Single cycle and transient force measurements in dynamic atomic force microscopy

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Karim Gadelrab,^a Sergio Santos,^a Josep Font^b and Matteo Chiesa^{*a}

The monitoring of the deflection of a micro-cantilever, as the end of a sharp probe mounted at its end, *i.e.* the tip, interacts with a surface, forms the foundation of atomic force microscopy AFM. In a nutshell, developments in the field are driven by the requirement of obtaining ever increasing throughput and sensitivity, and enhancing the versatility of the instrument to simultaneously map the topography and quantify nanoscale processes and properties. In the most common dynamic mode of operation, the motion of the driven cantilever is monitored at a single point on its longitudinal axis. Here, we show that from this single point a waveform is obtained that contains all the details about conservative and dissipative interactions. Then a formalism that accounts for multiple arbitrary flexural modes is developed for an indirectly driven cantilever. The formalism is shown to allow recovery of the details of the interaction even in the presence of complex and relevant hysteretic forces when the cantilever oscillates in the steady state. In a different approach, we develop a formalism that monitors the wave profile of the cantilever, *i.e.* the waveform at five different points on its longitudinal axis. With this formalism the interaction can be reconstructed during a single oscillation cycle even in the transient state of oscillation. Finally, we discuss the potential and advantages of the proposed methods and future technical challenges. Other standard and state of the art techniques and methods are also discussed and compared with the ones presented here. This work should also provide insight into the current high throughput–high sensitivity developments dealing with multifrequency dynamic AFM where information is recovered from multiple eigenmodes.

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1. Introduction

The capacity of the atomic force microscope AFM to image,^{1,2} probe^{3–5} and manipulate^{6,7} matter is a testament to its versatility. The instrument is currently employed by researchers in fields ranging from biology^{8,9} to semiconductor theory and devices¹⁰ and in hybrid systems.¹¹ With the AFM one can routinely image single nanostructures,^{12,13} map heterogeneous compositional^{14–18} and/or nanomechanical^{19–21} properties and/or processes,^{22,23} study molecular interactions^{24,25} and larger biological systems,^{26,27} identify single atoms,²⁸ molecules^{29,30} and/or chemical composition³¹ and structures,³² study the friction induced by single atomic motion³³ and, more recently, even discriminate bond order and symmetry.^{34,35} The fundamental principle however is relatively straightforward; atoms, nanostructures and surfaces are probed with high precision on the lateral and vertical axes *via* a nanoscopic tip mounted on a microstructure, typically a micro-cantilever, by monitoring its deflection.^{36,37}

Initially the AFM was developed to operate in the quasistatic or DC mode³⁶ but dynamic modes of operation were rapidly introduced^{38–40} to reduce lateral forces while imaging,⁴¹ enhance versatility⁴² and provide information related to chemical composition^{41–43} and dynamic processes such as those involved with irreversible loss of energy.^{44,45} In terms of nanoscale processes and properties, a main advantage of dynamic AFM (dAFM) modes over DC modes relates to their capacity to simultaneously probe both conservative and dissipative forces while tracking the topography for imaging.⁴⁶ Conservative and dissipative forces provide mechanical and chemical information about samples and about the atomic and/or nanoscale processes and phenomena²³ that give rise to the macroscale properties of matter.⁴⁷ Extracting such information robustly while enhancing the throughput and sensitivity is thus one of the main driving forces behind the recent developments in dAFM techniques.^{20,23,48–51} It is also worth noting that force reconstruction maps in DC modes, *i.e.* quasistatic modes, suffer from stability issues resulting in the so-called “jump-to-contact” where information for a range of distances is lost. Also the signal-to-noise ratio might be compromised by pink noise, *i.e.* noise is proportional to the inverse of the frequency. Still, the interpretation of forces in DC modes could be argued to be otherwise relatively simple, since the fundamental form of

^aLaboratory for Energy and Nanoscience (LENS), Center for Future Energy Systems (iFES), Masdar Institute of Science and Technology, Abu Dhabi, 54224, United Arab Emirates. E-mail: mchiesa@masdar.ac.ae

^bDepartament de Disseny i Programació de Sistemes Electrònics, UPC-Universitat Politècnica de Catalunya, Av. Bases, 61, 08242 Manresa, Spain

Hooke's law is used and the force is constant while imaging. On the other hand, interpreting data acquired from the dynamic modes of operation requires more detailed modeling and care as the tip follows a non-monotonic force trajectory during each oscillation cycle.⁵² Furthermore, both users and researchers have to deal with further complexity in electronics, differences in the operation of the several available feedback modes, fine tuning of the multiple operational parameters and the related requirements for dealing with elementary and even advanced concepts in vibration theory.

Among the most common dAFM modes of operation, the fundamental flexural mode of oscillation is excited and the dynamics are monitored *via* amplitude modulation³⁹ (AM) or frequency modulation⁴⁰ (FM) feedback systems. Conventionally, the motion of the cantilever is monitored at a single point on its longitudinal axis. In AM AFM the oscillation amplitude A typically decays, almost linearly, with decreasing cantilever separation particularly under ambient conditions. Furthermore the amplitude decay^{53,54} is robust enough to deal with the challenging topography¹⁹ in ambient and liquid environment.⁵⁵ In FM AFM, the amplitude is typically maintained constant while the resonant frequency, which shifts with decreasing cantilever separation, is a direct experimental observable.^{40,56} Conservative forces alone have long been recognized to control the frequency shift $\Delta\omega$ in dAFM and a relationship between the frequency shift and the conservative forces was also derived and robustly validated.^{56,57} Consequently, mapping of conservative forces has been possible in FM AFM for over a decade.⁵⁸ The FM AFM method of force reconstruction that was derived from these relationships, including the small amplitude and large amplitude approximations⁵⁶ and the more general form,^{57,59} is here termed the standard FM AFM method. In conventional AM AFM the oscillation amplitude A is kept constant by the feedback system by increasing and decreasing the cantilever separation z_c . The experimental observables are the amplitude A , the mean deflection and the phase shift ϕ . An interplay between conservative and dissipative forces however is responsible for the amplitude decay and the phase shift that make the study of the interaction particularly complex. In this respect, the more generally accepted theory in AM AFM states that the cosine of the phase shift provides information about conservative forces^{53,60} while its sine provides information about dissipation.^{44,45} Over the past decade, methods to reconstruct forces by inverting amplitude and phase shifts in standard AM AFM have also been proposed by several groups.^{61–63} It could be argued however that the most commonly employed method is one presented by Katan and Oosterkamp^{64,65} whereby the equivalence of the parameters controlling the dynamics in AM AFM and FM AFM is recognized. Then the relationship between the cosine of the phase shift, the conservative forces and the frequency shift is employed to exploit the standard FM formalism, *i.e.* the frequency shift is indirectly recovered from the cosine of the phase shift. These studies have thus exemplified that the standard FM AFM inversion method^{57,59} can be employed in both AM AFM and FM AFM^{21,66} with the use of observables only.

The standard FM AFM method as well as other proposed methods of force reconstruction in dAFM^{61–63} make use of the

integral form of the equation of motion and are based on the single mode/fundamental harmonic approximation. The most important implication from a practical point of view is that these methods typically require approaching the surface by decreasing the cantilever separation and acquiring data for a range of separations. In this way, the minimum distance of approach per cycle, *i.e.* d_m , covers a range of tip-sample distances that are directly mapped to a tip-sample force.^{57,62} For this reason such methods could be termed d_m methods, and, because of their working principle, they are generally low throughput methods. It is worth mentioning however that d_m methods extend to recent developments, typically termed multifrequency AFM; some multifrequency methods exploit the standard FM AFM method^{21,50} to reconstruct the tip-sample force from one of the modes. Generally, in multifrequency AFM, multiple flexural modes of the cantilever are externally excited^{49,51} and FM and/or AM feedback systems can be employed in one,⁶⁷ several⁶⁸ or all of the modes. Some modes can also be left free, *i.e.* open loop.^{69,70} While one mode is employed to track the sample's topography the other mode/s is/are employed to map nanomechanical properties thus enhancing the throughput and quantification capabilities of standard dAFM.¹⁹ Other multifrequency methods might simultaneously employ flexural and torsional excitation,⁷¹ drive the cantilever at two different frequencies close to the first resonance⁴⁸ or exploit band excitation⁷² to increase the throughput and quantification. In summary, multifrequency methods achieve high throughput and simultaneous quantification by cleverly circumventing the problems involved with the requirement of d_m methods for decreasing the cantilever separation at a point.^{19,21,50}

In a different approach, Stark and Heckl^{73,74} solved the differential equation of motion of the cantilever, rather than the integral equation as treated in the methods above, by accounting for higher modes and higher harmonics. In this way, in principle, the instantaneous tip-sample force can be reconstructed as a function of tip-sample distance or time.⁷⁵ This approach surmounts some of the disadvantages involved with the common assumptions and requirements^{59,66} for solving the integral form of the equation. In particular, no assumptions⁵⁹ regarding the nature of dissipative forces are required. This implies that the formalism is robust and recovers the true force even in the presence of complex hysteretic dissipative forces^{66,76} that might account for bond formation and rupture, capillary interactions or other relevant interactions.⁵⁹ Furthermore, the forces can be reconstructed in a single oscillation cycle. Albeit fractions of ms or more of oscillations per pixel are in practice required to reach the steady state and acquire a FFT to recover the higher harmonic amplitudes and phases.⁷⁵ On the other hand, by not depending on the minimum distance of approach d_m , the force can be reconstructed from a single cantilever-surface separation at a point. This can potentially lead to high throughput since the topography can be tracked while simultaneously mapping sample's properties *via* the higher harmonics.^{76,77} A main disadvantage of this technique relates to the difficulties in detecting the very small amplitudes of the higher harmonics. Experimentally, the amplitudes are excited by the non-linear tip-sample interaction,⁷⁸ *i.e.* the reaction of the sample. For the higher harmonic

amplitudes to be large enough to be detected, *i.e.* $\sim 1\text{--}10$ pm, high peak forces, which are detrimental for high resolution and soft matter imaging,⁷⁹ are required.^{75,77} In order to enhance harmonic excitation with lower peak forces, Sahin and coworkers proposed employing cantilevers where the resonances of the higher modes coincide with higher harmonics of the fundamental frequency.⁸⁰ Note that it could also be argued that the development of multifrequency AFM also originated from a similar idea,^{49,51} *i.e.* enhancement of harmonic excitation or detection from relatively small peak tip-sample forces. More recently, Sahin and coworkers²⁰ proposed and designed a T-shaped cantilever that allowed excitation of torsional modes and detects a sufficiently large number of torsional harmonics to reconstruct the tip-sample force with the standard peak forces of AM AFM. The topography is still recovered from the fundamental flexural mode and fundamental harmonic while sample's properties can be recovered from the torsional modes. In summary, there is a general trend in the community that is clearly directed towards exploiting multiple frequencies and higher eigenmodes with a view to enhance the sensitivity⁵⁴ and throughput,⁸¹ and to extract and quantify nanoscale properties robustly.^{27,51,82}

