electric fields are measurable at a certain frequency it is necessary to consider the back-gate and the cantilever as a capacitor. Whilst we have previously considered, in greater detail, the electrostatic forces between tip/cone/cantilever and the sample it is necessary to understand the dependence on the frequency of the system. For this we consider the more general form of the force dependence given in Eq. 2.18

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2 \quad (2.18)$$

Where the capacitance of the system is given by C , which is partially differentiated in the direction normal to the plates z . V denotes the potential difference between

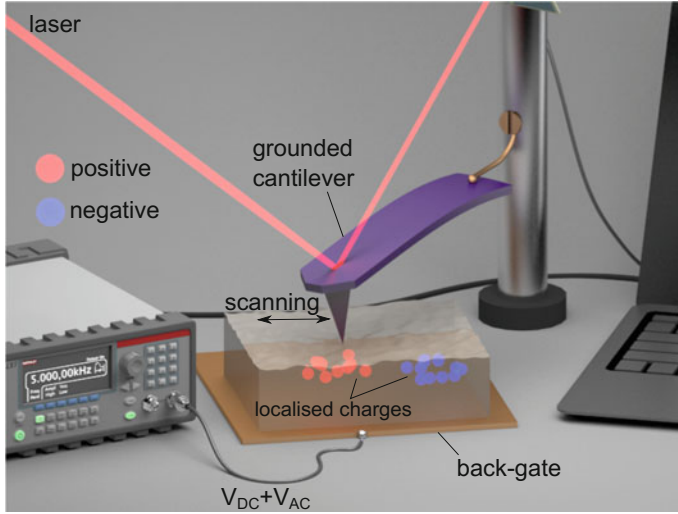


Fig. 2.13 Diagram of the basic operating principles of EFM and similar techniques. An AC+DC bias is applied between the tip and sample. Varying V_{DC} can be used to counteract local changes in surface charge density for example such as the difference between areas with a positive and negative charge. By changing the DC voltage during the scan so that no net force is seen by the cantilever and monitoring the applied DC voltage one can build a map of the local electrostatic environment

the plates. For the case of EFM one applies a DC+AC voltage between the cantilever and sample. There are however other sources of potential difference present which will depend on the sample measured such as the contact potential difference V_{CPD} and any voltage V_{SC} coming from a static charge on the surface of the material. Therefore the total voltage $V = (V_{DC} + V_{CPD} + V_{SC} + V_{AC} \sin(\omega t))$ should be input into Eq. 2.18 and the resultant equation can then be split into three components: the DC component, force at ω and 2ω given in Eqs. 2.19, 2.20 and 2.21

$$F_{DC} = \frac{1}{2} \frac{\partial C}{\partial z} ((V_{DC} + V_{CPD} + V_{SC})^2 + V_{AC}^2/2) \quad (2.19)$$

$$F_{\omega} = \frac{\partial C}{\partial z} (V_{DC} + V_{CPD} + V_{SC}) V_{AC} \sin(\omega t) \quad (2.20)$$

$$F_{2\omega} = -\frac{1}{4} \frac{\partial C}{\partial z} V_{AC}^2 \cos(2\omega t) \quad (2.21)$$

Typically EFM monitors F_{ω} for imaging however, some systems make use of $F_{2\omega}$ to measure the capacitive coupling to the sample [84]. Usually a corrective voltage is applied between the tip and the sample with the aid of a feedback loop.

This effectively removes the electrostatic forces acting on the cantilever providing a feedback signal to achieve zero electromechanical actuation, thus determining the zero total voltage.

2.3.3.3 Contact Electrostatic Force Microscopy

Whilst EFM and KPFM are conventionally non-contact mode techniques there have been efforts made to develop a contact method of electrostatic force microscopy [85, 86]. The purpose for this development is two-fold, firstly to obtain the maximum resolution of electrostatic fields on the sample and secondly to remove the coupling between topography and electrostatic interaction with the tip. However by choosing the contact regime for electrostatic force microscopy one also needs to take into account the effect of sample compliance.

2.3.4 Time-Resolved Techniques

In order to resolve time-dependant properties with an atomic force microscope one has a few options. Firstly, the direct signal from the photo-diode can be measured in real-time. One such example would be the mechanical response time of a resonator to an applied voltage. This could conventionally be done using an oscilloscope or other such device and would be an adequate solution for low frequency systems < 100 kHz. However as one progresses to higher frequency devices there are certain barriers that need to be overcome. Firstly the photodiode in the AFM has a limited bandwidth this may be in the region of a few MHz or a few tens of MHz if it is biased. As the frequency of device operation increases beyond this we start to see effects of wire capacitance in effectively filtering out the measured signal as well as unwanted inductance.

In dealing with high frequency signals one of the techniques commonly used in RF electronics is the principle of heterodyning. This is the phenomena where a fixed oscillator at frequency ω_1 is mixed through some non-linear interaction with the signal to be measured at ω_2 . Through this non-linear interaction we obtain two additional frequencies at $\omega_3 = \omega_1 \pm \omega_2$ where if ω_1 and ω_2 are chosen to be similar then one of the ω_3 will be of a suitably low frequency and will not suffer any of the effects of bandwidth limitation or the difficulty associated with detecting high frequency signals.

