Invited Paper

Nonlinear dynamics of atomic force microscope microcantilevers in liquid environments - a review

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Abstract: Surface forces at the liquid-solid interface play a fundamental role in a wide range of scientific disciplines including electrochemistry, energy storage, wetting, catalysis, environmental science, biochemistry, biophysics, and physical biology. Dynamic Atomic Force Microscopy (dAFM) is being increasingly used to quantify and map these forces with nanometer resolution. In dynamic AFM surface forces are sensed from the changes they cause in the nonlinear dynamics of the oscillating AFM cantilever. However, the dynamics of the AFM cantilever at liquid-solid interface differs significantly compared to air or vacuum environments due to both the low Q-factor of the cantilever in liquids as well as the unique nature of intermolecular forces at solid-liquid interface. In this article we review the state-of-art of understanding of nonlinear dynamics of AFM microcantilevers in liquid environments and outline the many open areas of research both in mathematical modeling and in experiments that remain to be explored.

Key Words: atomic force microscopy, AFM, liquid

1. Introduction
Dynamic atomic force microscopy (AFM) refers to a variety of nanoscale imaging methods where a microfabricated cantilever with a sharp tip is excited at a primary resonance and made to approach and scanned over a sample. The tip-sample interaction forces act between a few atoms on the tip and on the sample and can arise from a variety of surface interactions including van der Waals forces, chemical forces, elastic and inelastic interactions, and electrostatic forces. These tip-sample interaction forces, in most environments, are strongly non-linear functions of the oscillating tip position with rapid changes in gradients occurring over ~1nm changes in tip-sample gap. This implies that for the most part the dynamics of an AFM cantilever interacting with the sample surface need to be understood in the context of nonlinear dynamics using the analytical and computational tools of dynamical systems. An exception to this is when the tip oscillation amplitudes are much smaller than the lengthscale over which the force gradients change, which allows for a locally linear description of the cantilever dynamics. However this is a rare situation. The detection and quantification of tip-
sample forces using dAFM is thus, at its core, an inverse problem where the forces are described only in terms of the changes they cause to the nonlinear dynamics of the oscillating cantilever.

Interest in the use of dAFM at the liquid-solid interface has been driven by a growing demand for understanding surface forces in electrochemistry, energy storage, wetting, catalysis, environmental science, biochemistry, biophysics, and physical biology. Advances in dynamic AFM methods in liquid environments have enabled the study of fundamental physical processes at liquid-solid interfaces with high spatial and force resolution. For example dAFM has been used to detect and image the forces associated with the organization of solvation shells of water [1], self-assembly of molecules on surfaces [2], and electrochemistry [3]. As these advances drive many new experimental studies, it is important to understand the non-linear dynamics of the AFM cantilever at the liquid-solid interface in order to better interpret and quantify experimental data.

The nonlinear dynamics of AFM cantilevers in air or vacuum environments is well studied now (See [4] for a literature review). Some of the key results include: the co-existence of multiple stable oscillation states of resonantly excited cantilevers in tapping mode due to van der Waals and nanoscale repulsive interactions and their respective domains of attraction (i.e the attractive and repulsive regimes) [5]; the possibility of grazing bifurcations [6]; the possibility of chaotic dynamics and their control [7–10]; and the possibility of nonlinear modal interactions [11, 12].

However in order to understand cantilever nonlinear dynamics at the liquid-solid interface it is important to recognize several unique attributes of cantilever dynamics in liquid environments:

(a) The first is the major influence of viscous hydrodynamics which leads to low quality factors (Q factors) and natural frequency of the cantilever resonance in liquids. In liquids the quality factor (Q<sub>1-5</sub>) is generally two orders of magnitude smaller than in air and the natural frequency is generally two to four times smaller than in air. This arises from a combined added mass and added damping effect due to the surrounding liquid. The low Q-factors render inaccurate asymptotic approaches to the mathematical models of cantilever dynamics that rely on weak damping. Moreover the low Q factors mean that the different eigenmodes of the cantilever respond to excitation over a broader frequency bandwidth of forcing than in air or vacuum opening up an increased chance of nonlinear resonances such as combination resonances.