Here, we first discuss the advantages and disadvantages of period averaged methods for force reconstruction that are based on the minimum distance of approach d_m . In particular, we discuss the main cases where the standard FM AFM method of force reconstruction excels and where it fails. We then discuss a formalism based on the differential form of the equation of motion for standard rectangular cantilevers that has been recently put forward.⁸³ The formalism accounts for base motion, which is standard in commercial AFM systems, and also accounts for higher flexural modes and higher harmonics. From this formalism, a close form solution is found and expressed in terms of experimental observables. *Via* numerical simulations and the finite element FE method the formalism is shown to provide detailed information about realistic hysteretic dissipative forces where standard d_m methods fail. We term this formalism the modal analysis method and discuss its applicability provided a sufficiently high number of harmonics can be detected. As with standard and current force reconstruction methods, the modal analysis method presented here also requires monitoring the deflection of the cantilever, *i.e.* the waveform, at a single point on its longitudinal axis. The cantilever further has to oscillate in the steady state. Then, a second formalism is developed⁸³ that exploits the concept of monitoring the cantilever motion at five different points on its longitudinal axis. We term this second formalism the single cycle method and show that it is as powerful as the modal analysis method in the steady state.⁸³ With the single cycle method however, and by monitoring the wave profile of the cantilever at a finite number of locations on its longitudinal axis, transient phenomena can be probed, in principle, with sub-microsecond resolution. A discussion about the high temporal resolution of the method is given in terms of its potential to be employed experimentally to probe fast processes from those involved in phase transformation⁸⁴ and other irreversible interactions²³ to complex and fast biological phenomena.^{9,81,85,86} In the conclusions, the experimental challenges involving implementation are put into context and related

to current developments in advanced dAFM methods. Finally, some mathematical details are given in two appendices.

2. Force reconstruction schemes: assumptions and challenges

(a) Energy considerations

The DC mode of operation is commonly employed in AFM experiments to reconstruct the normal tip-sample force from the vertical deflection and the lateral or frictional forces from the lateral deflection.³⁷ Only dAFM methods are discussed in detail here however since the interpretation of DC force reconstruction is relatively straightforward.⁵² Moreover, some of the advantages of dAFM and DC methods have already been discussed in the introduction. Suffice it to say here that in DC modes compliant cantilevers typically reach a point of instability. The instability occurs in the attractive force region, arguably the most interesting region of the force from a chemical point of view.^{52,59,66} Stiffer cantilevers can compromise sensitivity⁸⁷ while employing compliant cantilevers in the DC mode has the disadvantage of magnifying noise *via* the effect of the $1/f$ noise (pink noise) factor.⁶⁵ In terms of force reconstruction, viscous dissipative forces are not probed in the DC mode.^{88,89} Finally, the interpretation of dissipative hysteretic forces from the DC signal could lead to ambiguity due to tip trapping or even tip sliding.⁹⁰ It should be noted however that more recent forms of DC operation, *i.e.* the Force Feedback Method (FFM), can be employed to eliminate issues related to tip trapping.⁹¹ Moreover, such methods might provide alternative means to the dynamic modes to probe conservative and hysteretic phenomena at different time scales.

With dAFM modes of operation the stability is provided to the cantilever dynamics *via* the energy stored in the cantilever E_c and *via* the energy inputted per cycle by the driving force E_{in} . This added stability allows operation of dAFM in (1) the pure non-contact mode of operation, where mechanical contact is never established, (2) the attractive regime where the average force per cycle is attractive, and (3) the repulsive force regime where mechanical contact occurs intermittently.^{92–94} Furthermore, by tuning E_c and/or E_{in} in dAFM, and for a given cantilever spring constant k , tip trapping can be avoided and any tip-sample distance can be reached (even in AM AFM⁶⁶) provided the oscillation amplitudes A and/or the free amplitudes A_0 respectively are large enough.^{95,96} The stability provided by E_c can be understood from the proportionality to k and A square.^{97,98} The oscillation amplitude A can be arbitrarily set as a set-point in dAFM. The stability coming from E_{in} is also arbitrarily selected by setting a given value of free amplitude A_0 where E_{in} increases with increasing A_0 .⁴⁴ Furthermore, in the steady state, the energy dissipated per cycle E_{dis} coincides with the energy provided by the driving force, *i.e.* $E_{in} = E_{dis}$, and this produces an extra channel for mapping compositional variations *via* phase imaging.^{44,45}

Physically, the tip-sample force F_{ts} is conservative if it depends on the tip-position z or, equivalently for a given z_c , the tip-sample distance d only; note the geometrical constraint *via* the cantilever-sample separation z_c where $d = z_c + z$.⁹² That is, a conservative force should be independent of the velocity and, in

particular, of the sense of motion and the history of tip-sample trajectories.^{59,76,99} The conservative part of the tip-sample force can be termed $F_c(d)^{63,76}$ and its contribution to E_{dis} should be zero. On the other hand, the energy dissipated per cycle E_{dis} is the work done per cycle by the dissipative forces present in the interaction.⁴⁵ The dissipative part of the force can be termed $F_{\text{dis}}(d, \dot{d})$. The net instantaneous force is then $F_{\text{ts}} = F_c + F_{\text{dis}}$. A qualitative discussion on some of these dissipative forces is given next; more general definitions⁵⁹ and assumptions⁷⁶ for modelling dissipative forces can be found in the literature.

Dissipative forces can be viscous or hysteretic.^{88,89} Viscous forces oppose the motion of the tip while hysteretic forces simply imply that the magnitude of the force depends on the tip's sense of motion⁶³ and possibly its trajectory's history.^{100,101} Furthermore, in dAFM, viscous forces are typically modelled as linear functions of the tip's velocity and, in more restrictive but common scenarios, as odd functions of velocity.⁵⁹ If the dissipative forces present in the interaction are odd functions of, and linearly dependent on, velocity, there are no constraints on the conservative forces that the standard FM AFM method can reconstruct.⁵⁹ The standard FM AFM method is discussed below and employed to reconstruct complex hysteretic interactions numerically.

(b) The equation of motion and force and energy reconstruction schemes

The equation of motion in dAFM is typically written in terms of a point mass, linear damping, a spring, a drive force and a non-linear force F_{ts} as follows^{3,92}

$$m \frac{d^2 z}{dt^2} + \frac{m\omega_0}{Q} \frac{dz}{dt} + kz = F_{\text{ts}} + F_{\text{D}} \quad (1)$$

where z is the tip-position relative to the unperturbed equilibrium position of the cantilever, k is the spring constant, Q is the quality factor due to dissipation with the medium, ω_0 is the angular resonance frequency, the effective mass is $m = k/\omega_0^2$, F_{D} is the driving force and F_{ts} is the net tip-sample interaction.⁴⁶ The main assumption in (1) is that the motion due to higher modes of oscillation can be neglected. This assumption is reasonable in ambient and vacuum environment where Q is high,^{102,103} i.e. $Q \sim 10^2$ to 10^5 . The assumptions in (1) are also reasonable in a liquid environment provided the free amplitude A_0 is low enough and provided directly excited cantilevers are employed;⁷⁹ note that base excitation is common in AFM. Moreover the drive frequency ω is sometimes set equal to the natural frequency ω_0 since this leads to convenient simplifications.⁴⁴

From (1), it can be shown that conservative forces, or more thoroughly, forces that are even functions of position,⁵⁹ are related to the virial $V_{\text{ts}} = \langle F_{\text{ts}} z \rangle \equiv \langle F_c z \rangle$ of the tip-sample interaction.⁵³ The expression relating $\langle F_c z \rangle$ to the frequency shift $\Delta\omega$ was initially proposed by Giessibl in 1997 (ref. 56) and by others later.^{104,105} Such expression is typically termed the integral equation of motion. Giessibl himself further inverted the expression and found a close form solution for the conservative force as a function of distance $F_c(d)$ for the small and the large amplitude A approximations. The small amplitude approximation typically requires amplitudes in the order of Å (ref. 106).

Later on, Sader *et al.* found⁵⁷ a close form solution for arbitrary amplitudes. This is in fact the standard FM AFM method for force reconstruction and reads

$$F_c^*(d) = \frac{2k}{|F_{\text{AD}}|} \int_{u=d}^{u=\infty} \left[\left(1 + \frac{A^{1/2}}{8\sqrt{\pi(u-d)}} \right) \Omega(u) - \frac{A^{3/2}}{\sqrt{2(u-d)}} \frac{d\Omega(u)}{du} \right] du \quad (2)$$

In (2) Ω is the normalized frequency shift as in $\Omega = (\omega_r - \omega_0)/\omega_0$ and ω_r is the effective resonant frequency.⁵⁹ Furthermore the conservative force F_c in (2) is normalized *via* the absolute of the minima of force, or force of adhesion $|F_{\text{AD}}|$, i.e. $F_c^* = F_c/|F_{\text{AD}}|$. Normalization is implied here, and throughout, by the asterisk, i.e. F_c^* . In FM AFM Ω is obtained experimentally and A is typically maintained constant as the cantilever separation z_c decreases. The implication is that the minimum distance of approach, i.e. d_m , decreases almost linearly with decreasing z_c , i.e. $d_m \approx z_c - A$. This approximation is reasonable¹⁰⁷ provided the mean deflection is small compared to A and provided the amplitudes of the higher harmonics are small, i.e. typically ~ 1 – 10 pm. This situation typically occurs when the value of Q is high enough as before.^{103,108} In this way, by decreasing the cantilever separation z_c the whole range of d_m is recovered smoothly by monitoring the variation in Ω . Furthermore, the force obtained by solving (2) at each point is that corresponding to $d = d_m$ and d_m can thus be directly equated to the tip-sample distance d by writing $F_c(d)$.

