Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Slow Dynamics of Water Confined in Newton Black Films

Supplementary Information

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A. Comparison of water dynamics in NVT and NVE ensembles

Dynamics of water in the films simulated in canonical (NVT) and microcanonical (NVE) ensembles are compared, as to reveal the possible influence of the velocity rescaling thermostat[1] to water dynamics. Fig. S1 displays $C_{\mu}(t)$ and MSD$_{xy}$ (t) of water from different layers of films (Fig. 3) with thicknesses 1.1 nm and 2.1 nm. It is clear that there are only little differences in water dynamics between the two ensembles. So the velocity rescaling thermostat hardly influences water dynamics. As the NVT simulations were performed for much longer time, more reliable results are expected. So in the other parts of this article, unless specified we only report results derived in the NVT runs.

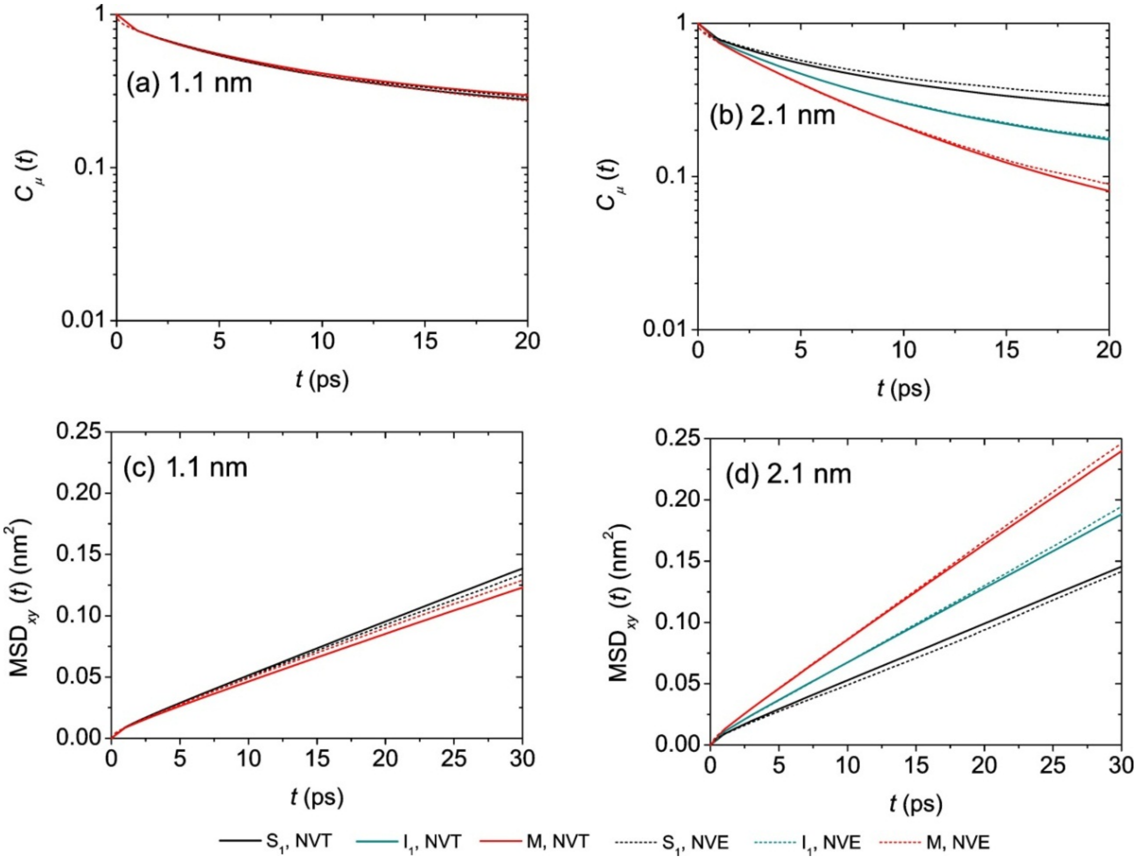

Fig. S1. $C_{\mu}(t)$ (a, b) and MSD$_{xy}$ (t) (c, d) of water from different layers of films with thicknesses 1.1 nm (a, c) and 2.1 nm (b, d) simulated in NVT and NVE ensembles.

