Electronic Supplementary Information for

Anomalous Cation Diffusion in Salt-doped Confined Bilayer Ice

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I. Ion diffusion in confined bilayer ice solidified by lateral pressures

We determined the lateral pressure of our system at different solution density ρ and found that the lateral pressure increases gradually with increasing ρ. The maximum lateral pressure at high ρ was a few hundreds of MPa. We performed another independent series of MD simulations of the confined system at different lateral pressures under the $NP_{xy}T$ ensemble (constant particle number, lateral pressure and temperature). The results showed that an enhanced ion diffusion (especially for Na^+) appears when the lateral pressure reaches tens or hundreds of MPa.

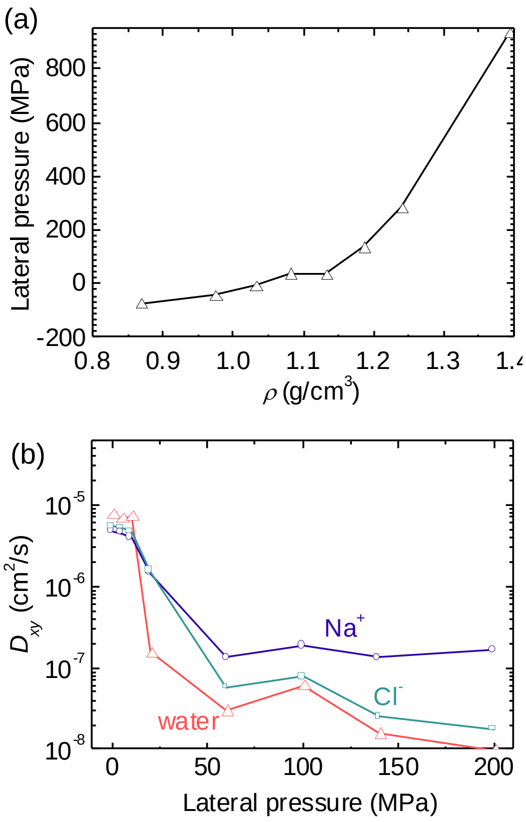

Figure S1 (a) Calculated lateral pressure as a function of ρ in the *NVT* simulations given in the main text. (b) Lateral diffusion coefficient D_{xy} for water and ions as a function of the lateral pressure applied in $NP_{xy}T$ simulations.

We also considered a larger system to explore the influence of surrounding bulk solution on the dynamics of the confined solution (Fig. S2). The confined solution in-between two parallel walls with a wall-wall separation h of 0.9 nm (same as that in the main text) was sandwiched by two water reservoirs containing 27702 water molecules. The length (L_z) and width (L_y) of the confining walls were 16.0 nm and 8.74 nm, respectively. Initially, Na^+ and Cl^- ions were randomly placed in the solution to obtain a salt concentration of 1 M. Following a 20ns *NPT* equilibration simulation at a lateral pressure P_{zz} of 0.1 MPa, P_{zz} was increased suddenly to 0.1 GPa and then a pressurization process with a step of 0.1 GPa per 1 ns was performed until 1 GPa, similar to a previous study[1]. Finally the system was equilibrated for another 100 ns at 1 GPa, with the last 40 ns used for determining diffusion coefficients. Other simulation details are the same as those described in the manuscript. During this process, Na^+ was found to diffuse with a rate of 3.98×10^{-8} cm^2/s, having a diffusion enhancement factor of ~8.3. The final concentrations of the confined solution and the bulk solution became 0.55 M and 1.07 M, respectively. These results suggest that the nanochannel, even when connecting to a surrounding bulk solution, can accommodate certain amount of ions (depending on ion size, channel dimension, surface properties, lateral pressure and solution concentration). Taking into account recent exciting experiments[2] on ion transport though nanochannels with a height of 0.67 nm, we expect that it is feasible to reproduce the present simulation results in future experiments.