In AM AFM however, Ω is not obtained directly as an experimental observable. Ω is indirectly recovered from the cosine of the phase shift⁵³ Φ which is directly observed experimentally.^{64,109} The relationship is

$$\Omega(d) = \left[\Omega_{\text{D}}^2 + \frac{F_0}{kA} \cos(\Phi) \right]^{1/2} - 1 \quad (3)$$

where Ω_{D} is the normalized drive frequency ω/ω_0 and where F_0 is the magnitude of the driving force, i.e. $F_0 = kA_0/Q$ when $\omega = \omega_0$. At this point, it is worth noting that in AM AFM the (normalized) oscillation amplitude A ($A^* = A/A_0$) varies with cantilever-sample separation z_c . In particular, while in AM AFM there is a functional relationship between A^* and d_m , i.e. $A^*(d_m)$, there is no one to one mapping from d_m to $F_c(d)$.¹¹⁰ Thus, the relationship $d_m \approx z_c - A$ assumed in (2) needs to be used with care. First, in AM AFM d_m does not necessarily decrease linearly with decreasing cantilever separation z_c .¹¹⁰ Second, there might be a missing region in d_m due to bistability.^{63,111,112} Third, due to the derivation of (2), where A is assumed to be constant during the measurements,⁵⁷ errors from variations in A might follow when acquiring data in AM AFM and by employing (2).⁶⁴ It has been shown *via* numerical integration however that errors in the recovery of F_c in AM AFM, and with the use of (2) and (3), might be 5% or less.^{64,66} Furthermore, the first two points can be dealt with in AM AFM by (i) choosing only the relevant region of d_m experimentally calculated with the standard expression $d_m \approx z_c - A$ and by (ii) driving with sufficiently large values of free amplitude⁶⁶ A_0 such that the bi-stability is avoided.^{92,95,113} In summary, since Ω can be measured directly in FM AFM and indirectly in AM AFM with (3), the conservative force F_c in (2)

can be reconstructed as a function of tip-sample distance d in both FM and AM AFM with the use of (2) and (2) and (3) respectively.

The energy dissipated per cycle E_{dis} can also be recovered in AM AFM with the use of

$$E_{\text{dis}}^*(d) = \frac{\pi k A_0 A(d)}{E_{\text{dis}}(M) Q} \left[\sin(\Phi) - \frac{A(d)}{A_0} \right] \quad (4)$$

where E_{dis}^* implies normalization with respect to maxima $E_{\text{dis}}(M)$ in E_{dis} in a given force–distance curve; similar expressions apply in FM AFM and other dAFM methods.^{44,114} From (4), E_{dis}^* can be mapped onto d_m , or d , from the relationship between A , Φ and d . It is now worth mentioning that there is no direct method for recovering a model free force F_{dis} in Newton, and as a function of distance d , from the integral equation of motion. Expressions (2) and (3) are employed next to reconstruct the conservative force in the presence of complex hysteretic dissipative forces.

(c) Reconstructing conservative forces in the presence of hysteretic forces

As stated, provided viscous forces are the only source of dissipation and these forces are (i) odd functions of tip-velocity $\dot{d}$ and (ii) linearly dependent on $\dot{d}$, (2) can be employed to reconstruct the conservative part of the force F_c .⁶⁶ That is, any errors from (2) are due to the single mode-single frequency^{59,64} and/or the small frequency shift⁵⁶ approximations only. Furthermore, and while these forces are not discussed in detail in this work, the two conditions above imply that^{63,76} $F_{\text{dis(A)}}(d, \dot{d}) = -F_{\text{dis(R)}}(d, \dot{d}) = -\eta(d)\dot{d}$ where $F_{\text{dis(A)}}$ is the viscous force on tip approach, $F_{\text{dis(R)}}$ is the viscous force on tip retraction⁶³ and η is a function of distance d only. The possible failure of (2) can be understood by realizing that in practical cases of interest η might depend on either the sense of motion, or the tip velocity $\dot{d}$ or both and not on d only. Then $\eta_{\text{(A)}}(d, \dot{d}) \neq \eta_{\text{(R)}}(d, \dot{d})$. Some realistic cases that might lead to the functions $\eta_{\text{(A)}}$ (tip approach) and $\eta_{\text{(R)}}$ (tip retraction) not being equivalent include (i) cases where different phenomena occur during tip approach and tip retraction, *i.e.* the formation and rupture of the capillary bridge or chemical bonds, or hysteretic sample deformation occurring when the samples are very compliant^{115,116} and (ii) cases where the tip oscillates in a different medium during tip approach and tip retraction, *i.e.* formation and rupture of the capillary bridge. In all these cases, expression (2) will then recover a value of $F_c(d)$ that is either that of the viscous independent path on tip approach only or that lying in between that of tip approach and tip retraction.^{66,76} In fact, the condition $\eta_{\text{(A)}}(d, \dot{d}) \neq \eta_{\text{(R)}}(d, -\dot{d})$ implies a viscous force equivalent to a hysteretic force since the magnitude $|\eta(d)\dot{d}|$ depends on the sense of motion.

Other than viscous forces, hysteretic forces are typically discussed in the literature.^{101,117} Hysteretic forces introduce ambiguity in terms of (2) since in these cases a single force cannot be defined at a given distance. More thoroughly, in the presence of hysteresis the tip-sample system is, by definition, metastable and dissipation will occur even in the absence of viscosity. The expression (2) however can still be employed to recover a single

value of F_c at a given distance d . It will be shown below (Fig. 2) that the recovered values of $F_c(d)$ with (2) depend on the nature of the hysteretic force. More thoroughly $F_c(d)$ depends on the relationship between the onset and breakoff distances on tip approach and retraction respectively. Next, two relevant hysteretic forces are defined and (2) is tested in their presence.

As a first type of hysteretic force, let us consider short range hysteresis. This is a key dissipative mechanism that is assumed to control nanoscale energy dissipation.^{41,88,118} Theoretical as well as experimental investigations have been conducted for years from the classical⁴¹ and atomistic perspectives,¹¹⁹ or by interpreting the data in terms of a combination of both.^{24,120,121} Short range hysteresis might originate from variations in surface energy, *i.e.* surface energy hysteresis. Some reports²⁴ have suggested that the molecular origin of surface energy hysteresis might relate to variations in the molecular configuration of the system. Others have observed short range hysteresis and interpreted it as sub-molecular motion of organic films.¹²² Here we consider a simple model for a short range hysteretic force F_i

$$F_i = -4\pi R \gamma_i, \quad d < a_0 \quad (5)$$

where γ is the surface energy¹²³ and $i \equiv a$ on tip approach and $i \equiv r$ on tip retraction.⁴¹ R is the tip radius and a_0 is the inter-molecular distance below which mechanical contact occurs. There are two important assumptions in (5). First, (5) does not take into account possible variations in surface energy γ as a function of distance d , that is, γ is constant during tip approach and tip retraction. Second, the onset d_{on} and breakoff d_{off} of the force coincide on tip approach and tip retraction at $d = a_0$, *i.e.* $d_{\text{on}} = d_{\text{off}} = a_0$. This situation might not be realistic experimentally but it is considered for completeness.

A second type of hysteretic force is considered here where the onset d_{on} and breakoff d_{off} distances do not coincide. Such forces have also been considered for over a decade by several groups and are thought to describe realistic phenomena.^{100,101,117,124–126} Here we term such form of hysteresis forces presenting $d_{\text{on}} - d_{\text{off}}$ mechanisms. Mathematically, a simple force presenting a $d_{\text{on}} - d_{\text{off}}$ mechanism can be described as follows

$$F_{\text{on-off}} = \begin{cases} 0 & d > d_{\text{off}} \\ 1 & d < d_{\text{on}} \\ 0 & d > d_{\text{on}}, \kappa = 0 \\ 1 & d > d_{\text{on}}, \kappa = 1 \end{cases} \quad (6)$$

where κ acts as a memory parameter that starts with $\kappa = 0$ and d is the tip surface separation measured from the sample surface ($d_{\text{off}} > d_{\text{on}}$). If the tip crosses d_{on} , where $d < d_{\text{on}}$, $\kappa = 1$. If the tip retracts past d_{off} , where $d > d_{\text{off}}$, $\kappa = 0$. From (2), the force $F_{\text{on-off}}$ is activated instantly (taking a value of 1) if the tip is closer to the surface than d_{on} ($d < d_{\text{on}}$) and the force persists provided the tip does not retract past d_{off} . Otherwise the force is discontinuously nulled. Physically, in the case of capillary interactions, d_{on} is identified with the distance at which van der Waals perturbations induce the formation of the capillary neck. Numerically d_{on} is approximately 3 times the height of the water layer according to theory.¹²⁷ The distance d_{off} is the distance at which the stability of the neck is compromised and it breaks.¹⁰¹ In the

case of physical or chemical bond formation and rupture d_{on} and d_{off} refer to the distances of formation and rupture of the bonds respectively.^{126,128}

