Quantification of surface displacements and electromechanical phenomena via dynamic atomic force microscopy

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Abstract
Detection of dynamic surface displacements associated with local changes in material strain provides access to a number of phenomena and material properties. Contact resonance-enhanced methods of atomic force microscopy (AFM) have been shown capable of detecting ~1–3 pm-level surface displacements, an approach used in techniques such as piezoresponse force microscopy, atomic force acoustic microscopy, and ultrasonic force microscopy. Here, based on an analytical model of AFM cantilever vibrations, we demonstrate a guideline to quantify surface displacements with high accuracy by taking into account the cantilever shape at the first resonant contact mode, depending on the tip–sample contact stiffness. The approach has been experimentally verified and further developed for piezoresponse force microscopy (PFM) using well-defined ferroelectric materials. These results open up a way to accurate and precise measurements of surface displacement as well as piezoelectric constants at the pm-scale with nanometer spatial resolution and will allow avoiding erroneous data interpretations and measurement artifacts. This analysis is directly applicable to all cantilever-resonance-based scanning probe microscopy (SPM) techniques.

Keywords: scanning probe microscopy, ferroelectrics, cantilever dynamics

Introduction
AFM-based detection of sample surface displacements associated with local changes in material strain provides access to a number of material properties and phenomena at the nanoscale such as polarization in ferroelectrics [1], thermal expansion due to Joule heating [2], light–matter interaction [3], ion dynamics in ionic conductors [4], mechanical stiffness [5, 6], and others. Quantitative measurements of dynamic surface displacements using an SPM probe can offer important insights into material functionalities at the nanoscale with high temporal resolution and is desirable for SPM-based characterization techniques such as piezoresponse force microscopy (PFM) [1, 7–9], electrochemical strain microscopy (ESM) [10, 11], atomic force acoustic microscopy (AFAM) [12, 13], and ultrasonic force microscopy (UFM) [14–16]. While these techniques have been developed...
decades ago, quantification of measured surface displacements is still elusive and would benefit the nanoscale characterization of functional materials. Furthermore, lack of quantitative and accurate measurement can lead to the misinterpretation of relevant material physics. Only if quantitative material parameters can be extracted, a correlation of nanoscale and macroscale material behavior and structure–function relationships can be derived. Many of the above-mentioned techniques utilize dynamic cantilever vibrations when in contact with the sample as a response to an external stimulus. To achieve better sensitivity and signal-to-noise ratio, these and similar techniques use harmonic stimuli, such as voltage bias applied to the tip, sample or probe vibrations, and the AFM photodetector signal is detected at the frequency of the stimulus using a lock-in technique. Resonance enhancement allows further significant improvement in the sensitivity of the measurements by setting the stimulus frequency equal or close to the resonance frequency of one of the cantilever vibrational modes [17, 18]. As a result, quantification efforts become more complex since contact cantilever dynamics need to be taken into account.

In many AFM-based techniques, a conducting AFM tip is placed into contact with a sample surface and a voltage bias is applied between the tip and an electrode beneath the sample. In particular, in electromechanical measurements, the electric field concentrated under the tip apex leads to a change in cantilever vertical position due to a change in the sample volume. The large strength of the highly localized field (on the order of $10^{8}$–$10^{9}$ V m$^{-1}$) can also be used as a local tool for material modifications [19–21], or for studies of material behavior in strong electric fields such as nanoscale melting [22] and water condensation [23]. Strong electric fields under the AFM tip can induce water dissociation and water-induced electrochemical reactions [24], material modifications and ionic conduction [25], i.e. phenomena that are of high relevance in nanoscale studies of organic and inorganic material systems. Such experiments require knowledge of the electric field strength and associated strain responses to understand the local functionality.

In turn, resonance enhancement makes the electromechanical techniques highly sensitive, enabling detection of tip displacements down to the sub-pm range. As a corollary, special attention should be given to possible parasitic effects, which may interfere with the measurements. One such effect is the presence of the electrostatic force acting on the cantilever shank and on the tip apex. The large electric field under the sharp apex of a probe tip can result in a force large enough to produce detectable apex displacements against the mechanical contact stiffness, especially in experiments with a strongly polarizable material, such as a high-permittivity dielectric [26]. The force on the apex is dependent on the local dielectric properties as well as topography of the surface, and can produce local contrasts superimposed onto the material electromechanical response of interest. Measurements of the force produced by the electric field may help manage and account for such side effects in the measurements.

