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Influence of Imaging Parameters on AFM Surface Potential Measurements in Aqueous Solutions

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Abstract—This paper presents surface potential measurements by closed-loop AC-KPFM in aqueous solutions. In contrast to conventional KPFM, the proposed method omits the use of a dc-bias, therefore preventing electrochemical & electrokinetic effects, enabling operation in water. The ability for reproducible surface potential measurements in aqueous solutions is demonstrated and the influence of key imaging parameters on its performance are investigated, in particular the excitation frequency of the drive signal. It is found that proper operation of AC-KPFM in water is only possible in a regime, where movement of the ions in the solution is suppressed. In the case of highly deionized water, an excitation frequency of $>30\,\text{kHz}$ is necessary to achieve a comparable performance as conventional KPFM operation in air.

Index Terms—kelvin probe force microscopy, surface potential, aqueous solution, solid-liquid interface

I. INTRODUCTION

Atomic force microscopy (AFM) [1] has a wide recognition in several scientific fields due to its diverse range of measurement modes. One of which is kelvin probe force microscopy (KPFM) [2], which enables the measurement of surface potential and charge distributions with nanometer resolution and high sensitivity. Electric surface potentials are of great scientific relevance as they play a key role in a variety of processes ranging from biomolecular interaction [3] and material sciences [4] to semiconductor devices [5].

With classical KPFM a cantilever tip is scanned in close proximity to a sample, while an ac voltage is applied to the conducting cantilever in order to modulate the electrostatic force. An additional dc-bias is used to nullify the cantilever deflection, leading to the local surface potential ϕ. Due to this dc-bias, KPFM is currently limited to measurements in vacuum or ambient conditions. However, several processes ranging from energy storage to ion channel activity take place at the solid-liquid interface and need to be observed in their natural environment, that is in most cases an aqueous solution. Here, the application of a dc-bias can induce electrokinetic effects (movement of solvated ions), electrochemical reactions or gas formation due to electrolysis in

the vicinity of the tip-sample system [6], preventing any controlled measurement.

Other techniques which circumvent the dc-bias by completely omitting its use and solely excite the cantilever with an ac voltage showed the feasibility of surface potential measurements in liquids [7], [8]. However, care must be taken when operating in aqueous solution due to the presence of mobile ions. Aside from induced ion motion due to the applied electric field affecting the potential distribution, other forces (e.g. electrophoretic, osmotic forces) can act on the cantilever and deteriorate the measurement. It is therefore key to use high excitation frequencies to ensure suppression of any ionic movement in the solution.

A derivation of conventional KPFM has been demonstrated recently, which replaces the dc-bias with a second ac voltage, while keeping the advantages of closed-loop operation, hence the name: AC-KPFM [9]. Due to the absence of a dc-bias, AC-KPFM is a promising approach for quantitative surface potential measurements in aqueous solutions. So far, it has only been demonstrated in air at ambient conditions and it remains unclear which influence mobile ions in the solution have on its performance and wether it is possible to assess its proper functionality during the measurement.

The contribution of this paper is a detailed analysis of the performance of AC-KPFM as a function of excitation frequency in aqueous solutions. Measurement parameters are discussed that must be set advisedly when operating AC-KPFM in an ion containing liquid. In the next sections, the setup for liquid AFM measurements is introduced, the AC-KPFM technique is briefly presented and experimental details are given. The experimental section includes an analysis of the influence of the lock-in reference phase and the excitation frequency on its surface potential measurement performance in deionized water.

II. SYSTEM DESCRIPTION AND AC-KPFM WORKING PRINCIPLE

The system of AC-KPFM is illustrated in Figure 1. As shown, the following voltage is applied to the conducting cantilever [9]:

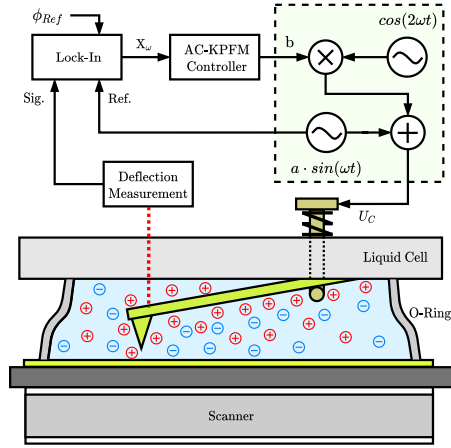$$U_C = a \cdot sin(\omega t) + b \cdot cos(2\omega t). \qquad (1)$$

Fig. 1: System for AFM surface potential measurements in liquids including the components on the top to perform AC-KPFM. A signal generator (dashed box) is used to apply the AC-KPFM signal U_C to the conducting cantilever and to provide the reference frequency to the lock-in-amplifier, which demodulates the measured cantilever deflection signal with regard to the reference phase ϕ_{Ref}. The in-phase output (X_ω) of the lock-in is nullified by a controller, which modulates the amplitude b, according to Eqn. (2).