For Fig. 1, the equation of motion (1) has been implemented in C and solved numerically with a fourth order Runge Kutta algorithm. A lock-in-amplifier has also been implemented in the simulation to recover the fundamental oscillation amplitude A and the phase shift Φ . Two standard^{92,129} conservative forces have been employed in the simulations. These are the long range London dispersion contribution to the van der Waals force F_{vdW} (7), considered *via* the Hamaker approach,¹³⁰ and the repulsive force due to mechanical contact F_{DMT} (8), considered *via* the Derjaguin Muller Toporov (DMT) model of contact mechanics¹³¹

$$F_{\text{vdW}} = -\frac{HR}{6d^2} \quad d > a_0 \quad (7)$$

$$F_{\text{DMT}}(d) = \frac{4}{3}E^*\sqrt{R}\delta^{3/2} \quad d \leq a_0 \quad (8)$$

where H is the Hamaker constant that accounts for the atoms of the tip-sample system interacting in a medium, E^* is the effective elastic modulus of the contacting bodies that accounts for mechanical properties and δ is the tip-sample deformation, *i.e.* $\delta = a_0 - d$. Note also that the surface energy and the Hamaker constant can be related *via*¹²³

$$\gamma = \frac{H}{24\pi a_0^2} \quad (9)$$

In the contact, *i.e.* when $d \leq a_0$, the force described by (5) has also been implemented. As discussed, this force can be employed to model surface energy hysteresis and introduces a form of metastability in the contact region that leads to energy dissipation in a cycle, *i.e.* $E_{\text{dis}} > 0$ provided $d < a_0$. A second source of dissipation has been implemented employing (6). As discussed, while also hysteretic in nature, the force in (6) activates at a distance d_{on} and deactivates if and only if the tip moves past a distance d_{off} on retraction, $d_{\text{off}} > d_{\text{on}}$. Such forces might act in the contact region, where mechanical and chemical processes occur, as well as in the long range where chemical affinity might affect the magnitude of the force as well as the distances d_{on} and d_{off} . Note that the range at which the $d_{\text{on}} - d_{\text{off}}$ mechanism dissipates

energy depends solely on where the $d_{\text{on}}/d_{\text{off}}$ distances are defined. Then, since the ability of (2) to recover the forces is not affected by the choice of $d_{\text{on}}/d_{\text{off}}$ distances, here, without loss of generality, we define them to be in the long range. In particular, we take $d_{\text{off}} > d_{\text{on}} > a_0$. Furthermore, in Fig. 1 the following cantilever-sample parameters have been employed: $k = 40 \text{ N m}^{-1}$, $f_0 = 300 \text{ kHz}$ (natural frequency), $Q = 450$, $A_0 \approx 25 \text{ nm}$, Young's modulus of the tip $E_t = 120 \text{ GPa}$, Young's modulus of the sample $E_s = 1 \text{ GPa}$ (then $E^* \approx 1 \text{ GPa}$), $R = 8 \text{ nm}$, surface energy of approach $\gamma_a = 10 \text{ mJ m}^{-2}$ and that of retraction $\gamma_r = 20 \text{ mJ m}^{-2}$, $d_{\text{on}} = 0.5 \text{ nm}$, $d_{\text{off}} = 1.5 \text{ nm}$ and $a_0 = 0.165 \text{ nm}$.

The net tip-sample force F_{ts} employed in the simulations is shown in Fig. 1 with the use of continuous black lines. Where the force is two, valued at a given distance d , the path of tip approach corresponds to the highest value and that of tip retraction corresponds to the lowest value. The conservative force F_c according to (2) is shown with the use of dashed blue lines. Several aspects are worth mentioning. First note that F_c follows very accurately (errors of less than 2%) the conservative long range force (black lines) prior to $d = d_{\text{on}}$. This corresponds to the London dispersion force modeled with (7). Second, the metastability of the $d_{\text{on}} - d_{\text{off}}$ mechanism in the $d_{\text{on}} = 0.5 \text{ nm} < d < 1.5 \text{ nm} = d_{\text{off}}$ region modeled with (2) is not recovered. In particular, the data show that when hysteretic forces presenting the $d_{\text{on}} - d_{\text{off}}$ mechanism are present, in the metastable region (2) recovers the force of the tip-approach path only and not that of tip retraction. That is, the conservative force according to (2) is the exact path of tip approach. Physically, this result implies that mechanisms related to bond formation and rupture in the long range, *i.e.* chemical and physical reactivity, and long range capillary interactions, amongst other phenomena, cannot be fully probed with (2). Furthermore, it can be shown⁶⁶ that the energy dissipation eqn (4) misses similar phenomena. Third, the discontinuity and overshoot in F_{ts} observed at $d = d_{\text{on}}$ result as a consequence of the onset of the hysteretic force (7). This is a consequence of the Gibbs phenomenon at the discontinuity.¹³² Fourth, during mechanical contact, *i.e.* $d < a_0$, the attractive hysteretic force in (5) acts. Recall that the main difference between this hysteretic force and the previous one is that here $d_{\text{on}} = d_{\text{off}}$. The implication of $d_{\text{on}} = d_{\text{off}}$ is that the standard FM AFM method for force reconstruction in (2) recovers a value of F_c lying in between the approach and retraction paths. Fifth, the accuracy of F_c from (2) deteriorates (not all data shown) as the tip further indents into the surface. This is a consequence of the assumptions in the derivation, *i.e.* the small frequency shift.⁵⁶ In summary, in the presence of hysteretic forces, the standard method of force reconstruction (2) will provide, at its best, an effective value of F_c lying in between the approach and retraction paths. More importantly, and considering that d_{on} might not coincide with d_{off} in practical cases, in most cases only the path of tip approach will be recovered. The physical implication is that the recovered values might lead to errors and inaccuracies when quantifying nanoscale phenomena. In particular, these errors might lead to miss-calculations of important nanoscale sample mechanical properties such as peak forces⁷⁹ and the related Young's modulus.²¹

The force reconstruction example described with the use of Fig. 1 has been discussed by employing the standard method for

Fig. 1 Simulation of a tip-sample interaction profile where conservative and hysteretic dissipative forces are simultaneously present in the interaction. F_{ts} (sim.) in continuous black lines stands for the force profile used in simulations while F_c (rec.) in dashed blue lines is the recovered conservative force according to the standard FM AFM method of force reconstruction in (2). When the force is double valued, the path of tip approach coincides with the highest values.

force reconstruction in FM AFM (2). Nevertheless, the outcome is general for methods, such as that in (2), that depend on inversion of the integral equation of motion and the minimum distance of approach d_m , and that have the standard assumptions involving even and odd functions of distance.^{59,62,63} In summary, ambiguity arises in terms of the value, and even the meaning, of conservative force in the presence of hysteretic forces. In practice however a highly sophisticated instrument such as the AFM should be able to provide detailed information about relevant nanoscale interactions, including those related to the above mechanisms, with no restrictions. In what follows, two methods are presented that overcome the limitations of force reconstruction methods based on the integral equation of motion.

3. Force reconstruction in steady state oscillation: the method of modal analysis

(a) The modal analysis formalism

The one dimensional Euler–Bernoulli beam equation that governs the dynamics of a rectangular beam can be written as follows¹³³

$$EI \frac{\partial^4}{\partial x^4} (u(x, t) + a_1 \dot{u}(x, t)) + a_0 \ddot{u}(x, t) + \mu(x) \ddot{u}(x, t) = f_{ts}(x, t) \delta(x - L) \quad (10)$$

$$\dot{u}(x, t) = \frac{\partial u(x, t)}{\partial t} \quad \text{and} \quad \ddot{u}(x, t) = \frac{\partial^2 u(x, t)}{\partial t^2}$$

In this equation, the elastic modulus $E(x)$ and moment of inertia $I(x)$ are assumed to be constant along the length of the cantilever L where x is the coordinate along the cantilever axis. The damping in the system is accounted for by a_0 and a_1 that are the mass proportional damping and the stiffness proportional damping parameters, respectively. The mass per unit length $\mu(x)$ is also considered as constant along the cantilever length and can be estimated from the density ρ and cross-section area A i.e. ($\mu = \rho A$). The tip-sample force f_{ts} is implemented in this formalism as an external force localized at the end of the cantilever using the delta function $\delta(x - L)$.

The boundary conditions that govern the cantilever motion are:

$$u(0, t) = y(t), \quad u'(L, t) = 0,$$

$$u'(0, t) = 0, \quad u'''(L, t) = 0.$$

where the derivatives are with respect to x . Here eqn (10), along with the boundary conditions, is written in terms of the absolute cantilever position $u(x, t)$ in an absolute inertial reference frame. This implies that the base motion is already incorporated in the expression. If the equation is projected onto a non-inertial reference frame by expressing the cantilever deflection $w(x, t)$ as

$$w(x, t) = u(x, t) - y(t) \quad (11)$$

where $y(t)$ is the base motion, the inertial terms appear naturally in the equation as an equivalent excitation force and all the

boundary conditions will be nulled. Substituting (11) into (10) results in

$$EI \frac{\partial^4}{\partial x^4} \left(w(x, t) + y(t) + a_1 \frac{\partial}{\partial t} \{w(x, t) + y(t)\} \right) + a_0 \frac{\partial}{\partial t} \{w(x, t) + y(t)\} + \mu \frac{\partial^2}{\partial t^2} \{w(x, t) + y(t)\} = f_{ts}(x, t) \delta(x - L) \quad (12)$$

The principle of separation of variables can now be applied to expand $w(x, t)$ as a series of eigenmodes where (see Appendix A)

$$w(x, t) = \sum_{m=1}^{\infty} \varphi_m(x) z_m(t) \quad (13)$$

$\varphi_m(x)$ is the normalized eigenfunction of the m th bending mode of a uniform thin rectangular beam. The eigenmodes are normalized i.e. $\varphi(L) = 1$ and, consequently, the measured tip deflection is $z_m(t)$.

Substituting (13) into (12), followed by multiplication with $\varphi_m(x)$ and integration over the length of the cantilever L , results in the following expression (see Appendix A)

$$EI z_m(t) \lambda_m^4 \alpha_m + a_1 EI \dot{z}_m(t) \lambda_m^4 \alpha_m + a_0 \dot{z}_m(t) \alpha_m + \mu \ddot{z}_m(t) \alpha_m + a_0 \beta_m \dot{y}(t) + \mu \ddot{y}(t) \beta_m = f_{ts}(L, t) \varphi_m(L) \quad (14)$$

$$\alpha_m L = \int_0^L \varphi_m^2(x) dx, \quad \text{and} \quad \beta_m L = \int_0^L \varphi_m(x) dx$$

Note that from 14 onwards summation over m is implied throughout. Eqn (14) can now be written in a more familiar form as (see Appendix A)

$$M_m \omega_m^2 z_m(t) + \frac{\omega_m M_m}{Q_m} \dot{z}_m(t) + M_m \ddot{z}_m(t) + [a_0 \dot{y}(t) \beta_m + \mu \ddot{y}(t) \beta_m] = f_{ts}(t) \quad (15)$$

In (15) the different terms in (14) are expressed in the form of generalized modal quantities, namely, generalized modal mass M_m and generalized modal quality factor Q_m . In fact the equation of motion described by (1) is simply the first mode in (15), i.e. $m = 1$, and standard methods involving the integral equation of motion, i.e. (2), are developed from it by ignoring higher modes, i.e. $m > 1$.