Here, we describe in detail the quantification of surface displacements with use of cantilever resonance at the first flexural contact resonant mode for the example of PFM measurements on ferroelectric materials. From this, material properties, such as the piezoelectric constant $d$, can be extracted. Steps toward quantification of $d$ through SPM-based techniques have been reported using different approaches. Most of them include low frequency measurements far away from contact resonance frequencies and the use of static sensitivity or background removal [27] or even double tip approaches [28]. Recently, interferometric approaches have been described which complimented PFM measurements on top electrodes [29] or even replaced PFM [30]. In both cases, additional hardware is required. Our goal is to provide a pathway to parameter quantification which is based on pure data analytics and advanced understanding of signal origins and so does not require additional hardware or specialty cantilevers when contact resonance enhancement is used for PFM. To this end, the cantilever mode shapes are calculated using an analytical model and the cantilever response functions extracted for a variety of cantilevers. We show that quantification of the surface and tip apex displacements can be achieved by performing a static calibration of cantilever sensitivity and application of a correction factor to account for the cantilever mode shape, depending on the cantilever and the tip–sample contact properties. In order to verify our approach, we compare theoretical data with PFM measurements using a variety of cantilevers with a range of properties on high-quality well-characterized ferroelectric materials. We extract the quantitative piezoelectric constant for a commercial periodically poled lithium niobate (PPLN) crystal and find an excellent match with a known value specified by the sample manufacturer. In addition, the ferroelectric switching process is evaluated for a ferroelectric epitaxial film of tetragonal Pb(Zr,Ti)O$_3$/Li$_2$SrMnO$_3$ (PZT/LSMO). All measurements are done in a controlled low-humidity environment (Ar-filled glove box). In the analysis, we are able to elucidate the influence of the cantilever properties and explain the measured scatter in PFM values obtained with different cantilevers.

**Resonance-enhanced dynamic cantilever displacements**

We begin with description of a general approach currently used for semi-quantitative cantilever displacement measurements. The amplitude of the AFM photodetector signal $V_{ph}^{\omega}$ produced by a harmonic displacement $u(t) = u_0 \sin(\omega t)$ of the sample surface in contact with the tip can be expressed as:

$$V_{ph}^{\omega} = s \theta(\omega) = sS(\omega)u_0$$

where $s$ is the conversion factor between the change of the cantilever slope $\theta$ at the position of the sensing laser beam and the photodetector output voltage, and $S(\omega)$ is the mechanical transfer function of the cantilever. The response of the cantilever $S(\omega)$ to a small harmonic excitation with an angular frequency $\omega$ close to an eigenfrequency of a resonant mode $\omega_0$ can be well described as a response of a simple
harmonic oscillator (SHO) with an oscillation amplitude [31, 32]:

$$|H(\omega)| = \frac{H_0\omega_0^2}{\sqrt{(\omega^2 - \omega_0^2)^2 + (\omega\omega_0/Q)^2}}$$

(2)

where $Q$ is the quality factor of the mode (typically on the order of 100 for the lowest flexural contact mode as observed in a large number of measurements by the authors), and the factor $H_0$ is directly proportional to the amplitude of the driving excitation. At resonance, $|H(\omega_0)| = H_0 \cdot Q$, and the slope amplitude $\theta(\omega_0) = s'\omega_0 \cdot Q$ ($s'$ is a conversion factor analogous to $s$ defined above). Correspondingly, for the amplitude of the photodetector signal:

$$V_{ph}(\omega_0) = s \cdot s' \cdot u_0 \cdot Q.$$  

(3)

The use of multifrequency measurements, such as band excitation (BE) or dual AC resonance tracking (DART) [33], allows for quantitative characterization of the cantilever response at a resonance. It allows precise measurements of the contact resonance frequency, Q-factor, and the amplitude $V_{ph}(\omega_0)$ at each pixel of the image. In particular, in BE, the measured contact resonance peak is fitted using equation (2), which provides the PFM amplitude, in units of Volts, of the photodetector signal. However, conversion of the PFM signal into parameters of the material response remains highly non-trivial. In particular, quantification of the cantilever displacement $u_0$ requires appropriate calibration of the $s \cdot s'$ product in equation (3), and it is usually performed by measuring the cantilever sensitivity by static force-distance curves, in which case:

$$V_{ph}^{\text{static}} = s \cdot \theta_{\text{static}} = s \cdot s'_{\text{static}} \cdot u_0.$$  

(4)

A complication arises because—generally—static and dynamic sensitivities of a cantilever are not equal: $s' \neq s'_{\text{static}}$. First, we note that during the static calibration, cantilever bending is much larger than in dynamic vibrations during dynamic detection techniques, and the force cannot prevent the slippage of the tip apex along the surface (bonded versus sliding indentation). Therefore, in the static calibrations, the cantilever shape is imposed exclusively by the vertical displacement of the cantilever free end in respect to the cantilever root (clamped end) equivalent to the displacement of the sample along the surface normal. In the static calibration, the distance of the tip apex slip along the surface is determined by the deformed cantilever shape and not by the force at the tip–sample contact. In turn in dynamics, the stiffness of the tip-surface junction will play a significant role, since it determines corresponding boundary conditions for the beam. However, the contact stiffness is position-dependent and is determined by local topography and indentation modulus of the materials involved [34]. Consequently, its effect cannot be inferred beforehand due to a lack of precise information about cantilever and/or sample properties.

