Supplementary Information

A hydrogen bond-modulated soft nanoscale water channel for ion transport through liquid-liquid interfaces

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1. Model and methods

1.1 Force fields

1.1.1 TIP3P water model

With the development of computer simulations, developing a water model which can accurately describe the properties of water under different conditions is essential. The multiple possible approximation (*e.g.*, quantum *vs.* classical, flexible *vs.* rigid) generates many computational models for water [1-8]. Since the existing water potential models are often developed based on the specific conditions, it is hard to choose a water model which is universal for all circumstances involving water. In this paper, we use the TIP3P water model [9] with a long-range Coulombic solver to simulate water molecules, which can accurately reproduce the density and structures of water molecules at the interfaces [10, 11]. Meanwhile, the consistence of simulated interfacial tensions with experimental results shows that the combination of this water model with decane model is nice. In theTIP3P model, each atom of water molecule is assigned with charge and LJ parameters. Additionally, the O-H bond and the H-O-H angle both are described by the *harmonic* style. The parameters of water molecules in our simulations are identical with those parameters reported by Price *et al.* [9] More detailed parameters are given in Table S1.

1.1.2 OPLS All-Atom force field

In this study, we employ the OPLS All-Atom (OPLS-AA) force field [12] to depict the interactions between decane molecules. Our group has proved its ability to reproduce the thermodynamic and interfacial properties of decane phase [10, 11]. The OPLS-AA force field is made up of the non-bonded interactions, bond stretching, angle bending and torsion interactions:

$$E = E_{ab} + E_{bond} + E_{angle} + E(\phi)$$
(S1)

The non-bonded interaction contains the standard 12/6 Lennard-Jones and Coulombic pairwise interactions, given by

$$E_{ab} = 4\varepsilon \left[\left(\frac{\sigma}{r_{ab}} \right)^{12} - \left(\frac{\sigma}{r_{ab}} \right)^6 \right] + \frac{Cq_a q_b}{\chi r_{ab}} \quad (r_{ab} < r_{cut})$$
(S2)

where ε is the depth of potential well, σ is the distance between atoms when the potential is zero, r_{cut} is the cutoff radius, C is a constant of energy-conversion, q_a and q_b are the charges of atom a and b, χ is the dielectric constant. When r_{ab} is greater than r_{cut} , we compute the long-range Coulombic forces using the Particle-Particle Particle-Mesh (PPPM) method. Potential parameters between different atoms are obtained using the Lorentz-Berthelot combining rule:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \qquad \varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$$
(S3)

The bond stretching and angle bending in molecules are described by the *harmonic* style, as

$$E_{bond} = K_{bond} \left(r_{ab} - r_0 \right)^2 \tag{S4}$$

$$E_{angle} = K_{angle} (\theta - \theta_0)^2$$
(S5)

where K_{bond} and K_{angle} are the bond and angle coefficients related to the energy, r_0 is the equilibrium bond length, θ_0 is the equilibrium bond angle.

The last term of the OPLS-AA force field is the torsion interaction described by the *opls* dihedral style, as follows:

$$E(\phi) = \frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)]$$
(S6)

where V_1 , V_2 and V_3 are the dihedral coefficients. The parameters of OPLS-AA force field for decane molecules are listed in Table S1.

1.1.3 Force field parameters for ions

The potential parameters for sodium and chloride ions which we used are the parameters reported by Lyubartsev *et al.* [13], which are proved to be accurate and effective for simulating the structures and dynamics of sodium/chloride ions in water phase. The detailed parameters for ions can be found in Table S1.

Water (TIP3P model) [1, 9]			
L-J potential parameters	σ (Å)	ε (10 ⁻³ eV)	charge (e)
0	3.188	4.423	-0.830
Н	0	0	0.415
Bond potential parameters	$K_{\text{bond}} (10^2 \text{ eV})$	$K_{\text{bond}} \left(10^2 \text{eV} \cdot \text{\AA}^{-2} \right) \qquad r_0 \left(\text{\AA} \right)$	
О-Н	19.514	0.9572	
Angle potential parameters	K_{angle} (eV·rac	$K_{\text{angle}} (\text{eV} \cdot \text{rad}^{-2}) \qquad \qquad \theta_0 (^{\circ})$	
Н-О-Н	2.385		104.52
Decane (OPLS-AA model) [12]			
L-J potential parameters	σ (Å)	$\varepsilon (10^{-3} \text{ eV})$	charge (e)
C, RCH ₃	3.500	2.862	-0.180
$C, R_2 CH_2$	3.500	2.862	-0.120
H	2.500	1.301	0.060
Bond potential parameters	$K_{\text{bond}} (10^2 \text{ eV})$	r_0 (Å) r_0 (Å)	
C-C	13.454	13.454 1.526	
C-H	14.365	1.090	
Angle potential parameters	K_{angle} (eV·rac	$K_{\text{angle}} (\text{eV} \cdot \text{rad}^{-2}) \qquad \qquad \theta_0 (^{\circ})$	
H-C-H	1.518	104.52	
H-C-C	1.518	109.50	
C-C-C	1.736	109.50	
Dihedral potential parameters	$V_1 (\mathrm{eV})$	$V_2 (\mathrm{eV})$	V_3 (eV)
C-C-C-C	0.0755	-0.0068	0.0121
H-C-C-C	0	0	0.0159
Н-С-С-Н	0	0	0.0138
Ions [13]			
L-J potential parameters	$\sigma(\text{\AA})$	$\varepsilon (10^{-3} \text{ eV})$	charge (e)
Na^+	2.586	3.706	1
Cl ⁻	4.4015	1.740	-1

Table S1. Force field parameters for water, decane and ions in our simulations.