(b) Secondly, the physical origin and magnitudes of interaction forces are different in liquids than in air or vacuum. For example attractive van der Waals forces and capillary forces, which can be significant in air, are much smaller at the interface of aqueous liquids and solids. Furthermore there are two additional forces in liquids that are not present in air or vacuum environments. First, insulating samples develop charge or have their surface charge modified in aqueous environments. These charges are screened by layers of opposing ions in the environment and repulsive electrostatic forces develop between these screening ionic layers. This is the electric double layer [13] force. Second, when the tip-sample separation becomes of the order of a few molecular diameters the liquid molecules become organized as a metastable phase with properties that are very different from those in the bulk of the liquid. The tip has to expend energy to push through this organized liquid to “contact” the underlying substrate. These additional tip-sample forces due to the interaction of solvent molecules with the surface (as well as nano-scale geometric confinement) are usually described in terms of solvation and hydration forces [13, 14].

In this review article we provide a review of recent results and open areas in nonlinear cantilever dynamics in liquid environments at the liquid-solid interface. Specifically excluded from this review are aspects of linear cantilever dynamics in liquids including hydrodynamic loading of cantilevers, eigenmodes in liquids, and cantilever frequency response to various excitation mechanisms in liquids for which we refer the reader to an exhaustive review in [15].

2. Early experimental evidence of cantilever nonlinear dynamics in liquids

Some of the most accessible experimental evidence for nonlinear cantilever dynamics has been from experimental time series data of resonantly driven cantilevers interacting with samples in liquid envi-
Fig. 1. Experimental evidence of cantilever nonlinear dynamics at the liquid-solid interface. (a) Deflection waveform of a (acoustically) resonant cantilever approaching a glass sample in water [16]; Deflection waveform of magnetically excited soft triangular cantilever in water on mica (c) and that for a magnetically excited rectangular cantilever (d) [17]. To be reproduced with permission.

Ronments. The first report measuring cantilever oscillations at the water-solid (water–glass) interface was made in [16]. Figure 1(a) shows the deflection waveform of a soft triangular cantilever in water that is acoustically excited (near its natural frequency) and approaches the sample (glass) through the extension of the Z piezotube. A key observation was that the amplitude envelope of the deflection waveform between points A and B was asymmetric about zero in Fig. 1(a). This was an unusual observation since if the oscillation waveform were described by a single harmonic, as it is in high Q factor conditions; the amplitude envelope is known to reduce symmetrically. A second important observation is that unlike in ambient settings, the cantilever oscillation waveform has time-localized anharmonic distortions (indicated by the vertical arrows), presumably at the instants when tip-sample contact occurs.

Further studies of this phenomenon were carried out in [17]. The deflection waveforms of a magnetically excited soft triangular cantilever (Fig. 1(c)) and soft rectangular cantilever (Fig. 1(d)) were recorded [17] as a function of time with the cantilever placed at increasingly close distances to a mica sample. The localized anharmonics near tip-sample contact were much more pronounced in the case of the rectangular cantilever, which exhibits the signature of an impulse or “ring down” response. The key observation made in [17] was that the frequency of the ring down corresponded to the resonance of the second eigenmode. This observation leads to the hypothesis that the second eigenmode is excited momentarily during interaction with the sample and quickly decays, in spite of the fact that the cantilever is at a primary resonance with excitation frequency nearly coincident with the natural frequency. This evidence suggested that the near contact dynamics of tapping mode cantilevers in
liquid environments can be complex and possibly involving multiple eigenmodes even under conditions of primary resonance.

3. Cantilever non-linear dynamics in liquids near primary resonance

Since the above early works, many further works have been carried out to understand aspects of cantilever nonlinear dynamics in liquids. Most [18–21] have attempted to use single degree of freedom models based on a single-mode discretization of the cantilever dynamics and low Q factors to predict the cantilever nonlinear dynamics in liquids.