Below, we analyze in detail cantilever vibration motion in response to periodic vertical surface displacement. The analysis is based on an idealized cantilever model shown in figure 1(a). The model is a beam of rectangular cross-section and a length $L$ rigidly clamped at one end. The beam is tilted in respect to the sample surface at an angle $\varphi$. A massless and rigid sensing tip of length $h$ is located at distance $L_2$ from the beam free end and makes a right angle with the beam. Boundary conditions at the tip–sample contact are represented by two Kelvin–Voigt linear elements with springs accounting for the contact stiffness $k_s$, $k_{s,\text{Lon}}$ and dashpots describing contact damping $\gamma_s$, $\gamma_{\text{Lon}}$ in directions normal to and along the surface respectively. This idealized model takes into account both normal and longitudinal contact stiffness contact damping and cantilever tilt. It, however, ignores the finite mass of the sensing pyramid, possible flexural deformations at its apex, as well as finite dimensions of its base. It also ignores possible deviations of the cantilever geometry from ideal specifications.

The problem for the forced harmonic oscillations of the cantilever model in figure 1(a) for excitation through the vertical displacement of the cantilever was solved analytically, and the solution is provided in [35]. We use this solution further in our analysis. Here, the analysis is restricted solely to the cantilever vibrations in the linear regime at the first flexural contact eigenmode at resonance excited by harmonic vertical displacements of the sample surface $u(t) = u_0 \exp(i\omega t)$. The cantilever tilt angle was set to $\varphi = 12^\circ$ in the calculations; cantilever dimensions $L$, $L_2$, and $h$ were used as provided by manufacturers. Further, it is assumed that $k_{s,\text{Lon}}/k_s = \gamma_{\text{Lon}}/\gamma_s$ and this ratio is independent of the contact stiffness.

In the Hertzian contact mechanics, for similar tip and sample materials and a circular contact, $k_{s,\text{Lon}}/k_s = 2(1 - \nu)/(2 - \nu)$, where $\nu$ is the Poisson ratio of the materials in contact [36]. The Poisson ratio varies from $\sim 0.1$ (e.g. diamond) to 0.5 (e.g. natural rubber), which yields $2/3 \lesssim k_{s,\text{Lon}}/k_s \lesssim 18/19$, with 0.81 being an average value (at $\nu \approx 0.36$) [37]. More accurate calculations for specific contact material pairs can be made using expressions given in [37–40]. They yield: $k_{s,\text{Lon}}/k_s = 4G^*/E^*$, where $E^* = [(1 - \nu_{\text{tip}}^2)/E_{\text{tip}} + (1 - \nu_s^2)/E_s]^{-1}$ and $G^* = [(1 - \nu_{\text{tip}})/G_{\text{tip}} + (1 - \nu_s)/G_s]^{-1}$, $E_{\text{tip}}$, $E_s$, are Young’s moduli, $G_{\text{tip}}$, $G_s$ are shear moduli, and $\nu_{\text{tip}}$, $\nu_s$ are Poisson ratios of tip (subscript ‘tip’) and sample (subscript ‘s’). For the tip, we use moduli values from [40]: $E_{\text{tip}}/(1 - \nu_{\text{tip}}) = 165.1$ GPa and $G_{\text{tip}}/(1 - \nu_{\text{tip}}) = 37.5$ GPa. In the model verification experiments described in the following sections, we carried out measurements on an LiNbO$_3$ single crystal and a ferroelectric epitaxial Pb(Zr$_{0.3}$Ti$_{0.7}$)O$_3$ (PZT) film. The elastic constants of LiNbO$_3$ [41] yield $k_{s,\text{Lon}}/k_s \approx 0.77$ for a surface normal to the c-axis of the signal crystal ($E = 199.3$ GPa, $G = 59.5$ GPa, $\nu = 0.266$). In turn, the elastic properties for the Pb(Zr$_{0.3}$Ti$_{0.7}$)O$_3$ ceramics [42, 43] and thin films [44] result in $k_{s,\text{Lon}}/k_s$ close to 0.85. The last value for the longitudinal and normal contact stiffness ratio was assumed in the further calculations.

Figure 1(b) shows a series of curves representing first resonant mode shapes for different contact stiffness $k_s/k_C$ calculated with use of the analytical model. Here, $k_C$ is the
static spring constant of the cantilever. As seen, with \( k^*/k_C \) increasing from a small value, the slope at the free end of the beam changes sign, crossing zero at about \( k^*/k_C = 10 \), increases, but then decreases with its shape approaching that at the clamped end for \( k^*/k_C \) approaching infinity. This trend is an effect of the longitudinal component of contact stiffness, which cannot be ignored in experiments with relatively hard materials. The inset in figure 1(a) illustrates the shape of the first contact flexural mode for a relatively stiff cantilever model used in the analytical calculations (adapted from [35]). See text for explanation of notation. The inset illustrates with a three-dimensional model the shape of the first contact flexural mode of an Olympus AC240 cantilever (material is silicon, length is 240 \( \mu m \), spring constant \( k_C = 2 \) N m\(^{-1} \), first-mode free resonance frequency is 70 kHz, sensing tip height is 14 \( \mu m \), contact stiffness in the model \( k^* = 390 \) N m\(^{-1} \) calculated using finite elements modeling with COMSOL v.4.4 software (COMSOL AB). (b) Calculated cantilever shapes for several values of normalized contact stiffness \( k^*/k_C \), where \( k_C \) is the cantilever spring constant; calculations were performed using the idealized model in panel (a). (c) Calculated cantilever slope amplitudes at resonance at the location of the sensing tip (where the laser spot is typically placed in experiments) as functions of contact stiffness for the softest and stiffest cantilevers used in this study. Positive and negative values reflect difference in slope sign for a given phase of sample surface oscillation. (d) Shape correction factors as functions of contact stiffness. Cantilever properties are provided in table S2 of the online supplementary data; \( k_C^*/k^* = 0.85 \).

