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A practical approach for standardization of converse piezoelectric constants obtained from piezoresponse force microscopy

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ABSTRACT

The ability to reliably measure electromechanical properties is crucial to the advancement of materials design for applications in fields ranging from biology and medicine to energy storage and electronics. With the relentless miniaturization of device technology, the ability to perform this characterization on the nanoscale is paramount. Due to its ability to probe electromechanical properties on the micro- and nano-scales, piezoresponse force microscopy (PFM) has become the premier tool for piezoelectric and ferroelectric characterization of a new generation of smart, functional materials. Despite its widespread use and popularity, PFM is a highly nuanced technique, and measurements on similar samples using different machines and/or in different laboratories often fail to agree. A comprehensive protocol for accurate quantitative measurements has not been presented in the literature, slowing the general uptake of the technique by reducing the ability of research groups to take full advantage of PFM for their characterization needs. Here, we present a procedure for PFM measurements, which outlines the practical aspects of quantitative PFM, from sample preparation to probe choice and use of control samples, and we substantiate these steps with original data on lithium niobate control samples. This quantitative characterization protocol is critical as society looks to smaller, greener alternatives to traditional piezoelectric materials for applications such as drug delivery, bio-microelectromechanical system sensors and actuators, and energy harvesting.

INTRODUCTION

Atomic force microscopy (AFM), in particular its voltage modulated variant piezoresponse force microscopy (PFM), has become an indispensable tool for the study of mechanical and electromechanical phenomena in a wide variety of functional materials.1,2 While traditionally used to investigate piezoelectricity (the linear coupling between stress and polarization, or electric field and strain) and ferroelectricity (a spontaneous polarization that can be reversed by the application of an external electric field) in ceramics and polymers, PFM has seen a renaissance in its use to probe biological materials. Recently, PFM has extended our knowledge of biological piezoelectricity in collagen fibrils,3 the M13 bacteriophage virus,4 spider silk,5 bovine intervertebral disk,6 and numerous peptide and protein assemblies.7–10 Due to the rapidly progressing need for biocompatible and biodegradable materials in fields such as energy harvesting and sensing, PFM is emerging as a vital tool for the local nanoscale analysis of this new generation of functional materials. To effectively examine a material’s electromechanical coupling properties, quantitative information is of crucial importance, as this allows the researcher to determine the suitability of this material for device applications.

In PFM, an oscillating electric field between the probe tip and sample results in local deformations of the sample surface, provided the sample is piezoelectric. The applied electric field will cause the
material to change shape by the converse piezoelectric effect. The probe is placed in contact with the sample and the piezoelectric response of the surface is detected as the first harmonic component, \( A_{1\text{th}} \), of the probe tip deflection \( A \), which is given as

\[
A = A_0 + A_{1\text{th}} \cos(\omega t + \varphi),
\]

where \( A_0 \) is the static surface displacement, \( \omega \) is the angular frequency of the applied AC bias, and \( \varphi \) is the phase of the electromechanical response underneath the tip. The first harmonic response is induced by the application of a periodic bias to the tip,

\[
V_{\text{tip}} = V_{\text{dc}} + V_{\text{ac}} \cos(\omega t)
\]

and is a direct consequence of the converse piezoelectric effect. However, this piezoresponse amplitude is not purely due to an electromechanical response but also contains electrostatic contribution, \( V_{\text{ele}} \), of the probe tip deflection and \( V_{\text{ele}} \cos(\omega t) \), which is given as

\[
A = A_{\text{piezo}} + A_{\text{ele}},
\]

where \( A_{\text{piezo}} \) is the useful piezoelectric contribution and \( A_{\text{ele}} \) is the parasitic electrostatic contribution. This unwanted contribution can originate from the interaction between the probe tip and the sample (local) or from the interaction between the cantilever body and the sample and/or underlying substrate (non-local). It will cause a deflection of the cantilever that is also linear with respect to the applied voltage and so will have the same dimension as the piezoelectric contribution (m/V). It is essential that this electrostatic contribution is minimized while maximizing the piezoelectric contribution as both will appear as a non-zero apparent "piezoresponse" when a voltage is applied to the sample under test. Due to the fact that the electrostatic contribution is linear with respect to the applied voltage and will appear at the low frequencies used in conventional PFM, steps must be taken to reduce this electrostatic contribution while keeping the useful piezoelectric contribution intact.\(^{16-18}\) While the two contributions cannot easily be differentiated, certain experimental procedures can be followed to minimize the unwanted contribution. Despite years of research in the area, the current methodologies have so far failed to produce any standardized quantitative interpretation of PFM data. This article provides a protocol for performing reliable and reproducible PFM measurements for the quantitative analysis of piezoelectric materials. The problem is comprehensive, precluding a single source solution suitable to all material types and measurement conditions. However, this protocol lays down a procedure allowing for best practice PFM characterization with accurate and unambiguous data acquisition as its goal.

