Electronic Supplementary Information

of

Mapping the Capacitance of Self-Assembled Monolayers at Metal/Electrolyte Interfaces at the Nanoscale by Inliquid Scanning Dielectric Microscopy

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S1. Sensitivity of the capacitance gradient to the tip interfacial capacitance

Figure S1. Tip-sample capacitance gradient as a function of tip-sample distance for a system with a uniform SAM with specific capacitance, $c_{SAM}=0.5 \,\mu\text{F/cm}^2$, and variable tip interfacial capacitance, $c_{tip}=0.2 \,\mu\text{F/cm}^2-70 \,\mu\text{F/cm}^2$. For comparison the case c_{tip} , $c_{SAM} >> 1000 \,\mu\text{F/cm}^2$ (thick line) is also shown. When $c_{tip}>c_{SAM}$ the capacitance gradient is almost insensitive to the actual value of c_{tip} . However, when $c_{tip}\leq c_{SAM}$ the capacitance gradient strongly depends on c_{tip} . Parameters: same as in Fig. 1b of the main text. For substrates with thin oxide layers (like highly doped semiconductor substrates) or for non ultra-thin dielectric layers on metals the condition $c_{tip}>c_{sub}$ is usually satisfied, and hence, the contribution of c_{tip} can be neglected, as we did in our earlier work (1). However, when ultrathin dielectric layers are present on metallic substrates one has $c_{tip}\leq c_{sub}$, and the contribution of the tip interfacial capacitance must be considered, as we did here.



S2. Characteristic tip parameters for fresh probes

Figure S2. (a) Raw oscillation amplitude at f_{mod} and (b) normal deflection versus distance curves for *N*=8 different fresh probes on a planar gold substrate in milliQ water. (c) Corresponding calibrated dC/dz curves. In the calibration we used the renormalization factor and photodiode sensitivity shown in (d) and the spring constant in (e). The renormalization has been done by imposing the same behavior at long tip sample distances z>1000 nm and a half cone angle equal to 20° (f). (g)-(i) Extracted tip interfacial capacitance, tip radius and capacitance gradient offset obtained by fitting theoretically calculated curves to the experimental curves in (c), under the assumption that the tip interfacial capacitance equals that of the gold substrate. The microscopic parameters were fixed to their nominal values: cone height 12.5 µm, cantilever width 3 µm and cantilever length 3 µm. The errors bars correspond to the standard deviation of *n*=3 approach curves.

S3. Renormalizing factor α

To account for any voltage drop in the circuitry at the frequencies of the measurement (in the 10's MHz range), or for inaccuracies in the several parameters to be determined (photodiode sensitivity, spring constant, etc.) we have included in the quantitative analysis a renormalizing factor, α , similarly to what we did earlier for measurements in humid conditions (2). The renormalizing factor is included as a multiplicative factor in the conversion of the raw data into the calibrated dC/dz values (see Eq. (3) of the main text). This factor accounts for any inaccuracy in the determination of the multiplicative factor $\frac{k}{mv_{ac}^2}$, which includes the spring constant, the photodiode sensitivity and the actual

voltage drop between tip and sample. To determine the parameter α , we have used the fact that in in-liquid SDM at tip sample distances satisfying H>z>>R the force acting on the tip is largely determined by the cone part of the tip (3),

$$\frac{dC(z)}{dz}\Big|_{z >> 1} \approx \frac{2\pi\varepsilon_{sol}}{\ln\left(\tan\left(\frac{\theta}{2}\right)\right)^2} \left[\ln\left(\frac{z+H}{z}\right) - \frac{H}{z+H}\right] + C_{offset}(L)$$
(S1)

Here, C'_{offset} accounts for the direct and indirect cantilever contributions discussed in Section S13, which has no relevance when analyzing capacitance gradient variations. In Eq. (S1) all parameters are known with a reasonable accuracy from the manufacturer. Therefore, by imposing dC/dz to be given by Eq. (S1) (or by the values corresponding to the numerical calculations) at long distances one can identify the renormalization factor. We have found that the value is on average close to 1 for fresh probes, $\alpha=1.1\pm0.1$ (see Section S2), but in long experiments larger deviations have been observed. We have shown that proceeding in this way the subsequent geometric tip parameters become realistic and close to the manufacturer specifications. It should be said, however, that this renormalization procedure does not impact much on the extracted interfacial capacitance values, but it does on the geometrical parameters extracted for the tip. S4. Additional data for Fig. 4: capacitance gradient approach curves.