To do so, we introduce a complex contact stiffness \( \tilde{k}^* = k^* + i k'' = k^* + i (\omega \gamma) \) and complex frequency \( \tilde{\omega} = \omega' + i \omega'' \). Q-factor of the resonance can be expressed through the real and imaginary parts of the complex frequency as \( Q = \omega'' / (2\omega') \). Here, \( \omega' \) has the meaning of the damped natural frequency of the contact resonance mode. For a strongly underdamped oscillator, \( \omega' \) is nearly equal to the resonant frequency at forced oscillations, and we set \( \tilde{\omega}_{1,c} = \omega_{1,c}(1 + i/2Q_{1,c}) \), where \( \omega_{1,c} \) and \( Q_{1,c} \) are the experimentally measured angular resonant frequency and Q-factor, respectively, of the first flexural contact resonant mode. The value of \( \tilde{\omega}_{1,c} \) is substituted for frequency in the characteristic equation of the cantilever beam \( N(\tilde{\omega}, \tilde{k}^*) = 0 \) (equation (S.8) in online supplementary data), and the equation is numerically solved for \( \tilde{k}^* \).
solved in respect to \( k^* \). The expressions for the characteristic equations are very lengthy to fit in the format of this paper and are provided in the online supplementary data. From the solution, the experimental contact stiffness \( k^* \) and the damping \( \gamma \) are:

\[
\gamma = \text{Re} k^* \quad \text{and} \quad \gamma = \text{Im} k^* / \omega_{1,c}.
\]

The characteristic equation can be further solved in respect to complex frequency for varying \( k^* \) to find resonant frequencies \( \omega_{1,c} \), slope amplitudes \( A_{01,c}(k^*) \), resonance Q-factors \( Q_{1,c}(k^*) \), and shape factors \( \lambda(k^*) \) as functions of \( k^* \) for a variety of cantilevers. However, first we need to make a choice for the model of contact damping. In the calculation of \( A_{01,c}(k^*) \) and \( Q_{1,c}(k^*) \) below, we applied the model used by Yuya et al [45] in measurements of storage and loss moduli of viscoelastic materials with contact-resonance AFM. For the purpose of our calculations, only the ratio of the contact damping parameter \( \gamma \) and contact stiffness \( k^* \) are of importance. Yuya et al, who used the Hertzian model for contact mechanics, elastic solution for the material Young’s modulus from nanoindentation, and elastic-viscoelastic correspondence principle, arrived at expressions that yield:

\[
\frac{\omega_{1,c}}{k^*} = \frac{E^*}{E^*} \tag{5}
\]

where \( E^* \) and \( E^* \) are reduced storage and loss moduli respectively. Following Yuya et al [46], we assumed that both \( E^* \) and \( E^* \) are material properties independent on details of the contact geometry and frequency in the range of typical contact resonance experiments. Therefore, \( \omega_{1,c}/k^* = \text{const.} \) or \( \omega_{1,c} = \alpha k^* \), where \( \alpha \) is a constant. This model describes a situation when energy dissipation in a dynamic process at the contact is proportional to the strain. The coefficient \( \alpha \) can be found in this case from experimental data and solution of the characteristic equation \( N(\omega, k^*) = 0 \) as \( \alpha = \text{Im} k^*/\text{Re} k^* \).

Alternatively, one may consider a model in which dissipation is proportional to the rate of the strain change. In this case, \( \gamma/k^* = \text{const.} \) and \( \gamma = \alpha k^* \) with \( \alpha = \text{Im} k^*/(\omega \cdot \text{Re} k^*) \).