B. Comparison of dynamics of water originally in a specific layer and remained in a specific layer

In Section 2 of the main text, we have discussed the two conventions in deriving dynamics behaviours of water. The first convention, as adopted by us in the main text, takes water originally in a specific layer into account. The second convention only accounts for water remained in a specific layer throughout the time interval. $C_\mu(t)$ and $\mathrm{MSD}_{xy}(t)$ derived by the two conventions respectively are shown in Fig. S2. These data are obtained from the NVE simulations, as NVE simulations export data with a much shorter time interval (0.05 ps) facilitating the calculation with the second convention. In any layer, $C_\mu(t)$ derived by the second convention decays obviously slower than that derived by the first convention. And $\mathrm{MSD}_{xy}(t)$ derived by the second convention is also obviously smaller. As the second convention accounts for water which does not leave a specific layer during the time interval, it is anticipated that those water molecules exhibit slower dynamics than others originally in that layer. On the other hand, the qualitative differences between water dynamics in different layers are consistent no matter which convention is used. As shown in Section 3.1 of the main text, water in the film with thickness 1.1 nm exhibits apparent homogeneous dynamics, while in the film with thickness 2.1 nm water closer to the interface exhibits slower dynamics. This conclusion still holds for dynamics behaviours derived by the second convention. So in quality the dynamics behaviours derived by the two conventions reflect the same interfacial influence. However, as the second convention causes the bias of neglecting the amount of water leaving the original environment, the first convention has been adopted in the main text.

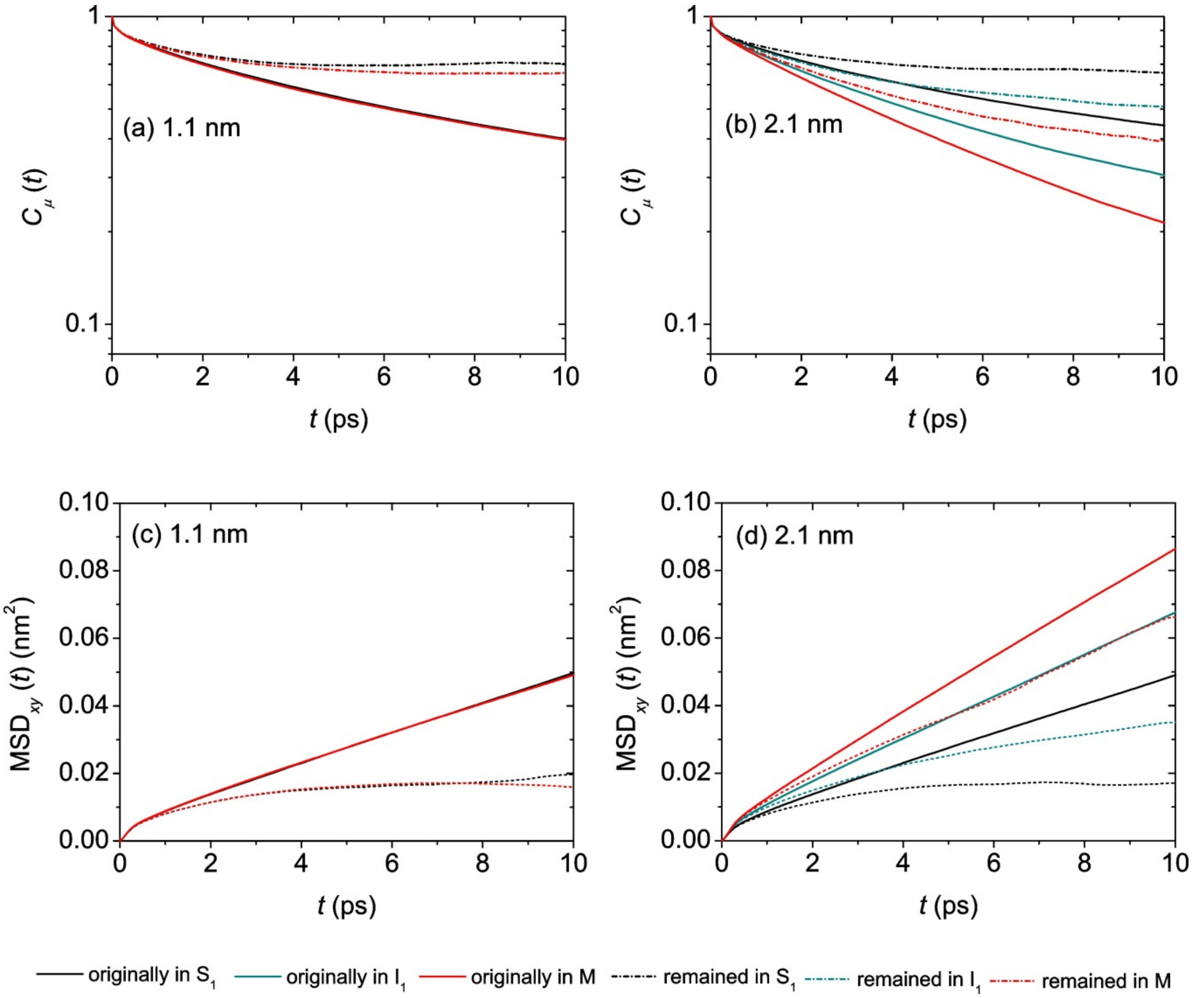

Fig. S2 $C_\mu(t)$ (a, b) and $\text{MSD}_{xy}(t)$ (c, d) of water originally in specific layers and remained in specific layers throughout the time interval. The film thicknesses are 1.1 nm (a, c) and 2.1 nm (b, d).