Inserting the cantilever voltage U_C into the formula of the electrostatic force: $F_{el} = \frac{1}{2}\frac{\partial C}{\partial z} \cdot (\phi - U_C)^2$, results in following force components acting on the cantilever:

$$F_{el} = \frac{1}{2}\frac{\partial C}{\partial z}\left\{\begin{matrix} \phi^2 + \frac{a^2+b^2}{2} & \\ +a\left[2\phi - b\right] & sin(\omega t) \\ -\left[2\phi b + \frac{a^2}{2}\right] & cos(2\omega t) \\ +ab & sin(3\omega t) \\ +\frac{b^2}{2} & cos(4\omega t) \end{matrix}\right\}, \quad (2)$$

where $\partial C/\partial z$ denotes the capacitance gradient at the tip-sample separation z and ϕ the local surface potential to be measured. A lock-in-amplifier locking on the reference frequency ω is used to demodulate the resulting cantilever deflection. The in-phase component X_ω is fed to a controller, which adjusts the amplitude b of U_C such that $X_\omega = 0$. At this point the electrostatic force component oscillating with ω is nullified, leading to the surface potential: $\phi = b/2$.

The choice of the lock-in reference phase ϕ_{Ref} determines the signal strength and sign of X_ω and hence the signal-to-noise ratio (SNR) of the measurement. If the sign of X_ω and the controller gains are coordinated to each other, stable operation within a 180° ϕ_{Ref} band is possible [10]. Outside this band, the sign of X_ω changes and the control-loop becomes unstable. Nevertheless, the quantitative value of the measured potential is not influenced by the choice of ϕ_{Ref} as long as it stays within the stable 180° band, as with conventional KPFM operation.
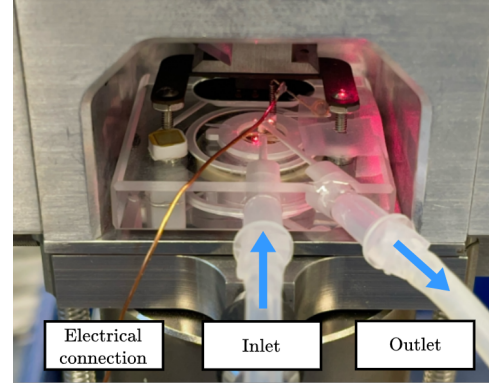

Fig. 2: View of the real setup with the AFM scan head and the used liquid cell. Two silicon tubes connected to a syringe containing the measurement solution and a drain-container are used as a solution inlet and outlet, respectively. The electrical connection to the AFM cantilever is provided via a cable soldered to the spring-clamp mechanism of the liquid cell.

III. SETUP AND EXPERIMENTAL DETAILS

A commercial AFM (Multimode 8, Bruker, USA) with an external signal generator (33522B, Keysight Technologies, USA) and an external lock-in-amplifier (7270, Ametek, USA) are used to implement the system as shown in Fig. 1. External components are used to minimize crosstalk induced artefacts in the surface potential measurement [11]. A PI controller (KPFM controller) is implemented on a rapid prototyping system (DS1005, dSpace, Germany), which modulates the amplitude b of the signal generator in order to nullify the in-phase deflection component X_ω. The value b is recorded along with the cantilever-sample separation to visualize the measured potential distribution. The reference phase ϕ_{Ref} of the lock-in-amplifier is adjusted throughout the experiments and given in the figure descriptions.