After that, the amplitude of the cantilever slope at the position of the sensing tip \( A_{01,c}(k^*) \) is calculated from the full analytical solution for the cantilever vibrations using the obtained values, and shape factors \( \lambda \) are determined as:

\[
\lambda = \frac{s'}{s_{\text{static}}} = \frac{A_{01,c}(k^*)}{Q_{1,c}(k^*)/\theta_{\text{static}}}. \tag{6}
\]

The expression for the static slope \( \theta_{\text{static}} \) corresponding to a static cantilever displacement equal to \( \theta_{0} \) can be readily derived from expression given in [46] for the case of sliding cantilever and neglecting correction from the friction force:

\[
\theta_{\text{static}} = \frac{3}{2} \frac{u_0}{L_1 \cos \varphi}. \tag{7}
\]

Figure 1(c) shows \( A_{01,c}(k^*) \) as functions of \( k^* \) calculated for a broad range of contact stiffness values from 5 N m\(^{-1}\) to 10\(^4\) N m\(^{-1}\) for two different cantilever geometries (see table S2 in the online supplementary data) for the damping model \( \omega_{1,c} = \alpha k^* \). Figure 1(d) displays the corresponding shape factors \( \lambda(k^*) \) for the two selected cantilevers. As seen, the \( A_{01,c}(k^*) \) curves for all cantilevers show a maximum over \( k^* \), which is an effect of the longitudinal contact stiffness (similar to that described in [46] for the quasi-static case). The exact shape of the curves and positions of maxima are strongly cantilever-dependent. The \( Q_{1,c}(k^*) \) curves (not shown) reflect a non-monotonic behavior of the Q-factor versus contact stiffness. As discussed in detail in [47], this is a result of mode-shape-dependent motion amplitude, and hence, dissipation, of the tip apex at contact. With increasing contact stiffness, the tip apex motion gradually ceases, and all Q-factors grow.

The choice of the contact dissipation model depends on properties of the specific material. However, importantly, the calculations show that the shape factors as functions of contact stiffness are nearly insensitive to the exact dissipation mechanism. In fact, calculations reveal that the shape factors change by less than 0.1% with change of the model for the contact damping from \( \omega_{1,c} = \alpha k^* \) to \( \gamma = \alpha k^* \) at \( k^* > 100 \text{ N m}^{-1} \). The shape factors are also very tolerant to the changes of the values of \( \gamma \), reflecting a weak dependence of the mode shape on the contact damping. For the contact stiffness range covered by the calculations, the shape factors strongly deviate from unity varying between 0 and 1.5, and therefore it is important that knowledge of the shape is accessed for accurate measurements of the sample surface displacements.

Note that for the displayed curves for cantilevers 1 and 5 the shape factors remain within 30% of unity in a broad range of the contact stiffness. Apparently, such cantilevers should be preferred in the measurements. Additionally, cantilever 5 will yield the largest slope amplitude at the resonance (as can be concluded from figure 1(c)) setting this probe model apart from others in terms of measurement sensitivity. Such knowledge can be used to compare data measured with different probes and to make an intelligent selection of cantilevers to be able to measure the cantilever displacement quantitatively. We further note that insofar as the contact stiffness can be measured to calculate the mode shape, the exact model of the contact mechanics, contact size, and particular tip–sample elastic properties are not important for determination of the shape correction factors. Furthermore, additional calculations showed that the shape factor is relatively weakly dependent on the ratio \( k^*_0/k^* \) (see figure S5 in the online supplementary data), especially for stiffer cantilevers.

**Piezoelectric constant of a periodically poled lithium niobate crystal**

In order to verify the model developed in the previous section, we apply the data correction to PFM measurements of a piezoelectric constant of a PPLN crystal (Bruker). In PFM, the dynamic cantilever displacement \( D_{ac} \) is caused by a local sample volume expansion resulting from the inverse piezoelectric effect and is proportional to the piezoelectric constant \( d \). In our case, \( D_{ac} \) is synonymous with the so-called PFM signal. Since \( d \) is a material property, the cantilever displacement should be independent of the cantilever properties.

The PFM experiments were carried out using the BE technique, which is capable of measuring amplitude and phase responses of a cantilever in a frequency band
encompassing a resonant peak [31, 48]. The use of such a technique is crucial here since the model described above requires inputs of a contact resonance frequency as well as a Q-factor, which cannot be extracted from single-frequency measurements. During BE, the full contact resonance peak is acquired and fitted with the SHO model equation (2) to extract response amplitudes and resonance quality factors. All the measurements were performed in an Ar-filled glove box to minimize the effect of the surface water layer and to keep environmental conditions constant for all measurements. The H2O level in the glove box was <0.1 ppm as measured by the standard moisture probe in the glove box. Two varieties of metal-coated cantilever probes with stiffness values 0.6 N m⁻¹ and 3.9 N m⁻¹ were used (MikroMash and Nanosensor). Cantilever properties are listed in table S1 of the online supplementary data. All the probes were calibrated through force-distance curves and thermal tunes to extract the static cantilever sensitivity and spring constant (stiffness). During the PFM measurements, the contact force was kept at about 120 nN for all the probes.

Before performing quantitative measurements, it is necessary to understand the main PFM signal components and image contrast mechanisms. This becomes obvious from the PFM images taken on the PPLN sample (figure 2(a)), which show strong asymmetry in signal strength between ferroelectric domains of opposite orientations (blue and red areas in figure 2(a)) as seen from the histogram in the inset in figure 2(a). Since no contrast was observed in the corresponding images of the contact resonance frequency and quality factor, this asymmetry will remain after data quantification.

