Supplemental Information:
Ion-Specific Adsorption and Electroosmosis in Charged Amorphous Porous Silica

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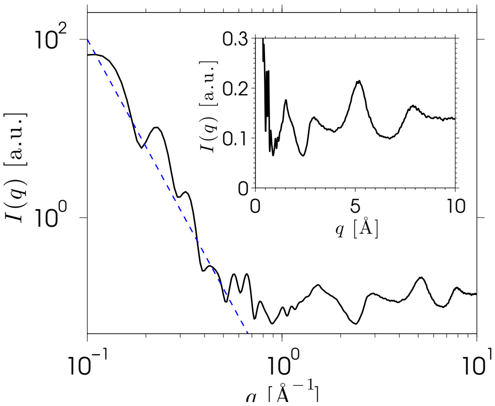


FIG. S1: The results of a neutron scattering simulation for an amorphous silica slit pore. The decaying part (small q-values) corresponds to lengths spanning the channel. The fit of this decay indicates a Porod exponent close to 4 (dashed line), which corresponds to that for a smooth surface.

TABLE S I: Lennard-Jones parameters and charges taken from the literature. The charges of the surface groups are such that a fully hydroxylated surface is charge neutral, while each dangling oxygen atom has a negative elementary charge. Since the partial charge of the hydrogen atom is smaller than an element charge there is a difference between the charge of hydroxylated and dangling oxygen atoms, the latter of which is indicated with Si-O*.

	σ [Å]	ϵ/k_B [K]	q [e]	Ref.
Ions				
Na^+	2.1845	84.7616	+1	1
K^+	2.8331	140.6332	+1	1
Cs^+	3.3640	198.4871	+1	1
Sr^{2+}	3.1	125.81	+2	2
Cl^-	4.9178	5.8683	-1	1
Water (TIP4P/2005)				
O	3.1589	93.19685		3
H			+0.5564	3
M			-1.1128	3
Silica				
Si	3.795	64.17773	+2	4
O	3.154	78.02117	-1	4
O (Si-O*)	3.154	78.02117	-1.5	4
H			+0.5	

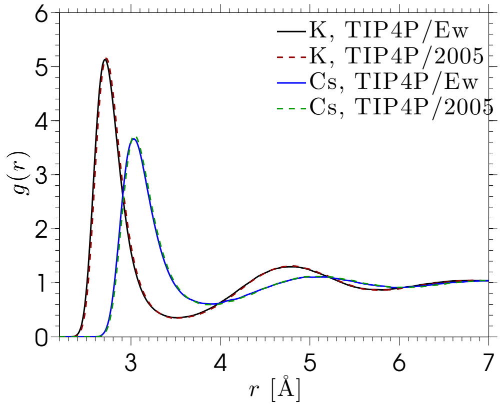


FIG. S2: Comparison between the hydration of K^+ and Cs^+ solvated in TIP4P/Ew water (solid lines) and the same ions in TIP4P/2005 water (dashed lines). The temperature of the solution is 300 K and the pressure is 1 atm.