Note also that the effect of base excitation (quantity in square brackets) is translated into an equivalent excitation force. Further modifications are seen in terms of the tip-sample force. Here the explicit dependence of $f_{ts}(t)$ on time only is understood from the point of view that the force acts at the end of the cantilever only. Then, $\varphi(L)$ is simply 1 due to normalization.

By using the decoupled m equations in (15), the cantilever response to any arbitrary periodic base excitation can be derived. This is done by writing the equation in the frequency domain to express the steady state dynamics as follows

$$M_m z_m(j\Omega) \left\{ \omega_m^2 + \frac{j\Omega \omega_m}{Q_m} - \Omega^2 \right\} + \beta_m y(j\Omega) \times [j\Omega a_0 - \mu \Omega^2] = f_{ts}(j\Omega) \quad (16)$$

Note that (16) now contains the angular frequency of the base excitation Ω . Also note that (16) is satisfied for m mode shapes of the cantilever for every harmonic n ; $n = 0$ is the static solution (DC deflection of the cantilever). An accurate representation of the force profile is obtained by taking a sufficient number of modes m and harmonics n (ref. 74–76). With this understanding and from (16) we express the n th harmonic of the tip-sample force as

$$M_m A_{mn} e^{j\alpha_{mn}} H_{mn} + \beta_m A_{dn} e^{j\theta_n} [jn\Omega a_0 - \mu n^2 \Omega^2] = F_n e^{j\gamma_n} \quad (17)$$

where the phasor representation is employed to express $z_m(jn\Omega)$ with an amplitude A_{mn} and phase α_{mn} for the m th mode and n th harmonic.

The base excitation $y(jn\Omega)$ has no modal dependence so A_{dn} and θ_n are the amplitude and phase of the n th harmonic of the base excitation respectively. The quantity H_{mn} is used in (17) to replace the quantity in brackets in (16). Then, the system of equations in (17) needs to be solved for every harmonic n . This results in a complex force term f_{ts} (magnitude F_n and phase γ_n). Finally, taking into account that the measurable quantities are the amplitudes and phases of each harmonic, it follows that

$$A_n e^{j\alpha_n} = \sum_{m=1}^{\infty} A_{mn} e^{j\alpha_{mn}} \quad (18)$$

(b) Numerical example with the modal analysis

Without the loss of generality we next demonstrate the analysis for a three mode system while the final expression can be easily extended to any number of modes and harmonics. In the matrix form (17) reads

$$\begin{pmatrix} M_1 H_{1n} & 0 & 0 \\ 0 & M_2 H_{2n} & 0 \\ 0 & 0 & M_3 H_{3n} \end{pmatrix} \begin{pmatrix} A_{1n} e^{j\alpha_{1n}} \\ A_{2n} e^{j\alpha_{2n}} \\ A_{3n} e^{j\alpha_{3n}} \end{pmatrix} + A_{dn} e^{j\theta_n} (jn\Omega a_0 - n^2 \Omega^2 \mu) \begin{pmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \end{pmatrix} = F_n e^{j\gamma_n} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad (19)$$

which when multiplied by the inverse of the MH matrix

$$\begin{pmatrix} A_{1n} e^{j\alpha_{1n}} \\ A_{2n} e^{j\alpha_{2n}} \\ A_{3n} e^{j\alpha_{3n}} \end{pmatrix} + A_{dn} e^{j\theta_n} (jn\Omega a_0 - n^2 \Omega^2 \mu) \begin{pmatrix} 1/M_1 H_{1n} & 0 & 0 \\ 0 & 1/M_2 H_{2n} & 0 \\ 0 & 0 & 1/M_3 H_{3n} \end{pmatrix} \begin{pmatrix} \beta_1 \\ \beta_2 \\ \beta_3 \end{pmatrix} = F_n e^{j\gamma_n} \begin{pmatrix} 1/M_1 H_{1n} & 0 & 0 \\ 0 & 1/M_2 H_{2n} & 0 \\ 0 & 0 & 1/M_3 H_{3n} \end{pmatrix} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \quad (20)$$

Finally, the n th harmonic of the tip sample force is

$$F_n e^{j\gamma_n} = \frac{A_n e^{j\alpha_n} + A_{dn} e^{j\theta_n} (jn\Omega a_0 - n^2 \Omega^2 \mu) \sum_{k=1}^{k=m} \frac{\beta_k}{M_k H_{kn}}}{\sum_{p=1}^{p=m} \frac{1}{M_p H_{pn}}} \quad (21)$$

And the instantaneous (net) tip sample force is

In the standard dAFM, the base motion occurs at a single frequency Ω . Thus, $A_{dn} = 0$ for all n but $n = 1$. Furthermore, as the modal analysis assumes steady state oscillation, t has to cover only one cycle of oscillation to fully reconstruct the tip-sample force. In practice however, several cycles are necessary per pixel, depending on the topography, in order to reach the steady state and perform the FFT. Reaching the steady state with standard cantilevers in dAFM under ambient conditions typically requires oscillation of ~ 1 ms. In a liquid environment, where the Q factor is orders of magnitude smaller, the steady state might be reached in fractions of ms. This is the temporal limitation of the modal analysis as presented here and it is, in principle, similar to the limitations of the standard AM AFM where imaging in the steady state is required.⁴⁶

The validity of the formalism is next tested by employing numerical results obtained from finite element FE simulations using a commercial package (Ansys). In FE, a beam element BEAM188 is utilized as a 1D element to simulate the AFM cantilever. A mesh refinement study is conducted to ensure mesh independent results. The cantilever oscillates because of the base excitation and the tip-sample force includes both types of hysteresis (5) and (6) discussed with the use of Fig. 1. The absolute tip position $u(L, t)$ is then extracted and from this and the use of (13) the cantilever deflection is determined. Fig. 2 shows an FFT of the signal and four oscillations of the steady state cantilever deflection as a function of time in the inset. The FFT shows the presence of harmonic amplitudes and the inset demonstrates the distortion of the waveform that generates

the harmonics. From the amplitude spectrum, one can deduce the number of eigenmodes that significantly contribute to the cantilever oscillation, or, more thoroughly, the number of harmonics that could be detected from an experimental point of view. The resonances of the modes are shown in the figure with the use of dashed blue lines. Note that these do not typically coincide with higher harmonics. In the case of Fig. 2, harmonics contribute with amplitudes in the pm range or larger up to the

Fig. 2 Finite element simulation of a vibrating cantilever. The amplitude spectrum of the deflection waveform shows equally spaced amplitudes of the higher harmonics. The plot can point out the significant number of modes that can describe the cantilever motion (four modes). The inset shows four cycles of the steady state tip deflection $w(L, t)$ of the cantilever as a function of time. Some wave distortion can be observed due to the presence of higher harmonics. Simulation parameters: $L = 160 \mu\text{m}$, $A = 25 \times 5 \mu\text{m}^2$, $\rho = 2300 \text{ kg m}^{-3}$, $E_t = 200 \text{ GPa}$, and $Q_1 = 20$.

4th eigenmode. Frequencies closer to higher modes have even smaller amplitudes that would therefore be buried under the base noise in experiments. The relevant question is whether the harmonics that, in principle, could be experimentally detected suffice, *i.e.* up to the 4th mode, to observe the details of the approach and retraction paths where (2) fails, *i.e.* the meta-stable regions.

According to (21), the full waveform for $f_{ts}(t)$ can be recovered from the harmonic components by employing (22). It is instructive however to discuss the contribution of each mode, the relevant number of harmonics n that should be considered when considering a given number of modes m and the details that can be recovered in each case. This is shown in Fig. 3 and 4 and is the aim of the discussion that follows. The force employed in the simulations is similar to that discussed in Fig. 1 and comprises hysteretic dissipative forces (5) and (6) and conservative forces (7) and (8) like before. The net force in the simulations is shown with the use of continuous black lines and the reconstructed force according to (22) is shown with the use of blue lines. First in Fig. 3a a single mode has been implemented and the contribution from the higher mode signal has been ignored. This is equivalent to employing (1) as the equation of motion or to employing $m = 1$ only in (21). The reconstructed force $F_{ts}(\text{rec.})$ in blue lines has been acquired with the use of 3 harmonics only since these are the harmonics towards which the first mode contributes the most. It can be readily observed that while the reconstructed force $F_{ts}(\text{rec.})$ already has a tendency to follow the true force $F_{ts}(\text{sim.})$ errors in peak forces can be as large as 40%. However, the area under the curve, *i.e.* the energy dissipated in the interaction E_{dis} , already accounts for over 95% of the total dissipated energy. This is in agreement with previous studies⁷⁶ and in accordance with^{101,134} the use of (4), *i.e.* the single mode-single frequency approximation, in previous reports.¹³⁵ The consequences of employing 50 harmonics to reconstruct the force when employing the single mode approximation are shown in Fig. 3a with the use of grey lines. It is clear that the error is dramatic and stems from the fact that harmonics higher than the third are encoded mainly in

Fig. 3 FE simulations *versus* the modal analysis scheme for force reconstruction. The force employed in the simulations is shown in black $F_{ts}(\text{sim.})$. The blue curve $F_{ts}(\text{rec.})$ is the force reconstructed by utilizing the relevant number of harmonics for every mode. (a) For mode 1 we use 3 harmonics, (b) for mode 2 10 harmonics and (c) for mode 3, 27 harmonics. Note that from the second mode alone an accurate estimation of the maximum indentation depth and the hysteretic part inside the material, *i.e.* the region of mechanical contact, is recovered already. In gray, a fixed number of harmonics (50 harmonics) have been employed to reconstruct the force when employing 1, 2 and 3 modes respectively. The number 50 is instructively chosen because it is the number of harmonics employed with the 4 mode approximation. It is clear that increasing the number of harmonics alone does not lead to accurate reconstruction unless the right number of modes is considered. Simulated force parameters: $d_{\text{on}} = 1.5 \text{ nm}$, $d_{\text{off}} = 4.5 \text{ nm}$, $H = 3 \times 10^{-19} \text{ J}$, $R = 15 \text{ nm}$, $\gamma_a = 10 \text{ mJ m}^{-2}$, $\gamma_r = 40 \text{ mJ m}^{-2}$, $E_s = 10 \text{ GPa}$, and $A_d = 1.5 \text{ nm}$.