C. Multiexponential fitting parameters for dipole reorientational time correlation functions

Table S1. Multiexponential fitting parameters for dipole reorientational time correlation functions

Film thickness (nm)	A_1	τ_1 (ps)	A_2	τ_2 (ps)	A_3	τ_3 (ps)	A_4	τ_4 (ps)	A_5	τ_5 (ps)	τ_μ (ps)
0.5	0.18	0.61	0.20	8.82	0.22	59.07	0.21	373.69	0.20	3500.52	780.14
0.6	0.17	0.53	0.22	6.78	0.23	40.08	0.21	226.13	0.17	1671.90	347.35
0.8	0.19	0.64	0.32	7.40	0.23	48.85	0.15	278.05	0.11	2174.10	300.61
0.9	0.21	0.78	0.41	8.18	0.24	58.88	0.15	640.01	-	-	112.79
1.1	0.18	0.63	0.47	6.88	0.21	46.77	0.14	594.84	-	-	95.06
1.3	0.17	0.57	0.49	6.25	0.18	35.42	0.15	307.44	-	-	56.03
1.5	0.14	0.39	0.45	4.65	0.28	12.82	0.13	112.42	-	-	20.52
1.7	0.17	0.61	0.64	6.38	0.18	61.83	-	-	-	-	15.58
1.9	0.14	0.42	0.65	5.28	0.21	22.57	-	-	-	-	8.23
2.1	0.13	0.40	0.66	5.08	0.21	17.48	-	-	-	-	7.08
2.4	0.13	0.39	0.63	4.90	0.24	14.56	-	-	-	-	6.65
2.6	0.13	0.38	0.59	4.81	0.28	12.23	-	-	-	-	6.29

D. Coordination modes distributions of water

The coordination mode of a water molecule is determined according to the hydrogen bonds (HB) formed between it and surrounding water molecules and/or sulfate groups. The oxygen atom which forms a HB with a hydrogen atom is seen as the accepter, while the oxygen atom which forms a covalent bond with that hydrogen atom is seen as the donor. The HB between two water molecules is determined by the widely employed geometric definition: The donor-accepter distance is less than 0.35 nm, the hydrogen-donor-accepter angle is less than 30°, and the hydrogen-accepter distance is less than 0.245 nm.[2, 3] The HB between a water molecule and a sulfate group is determined by a looser geometric definition without considering the hydrogen-accepter distance.[4]

The coordination modes distributions are shown in Fig. S3. The coordination mode "O2H1H1" which exhibits a tetrahedral structure (Fig. 7a) has the largest population in all the situations. The distribution of different coordination modes in the M layer of the film with thickness 2.1 nm is similar to that in the pure water slab (Fig. S3b,c). Coordination modes "O2H1H1", "O1H1H1", "O2H0H1" and "O3H1H1" have obvious higher proportions in the M layer than in the I and S layers, and the proportions of "O0H1H1" and "O0H0H1" are lower due to less Na^+ ions in the M layer (Fig. 3b). The coordination modes characterizing HBs with sulfate groups such as "O2H1H'1", "O1H1H'1" and "O0H'1H'1" appear in the I and S layers. In the film with thickness 1.1 nm, there are only minor differences in water coordination modes distributions among different layers (Fig. S3a). Due to the thin film thickness, even water in the core can form HBs with sulfate groups, and the Na^+ ions concentration in the M layer is not much smaller than those in S layers (Fig. 3a), so that the differences in coordination modes distributions are not so obvious.