Figure S3. Capacitance gradient approach curves measured on the SAM and on the center of the largest scratched area in Fig. 4 of the main text (black and blue continuous lines, respectively). The dashed red lines correspond to the fitted theoretical curves obtained by using the model shown in Fig. 3f. The parameters obtained from the fitting are: $c_{SAM}=0.7\pm0.3 \ \mu\text{F/cm}^2$, $c_{scr}=1.1\pm0.2 \ \mu\text{F/cm}^2$, $R=151\pm8 \ \text{nm}$ and $C'_{offset}=1.5\pm0.05 \ \text{aF/nm}$ (with $c_{tip}=2.7 \ \mu\text{F/cm}^2$ and $\alpha=1.2 \ \text{fixed}$). The remaining parameters were let to their nominal values: $\theta=20^\circ$, $H=12.5 \ \mu\text{m}$, $W=3 \ \mu\text{m}$, $L=3 \ \mu\text{m}$. The green symbols correspond to the values on the SAM layers in Fig. 4a, used to determine the tip sample-distance.

S5. Estimation of the spatial resolution



Figure S4. (a) Topographic image (same as Fig. 5a) with the SAM contour highlighted. (b) and (c) Superposition of the contour of the topographic image on the experimental and theoretical SDM images shown in Figs. 5b and 5d of the main text, respectively. The superposition of the topographic contour on the electrical images show that many of the topographical features, but not all of them, are electrically resolved. To estimate the spatial resolution in the electrical images, we have identified the smallest topographical features in (b) and (c) that are electrically resolved. From this analysis spatial resolutions of ~75 nm and ~50 nm can be estimated from (b) and (c) respectively, respectively. Examples of features showing such dimensions and that are electrically resolved are highlighted by the arrows.

S6. Influence of c_{tip} in the analysis of the data from Figure 2.

In the extraction of the interfacial capacitance of uniform SAMs in Fig. 2 the value of the interfacial capacitance of the tip has been determined by assuming it to be equal to that of the bare gold substrate, $c_{tip}=c_{gold}$, since both the tip and substrate were made of gold. With this assumption, we obtained $c_{tip}=c_{gold}\sim 2.7 \,\mu\text{F/cm}^2$, which is in the range of values determined from fresh probes (see Section S2). However, it may happen that this assumption is not fully satisfied since the surface properties of the tip and of the gold substrate can still show different interfacial capacitances (e.g. due to differences in surface contamination or roughness, for instance). We have analyzed the effect of relaxing the assumption $c_{tip}=c_{gold}$ in the extracted values of c_{SAM} and c_{gold} . To this end we have considered different values for c_{tip} for a given tip geometry and extracted the corresponding values of c_{gold} and c_{SAM} . We have observed that the extracted values vary according to the series capacitance combination relationships (see Fig. S5)

$$c_{SAM} = \frac{1}{\frac{1}{c_{iip,0}} + \frac{1}{c_{SAM,0}} - \frac{1}{c_{iip}}} \qquad c_{gold} = \frac{1}{\frac{1}{c_{iip,0}} + \frac{1}{c_{gold,0}} - \frac{1}{c_{iip}}}$$
(S2)

where $c_{tip,0}$, $c_{gold,0}$ and $c_{SAM,0}$ correspond to the values extracted assuming $c_{tip}=c_{gold}$. The dependency predicted by Eq. (S2) sets some upper and lower bounds to the extracted specific capacitances. For instance, the minimum value of c_{tip} compatible with the experiments is $c_{tip,min}=(1/c_{tip,0}+1/c_{gold,0})^{-1}=c_{tip,0}/2=1.35 \ \mu\text{F/cm}^2$. For this value, $c_{gold,max}$ will tend to infinity (negligible effect) and $c_{SAM,max}=(1/c_{SAM,0}-1/c_{tip,0})^{-1}$ (red dashed line in Fig. S5). On the other hand, for the maximum value of c_{tip} (infinite, negligible effect), the minimum values that can be obtained are $c_{gold,min}=c_{gold,0}/2=1.35 \ \mu\text{F/cm}^2$ and $c_{SAM,min}=(1/c_{tip,0}+1/c_{SAM,0})^{-1}$ (black dashed line in Fig. S5). Therefore, assuming different values for c_{tip} can give rise to different absolute values for c_{SAM} and c_{gold} according to Eq. (S2), the more different the closer to the c_{tip} value (for instance for n=11 the variation is almost negligible).