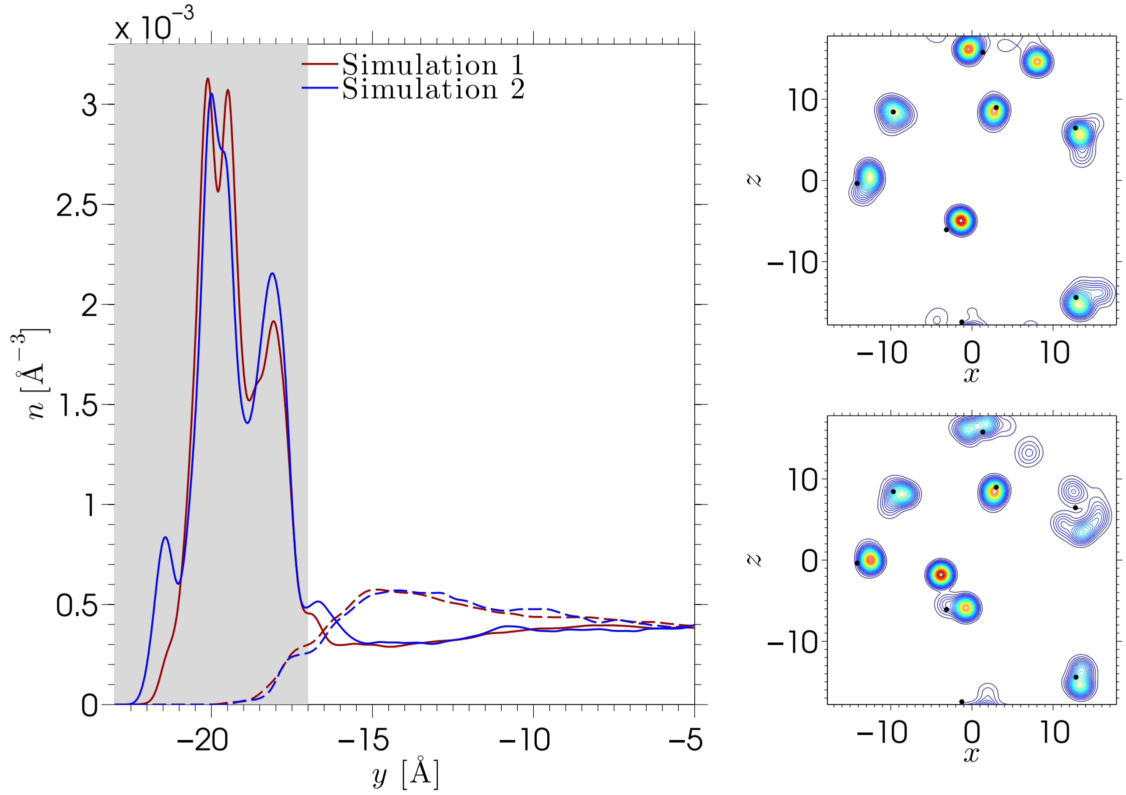
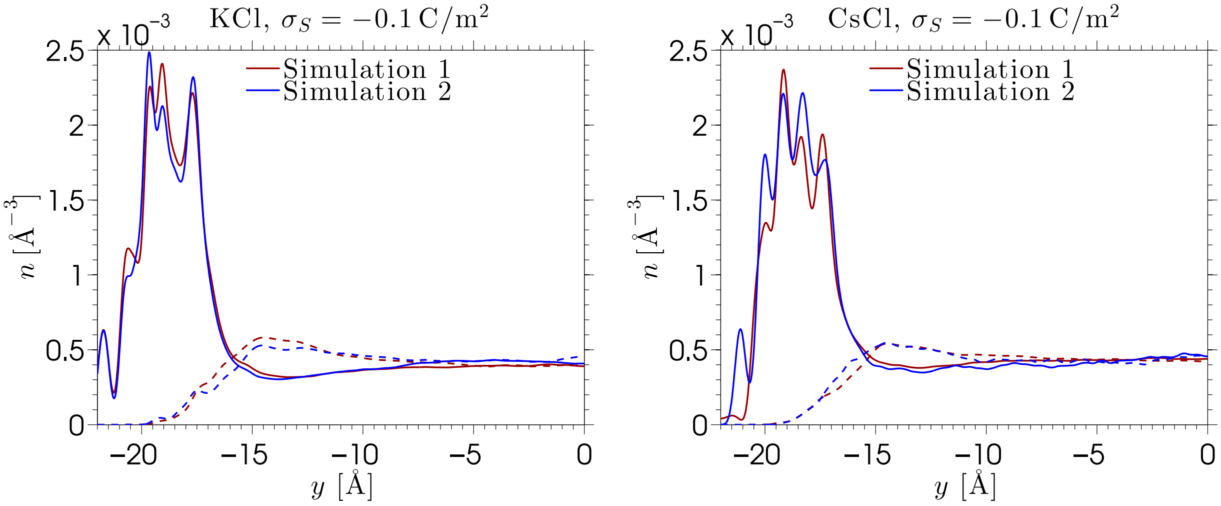


