

Supporting Information

Molecular Dynamics Simulations of Nanoscale Friction on Illite Clay: Effects of Solvent Salt Ions and Electric Double Layer

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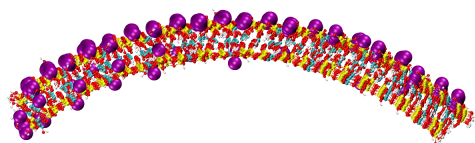
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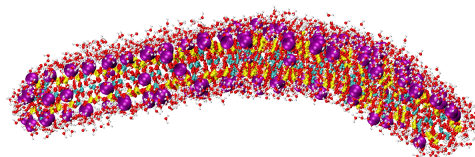
S1. Mechanical stability evaluation of one-layer illite platelet

Unlike swelling T-O-T clays such as montmorillonite, where charge substitutions in the octahedral layer lead to weak surface charges and mobile counter ions, illite exhibits strong surface charges due to Si^{4+} substitutions by Al^{3+} in the tetrahedral layers, causing K^+ counter ions to remain tightly bound to the surface, which is crucial for its stability and surface properties. To evaluate the impact of ion distribution on stability, we compared the mechanical stability of two one-layer illite platelets: one with K^+ counter ions exclusively on one side (Platelet 1) and the other with K^+ ions distributed equally on both sides (Platelet 2) in vacuum and partially solvated environments. In both vacuum and 20 wt. % water conditions, Platelet 1 exhibited significant distortion (Figure S1) due to the initial asymmetric placement of K^+ counter ions, which remained predominantly on one side, leaving the opposite side with a strong net negative charge. This imbalance caused the positively charged side to move to cover and neutralize the negatively charged side, thereby causing irreversible deformation, manifested by the insertion of K^+ ions into the enlarged Si-O gaps on the upper surface of the deformed illite platelet. This deformation is consistent with the finding by Jia et al., 2023¹. In contrast, Platelet 2 remained flat and stable throughout the entire 30 ns production run (Figure S1). This illustrates the importance of a well-balanced distribution of K^+ ions.

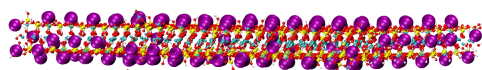
(a)



(b)



(c)



(d)

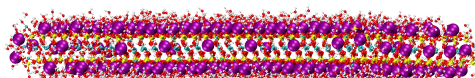


Figure S1. A one-layer illite platelet with K^+ on one side (Platelet 1, a and b) and a one-layer illite platelet with equivalent K^+ on two sides (Platelet 2, c and d) in vacuum and 20 wt. % water after 30 ns production MD simulations.

S2. Non-bonded and bonded parameters for original ClayFF atoms

ClayFF was employed to describe both nonbonded interactions (Table S1) and bonded interactions (Table S2 and S3) among the original ClayFF atoms². The parameters for nonbonded interactions of Mg^{2+} are taken from Åqvist^{3,4}.

Table S1. Non-bonded parameters for original ClayFF atoms.

Atom name	Atom number	Mass	Charge	$\sigma(\text{nm})$	$\epsilon(\text{kJ/mol})$	Description
hw	1	1.008	0.4238	0.0	0.0	Water hydrogen
ho	1	1.008	0.4250	0.0	0.0	Hydroxyl hydrogen
ow	8	16.000	-0.8476	0.316554	0.650194	Water oxygen
oh	8	16.000	-0.9500	0.316554	0.650194	Hydroxyl oxygen
ob	8	16.000	-1.0500	0.316554	0.650194	Bridging oxygen
obts	8	16.000	-1.1688	0.316554	0.650194	Bridging oxygen with tetrahedral substitution
ohs	8	16.000	-1.0808	0.316554	0.650194	Hydroxyl oxygen with substitution
st	14	28.086	2.1000	0.330203	7.701E-06	Tetrahedral silicon
ao	13	26.982	1.5750	0.427124	5.564E-06	Octahedral aluminum
at	13	26.982	1.5750	0.330203	7.701E-06	Tetrahedral aluminum
na	11	22.990	1	0.235001	0.544338	Aqueous sodium ion
k	19	39.098	1	0.333400	0.418400	Aqueous potassium ion
cs	55	132.905	1	0.383104	0.418400	Aqueous cesium ion
mg	12	24.305	2	0.16444	3.663385	Aqueous magnesium ion
ca	20	40.078	2	0.287199	0.418400	Aqueous calcium ion
cl	17	35.453	-1	0.439997	0.418818	Aqueous chloride ion

