Zeta Potential Determination from Molecular Simulations

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Supporting Information

Example Gromacs and LAMMPS input files can be found at

http://home.prf.jcu.cz/~predota/zeta/biriukov/

Table S1. Force Field Parameters Employed in This Work[a]

atom	model	q [e]	σ [Å]	ε [kJ mol^{-1}]
Na^+	ECC[1]	+0.75	2.115	0.544284
	full-rutile[2]	+1	2.583	0.4184
	full-quartz[3]	+1	2.15954	1.47545
Rb^+	ECC[4]	+0.75	2.97	1.86231
Sr^{2+}	ECC[4]	+1.5	2.97	0.4947
Ca^{2+}	ECC[5]	+1.5	2.6656	0.5072
Cl^-	ECC[6]	−0.75	4.1	0.4928
	full-rutile[2]	−1	4.4401	0.4184
	full-quartz[3]	−1	4.83045	0.0534924

[a]Force field parameters for rutile (110) surfaces are summarized in ref 4. Lennard-Jones parameters and original 'full' charges of quartz (101) surface atoms are summarized in ref 7, while 'ECC' charges are summarized in Table S2. Force field parameters for oxalic acid anions are summarized in Ref 8 (the ECCR-P parameterization of hydrogenoxalate has been used).

Table S2. ECC Charges of Quartz (101) Surface Atoms[a]

surface charge density [C/m^2]	bulk atoms		SiOH atoms			SiO^- atoms	
	Si_s	O_s	Si_h	O_h	H_h	Si_{o-}	O^-
−0.03	2.0598	−1.0312	2.06505	−0.9352	0.4218	1.97005	−0.9812
−0.06	2.0588	−1.0322	2.0637	−0.9362	0.4208	1.9677	−0.9822
−0.12	2.0566	−1.0344	2.0616	−0.9384	0.4186	1.9658	−0.9844

[a]The variable charge atoms are summarized here. The charges of bulk SiO_2 atoms are $q(Si_B) = 2.1$ and $q(O_B) = -1.05$ as in ref 7.