FIG. S3: Comparison between two independent simulations of a NaCl solution confined between silica walls with a surface charge of $\sigma_S = -0.1\,\mathrm{C/m^2}$. The ion density profiles are shown on the left. The grey shaded area denotes the region of the Stern layer. The time-averaged in-plane cation distribution in the Stern layer near a wall is shown in the figures on the right. The figure on the top corresponds to simulation 1 and the figure on the bottom to simulations 2. The black dots indicate the locations of the charge sites at the wall, while the colored contours show the distribution of the adsorbed cations. The in-plane structure is averaged over a period of 5 ns. The figures show that each charge site is compensated by at least one cation, while the additional ions due to overscreening are often also located near a charge site.



(a) (b)

FIG. S4: Comparison between two independent simulations of KCl (a) and CsCl (b) solutions confined between silica walls with a surface charge of $\sigma_S = -0.1\,\mathrm{C/m^2}$.

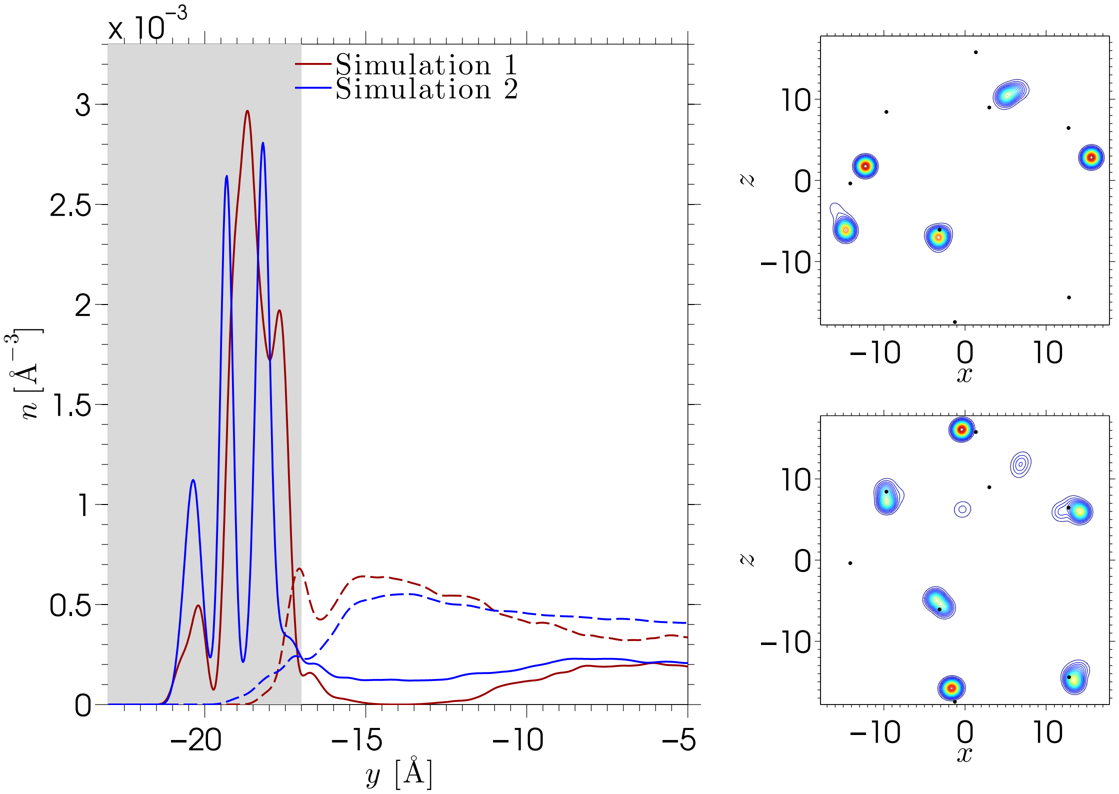


FIG. S5: Comparison between two independent simulations of a $SrCl_2$ solution confined between silica walls with a surface charge of $\sigma_S = -0.1\,\mathrm{C/m^2}$. The ion density profiles are shown on the left. The grey shaded area denotes the region of the Stern layer. The time-averaged in-plane cation distribution in the Stern layer near a wall is shown in the figures on the right. The figure on the top corresponds to simulation 1 and the figure on the bottom to simulations 2. The black dots indicate the locations of the charge sites at the wall, while the colored contours show the distribution of the adsorbed cations. The in-plane structure is averaged over a period of 5 ns. The figures show some of the cations are not located at charge sites. These ions found a local minimum energy and were probably not able to migrate to different lower energy state.

