The determination of the magnitude of the piezoelectric coefficients (PCs) is still a rewarding experimental challenge. Although several methods have been utilized (measuring the resonance frequencies of specifically cut samples \[\varepsilon\], determining the velocity of sound \[\varepsilon\], utilizing a Berlincourt meter \[\varepsilon\] or using optical heterodyne interferometry \[\varepsilon\]), they all suffer from being cumbersome and the published values vary strongly. In the past years piezoresponse force microscopy (PFM) has become a standard tool for investigating ferroelectric and thus piezoelectric samples \[\varepsilon\] making use of the converse piezoelectric effect. A detailed description of PFM can be found elsewhere \[\varepsilon, \varepsilon\]. However, despite its ultra-high vertical resolution in the sub-picometer regime, it is not applied for the precise determination of PCs. This is mainly due to the fact, that even well established PCs could not be reliably confirmed with PFM. Interestingly, the failure of PFM measurements with high quantitative accuracy is mostly due to the incorrect calibration of the instrument. However, even with appropriate calibration, PFM is not capable of determining piezoelectric coefficients.

In this contribution, we will show why the calibration technique generally referred to \[\varepsilon\] leads to wrong PFM-calibration constants. We will in return present a reliable calibration procedure. We will further more focus on the difficulties to determine PCs with high accuracy with PFM. It will unfortunately turn-out that a precise determination of PCs with PFM is generally not possible.

Piezoresponse force microscopy is based on the deformation of the sample due to the converse piezoelectric effect. The PFM is a scanning force microscope (SFM) operated in contact mode with an alternating voltage \(U_{tip}\) applied to the tip. In piezoelectric samples this voltage causes thickness changes \(\Delta t\) and therefore vibrations of the surface which lead to oscillations of the cantilever that can be read out with a lock-in amplifier. In order to obviate misunderstandings we briefly define the symbols used later on for the outputs of the lock-in amplifier (LI). A LI-signal can generally be described in a circular coordinate system as a vector \(\mathbf{P}\) with an appropriate length \(P\) and an angle \(\theta\) with respect to the reference signal. This is the way the signals are read-out from a single-phase LI. In case of a dual-phase LI, the two output signals can optionally also be displayed in a cartesian coordinate system thus resulting in the output signals \(P^X\) and \(P^Y\). Note that adjusting the phase \(\phi\) of the reference signal corresponds to a rotation of the coordinate system. In the following we will adapt the usual notation naming the output signals \(P\) and \(\theta\) \((\phi = 0)\) of the LI the PFM-signals, subscripts specify the particular sample.

In general the calibration of the SFM for PFM-measurements is performed according to the hence often cited work by Christman et al. \[\varepsilon\]. In brief, a piezoelectric sample with known PC is brought into the PFM-setup. Due to its very precisely determined PC an \(\alpha\)-quartz-plate \((d_{11} = 2.3 \pm 0.05 \text{ pm/V})\) is generally used for this purpose. One presumes thus to obtain the relation between the PFM-signal \(P_\alpha\) and the vibration amplitude \(\Delta t = d_{11} U_{tip}\) of the surface, leading to a PFM-calibration constant \(k_{PFM} = \Delta t/P_\alpha = d_{11} U_{tip}/P_\alpha\). Thus by measuring \(P\) of any other sample one presumes to determine its particular PC as

\[
d = k_{PFM} P/U_{tip} = d_{11} P/P_\alpha.
\]

However, due to the system-inherent background \[\varepsilon\] this calibration procedure and thus the precise determination of PCs fails. This background, present in current SFM setups, shows-up as a frequency dependent contribution to the PFM-signal, probably caused by a wealth of mechanical resonances of the SFM-head. The amplitude of the background \((1–10 \text{ pm/V})\) scales linearly with \(U_{tip}\), its phase varies randomly. Possible consequences of the background-adulterated PFM-signals have been presented in detail elsewhere \[\varepsilon\]. Hitherto attempts to suppress the background by modification of the SFM-head...
failed.

