

Quantitative Surface Potential Measurements by AC Electrostatic Force Microscopy

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Abstract—Electric charge distributions and the associated surface potentials at the nanoscale play a key role in many areas from material sciences to biology. The increasing field of sample analysis in liquid environments of biologically relevant ionic concentration demands for invasive-free measurements, hardly achievable with current techniques. This paper presents the development of a novel Atomic force Microscopy measurement mode, termed AC-EFM, enabling quantitative surface potential measurements at the nanoscale. It circumvents the use of a dc-bias, which leads to parasitic electrochemical effects in liquids in conventional methods, by the application of an amplitude modulated high frequency voltage. The surface potential is measured through the shift in cantilever resonance frequency, which itself is detected by a phase-locked loop. Measurements with externally applied sample potentials validate the derived model and experiments on a standard KPFM sample show improved spatial resolution, when compared to conventional methods. The capability of AC-EFM to quantitatively measure surface potentials at the nanoscale without the use of a dc-bias is demonstrated.

Index Terms—atomic force microscopy, electrostatic force microscopy, surface potential

I. INTRODUCTION

Since its first introduction in 1986, atomic force microscopy (AFM) [1] has been used as an analysis tool in a wide variety of scientific fields, ranging from material science applications [2] to more recent usage in biological cell analysis [3], [4]. Since then, many AFM modes has evolved, enabling the measurement and characterization of intrinsic sample properties such as mechanical [5], magnetic [6] or electrical features [7] at the nanoscale. In the case of measuring electric surface charges or the associated potential distribution, several different techniques have been developed, among which kelvin probe force microscopy (KPFM) [8] is the most widely used.

In KPFM a conducting AFM cantilever is held in close proximity (few tens of nm) to a sample surface whose surface potential distribution is to be measured. The electrostatic force interaction on the cantilever is modulated by an ac-voltage, usually oscillating with the resonance frequency of the cantilever to maximize the signal-to-noise ratio (SNR) [9]. The cantilever deflection, resulting from this electrostatic force, is measured and controlled to zero by an additional dc-bias. This, in addition with a lateral scan above the sample surface, results

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in a map of the samples potential distribution. However, due to this dc-bias, KPFM can not be used in aqueous media [10], which is important for e.g. biological AFM applications. A dc-electric field between cantilever and sample induces parasitic electrochemical effects, ranging from motion of the solvated ions to gas formation due to electrolysis [11] potentially damaging the sample and making any controlled measurement impossible.

Several derivations of KPFM have been developed in the recent years tackling this issue. Some of them circumvent the need for a dc-bias by completely omitting its use and by measuring the potential distribution in an open-loop configuration [12]. Another approach replaces the dc-bias with a second high frequency ac-voltage and uses its amplitude for the nullification of the electrostatic force [13], [14]. While these methods are generally able to operate in aqueous media [15], [16], they are still restricted to measurements in low-ionic concentrations (~ 10 mM). Higher concentrations of biological relevance (> 100 mM) require excitation frequencies of several MHz [17], which is not achievable with the current limitation in cantilever design (i.e. resonance frequency). Only in this case a static and homogeneous medium between cantilever and sample is guaranteed, as induced motion of solvated ions in the liquid is suppressed.

A technically different but KPFM-related AFM measurement mode is electrostatic force microscopy (EFM) [18]. Here, no external electric signals are applied to the cantilever, which is solely mechanically excited and therefore enables its use in any medium. The electrostatic interaction with the sample potential manifests itself in a shift of the cantilever resonance frequency which is tracked and measured by means of a phase-locked loop (PLL). However, since no nullification of the electrostatic force is done, EFM only provides a qualitative measure of the potential distribution.

The contribution of this paper is the development of electrostatic force microscopy towards quantitative potential measurements. It adapts the use of the electrical cantilever excitation from KPFM, by employing an amplitude modulated high frequency ac-voltage. Its frequency is decoupled from the cantilever resonance frequency and can therefore be chosen arbitrarily-high. This eventually opens the possibility for invasive-free electric potential measurements in aqueous media of high ionic concentration. Here we present the basic principle and experimental setup of the developed mode, which

to calculate the surface potential distribution ϕ .