Recently, we have shown that electrostatic tip–sample interactions can strongly contribute to the measured cantilever displacements [49, 50]. The electrostatic force F is proportional to the applied voltage squared: F = \( \frac{1}{2} C^* \cdot V^2 \). In electrostatic force microscopy and traditional non-contact Kelvin probe force microscopy (KPFM), \( C^* \) is typically negative and equal to the derivative of the capacitance of the probe as a function of the probe-sample distance: \( c/dz \). In contact, \( dc/dz \) becomes undefined, and \( C^* \) has to be viewed as a proportionality coefficient between the force and voltage with local and global contributions from the tip apex, tip cone, and cantilever shank [51, 52]. With a sinusoidal voltage \( V_{ac} \) superimposed on a dc bias \( V_{dc} \), \( V = V_{dc} + V_{ac} \cdot \sin(\omega t) \), the amplitude of the first harmonic of the electrostatic force \( F_{ac} \) can be written down as: \( F_{ac} = C^* \cdot V_{ac} \cdot V_{dc} \) or \( F_{ac} = C^* \cdot V_{ac} (V_{dc} - V_{SP}) \) in the presence of a surface charge, with \( V_{SP} \) being the corresponding surface potential. In the case of PPLN, a measurable surface potential is always present as seen in the image in figure 2(b), which was recorded using peak force (PF) KPFM. This fact needs to be considered in the further data analysis. Depending on the contact stiffness \( k^* \), an electrostatic force can result in a measurable cantilever displacement \( D_{ac} = F_{ac}/k^* \) with a linear dependence of \( D_{ac} \) on \( V_{dc} \). In turn, for the piezoelectric contribution, \( D_{ac} \) is independent of \( V_{ac} \) unless domain switching takes place: \( D_{ac} = d \cdot V_{ac} \). Both contributions are schematically shown in figure 2(c) where domains with opposite polarization orientations correspond to positive and negative \( D_{ac} \).

In the following, we denote the cantilever displacements due to piezoelectricity and electrostatics as \( D_{PE} \) and \( D_{ES} \) respectively. Figure 2(d) schematically illustrates the combined effect of piezoelectric and electrostatic contributions. The original symmetric piezoelectric contribution \( +/− D_{PE} \) is shifted by \( D_{ES} \), resulting in unequal values of cantilever displacements \( D_{ac,1} \) and \( D_{ac,2} \) for domains pointing up and down respectively. This directly affects the PFM imaging, which is performed at 0 Vdc. In a range of \( V_{SP} \) and the slope \( m \) of the dependency of \( D_{ac} \) on \( V_{dc} \), the asymmetry can be so strong that no phase flip is observed between different domains.

In order to distinguish between piezoelectric and electrostatic contributions, we apply a combination of KPFM and on-field switching-spectroscopy PFM (SS-PFM) [53] in two sequential measurements on the same area across a sparse grid. During the on-field PFM voltage spectroscopy, \( V_{ac} \) and \( V_{dc} \) are applied simultaneously and piezoelectric as well as electrostatic signal contributions are measured. After that, open-loop KPFM is performed in non-contact mode with the same voltage sequence as used for the on-field PFM measurements. The KPFM provides the distribution of \( V_{SP} \), while the on-field PFM voltage spectroscopy yields \( m \) as well as \( D_{ac,1} \) and \( D_{ac,2} \) over domains with opposite orientations. Combining this information, \( +/− D_{PE} \) can be calculated. It is noteworthy that \( V_{dc} \) applied to measure the on-field PFM curves has to be small enough to avoid injecting charges from the tip and altering the domain structure underneath it. Both can be challenging for ferroelectric thin films. In contrast, for PPLN crystals, the coercive voltages are high, and only charge injection needs to be considered. Here, it has been found that fresh tips can inject some charge into the PPLN when a tip is still sharp. After a few measurements, charge injection typically becomes negligible, which is attributed to tip wear increasing the tip radius and, thus, decreasing the local electric field driving the charge injection.

Measurements on the PPLN crystal were performed with two different cantilevers, A and B, of different stiffness as summarized in table S1 of the online supplementary data. Figure 3(a) shows the on-field PFM signal plots for the two cantilevers measured on a 128 × 64 grid over a 50 μm × 50 μm area and averaged over oppositely oriented domains before any data quantification. The plots are straight lines without any hysteresis (compare with figure 2(d)). As expected, the softer cantilever shows a larger slope \( m \) corresponding to a higher sensitivity to the electrostatic forces. Based on the cantilever geometry, free as well as contact resonance frequencies and Q-factors, contact stiffness \( k^* \) and shape factors \( \lambda \) were calculated for each point of the grid using the model of the previous section. The resulting histograms are shown in figures 3(b) and (c) respectively.