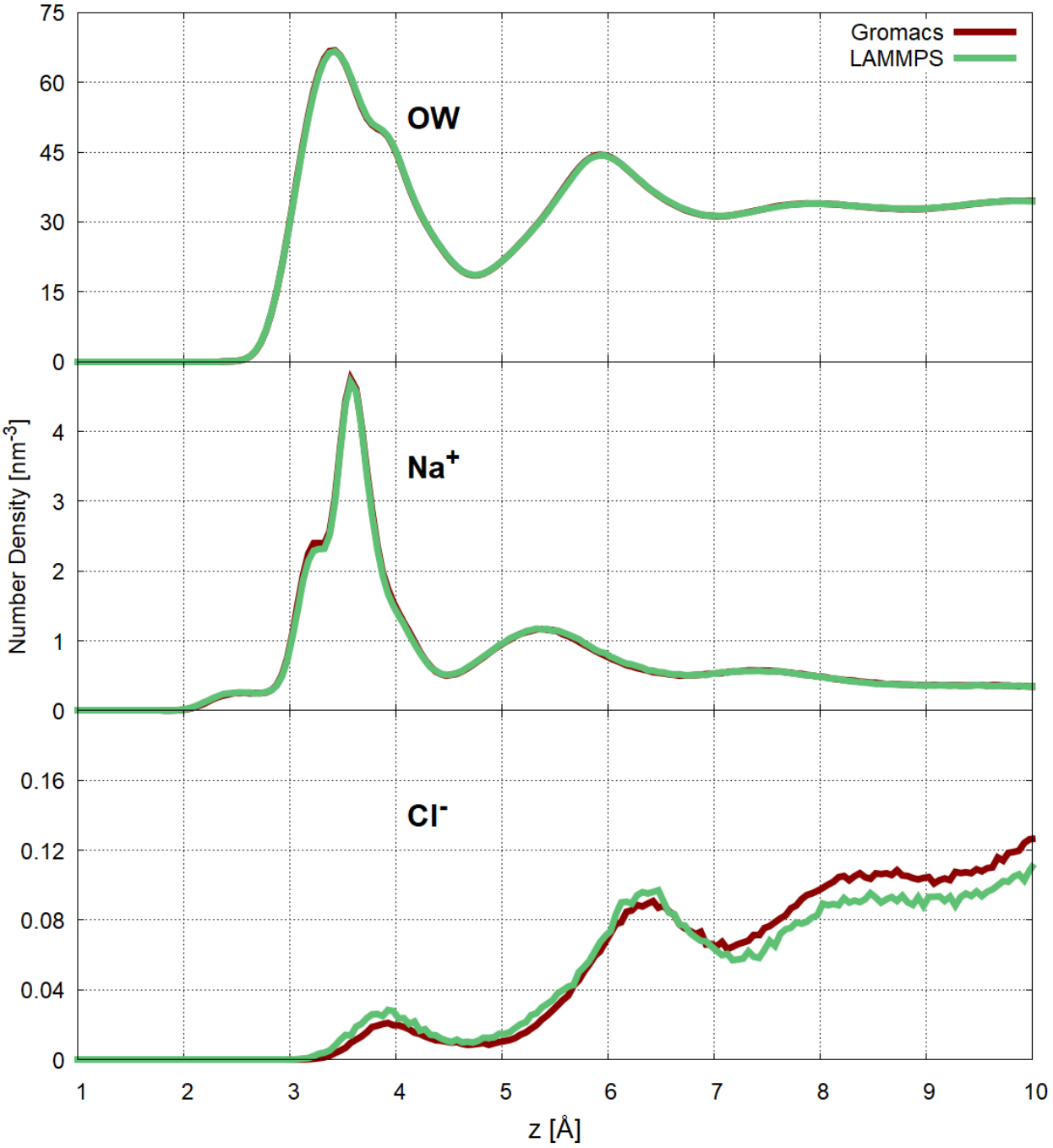

Figure S1. Axial number density profiles of water and ions of 0.33 M NaCl solution at the most negatively charged (−0.12 C/m^2) quartz (101) surface from the equilibrium MD simulations performed in different software packages. Note different vertical scales.

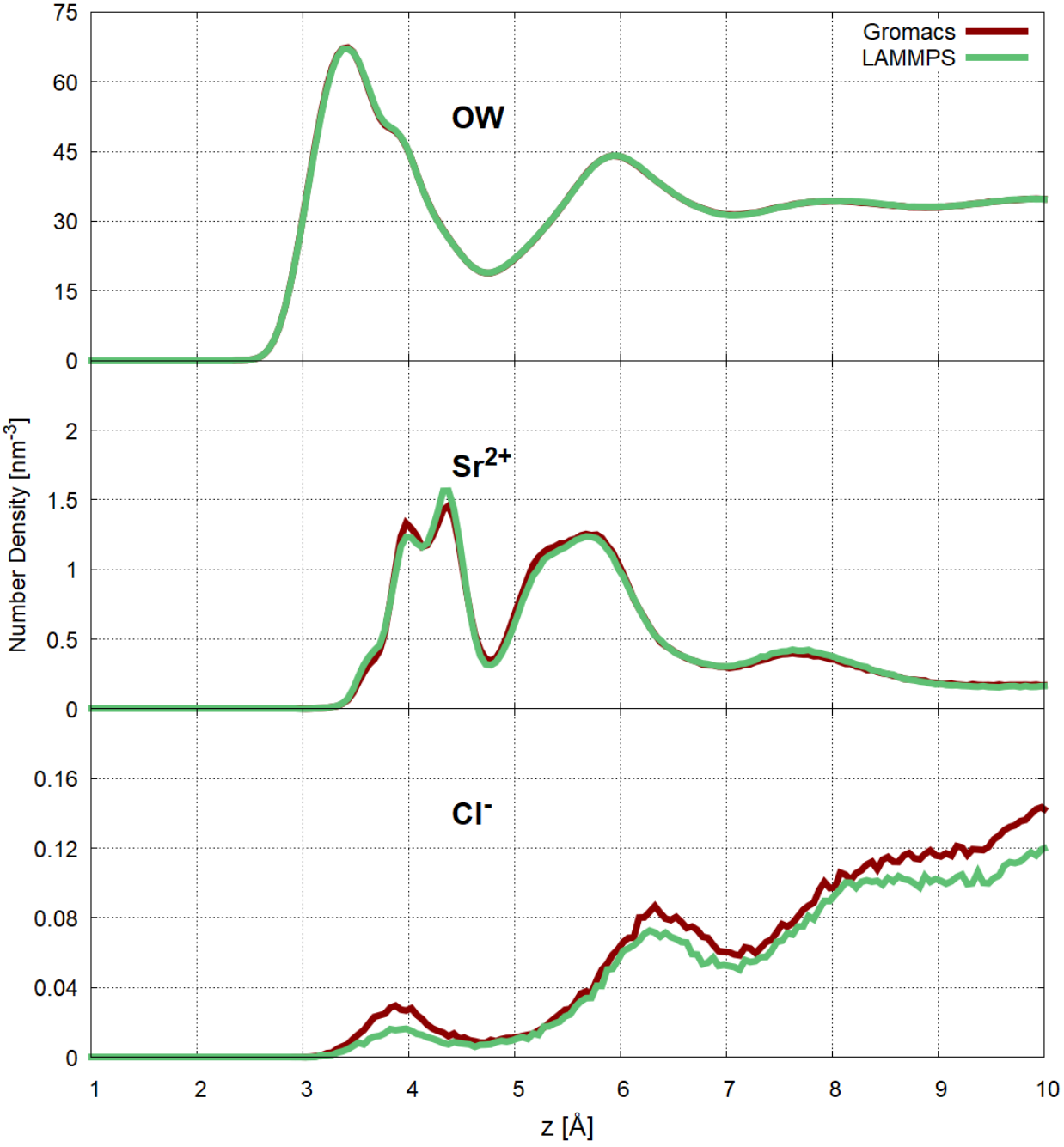

Figure S2. The same as Figure S1, but for 0.15 M $SrCl_2$ solution.

