Supplementary Information

Collective Dehydration of Ions in Nano-Pores

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Asymmetry of the pre-final FTT

While the collapsed pore at high salt concentration invariably ends with a mostly symmetrical interface f), the pathway to reach this final state may vary, depending on the degree of asymmetry present in the pre-final transition. For example, an exceedingly asymmetric interface e) can be produced if the pre-final transition is due to a collective dehydration / adsorption of only one hydrated-ion layer to its nearest surface. The very asymmetric structure illustrated at interface e) in Figure SI1 below is not necessarily the only possible scenario and configurations with mixed symmetry may indeed be the norm. The phenomenon of asymmetry of the pre-final FTT is particularly pronounced in the model-slit-pore experiment, but may also occur in any common pore geometry.

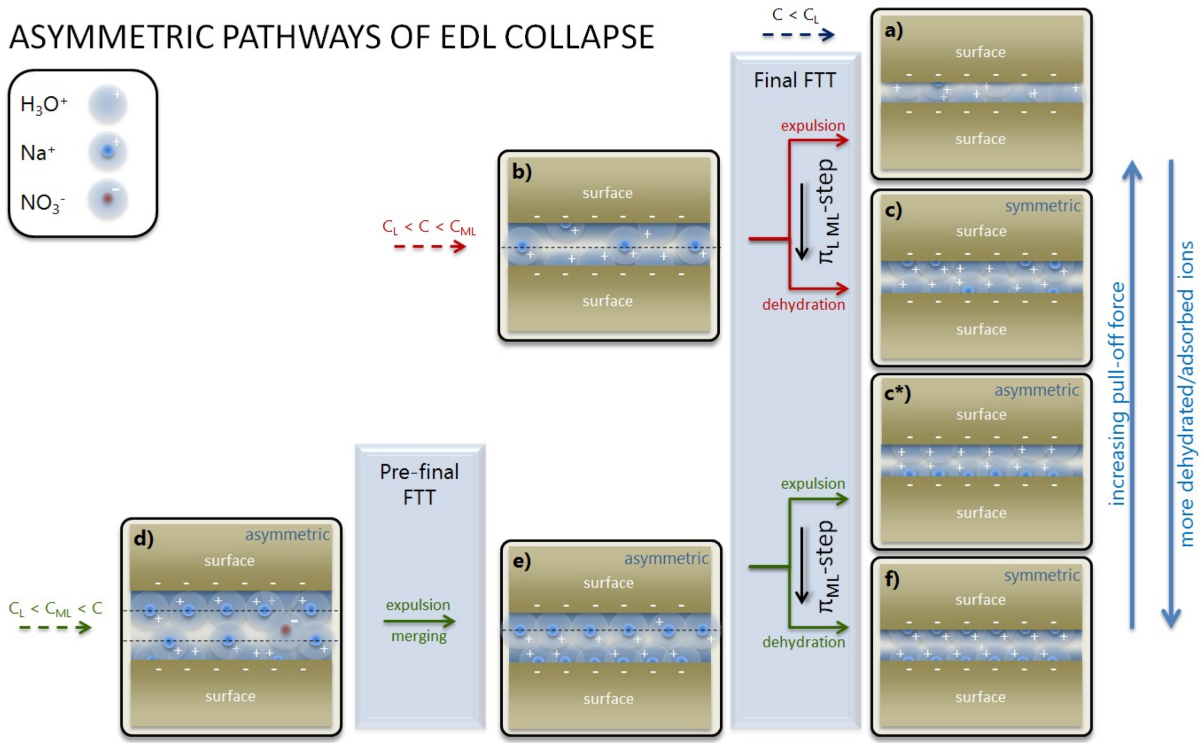

Figure SI1: Purely asymmetric pathways of EDL collapse showing the asymmetric modes; the dashed black pathway ending with interface a) corresponds to a low salt concentration without layering; the red pathways (b-a and b-c) are enabled with single hydrated-ion layering, the change of interface from a) to c) gives rise to the $\Delta\pi L$-step; the green pathways (d-e-c* and d-e-f) are enabled by multiple layering, allowing the existence of a pre-final FTT preceding the final FTT that gives rise to the $\Delta\pi_{ML}$-step. The interface e) is asymmetric, since one of the hydrated-ion layers of interface d) has been dehydrated. In terms of total number of dehydrated ions, both interfaces c) and c*) are similar, leading to similar pull-off forces, but one is symmetric and the other is asymmetric. Hydrated-ion layering is indicated by dashed lines. The bifurcation points highlight the switching mechanisms that give rise to the observed quantization of adhesion. In contrast to Figure 4, the purely asymmetric pathways are shown; the real situation seems to involve a mixture of symmetric and asymmetric pathways.

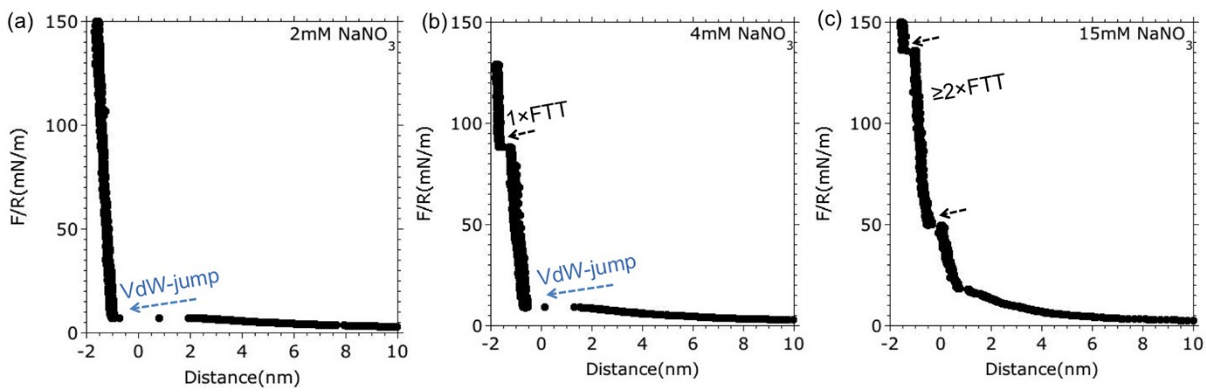

Figure SI2: Force distance curves measured at three selected salt concentrations using the same pair of mica surfaces (a) low salt concentration where the VdW attraction dominates at small separations (b) intermediate salt concentration where single FTTs are present and (c) high salt concentration where multiple layering of ions (≥2 FTTs are present). The "zero" on the distance scale was determined in an unloaded mica-mica contact in neat water at equilibrium with atmosphere before adding salt to the system. The apparently negative distances are a real systematic artefact related to the compression of the mica spacer layers. Mica has a higher modulus than the confined fluid, but also contributes ≳1000x more to the optical path in the Fabry-Pérot interferometer.