Dual-frequency resonance-tracking atomic force microscopy

Brian J Rodriguez\textsuperscript{1,2}, Clint Callahan\textsuperscript{3}, Sergei V Kalinin\textsuperscript{1,2,4} and Roger Proksch\textsuperscript{3,4}

\textsuperscript{1} Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
\textsuperscript{2} The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
\textsuperscript{3} Asylum Research, Santa Barbara, CA 93117, USA

E-mail: sergei2@ornl.gov and roger@asylumresearch.com

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Abstract

A dual-excitation method for resonant-frequency tracking in scanning probe microscopy based on amplitude detection is developed. This method allows the cantilever to be operated at or near resonance for techniques where standard phase locked loops are not possible. This includes techniques with non-acoustic driving where the phase of the driving force is frequency and/or position dependent. An example of the latter is piezoresponse force microscopy (PFM), where the resonant frequency of the cantilever is strongly dependent on the contact stiffness of the tip–surface junction and the local mechanical properties, but the spatial variability of the drive phase rules out the use of a phase locked loop. Combined with high-voltage switching and imaging, dual-frequency, resonance-tracking PFM allows reliable studies of electromechanical and elastic properties and polarization dynamics in a broad range of inorganic and biological systems, and is illustrated using lead zirconate–titanate, rat tail collagen, and native and switched ferroelectric domains in lithium niobate.

In scanning probe microscopy (SPM), changes in the resonance frequencies of the cantilever as it interacts with the surface can provide a direct measure of tip–surface interactions. Since the seminal work by Albrecht et al \cite{1}, resonant frequency detection has emerged as the functional basis of techniques such as non-contact atomic force microscopy (NC-AFM) \cite{2} and contact techniques like atomic force acoustic microscopy (AFAM) \cite{3}. Frequency tracking in the NC-AFM case is typically implemented using phase locked loop (PLL) circuitry or logic that utilizes the measured phase lag between excitation and response signals as the error signal for a feedback loop that maintains the cantilever phase at a constant value (typically 90° at resonance) by adjusting the frequency of the excitation signal. The high sensitivity of PLL-based frequency tracking methods allows precise control of tip–surface interactions, enabling atomic-resolution imaging and dissipation probing in NC-AFM. Furthermore, resonance enhancement minimizes contributions of non-thermomechanical noise sources (e.g. 1/f and laser shot noise) to the signal, increasing the signal to noise ratio and allowing weak conservative and dissipative tip–surface interactions to be probed.

The PLL methods are ultimately based on the fact that for a constant driving force, the phase and amplitude of the system response are directly determined by proximity to the resonance. The inherent limitations of phase-detection based resonant frequency tracking methods are that the phase and amplitude of the excitation signal should be (i) independent of the tip position and (ii) independent of the drive frequency. In other words, the phase and amplitude of the driving force should be known at each point. Any measurement where one or both of these conditions is not met will at least limit the interpretability and often the stability of a PLL.

These conditions are typically met for techniques in which the driving force is constant and is independent of tip location.
Figure 1. Schematic diagram showing the amplitude (red) and phase (blue) cantilever response over antiparallel domains. The phase is offset by 180° over antiparallel domains, demonstrating that it cannot reliably be used as a feedback signal for a PLL.

and tip–surface separation, e.g. imaging with a magnetic excitation. For techniques based on acoustic excitation of the cantilever base (NC-AFM) or the sample (AFAM), the implicit assumption is that the phase and amplitude of the driving force acting on the cantilever are related to the phase and amplitude of the driving voltage provided by the microscope electronics through a frequency-independent phase offset and an amplitude proportionality factor. The frequency dispersion of typical instrumental transfer functions is typically small, justifying this approximation for small frequency shifts. However, in the presence of internal resonances of the piezodriver or large frequency shifts, this assumption can fail [4].