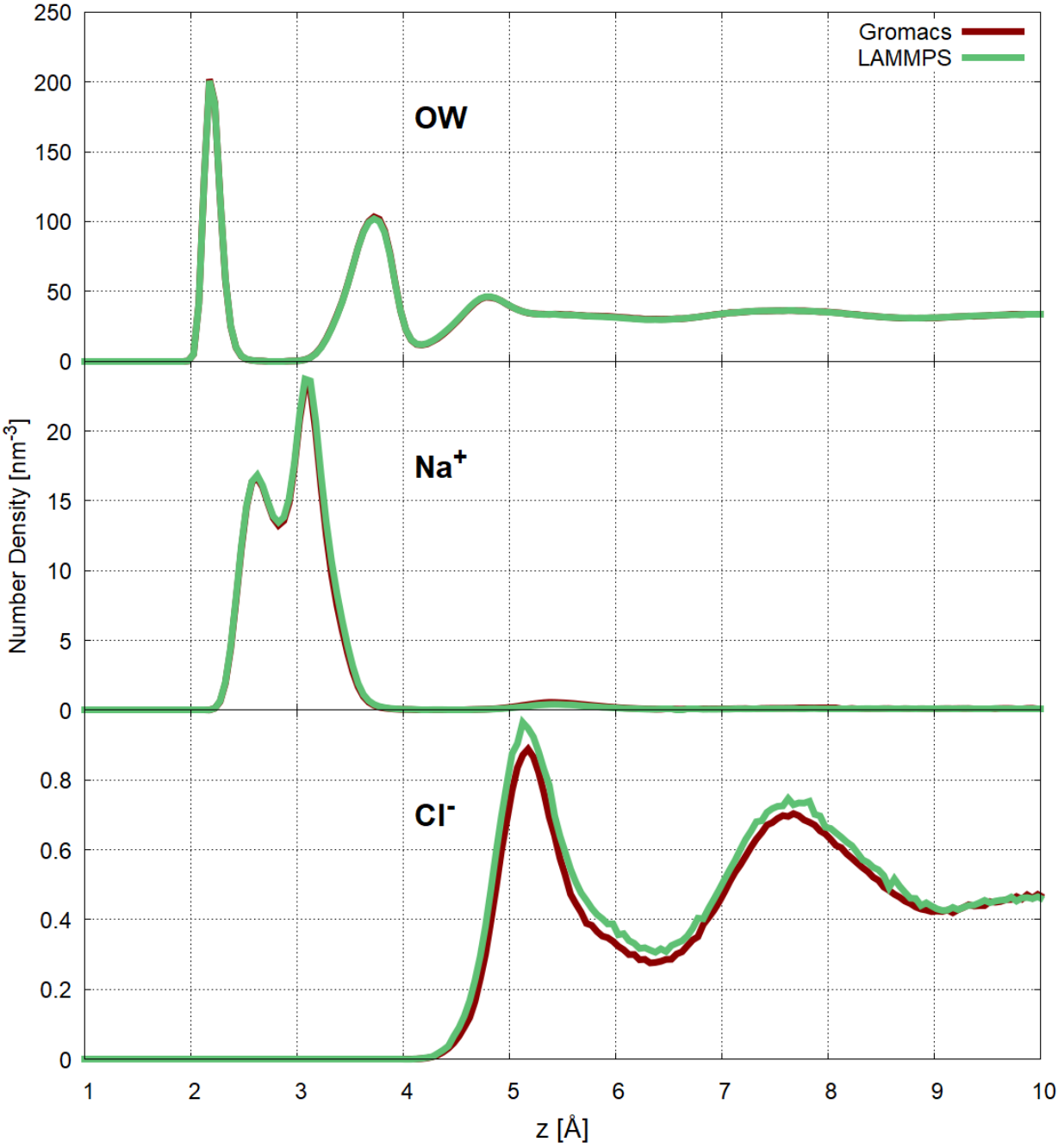

Figure S3. Axial number density profiles of water and ions of 0.45 M NaCl solution at the negatively charged (-0.208 C/m^2) rutile (110) surface from the equilibrium MD simulations performed in different software packages. Note different vertical scales.

