

Supplementary Information

Comparative molecular dynamics simulations of charged solid-liquid interfaces with different water models

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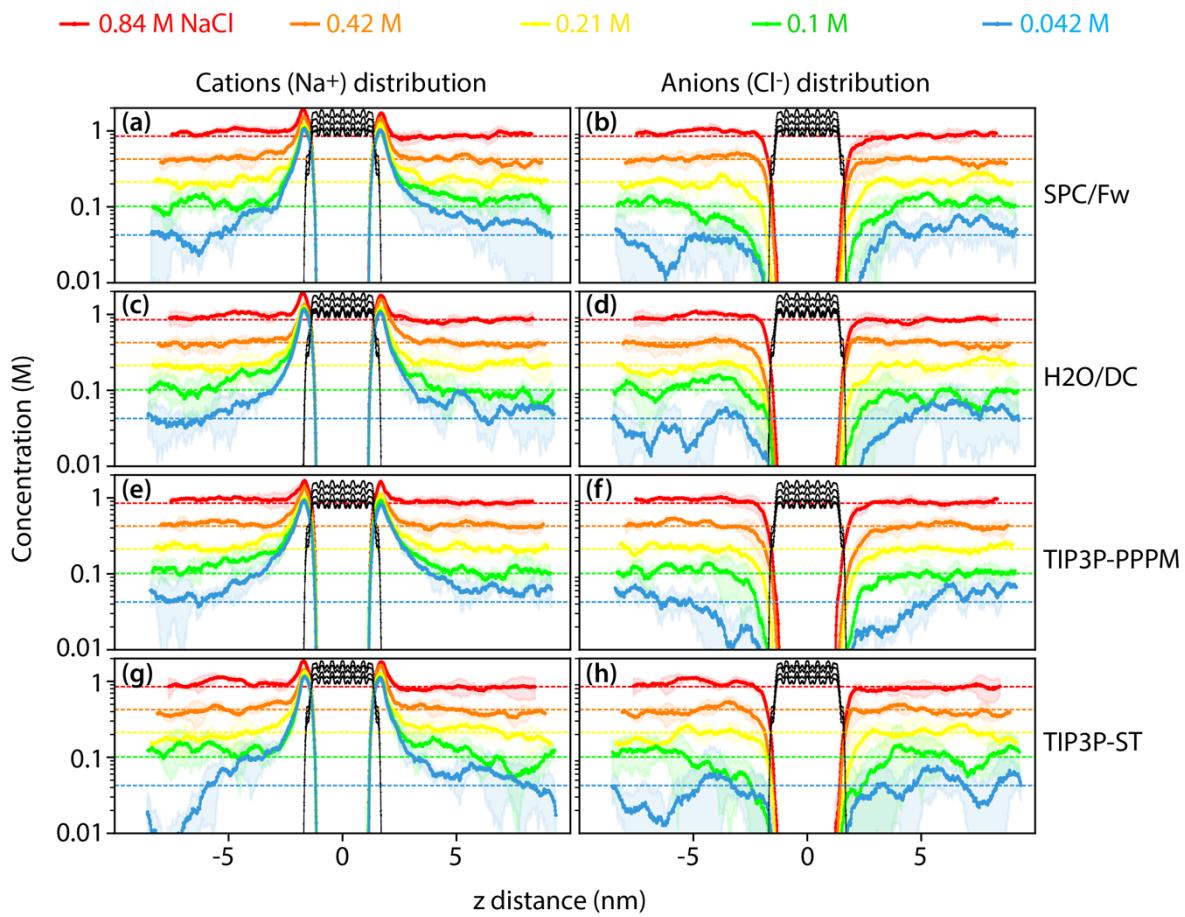


Figure S1: Effect of the salt concentration on the ion distribution near solid-liquid interface for the selected water models. The cation and anion distribution near a solvated silica surface is shown for SPC/Fw (a) and (b), respectively, H₂O/DC (c) and (d), TIP3P-PPPM (e) and (f), and TIP3P-(g) and (h). The different colours represent the different bulk ionic concentrations (horizontal dashed line) with the silica density appearing in black.