the higher modes of oscillation rather than in the first mode.^{102,103} From this, it follows that increasing the number of harmonics alone does not lead to accurate reconstruction unless the right number of modes is considered. Next, in Fig. 3b two modes have been implemented. The same true force $F_{ts}(\text{sim.})$ has been employed in the simulations. In order to reconstruct the force $F_{ts}(\text{rec.})$ with the use of (21) and (22) however, 10 harmonics have been employed since these are the harmonics mainly encoded by the first and second modes. The error in the peak force is now approximately 5–10%. This is good considering that complex hysteretic forces, such as those in (5) and (6), are present in the interaction and that only two modes and 10 harmonics have been considered. The errors in the points of discontinuity however are still large and lead to

Fig. 4 Force reconstruction in the steady state using the method of modal analysis. (a) Force waveform as a function of time. The reconstructed force (dashed blue lines) using (22) is in very good agreement with the force F_{ts} (sim.) employed in FE (black lines) producing peak forces with errors $\sim 2\%$ or less. (b) Approach (red) and retraction (blue) reconstructed force curve as a function of the absolute tip position $u(L, t)$. The short range hysteretic region is very well captured even if the Gibbs phenomenon can still be observed at the points of discontinuity. Simulation parameters as in Fig. 3.

large errors in the approach and retraction paths. This is particularly noticeable in the metastable regions such as the long range hysteretic force modeled by (6); note the errors in the area lying between the $d_{on} - d_{off}$ distances there. The source of these errors can be appreciated when trying to employ 50 harmonics to reconstruct the force with the 2-mode model. This is shown in Fig. 3b with the use of grey lines as before. The deviations in force when 50 harmonics are employed are due to the fact that a significant part of the signal is still encoded in higher modes. In Fig. 3c, three modes have been employed to recover the force F_{ts} (rec.) with the use of the corresponding 27 pertinent harmonics. The peak forces are now recovered with errors smaller than 5% and the metastable regions are identified as enclosed areas; recall that identifying the metastability due to the presence of hysteretic forces was one of the motivations for the development of the present formalisms. The fact that some signals are still encoded in the higher modes and harmonics can be deduced from the errors resulting when 50 harmonics are included in this particular 3 mode model (grey lines). Still, from Fig. 3, it follows that 3 modes and 27 harmonics are, in principle, sufficient to extract information about complex dissipative forces such as the two hysteretic forces modeled with the use of (5) and (6) leading to up to four discontinuities per cycle. Sufficient here implies that the difference in approach and retraction paths results in forces larger than, *i.e.* at least double as in Fig. 3c, the error in force due to the undulation which results from the superposition of harmonic waves. In the case of the fundamental frequency employed in this work, *i.e.* $f_0 \sim 300$ kHz, the implication is that the details of the tip-sample force, and in particular of complex hysteretic processes, are encoded in frequencies up to 7–8 MHz. Importantly, peak forces are recovered independent of the indentation depth. That is, there are no assumptions, such as small perturbation assumption, as in the case of (2).

In Fig. 4 the multimodal formalism is shown to lead to the recovery of the approach and retraction paths employed in the FE simulation F_{ts} (sim.) (black lines) as a function of time (Fig. 4a) and tip position (Fig. 4b). Arguably, the fact that the reconstruction closely follows the force can be better shown in

Fig. 4b when plotted as a function of d but the figures are equivalent. In the force plot in Fig. 4b the reference value for the tip position $u(L, t)$ is arbitrary since, as in the experimental case, the location of the sample surface is unknown. Still, it is a common practice to locate the zero value where the force starts to increase, *i.e.* coinciding with the onset of repulsive forces. The metastability in the force is observed at the relevant distances $d_{on} \leq d \leq d_{off}$, where the sudden discontinuity of the force is translated into a steep decrease in the reconstructed force. In Fig. 4b the paths of approach (red) and retraction (blue) in the region of mechanical contact are reconstructed with negligible errors relative to the force F_{ts} (sim.) in the simulation. The oscillatory behavior of the recovered force signal in both the approach and retraction paths is a consequence of the superposition of harmonic waves and should die off only in the limits n and $m \rightarrow \infty$. Over-shooting at the points of discontinuity of force will always be present however as a consequence of the Gibbs phenomenon.^{76,132} Importantly, 4 modes and 50 harmonics with an FFT resolution of about 30 Hz have been employed in Fig. 4. The finite value of FFT resolution has limits that also contribute to the error in the force reconstruction scheme. Such limitations are due to the computational cost of the FE method and numerical noise. These two particular sources of errors should not be so important in experiments where the steady state can be maintained for seconds or more and where longer signals (tens of milli-seconds) can be easily recorded and analyzed experimentally.

The modal analysis formalism and the discussion on Fig. 2–4 have shown that the main drawbacks and limitations of standard force spectroscopy or reconstruction measurements, as described in the previous section, can be overcome. Nevertheless, while modal analysis is a powerful approach to capture the details related to discontinuous and hysteretic phenomena, as for example what can be described with the use of (5) and (6) or similar models, there is a fundamental assumption that deserves consideration. Note that in order to recover the details of the instantaneous tip-sample force, neither conservative nor dissipative forces should vary during measurements. That is, forces can be arbitrary but, for a given set of conditions and tip history, the tip-sample forces should remain constant after the cantilever reaches the steady state. Then an FFT can be acquired. Practically, under ambient conditions it is required that the tip-sample forces do not vary for several milliseconds when the tip oscillates in a particular position on the sample.⁷⁶ The practical implication is that such an approach might not capture dynamic phenomena that have time scales shorter than the time needed by the cantilever to reach the steady state, *i.e.* $\sim$ ms. On the other hand, eqn (22) and the distortion of the waveform in Fig. 2 imply that a single cycle already contains all the information related to the instantaneous tip-sample force. It should then be expected that a suitable formalism would allow us to carry out single cycle force reconstruction without limitations related to the steady state or the number of cycles required to perform an FFT. This is the subject of the next section and it is based on moving from monitoring the cantilever at a single point on its longitudinal axis to monitoring the

motion at several locations. This is a change of paradigm that provides information on the cantilever dynamics that leads to the recovery of the tip-sample and sample's properties in a single cycle or faster.

4. Transient phenomena and the differential quadrature method (DQM)

The way in which the formalism of cantilever dynamics has been posed above might require some changes for single cycle force measurements. More specifically, consideration should be given to the way in which the tip-sample force is taken into account. In the previous method, *i.e.* modal analysis, the force is localized at the end of the cantilever and modeled with a delta function as in (10).⁸³ The boundary conditions, however, are those of a free vibrating cantilever so the mode shapes can be evaluated in this way and employed to reconstruct the force. The tip-sample force that is being probed however is in fact acting normally to the cantilever axis. That is, there is a shear force acting at the cantilever's end (see boundary conditions that apply to (10)). Thus, the instantaneous force acting on the cantilever can be estimated from the third (spatial) derivative of the cantilever deflection. Practically however, it is clear that this is challenging by noting that the force has a dependence on the tip sample's separation.¹³⁶ Thus, the instantaneous shape of the cantilever has to be spatially sampled with infinite resolution to perform numerical differentiation. Here we can invoke the differential quadrature method DQM¹³⁷ which is a numerical approach that can evaluate such derivatives accurately with a considerably small number of sampling points along the cantilever axis. DQM is an efficient discretization method that transforms a non-linear boundary-initial-value problem and the corresponding boundary conditions into a coupled set of ordinary differential equations that govern the time evolution of the system.¹³⁸ DQM has already proved to provide highly accurate solutions for many problems in applied sciences^{139,140} and more specifically in the field of structural dynamics.^{141,142} In DQM the derivative of a function with respect to a variable at a given point is approximated as a weighted linear sum of the function values at all discrete points in the range of that variable.¹³⁸ In terms of dimensionless variables, the r th order derivative of a function $w(\zeta)$ at $\zeta = \zeta_i$, defined between 0 and 1 with N discrete grid points, is given by.

$$\left[\frac{d^r w}{d\zeta^r} \right]_{\zeta=\zeta_i} = \sum_{j=1}^N A_{ij}^{(r)} w_j, \quad i = 1, 2, 3, \dots, N \quad (23)$$

The elements of $A_{ij}^{(r)}$ are the weighting matrix coefficients corresponding to the r th order derivative. The details of calculation of $A_{ij}^{(r)}$ are provided in Appendix B. For completeness, a simpler form of (10) is employed where the stiffness proportional damping coefficient is neglected. Then

$$EI \frac{\partial^4}{\partial x^4} (w(x, t) + y(t)) + a_0 \frac{\partial}{\partial t} \{w(x, t) + y(t)\} + \mu \frac{\partial^2}{\partial t^2} \{w(x, t) + y(t)\} = 0 \quad (24)$$

and

$$w(0, t) = 0, \quad w''(L, t) = 0$$

$$w'(0, t) = 0, \quad w'''(L, t) = \frac{f_{ts}}{EI}.$$

The force term does not appear as a boundary condition. A dimensionless variable $\zeta = x/L$ is introduced in order to rewrite the partial differential equation, *i.e.* the governing equation of motion of the cantilever. The result is

$$\frac{EI}{L^4} w^{(4)}(\zeta, t) + a_0 \dot{w}(\zeta, t) + \mu \ddot{w}(\zeta, t) = -a_0 \dot{y}(t) - \mu \ddot{y}(t) \quad (25)$$

$$w(0, t) = 0, \quad \frac{\partial^2 w(1, t)}{\partial \zeta^2} = 0,$$

$$\frac{\partial w(0, t)}{\partial \zeta} = 0, \quad \frac{\partial^3 w(1, t)}{\partial \zeta^3} = \frac{L^3}{EI} f_{ts}.$$