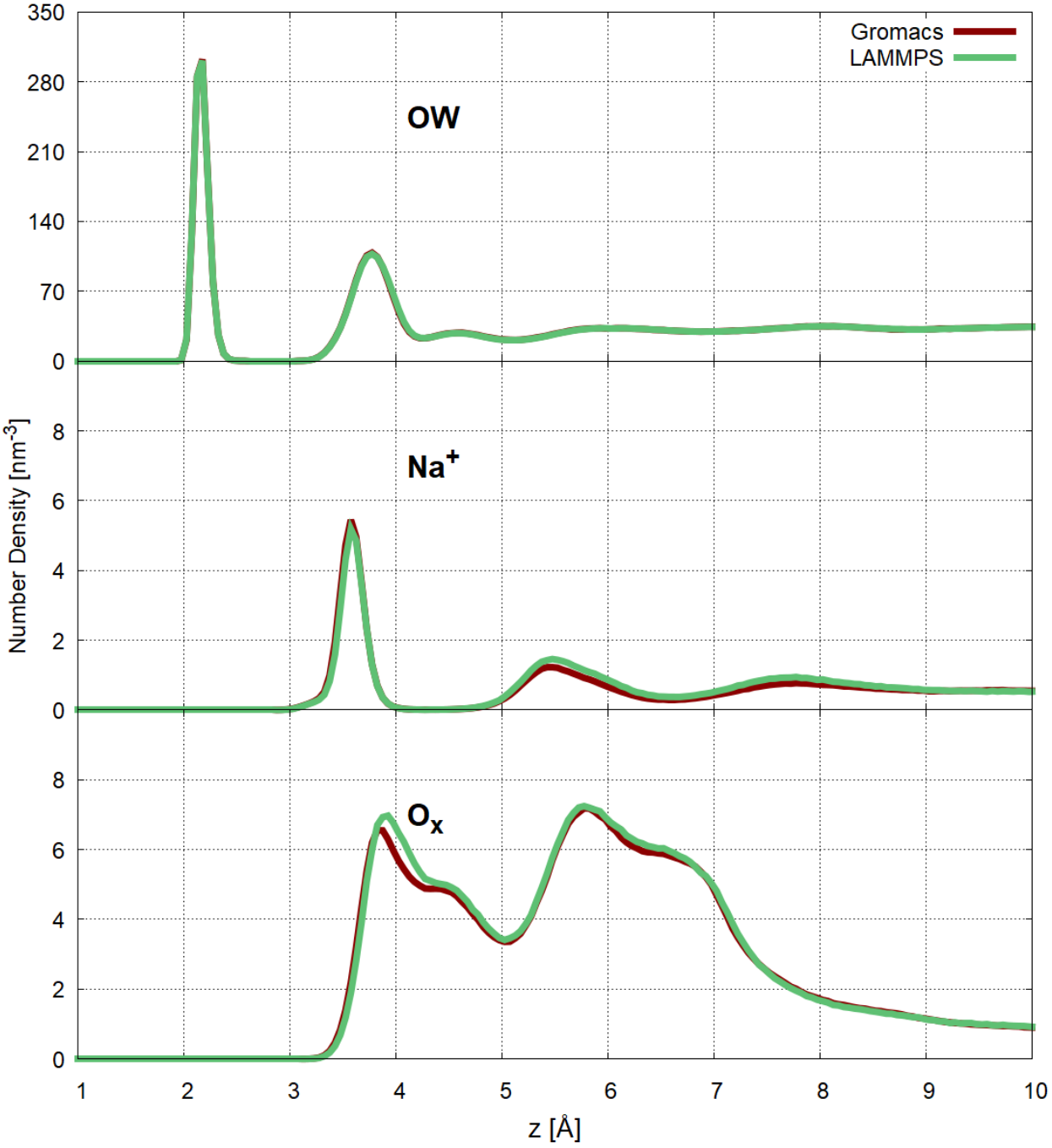

Figure S4. The same as Figure S3, but for 0.29 M $Na_2C_2O_4$ solution at the positively charged $(+0.104\,C/m^2)$ surface.

Table S3. Number of Species, Bulk Concentrations, and System Conditions of NEMD Simulations.

№ of set	surface	salt	model	surface charge density [C/m^2]	T [K]	# of cations	# of anions	# of water	bulk ionic concentration [M]	figures[a]
1	quartz	NaCl	ECC	0.00	298.15	24	24	3745	0.37	5A, 7A
				−0.03		32			0.40	
				−0.06		40			0.45	
				−0.12		56			0.48	5A, 5B, 7A
2	quartz	NaCl	ECC	0.00	298.15	16	16	3745	0.25	6, 7A, 7B, S5, S7, S8
				−0.03		24			0.28	6, 7A, 7B, S5, S7
				−0.06		32			0.31	
				−0.12		48			0.33	2–4, 6, 7A, 7B, S1, S5, S6, S7, S9
3	quartz	NaCl	ECC	0.00	298.15	8	8	3745	0.12	7A
				−0.03		16			0.16	
				−0.06		24			0.16	
				−0.12		36	4		0.14	
4	quartz	NaCl	ECC	0.00	298.15	4	4	3745	0.07	7A
				−0.03		8	-		0.05	
				−0.06		16			0.06	
				−0.12		32			0.07	
5	quartz	NaCl	full-quartz	0.00	298.15	16	16	3745	0.24	4
				−0.03		24			0.26	
				−0.06		32			0.30	
				−0.12		48			0.34	
5	quartz	RbCl	ECC	0.00	298.15	16	16	3745	0.26	6
				−0.03		24			0.30	
				−0.06		32			0.31	
				−0.12		44	12		0.29	

6	quartz	$CaCl_2$	ECC	0.00	298.15	8	16	3762	0.12	6
				−0.03		12			0.15	
				−0.06		16			0.14	
				−0.12		24			0.15	
7	quartz	$SrCl_2$	ECC	0.00	298.15	8	16	3762	0.13	6, S8
				−0.03		12			0.15	6
				−0.06		16			0.15	
				−0.12		24			0.15	6, S2
8	quartz	NaCl	ECC	0.00	373.15	16	16	3745	0.25	7B
				−0.03		24			0.29	
				−0.06		32			0.31	
				−0.12		48			0.33	7B, S9
9	rutile	NaCl	ECC	+0.1	298.15	11	29	2182	0.41	4, 5A
				0.0		17	17	2200	0.42	
				-0.1		34	16	2186	0.38	4, 5A, 5B
				-0.2		56	20	2164	0.45	4, 5A, S3
				-0.4		94	22	2128	0.39	4, 5A
10	rutile	NaCl	full-rutile	+0.1	298.15	11	29	2176	0.35	4
				0.0		18	18	2200	0.43	
				-0.1		38	20	2176	0.43	
				-0.2		56	20	2158	0.36	
				-0.4		94	22	2128	0.38	
11	rutile	$Na_2C_2O_4$	ECC	+0.2	298.15	24	24, 12[b]	2138	0.26[c]	8
				+0.1		30	24	2166	0.29	8, S4
				0.0		24	12	2204	0.28	8
				-0.1		54	18	2162	0.31	
12	rutile	$Na_2C_2O_4$	ECC	+0.2	298.15	5	17, 7[b]	2150	0.09[c]	8
				+0.1		6	12	2180	0.07	
				0.0		8	4	2210	0.10	