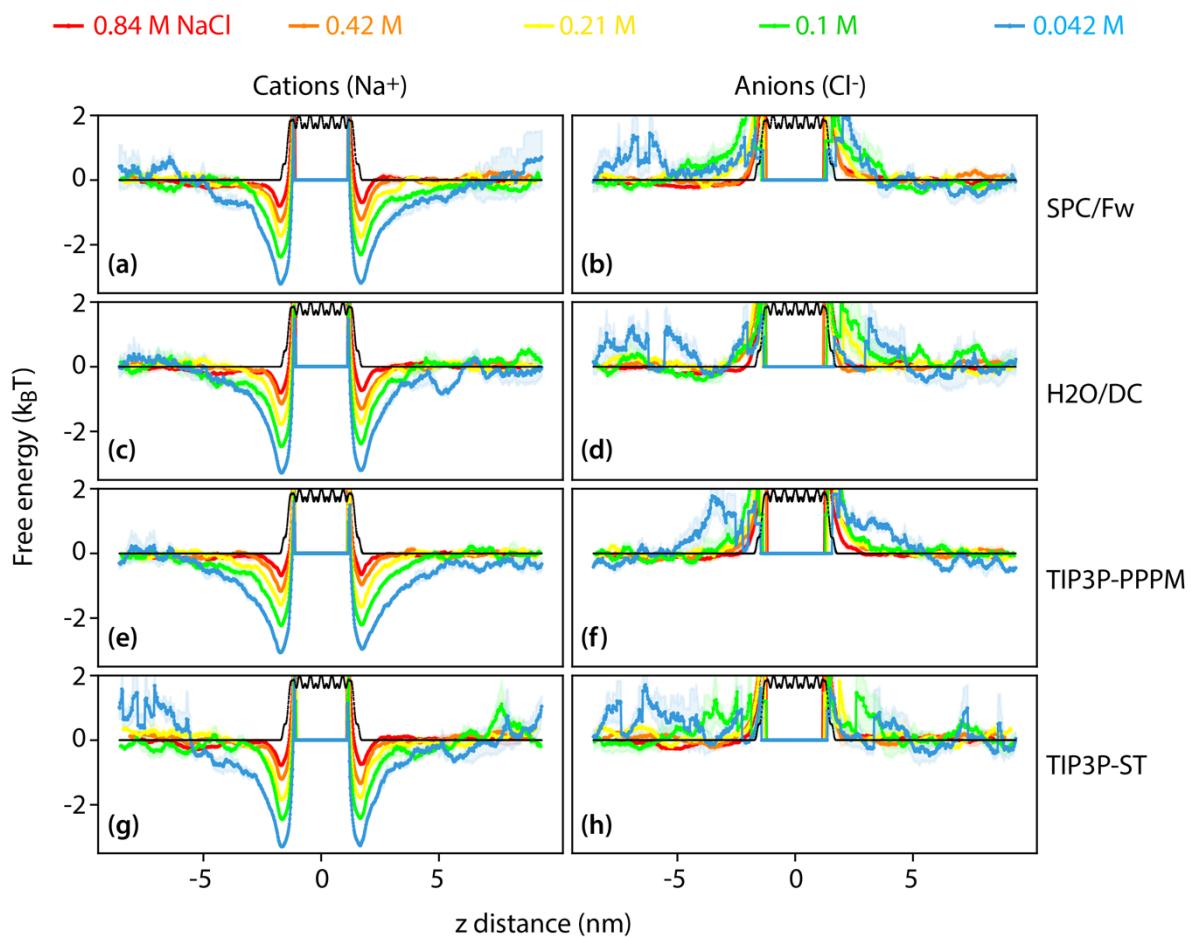


Figure S2: Effect of the salt concentration on the free energy of the ions near solid-liquid interface for the selected water models. The cation and anion free energy distribution near a solvated silica surface is shown for SPC/Fw (a) and (b), respectively, H₂O/DC (c) and (d), TIP3p-PPPM (e) and (f), and TIP3P-(g) and (h). The different colours represent the different bulk ionic concentrations with the silica density appearing in black.