Overall gold coated cantilevers (TAP300GB-G, BudgetSensors, Bulgaria) with a measured resonance frequency in air of $f_0 = 225.6$ kHz and a stiffness of $k = 22.88$ Nm are used. If not otherwise stated, lift heights of 50 nm, drive amplitudes of $a = 2$ V and drive frequencies of $\omega_L = 2\pi \cdot 120$ Hz, $\omega_H = 2\pi \cdot 1$ MHz are used. Here, we want to emphasize that the choice of ω_H is not limited by the system and can be chosen to be much higher.

Measurements are performed on a standard KPFM sample (BudgetSensors, Bulgaria). This sample features stripes with alternating material (Aluminium and Gold) and equal height, separated by a 500 nm wide trench. This enables measurements of the materials work functions, while minimizing potential crosstalk of topographical features. In addition, it allows the application of external voltages, which is used to mimic known surface potential distributions.

IV. RESULTS AND DISCUSSION

A. Model Verification

To verify the derived model as given by Eq. (3)-(6), parameter sweeps are performed and the resulting static and dynamic frequency shifts, Δf_0 and Δf_{2-L} , are recorded. Fig. 2(a) and (b) show the influence of the surface potential ϕ and the drive amplitude a on the static frequency shift Δf_0 . The parabolic dependence is clearly visible, and fully overlaps with the theoretical fits. In Fig. 2(c) the amplitude of the dynamic frequency shift Δf_{2-L} is shown as a function of the drive amplitude a . Again, as given by Eq. (5), it fits the theoretical formulation with no dependence on the surface potential ϕ . These two measured components ($\Delta f_0, \Delta f_{2-L}$), together with the knowledge of the cantilever voltage U_C , are then used in the upcoming steps to calculate the quantitative surface potential ϕ as derived in Eq. (6).

B. Measurement Procedure

To be able to calculate the surface potential, the static and dynamic frequency shift components need to be extracted out of the recorded Δf signal. This process is visualized in Fig. 3. Here, the scanning motion of the AFM is disabled and an external rectangular voltage is applied to the sample, in order to mimic a surface potential distribution. In (a) the recorded Δf -Map is shown, where the amplitude of the applied signal is set as indicated. The cross-section of the applied voltage and measured frequency shift is shown in (b) and (c), respectively. Since the dynamic part of the frequency shift does not depend on ϕ , its amplitude stays constant throughout the measurement. The static frequency shift Δf_0 however, changes with the high and low side of the applied potential, as expected. The individual components of the signal are extracted by calculating the mean value and the spectral components over a predefined time-window. The length of this window defines the trade-off between measurement accuracy and speed and is chosen to be exactly one period of the dynamic frequency shift Δf_{2-L} (i.e. $2/\omega_L$).

The two components of each high- and low-section are extracted and given in Table I. From these values and the known drive amplitude $a = 2$ V, the potentials (ϕ_1, ϕ_2) are calculated, leading to the measured amplitude of the applied rectangular signal: $\Delta\phi = \phi_1 - \phi_2$. Good agreement between the applied signal amplitude and the measurement is observed, validating the ability of AC-EFM to quantitatively measure the samples surface potential.

C. Voltage accuracy and spatial resolution

With the working measurement procedure, accuracy and spatial resolution of AC-EFM are analyzed. Figure 4 shows the measured surface potential, again with the scanning motion