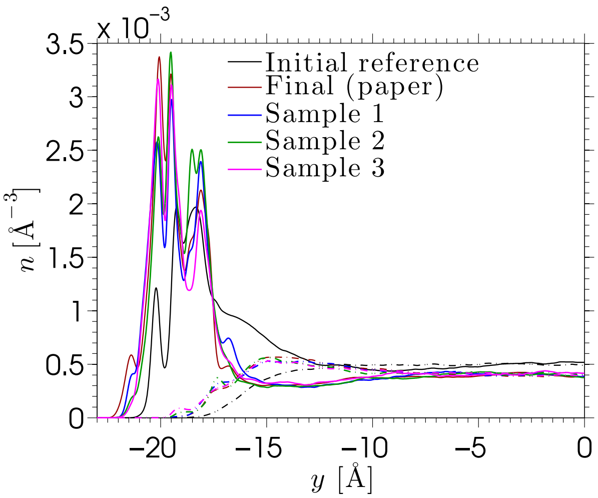
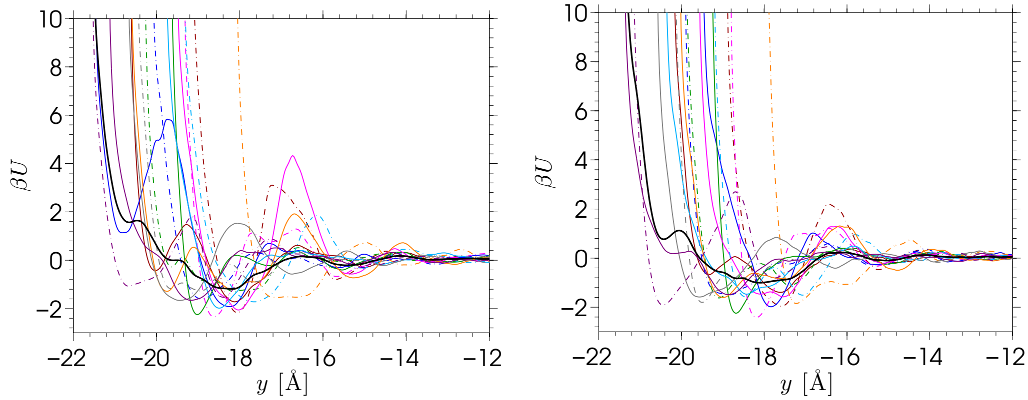
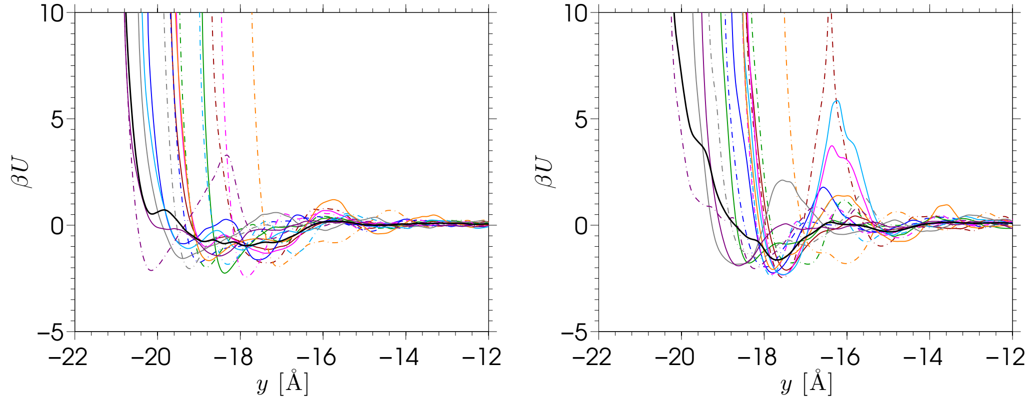