The operating principle of PFM is detailed in Fig. 1. The oscillations of the sample surface can deflect the cantilever vertically (out-of-plane), which is known as vertical PFM or VPFM, or laterally (in-plane), known as lateral PFM or LPFM. Quantification of the VPFM signal yields the effective longitudinal piezoelectric coefficient \( d_3^{\text{eff}} \). Similarly, quantification of the LPFM signal yields the effective shear piezoelectric coefficient \( d_3^{\text{eff}} \). This notation comes from the commonly used laboratory coordinate system, where the 3-axis is normal to the surface of the material under test and the 1-axis is oriented along the long cantilever axis.\(^{19}\) However, if the exact crystallographic orientation is known for the material in question, these effective coefficients can be interpreted as the exact piezoelectric tensor components.

Despite the apparent simplicity of the technique, there are various practical considerations that must be considered when performing PFM experiments, particularly when exact quantitative information is required. These considerations motivated our
development of an extensive protocol for ensuring collection of accurate, unambiguous, and high-quality data when carrying out electromechanical characterization of piezoelectric materials using PFM. The steps in this protocol are discussed in depth and the most vital of these, the probe choice, is substantiated with experimental data on two commercially available standard samples. Measurements on these standard samples are presented to indicate ideal measurement conditions that allow correct interpretation of the true electromechanical response and thus, calculation of accurate quantitative piezoelectric coefficients.

MATERIALS AND METHODS

PFM measurements were carried out using an NT-MDT Ntegra Spectra scanning probe microscope (SPM) operated in a contact mode. An AC voltage was applied between the conductive probes and grounded samples at a frequency of 21 kHz. This frequency is well below the contact resonance of the tip–sample system, preventing any unwanted amplification of the signal. The probe free resonances varied from 550 kHz for the probe with the lowest spring constant to 30 kHz for the probe with the lowest spring constant. The LPFM signal can also be highly frequency dependent at higher frequencies.20 We observed no frequency dependence in the region of 20 kHz, and so this was selected as a suitable low frequency. For the purpose of these measurements, single frequency PFM was used. Seven different AFM probes with varying tip coatings, tip radii, spring constants, and cantilever lengths were used for piezoelectric characterization. Exact spring constants for the probes were calculated using the Sader method.21 All probes were manufactured by NT-MDT and their properties are summarized in Table I.

Lithium niobate (LN) was used as a standard sample for all measurements. LN is a ferroelectric crystalline material belonging to the piezoelectric point group 3m and can contain several types of domain structures.22,23 In order to investigate both VPFM and LPFM signal quantification, it is necessary to use two different cuts of LN. Periodically poled lithium niobate (PPLN) (NT-MDT, Russia) and Y-cut LN (Siegent Wafer, Germany) were used for VPFM and LPFM, respectively. PPLN is a commercially available form of Z-cut LN where alternating domains have been poled in opposite directions. Measuring the VPFM signal on the Z-cut face of LN will yield the material’s $d_{33}$ piezoelectric coefficient, corresponding to a strain in the $3$-direction due to an electric field applied in the same direction. This coefficient is generally accepted to be in the region of 6–8 pm/V.24–27 For the case of Y-cut LN, it is possible to probe the non-zero $d_{33} = d_{15}$ coefficient, which is generally accepted to be in the region of 68–70 pm/V.24,25 In the case of the converse piezoelectric effect, the $d_{33}$ coefficient refers to a strain about the $1$-direction when an electric field is applied in the $2$-direction. Applying an electric field to the $Y$-cut face and measuring the lateral deflection of the probe when it is parallel to the $1$-direction allows this $d_{33}$ coefficient to be detected, denoted hereafter using its equivalent in the conventional $d_{15}$ notation. This notation is further explained in Fig. S4 of the supplementary material.