				-0.1		30	6	2180	0.13	
13	rutile	$Na_2C_2O_4$	ECC	+0.2	298.15	2	16, 5, 1[c]	2155	0.05 (0.02)[f]	8
				+0.1		3	10, 1[d]	2185	0.05 (0.03)[f]	
				0.0		3	1, 1[d]	2210	0.02 (0.03)[f]	
				-0.1		21	1, 1[d]	2190	0.03 (0.03)[f]	

[a]The last column shows in which figures data from a particular simulation were used. [b]Number of oxalate and hydrogenoxalate ions, respectively. [c]Number of oxalate, hydrogenoxalate, and chloride ions, respectively. [d]Number of oxalate and chloride ions, respectively. [e]Total salt concentration including both (hydrogen)oxalate contributions. [f]In parentheses, the concentration of background NaCl salt is given.

Table S4. Technical Settings of Molecular Dynamics Simulations Performed in This Work

setting	Gromacs	LAMMPS
timestep [fs]	2	
cut-off [Å]	12	
mixing rules for interatomic Lennard Jones interactions	Lorentz-Berthelot	
treatment of long-range electrostatic interactions	Particle Mesh Ewald (PME)	Particle-Particle Particle-Mesh (PPPM)
slab correction for long-range electrostatic interactions	EW3DC	
algorithm to constrain hydrogen bonds	LINCS	SHAKE

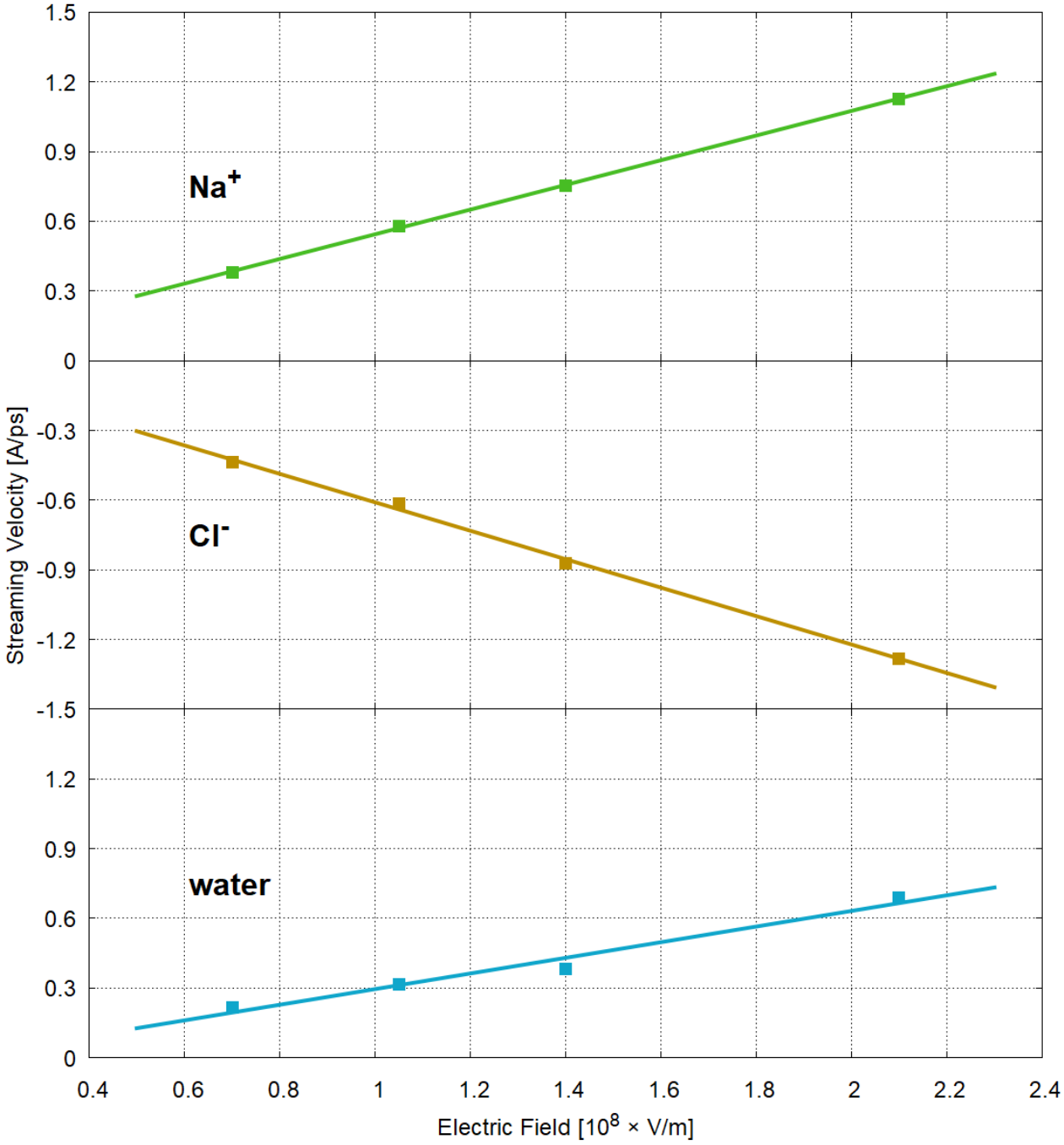

Figure S5. The dependence of streaming velocity as a function of applied electric field for sodium (top), chloride (middle), and water (bottom), for the system with 0.33 M NaCl solution at the most negatively charged (–0.12 C/m^2) quartz (101) surface. Note that for ions we report the velocity with respect to water, while the velocity of water is given relative to the surface. Consequently, the bulk mobility of ions