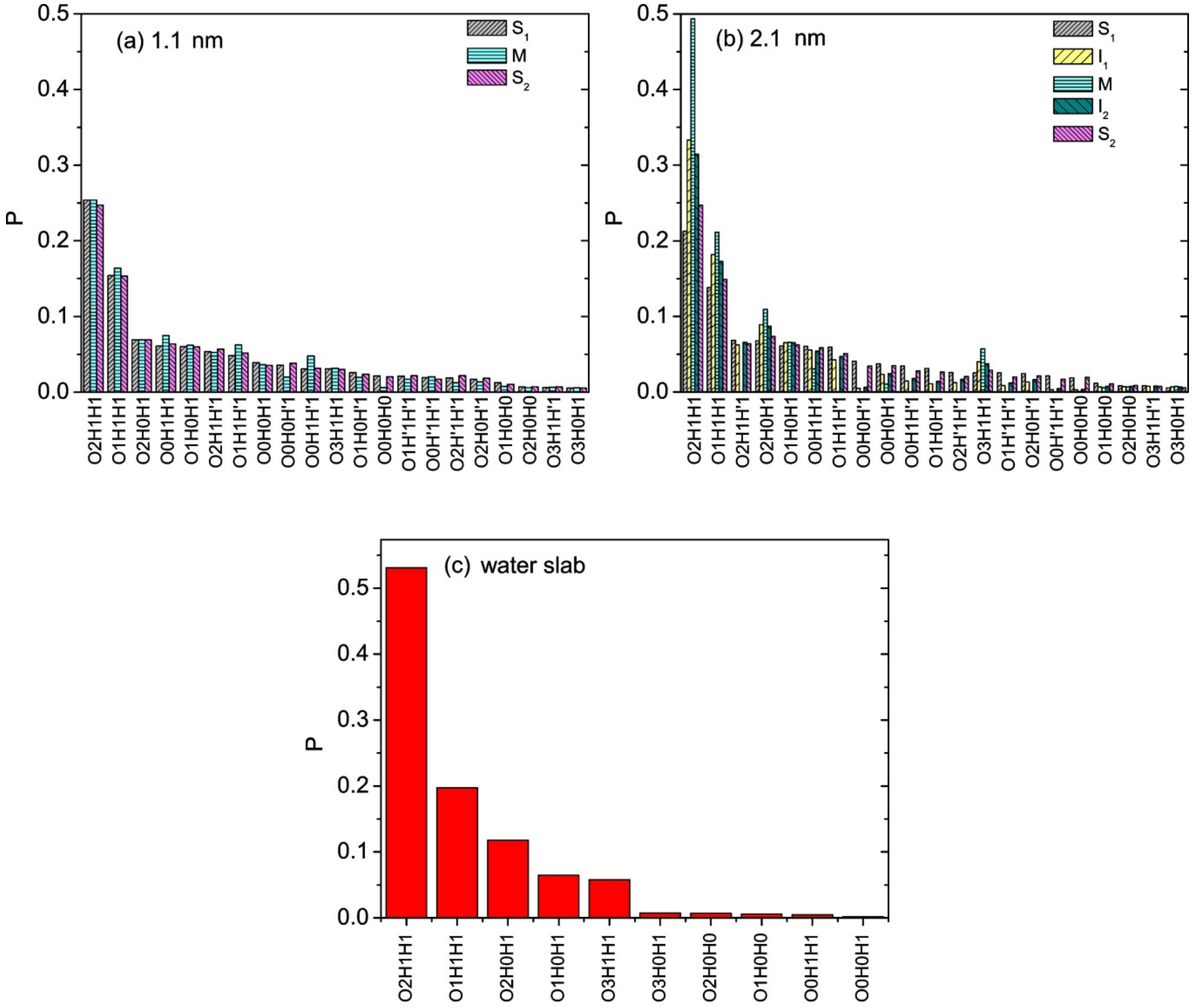

Fig. S3. Probability distributions of coordination modes of water in different layers of films with thicknesses 1.1 nm (a) and 2.1 nm (b) and in the pure water slab (c).

E. Relation between water and Na$^+$ ions

The relation between water and Na$^+$ ions is revealed by studying the S_1 layer of the film with thickness 1.1 nm. Water molecules are classified into 4 kinds (O0, O1, O2 and O3) according to the number of HBs they accept. The radial distribution function (RDF) and coordination number (CN) of Na$^+$ ions around every kind of water molecules are shown in Fig. S4. An obvious peak of the RDF appears at about 0.24 nm around “O0” and “O1” water molecules, absent around “O2” and “O3” water molecules. The peak around “O0” water molecules is much higher than that around “O1” water molecules. The CN corresponding to the peak is a little higher than 1.0 around “O0” water molecules and it is about 0.5 around “O1” water molecules. It reflects that most “O0” water molecules are stably coordinated by one Na$^+$ ion as illustrated in Fig. 7b in the article. And about half “O1” water molecules are coordinated by a Na$^+$ ion.