In order to translate the cantilever deflection, measured by the AFM system as nanoamperes (nA), to the units of piezoresponse which are in picometres (pm), a conversion factor must be established. This conversion factor is known as the inverse optical sensitivity (IOS) and links the cantilever deflection to the actual height change of the sample surface. In the present study, we are interested in quantifying both vertical and lateral cantilever deflections so the inverse optical sensitivities in both the vertical (IOSV) and lateral (IOSL) modes were calculated for each probe used. Equation (4) relates the unit of piezoresponse as measured by the PFM photodiode system (nA) to the actual displacement of the sample surface (pm). The vertical inverse optical sensitivity (IOSV) is easily determined from the slope of the linear section of a force–distance curve performed on a hard substrate. IOSV was determined for each probe before measurements were taken. The gain and input are experimental amplification factors that are both required to increase the signal to noise ratio during PFM experiments. Both are set to 10, enhancing the amplitude signal by 100 times. This is then compensated for in the quantification process by dividing by both factors in Eq. (4). The $d_{33}$ coefficient can then be determined using Eq. (5).

$$Displacement\ (pm) = \frac{Amplitude\ (nA)}{Gain \times Input \times IOS (nA/nm)} \times 1000,$$

Equation (4)

$$d_{33}\ (pm/V) = \frac{Displacement\ (pm)}{Voltage\ applied\ (V)}.$$

Equation (5)

### Table I. Probe properties. All length and tip radius values are from manufacturer specifications and are approximate. Probe spring constants were calculated using the Sader method. See below for details of the inverse optical sensitivity (IOS) calculation. All seven probes were unused prior to the reported measurements with intact conductive coatings. The laser spot (Fig. 1) was aligned at approximately 70% of the length of the cantilever from the fixed end and all cantilevers were rectangular in shape.

| Probe name | Tip coating  | Spring constant (N/m) | Length (µm) | Tip radius (nm) | IOSV (nA/nm) | IOSL (nA/nm) |
|------------|--------------|-----------------------|-------------|----------------|---------------|---------------|
| C/Pt-A     | Platinum     | 0.67                  | 265         | 30             | 0.022         | 0.001 24     |
| NC/Pt-B    | Platinum     | 5.72                  | 125         | 30             | 0.039         | 0.004 68     |
| NC/Pt-A    | Platinum     | 11.03                 | 95          | 30             | 0.060         | 0.009 47     |
| HR/Pt-B    | Platinum     | 19.68                 | 125         | 30             | 0.048         | 0.005 76     |
| HR/Pt-A    | Platinum     | 34.30                 | 95          | 30             | 0.058         | 0.009 15     |
| HR/DCP-B   | Doped-diamond| 41.62                 | 125         | 100            | 0.059         | 0.007 08     |
| HR/DCP-A   | Doped-diamond| 85.77                 | 95          | 100            | 0.076         | 0.012 00     |
To calculate the $d_{33}$ coefficient, the lateral inverse optical sensitivity must be determined. IOS$_L$ can be determined using a simple geometrical relationship between the length of the cantilever, $L$, the height of the tip, $h$, and the ratio of the vertical sensitivity to the lateral sensitivity, $R$,

\[ R = \frac{\text{IOS}_V}{\text{IOS}_L} = \frac{2L}{3h} \quad (6) \]

Equations (4) and (5), with IOS$_V$ replaced by IOS$_L$, can then be used to determine the $d_{33}$ coefficient.

**RESULTS AND DISCUSSION**

**Measurement protocol**

The following details an extensive 6-step protocol that can be used by researchers hoping to generate accurate, unambiguous PFM data for characterization of the piezoelectric properties of functional materials. The first four steps describe useful and practical tips that can help identify and avoid artefacts that may cause spurious results, while the final two steps identify key areas that need to be addressed when quantitative information is valuable to the researcher. These final two steps are elaborated on with the use of original data, which provides valuable insights into the various factors affecting the quantification of the PFM signal.

**Sample preparation**

The first step involves ensuring that the sample is prepared in a correct, standardized way. The sample should be mounted on a non-piezoelectric, grounded, conductive substrate such as ITO glass. The sample should be fixed to this substrate, with, for example, conductive silver paste. If the sample is not sufficiently fixed to the substrate, low frequency resonances can occur, often in the range used for the conventional PFM (20–40 kHz), which creates an unwanted artificial “piezoresponse.” If the sample has been placed on the substrate through a method such as drop casting and the surrounding solvent has evaporated, the crystals left behind will often be naturally adhered to the substrate. This scenario is most preferable for smaller crystals that are not compatible with other fixing methods. If no method of fixing the sample is possible, it must be ensured that the piezoresponse is not frequency dependent in the region of the chosen scanning frequency.