The inverse proportionality factor between c_{SAM} and the number of methyl groups (which depends on the SAM dielectric constant, ε_{SAM}) remains, however, the same. Indeed, by using Eq. (1) of the main text one has

$$c_{SAM} = \left(\frac{d_C n}{\varepsilon_0 \varepsilon_{SAM}} + \frac{1}{c_{0,0}} - \frac{1}{c_{ip}}\right)^{-1} = \left(\frac{d_C n}{\varepsilon_0 \varepsilon_{SAM}} + \frac{1}{c_0}\right)^{-1}; \qquad \frac{1}{c_0} = \frac{1}{c_{0,0}} - \frac{1}{c_{ip}}$$
(S2)

where only the excess capacitance c_0 gets modified. Therefore, varying the value of c_{tip} does not influence the value of the extracted ε_{SAM} , as we mentioned in the main text.



Figure S5. Interfacial capacitance values obtained for the uniform SAMs under the assumption $c_{tip}=c_{gold}=2.7 \ \mu\text{F/cm}^2$ (black symbols). The interfacial capacitance obtained for the bare gold substrate is shown by the grey symbol and assigned the *n*=0 ordinate. These data are the same as those in Fig. 2b of the main text. Idem but assuming $c_{tip}=1.7 \ \mu\text{F/cm}^2$ and keeping the same tip geometry (red and pink symbols). Specific capacitances for the SAM and gold substrates predicted by Eq. (S2) (empty blue symbols). The black and red dashed lines represent the minimum and maximum values of c_{SAM} compatible with the experiments.

Other possible sources of uncertainty in the extraction of c_{SAM} , such as the voltage drop in the external circuit, the spring constant of the photodiode sensitive, all contribute as a multiplicative factor to the extracted values of the capacitance gradient. We have checked that a global multiplicative factor can affect the values of the tip radius, half cone angle or tip interfacial capacitance, but it does not affect the extracted values for the interfacial capacitance of the SAM.

S7. Analysis of the frequency dependence of the force and impedance in Figure 6d.

For frequencies $f < f_{RbCint} = (2\pi R_bC_{int})^{-1} \sim 1$ kHz, where C_{int} is the total system interfacial capacitance and R_b the bulk electrolyte resistance, ions form ac space charge layers at both the tip and sample surfaces, which fully screen the applied voltage. In this frequency range, large electric and osmotic forces act on the tip, with a similar magnitude and opposite phase (see Section S8), resulting in a relatively small net force. This force, however, is not sensitive to the local electric properties of the SAM, except for z<L_D (see Section S8). The impedance, on its side, shows a capacitive behavior determined by C_{int}. Here, $R_b = L_{eff} / (\sigma A_{tip}) = 11.2 \text{ M}\Omega$ and $C_{int} = A_{tip} \varepsilon_0 \varepsilon_{sol} / L_D = 13.3 \text{ pF}$, where $A_{tip} = 595 \text{ }\mu\text{m}^2$ is the area of the tip and $L_{eff} = 5 \text{ }\mu\text{m}$ is an equivalent 1D characteristic length of the system. Since $A_{tip} < <A_{subs} = 33850 \text{ }\mu\text{m}^2$, where A_{sub} is the substrate area, C_{int} is mostly determined by the tip space charge layer, and hence insensitive to properties of the finite size SAM.

For $f_{RbCint} < f < f_{RbCb} = (2\pi R_b C_b)^{-1} \sim 170$ kHz, where C_b is the bulk electrolyte capacitance, the ac space charge layers do not fully form and some ac potential drops in the electrolyte solution giving rise to a resistive behavior determined by the bulk resistance, R_b . In this

frequency range, both osmotic and electric forces decrease with frequency, but they are still very similar in magnitude giving rise again to a relatively small net force (see Section S8), which is still non-local (i.e. the forces with and without the finite SAM are the same). Since the impedance is determined by R_b , it is not sensitive to the SAM properties neither.