Table S2. Bond parameters for OH bonds with different types of O atoms

Bond parameter	Bond length r in nm	Harmonic force constant k_r in $\text{kJ}/(\text{mol}\cdot\text{nm}^2)$
O-H bond in water	0.1	463700
O-H bond in hydroxyl group	0.1	463700
O-H bond with bridging oxygen with tetrahedral substitution	0.1	463700

Table S3. Angle parameters for H-O-H and M-O-H angles

Angle parameter	Angle q in degree	Harmonic force constant k_q in $\text{kJ}/(\text{mol}\cdot\text{rad}^2)$
H-O-H	109.47	383.00
M-O-H (M: metal ions)	109.47	251.04

S3. Friction force traces on the two-layer illite platelet in pure water and 0.62 M different salt solutions under a 10 nN normal force.

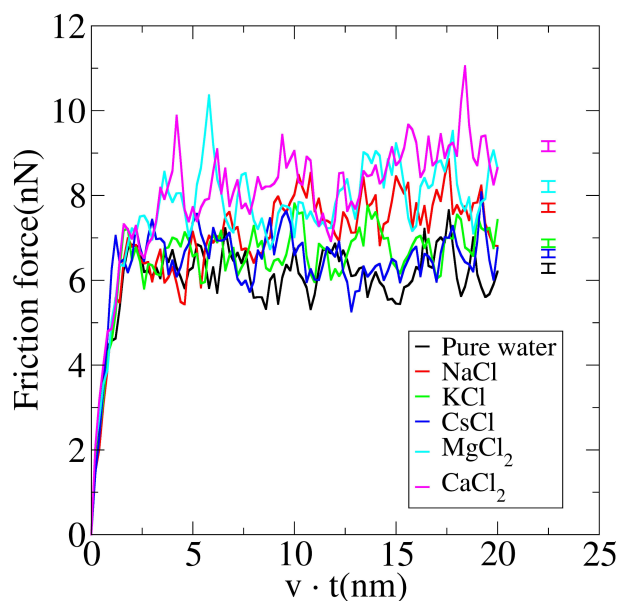


Figure S2. Friction force traces on the two-layer illite platelet in pure water and 0.62 M different salt solutions under a 10 nN normal force. The average friction forces of the last 5 nm of sliding, along with their uncertainties estimated using the block averaging method, are shown to the right of the friction force traces.

S4. Complete density profiles of ions adjacent to the illite clay surface in NaCl, KCl, CsCl, MgCl₂ and CaCl₂ solutions