**Laser alignment**

Incorrect alignment of the optical detection system can cause artefacts such as crosstalk between the vertical and lateral channels. To assess if this crosstalk is present in the system, the probe should be far away from the sample under test and the cantilever excited to vibrate at its first standard resonance frequency. While the probe is driven at this frequency, the amplitude in the vertical and lateral channels can be monitored. A high signal should be evident in the vertical channel at the resonance frequency of the cantilever. Any signal in the lateral channel must originate from crosstalk since torsional (lateral) vibration modes have a much higher resonance frequency, and so these modes should not be induced at the cantilever’s first standard resonance frequency.

This crosstalk can be compensated for with the use of an electronic circuit. It has also been shown that aligning the laser away from the free end of the cantilever (at a position ∼60% of the length of the cantilever from the fixed end) can result in decreased buckling and electrostatic contributions, at the cost of a partial loss in sensitivity. This can be useful when a softer sample necessitates the use of a probe with a lower spring constant.

**Operating frequency**

The frequency of the applied electric field should be low and far away from the resonance frequency of the cantilever to prevent any resonance enhancement of the signal. 20 kHz is usually a suitable frequency for conventional PFM measurements. Additionally, the LPFM signal becomes meaningless at higher frequencies due to the onset of sliding friction, and so lower frequencies are required for accurate quantification of shear piezoelectricity. A frequency sweep should be conducted in the neighborhood of the chosen frequency to ensure there are no resonances present. This only applies to non-resonance enhanced PFM techniques. Resonance enhanced methods such as dual AC resonance tracking PFM (DART-PFM) also exist. While these methods allow for enhanced signal-to-noise ratios and the use of lower electric fields, quantitative analysis is often not possible and is only attainable with accurate knowledge of the cantilever-sample dynamics. Since not all PFM systems allow for the easy implementation of resonant enhanced techniques, only single frequency PFM is discussed here.

**Applied voltage**

The applied voltage induces the electric field within the sample, which then causes a piezoelectric sample to deform by the converse piezoelectric effect. Increasing this voltage should cause the sample to deform to a greater degree, thus increasing the signal-to-noise ratio. However, this cannot be increased indefinitely. Electrostatic and other parasitic contributions can also increase proportionally with the applied voltage. Additionally, some thin-film and delicate samples are not compatible with high voltages and will experience dielectric breakdown and significant damage when high voltages are used.

**Probes**

Probe choice is the most crucial factor when quantitative PFM characterization is required. To ensure any electrostatic contributions to the electromechanical response are minimized, a stiff probe should be used. The electrostatic term is proportional to 1/k, where $k$ is the spring constant of the cantilever. A probe with $k < 1$ N/m should never be used for quantification as the electrostatic term will be amplified. In general, probes with $k > 5$ N/m should give reasonable results, but electrostatic contributions may still be present. The choice of probe stiffness will also depend on the sample under test as a stiff probe will damage a soft material. As a result, accurate quantitative measurements on very soft materials may not be possible with the conventional PFM, but may be possible with the use of more advanced techniques. Another potential parasitic contribution which can be relevant in PFM experiments is flexoelectricity, which is mechanoelectrical coupling.
between a strain gradient and electric polarization (and conversely, electromechanical coupling between an electric field gradient and mechanical stress). Flexoelectricity can be present when large gradients in the strain or electric field are present. In PFM, the large electric field gradient around the probe tip can theoretically cause a flexoelectric strain, which can contribute to the piezoresponse signal. However, the significance of this effect diminishes with increasing contact force, which is provided by stiff probes. The conductive coating of the probe is also a relevant parameter. While most probes have platinum coatings, doped diamond is a more expensive alternative that provides greater stability for electrical measurements and a longer probe lifespan, albeit with increased tip radius and decreased resolution. Detailed insight into how probe choice affects both VPFM and LPFM signal quantification is provided below.