Finally, for $f > f_{RC}$ ions cannot follow any more the ac applied voltage, no ac space charge layers form and no ac ion conduction processes take place in the bulk electrolyte, and the system shows a pure capacitive behavior determined, this time, by the bulk capacitance, $C_b = \varepsilon_0 \varepsilon_{sol} A_{tip}/L_{eff} = 82.2$ fF, which is dominated by the tip area, and is not sensitive to the local capacitance of the SAM. In this frequency range the ac osmotic force tends to vanish, and the electric force becomes dominant and frequency independent (see Section S8). The resulting net force is then determined by the electric force, which is sensitive to the presence of the finite size SAM layer (i.e. it is local). In this frequency range, the net force can be related to the (high frequency) system capacitance gradient through the relation $F_{2\omega}=1/4 dC/dz v_{ac}^2$, where v_{ac} is the amplitude of the ac voltage (for modulated voltages the measured force harmonic is the ω_{mod} harmonic, $F_{\omega mod}$, and the prefactor is 1/8, see Section S9).



S8. Additional data for Figure 6d: Electric and osmotic force components.

Figure S6. Electric (blue symbols) and osmotic (red symbols) 2ω -force components of the total forces (black symbols) displayed in Fig. 6d of the main text, for the tip on (a) a bare and (b) finite size SAM layer, respectively. The data for the total 2ω -force (black symbols) are the same as in Fig. 6d. The total 2ω -force harmonic has been obtained by Fourier transforming the sum of the electric and osmotic forces in the time domain.



S9. Force and impedance frequency response for z<L_D

Figure S7. (a)-(d) Idem as in Fig. 6 of the main text but for z=10 nm. Since the Debye screening length is $L_D=30$ nm the calculations correspond to the condition $z < L_D$. The overlap of the ac space charge layers makes the net force sensitive to the local electric properties of the sample underneath in the whole frequency range, although the higher variation is still observed in the high frequency range beyond the dielectric relaxation frequency of the electrolyte.

S10. Harmonic analysis of the force in SDM with amplitude modulated voltages

In in-liquid SDM one applies an amplitude modulated voltage of the form

$$V(t) = V_{dc} + \frac{V_{ac}}{2} \left(1 + \cos\left(\omega_{mod}t\right)\right) \cos\left(\omega_{el}t\right)$$
(S3)

where a dc term has also been included for generality, and which represents either a contact potential or an actual dc applied voltage (see Figs. S8a). The applied voltage in Eq. (S3) has a dc component and three harmonics at frequencies ω_{el} , $\omega_{mod}-\omega_{el}$ and $\omega_{mod}+\omega_{el}$

$$V(t) = V_{dc} + \frac{v_{ac}}{2} \cos(\omega_{el}t) + \frac{v_{ac}}{4} \cos\left[(\omega_{el} - \omega_{mod})t\right] + \frac{v_{ac}}{4} \cos\left[(\omega_{el} + \omega_{mod})t\right]$$
(S4)

(see Fig. S8b). If the force depends quadratically on the applied voltage, then 11 harmonics will be generated on the oscillation amplitude (see Figs. S8c and S8d). Of the different harmonics, the dc, ω_{mod} and $2\omega_{mod}$ appear at low frequencies (around the modulation frequency), while the remaining ones appear at high frequencies (around the electrical frequency). The amplitudes of the low frequency harmonics are related to the amplitude of the dc and ac voltages through the following coefficients

$$\left[v(t)^{2}\right]_{dc} = v_{dc}^{2} + \frac{3}{16}v_{ac}^{2}; \qquad \left[v(t)^{2}\right]_{\omega_{\text{mod}}} = \frac{1}{4}v_{ac}^{2}; \qquad \left[v(t)^{2}\right]_{2\omega_{\text{mod}}} = \frac{1}{16}v_{ac}^{2} \qquad (S5)$$