does not depend on interfacial structure, while the mobility of water is sensitive to changes at the interface. This explains small deviations in the linear fit for the water velocity, since a too strong electric field can disturb the ionic structure near the surface, and furthermore, affect the relative motion of liquid layers.

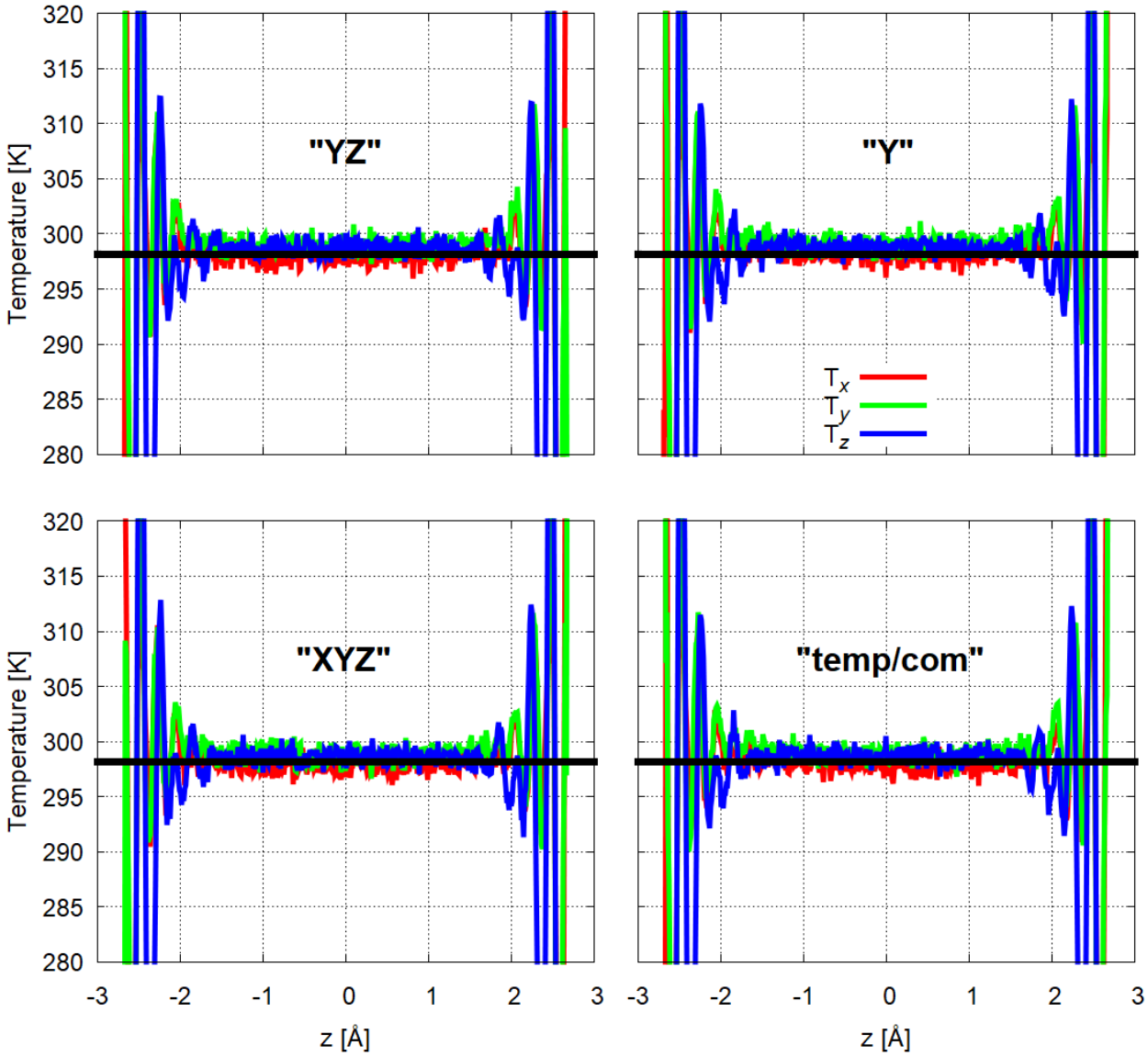

Figure S6. Temperature as a function of *z*-coordinate calculated separately from all velocity components of water and ions at the most negatively charged (−0.12 C/m^2) quartz (101) surface in 0.33 M NaCl solution, applying different thermostats. Zero is normalized to the center of the simulation box. Huge oscillations in the regions closest to the surfaces (around −2 and 2 Å) originate from few molecules in very low density domains and do not affect the results.