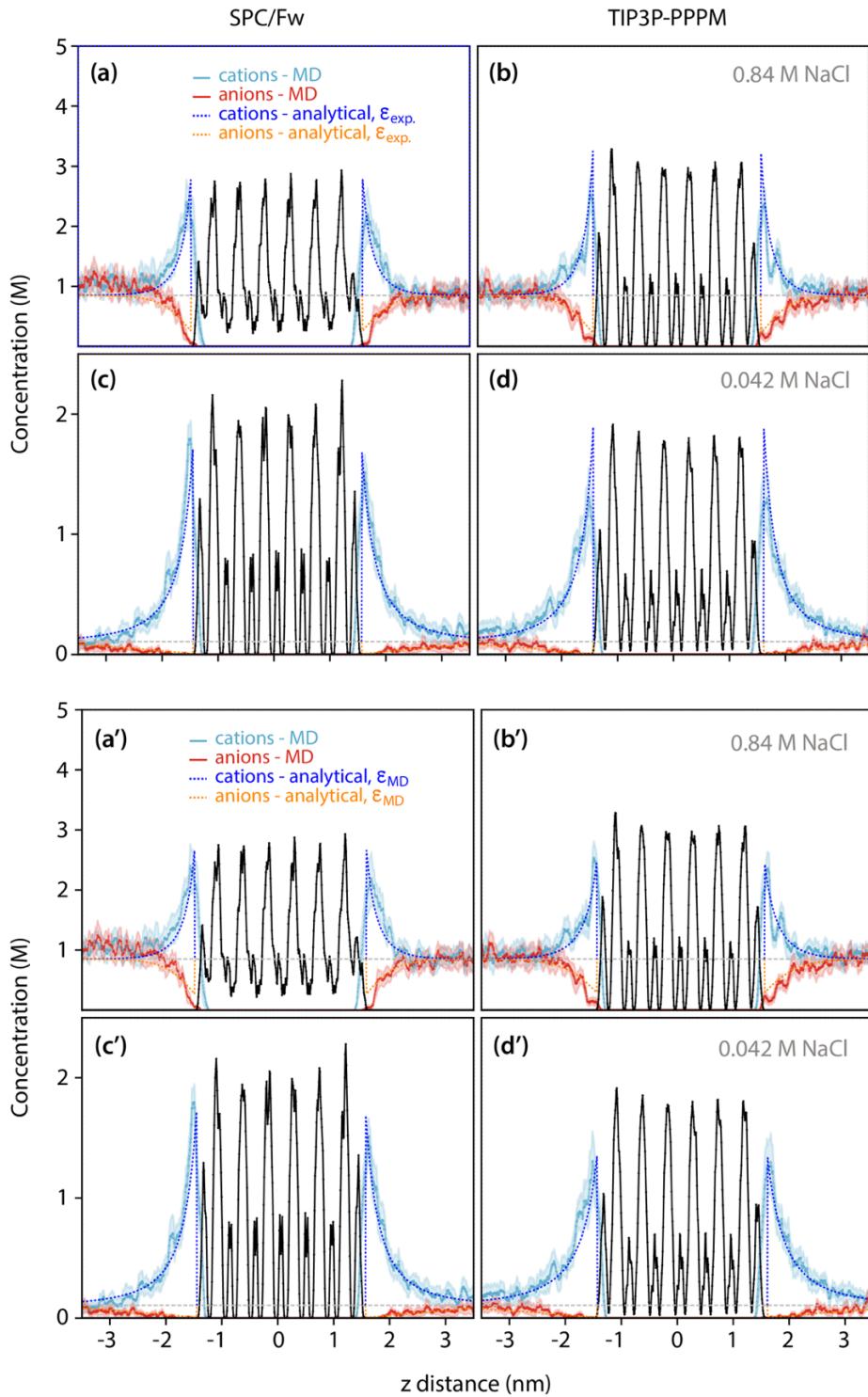


Figure S3: Ion density profiles obtained with SPC/Fw and TIP3P-PPPM at two salt concentrations. For comparison, analytical predictions from Gouy-Chapman model are given using the with experimentally measured dielectric constant for water ϵ_{exp} . (a-d) and with the constant ϵ_{MD} derived from MD simulations (a'-d'). The SPC/Fw water model tends to underestimate the counter-ion density near the silica surface at 0.84 M, and effect more marked when the MD calculated dielectric constant is used. However, the predictions made by TIP3P-PPPM water are in a good agreement with the analytical solution despite its poor ability to predict the dielectric constant accurately. The counter-ion and co-ion concentration profiles near the charged silica surface are given at 0.84 mM NaCl and 0.042 M NaCl for SPC/Fw with analytical predictions based on ϵ_{exp} . (a, c) and ϵ_{MD} (a', c') respectively. The counter-ion and co-ion concentration profiles at 0.84 M NaCl and 0.042 M NaCl for TIP3P-PPPM with analytical predictions based on ϵ_{exp} . (b, d) and ϵ_{MD} (b', d') respectively.