Note that, even in the absence of a dc voltage, a dc force appears on the probe which can induce its static bending. The ω_{mod} and $2\omega_{mod}$ harmonics are independent from the dc potential, and hence, they are the most suitable to address independently the electric polarization properties of the sample. We have measured the ω_{mod} harmonic since it is four times larger than the $2\omega_{mod}$, and hence it provides a better signal to noise ratio. We have experimentally verified the square dependence of the oscillation amplitude on the applied ac voltage and the relation between the amplitudes of the ω_{mod} and $2\omega_{mod}$ oscillation harmonics (Figs. S8e and S8f). Experimentally the ration between the ω_{mod} and $2\omega_{mod}$ and $2\omega_{mod}$ is ~3,35:1, close to the 4:1 ideal relationship.



Figure S8: (a) Schematic representation of the amplitude modulated voltage in Eq. (S3) with the meaning of the different parameters (V_{dc} , v_{ac} , f_{el} and f_{mod}). (b) Fourier transform of the amplitude modulated voltage in (a). Each peak is labelled with its frequency position and amplitude. (c) Schematic representation of the square of an amplitude modulated voltage. (d) Fourier transform of (c). The low frequency peaks are labelled with its frequency position and amplitude. (e) Experimental oscillation amplitude spectra corresponding to a conductive AFM probe (k=0.5 N/m, f_0 =65 kHz) in milliQ solution close to a bare metal substrate with an amplitude modulated voltage applied with V_{dc} = 0 V, f_{el} =32 MHz, f_{mod} =2 kHz and different v_{ac} . As predicted, two low frequency harmonics

at f_{mod} and $2f_{mod}$ are observed. (f) Dependence of the oscillation amplitudes of the f_{mod} and $2f_{mod}$ harmonics as a function of the amplitude of the ac voltage applied (symbols). As predicted, both harmonics follows a quadratic dependence on the amplitude of the ac applied voltage (continuous lines), with a ratio of amplitudes ~3.35:1, close to the ideal 4:1 ratio (dashed line).



S11. Electric force acting on a tip with an interfacial capacitance

Figure S9: Schematic representation of the forces acting on a metallic tip covered by an uncharged ultrathin dielectric layer representing the tip interfacial capacitance.

The presence of an interfacial capacitance on the tip, represented by an ultrathin dielectric layer, complicates the calculation of the force acting on the tip as compared to the case of a bare metallic tip. This situation is common to different fields of research in which abrupt dielectric interfaces are present and the forces need to be numerically calculated, as for instance in the calculation of molecular electrostatic forces in the framework of the Poisson-Boltzmann equation (4) (5). The forces acting on the tip under this situation are schematically shown in Fig. S9. If the dielectric layer is assumed to be able to mechanically transmit the force acting on it, then the total force acting on the tip is

$$\vec{F}_T = \vec{F}_{Metal} + \vec{F}_{in} + \vec{F}_{out}$$
(S7)

Each one of these forces is calculated by integration of the Maxwell stress tensor on the corresponding surface. The relative dielectric constants of the ultrathin insulating layer, ε_{ins} , and of the electrolyte solution, ε_{sol} , are in general different, so that the normal component of the electric field across the insulating layer/electrolyte interface is

discontinuous, and so they are the electric forces on both sides of the interface. In the absence of fixed charges at the interface, one can show that the net force acting on the interface is given by (4), (5)

$$\vec{F}_{in} + \vec{F}_{out} = -\frac{1}{2} \left(\varepsilon_{sol} - \varepsilon_{ins} \right) \int_{S_{ins}} \left(\vec{E}_{in} \cdot \vec{E}_{out} \right) \hat{n}_{out} dS$$
(S8)

where S_{ins} is the surface of the insulating layer, \hat{n}_{out} the normal vector to this surface pointing outwards, and \vec{E}_{in} and \vec{E}_{out} the electric fields in the inner and outer surfaces of the insulating layer, respectively. This relation confirms that the in and out forces acting at the dielectric/solution interface do not cancel each other, in general. Accordingly, to compute the total electric force acting on the tip one should calculate the three forces appearing in Eq. (1). However, since the insulating layer is assumed to be very thin, in practice one can assume that the electric field across it is constant (as in a 1D geometry). Under this condition the force acting on the metal tip surface and in the interior part of the insulating interface cancel each other. Therefore, to a good approximation the total force is given by the force acting on the outside of the insulating layer

$$\vec{F}_T \approx \vec{F}_{out}$$
 (S9)

We have checked the validity of this approximation for the tip geometry, parameters and frequencies used in the manuscript and obtained an error in the calculation of the capacitance gradient by assuming the approximation in Eq. (S9) inferior to \sim 3 zF/nm, which is much smaller than the noise of the measurements \sim 100 zF/nm. Therefore, we calculated the total force by just calculating the force acting on the outer part of the ultrathin dielectric layer.