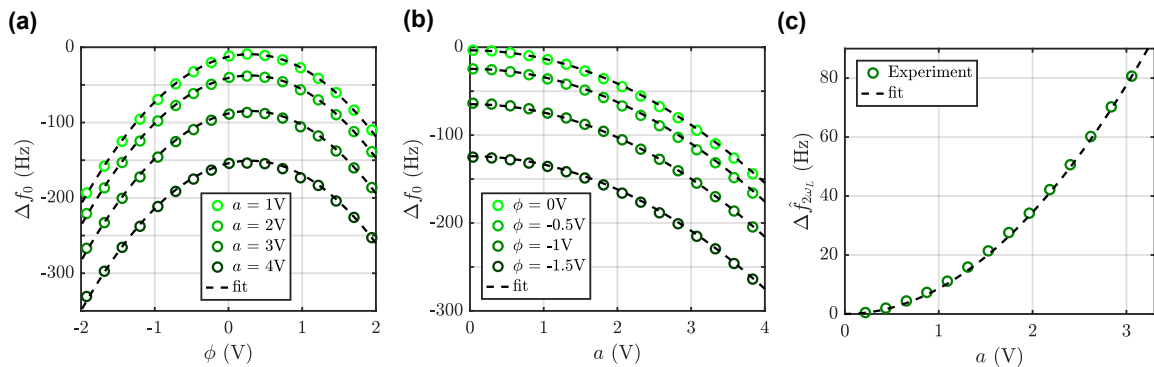


Fig. 2: (a) Dependence of the static frequency shift Δf_0 on the surface potential ϕ for different drive amplitudes a . (b) Dependence of the static frequency shift Δf_0 on the drive amplitude a for different surface potentials ϕ . (c) Dependence of the dynamic frequency shift Δf_{2-L} on the drive amplitude a (surface potential ϕ has no impact). Dashed lines in each Figure represent fitted curves using Eq. (5) with $f_0 = 225.6$ kHz, $k = 22.88$ Nm and $2C/z^2 = 0.0153$. The offset of the parabolas in (a) to the zero point (0.28 V) can be explained by the natural work function difference between the varying materials of the cantilever and the sample.

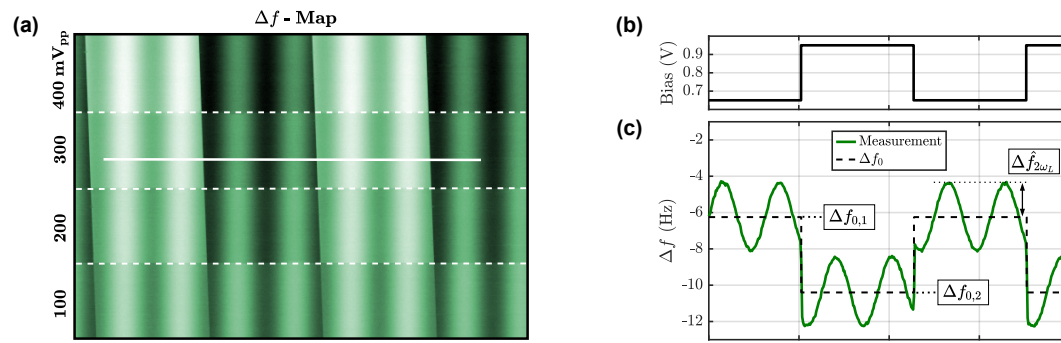


Fig. 3: (a) Measured Δf signal on a bare gold substrate with the xy-scanning motion disabled. Each vertical quarter represents a different amplitude of the applied voltage signal (given on the left), which is roughly synchronized with the line scanning rate. (b) Applied bias voltage at the cross section as indicated in (a), with the simultaneously measured Δf signal in (c). The components Δf_0 and $\Delta f_{2\omega_L}$ are highlighted for clarity. (extracted data in Table I)

Sample Bias (mVpp) + offset (V)	$\Delta f_{0,1}$ (Hz)	$\Delta f_{0,2}$ (Hz)	$\Delta f_{2\omega_L}$ (Hz)	$\Delta\phi$ (mV)
400 + 0.8	-6.10	-11.66	1.86	391
300 + 0.8	-6.13	-10.29	1.86	308
200 + 0.8	-6.80	-9.61	1.86	205
100 + 0.8	-7.09	-8.45	1.86	104

TABLE I: Extracted data from Figure 3. The corresponding potentials ϕ are calculated for each section and their difference $\Delta\phi = \phi_1 - \phi_2$ is shown. Only minor deviations in the single mV range to the applied signal amplitude (highlighted) are observed.

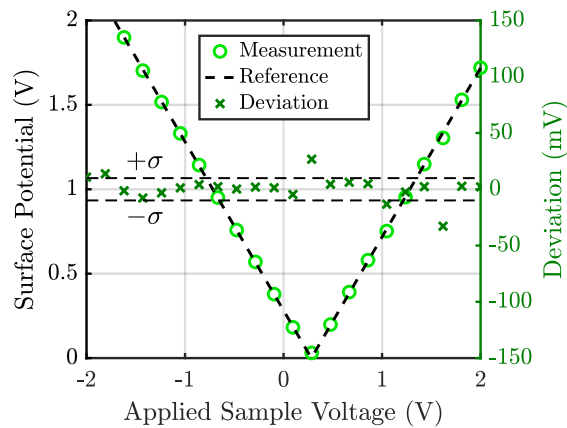


Fig. 4: Measured surface potential on a bare gold substrate using AC-EFM (only positive values shown) as a function of the applied sample voltage. The difference from the applied voltage is given on the right y-axis with a standard deviation of $\sigma = 9.9$ mV.

