Supplementary information for

Nanoscale electric polarizability of ultrathin biolayers on insulator substrates by electrostatic force microscopy

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S1-Electric interaction of a sharp silicon tip with an insulating substrate

The sharp silicon tips used in this work present a double angle cone geometry as schematically shown in Fig. S1a. We will show here that with insulating substrates effective *single-angle* cone models cannot be used in any range of distances to represent them, contrary to the case of metallic substrates[27,70] where this can be done at short distances, due to both indirect effects associated to the microscopic probe geometry,[41,45] and to the mixing of micro- and nanoscopic contributions.[70] Thus, it is necessary to use a complete double angle cone model as we did in the article.

Figure S1b shows calculated capacitance-gradient curves, dC/dz (z,ε_r), on an insulator substrate with $\varepsilon_{r,sub}$= 6 as a function of the tip-substrate distance, z, for a sharp probe with geometric parameters H = 12.5 µm, L = 0 µm, Θ = 25º, θ = 10º and R = 5 nm, and sharpened cone heights h_{cone}=100 nm, 300 nm and 600 nm. The approach curves depend on the height of the sharpened cone end, h_{cone}, and they decrease with increasing h_{cone}. One would conclude that this decrease corresponds to the decrease in the effective interaction area produced by the fact that the microscopic cone is farther from the substrate for higher nanoscopic cone heights, in a similar way as to what we found for metallic substrates[70]. However, when fitting the data shown in Fig. S1b with a single-angle model using the equivalent geometric parameters, R_{eq} and θ_{eq}, obtained from fitting the corresponding curves on a metallic substrate (data not shown, see Ref. 45), one obtains a dielectric constant for the substrate smaller than the one used to generate the data. The values of the effective dielectric constant obtained depend on the value of the sharpened cone height, h_{cone}, and on the distance range included in the analysis, as shown in the inset of Fig. S1b, where we show the effective dielectric constant seen by an effective single angle cone model for three different substrates ($\varepsilon_{r,subs}$ = 3, 6 or 9) and three different ranges of distances, z_{range}= 300, 150 and 50 nm, in each case. We observe that the effective dielectric constants given by the single angle model systematically depart from the nominal ones, showing a decrease when increasing h_{cone} until a saturation value is reached for large h_{cone}. For instance, for a typical value of h_{cone}=200 nm one obtains for a substrate with $\varepsilon_{r,subs}$ = 6 the following single angle model effective dielectric constants, $\varepsilon_{r,eff}$=5.5, 5.4 and 5.1, for distances of z_{ref}=300, 150 and 50 nm, respectively. Similar tendencies are observed for other dielectric constant values. This fact indicates that, if a single-angle cone model is used to obtain the effective tip geometry of a sharp probe by fitting an approach curve on a metallic substrate, this geometry would give an interaction with an insulator substrate equivalent to reducing the dielectric constant of the substrates in a range between a 8%-15%, depending on the range of the capacitance gradient curve considered. In particular, for short range curves (z_{ref}=50 nm), for which double angle models and effective single angle models can be made fully equivalent on metallic substrates[27,70], such an equivalency is not maintained for an insulator substrate, since for a given set of data both models would not predict the same dielectric constant of the insulator substrate.