A typical way of transforming the units of \( D_{ac} \) from volts (as measured at the photodetector) to picometers is to use an (inverse) static cantilever sensitivity \( S = \left( s \cdot s_{static}\right)^{-1} \) as described at the beginning of the previous section (equation (4)). Figure 3(d) compares this approach versus our
model incorporating the resonant mode shape through the factor $\lambda$. It can be seen that using the static sensitivity only, the extracted values overestimate the surface displacement (i.e., $\lambda > 1$). The distributions of the values for cantilever B are noticeably different between the two methods, showing that it is necessary to apply the cantilever shape correction. Still, despite the improved data quantification, different cantilevers yield significantly different values of $D_{ac}$. This can be explained by variations of the surface potential $V_{SP}$ revealed by the histograms in figure 3(e). The alterations of the surface potential can be associated with the contact electriification that occurs during scanning in contact mode [50, 54–56]. However, $V_{SP}$ changes of about $+/-1$ V were also observed between different days, which might be related to unknown environmental factors. These observations demonstrate the importance of combining the PFM measurements with the surface potential characterization.

After quantification of the shape factor $\lambda$, $V_{SP}$ and $m$, the contributions from electrostatics, $D_{ES}$, and piezoelectricity, $D_{PE}$, can be separated and plotted, as displayed in figure 4. These measurements were carried out in two different areas for each of the two probes. Figure 4(a) shows the electrostatic contribution. As seen, $D_{ES}$ (at $V_{dc} = 0$ V and $V_{ac} = 2$ V$_{pp}$) can be between 0.5 and 2 pm depending on the surface potential. Further, we compare $D_{PE}$ with the piezoelectric constant value $d_{PE}$ specified by the PPLN crystal provider. In figure 4(b), the measured piezoelectric constants are displayed together with the value 7.5 pm V$^{-1}$. It can be seen that both the cantilevers yield values approaching the manufacturer-specified macroscopic one for domains of both orientations, and the results are independent of the surface potential. This shows the potential for PFM to become a quantitative characterization technique when all signal-contributing mechanisms and the cantilever dynamics are considered. It also demonstrates a problem arising for weak ferroelectric materials with low piezoelectric constants. For $V_{ac} = 2$ V$_{pp}$, the electrostatic contribution was evaluated to be between 0.5 and 2 pm. If a piezoelectric constant were one order of magnitude lower, for example, the piezoelectric contribution would be in the same range as the electrostatic contribution and, hence, would be difficult to detect.

**Figure 2.** (a) PFM image of domains on the PPLN crystal obtained with $V_{ac} = 2$ V$_{pp}$ using BE before any calibration/quantification. The inset shows a histogram of the data points in the image. (b) Surface potential image obtained with PF-KPFM on the PPLN crystal. (c) and (d) Schematic analysis of piezoelectric and electrostatic signal contributions considered separately in (c) and combined in (d).
Ferroelectric switching properties of an epitaxial PZT thin film

In a second example, a different set of PFM measurements was performed on a 50 nm thick ferroelectric (001) Pb(Zr0.2Ti0.8)O3/(La,Sr)MnO3 film grown epitaxially with pulsed laser deposition on an SrTiO3 (001) substrate. The polar axis in the film is directed along the normal to the film surface. As before, we employed SS-PFM [53] to measure on- and off-field PFM hysteresis loops. All experimental data for the PZT film were recorded at a single point. Due to the high quality and uniformity of the epitaxially grown ferroelectric film, significant lateral variations in sample behavior could not be observed, which allowed for single point measurements. The measurements were performed with a total of five different cantilevers as summarized in table S2 of the online supplementary data. As the first quantification step, only the static sensitivity S was used to express $D_{ac}$ in picometers. The on-field curves shown in figure 5(a) are hysteretic due to ferroelectric polarization switching (flip to the opposite direction). In addition, a tilt in the curves is observed due to the electrostatic contribution, which strongly depends on the probe. Figure 5(b) shows the slope as function of cantilever stiffness from this as well as the two cantilevers used for PPLN. In general, the slope is higher for lower stiffness but saturates for higher one.

In the case of the PZT thin film, we assume that the surface potential is not constant during the measurement since domain switching occurs. Therefore, we cannot apply the same combination of KPFM and SS-PFM approach as for the PPLN crystal. Instead, we turn our attention to the off-field PFM loops shown in figure 6(a). During the off-field loop acquisition, $V_{ac}$ is applied after $V_{dc}$ voltage pulses, and electrostatic signal contributions are minimized. However, there is still a strong cantilever-dependence when only static sensitivity is used to extract the surface displacement in picometers. This again demonstrates that the static sensitivity of a probe cannot serve to correctly predict the intensity of the

Figure 3. (a) PFM signal $D_{ac}$ as a function of $V_{dc}$ measured on a 128 × 64 point grid over a 50 μm × 50 μm area with two different cantilevers, A and B, and averaged over oppositely oriented domains. Histograms of (b) contact stiffness $k^*$ and (c) shape factor $\lambda$ measured in the same area for cantilevers A and B. (d) Histograms of $D_{ac}$ expressed in picometers with use of the static sensitivity $S$ (top) and the shape factor $\lambda$ (bottom). (e) Histograms of the measured surface potential $V_{SP}$ for two areas over the PPLN crystal.
cantilever response at the first-mode resonance in a PFM experiment.