On the other hand, the observation (Fig. 1) that the experimental oscillation waveform appeared include contributions from the second eigenmode prompted the authors in [17] to propose a two eigenmode model of the cantilever probe in order to capture the complex dynamics of oscillating probes interacting with samples in liquid medium. More generally, an N degree-of-freedom (DOF) model follows from a Galerkin discretization of the Bernoulli-Euler beam equation, which retains the first N normal eigenmodes and yields a reduced-order model

\[
\begin{align*}
\ddot{q}_1 + \frac{Q_1}{\omega_1^2} \dot{q}_1 + q_1 &= \frac{F_1(t)}{k_1} + \frac{F_{ts}(d, \dot{d})}{k_1} \\
\ddot{q}_2 + \frac{Q_2}{\omega_2^2} \dot{q}_2 + q_2 &= \frac{F_2(t)}{k_2} + \frac{F_{ts}(d, \dot{d})}{k_2} \\
\vdots
\end{align*}
\]

where the dots represent temporal derivatives, \( F_{ts} \) is the tip-sample interaction force, \( d = q_1 + q_2 + \cdots + q_N \) is the instantaneous gap between the tip and sample. The contribution of the \( j \)th eigenmode to the tip deflection is \( q_j \). \( k_j, Q_j, \) and \( F_j \) are the corresponding equivalent stiffness, natural frequency, quality factor and modal forcing. In this model it is worth reiterating that in normal tapping mode operation the frequency of excitation is tuned to the fundamental natural frequency \( \omega_1 \). Such models have been validated with experimental data [17, 22] using a variety of magnetically excited cantilevers on different samples in buffer solutions. These works have assumed that at high buffer solution concentration the tip-sample interaction models can be suitably described by Hertzian contact mechanics, an assumption which as we will see in this review article, does not capture the true physics of tip-sample interaction in high ionic concentration liquids.

In Fig. 2 we summarize the results from [22] where a 0.1 N/m rectangular microcantilever is driven at its first eigenmode frequency in a buffer solution (300mM KCl, 20mM tris-HCl) at an initial amplitude of \( \approx 14 \) nm, and brought closer to a patch of the extracellular face of purple membrane (soft membrane of the Halobacterium salinarium) supported on a mica surface (stiff). Under gentle imaging conditions (set point amplitude ratio \( \approx 95\% \)), the measured oscillation waveform of the tip motion is plotted in Fig. 2(b) where a distinct distortion of the harmonic response is observed when the tip taps the sample, and the spectral content of cantilever vibration shows a cluster of higher harmonics of the drive frequency that is amplified near the natural frequency of the second eigenmode. This local distortion has been observed [17, 22] for all cantilevers tested on both soft and hard samples in liquids and in all cases the second eigenmode frequency was not near an integer multiple of the fundamental drive frequency.

To explain this phenomenon a two eigenmode model for the cantilever dynamics interacting with the sample with realistic tip-sample interaction models in buffer solutions was developed [17, 22]. Figure 2(d) shows the simulation results that clearly show that the local distortion in the tip oscillation waveform is due to the second (undriven) eigenmode, which is excited in a transient fashion at each impact and decays before the next tap event. This phenomenon was termed the momentary excitation of the second eigenmode. Because the momentary excitation occurs once every drive time period, its spectral content consists of higher harmonics of the drive frequency resulting in the enhancement of
Fig. 2. Theory vs. experimental studies of tip motion of magnetically excited cantilevers on mica and purple membrane samples in buffer solution [22]. (a) A schematic of the experimental set up with a magnetic 0.1 N/m rectangular microcantilever imaging purple membrane on mica in a buffer solution under gentle imaging conditions (free amplitude=14 nm, setpoint amplitude ratio=95%). (b) Experimental waveform acquired while tapping on mica and (c) the discrete Fourier transform of the signal. When simulations were performed with a two-eigenmode model tapping on mica, (d) it became clear that the second eigenmode is momentarily excited and decays before the next tap, (e) the discrete Fourier transform of the simulated response of the first and second eigenmode, showing that the momentary excitation leads to a cluster of higher harmonics, esp. 8th-12th harmonics near the natural frequency of the second eigenmode. (f-g) show the phase space trajectories of the simulated time series in (d) where $q_1$ and $q_2$ refer to contribution of the first and second eigenmodes to the overall tip response. To be reproduced with permission.

Examining the phase space trajectories (Figs. 2(f), (g)) of the first and second eigenmode response makes it clear that while the driven eigenmode evolves to a steady state near-harmonic periodic solution, the second eigenmode is significantly perturbed during each tap and undergoes oscillatory decay before the next tap. This is a non-resonant interaction between the first and second eigenmode since the second eigenmode frequency is not near an integer multiple of the first and occurs due to the low Q-factor (high damping) of the cantilever eigenmodes in liquid environments. Such modal interactions are not typically observed in the dynamics of harmonically excited, resonant, lightly damped structures.