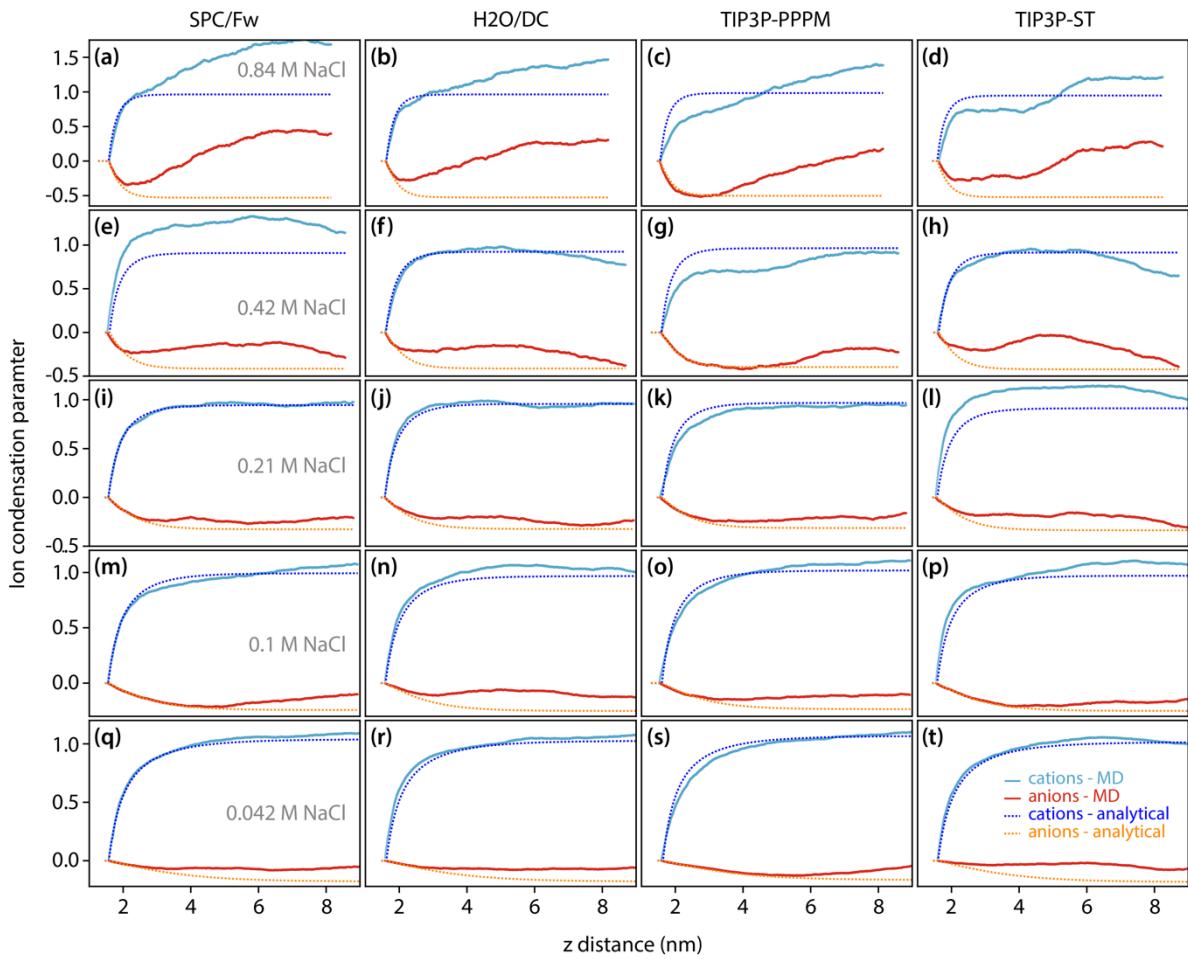


Figure S4: Comparison of the condensation parameter obtained at various salt concentrations for the selected water models. The results are compared with analytical prediction from the Gouy-Chapman model. Counter-ion (blue) and co-ion (red) condensation profiles are shown with a solid line for the MD simulations and a dashed line for the analytical predictions. The SPC/Fw -derived condensation parameter is given for 0.84 M NaCl (a), 0.42 M NaCl (e), 0.21 M NaCl (i), 0.1 M NaCl (m) and 0.042 M NaCl (q) respectively. The H2O/DC -derived condensation parameter is given for 0.84 M (b), 0.42 M (f), 0.21 M NaCl (j), 0.1 M (n) and 0.042 M (r) respectively. The TIP3P-PPPM -derived condensation parameter is given for 0.84 M (c), 0.42 M (g), 0.21 M NaCl (k), 0.1 M (o) and 0.042 M (s) respectively. The TIP3P-ST -derived condensation parameter is given for 0.84 M (d), 0.42 M (h), 0.21 M NaCl (l), 0.1 M (p) and 0.042 M (t) respectively.

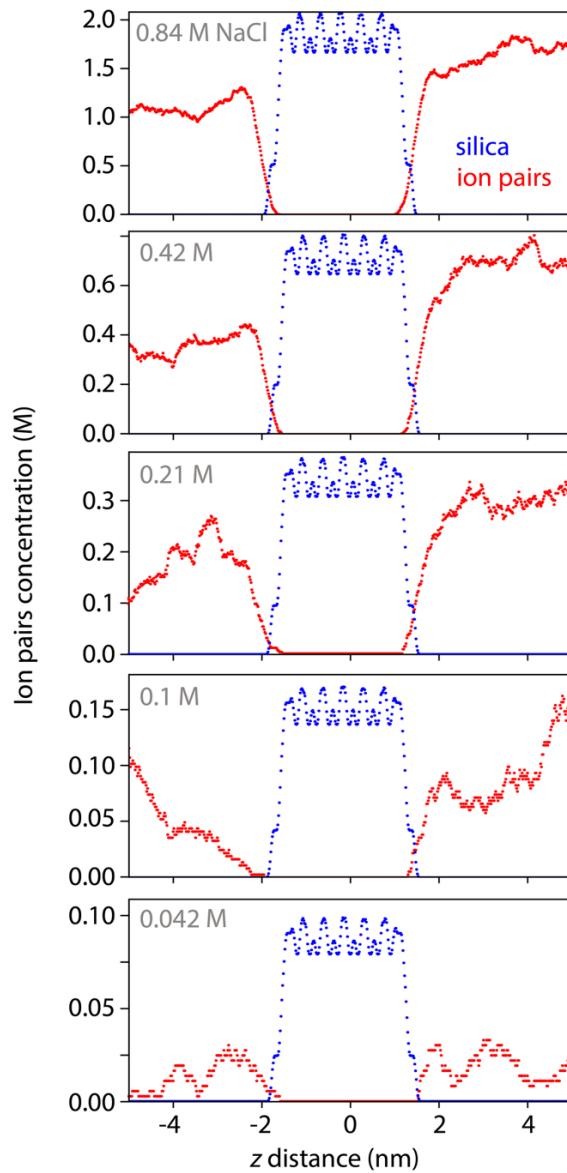


Figure S5: Concentration of ion pairs as a function of z distances for different concentrations of NaCl in SPC/E water. The concentration of pairs increases non-linearly with the salt concentration. This supports the idea that effects due to ion pairs dominate at higher concentrations