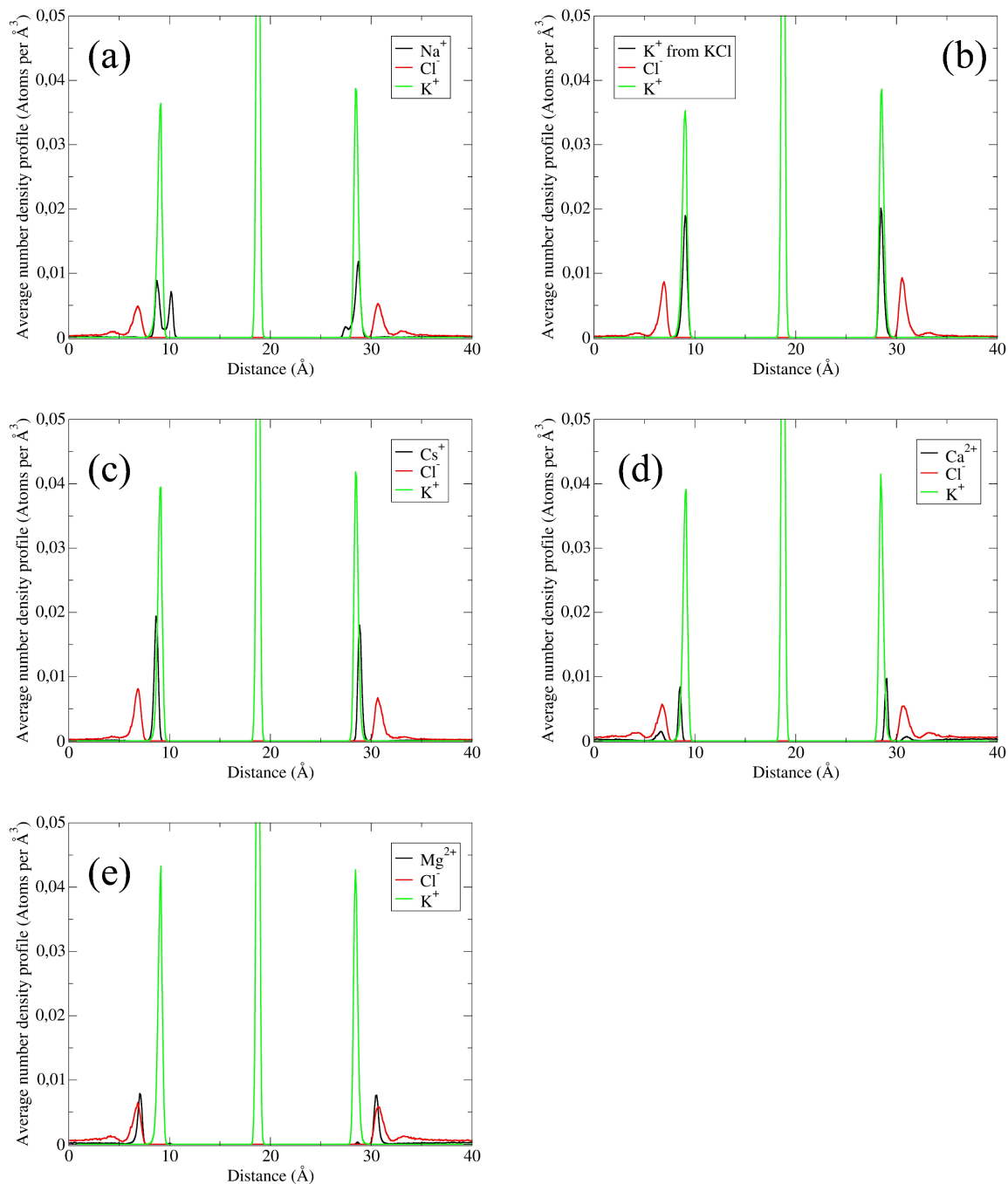


Figure S3. Density profiles of different ions outside the illite clay surface in (a) NaCl, (b) KCl, (c) CsCl, (d) MgCl₂ and (e) CaCl₂ solutions. The middle green peak, representing interlayer K⁺, is truncated due to its excessive height, which obscures the other peaks.

S5. Overall diffusion coefficients of cations and water in different salt solutions

The overall diffusion coefficients in the XY, Z and XYZ dimensions were obtained by fitting the average mean square displacement (MSD) in different time ranges. For cations, D_{xy} and D_{xyz} were fitted using average MSD data in the time range of 1 to 10 ns while D_z was fitted from 0.5 to 2.5 ns, as the average MSD curve in this range exhibited better linearity. For water molecules, all diffusion coefficients were obtained from the average MSD from 0.5 to 2.5 ns due to the computational cost associated with their large number. Corresponding average MSD plots are provided in Figure S5 and S6.