At this point it is worth asking the question why this modal interaction becomes so important in describing cantilever tapping mode dynamics in liquids under conditions of primary resonance when single-mode approximations work so well in ambient/vacuum settings. The answer to this important question lies in the low Q-factors in liquids. In air or vacuum, the Q-factors are high and the resonance bandwidths of the fundamental and higher eigenmodes are quite narrow. As a result significant nonlinear transfer of energy between cantilever eigenmodes can only occur when the second eigenmode natural frequency is an integer multiple of the fundamental frequency $\omega_2 \sim n\omega_1$ or if the excitation frequency $\omega_{dr}$ is in some strict rational mathematical relationship with respect to the cantilever resonance frequencies: $m\omega_{dr} + n\omega_1 + p\omega_2 \sim 0$. These conditions have been produced in specially constructed cantilevers ([11, 12]) but are impractical to fabricate since there is a large variability in cantilever modal structure within a wafer and between wafers. On the other hand in liquid environments, multiple higher harmonics of the drive frequency lie within the resonance bandwidth of the second eigenmode due to the low Q-factor allowing for significant nonlinear transfer of energy between modes.

Further studies of the anharmonics near tip-sample contact were undertaken by [23] where the dynamics of magnetically excited soft cantilevers (stiffness < 0.1 N/m) were simulated while tapping on the 8th-12th harmonics that lie in the vicinity of the second eigenmode natural frequency (Fig. 2(e)).
mica and purple membrane samples in high concentration buffers. The mathematical model consisted of a two-degree of freedom discretization of the cantilever with well calibrated modal parameters along with a Hertzian contact mechanics model describing contact and short-range forces. As shown in sample results from [23] (Fig. 3), as the cantilever set point amplitude is reduced the momentary excitation leads to the possibility of multiple impacts or contact events occurring during a single tap event. The transition between single impact taps and 2 impact taps was described in terms of a secondary bifurcation of a grazing trajectory. A signature of transition from single to multiple tap solutions was identified and demonstrated with experimental results. However, these results are quite sensitive to the presence of hydration or solvation forces within a thin highly viscous layer of organized water on the interface which cushions the impact forces and reduces momentary excitation and the possibility of multiple impacts during a tap event.

4. Nonlinear dynamics while operating at higher eigenmodes in liquids

The preceding sections have mainly focused on situations where the cantilever is excited near its first natural frequency. However, many newer methods aim to excite the cantilever at its second (or higher) natural frequency, with the goal of achieving increased contrast, better compositional contrast, or both. For example, because the stiffness and quality factor of the second eigenmode is higher than that of the first, stable imaging may be possible at smaller oscillation amplitudes [24], the phase contrast may be better [25], and for some situations the undesirable “forest of peaks” in acoustic drive [26] may be reduced. In addition, the second eigenmode is also driven as a part of bimodal AFM [27].

In this section, we review the results of [28] (and also revisited in [29]). In that work, the dynamics of AFM cantilevers in liquids were investigated when the cantilever is driven at its second natural frequency. From prior work in air or vacuum this ought not to be essentially different from operating at the fundamental natural frequency. In fact the results can be surprisingly different.

An example experimental approach curve of a Mikromasch CSC37B cantilever on mica in buffer solution is shown in Fig. 4(a). The experiment is also compared to simulation (using the VEDA – Virtual Environment for Dynamic AFM - simulator [29]) using a 3 eigenmode model with tip-sample interaction force ($F_{ts}$) for the Biolever in water tapping on mica. Examples of oscillations with (a) single, (b) double, and (c) triple impacts corresponding to setpoint amplitude ratios of 95%, 90%, and 85% respectively [23]. To be reproduced with permission.

**Fig. 3.** Numerical simulation of the photodiode deflection $u = q_1 + q_2$ and tip sample interaction force ($F_{ts}$) for the Biolever in water tapping on mica. Examples of oscillations with (a) single, (b) double, and (c) triple impacts corresponding to setpoint amplitude ratios of 95%, 90%, and 85% respectively [23]. To be reproduced with permission.
interactions described by a Hertz model. Surprisingly, there are some interesting jumps up and down in the first harmonic amplitude, which are reproduced in both the experiment and simulation. Attractive forces can cause a similar behavior \[5\], but the simulation has no attractive forces so that cannot be the cause in this case.