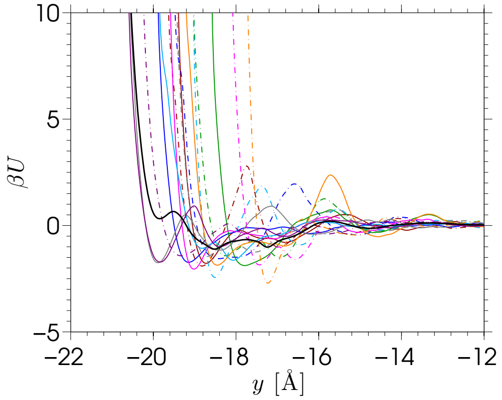
FIG. S6: Three simulations for NaCl started from an ion distribution in which no overscreening occurs. The figure shows the ion density profiles after equilibrating the system for 6 ns and averaging over the subsequent 5 ns.



(a) Na$^+$ (b) K$^+$

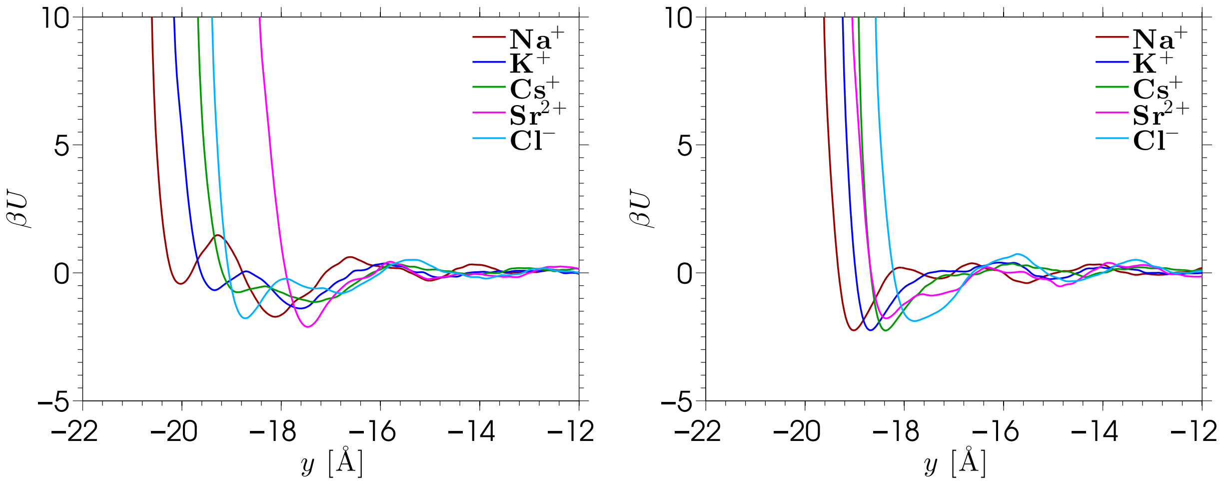


(c) Cs$^+$ (d) Sr^{2+}



(e) Cl$^-$

FIG. S7: The potential of mean force of a single ion near a neutral wall for each of the ion species included in this study. The thin lines are the free energy profiles corresponding to different locations across the silica surface, the solid black line indicates the average free energy profile with the average procedure shown in Figure S9. The colors codings in the different subfigures are consistent so that comparison of different ions at the same x-z position is possible. This comparison has been shown for 2 points in Figure S8



(a) Point 1 (b) Point 2

FIG. S8: The potential of mean force of each of the ion species at a single fixed x-z position. The difference between both figures show how the local environment close to the surface can affect ion hydration and thus the effective ion-surface interaction. Figure (a) shows a difference in the hydration behavior of the different ions, while figure (b) primarily shows a horizontal shift between the profiles, approximately consistent with the differences in the Lennard-Jones radii of the ions.