Employing the DQM approximation, the following set of equations directly follows.

$$\ddot{w}(\zeta, t) + \frac{a_0}{\mu} \dot{w}(\zeta, t) + \frac{EI}{\mu L^4} \sum_{j=2}^N A_{ij}^{(4)} w_j = -\frac{a_0}{\mu} \dot{y}(t) - \ddot{y}(t), \quad (26)$$

$$i = 2, 3, \dots, N$$

$$\sum_{j=2}^N A_{ij}^{(1)} w_j = 0, \quad \sum_{j=2}^N A_{ij}^{(2)} w_j = 0, \quad \sum_{j=2}^N A_{ij}^{(3)} w_j = \frac{L^3}{EI} f_{ts}.$$

Both (26) and the corresponding boundary conditions have been recently employed to simulate and interpret the dynamics of an oscillating cantilever in the presence of conservative forces (7) and (8). The study shows how the resonant frequencies, as well as the mode shapes, of the cantilever behave as a function of tip sample separation.¹³⁶ Then the boundary conditions are incorporated into (26) in order to reduce the number of coupled equations to solve.¹⁴³ The system of equations is equivalent to

$$\ddot{w}(\zeta, t) + \frac{a_0}{\mu} \dot{w}(\zeta, t) + \frac{EI}{\mu L^4} \sum_{j=4}^N A_{ij} w_j = -\frac{a_0}{\mu} \dot{y}(t) - \ddot{y}(t), \quad (27)$$

$$i = 4, 5, \dots, N-1$$

$$\sum_{j=4}^N C_j w_j = \frac{L^3}{EI} f_{ts} \quad (28)$$

where

$$A_{ij} = A_{ij}^{(4)} + A_{i2}^{(4)} \eta_j + A_{i3}^{(4)} \chi_j$$

$$C_j = A_{Nj}^{(3)} + A_{N2}^{(3)} \eta_j + A_{N3}^{(3)} \chi_j$$

with

$$\eta_j = \frac{A_{13}^{(1)} A_{Nj}^{(2)} - A_{1j}^{(1)} A_{N3}^{(2)}}{A_{12}^{(1)} A_{N3}^{(2)} - A_{13}^{(1)} A_{N2}^{(2)}}$$

$$\chi_j = \frac{A_{1j}^{(1)} A_{N2}^{(2)} - A_{12}^{(1)} A_{Nj}^{(2)}}{A_{12}^{(1)} A_{N3}^{(2)} - A_{13}^{(1)} A_{N2}^{(2)}}$$

The aim here is force reconstruction in a single oscillation cycle. For this purpose, we focus our attention on eqn (28). The procedure can be described as follows: (1) the deflection of the cantilever in the time domain is recorded, simultaneously, at specific locations on the cantilever according to the grid defined in Appendix B and for any period of time. (2) The deflections at each point are added, after scaling by a weighting coefficient C_j . (3) The waveform of the force, *i.e.* the instantaneous tip-sample force $f_{ts}(t)$, is this summation multiplied by EI/L^3 as in eqn (28).

No assumptions related to cantilever motion are made in this approach except that the governing equation of motion is assumed to be described by the Euler–Bernoulli equation (small deflection assumption). The implication is that the formalism describes both the steady and the transient states of motion. Practically, this results in enhanced temporal resolution and a true single cycle analysis. In fact, it will be also shown below, that, in principle, the temporal resolution is as high as the discrete measurement of the displacement of the cantilever.

FE is employed next to demonstrate the use of eqn (28). Again, a base excited cantilever is simulated and vibrated in the presence of dissipative hysteretic forces as modeled by (5) and (6) and with conservative forces (7) and (8). The assumption of base motion does not affect the generality of the formalism or the concepts developed in this work; modification would lead to a formalism for directly excited cantilevers. In the simulation, the cantilever deflection is recorded at specific points along its axis as defined by grid spacing as illustrated in Fig. 5a with a

cantilever and the five points at which waveforms have been recorded. Initially, it turns out that an eight point grid is necessary, and sufficient, to obtain results with sufficient accuracy. However, from (28), the summation is seen to start from four after including the boundary conditions. Thus, experimentally, the deflection has to be recorded at five different locations along the cantilever axis as shown in Fig. 5a. The distortion in the cantilever motion is more pronounced at distances closer to the base. This can be subtly observed from Fig. 5a and accuracy demonstrated in the simulations (not shown). The 5 locations of the cantilever from which waveforms have been recorded are numbered in the illustration in Fig. 5a and correspond to the 5 numbered waves in the figure. If the length of the cantilever is L , the normalized vector positions are $x/L = 0.3570, 0.6430, 0.8689, 0.9759$, and 1.0000 . The positions have been drawn to scale in the illustration. The waveform of the force, as reconstructed by the DQM method (blue lines), is shown in Fig. 5b. The DQM reconstructed force closely follows the tip-sample force employed in the FE simulations (black lines). This can be better observed in Fig. 5c where the x axis is the tip position. The DQM reconstructed force captures all the features of the force curve including the peak forces with negligible errors, *i.e.* $\sim 1\%$, the points of discontinuity with errors that are less than 15% of that of the adhesion force, the approach and retraction paths and the corresponding metastable regions due to hysteretic forces in the long range and in the mechanical contact region. The force plots in Fig. 5a have been generated as the cantilever was still building up the momentum to reach the steady state (see Fig. 5a). Physically, this implies that the tip-sample force has been reconstructed during the transient state of cantilever vibration. This could have not been achieved with the formalism in Fig. 3 and 4 where oscillation in the steady state was required.

A FE simulation is conducted next where a dynamic tip-sample force is employed. In this case, the expression for the tip-sample force varies during a given simulation emulating transient processes occurring in the tip-sample junction. One could think of cases where a tip interacts with water layers on a sample's surface and where the volume of water increases with time due to the proximity of the tip and the resulting confinement and condensation. Similar fast processes might result from the segregation of matter on the surface on reaching thermodynamic equilibrium,¹⁴⁴ the creeping or plastic deformation occurring on the tip and/or the sample,¹⁴⁵ the motion of ions on the surface,¹⁴⁶ charge transfer¹⁴⁷ or as fast events in biological interactions.⁸⁶

An example that shows the probing of transient phenomena is shown in Fig. 6. As the cantilever oscillates, the force profile is instantaneously replaced from force profile 1 to 2. Force (1) (black lines in Fig. 6a–c) includes short and long range hysteresis forces as modeled with (5) and (6). Force (2) (blue lines in Fig. 6a–c) includes conservative forces (7) and (8) and the force of adhesion F_{AD} , *i.e.* $d < a_0$, only. In the FE simulation force (1) was instantaneously replaced by (2) as the cantilever vibrated, *i.e.* after approximately the third period of oscillation as shown in the figure; note the change in color from black to blue. In both the experiment and simulations, an instantaneous

Fig. 5 Force reconstruction using DQM and compared to finite element FE simulations. (a) The tip deflection waveform recorded at five grid points along the cantilever axis as a function of time. The location of the forces is shown in the illustration of the cantilever and numbered from 1 to 5 accordingly. (b) Verification of the validity of the DQM force reconstruction method (blue) using FE (black) in the simulations. (c) Force profile as a function of the absolute tip position. Simulated force parameters: $D_{on} = 0.5$ nm, $D_{off} = 1.5$ nm, $H = 3 \times 10^{-19}$ J, $R = 20$ nm, $\gamma_a = 10$ mJ m $^{-2}$, $\gamma_r = 40$ mJ m $^{-2}$, $E_s = 10$ GPa, $Q_1 = 500$, and $A_d = 200$ pm.

Fig. 6 Transient force field reconstruction with the DQM method. (a) Force and (b) tip position as a function of time in a transient state. In the finite element FE simulation, two forces are involved and replaced instantaneously. Force (1) is shown with the use of black lines and includes conservative forces and short and long range hysteretic forces. Force (2) is shown with the use of blue lines and dissipation is not included. (c) 3D force plot as a function of absolute tip position and time showing the transition from (1) to (2). (d) Projected forces against the absolute tip position. Parameters as in Fig. 5.

replacement of force induces transient cantilever vibrations but (28) can cope with these situations as shown in Fig. 6c and d. Fig. 6c shows a 3D plot of the tip-sample force as a function of time and tip position. The transition between force profiles occurs approximately at the center of the plot, *i.e.* at time $\approx 47 \mu\text{s}$. The resulting reconstructed force as a function of tip position (DQM) is shown in Fig. 6d.

The objective of this work has been to discuss and examine the advantages and disadvantages of force reconstruction techniques. Ultimately the goal is to probe material properties, chemical reactivity and other complex phenomena. The formalism in this section has shown that phenomena can be accurately quantified even in the transient state of cantilever vibration. An important issue however remains to be addressed. While standard force reconstruction methods are very robust^{59,64,66} the formalisms presented here will be developed next in order to detect variations in the output signal with sufficient accuracy. In particular, the accuracy of the modal analysis depends on acquiring of a FFT with sufficient resolution, *i.e.* with pm resolution. Technologically, attaining such a resolution might be challenging but not unachievable and methods for detection will steadily improve together with improvement of feedback systems, electronics and optics. Moreover, even with the current and standard optical lever method,¹⁴⁸ the waveform for a tip oscillating at a constant separation from the surface can be recorded for any duration. Phenomena such as thermal drift and other specific challenges should also be addressed not only technologically but also by learning from the system, *i.e.* there could be an optimum set of cantilever operational parameters or deviations from standard set-ups which might prove better suited for the implementation of the present formalisms. Other issues relate to the calibration

of the amplitude from volts to nm, *i.e.* InvOLS,¹⁴⁹ and the modal quantities such as M_m , Q_m and ω_m .^{17,150,151}

The DQM method can be employed in the steady state and has the advantage to be valid in the transient state also. Experimentally implementing the DQM method as discussed in this work however might present more challenges in particular with conventional AFM setups. For the implementation of the DQM method, it would be more convenient to modify the instrument. A multi-laser system could be employed to monitor the cantilever shape at various locations on the cantilever. Some groups and manufacturers are currently dealing with similar issues.¹⁵² Some have mapped the waveform of the cantilever during the tip-sample interaction. Others, *i.e.* Kiracofe and Raman,¹⁵³ employed a Doppler vibrometer and successfully decoupled the motion of the cantilever at its base and at its end. Still others scanned the cantilever's surface, *i.e.* Reinstaedtler *et al.*,¹⁵⁴ by employing an optical Michelson heterodyne-interferometer. In the latter case, with current and standard set-ups, like with the Cypher AFM (Asylum Research Corporation, an Oxford instruments company), the laser spot can be employed to automatically scan along the cantilever's axis by disabling the feedback loop. In this way, the full cantilever's waveform can be monitored. In summary, while there are many challenges that need to be met in order to detect the cantilever's wave profile with enough details, the reward might be great enough for the community to pursue it. Thus, in the near future, standard AFMs might ship with the required hardware and software to conduct the experiments proposed in this work.