Insight into the behavior causing the jumps can be gained from a time history plot. Figure 4(f) shows the simulated and experimental time histories of observed deflection near Z=1 nm. The tip does not tap on the sample every drive cycle; rather, there is a pattern that repeats once every four drive cycles. This is a period-4 response, which corresponds to a significant cantilever response at 1/4 the drive frequency. In essence, when the tip taps on the sample, the sudden impact transfers energy from the driven harmonic to both higher and lower frequencies (i.e. the first and third eigenmode) (for example as described in \[30\]) as shown in Fig. 4(a). The response of the first eigenmode causes the tip to rebound off the sample so far that it does not tap the sample on the next drive cycle and a subharmonic motion is created.

Therefore, if we set an additional lock-in to monitor the response at frequencies below the excitation frequency (Figs. 4(d) and (e)) we see that the jump downs in the first harmonic amplitude correspond to jump ups in the 1/4 and 1/3 harmonic amplitude indicating the onset of subharmonic response. Depending on the cantilever parameters and operating conditions, two, three, or even five drive cycle patterns are possible.
Importantly, the subharmonic response depends on sample material properties (e.g., ratio of cantilever stiffness to sample stiffness). For example, softer cantilevers on stiffer samples lead to stronger subharmonics, and stiffer cantilevers on softer samples lead to weaker subharmonics. Therefore, the phenomenon of subharmonic response can also be used for mapping compositional contrast. On the other hand, the energy transfer between eigenmodes means that classical formulas for tip-sample energy dissipation such as [31] are not applicable in this situation.

In conclusion, the operation of dAFM in liquid environments using the second cantilever eigenmode opens up a unique subharmonic energy transfer mechanism to the first eigenmode. This mechanism can offer new opportunities to map compositional contrast but can also challenge the interpretation of conventional energy dissipation spectroscopy.

5. Nonlinear frequency response of microcantilevers at the liquid-solid interface

An important implication of the works discussed in section 3 is that understanding the nonlinear dynamics of the AFM in liquids requires the observation and prediction of processes that happen over a wide frequency bandwidth. It is not sufficient to study the dynamics only at a single frequency. This is a limitation of most of the existing work on non-linear dynamics in liquids [17, 18, 23, 30, 32, 33], and [34]. Although these studies do provide insight, they show only a small slice of the entire response. The only studies of the dynamics over a wider frequency range that the authors are aware of are [18–21].

In this section, we review the results of [35], where the non-linear frequency response of AFM cantilevers was studied at the liquid-solid interface over a wide bandwidth. The experiments in this work consisted of multiple frequency sweeps (amplitude and phase as a function of excitation frequency) of cantilevers at various distances from the sample surface. Typical results on mica are shown in Fig. 5. The black dashed line corresponds to data acquired when the cantilever is far enough away from the sample that there is no significant tip-sample interaction (i.e., the response is linear). Each successive curve is acquired as the cantilever is positioned progressively closer to the sample. It can be seen that as the cantilever position approaches the sample, the response does not remain linear. Instead it is significantly distorted. Based on these and other experiments, as well as numerical simulations, the authors in [35] drew several main conclusions:

(a) First, due to the non-linear tip-sample interactions and the low quality factors, it is possible for the resonance peak to split into two distinct resonance peaks. The secondary resonance peak appears at one-half the frequency of the main resonance peak and is referred to as a superharmonic resonance. (e.g., the two peaks in the black solid line in Fig 5(a)). Both resonance peaks involve significant response at higher harmonics (a well known hallmark of non-linear behavior). The superharmonic resonance involves a large response at the second harmonic (i.e., mainly first eigenmode responding), whereas the primary resonance involves a large response at many higher harmonics (i.e., the second eigenmode also responds). This can be seen in Figs. 5(c) and 5(d). Time histories of the responses can be seen in Figs. 5(e) and (f). Both time histories show a distortion of the waveform when the tip taps on the sample.

(b) Higher quality factor was shown to suppress the superharmonic resonance, which is why this phenomenon is only seen in liquid environments and not in air or vacuum. On the other hand, a higher quality factor creates a significantly more non-linear response at the primary resonance. In fact, jump phenomena (i.e., discontinuous changes in the amplitude-frequency curve), which have been known in air for a long time, can be seen in liquids for modest quality factors (Q approximately 6 or higher).