Figure 1 depicts the situation showing PFM-signals in a vectorial diagram. Note that $\mathbf{D}_a$ denotes the contribution of the calibration sample to the PFM-signal which should not be confused with its piezoelectric coefficient $d_a$. For the sample to be measured the same notation $(\mathbf{D}$ and $d)$ applies. Starting from scratch: the background $\mathbf{P}_b$ results in PFM-signals of $P_b$ and $\theta_b$. The contribution of the calibration sample adds on the background as $\mathbf{P}_a = \mathbf{P}_b + \mathbf{D}_a$ thus resulting in the PFM-signals $P_a$ and $\theta_a$. The sample to be measured finally leads to the PFM-signals $P$ and $\theta$. From simple geometrical considerations can be seen that

$$P_a = \sqrt{P_b^2 + D_a^2 + 2P_bD_a \cos \theta_b} . \quad (2)$$

The same expression applies for $P$ substituting $D_a$ by $D$. It is now self-evident that for $\mathbf{P}_b \neq 0$ and thus $\mathbf{P}_a \neq \mathbf{D}_a$ the procedure described previously for calibrating the PFM and consequently the determination of $d$ fails.

An example shows the significance of the situation described above. In Fig. 1 the different contributions to the PFM-signals are shown in realistic proportions when using $\alpha$-quartz ($d_{11} = 2.3 \text{pm/V}$) for calibration. Let us assume the background to have an amplitude of $P_b = 8 \text{ pm/V}$ at an angle of $\theta_b = 60^\circ$ and the sample to have a PC of $d = 7 \text{ pm/V}$. Using Eqs (1) and (2) would lead to $d = d_{11} P/P_a \simeq 3.2 \text{ pm/V}$ which is wrong by a factor of more than two.

To overcome the above mentioned difficulties it is essential to conduct a reliable calibration of the PFM. Therefore three steps have to be accomplished:

- Calibration of the z-scanner of the SFM. This can be accomplished with a height standard.
- Determination of thickness change $\Delta t$ of the calibration sample at a specific voltage $U_{\text{tip}}$ and frequency $f$ applied to the tip. This measurement is performed with the "height-modus" of the SFM. Therefore a piezoceramic sample with a large PC $(\sim 500 \text{ pm/V})$ is most appropriate. The frequency $f$ must be low with respect to the feedback loop of the SFM thus the z-scanner can fully follow the movement $(f \sim 0.1 – 1 \text{ kHz})$.
- With the piezoceramic sample used in the step before, using the same voltage and the same frequency applied to the tip the PFM can now be calibrated just by disabling the feedback-loop and measuring the output $P_{\text{PZT}}$ of the lock-in amplifier. One thus gets the wanted calibration constant $k_{\text{PFM}} = \Delta t_{\text{PZT}} / P_{\text{PZT}}$.

Another possibility to calibrate the SFM by determining the detector sensitivity via a force-distance measurement and then calculating the expected PFM-signal [11]. This calibration method has a disadvantage since it is a low-frequency measurement whereas for PFM usually frequencies in the kHz regime are used. It is thus not performed under the same conditions than the PFM measurements.

Now, after calibration of the PFM, the main problem for determining reliable PCs with the PFM remains the background. Although the origin of the background is not fully understood, it can be attributed to resonances of the whole SFM setup, i.e. head of the microscope, and sample & sample stage, depending on the specific realization of the top electrode. Therefore two situations have to be discussed individually: (a) the tip and (b) a large area metallization acting as top electrode. In both cases the backside of the sample is covered with a large area electrode (Fig. 2).

Tip as electrode. This is the standard configuration for PFM-measurements yielding a high lateral resolution. In this situation, the electric field inside the crystal can reach values of up to $E \approx 10^9 \text{ V/m}$ just underneath the tip, depending on the tip radius and the dielectric

FIG. 1: Output signals of the lock-in amplifier in the X-Y-plane. The system-inherent background is $\mathbf{P}_b$. A piezoelectric standard sample with a piezoelectric coefficient $d_a$ contributes $\mathbf{D}_a (\rightarrow)$ to the resulting PFM-signal $\mathbf{P}_a$. Same applies for the sample with the PC to be measured: it’s contribution to the measured signal $\mathbf{P}$ is $\mathbf{D} (\rightarrow\rightarrow)$.

FIG. 2: (a) The tip acting as electrode. Only a very small volume of the sample (some $\mu$m$^3$) contributes to the deformation. (b) A large area top electrode. Beneath the central part of the electrode, the whole volume of the sample expands homogeneously. Near the edges clamping influences the deformation.
constant of the sample. However, due to the strong in-
homogeneity caused by the sharp tip, \( E \) decays within
\( \leq 1 \, \mu m \) inside the sample [12]. The piezoelectrically ex-
cited region is thus only a few \( \mu m^3 \) (Fig. 2(a)). This has two important consequences on PFM-imaging: (i) the
whole sample is at rest, the background is only due to the
SFM-head (incl. cantilever) and can thus be determined e.g.
with a glass plate [8]; (ii) Due to clamping of the sur-
rounding material the crystals deformation is drastically
reduced. The values measured in this way were found to be
too small by a factor of up to three [13]. As a result
measurements with the tip acting as electrode are not
suited for the determination of PCs with high accuracy.