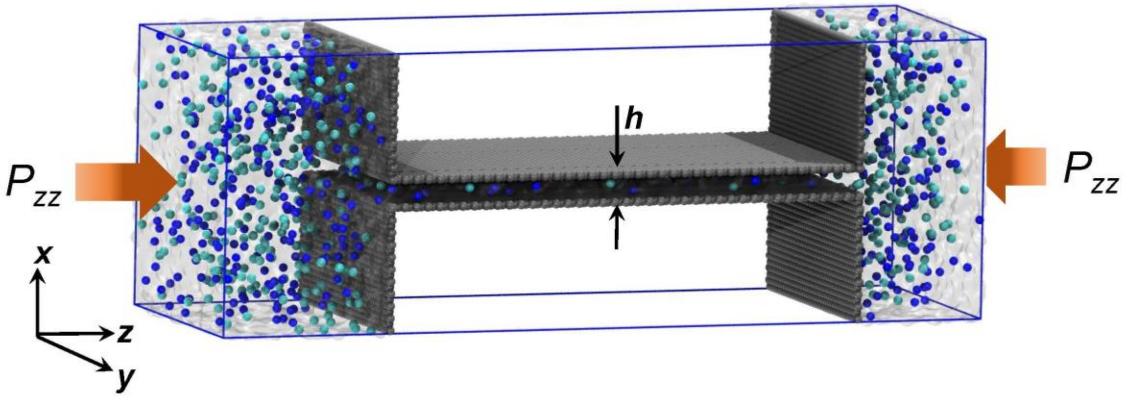

Figure S2 Simulation system of a confined 1 M NaCl solution connecting to a surrounding bulk solution. The simulation box is marked by the blue rectangle. A lateral pressure P_{zz} was applied to the system to induce the solidification of the confined solution.

II. Snapshots of confined salt solutions in liquid and solid-like states

The snapshots of the simulation system of a bilayer liquid and a bilayer water are shown in Figs. S1a and S1b, respectively. As expected, we found a disordered arrangement of the oxygen atoms of water molecules in the bilayer water (Fig. S1a) and a well ordered hydrogen-bonding network in the bilayer ice (Fig. S1b).

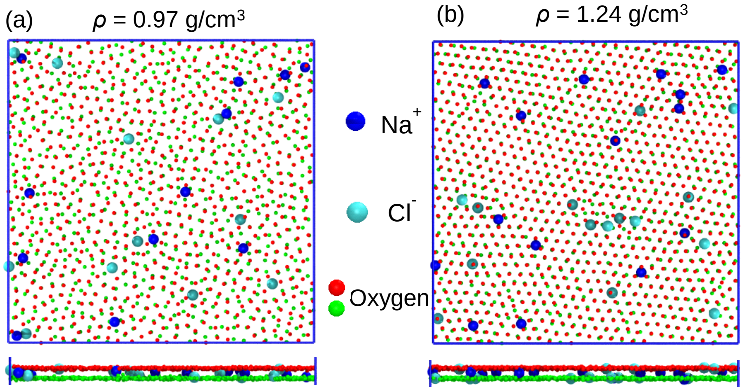

Figure S3 Instantaneous snapshots from MD simulations showing the top (top panel) and side (bottom panel) views of a low-density bilayer liquid water (a) and a high-density bilayer ice crystal (b) containing Na^+ and Cl^- ions. Oxygen atoms of water molecules in the upper and lower water planes are shown as red and green spheres, respectively. For clarity, hydrogen atoms of water are not shown.