Finally, in methods based on the electrical excitation of the tip such as Kelvin probe force microscopy (KPFM) [5] and piezoresponse force microscopy (PFM) [6], the relationship between the phase of the excitation force and driving voltage strongly depends on material properties and in fact contains location-specific information on local properties, violating condition (i) above. In these cases, the amplitude and phase of local response are a convolution of material response to an external field, and the cantilever response to a material generated force, which cannot be separated unambiguously. For example, in PFM the phase of the cantilever response changes by 180° across antiparallel domain walls, and thus cannot be reliably used as a feedback signal, as illustrated in figure 1. In this figure, the material generated piezoelastic force has a 180° offset between the different polarization directions on the sample surface (plotted as a blue curve in each graph).

As with many SPM techniques, PFM can benefit from an enhanced signal to noise level if the cantilever is operated on resonance [7, 8]. However, since PFM also relies on the relative phase of the drive and response for determining domain alignment, there can be significant crosstalk between the sample topography (and by extension, the contact stiffness) and the measured phase and amplitude of the cantilever. This effect is especially problematic when the cantilever is operated at or near a resonance [9, 10]. Previously, a resonance-enhanced PFM based on the rapid detection of an amplitude–frequency response curve at each pixel (10–100 ms per pixel) has demonstrated the need for independent detection of resonant frequency and electromechanical response [11]. Here, we develop and implement a dual-frequency excitation method [12, 13] that allows amplitude-based resonant frequency tracking in PFM and other techniques.

The principle of the method is illustrated schematically in figure 2(a). In this apparatus, the potential of the conductive cantilever is the sum of two oscillating voltages with frequencies at or near the same resonance. The resulting cantilever deflection is digitized and then sent to two separate lock-in amplifiers, each referenced to one of the drive signals. By measuring the amplitudes at these two frequencies, it is possible to measure changes in the resonance behavior and furthermore, to track the resonant frequency. The amplitude–frequency curve for a typical surface tune is schematically indicated by the solid line in figure 2(b). In the dual-frequency resonance-tracking (DFRT) method described herein, this response is measured at two drive frequencies, \(f_1\) and \(f_2\), yielding amplitudes \(A_1\) and \(A_2\). The difference between these two frequencies \(\Delta f = f_2 - f_1\) is typically chosen such that \(\Delta f \geq 2BW\) where \(BW\) is the imaging bandwidth, typically on the order of 1 kHz. For the cantilevers used in this work, it typically implied amplitudes \(A_1\) and \(A_2\) respectively. The drive frequencies were also typically chosen such that \(A_2 - A_1 \approx 0\), though this is not a requirement of the technique.

Referring to figure 2(b), a change in the contact stiffness of the tip–surface contact during scanning results in a shifted response curve shown as a dashed line. For the dashed curve, the measured amplitudes become \(A_1'\) and \(A_2'\) respectively. The
decrease (increase) of the resonant frequency results in the decrease (increase) of the amplitude difference signal, $A_2' - A_1' < 0$ ($A_2' - A_1' > 0$). Hence, the amplitude difference signal can be used as an input to a feedback loop to maintain the two drive frequencies bracketing the resonant frequency of the cantilever. In our implementation of this method, the two frequencies $f_1$ and $f_2$, chosen such that $\Delta f$ is constant, are updated to maintain $A_2' - A_1' = 0$.

We accomplish this using a digital proportional-integral gain controller, although other feedback loop implementations are certainly possible. For a symmetric peak, the resonant frequency is then determined as $f_c = (f_2 + f_1)/2$. For a constant driving force (e.g., acoustic excitation), it is also possible to quantify damping and non-conservative tip–surface interactions from the measured amplitude(s). For PFM and similar techniques, determination of the damping requires additional measurements (e.g. three excitation frequencies), to be reported elsewhere [14]. Note that many more forms of frequency feedback based on multiple excitation signals can also be implemented. Examples include more complex functions of the measured amplitudes, phases, in-phase and quadrature components, the cantilever deflection, and lateral and/or torsional motion.