**Large area electrode.** To avoid the problem of clamp-
ing and to minimize any effect of electrostatic interac-
tion between the cantilever and the sample, a large area
electrode of some \( \mu m^2 \) is evaporated on top of the sam-
ple. Electrical contact is performed directly to the elec-
 trode through an external wire, short-circuited with the
tip (Fig. 2(b)). Besides being unclamped in the center of
the electrode, this configuration offers another advan-
tage in comparison to the situation with the tip acting
as electrode: The electrical field applied to the crystal is
well defined as it is homogeneous across the whole sample
thickness. In this configuration, however, the background
is no longer independent of the sample which turns out
to be a probably irresolvable drawback. Since the whole
sample is piezoelectrically excited, sample and sample-
holder also contribute to the background. A series of
experiments with different fixations of the sample (stick-
ing it with epoxy on a large lead block, embedding it in
rubber, or suspending it freely) failed. Every mounting
showed its own frequency dependence of the PFM-signal
why a determination of the background is not possible.
Thus, measurements with the large area electrodes are
not suited for the determination of PCs with high accu-
cracy.

Of course the immediate question arises whether there
is any possibility to circumvent the drawbacks presented
above, thus enabling a precise determination of piezo-
electric coefficients. A reliable measurement of PCs with
the tip acting as electrode can be excluded as it fails
due to clamping, i.e., a fundamental physical reason. For
the measurements using large top electrodes, however,
the situation is different since so far technical deficien-
cies cause the failure. In the following we will discuss
three approaches that might overcome the difficulties
mentioned above.

(1) In principle, one can think about a SFM-setup sup-
pressing any kind of background. Although difficult to
realize, it is not impossible. As a reminder the amplitude
of the background is of the order of 10 \( \mu m/V \), which, us-
ing standard PFM settings (10 V applied to the tip) be-
comes comparable to the radius of an atom. The same
scale applies for the PCs to be measured. Obviously the
specific SFM we used (SMENA from NT-MDT) is not of
low quality but lock-in detection is amazingly sensitive.
Note that in order to become interesting for the deter-
mination of PCs, the background needs to be reduced at
least by two (!) orders of magnitude. Taking this into
account, building a ”background-free” SFM appears as a
remarkably serious challenge.

(2) Another approach to circumvent the back-
ground-problem is based on multi-domain samples. Measuring
the PFM-signals on both domain faces (with the same
background) would automatically yield the correct PC
of the sample [8]. Apparently straightforward, this ap-
proach results in new troubles: the clamping between
adjacent domains. As expected from theoretical con-
siderations, and verified experimentally [14], the surface
def ormation is affected on a length scale similar to the
thickness of the sample. Thus, for a 500 \( \mu m \) thick sample,
valuable values for the piezomechanical deformation can
only be obtained at a distance of \( > 500 \mu m \) from any do-
main boundary. As a first consequence, the use of a large
bi-domain sample is required. Furthermore, the sample
has to be transferred by more than 1 mm for measuring
reasonable PFM-signals on both domain faces. Unfortu-
nately, when performing such crucial changes in the me-
chanical setup, the background can not be presumed to
remain unchanged. This, however, is an absolute condi-
tion for the quantitative analysis of a multi-domain mea-
surement as proposed here. Even worse, there is no way
to find-out, whether the translation of the sample did
affect the background or not.

One could think, of course, to reduce this difficulty
using thinner crystals, e.g., 50 \( \mu m \) thickness, thus scaling
the problems described above by one order of magnitude.
But also a 100 \( \mu m \) translation is still too much. Since for
this measurement, the samples must be free-standing, to
make them even thinner is not trivial. Thus although
seemingly easy, this approach also suffers a series of draw-
backs not yet resolved.

(3) Finally, and so far the only realizable solution to the
problems described above consists of using very particu-
lar settings for the PFM, avoiding the contribution of the
background by applying frequencies of \( \ll 1 \) Hz to the tip,
thus excluding the resonances of the setup. This requires
of course to disable the feedback of the SFM. Due to the
very long integration time of several minutes, necessary
for obtaining reliable data, those measurements can only
be carried out when the environment of the setup is at
quiet as possible. Although this measurement scheme
might provide the best data for PCs when using PFM,
it is not a detection method suitable to provide reliable
values of high accuracy due to inherent drift and noise in
current SFM setups.

In this contribution, we extensively discussed the ca-
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