The results for D_z and D_{xyz} are shown in Figure S4. In all cases, the average values of D_z and D_{xyz} are consistently smaller than the corresponding D_{xy} , a behavior attributed to the electric field generated by the negatively charged illite surface, which suppresses diffusion in the surface-normal direction. Moreover, the average D_{xyz} of divalent cations and water in divalent salt solutions are lower than those of monovalent cations, similar to the trend observed for D_{xy} as discussed in the main text. This consistent pattern highlights that the reduced diffusion of cations and hydration shells in divalent systems impedes the mobility of an illite platelet sliding across an infinite illite surface.

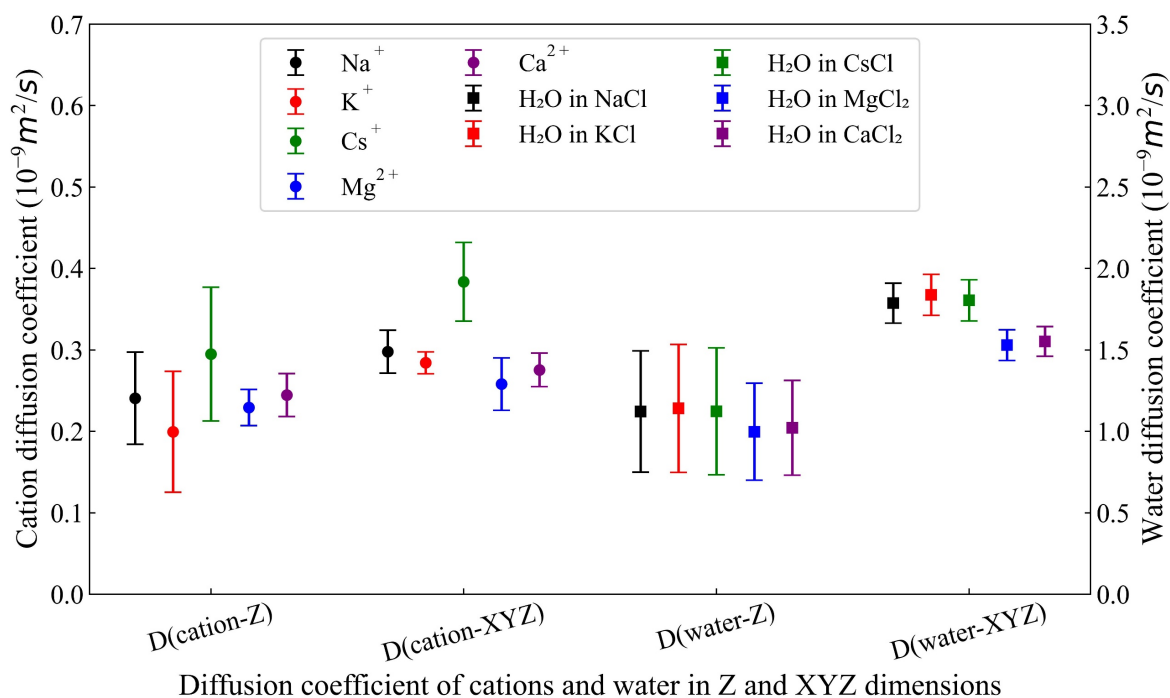


Figure S4. Overall diffusion coefficients of cations and water in different salt solutions in the Z and XYZ dimensions.