(c) The authors in [35] then used numerical simulation to reproduce these results. In addition to the multiple eigenmode model already described, it was found that a tip-sample interaction force model consisting of two parts was needed to match the experimental results. The first is a hydration force and the second is the Hertz contact force. In intermittent contact on hard samples, the Hertz contact force leads to a significantly stronger non-linearity than the hydration forces (the hydration forces...
Fig. 5. Experimental frequency sweeps for a 2 N/m magnetically excited cantilever in 500-mM KCl solution on mica (from [35]). The Z distances range from approx. 7 nm to approx. −0.5 nm in increments of 0.5 nm. Amplitudes and phases of the 1st, 2nd and 6th harmonics of excitation (a) $A_1$, (b) $\phi_1$, (c) $A_2$, (d) $A_6$. Interestingly, the resonance splits into two distinct peaks in $A_1$, one of which corresponds to a large $A_2$ and the other to a large $A_6$. $\phi_1$ shows an interesting reversal above resonance and surprisingly $\phi_1 = 90^\circ$ at the natural frequency. (e) and (f) Time histories. The signal has been comb filtered to keep only the first seven harmonics. The waveform shows a distinctive distortion after tapping on the sample. (e) corresponds to the black dot marked “X” in (a). (f) corresponds to the dot marked “Y”. Insets: zoom-in on boxed regions. To be reproduced with permission.
tend to reduce the peak interaction forces). Therefore, the non-linear response is strongly influenced by which of the two types of forces is most dominant. When using larger stiffness cantilevers and larger free amplitudes the tapping forces are larger, so that the role of the hydration forces is decreased and stronger nonlinear response emerges. For very stiff cantilevers (\( > 40 \text{ N/m} \)), the effect of the hydration forces is negligible, and the non-linearity is governed by the ratio of cantilever stiffness to sample stiffness.

(d) Further, different solid-liquid interfaces exhibit characteristic forces, and therefore lead to distinctly different cantilever dynamic responses. Experimental data in [35] showed that the experiment results on HOPG (which is hydrophobic) are quite different than the results in Fig. 5 for mica (which is hydrophillic).

(e) Finally, magnetic excitation can potentially excite the second eigenmode strongly in the linear system response, even when driving near the first natural frequency. This can be seen in the black dashed line in Fig. 5(b). If there was no response of the second eigenmode, the phase would increase asymptotically to 180 degrees as frequency increased. However, the second eigenmode responds out of phase with the first and causes the phase to decrease as the frequency increases past the first natural frequency. This response must be considered in quantitative calculations, even for linear small-amplitude AFM.

All these results confirm previous results that AFM cantilever dynamics in liquids are qualitatively different than the dynamics in air/vacuum, and are caused by the interplay between the unique surface forces in liquids and the low quality factors in liquids, as introduced in Section 1.

6. Applications of nonlinear response in liquids

The fact that the cantilever dynamics at the liquid–solid interface is quite nonlinear is not only of academic interest but it also provides many new possibilities for innovation in nanoscale imaging using AFM. In tapping mode AFM the cantilever is excited at a single frequency usually near its fundamental natural frequency and the amplitude of the cantilever response at that frequency is maintained constant while scanning over the sample. As we have seen though, the cantilever dynamics at the liquid-solid interface is far from a pure harmonic tone and the tip-sample interaction nonlinearity generates many harmonic components besides the one at the drive frequency. This spectral content beyond the amplitude of the driven harmonic is uncontrolled and changes depending on the local material properties of the sample allowing the possibility of many new channels of material property information to be acquired as the sample is being scanned in tapping mode.