Control samples

Before measurements are conducted on the sample under test, positive and negative controls must first be used to verify that the chosen probe and the PFM system in general are operating correctly and producing accurate quantitative data. Control samples should be standard samples that have extensively characterized properties and can therefore be used to standardize a measurement. Both positive controls, where the sample has a well-known non-zero coefficient, and negative controls, where piezoelectricity is symmetry forbidden and theoretically zero, must be used. Control samples should be thoroughly cleaned before use to remove any contamination and dead layers. Commercially available periodically poled lithium niobate (PPLN) is a very useful positive control and has a known $d_{33}$ coefficient of $6–8$ pm/V detailed in the literature. PPLN is particularly useful as it also gives the researcher an idea of the kind of electrostatic contributions that may be present with the probe in use. To do this, one simply must observe the difference (if any) in the amplitude of the “positive” and “negative” domains. While these domains are oppositely oriented ($180^\circ$ out of phase), the amplitude of piezoelectric response should, in theory, be equal. However, it is well-known that an electrostatic contribution will cause an increase in the piezoresponse amplitude in the positive domain and a decrease in the negative domain. With a PPLN crystal and this knowledge, the electrostatic contribution can be quickly estimated and the $d_{33}$ value can be verified using point measurements. Point measurements refer to when the voltage is varied between two set points and the piezoresponse recorded simultaneously with the probe held stationary and in contact with the sample. The combination of a relatively stiff probe and correct laser alignment should allow the three criteria for correct PFM measurements on an ideal ferroelectric sample to be satisfied. First, measurements should be frequency independent below the first contact resonance frequency. Second, the amplitude should be independent of the ferroelectric domain polarization direction. Finally, the phase shift across oppositely polarized domains should be $180^\circ$. An additional fourth stipulation can be added specifically for the case of PPLN, which is that the lateral amplitude and phase responses should show a negligible signal. In PPLN ($Z$-cut lithium niobate), the longitudinal $d_{33}$ coefficient should dominate with negligible contributions from shear or transverse components of the piezoelectric tensor. While PPLN is ideal as a control for the VPFM signal, Y-cut lithium niobate (Y-cut LN) can be used as a control for quantification of the LPFM signal as it has a well-known piezoelectric $d_{33}$ coefficient of $68–70$ pm/V.

Any non-piezoelectric material can act as a negative control. Amorphous glass and conductive glass such as indium tin oxide (ITO) glass are useful negative controls as piezoelectricity is precluded due to the lack of a crystal symmetry in these materials. However, care should be taken as some types of glass such as float glass can have electromechanical responses. The purpose of using a negative control is first, to verify that the system is measuring very close to zero for such a sample, and second, to estimate the inherent background signal for the system. It will not be possible to accurately distinguish and quantify piezoelectric coefficients that are close to this background. Three significant potential problems may be encountered at this step.

First, if the system is quantifying larger than expected on the positive control, conduct a voltage sweep to check for non-linear effects. If these are present, a stiffer probe and/or lower applied voltage must be used. If there is a region where the deformation response with respect to voltage is linear, this voltage range should be used. If there is a significant electrostatic contribution, a stiffer probe should be used to negate this. A frequency sweep can also be used to check for any low frequency resonances, performed by varying the frequency of the applied electric field while monitoring the piezoresponse amplitude. These resonances can occur if the sample is not properly secured, creating a false enhancement of the piezoresponse signal. These resonances can also occur if the probe is not placed securely in the probe holder. In the ideal case, the only resonance visible on a frequency sweep will be that of the cantilever’s resonance frequency (if the probe is not in contact) or that of the tip-sample system (if the probe is in contact with the sample). For stiff probes, these frequencies should be of the order of hundreds of kHz, much higher than those used for the conventional single frequency PFM.

Second, if the system is quantifying lower than expected on the positive control, the likely scenario is that the probe’s conductive coating has worn out. This can happen due to repeated scanning or joule heating caused by voltage sweeps. If this is the case, a new probe must be used. In general, diamond coated probes last much longer and are more stable than platinum coated probes, with the trade-off of higher cost and decreased resolution due to the larger tip radius. Lower than expected signals can also be measured if the positive control sample has not been sufficiently cleaned prior to measurements. Contamination and dead layers will cause the actual voltage-drop across the piezoelectric sample to be less than what is being applied to the probe which will then cause a strain that is smaller than expected.

Third, if the system is showing a large non-zero measurement on the negative control, the probe may be contaminated. In this case, it must be cleaned or changed. If the sample or probe is not properly secured in its respective holder, resonant enhancement of the signal can occur, artificially amplifying the small background to much larger values.

Several factors influence the quality of the signal that can be obtained when carrying out a PFM experiment. These variables become extremely important when quantitative information is
required. While simply visualizing ferroelectric domains can provide useful qualitative information, accurately measuring the exact piezoelectric coefficients requires much more careful consideration of the factors that affect the PFM signal.