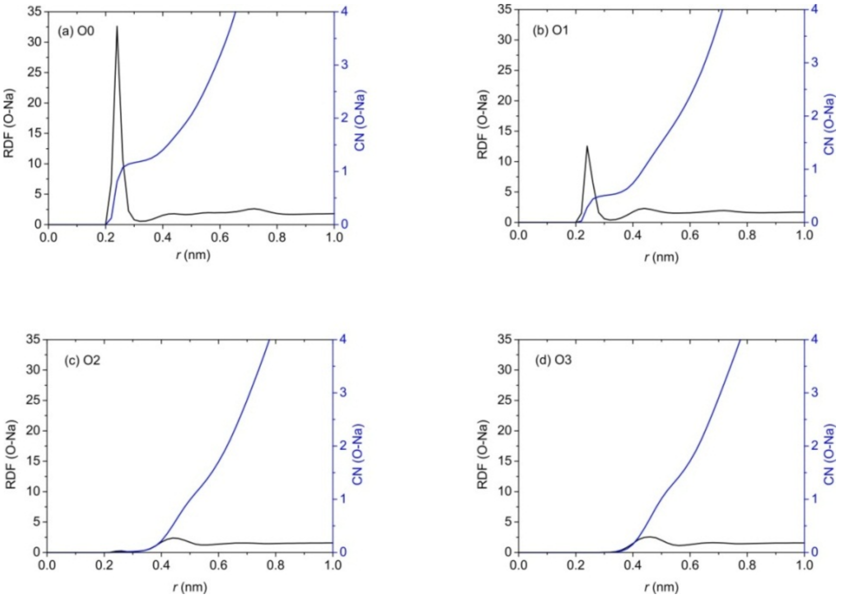

Fig. S4. Radial distribution functions (RDF) and coordination numbers (CN) of Na$^+$ ions around oxygen atoms of water accepting 0 (a), 1 (b), 2 (c), 3 (d) HBs.

F. Electrostatic field and water orientation across the film

The electrostatic field E_z across a film is calculated using Gauss theorem:

$$E_z = \frac{1}{\varepsilon_0} \int_{-\infty}^{z} \rho(z') dz' \qquad (S1)$$

where $\rho(z')$ is the charge density. Now we consider the contributions of ions (surfactant anions and counterions) and water to E_z separately as done by Bresme and Faraudo.[5] Eq. (S1) is rewritten by replacing $\rho(z')$ with ionic charge density $\rho_i(z')$ and water charge density $\rho_w(z')$ respectively:

$$E_{z,i} = \frac{1}{\varepsilon_0} \int_{-\infty}^{z} \rho_i(z') dz' \qquad (S2)$$

$$E_{z,w} = \frac{1}{\varepsilon_0} \int_{-\infty}^{z} \rho_w(z') dz' \qquad (S3)$$

where $E_{z,i}$ is related to the electric displacement D_z as $D_z = \varepsilon_0 E_{z,i}$, and $E_{z,w}$ is related to the polarization P_z as $P_z = -\varepsilon_0 E_{z,w}$. Fig. S5 illustrates the individual contributions of ions and water to E_z. It is clear that the intensity of $E_{z,w}$ is comparable to that of $E_{z,i}$, showing the strong polarization of water in the films. The polarization of water is also reflected by water orientation, which is characterized by the tilt angle (θ). Fig. S5 also shows the orientation of water, which prefers to point towards the interface. Only at the midpoints of the films $\langle \cos \theta \rangle$ and the electrostatic fields are zero due to the symmetry of the film, reflecting water molecules across the film are all under obvious polarization effects.