III. Determining whether ions can diffuse in bulk ice

We carried out additional MD simulations on an ion-containing bulk ice to explore the diffusion of ions along the ice lattice. The initial configuration of ice Ih was created by the GenIce program.[3] Na^+ and Cl^- ions were introduced by randomly replacing a few water molecules to achieve a NaCl concentration of 0.5 M (Fig. S3a). The final system contains 3394 water molecules, 31 Na^+ and 31 Cl^- ions, and measures 4.69 nm × 4.41 nm × 5.42 nm in dimension. The simulation was performed at 260 K and 1 atm. Other parameters such as the L-J potential parameters were identical to those used for the confined system described in the main text. During the initial ~300 ns relaxation simulation, a few ions were found to be able to move inside the ice to form ion pairs (Figure S3b, top left and top right panels). After equilibration (e.g, ≥ 500 ns), we found that ions rarely hop inside the bulk ice (Figure S3b, bottom left and bottom right panels). The determined diffusion coefficients for water, Na^+ and Cl^- during the equilibration period are 7.5×10^{-10}, 8.0×10^{-10} and 4.0×10^{-10} cm^2/s, respectively. We also considered an ice system with a low concertation of 16 mM, which contains 3454 water molecules, a single Na^+ ion and a single Cl^- ion. As expected, we found no hopping of these two ions during a 1000 ns MD simulation. These results suggest that no significant enhancement in ion diffusion occurs in the bulk ice Ih, in agreement with a previous study.[4]

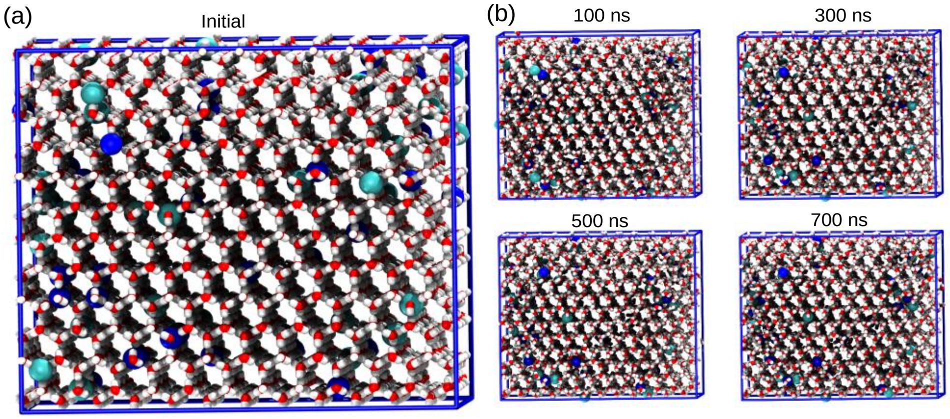

Figure S4 Ion diffusion in bulk ice Ih. (a) Starting configuration of a bulk ice Ih containing Na^+ and Cl^- ions. (b) Evolution of the system in a 700 ns MD simulation.

Table S1. Lennard-Jones parameters (σ and ε) for all components in the system

Particles	σ (nm)	ε (kJ/mol)
wall atoms	0.320	1.0315
water oxygen	0.312	0.6694
water hydrogen[a]	0	0
Cl-	0.442	0.4928
Li^+	0.213	0.0765
Na^+	0.333	0.0116
K^+	0.493	0.0014
Rb^+	0.562	7.15×10^{-4}
Cs^+	0.672	3.39×10^{-4}

[a] A specialized set of L-J parameters was used to describe the interaction between the hydrogen atoms of water and the wall atoms: $\sigma_{\text{wall-H}}$ = 0.284 nm $\varepsilon_{\text{wall-H}}$ = 0.415 kJ/mol, as done in earlier studies[5-6].

Table S2 Ion diffusion in simulations with a 10-fold lower $\varepsilon_{\text{wall-wall}}$ or with a TIP4P water model[a]

Diffusion coefficient	TIP5P $\varepsilon_{\text{wall-wall}}$ = 1.03 kJ/mol[b]	TIP5P $\varepsilon_{\text{wall-wall}}$ = 0.103 kJ/mol	TIP4P $\varepsilon_{\text{wall-wall}}$ = 1.03 kJ/mol
D_{water} (cm^2/s)	9.357×10^{-10}	6.800×10^{-9}	6.172×10^{-9}
$D_{\text{Na+}}$ (cm^2/s)	4.194×10^{-8}	1.391×10^{-7}	4.013×10^{-7}
$D_{\text{ion}}/D_{\text{water}}$	44.8	20.5	65

[a] The density of salt solutions in all simulations is 1.24 g/cm^3.

[b] This column lists parameters and associated data shown in the main text.

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