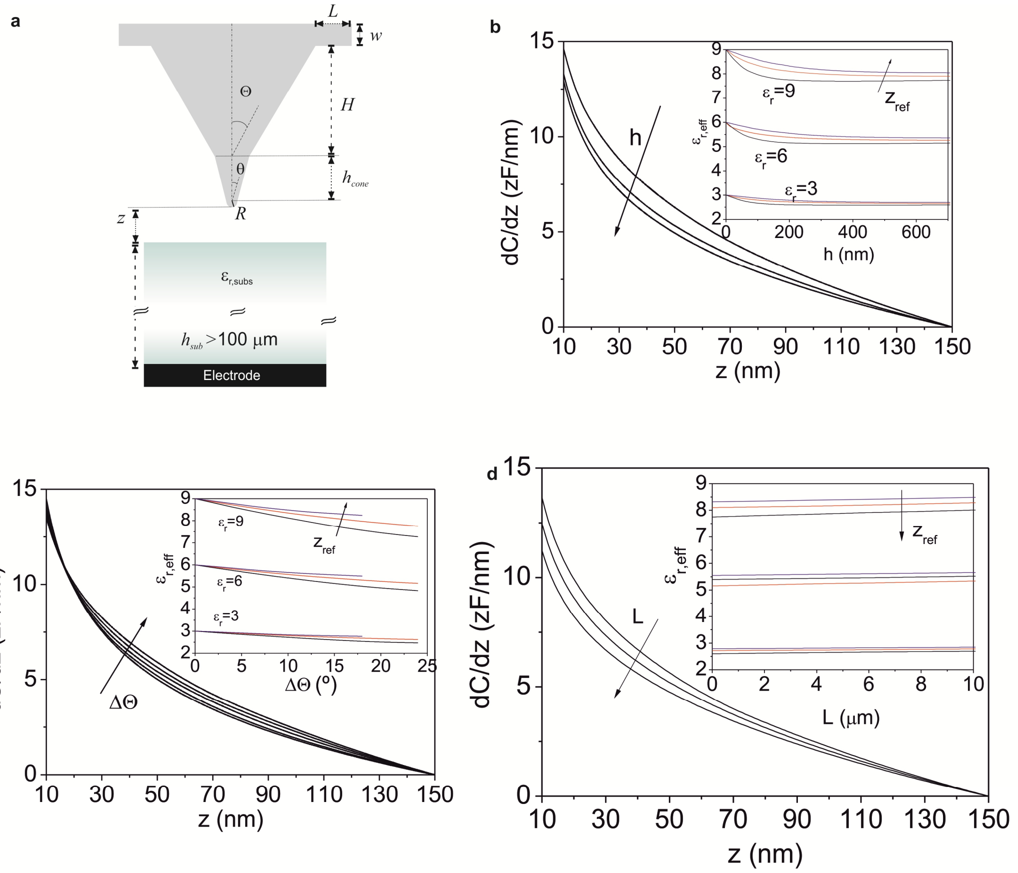

Fig. S1. (a) Schematic representation of the model corresponding to a sharp probe interacting with a thick dielectric substrate. Calculated capacitance gradient approach curves on an insulator substrate ($\varepsilon_{r,subs}$=6) for probes by varying (b) the sharpened cone heights, h_{cone}=100, 300 and 600 nm (from top to bottom), (c) the cone sharpening angle $\Delta\Theta=\Theta-\theta$ (0-24º nm), from bottom to top and (c) the cantilever radii L=0, 5, 10 μm, from top to bottom. The default geometric parameters are: H=12.5 μm, w=3 μm, L=0 μm, Θ=25º, θ=10º, h_{cone}=200 nm and R=5 nm. Insets: Effective dielectric constant of the substrate obtained by fitting the results in the main figures with a single angle cone model with equivalent radius and angle obtained from fittings of the corresponding approach curves on a metallic substrate. Three fitting ranges, z_{ref}=50nm (black curves), z_{ref}=150nm (red) and z_{ref}=300nm (blue) and three relative dielectric constants of the substrate, $\varepsilon_{r,sub}$=3,6 and 9 are analyzed.