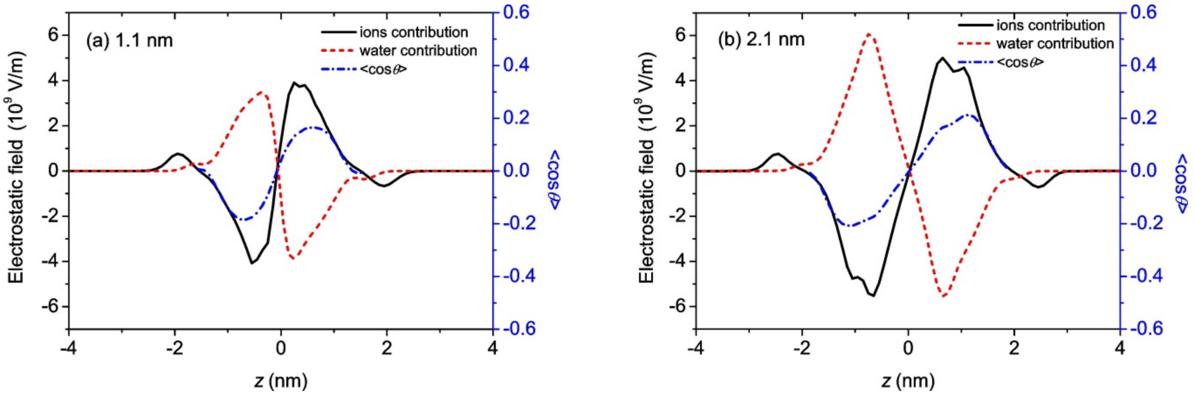

Fig. S5. Contributions of ions and water to the electrostatic field and orientations of water across the films with thicknesses 1.1 nm (a) and 2.1 nm (b).

G. Reorientational dynamics dependence on water orientation

The reorientational dynamics dependences on water orientations were studied for water molecules with different coordination modes in different layers of the two films (Fig. S6-S9). In the S_1 and I_1 layers (Fig. S6 and S7), water of coordination modes “O2H0H1” and “O3H1H1” exhibit reorientational dynamics which are strongly dependent on θ, similar to the case of water of coordination mode “O2H1H1” shown in the main text. Water of coordination modes “O1H0H1” and “O1H1H1” exhibit weaker θ dependent dynamics. The dependences are much weaker for water of coordination mode “O0H0H1”. The θ dependent reorientational dynamics are determined by the macroscopic electrostatic field. The local influences of Na^+ ions are responsible for weakening the macroscopic electrostatic field influence on water reorientational dynamics. Water coordinating sulfate groups (O2H1H'1) also exhibits obvious θ dependent reorientational dynamics.

Water molecules in the M layers of the two films exhibit not obvious θ dependent reorientational dynamics (Fig. S8 and S9), as they are influenced almost equally by the two interfaces. Water molecules with θ in the range from 72° to 108° exhibit slightly faster reorientational dynamics, as their orientations deviate most from the polarized direction of either interface.