S12. Electric currents model

The electric currents model consists of the divergence of the total current densisty,

$$\nabla \cdot \vec{J}_T(\vec{r},t) = 0 \text{ (S10)}$$

where \vec{J}_T is given by

$$\vec{J}_{T}(\vec{r},t) = \vec{\nabla} \left(\varepsilon_{0} \varepsilon_{r} \frac{\partial \phi(\vec{r},t)}{\partial t} + \sigma \phi(\vec{r},t) \right)$$
(S11)

with ϕ being the electric potential, ε_r the relative dielectric constant and σ the conductivity. ε_r is equal to ε_{sol} and ε_{tip} in the electrolyte and tip thin insulating layer, respectively. Moreover, σ is equal to σ_{sol} in the electrolyte and to 0 in the tip insulating layer. Eqs. (S10) and (S11) are supplemented by the current continuity equation at the tip insulating layer/electrolyte interface

$$\hat{n} \cdot \vec{\nabla} \left[\sigma_{sol} \phi(\vec{r}_{int}^{+}, t) + \varepsilon_0 \varepsilon_{sol} \frac{\partial \phi(\vec{r}_{int}^{+}, t)}{\partial t} - \varepsilon_0 \varepsilon_{tip} \frac{\partial \phi(\vec{r}_{int}^{-}, t)}{\partial t} \right] = 0 \quad (S12)$$

where \hat{n} is the unit vector normal to the interface. The boundary conditions of the problem are

$$\phi(\vec{r}_{tip},t) = V(t); \quad \vec{r}_{tip} \in S_{tip} \text{ (S13)}$$
$$\hat{n} \cdot \vec{\nabla} \left(\varepsilon_0 \varepsilon_{sol} \frac{\partial \phi(\vec{r}_{subs},t)}{\partial t} + \sigma_{sol} \phi(\vec{r}_{subs},t) \right) = -c_{subs} \frac{\partial \phi(\vec{r}_{subs},t)}{\partial t}; \quad \vec{r}_{subs} \in S_{subs} \text{ (S14)}$$

where $V(t) = v_{ac} \cos(\omega t)$ is the voltage applied and ω the angular frequency. Here, c_{subs} represents either c_{gold} , c_{SAM} , c_{scr} or a distribution of them. The force acting on the tip is calculated from the solution of Eqs. (S10)-(S14) by integration of the projection of the Maxwell stress tensor in the vertical direction on the surface of the tip insulating layer, S_{ins} (see Section S9)

$$F_{el,z} = \int_{S_{ins}} f_{el,z} dS; \quad f_{el,z} = n_z (E_z E_z - \frac{1}{2}\vec{E}^2) + n_y (E_z E_y) + n_x (E_z E_x)$$
(S15)

where $\vec{E} = -\vec{\nabla}\phi$ is the electric field.

S13. Cantilever effects in in-liquid SDM

In in-liquid SDM measurements, the cantilever has a direct contribution to the force (as in air), which can be modelled, to a good approximation, as a parallel plate capacitor in parallel with the tip capacitance. For tip sample distances shorter than the cone height this contribution is independent from tip-sample distance and contributes as a capacitance gradient offset. In addition to this direct contribution, there is also an indirect contribution of the cantilever, since it reduces the force acting on the rest of the tip, similarly to what happens for SDM measurements on thick dielectric substrates in air (*6*), (*7*). This effect, in the case of in-liquid SDM, can be accounted for by introducing a capacitance gradient offset, as shown in Fig. S10a. The fact that this offset is positive means that the indirect cantilever effect reduces the force acting on the tip. The dependence of the offset on the disk cantilever radius is shown in Fig. S10b for the given geometry, and for two different interfacial capacitances of the substrate. As it can be seen, the capacitance gradient offset is independent from the sample specific capacitance.