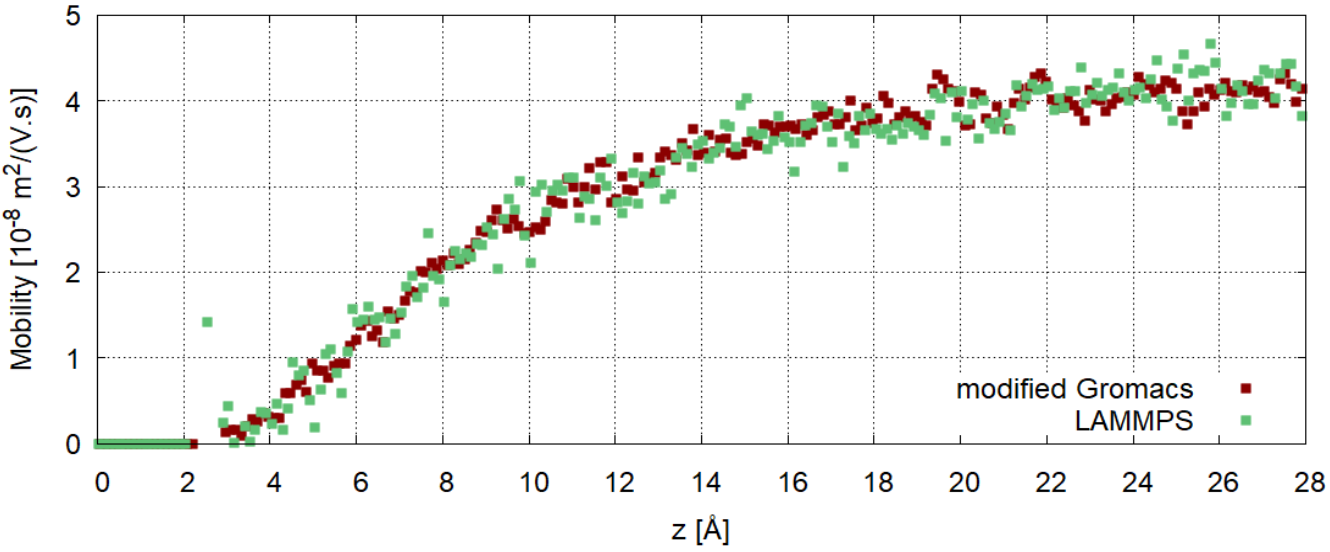

Figure S7. Comparison of distance-dependent mobilities of water at the most negatively charged ($-0.12\ C/m^2$) quartz (101) surface in NaCl solution calculated on-the-fly in LAMMPS simulation or post-processed from trajectories obtained in Gromacs with modified source code implementing the "YZ-thermostat" .