**Vertical-PFM (VPFM) signal quantification**

In order to investigate VPFM quantification, $30 \times 10 \mu m^2$ scans were carried out with each probe on the same region of the PPLN sample. For each scan, the surface topography, VPFM amplitude (magnitude of electromechanical response) and VPFM phase (direction of electromechanical response) signals were recorded. Additionally, ten individual point measurements of piezoelectricity were recorded from the same area. Point measurements, where the voltage is varied and the piezoresponse recorded simultaneously with the probe held stationary and in contact with the sample, are the preferred method for PFM quantification because the measurement is independent of any scanning artefacts or background signals that might otherwise be present. The resultant data will be linear for a true piezoelectric response, and the slope of the line of best fit will yield the relevant piezoelectric coefficient in units of picometers per volt (pm/V). Representative point measurements are included in the supplementary material. Figure 2 illustrates the relationship between the spring constant of the probe used and the average value of ten such measurements on PPLN with that probe.

The measured piezoelectric $d_{33}$ coefficient remains mostly constant very close to 7 pm/V for the three probes with the highest spring constant values. As the probe spring constants decrease further, from approximately 34 N/m to 6 N/m, the average $d_{33}$ coefficient increases toward 8 pm/V. Finally, as the probe spring constant decreases below 1 N/m, the average $d_{33}$ coefficient increases to a value in excess of 9 pm/V. The increase in the observed $d_{33}$ coefficient is in line with Eq. (3) and is driven by an increasing electrostatic contribution due to the decreasing probe spring constants. Spring constants greater than 34 N/m result in minimal electrostatic contributions, shown here by the almost identical results obtained for the three probes with spring constants ranging from 34 to 86 N/m. A small increase in the electrostatic contribution is evident as the spring constant further decreases to 6 N/m. However, the measured $d_{33}$ coefficient of the PPLN sample remains within the expected value from the literature even for a probe of spring constant as low as 6 N/m. It is not until a probe with a low spring constant of 0.7 N/m is used that the measured value exceeds that of the expected value from literature, reaching a peak value of 9.2 pm/V. It can be concluded that stiff probes nullify the electrostatic contribution, which appears to be at a minimum when probes above approximately 30 N/m are used. Probes with lower spring constants down to approximately 5 N/m can be used with caution, depending on the sample and the degree of accuracy required. Probes with spring constants less than 1 N/m should not be used where quantitative measurements are required.
To further investigate probe suitability to VPFM quantification, it is necessary to look at the PFM amplitude and phase signals collected during scanning. Figure 3 shows scans collected using a doped diamond coated probe with a spring constant of 86 N/m and is representative of accurate, artefact-free measurements on PPLN. Figure 4 shows the scans collected using a platinum coated probe with a spring constant 0.7 N/m and is demonstrative of improper, artefact-laden measurements. In both Figs. 3 and 4, (a) shows the VPFM amplitude and (b) shows the VPFM phase, along with corresponding graphs showing a cross section of the signal taken vertically across the poled regions. Topography images showing very low roughness of several nanometres are included in the supplementary material. All images are 30 × 10 μm² and were collected with a 12 V AC bias applied to the conductive probe.

Figure 3 demonstrates a perfect VPFM signal on PPLN. Figure 3(a) shows identical piezoresponse amplitude in each domain which drops close to zero at the domain wall. While the amplitude drops significantly towards zero at the domain wall, it does not reflect the true zero amplitude value at the domain wall due to the fact that the actual domain wall is extremely thin (<10 nm), and the probe is only in contact with the true domain wall for a tiny fraction of a scan line. Thus, due to the speed of the moving probe and the capture resolution of the image, it is not always possible to observe the full drop to zero and for the same reasons, the amplitude can then appear slightly different at different domain walls. The amplitude is independent of the ferroelectric polarization which, as we see in Fig. 3(b), switches between approximately 0° and 180° across the poled regions. The average difference in the piezoresponse amplitude between domains is 2 pm, which, at 12 V applied voltage, corresponds to a difference of just 0.17 pm/V. This is similar to the noise level measured on a non-piezoelectric control such as glass.44

Figure 4 demonstrates improper VPFM piezoresponse data. Various “skips” are evident in Fig. 4(a). This is an imaging artefact that platinum coated probes can be prone to and is attributed to a sudden release of contaminants from the tip or a sudden change of the conductive layer on the tip, changing the electric field distribution and thus the VPFM signal.40 This artefact is exclusive to PFM imaging and does not affect PFM point measurements. Two of the platinum coated probes used in this work caused skipping artefacts and none of the doped diamond coated probes caused skipping. The amplitude image and the cross section [Fig. 4(a)] show a significant difference in the piezoresponse amplitude between domains, while the phase image and cross section confirm a 180° difference between adjacent domains. The average difference in the piezoresponse amplitude between domains is 36 pm, which corresponds to 3 pm/V. This is a significant proportion of the overall signal and introduces massive error to the measurements of piezoresponse should they be derived solely from a VPFM amplitude image.