Overall gold coated cantilevers (TAP300GB-G, BudgetSensors, Bulgaria) with a measured resonance frequency in water of 110 kHz and a nominal stiffness of 40 N/m are used throughout all measurements. As test-sample a gold coated p-doped silicon substrate, manufactured by e-beam evaporation (Micro-To-Nano, Netherlands), is used. Pieces of 5x5 mm are cut out and glued onto an AFM specimen disc via conductive silver paint. The cantilever is loaded in the cantilever holder (MTFML, Bruker, USA) via a spring-clamp mechanism, which also provides electrical connection. An s-shaped o-ring is inserted around the cantilever to seal the liquid cell and to prevent leakage. After insertion of the sample disk onto the AFM scanner, the liquid cell is placed into the AFM scanhead, where a conformal seal of the o-ring around the sample is ensured. The measurement solution (milliQ water) is inserted by a syringe connected to the inlet-port of the liquid cell (see
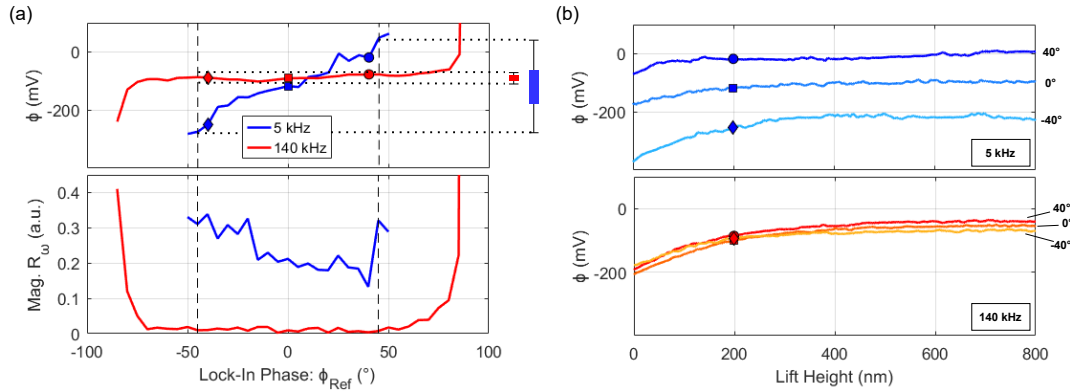
Fig. 3: (a) Measured surface potential at a tip-sample separation of 200 nm as a function of lock-in phase for two different drive frequencies (top) with the residual cantilever oscillation amplitude (bottom). (b) Measured surface potential as a function of lift height for an excitation frequency of 5 kHz (top) and 140 kHz (bottom) for three different lock-in phases as marked in (a).

Fig. 2). After alignment of the laser for the deflection measurement and engaging the cantilever to the sample, standard AFM force curves are performed. During the force curves, AC-KPFM is operated and the amplitude b, needed to nullify the in-phase deflection component X_ω, together with the residual cantilever deflection amplitude $R_\omega = \sqrt{X_\omega^2 + Y_\omega^2}$ is recorded.

IV. INFLUENCE OF MEASUREMENT PARAMETERS ON AC-KPFM PERFORMANCE

A. Lock-In reference phase & Lift height dependence

Figure 3 shows the measured surface potential ($\phi = b/2$) as a function of tip-sample separation (i.e. lift height) and lock-in reference phase ϕ_{Ref} for two different excitation frequencies (blue: ω =5 kHz / red: ω =140 kHz). The measurement with an excitation frequency of 140 kHz shows a stable operation that is independent on the lock-in reference phase within a ~180° band (Fig. 3(a)). The cantilever oscillation amplitude R_ω can be nullified by the AC-KPFM technique and the measured surface potential at a lift height of 200 nm is constant, which indicates proper operation at this frequency as it mirrors the expected behaviour. In contrast to this a strong dependence of the measured surface potential on ϕ_{Ref} is observed for the low frequency excitation at 5 kHz. Additionally, the controller can not nullify the cantilever deflection, as a residual amplitude R_ω is still present.

Figure 3(b) shows the measured surface potential as a function of the lift height for an excitation frequency at 5 kHz and 140 kHz, respectively. In the case of low frequency excitation (top) the measured potential curves are highly influenced by the lock-in reference phase ϕ_{Ref}. For the high frequency operation (bottom), the measurement shows nearly the same result, regardless of ϕ_{Ref} (as long as it stays within the stable 180° band). In addition, a distinct dependence of

the surface potential on the lift height can be observed in both cases. This is expected due to the buildup of the so-called electric double layer (EDL), which evolves when a surface is immersed in an ion containing liquid [12]. However, this effect is independent on the analysis of imaging parameters on the AC-KPFM performance, which is the focus of this work.