1.2 Simulation details

In this paper, the Nose-Hoover style non-Hamiltonian equations of motion [14, 15] are adopted to generate positions and velocities of atoms in the system from the NPT ensembles. The schemes of time integration follow the time-reversible measure-preserving Verlet and rRESPA integrators raised by Tuckerman *et al.* [16] The parameter T_{damp} for temperature relaxation is 0.2 K, while the P_{damp} determining the time scale for pressure relaxation is a value of 1.0 ps. It is generally accepted that a good choice of P_{damp} is about 1000 timesteps. A small value of P_{damp} means the long equilibrium time for pressure. To reduce the storage requirements for data analysis, we output the coordinates of ions and molecules every 10000 timesteps, *i.e.*, 1.0 ps.

Due to the charged properties of ions, the long-range Coulombic interactions play an important role in the simulations. Thus, we adopt the PPPM solver to calculate the long-range Coulombic force. In this method, 3d FFTs are used to solve Poisson's equation on the mesh mapping atom charge, then interpolates electric fields on the mesh points back to atoms. The PPPM is a faster solver because it scales as Nlog(N) where N is the total atom numbers, which is far less than the Ewald summation (N^(3/2)). In our study, the accuracy of PPPM is 1.0×10^{-3} eV/Å and the grid of the mesh is $10 \times 10 \times 30$, which have been proven to be reasonable [11].

1.3 Model validation

Our group has demonstrated the reasonableness and reliability of the simulation models used in this study by comparing the simulated densities, interfacial thickness, interfacial tension (IFT), diffusion coefficients of ions with the experimental or theoretical results under different temperature and pressure conditions [10, 11]. The comparison showed that these potentials can accurately reproduce the thermodynamic and interfacial properties of water, decane and ions, such as the density, diffusion coefficients and interfacial tension. Moreover, effects of electric field on the simulation models were also discussed by analyzing the variation of energies with external forces (E). The results showed that the electric field does not create an unphysical system and the effects of electric field on the simulation results can be ignored [17]. Besides, the extensive applications of the potential in other literatures [18-21] also validated the reliability and accuracy of these potential models to reproduce the oil-water-ions systems.

We also compare the conformation or orientation of water molecules at interface with or without an electric field (E = 0.1 eV/Å) for NaCl concentration c = 0.1 mol/L (see Figure S1). The electric field has a little effect on the orientation of water molecules at interfaces. The slight difference is due to the stronger aggregation of ions at interface with an electric field, which slightly disturbs the orientation of water at interfaces. Therefore, we believe that the external electric field is sufficiently small and thus can be negligible.



Figure S1. The orientation of water molecules at interfaces for NaCl concentration c = 0.1 mol/L with or without the electric field (E = 0.1 eV/Å). Angle α represents the angle between the dipole moment of water molecule and the normal direction of interface.

2. Transport velocity of ions

We know from Figure 3(a) that the persistence time of water channel, which reflects the stability of water channel, increases with ionic concentration. Apparently, the stability of water channel has an important influence on the dynamics of ions, such as transport velocity. Considering the fluctuations of water channel formation, we calculate the time-averaged transport velocity of ion only during the persistence time of water channel. Due to the fluctuations of ions transport velocity along the axis direction of water channel, as shown in Figure S2. We can find that the number density distribution of ions with ionic velocity follows normal distributions. Due to the applied electric field, sodium and chloride ions are opposite. Here, we focus on the magnitude of ionic velocity. By fitting these curves with the normal distribution equation, we can obtain the time-averaged transport velocities of ions as a function of ions as a function are opposite. Here, we focus on the magnitude of ionic velocity. By fitting these curves with the normal distribution equation, we can obtain the time-averaged transport velocities of ions as a function of ionic concentration, as shown in Figure 3(b).



Figure S2. The number density distribution of ions as a function of ion velocity along *z*-direction under the conditions of NaCl concentration c = 0.50 mol/L and $E = 1.0 \times 10^{-1} \text{ V/Å}$.

3. Number of hydrogen bonds

Figure S3 shows the total number of H-bonds and the number of H-bonds per water molecule in the water channel under different ionic concentrations. We can find that with ionic concentration rising, the total number of H-bonds increases while the number of Hbonds per water molecule decreases slightly. The increase of total number of H-bonds in the water channel with ionic concentration is due to the increase of channel diameter, which carries more water molecules. For the slight decrease of number of H-bonds per water molecule with ionic concentration increasing, we attribute to the layered ordering structures of water molecules near channel surface induced by the confinement of channel sizes. The layered ordering structures of water molecules break the tetrahedral hydrogen bonding network between water molecules in bulk phase, thus slightly reducing the number of H-bonds per water molecule.

In addition, we compare the number of H-bonds per water molecule (n_{HB}) in the water channel with that in carbon nanotubes. As shown in Figure S3, the number of H-bonds per water molecule in the water channel decreases slightly from 1.2 to 0.8 with ionic concentration increasing (i.e., the diameter of water channel increases from 1.6 nm to 2.3 nm). The number of H-bonds per water molecule in the water channel is consistent with that inside carbon nanotubes (n_{HB} =0.87) [22]. However, the variation trend of n_{HB} in the water channel is different from that in carbon nanotubes, which shows an increasing dependence on the diameter of nanotubes [23]. This difference may be due to the fluctuation of water channel induced by the ions transport, which needs to be further investigated.



Figure S3. The number of H-bonds in the water channel as a function of NaCl concentration under $E = 1.0 \times 10^{-1} \text{ V/Å}$.

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