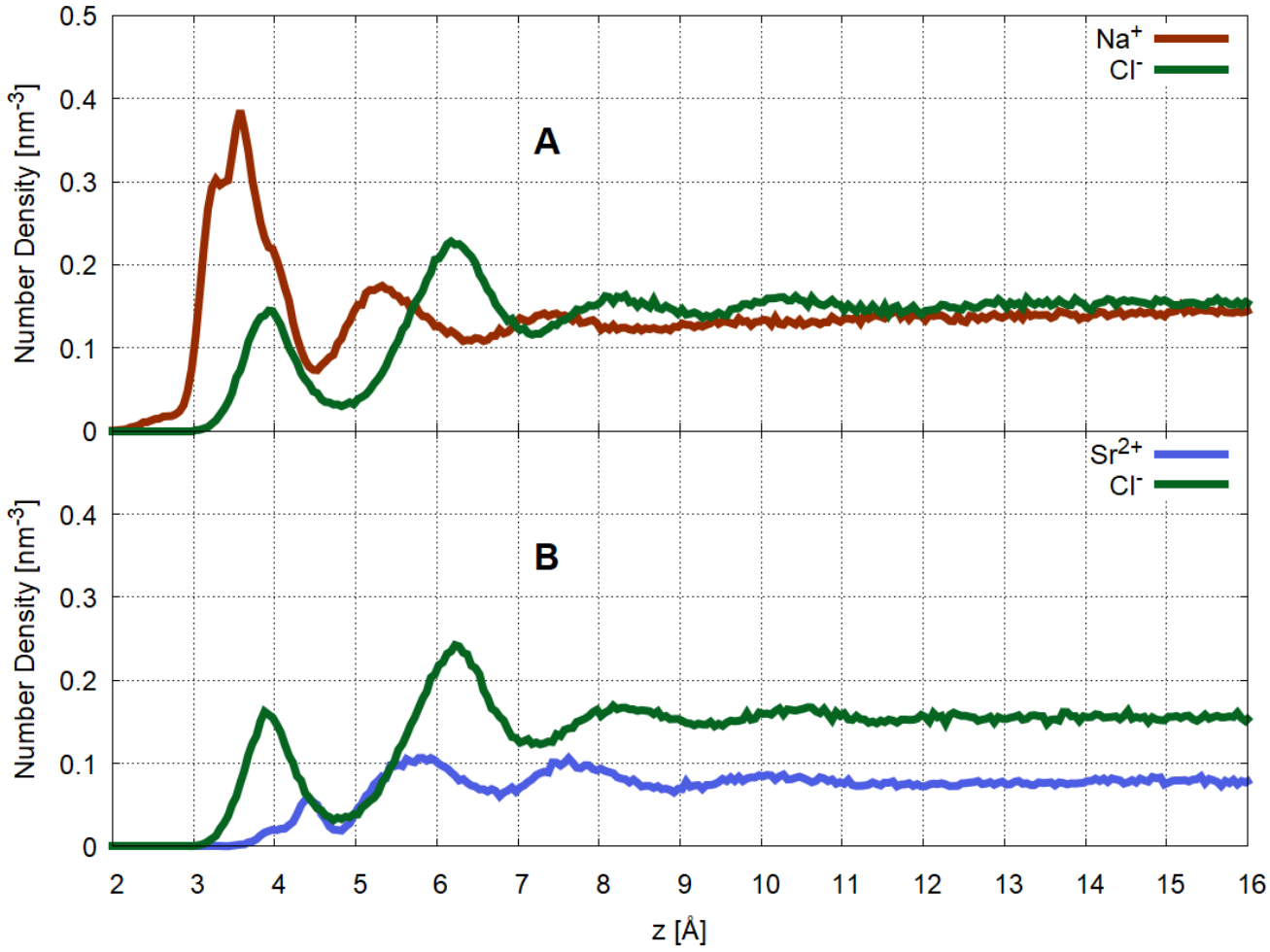

Figure S8. Axial number density profiles of ions at the neutral quartz (101) surface in (**A**) 0.25 M NaCl and (**B**) 0.13 M $SrCl_2$ solutions.

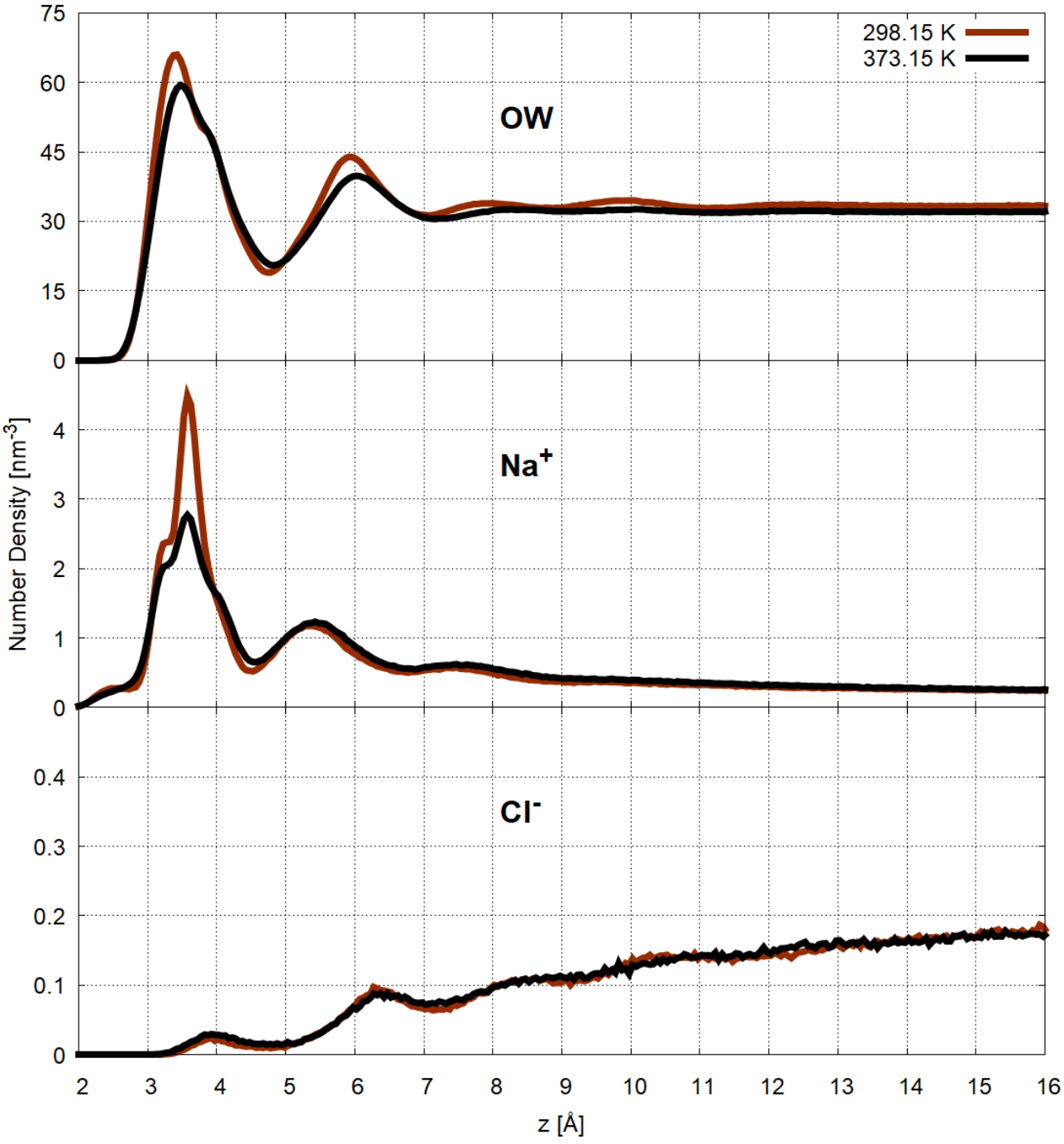

Figure S9. Axial number density profiles of water and ions of 0.33 M NaCl solution at the most negatively charged (–0.12 C/m^2) quartz (101) surface at different temperatures.

References

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