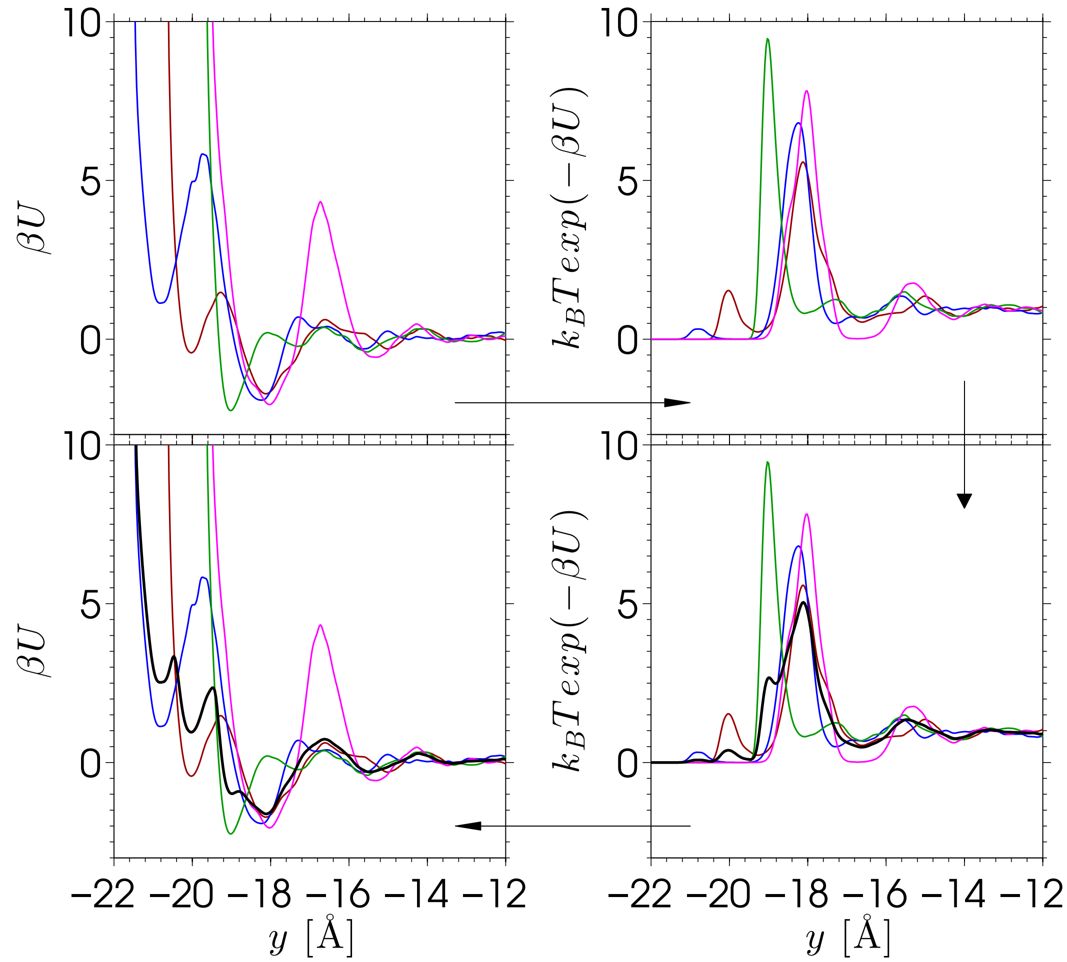
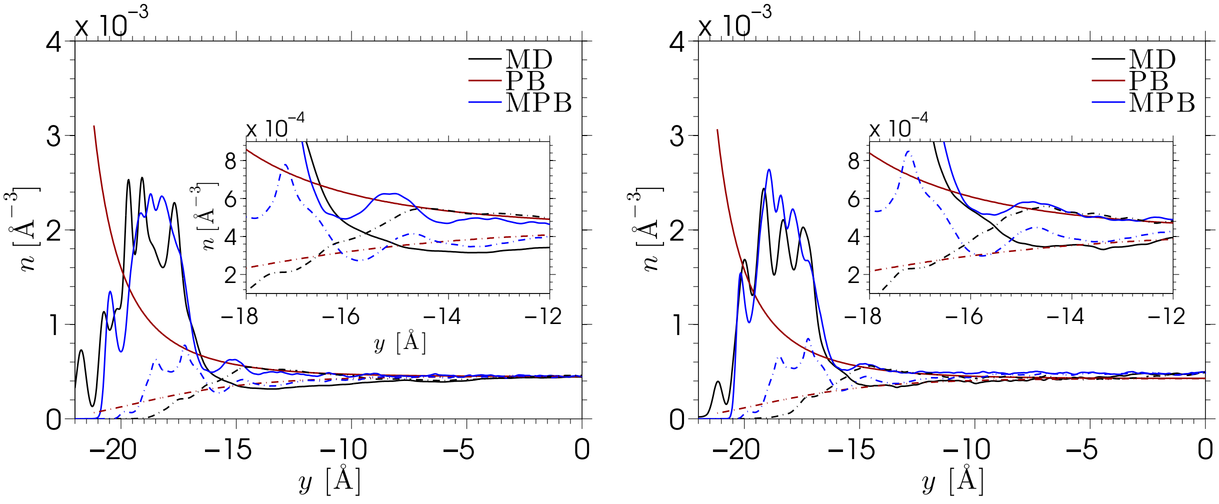
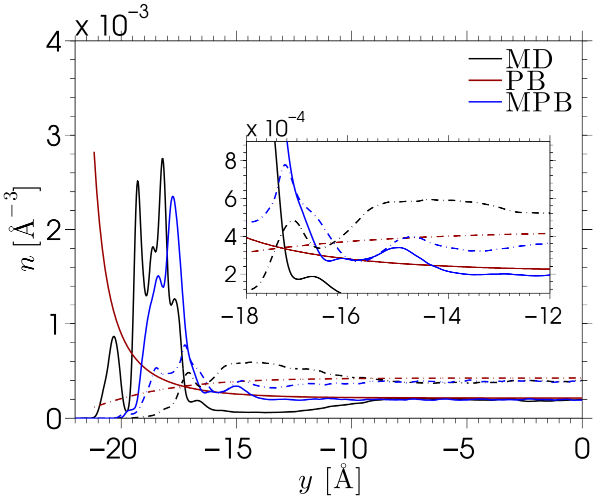