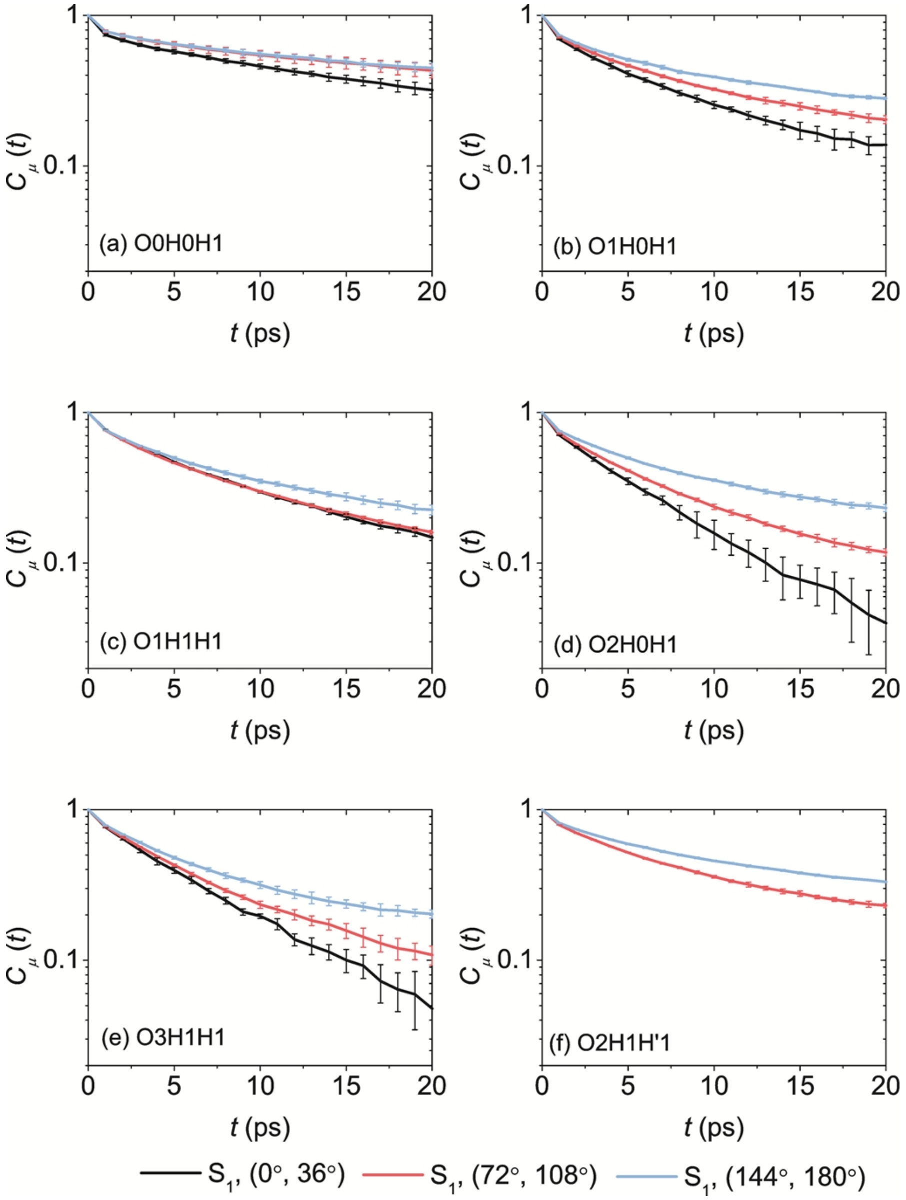

Fig. S6. The dependences of $C_\mu(t)$ on initial tilt angles of water with different coordination modes in the S$_1$ layer of the film with thickness 1.1 nm.

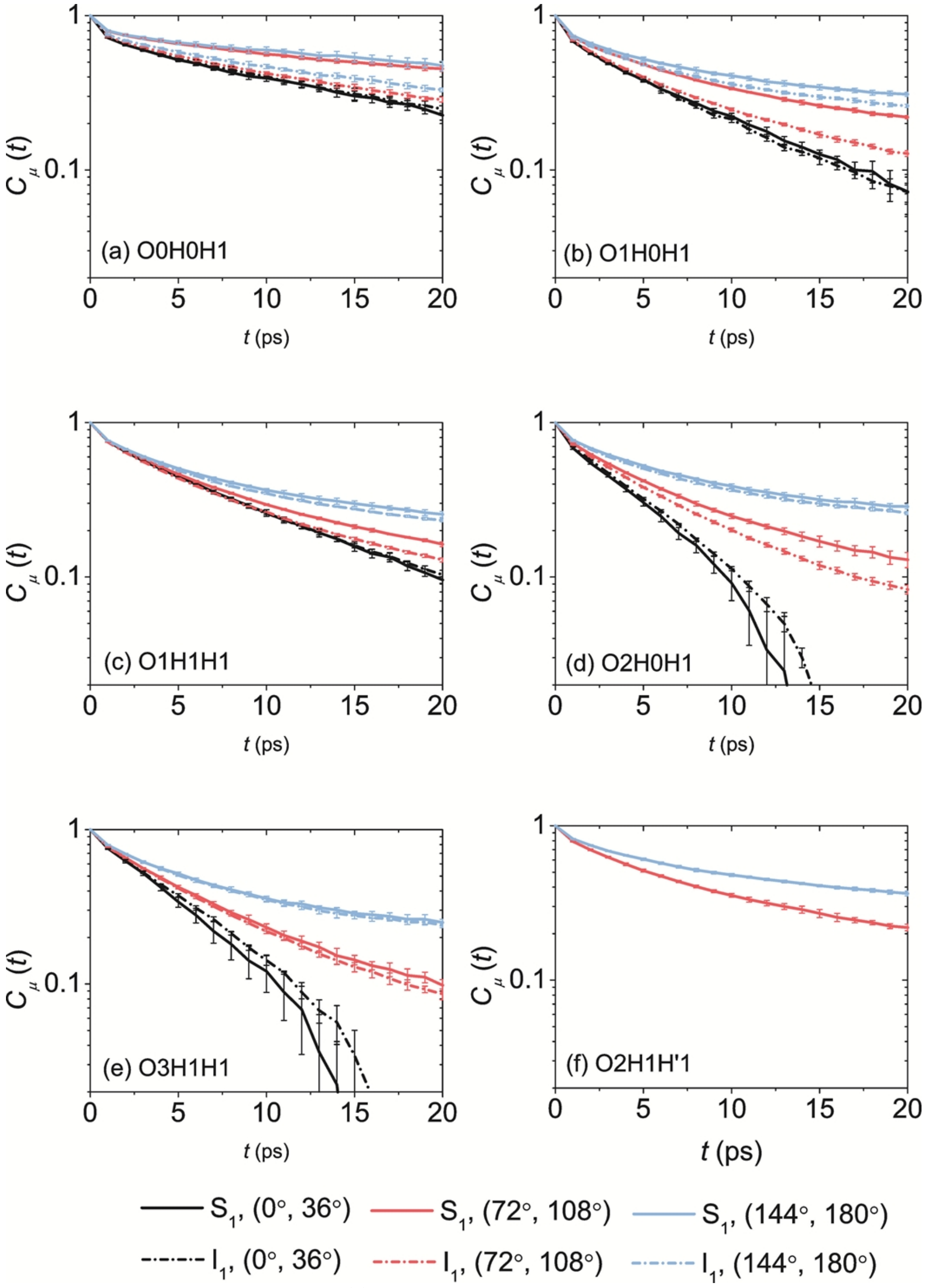

Fig. S7. The dependences of $C_\mu(t)$ on initial tilt angles of water with different coordination modes in the S_1 and I_1 layers of the film with thickness 2.1 nm.