This trend is maintained for all the probes used. Figure 5 shows the relationship between the probe spring constant and the
average difference between piezoresponse across adjacent domains, measured in pm/V.

For the two stiffest probes, those being the doped diamond coated probes with spring constants of 86 N/m and 42 N/m, the average difference in the piezoresponse between adjacent domains is of the order of 0.2 pm/V and is very close to the noise level for measurements. Moving to the less-stiff platinum coated probes, the average difference increases considerably, ranging from approximately 1 pm/V (for the probe with a spring constant 34 N/m) to 3 pm/V (for the probe with a spring constant of 0.7 N/m). Clearly, the electrostatic contribution manifests differently and to a greater degree during PFM imaging as opposed to PFM point measurements. Quantification from a PFM amplitude image alone is never advised. For example, while Fig. 3(a) shows domains of equal magnitude, the 100 pm displacement at 12 V applied bias is equivalent to a piezoelectric coefficient of 8.3 pm/V, which is significantly larger than 7 pm/V measured from point measurements on the same area. It can be concluded that stiff and, in particular, doped diamond coated probes, provide the most stable, electrostatic free and instrumental background free images for qualitative studies of the shape, size, and distribution of ferroelectric domains. However, caution should be observed when the magnitudes of piezoelectric coefficient are of interest. While the relative magnitudes can be investigated using the appropriate probes, the absolute magnitude of piezoelectric coefficients cannot be reliably calculated from piezoresponse amplitude images alone. When this data is required, PFM point measurements provide the most accurate and reliable measurements that are independent of any scanning or imaging artefacts.

**Lateral-PFM (LPFM) signal quantification**

Quantification of the LPFM signal is traditionally more difficult and prone to error compared to the VPFM signal and is still not as widely implemented. For the VPFM signal, conversion of the unit of piezoresponse as measured by the photodiode to the actual sample surface displacement takes into account the length of the cantilever and the height of the probe tip. While other methods of LPFM calibration exist, this remains the simplest, most straightforward means of direct, sensitivity-based quantification similar to that used for the VPFM signal. For the purpose of assessing LPFM quantification, this is the method used here to derive IOSV values from the easily obtained IOSV values (see the section on Materials and Methods).

As before, 30 × 10 μm² scans were carried out with each probe on the same region of the Y-cut LN sample. For each scan, the surface topography, LPFM amplitude and LPFM phase signals were recorded. Additionally, ten individual point measurements of piezoresponse were recorded from the same area with each probe, this time recording the LPFM amplitude as the voltage was varied. As this Y-cut LN sample is not poled, PFM imaging recorded no significant features and the images contained no contrast indicative of ferroelectric domains. In accordance with the high d_{15} shear piezoelectric coefficient of LN oriented in this way, the LPFM amplitude images displayed a large signal far above the background for LPFM measurements [Fig. S3(a) in the supplementary material]. Given the lack of domains, no phase contrast was observed suggesting the piezoelectric effect in the region was oriented in the same direction throughout [Fig. S3(b) in the supplementary material].

Quantifying the lateral piezoresponse using the calculated IOSV values results in a substantial variance in the calculated shear piezoelectric coefficient of the sample. The values strongly depend on the probe used, as illustrated in Fig. 6. The highest recorded average value is 413.9 pm/V and the lowest is 18.4 pm/V. When compared with VPFM quantification, LPFM quantification fails to give consistent, reliable results. Interestingly, the LPFM signal does not seem to be substantially affected by the electrostatic interactions in the same manner as the VPFM signal with no clear correlation existing between the probe spring constant and the LPFM amplitude. While a substantial increase is observed for the probe with the smallest spring constant, this is likely due to other factors which we discuss below. Further analysis into the relationship between the signal and the probe used reveals a dependence on other factors, namely, the conductive coating, and thus the tip radius, and the cantilever length.

**Table II** shows the probe properties along with the measured d_{15} coefficient for each probe. Some trends begin to emerge which can help identify which factors most critically affect the LPFM amplitude signal. Referring to the method of obtaining the IOSV as

![FIG. 6. Experimentally measured shear piezoelectric d_{15} coefficient of Y-cut LN for each probe of varying spring constant. Black dashed line represents the ideal value of 69 pm/V. Only one probe out of seven provides an accurate value coming within 2.2% of the d_{15} piezoelectric coefficient of LN, measuring a value of 67.5 pm/V. Probe 2 is the only other probe that provides an approximately correct value, coming within 15.1% of the ideal d_{15} piezoelectric coefficient. Error bars are not visible due to their small size.](image-url)
TABLE II. Probe properties related to LPFM quantification, along with the $d_{15}$ coefficient obtained from IOSL calibration. Probes are numbered 1–7 to ease identification in the text.

