Supplementary Information

Mechanisms of Electrotunable Friction in Friction Force Microscopy Experiments with Ionic Liquids

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Simulations of friction for a negatively charged tip.

The computations presented in the main text correspond to the uncharged tip. We have also performed simulations for the charged tip with the surface charge density of -16 μC/cm^2. Charging of the tip has a minor impact on the distribution of ions in the region confined between the tip and electrode, and on the magnitude of the friction force, and it does not modify the dependence of the friction force on the substrate surface charge density, q_s, and the microscopic mechanism of friction. In Figure S1, we report the time-averaged number densities of different charged groups of the ionic liquid layer across the confined region. A comparison of this figure with Figure 3 in the text shows that in the case of negatively charged tip the density of confined cations is higher than that found for the uncharged tip. Also here the tilting of cations at negatively charged and uncharged electrode surfaces is more pronounced than for the uncharged tip.

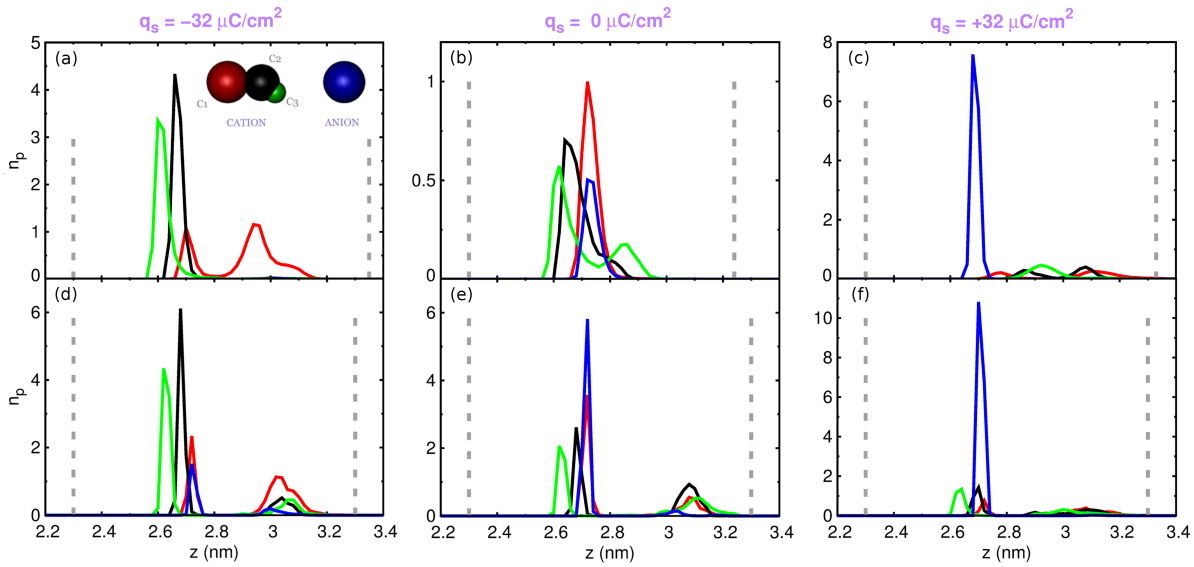


Figure S1. Number density of beads, n_p, corresponding to different charged groups across the region confined between the charged tip and substrate. Results in panels (a-c) calculated for the weak ion-substrate interaction $\varepsilon_{is} = 0.23$ kJ/mol, whereas the results in (d-f) found for the strong ion-substrate interaction $\varepsilon_{is} = 70$ kJ/mol. The first, second, and third columns correspond to the substrate surface charge densities of -32, 0, and +32 μC/cm^2, respectively. In each of these panels, the vertical left and right dashed lines show the position of surface layers of substrate atoms and the tip apex, respectively.

The results of simulations of friction performed for the charged tip, which are presented in Figure S2, show the same trends in the dependence of friction on the electrode surface charge density and similar magnitudes of the force as the results obtained for the uncharged tip (see Figure 5). Two strictly different scenarios for the variation of *F(q,)* were demonstrated in this case as well, which are determined by the regime of motion of the confined IL relative to the substrate and tip. In the range of negative electrode charges and $\varepsilon_{is} = 70$ kJ/mol, we found slightly higher values of the friction force for the charged tip compared to that for the uncharged tip. This effect results from the enhancement of commensurability between the structures of IL layer and the charged tip.