The parameters extracted from the off-field loops to characterize the ferroelectric switching properties include the loop opening $\Delta D_{ac}$ at 0 Vdc (related to switchable polarization of the ferroelectric film) and the coercive voltage $V_c$. These parameters are shown in figures 6(b) and (c) as function of a cantilever stiffness $k_c$ for all the probes. The coercive voltages were determined through the phase flips in the PFM phase loops. It can be seen that there is a non-monotonic trend for the loop opening without clear dependencies on any cantilever properties, including cantilever length, cantilever area, free resonance frequency, contact resonance frequency and Q-factor. From the experimental data, it is obviously impossible to compare directly two different measurements with two different cantilevers. In turn, the coercive voltages (figure 6(c)) show only weak variability with the cantilever choice.

As described above, for each cantilever the tip–sample contact stiffness $k^*$ was determined from experimental values of the contact resonance frequencies and cantilever geometry. From this, the shape factor $\lambda$ was calculated for every cantilever (figure 6(d)) and compared with the experimentally measured ferroelectric loop opening plotted versus contact stiffness $k^*$. As evident, there is a very good match between the trends of the measured PFM loop opening and the calculated shape factors, validating both the model and the data processing procedure. There is no exact correlation between data and theory, which is unsurprising considering the use of an idealized model.
We note a relatively large range of the contact stiffness obtained with different cantilevers. The contact stiffness $k^*$ varies from $\approx 70$ N m$^{-1}$ to $\geq 250$ N m$^{-1}$. In the simplest model of the contact mechanics, $k^*$ is directly proportional to the tip–sample contact radius [36], and the large range of $k^*$ may point to a similar, large range of contact radii associated with different probes, which would significantly affect electric field strength in the sample and sample volume involved in the piezoeffect. Thus, a large difference in the electro-mechanical response may be expected in different cantilevers based on the range of the contact stiffness. However, as was noted above, the variability of the coercive fields obtained with different cantilevers is small, showing that the electrical properties of the tip–sample contact and transfer of the electric field into the PZT film are close for different cantilevers, even though the mechanical properties of the junctions are significantly different. This fact is worth special notice and further future studies. It can be assumed that the adhesion forces at the tip–sample contact (not accounted for in the Hertzian model) play a major role in determining contact stiffness. Both electrical and mechanical properties of the tip–sample junction depend on the tip apex shape and condition (such as contaminations) [57]. It can be speculated that the electrical shape of the probe apex is determined by the Si tip shape and coating and varies little, while the mechanical stiffness is strongly dependent on the tip apex state and contaminations, which were not controlled in our experiments. The small variability of the coercive field allows us to consider the piezoresponse of the PZT film as nearly identical for the different cantilevers used to obtain the data shown in figure 6. Therefore, deviations of the

Figure 6. (a) Off-field PFM hysteresis loops for cantilevers with different stiffness. Cantilever static sensitivities $S$ were used to convert the microscope signal into picometers for the plots, (b) Loop opening at 0 V$_{dc}$ and (c) coercive voltages $V_c^+$ and $V_c^-$ extracted from the measured off-field PFM loops in (a) and shown versus cantilever stiffness. (d) Comparison of the measured loop opening from (b) and corresponding calculated shape factors shown versus contact stiffness. The contact force was 120 nN in all measurements. Cantilever properties are provided in table S2 of the online supplementary data.
experimental data from the model results should be attributed to other factors, such as inaccuracies in determination of cantilever parameters, e.g. length and pyramid height and area, as well as imperfections of the cantilever shape [35]. We further note that the position of the laser spot along the cantilever length may change the results as well. This was not investigated in this work, where the laser spot was aligned the same way (above the sensing tip) for all cantilevers.

Conclusions

In conclusion, contact-resonance-enhanced AFM techniques used to study electrical and mechanical material properties on the nanoscale can be made more quantitative by taking into account the cantilever beam shape in the first eigenmode, which is a strong function of the tip–sample contact stiffness. Here, we have introduced a method to quantify surface displacements with high accuracy based on an analytical model of AFM cantilever vibrations. The proposed method was verified with two different high-quality well-characterized ferroelectric materials and a variety of cantilevers, through measurements of piezoelectric constant in resonance-enhanced piezoresponse force microscopy in a controlled environment. First, we measured nanometer-scale piezoelectric constant of a commercial periodically poled lithium niobate crystal and found an excellent match with the known macroscopic value specified by the sample manufacturer. In these experiments, we have for the first time introduced a methodology to quantitatively measure piezoelectric constants independently of cantilever properties and other factors in PFM measurements. Second, the technique was verified with use of a well-defined ferroelectric film. The comparison of the variations in the hysteresis loop opening measured at varying contact stiffness with a number of cantilevers showed excellent agreement with the calculated factors for the cantilever shape correction. We find that the shape correction factors are strongly dependent on the cantilever choice, and for certain cantilevers, they remain close to unity in a broad range of contact stiffness. This is important for the simulation-guided cantilever choice tailored for dynamic AFM-based characterization techniques. From a broader perspective, these results are of a significant value for quantitative measurements with a range of SPM-based techniques.

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