S6. Average mean square displacement (MSD) plots of different cations in the XY, Z and XYZ dimensions over 30 ns simulations

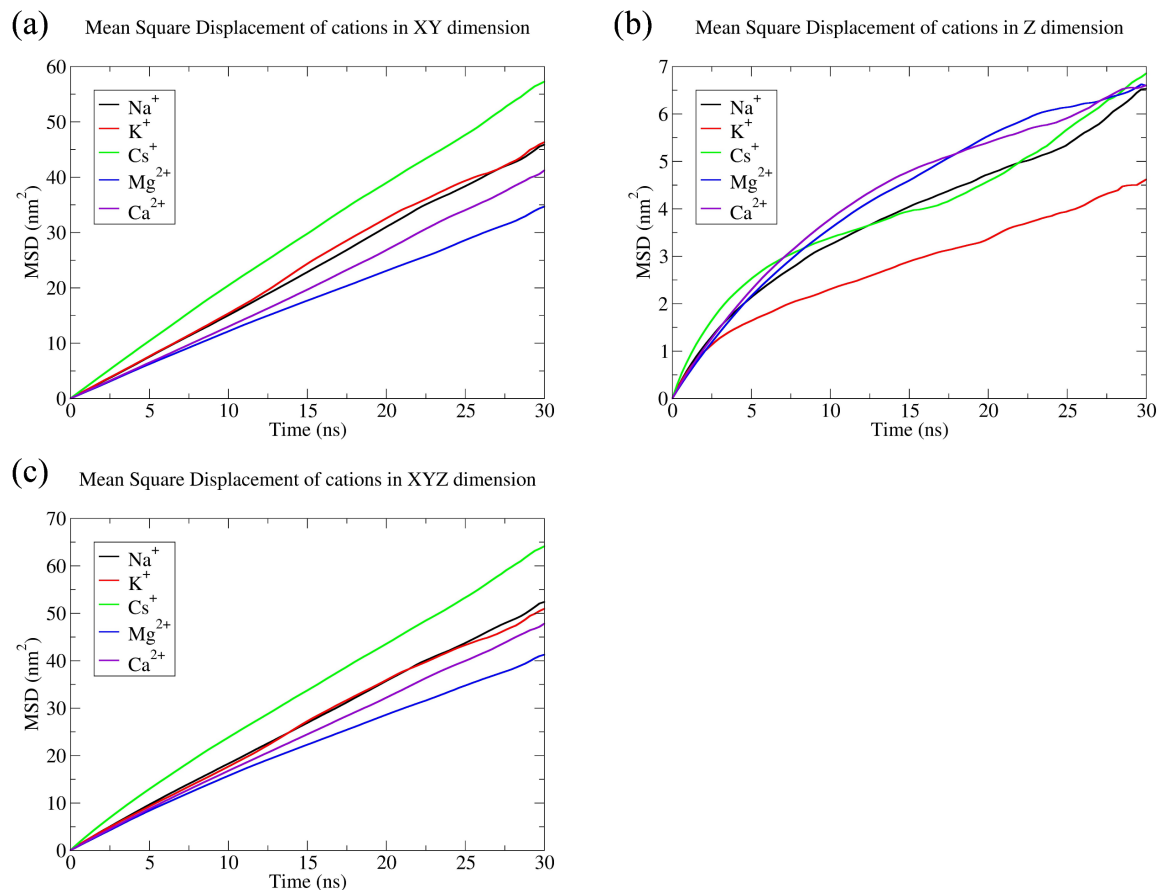


Figure S5. Mean square displacement (MSD) of Na^+ , K^+ , Cs^+ , Mg^{2+} and Ca^{2+} cations in (a) XY, (b) Z and (c) XYZ dimensions.

S7. Average mean square displacement (MSD) plots of water molecules in different salt-containing systems in the XY, Z and XYZ dimensions over 30 ns simulations