A similar analysis can be performed by varying the sharpening angle of the probe, $\Delta\Theta=\Theta-\theta$. In Fig. S1c we show the dependence of the capacitance gradient approach curves on a dielectric substrate with relative dielectric constant $\varepsilon_{r,sub}$ = 6 by using a probe with geometry H=12.5 μm, L=0 μm, h_{cone}=200 nm, θ=10º and R=5 nm and different sharpening angles in the range 0º–24º (from bottom to top). The sharpening angle $\Delta\Theta$=0º corresponds to a single angle cone model. We observe that by increasing the cone sharpening, the approach curve increases at far distances, but decreases at shorter distances. This result is a consequence of the fact that by increasing the microscopic cone angle the effective area of the probe interacting with the substrate increases at large distances (direct contribution), as for the approach curves on metallic substrates[70], but at the same time this increase induces an indirect effect on the local force acting on the probe that appears at shorter distances (indirect effect). Further details on indirect effects of the microscopic parts of the probe on the local interaction on insulating substrates are given elsewhere[41,45]. The overall effect of the direct and indirect contributions is reflected on the effective dielectric constants extracted from fitting the curves of Fig. S1b using a single-angle model with the geometric parameters, R_{eq} and θ_{eq}, obtained from the fitting of the corresponding curves for a metallic substrate (data not shown, see Ref. 70). The effective dielectric constants clearly depend on the sharpening angle and range of the approach curve analyzed, again being systematically smaller than the one used in the numerical calculations to generate the data and showing a larger departure from that value for the shortest range of distances. For instance, for a characteristic sharpening angle of $\Delta\Theta$=15º, we obtain for a substrate with relative dielectric constant ε_r=6, the following effective dielectric constants from the single angle cone model, $\varepsilon_{r,eq}$=5.5, 5.4 and 5.1, for reference distances of z_{range}=300, 150 and 50 nm, respectively, i.e. again an underestimation in the range 8%-15%. This result again shows that with a dielectric substrate one cannot use any effective single angle cone model that reproduces accurately the electrostatic interaction with an insulator substrate.

Finally, we have investigated also the effect of the cantilever radius, L, on the electrostatic interaction between the sharp tip and the dielectric substrate. In this case, the interaction decreases as the cantilever radius increases (Fig. S1d), in a similar way as we observed for single angle tip models[45]. This effect is due to the indirect effect of the microscopic parts of the probe in the local tip-sample interaction. The effective dielectric constant obtained from the corresponding effective single angle cone model with the same cantilever radius can be seen to be independent from the cantilever radius and only dependent on the range of the approach curve. This means that the effect of the cantilever in a single and double angle models is the same, and that the sharpened geometry of the latter does not add additional dependencies on this parameter. In this case, one can use the results valid for single angle cone models on insulator substrates[41].

In summary, we have shown that the electrostatic interaction between a sharp probe and an insulator substrate depends on both the microscopic and nanoscopic probe geometry, and that effective single angle cone models can not be used to reproduce quantitatively this interaction. This is the reason why the full double angle cone geometry is used in the paper.

S2-Calibration curves and calibration parameters

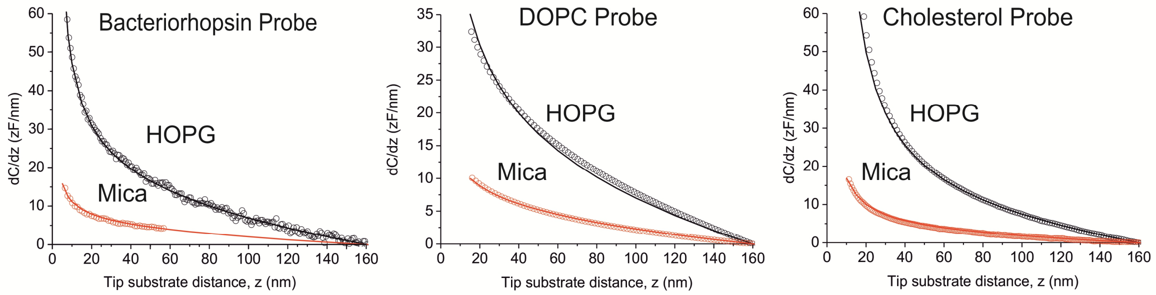

Fig. S2: (Symbols) Experimental calibration curves taken on the metallic (HOPG, black symbols) and insulator (mica, red symbols) substrates for the three probes used, respectively, in the bacteriorhodopsin, DOPC and cholesterol experiments. (Continuous lines) Fitted theoretical curves corresponding to the probe model shown in Fig. S1a. The resulting geometric parameters for each probe are shown in table S1.

Table S1. Geometrical parameters of the probes used in the experiments of the paper obtained from the tip geometry calibration process. The dielectric constant of the mica substrate is assumed to be $\varepsilon_{r,subs}$=6.5.

Probe	R (nm)	h_{cone} (nm)	θ (º)	Θ (º)	L (µm)	H (µm)	w (µm)
PM	5.5	400	7.4	25	13	12.5	2
DOPC	2.8	400	11.2	24	7	12.5	2
Chol	19.5	400	2.6	15	27	12.5	2