We implemented DFRT-PFM on a commercial SPM system (Asylum Research MFP-3D). Measurements were performed using Pt–Ir coated (Olympus ElectriLevers) and Au coated (Olympus TR400PB) cantilevers. The system is additionally equipped with a prototype high voltage module (power supply, amplifier, tip holder, and sample holder) that allows application of dc voltages up to $\pm 220$ V and imaging at ac voltages up to 110 V$_{pp}$ (in the dual-excitation mode) at frequencies of 300–400 kHz. This enables polarization switching in high-coercivity materials such as single-crystal periodically poled LiNbO$_3$ and imaging of weakly piezoelectric material (\(\sim 1–5 \text{ pm V}^{-1}\)) such as dentin, collagen, and other biopolymers.

Figure 3 illustrates DFRT-PFM imaging of a model lead zirconate–titanate (PZT) polycrystalline surface. The deflection image in figure 3(a) shows several topographic steps clearly visible in differential contrast. The corresponding resonant frequency image exhibits significant (\(\sim 2 \text{ kHz}\)) variations of the contact resonant frequency associated with topographic variations due to changes in the tip–surface spring constant. Large-scale variations in the frequency image, presumably due to changes in elasticity from grain to grain in the bulk ceramic sample and/or surface contamination are also visible on larger images (not shown). Note that for resonant frequencies of \(\sim 310 \text{ kHz}\) and typical $Q$ factors on the order of \(\sim 100\), the width of the resonant peak is \(\sim 3 \text{ kHz}\). Imaging this with the DFRT-PFM technique has two implications we mention here: (i) operating near resonance yields a \(\sim 10–100\)-fold increase in the electromechanical response over non-resonant, constant-frequency PFM while (ii) at the same time avoiding crosstalk between changes in the contact stiffness and the PFM signal by tracking the resonance frequency.

Because we take advantage of the natural cantilever resonance and avoid artifacts associated with changes in the contact stiffness, DFRT-PFM is a promising technique for high-resolution imaging of weakly piezoelectric biopolymers in e.g., calcified and connective tissues [15, 16]. While the combination of optical activity and polar bonding renders piezoelectricity ubiquitous in these materials, high-veracity structural imaging by PFM was demonstrated to date only for dentin and artificially prepared collagen films [16]. For
Figure 3. (a) Topography error signal, (b) resonance frequency, (c) piezoresponse amplitude and (d) piezoresponse phase images of the lead zirconate–titanate (PZT) ceramic surface. The images are obtained at $\Delta f = 6.5$ kHz and $V_{ac} = 44$ V.

Figure 4. (a) Topography error signal, (b) resonance frequency, (c) piezoresponse amplitude and (d) piezoresponse phase images of the mouse tail collagen. The images are obtained using a high-voltage PFM module at $\Delta f = 10$ kHz and $V_{ac} = 66$ V.

most biosystems, surface topographic features strongly correlate with the molecular orientation, precluding unambiguous separation of intrinsic electromechanical response and topographic effects. DFRT-PFM imaging of rat tail collagen is illustrated in figure 4. The deflection image in figure 4(a) clearly shows the characteristic periodicity of collagen fibrils. The corresponding resonant frequency map in figure 4(b) shows strong variations of the resonant frequency along the
Figure 5. (a), (d), (g) Resonance frequency, (b), (e), (h) piezoresponse amplitude and (c), (f), (i) piezoresponse phase images of the periodically poled lithium niobate surface. Shown are images of the (a)–(c) native domain structure, (d)–(f) an intrinsic domain and (g)–(i) domains switched by $\pm 176$ V (locations marked in (e)). The images are obtained at $\Delta f = 4$ kHz and $V_{ac} = 66$ V. The frequency images have been flattened to account for minute changes of contact radius from line to line.