Figure S10. (a) Capacitance gradient of the tip-substrate system (cone+apex only) calculated for tips with different disk cantilever lengths and for different specific capacitances of the sample in the range 0.1 μ F/cm²–100 μ F/cm² and an interfacial capacitance of the tip c_{tip} =67 μ F/cm² (almost negligible effect). (b) Dependence of the capacitance gradient offset induced by the cantilever on the force acting on the tip as a function of the cantilever size. Parameters of the calculations: R=30 nm, θ =20°, H=12.5 μ m, W=3 μ m, ε_{sol} =78.

S14. Nernst-Planck-Poisson model

The Nernst-Planck-Poisson model consists of the continuity equations for the ion number densities, $n_{\pm}(\vec{x},t)$, coupled to the Poisson equation for the electric potential, $\phi(\vec{x},t)$, i.e.

$$\frac{\partial n_{\pm}}{\partial t} + \vec{\nabla} \cdot \vec{J}_{\pm} = 0$$
(S16)

$$-\mathcal{E}_0 \mathcal{E}_{sol} \nabla^2 \phi = e \left(n_+ - n_- \right) (S17)$$

Here, ε_{sol} is the relative dielectric constant of the electrolyte (assumed to be frequency and electric field independent) and *e* the electron charge. Moreover, \vec{J}_{\pm} are the ion number flux densities, which, in the dilute concentration limit, are given by

$$\vec{J}_{\pm} = -D\vec{\nabla}n_{\pm} - \mu n_{\pm}\nabla\phi \text{ (S18)}$$

where *D* is the ion diffusion coefficient and μ the ion mobility, assumed to be equal for both ionic species. The diffusion coefficient and the mobility are assumed to be related though Einstein's relation for dilute electrolytes, $D=(k_BT/e)\mu$, where k_B is Boltzmann's constant and *T* the temperature. The tip, SAM and metal substrate are assumed to show blocking properties (no ion or charge exchange with the electrolyte), and hence the interfaces are described by means of no-flux boundary conditions

$$\hat{n} \cdot \vec{J}_{\pm} \Big|_{S_{SAM}} = 0; \quad \hat{n} \cdot \vec{J}_{\pm} \Big|_{S_{subs}} = 0; \quad \hat{n} \cdot \vec{J}_{\pm} \Big|_{S_{tip}} = 0$$
(S19)

where S_{SAM} , S_{subs} and S_{tip} refers to the SAM layer, metal substrate and tip, respectively. Within the thin dielectric film, we solved for the Laplace equation (no net volumetric charge assumed)

$$\nabla^2 \phi = 0; \quad \vec{r} \in V_{film (S20)}$$

We assumed the continuity conditions for the electric potential and total current at the thin film/electrolyte interface

$$\phi\left(r_{SAM}^{-},t\right) = \phi\left(r_{sol}^{+},t\right);$$

$$\hat{n} \cdot \vec{J}_{T}\left(r_{SAM}^{-},t\right) = \hat{n} \cdot \vec{J}_{T}\left(r_{sol}^{+},t\right);$$

$$\vec{J}_{T,sol}^{+} = \varepsilon_{0}\varepsilon_{sol}\frac{\partial \vec{E}}{\partial t} + e\vec{J}_{+} - e\vec{J}_{-}; \quad \vec{J}_{T,SAM}^{-} = \varepsilon_{0}\varepsilon_{SAM}\frac{\partial \vec{E}}{\partial t}$$
(S21)

In the absence of fixed interfacial charges, and considering the zero-flux boundary condition the continuity conditions, Eq. (23) is equivalent to the continuity of the displacement vector, i.e.

$$\hat{n} \cdot \left[\varepsilon_{SAM} \vec{E} \left(r_{SAM}^{-}, t \right) - \varepsilon_{sol} \vec{E} \left(r_{sol}^{+}, t \right) \right] = 0 \quad (S22)$$

Finally, for the boundary conditions on the electric potential at the tip and at the metallic substrate one takes

$$\phi_{S_{tip}} = -\phi_{S_{Metal}} = \frac{v_{ac}}{2} \cos\left(\omega t\right)$$
(S23)

where v_{ac} and ω are the amplitude and frequency of the applied potential.