B. Dependence on excitation frequency

To further analyze the performance and measurement accuracy of AC-KPFM in aqueous solutions, the dependence of the measured surface potential on ϕ_{Ref} and the drive frequency is analyzed. To this end, the lock-in reference phase is swept 90° around the phase of the cantilever transfer function at each measurement frequency (area between dashed lines in Fig. 3(a)). The standard deviation of the measured surface potential is then calculated within this band for various lift heights (as shown in the boxes right to Fig. 3(a) for a lift height of 200 nm). The average of these standard deviations for each drive frequency is plotted in Figure 4. It can be seen that the standard deviation, which can be interpreted as the uncertainty of the measurement, gradually decreases with rising excitation frequency. At frequencies above ~30 kHz it converges to a value of ~15 mV, which is comparable to KPFM operation in air [13] and is sufficient for most applications.

V. DISCUSSION

Although deionized water is used in this experiment, a finite portion of ions is still present in the solution as the containment is not perfectly clean and the known fact that water is subject to self-dissociation [14]. The observed effects in the experiments can be explained by ionic motion within the cantilever-sample system. In the case of high frequency
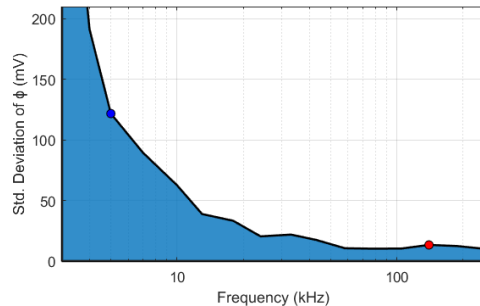
Fig. 4: Standard deviation of the measured surface potential for a given drive frequency in deionized water over a ϕ_{Ref} band of $90\,°$. The blue and red dot correspond to the measurements in Figure 3.

excitation (Fig. 3(a) red), movement of the ions in the solution due to the applied electric field is mostly suppressed. Therefore, spurious forces like electrophoretic or osmotic pressure on the cantilever do not occur. The resulting force on the cantilever is of pure electrostatic nature, which can be nullified by the AC-KPFM technique ($R_\omega \sim 0$). For a low frequency excitation on the other hand the solvated ions in the solution are able to follow the polarity of the applied voltage (as illustrated by the ions in Fig. 1). The induced ionic movement not only creates a direct force on the cantilever but also due to the resulting concentration gradient an osmotic force, both oscillating with the drive frequency ω. Hence, they get demodulated by the lock-in-amplifier and together with the electrostatic force they add up to the total cantilever deflection amplitude R_ω. In this regime, AC-KPFM is not able to nullify the cantilever oscillation amplitude: $R_\omega \neq 0$, as it only impacts the electrostatic force (Fig. 3(a) blue). Therefore, a flawed surface potential may be recorded. This indicates that AC-KPFM does not operate properly in a regime, where ionic movement is responsible for the predominant force on the cantilever. The results in Figure 4 further validate and are consistent with the idea of suppressed ionic motion at higher frequencies as the dependence of the measured potential on ϕ_{Ref} gradually declines with rising excitation frequency and stabilizes for drive frequencies beyond $30\,\mathrm{kHz}$ for this case. Increased ionic concentration is expected to shift this frequency border even higher. However, this paper is focused on the feasibility of AC-KPFM, not on its dependence on ionic concentration, which is part of ongoing work.

In summary it is shown, that proper AC-KPFM operation and reproducible results in aqueous solutions are only possible when excitation frequencies are used, which put the tip-sample system in a static regime, where ionic motion is suppressed. In this case the feedback controller is able to nullify the cantilever deflection and the measured surface potential is uninfluenced by the choice of the lock-in reference phase.

VI. Conclusion

The behaviour and performance of closed-loop AC-KPFM to measure the surface potential in aqueous solutions is analyzed. Influence of key imaging parameters on its operation are experimentally tested and the results are discussed. Spurious forces due to ionic motion in the solution (e.g. osmotic pressure), caused by the applied electric field, can deteriorate the measurement, which enables correct functionality only at high excitation frequencies.

During the operation of AC-KPFM in water, its functionality can be verified by checking wether the measured potential is independent on the lock-in reference phase and wether the cantilever deflection amplitude can be controlled to zero. Only in this case, the forces on the cantilever are of pure electrostatic nature and proper operation is enabled.

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