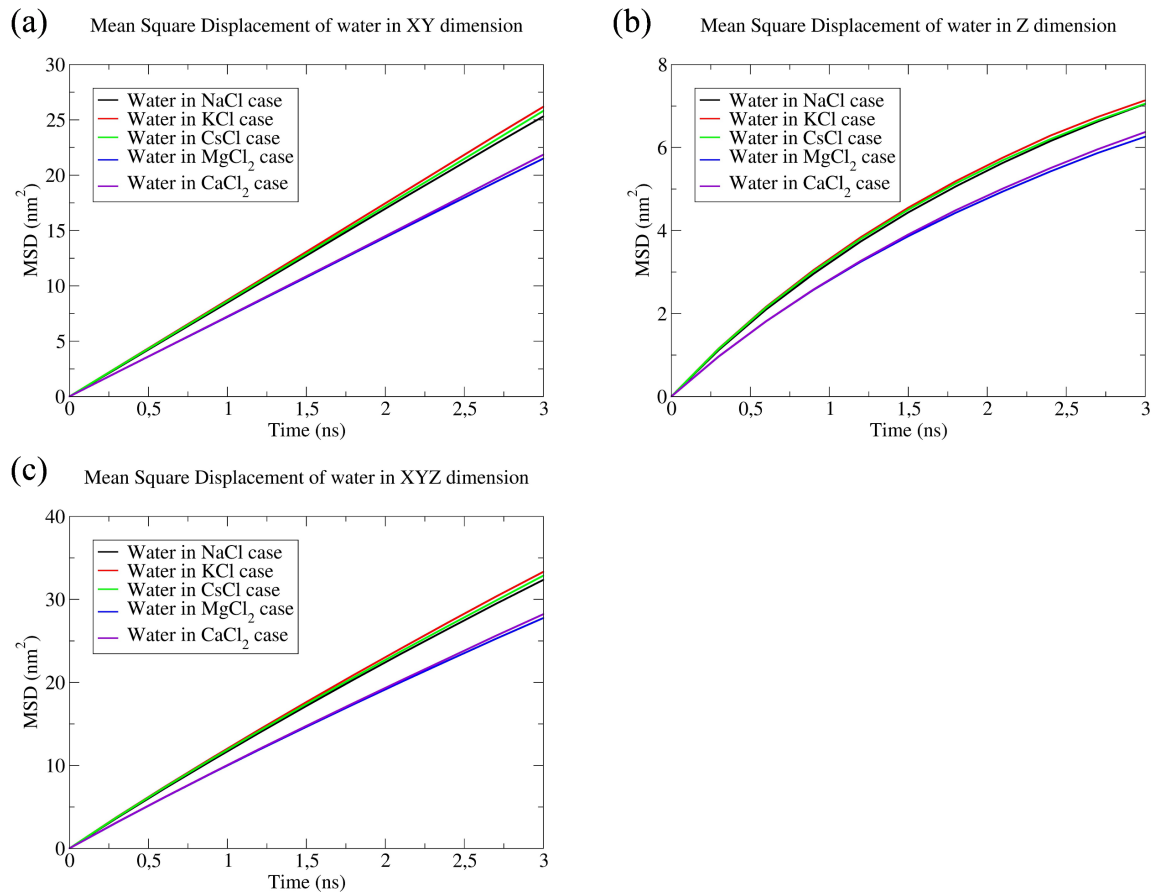


Figure S6. Mean square displacement (MSD) of water in NaCl, KCl, CsCl, MgCl₂ and CaCl₂ in (a) XY, (b) Z and (c) XYZ dimensions.

References

- 1 Jia, J., Wu, D., Lin, J. & Jiang, X. Molecular dynamics simulation of illite: From particle associations to hydration properties. *Applied Clay Science* **234**, 106850 (2023). <https://doi.org/https://doi.org/10.1016/j.clay.2023.106850>
- 2 Cygan, R. T., Liang, J.-J. & Kalinichev, A. G. Molecular Models of Hydroxide, Oxyhydroxide, and Clay Phases and the Development of a General Force Field. *The Journal of Physical Chemistry B* **108**, 1255-1266 (2004). <https://doi.org/10.1021/jp0363287>
- 3 Åqvist, J. Ion-water interaction potentials derived from free energy perturbation simulations. *The Journal of Physical Chemistry* **94**, 8021-8024 (1990). <https://doi.org/10.1021/j100384a009>
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