As a final note, it could be argued that (by allowing $\sim 1 \text{ ms}$ per pixel) the modal analysis could be potentially employed in air applications and with the use of standard cantilevers to recover the true instantaneous force at approximately 1000 pixels per s.

Cantilevers with lower or similar Q factors but higher resonant frequencies might be used to increase the throughput. In fact, as an advantage over methods relying on the fundamental frequency only, in principle, compliant cantilevers should not involve larger errors in the modal analysis. Furthermore, in a liquid environment, the throughput might be much larger since the time to reach the steady state significantly decreases in such a highly damped environment. The two pass technique,⁷⁶ at two different cantilever separations, might further be employed to directly obtain the viscosity independent approach and retraction paths. The two pass technique would not be detrimental in terms of throughput since the trace and retrace are commonly acquired in AFM experiments. The only difference here would be that the cantilever separation would be different in the trace and retrace pass. The above advantages also apply to the single cycle technique, *i.e.* the DQM method. The DQM method has the further advantage of allowing reconstruction of the force while the cantilever is oscillating in the transient state, *i.e.* during variations of the tip-sample force. Thus single cycle methods might be employed to provide feedback on either conservative or dissipative forces, or derivations of these, since transient phenomena can be detected. Such a feedback should lead to faster scans by, in principle, providing a pixel per cycle. For a cantilever vibrating at 70 kHz this translates into approximately 1 image per second when considering standard AFM images of 256×256 pixels per image. Higher throughput might of course be obtained by increasing the drive frequency even though this might lead to further technological challenges related to waveform detection. In summary, higher sensitivity typically involves higher accuracy and precision in any field while higher throughput typically involves higher sophistication in terms of electronic equipment and theoretical development, *i.e.* note that in the multifrequency and related techniques discussed in the introduction several lock-in-amplifiers or external electronic equipment is required. While the proposed methodologies in this work are no exception to this rule, technological developments will likely follow that will meet these requirements.

5. Conclusion

The present work has discussed force reconstruction techniques with an emphasis on complex hysteretic forces. The performance of standard force reconstruction methods has been examined under such situations and concluded to be inaccurate in some cases. In particular, standard force reconstruction methods typically produce effective forces in the presence of hysteresis. Two formalisms based on the differential equation of motion have also been presented and shown to be capable of simultaneously dealing with high sensitivity and high throughput scanning. These are the modal and the DQM method respectively. The first methodology is standard in that it exploits the output signal at a given location on the cantilever's axis, *i.e.* at the end of the cantilever. The second methodology arguably involves a change of paradigm since it exploits the full wave profile, even though in this case signals have to be recorded at five points only.

With both methodologies the force can be recovered without imposing any restrictions and the true instantaneous values are obtained on both tip approach and tip retraction. This implies that phenomena that are induced on tip approach and that differ from the phenomena that occur on tip retraction, *i.e.* bond formation and rupture, can be probed and quantified. This can be summarized by stating that the true and instantaneous force profile is recovered. Amongst others, the present methodologies have overcome (1) limitations of standard force reconstruction methods that are based on the integral equation of motion and produce effective values, (2) limitations of current and standard techniques that fail in the presence of hysteretic forces, (3) limitations in the throughput of reconstruction techniques that require probing of the whole cantilever-sample separation and (4) limitations of force reconstruction techniques that require that the tip-sample forces do not change from cycle to cycle. The limitations of the techniques presented in this work have also been discussed in terms of practical implementation. In particular, the main challenges involve detection of the full wave profile, or the waveform at a single location, with enough accuracy. It is expected however that theoretical developments, more accurate electronic and control equipment and careful experimentation should tell what the limitations are. In summary, future advances should only increase the accuracy of the proposed methods and, since the reward is great enough, it is expected that the interest of the community in this field and direction will only increase.

Appendix A. Steady state force reconstruction (modal analysis)

The solution for a freely vibrating cantilever can be found in dynamics textbooks¹⁵⁵ but a review is given here. The modal analysis requires solving an eigenvalue problem. For a free vibrating cantilever the characteristic equation is

$$\cos \lambda_m L \cosh \lambda_m L = -1 \text{ and } \lambda_m L = \omega_m^{1/2} \left(\frac{EI}{\rho A L^4} \right)^{1/2} \quad (\text{A1})$$

where ω_m is the angular resonance frequency of the m th mode.

There are an infinite number of solutions, *i.e.* $\lambda_1 L = 1.875$, $\lambda_2 L = 4.694$, $\lambda_3 L = 7.854$, *etc.* The eigenvectors or mode shapes $\varphi_m(x)$ must satisfy the boundary conditions given by

$$\varphi_m(0) = \varphi'_m(0) = \varphi''_m(L) = \varphi'''_m(L) = 0.$$

Then

$$\varphi_m(x) = \frac{1}{2} \left[\cos \lambda_m x - \cosh \lambda_m x - \frac{\cos \lambda_m L + \cosh \lambda_m L}{\sin \lambda_m L + \sinh \lambda_m L} \times (\sin \lambda_m x - \sinh \lambda_m x) \right] \quad (\text{A2})$$

The eigenvectors are orthonormal in that

$$\int_0^L \varphi_m(x) \varphi_n(x) dx = \delta_{mn} \quad (\text{A3})$$

where δ_{mn} is the Kronecker delta. The eigenfunctions describe the cantilever motion as a coordinate system as is seen in (13). Substituting into (12) and employing (A3) leads to

$$\begin{aligned} EI z_m(t) \int_0^L \varphi_m^{(4)}(x) \varphi_m(x) dx + a_1 EI \frac{\partial z_m(t)}{\partial t} \int_0^L \varphi_m^{(4)}(x) \varphi_m(x) dx \\ + a_0 \frac{\partial z_m(t)}{\partial t} \int_0^L \varphi_m^2(x) dx + \mu \frac{\partial^2 z_m(t)}{\partial t^2} \int_0^L \varphi_m^2(x) dx \\ + a_0 \frac{\partial y(t)}{\partial t} \int_0^L \varphi_m(x) dx + \mu \frac{\partial^2 y(t)}{\partial t^2} \int_0^L \varphi_m(x) dx \\ = \int_0^L f_{is}(x, t) \delta(x - L) \varphi_m(x) dx \end{aligned} \quad (A4)$$

where

$$\varphi_m^{(4)}(x) = \frac{d^4 \varphi_m(x)}{dx^4}, \text{ and } \varphi_m^{(4)}(x) = \lambda_m^4 \varphi_m(x)$$

where the integrals in (A4) take definite values. For this reason the system simplifies to (14). The modal equations (uncoupled) form an equivalent set of equations that resemble harmonic oscillator motion with generalized modal parameters with the generalized mass $M_m = \mu \alpha_m$ and the generalized stiffness $K_m = EI \alpha_m \lambda_m^4$. The resonant frequencies are

$$\omega_m = \sqrt{\frac{K_m}{M_m}} \quad (A5)$$

Furthermore a generalized damping term Λ can be defined as

$$\Lambda = a_0 \alpha_m + a_1 EI \lambda_m^4 \alpha_m = 2 M_m \omega_m \left(\frac{a_0}{2 \mu \omega_m} + \frac{a_1 \omega_m}{2} \right) = 2 M_m \omega_m \Pi_m \quad (A6)$$

or in terms of the quality factor Q

$$\Lambda = 2 M_m \omega_m \Pi_m = \frac{M_m \omega_m}{Q_m} \quad (A7)$$

From the above expressions (15) follows.

Appendix B. Transient state force reconstruction: DQM

The weighting coefficients $A_{ij}^{(n)}$ of the n th order derivative can be determined through the recurrence formulae in DQM. In particular, the off-diagonal elements of the weighting coefficient matrix of the first order derivative are

$$A_{ij}^{(1)} = \frac{\prod_{\tau \neq i}^N (\zeta_i - \zeta_\tau)}{(\zeta_i - \zeta_j) \prod_{\tau \neq j}^N (\zeta_j - \zeta_\tau)} \quad i, j = 1, 2, 3, \dots, N \text{ and } i \neq j \quad (B1)$$

The off-diagonal elements of the weighting coefficient matrix of higher order derivatives are given by

$$A_{ij}^{(r)} = r \left[A_{ij}^{(r-1)} A_{ij}^{(1)} - \frac{A_{ij}^{(r-1)}}{\zeta_i - \zeta_j} \right] \quad i, j = 1, 2, 3, \dots, N \text{ and } i \neq j \quad (B2)$$

The diagonal elements of the weighting coefficient matrix are

$$A_{ii}^{(r)} - \sum_{\tau \neq i}^N A_{i\tau}^{(r)} \quad i = 1, 2, 3, \dots, N \quad (B3)$$

The final step involves obtaining the shifted Chebyshev–Gauss–Lobatto points which are obtained via basic mesh points p_i with a stretching coefficient $\varepsilon = 0.4$ (ref. 156). Then it follows that

$$p_i = \frac{1}{2} \left[1 - \cos \left(\frac{i-1}{N-1} \pi \right) \right] \quad i = 1, 2, 3, \dots, N \quad (B4)$$

$$\zeta_i = (1 - \varepsilon)(3p_i^2 - 2p_i^3) + \varepsilon p_i, \quad i = 1, 2, 3, \dots, N \quad (B5)$$

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