2.3.4.1 Heterodyne Force Microscopy (HFM)

Heterodyne force microscopy was first implemented [87] as a means of detecting the dynamic mechanical properties of materials such as visco-elastic behaviour. By using the heterodyne principle it is possible to measure the dynamic mechanical properties

of a material at high frequencies, well above those accessible to conventional SPM techniques.

HFM works by oscillating the tip and sample at two slightly dissimilar frequencies, usually in the MHz regime. Then by using the non-linear tip-surface interaction as the mixer, the two frequencies are combined. This can be demonstrated by approximating the tip-surface interaction as [87]

$$F_{ts} = kz_0 - \chi z_0^2 \quad (2.22)$$

Where $z_0(t)$ denotes the distance between tip and sample and can be thought of as the difference of the tip and sample vibrations $z_0(t) = z_t(t) - z_s(t)$ and

$$z_t(t) = A_t \sin(\omega_t t) \quad (2.23)$$

$$z_s(t) = A_s \sin(\omega_s t + \omega_s \tau) \quad (2.24)$$

where ω represents the angular frequency and $\omega_s \tau$ denotes the phase attributed to the dynamic mechanical phenomena on the sample surface, with τ being the characteristic timescale of the phenomena such as the stress relaxation in a visco-elastic material. Inserting Eqs. 2.24 and 2.23 into 2.22 we obtain the DC and low frequency terms acting on the cantilever

$$F = \chi \left[\frac{1}{2} (A_t^2 + A_s^2) - A_s A_t \cos(t(\omega_t - \omega_s) - \omega_s \tau) \right] \quad (2.25)$$

From Eq. 2.25 it can be seen that the action at the difference frequency has preserved the phase which came from the dynamic phenomena at high frequency ($\omega_s \tau$); this, combined with a known vibration amplitude of the tip, also known as the local oscillator, allows one to preserve the amplitude and phase of the response at high frequency to a more manageable lower frequency. It is important to understand the difference between the beating and mixing effects as is illustrated in Fig. 2.14.

In Fig. 2.14 we see that for a detection system limited in speed to below 1/period of the beating the total signal detected will be 0, this is not the case for mixing. Given this information one would assume that beating does not play a role in HFM however it has been shown that beating does in fact play a certain role in image contrast [88]. This is due to the real motion of the cantilever provided by the beating signal and how this feeds back into the tip-surface interaction providing an additional force. This was found to be the case for all but quadratic tip-sample interactions [88].

As all of the mixing is taking place at the tip-surface point-contact there is no need for a fast detection system to be present in the AFM. The limiting factor for this is usually the response time of the photo-diode so, provided the mixed frequency is less than this, detection should not be an issue. By monitoring the phase of the heterodyne signal one can see any changes in the dynamic response of the sample.

Whilst not a widely used technique there have been sufficient studies into the mechanisms behind the contrast in HFM. Initially it was thought that, along with

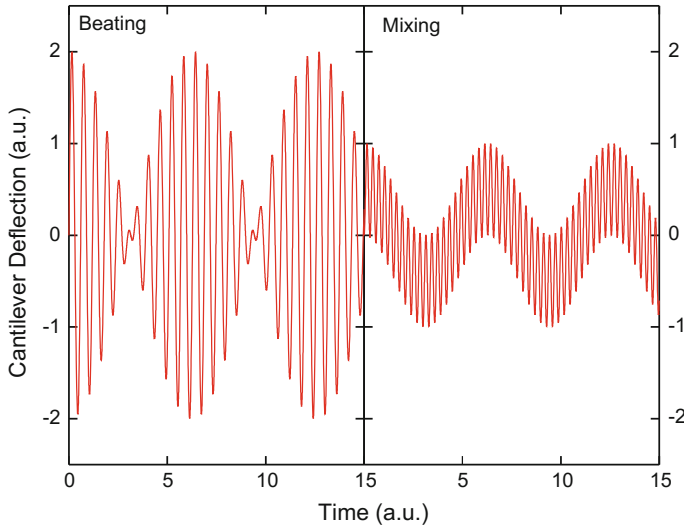


Fig. 2.14 The difference between beating and mixing is demonstrated where the beating signal is the sum of two Sine waves ($S_1 + S_2$) differing in frequency whereas the mixing is the multiplication of the same two Sine waves ($S_1 S_2$)

ultrasonic force microscopy (UFM), Rayleigh scattering was responsible for the nanoscale contrast in UFM and HFM [89]. This was later analysed quantitatively and it was found that Rayleigh scattering was several orders of magnitude smaller than what was observed experimentally [90] and was not the main cause of the contrast. In addition, it was proposed that the contrast mechanism depended on the sample type where for nanoparticles embedded in a polymer substrate the contrast was due to energy lost through the friction of the nanoparticle with the surroundings. For much stiffer samples the proposed mechanism was through a variation in the sample stiffness [90] making both HFM and UFM near-field techniques.

2.3.4.2 Electrostatic Heterodyne Force Microscopy (Non-Contact)

In the preceding section we have discussed the method of HFM whereby the tip and sample are vibrated mechanically through a piezo actuator, providing information on the time-dependant properties of the sample. There is however much interest in studying time-dependant electrostatic properties in micro/nano electronic devices, to do this the piezo actuators have been replaced with high frequency electric fields [91, 92]. In these studies the cantilever is however not in contact with the surface and the non-linear electrostatic interaction is used as the mixer in-place of the tip-surface interaction. The spacing between the tip and the sample in both cases was 100 nm [92] and 500 nm [91].

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