One area of recent interest and growth has been the use of higher harmonics imaging in liquid environments where the cantilever vibration at integer higher harmonics of the drive frequency are mapped while scanning the sample in tapping mode. Higher harmonic imaging in air or vacuum environments is quite difficult to implement in practice because the higher harmonic amplitudes are orders of magnitude smaller than the amplitude of the fundamental harmonic in the cantilever spectrum [36]. However, when cantilevers are immersed in liquids, the higher harmonics are enhanced due to the strong anharmonic distortions produced in the oscillation waveforms as we have seen. The earliest higher harmonic images, taken by Van Noort et al. [32], included 2nd and 3rd harmonic images of DNA imaged in liquid (See Fig. 6(a)). Preiner et al. [37], have demonstrated molecular resolution of a bacterial S-layer in a second harmonic image (Fig. 6(b)) and Thompson et al. [38] have collected 2nd-4th harmonics on \textit{Staphylococcus aureus} bacteria cells (Fig. 6(c)). Xu et al. [22] mapped the cantilever vibration harmonics that lie close to the second eigenmode frequency while the cantilever was excited near its fundamental frequency. Figure 6(d) shows a 9th harmonic image of a double layer of purple membrane on a mica substrate. The 9th harmonic image is able to distinguish the single layer of purple membrane from the double layer, which is expected to be softer.

The link between the amplitude and phase of the higher harmonics and the material properties of the sample is an ongoing area of research and has been studied using simulations of single mode models and two-mode models [22, 38]. In addition to their physical interpretation, one important issue is to understand which higher harmonic is more sensitive to which material property and under
Fig. 6. Using cantilever nonlinear dynamics in liquids for new imaging methods. (a) Second harmonic image of DNA on a mica substrate [32], (b) Second harmonic image of a bacterial S-layer [37], (c) 2nd harmonic amplitude contrast on *S. aureus* bacterium trapped in a filter [38] while scanning in tapping mode (d) 9th harmonic image distinguishing a single layer from a double layer of purple membrane on a mica substrate [22]. To be reproduced with permission.

what circumstances. While the second harmonic proposed originally in [32] is typically the largest in magnitude, the authors in [22] have demonstrated that the 9th harmonic amplitude can be much more sensitive under certain imaging conditions when it can be easily detected.

7. Outlook

In this article we have attempted to provide a snapshot of the state-of-art of AFM cantilever nonlinear dynamics in liquid environments which continues to be an important growth area for AFM and yet offers many opportunities for new dynamical systems based approaches. In conclusion, we would like to highlight some key areas where much work remains to be done in advancing this rapidly evolving field:

(a) While we have discussed higher harmonic imaging, these days bimodal AFM where the cantilever is simultaneously excited in two different eigenmodes is gaining increased use in liquid environments [39, 40]. Cantilever dynamics under this two-frequency excitation condition is expected to reveal many unique phenomena in cantilever dynamics in liquids. While better understood in air or vacuum, the cantilever dynamics with bimodal excitation under liquid environments remains a little studied but important area of research.

(b) Most nonlinear dynamics studies discussed in this review article assume deterministic dynamics of the cantilever. For very soft cantilevers as used for imaging soft biological samples, thermal noise due to Langevin forces become very relevant and need to be included in a systematic way in the analysis. Additionally soft viscoelastic samples in liquid environments undergo several relaxation processes so that the surface response to intermittent tapping is not well represented by simple viscoelastic contact mechanics models. Surface relaxation effects then allow for time-delay effects to enter the system dynamics where the surface position in one tap event depends on how the tip interacted with
the sample in the last tap. These open up many new areas where cantilever nonlinear dynamics can be studied in liquid environments.

(c) We have focused in this review article on the study of near resonant cantilever dynamics. In liquid environments little operational penalty is placed on using AFM of resonance due to the low Q-factors. On the other hand the cantilever dynamics under off-resonance conditions can be quite complicated and needs to be understood since many new imaging modes in liquids use such excitations ([41, 42]).

(d) The papers highlighted in this article have by and large used relatively stiff samples in liquid environments (Young’s modulus > 100 MPa). However when dynamic AFM is used to study living or fixed cells in buffer solutions (Young’s modulus 10kPa-100kPa), the samples are much softer and viscoelastic compared to typical studies of polymers or mica/graphite/glass at solid-liquid interfaces. Understanding the cantilever dynamics when coupled to such soft materials remains an open area of research.

(e) Recent studies using tapping mode AFM have demonstrated atomic resolution can be attained at liquid-solid interfaces if the cantilever dynamics are “tuned” correctly to the right conditions. The relationship between cantilever nonlinear dynamics and atomic resolution imaging remains an open and important question– can nonlinear dynamics help in atomic resolution imaging or does it reduce imaging resolution?

These are some possible avenues that several research groups are already looking into and where we can expect exciting new developments in the near future.

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