| Probe No. | Probe name   | Tip coating | Spring constant (N/m) | Length (µm) | Tip radius (nm) | IOSL (nA/nm) | $d_{15}$ (pm/V) |
|-----------|--------------|-------------|-----------------------|-------------|----------------|--------------|-----------------|
| 1         | C/Pt-A       | Platinum    | 0.67                  | 265         | 30             | 0.00124      | 413.9          |
| 2         | NC/Pt-B      | Platinum    | 5.72                  | 125         | 30             | 0.00468      | 58.6           |
| 3         | NC/Pt-A      | Platinum    | 11.03                 | 95          | 30             | 0.00947      | 26.2           |
| 4         | HR/Pt-B      | Platinum    | 19.68                 | 125         | 30             | 0.00576      | 34.9           |
| 5         | HR/Pt-A      | Platinum    | 34.30                 | 95          | 30             | 0.00915      | 18.4           |
| 6         | HR/DCP-B     | Doped diamond| 41.62                | 125         | 100            | 0.00708      | 111.0          |
| 7         | HR/DCP-A     | Doped diamond| 85.77                | 95          | 100            | 0.01200      | 67.5           |

An interesting observation can be made by comparing the calculated coefficients for the doped diamond coated probes and the platinum coated probes. The $d_{15}$ coefficient for the "short" doped diamond coated probe (probe 7) is 3.7 times larger than that for the "short" platinum coated probe (probe 5). This trend is followed for the "long" probes, with the "long" doped diamond coated probe (probe 6) quantifying 3.2 times larger than the "long" platinum coated probe (probe 4). This factor of 3.2–3.7 seems to correlate with the ratio of the different probe tip radii, where the diamond coated probes typically have a tip radius of ≈100 nm compared with the tip radius of ≈30 nm of the platinum probes. While this trend appears to persist for the platinum coated probes with higher spring constants (probes 4 and 5), it breaks down when measurements on probes 2 and 3 are compared with doped diamond coated tips of the same length. This suggests that the probe tip radius plays a key role in LPFM quantification, but the relationship between the probe tip radius and the LPFM signal is not always linear as it can also be influenced by other factors.

In summary, it is clear that the method proposed by Peter et al. is unsuitable for most commercially available probes. The formula for calculating IOSL contains a dependence on the length of the probe that systematically inflates the apparent shear piezoelectric coefficients for longer probes, resulting in the hugely overestimated $d_{15}$ coefficient calculated using probe 1. Additionally, the formula contains no dependence on the probe tip radius, which we show the LPFM signal to be highly dependent on. Despite this, one type of probe tends to give accurate results following this method. These are the short, doped diamond coated probes (probe 7). Provided the correct $d_{15}$ value for Y-cut LN is verified before use, these types of probes can be used along with this method of LPFM quantification. For all other probes, a scaling factor method should be used whereby the uncalibrated piezoresponse amplitude on a known standard sample with a known shear piezoelectric coefficient, such as Y-cut LN, is compared with that of the sample of interest. This method has been used to determine the shear piezoelectric coefficient in peptide nanotubes.

CONCLUSION

Despite the absence to date of a rigorous protocol to generate reliable quantitative data from the conventional PFM, the technique remains the most suitable method for the detection and measurement of piezoelectricity in small and often fragile crystalline materials. For unambiguous interpretation of data, a standardized approach is essential. We have demonstrated that reliable quantitative PFM measurements of piezoresponses below 10 pm/V are possible with a conventional system that does not require any modifications such as an interferometric displacement sensor (IDS) or resonance enhanced techniques. A protocol for best-practice measurements has been outlined that will allow researchers to identify the common pitfalls associated with conventional PFM measurements, along with potential solutions to these common problems. Importantly, two commercially available samples of lithium niobate were used to quantify the effect that probe choice has on the quantitative PFM signal for both VPFM and LPFM. These samples should be recognized by researchers as the gold standard for verification and calibration of PFM measurements, finally allowing the realization of a "round-robin" approach that should see consistent and reliable agreement between PFM measurements.
measurements carried out on samples from different laboratories around the world.

SUPPLEMENTARY MATERIAL

See the supplementary material for further details of PFM quantification, PFM point measurements, AFM topography images, and LPFM images.

AUTHORS’ CONTRIBUTIONS

All authors contributed equally to this work.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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