The grooves on the fibril are associated with a significant increase of the resonant frequency ($\sim 3–4$ kHz), consistent with an increase of local contact area and contact stiffening. In addition, strong variations in resonant frequency are visible perpendicular to the fibril axis. Circled in figure 4(b) is a region with significantly depressed ($\sim 4–5$ kHz) local resonant frequency, corresponding to a suspended segment of the collagen fibril. This softening is observed despite the fact that the fibril radius ($\sim 150$ nm) is significantly larger than the tip radius ($\sim 10–20$ nm from resolution). This observation strongly suggests that the elastic response of the fibril is non-local, indicative of a softer internal core surrounded by stiffer outer shell. Finally, the PFM images in figures 4(c) and (d) illustrate only weak amplitude contrast and relatively small ($\sim 20^\circ$) phase variations within the fibril. This behavior is consistent with that expected for a non-piezoelectric material. The response in this case is the surface deformation induced by the tip–surface electrostatic forces, rather than intrinsic electromechanical coupling in the material, and frequency data can be analyzed similarly to AFAM [3]. The lack of significant measurable electromechanical response in the collagen fibril is not surprising and can be ascribed to the surface being covered by a proteoglycan layer that precludes electrical tip–surface contact, and possibly surface conductivity of humid collagen.

Finally, DFRT-PFM studies of polarization switching are illustrated for single-crystal lithium niobate (LN) (Crystal Technologies). The resonant frequency image of the LN surface in figure 5(a) illustrates an almost uniform surface. Corresponding PFM amplitude and phase images in figures 5(b) and (c) show a macroscopic $180^\circ$ domain wall and two inversion domains which are typical for this material. Higher-resolution DFRT-PFM images of pre-existing domains in figures 5(d)–(f) illustrate strong frequency contrast, and nearly constant PFM amplitudes within and outside the domain. To assess the noise performance of this technique, we adjusted the drive amplitude, feedback gains, set-points and other imaging parameters to typical values and then acquired frequency images at a fixed point (zero scan size). The frequency noise was then computed using standard image roughness calculations. These measurements, made with a bandwidth of 1 kHz, yielded rms frequency noise levels between 1 and 10 Hz, depending on the contact set-point. The noise measurements depended strongly on the contact set-point (increasing the loading force decreased the noise) and the drive amplitudes.

In comparison, shown in figures 5(g)–(i) are DFRT-PFM images of domains switched by the application of three $176$ V magnitude pulses for $\sim 10$ s in three adjacent locations. Note the significant change of resonant frequency and the strong amplitude depression in the newly fabricated domain. This
contrast can be attributed to the transient behavior of the LN surface due to defect-dipole reorientation [17] and surface screening [18] strongly modifying electromechanical response. These observations suggest that the temporal evolution of resonant frequencies and electromechanical responses in systems with screening (all ferroelectrics in ambient), or phase separation (relaxor ferroelectrics) dynamics can provide new approaches to study these phenomena.

To summarize, we have developed a dual-excitation method for resonant-frequency tracking in SPM based on amplitude detection. This approach allows the limitations of frequency tracking in techniques with strongly position-dependent response phase to be overcome. This approach is implemented for PFM, and imaging at 0.3–1 Hz rates with <0.2 kHz frequency noise is demonstrated. These characteristics make this approach ideal for techniques such as PFM, AFAM and polarization and dielectrophoretic force microscopies in liquid, in which resonant frequencies change significantly (∼0.1–40 kHz) across the surface. DFRT-PFM imaging of model PZT surface showed strong variation of resonant frequency at the topographic steps and lack of topographic effects in resonant PFM amplitude, illustrating effective decoupling of the two. DFRT-PFM of collagen fibrils has shown clear elastic contrast within the fibril at 64 nm periodicity, and between suspended and bound segments. At the same time, the fibril is non-piezoelectric within the detection limit, presumably due to the surface proteoglycan layer or surface conductivity. Finally, the strong effects of surface chemistry and screening conditions on the resonant frequency of the PFM cantilever on an LN surface is shown, paving the way for dynamic studies of slow polarization-mediated phenomena. Future development of this method will include detection at more than two frequencies, necessary for unambiguous determination of damping in PFM-type experiments and allowing measurements of tip-sample damping variations.

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