The 1D version of this model can be solved analytically in the linear regime (8), (9). However, for 3D geometries like the tip-plane geometry relevant for in-liquid SDM measurements, no analytical solution can be derived, and one must resort to numerical calculations, as we did in the manuscript.

S15. Comparison between the force predictions of the electric currents and Nernst-Planck-Poisson models.

In the main text we have calculated the force acting on the tip by using the currents model described in Section S12. Here we show that this model, for frequencies higher than the dielectric relaxation frequency of the electrolyte, gives the same forces as those calculated by the physically more accurate Nernst-Planck-Poisson (NPP) model described in section S14 and that includes electro-osmotic effects. For completeness, we also include in the comparison a simple electrostatic model.

Figures S11a, S11b and S11c show schematic representations of the NPP, electric currents and electrostatic models (the later consisting of just the Laplace's equation). In the electric currents model, we assumed the presence of tip and substrate interfacial capacitances determined by the Debye screening length (and the dielectric constant of the electrolyte). With this assumption, the impedance spectra predicted by the NPP and the electric currents models are almost undistinguishable (Fig. S11d). Instead, the electrostatic model predicts a pure capacitive impedance, as expected. The total force acting on the tip according to the NPP, electric currents and electrostatic models are given by the solid symbols (red, blue and black, respectively) in Fig. S11e. For the NPP model the total force is the resultant of the electric and osmotic forces (9). For the electric currents model the force is evaluated at the surface of the tip. We have also included the the force evaluated at the surface of the tip insulating layer (empty blue symbols). The former case assumes that the insulating layer (space charge) can not mechanically transmits the force to the tip, while the later one assumes that it does. For comparison, we have also plotted the electric and osmotic force contributions (empty square and triangles in Fig. 11Se, respectively, almost indistinguishable except at high frequencies). We note that even though the impedance for the NPP and electric currents models are almost identical, the predicted forces are very different. They only agree at high frequencies beyond the electrolyte dielectric relaxation frequency. In this range, they also coincide with the predictions of the electrostatic model. We note that the force predicted by the electric currents model in the case of assuming that the insulating layer does not transmits mechanically the force (solid blue symbols) agrees with the electric force predicted by the NPP in a broader range of frequencies. However, since the electric currents model does not include the osmotic force, it cannot predict the total force acting on the tip in this wider frequency range (similar conclusions were reached from the analysis of the 1D

model in Ref. (9)). These conclusions remain valid also for the case that a compact layer is considered on either the tip or the substrate (or both), as shown in Ref. (9).



Figure S11: (a)-(c) Schematic representation of three different physical models (electrodiffusive or NPP model, electrics currents and electrostatics, respectively) used to analyze the force acting on the tip in in-liquid SDM. In the electric currents model interfacial capacitances equal to the space charge diffusive capacitances, determined by the Debye screening length and solution dielectric constant, are assumed. (d) Impedance spectra calculated from the three models. (e) Force acting on the tip predicted by the three models (solid symbols). For the NPP model, we also plot the separate contributions of the electric and osmotic forces (empty red symbols). For the electric currents model we also plotted the force calculated outside of the tip thin insulating (blue empty symbols). Parameters: 1:1 symmetric electrolyte, ionic concentration c=1 mM, solution dielectric constant $\varepsilon_{sol}=78.5$, temperature T=298 K and ionic diffusion coefficient $D=10^{-9}$ m²/s. The ionic mobility is given by Einstein's relationship, $\mu=D/k_{\rm B}T=3.9$ 10⁻⁸ m²V/s, where k_B is the Boltzmann constant, and the conductivity of the solution by $\sigma=2 \ e \ \mu \ n=7.5 \ 10^{-3}$ S/m, where e is the electron charge. The Debye screening length is $L_D=(\varepsilon_0 \varepsilon_{sol} k_B T/2 \ e^2 \ c)^{1/2}=10$ nm. The tip geometric parameters are: R=70 nm, $\theta=18^\circ$, H=12.5 µm, W=3 µm, L=3 µm.

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