disabled, while linearly sweeping the applied voltage on the sample. As stated in the derivation of AC-EFM the sign of ϕ is lost during the measurement, explaining the two mirrored branches (only positive value shown) around the zero position at 0.28 V, which is again attributed to the natural difference in work function of the cantilever and sample metal coating. The difference of the measured surface potential to the known reference (i.e. the measurement error) is shown on the right y-axis and has a standard deviation over this 4 V range of $\sigma = 9.9$ mV, which is comparable to conventional KPFM measurements [20].

Assessing the spatial resolution of AC-EFM is done via measuring the work function distribution of a 5 μm wide aluminum stripe between two gold electrodes. Figure 5(a) shows the topography of the sample with the measured potential distributions using conventional KPFM and AC-EFM in (b) and (c), respectively. The most obvious difference between the two images is the increase in spatial resolution in AC-EFM. This arises from its dependence on the second derivative of the tip-sample capacitance (cf. Eq (3)) as opposed to the proportionality to its first derivative in standard KPFM. This effect is also exploited within frequency-modulated and heterodyne KPFM, which is discussed in more detail elsewhere [20]. In (c), the decreasing potential of the center-electrode (aluminum) towards its edges is attributed to be a result of non-uniform oxidation, which is generally more present at metal edges. Since gold is not subject to oxidation, this effect is not visible on the left and right electrode. Conventional KPFM in (b) on the other hand is not able to resolve this sample feature.

In summary it has been shown, that the introduced AFM mode enables a quantitative measurement of surface potential distributions at the nanoscale with the use of an amplitude modulated ac-voltage of arbitrarily choose-able carrier frequency. This development paves the way for electrical AFM measurements in aqueous solutions with biologically relevant ionic concentrations, which is part of ongoing and future work.

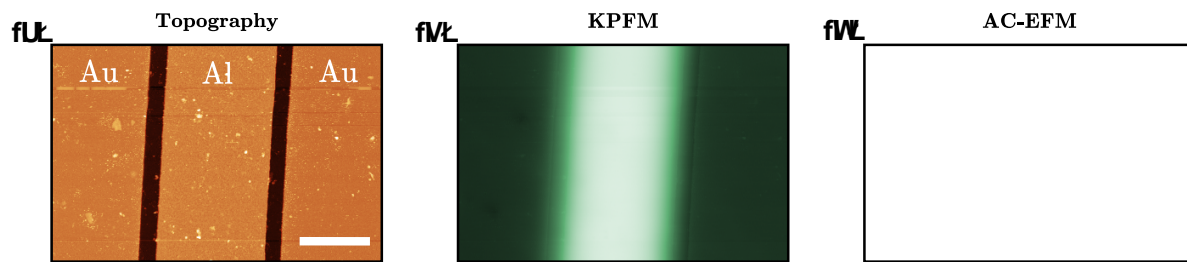


Fig. 5: (a) Measured Topography of the Gold-Aluminum sample. Some dust particles are visible on the sample surface (scale bar: 3 μm / color scale: 100 nm). (b) Measured potential distribution using conventional KPFM (color scale: 1.3 V). (c) Measured potential distribution using AC-EFM (color scale: 1.3 V).

V. CONCLUSION

The herein developed AFM measurement mode enables quantitative determination of distributed surface potentials on the nanoscale. An amplitude modulated high frequency signal is applied onto a mechanically oscillating AFM cantilever. This voltage, in combination with the sample potential, generates an electrostatic force that modifies the effective stiffness of the cantilever. The resulting change in resonance frequency is measured by a phase-locked loop and used in a post-processing step to calculate the surface potential distribution. Measurements on an aluminum-gold test sample validate the derived model and show measurement uncertainties of 9.9 mV.

With its use of a voltage whose carrier frequency can be arbitrarily chosen, AC-EFM is a promising candidate for surface potential measurements in aqueous solution of high ionic concentration, which is currently not possible with state of the art techniques. Future work will therefore focus on the adoption of the current setup for operation in liquid environment.

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