FIG. S9: A schematic point-by-point overview of how the average potential of mean force is obtains. This example shows only four profiles for the sake of clarity, while 18 profiles are used in our calculations. As mentioned in the main article, the arithmetic average of the density of states needs to be calculated, rather than a direct average of the interaction energies.



(a) KCl (b) CsCl



(c) $\mathrm{SrCl_2}$

FIG. S10: Ion distribution profiles for KCl (a), CsCl (b), and $\mathrm{SrCl_2}$ (c) solutions near a surface with charge density $\sigma_S = -0.1\,\mathrm{C/m^2}$. The full lines correspond to cation distributions, while the dashed-dotted lines corresponds to anion distributions.

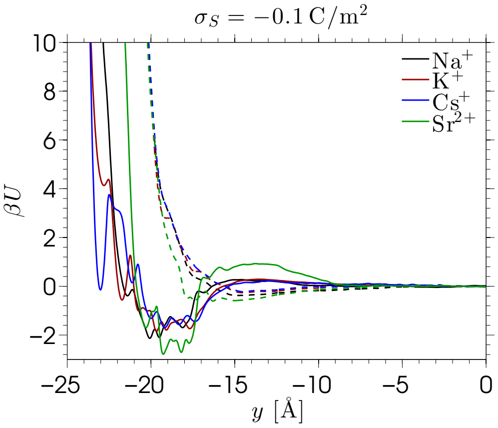


FIG. S11: Free energy profiles of the ions in the various electrolyte solutions calculated from the normalized density profiles $n(y)/n_0$. The full lines denote the cation energy profiles for Na$^+$ (black), K$^+$ (red), Cs$^+$ (blue), and Sr^{2+} (green). The dashed lines denote the chloride energy profiles corresponding to the cation profile in the same colors.

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