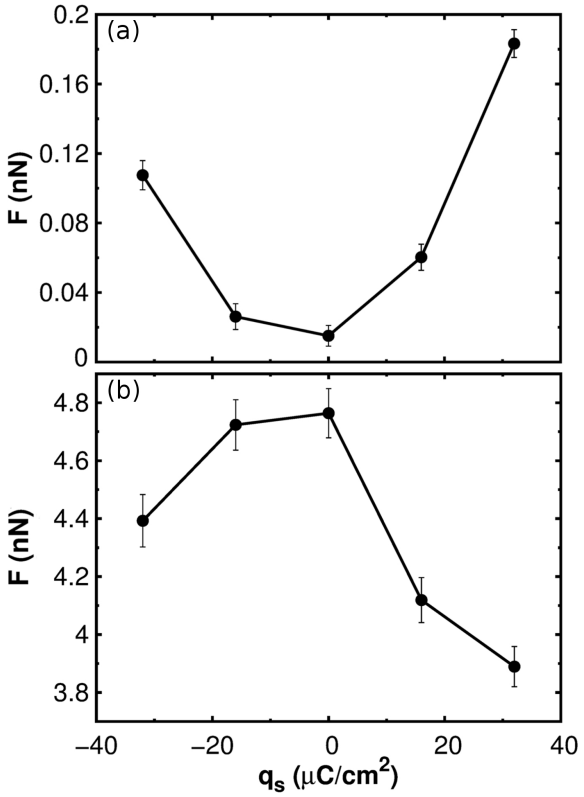


Figure S2. Friction force as a function of substrate surface charge density calculated for the negatively charged tip with the surface charge density of -16 μC/cm^2. Top panel presents the results obtained for ion-substrate interaction $\varepsilon_{is} = 0.23$ kJ/mol, where the slippage occurs at the interface between the ionic liquid layer and the substrate, whereas the bottom panel shows results obtained for $\varepsilon_{is} = 70$ kJ/mol, where the slippage takes place mainly at the interface between the tip and the ionic liquid layer.

Effect of electrode charging on commensurability between the tip lattice and the structure of underlying ionic layer.

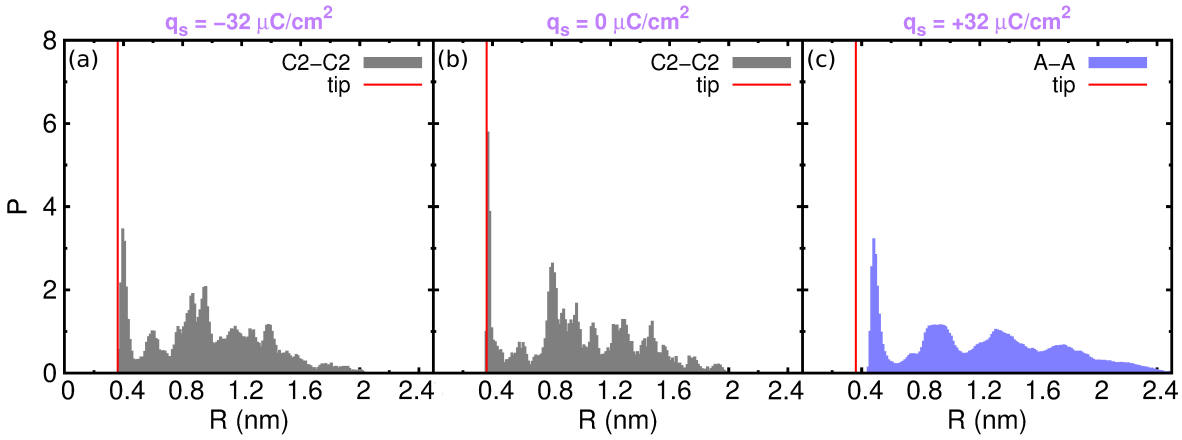


Figure S3. Time averaged distributions of the distances between the beads representing ions in the layer confined between the tip and the substrate. The first, second and third panels correspond to the substrate surface charge densities of -32, 0, and +32 μC/cm^2, respectively. The red line in each panel corresponds to the lattice spacing in the tip, 0.36 nm. For charge densities of -32 and 0 μC/cm^2 the distances between C2 cation beads are considered, and for q_s = +32 μC/cm^2 the distribution of the distances between anions is presented.

To describe the effect of surface charge density on commensurability between the tip lattice and the structure of confined ionic layer noted in the main text for the case of strong ion-substrate interaction, $\varepsilon_{is} = 70$ kJ/mol, we plot in Figure S3 the time averaged distributions of the distances between the beads representing ions located below the tip. For charge densities of -32 and 0 μC/cm^2, C2 cation beads give the main contribution to the interaction between the tip and the IL layer, and correspondingly in the panels (a) and (b) of Figure S3 we present the distributions of distances between these beads. Differently, for the positively charged electrode (q_s = +32 μC/cm^2) mainly anions are present in the confined region, and the distribution of the distances between anions is presented in panel (c).

A commensurability between the tip and IL layer structures should be manifested as an overlap between the red line and peaks in the distributions of distances between the ions. Figure S3 shows that the strongest overlap occurs for the uncharged electrode indicating on a pronounced commensurability between the structures of the tip and the underlying IL layer. While only a minor difference in overlaps is found for q_s =-32 and 0 μC/cm^2 (see panels a and b), a space separation between the red line and the distance distribution calculated for q_s =+32 μC/cm^2 (see panel c) clearly indicates on the incommensurability between the structures of the tip and the underlying IL layer for the positively charged electrode. As noted in the main text stronger commensurability between the contacting structures in relative motion corresponds to higher friction force. These calculations provide a strong support for the explanation of the charge dependence of friction presented in the main text.