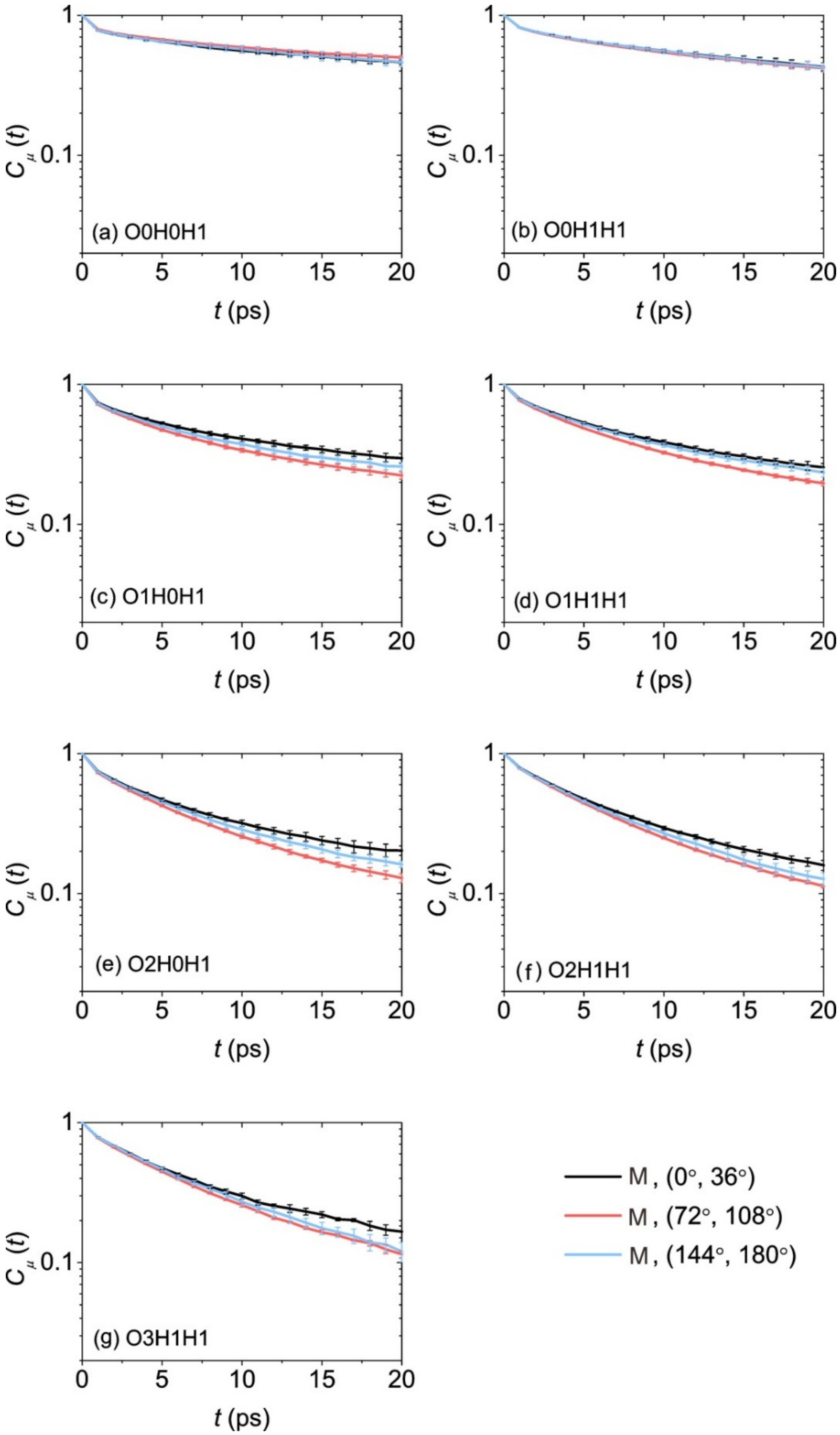

Fig. S8. The dependences of $C_\mu(t)$ on initial tilt angles of water with different coordination modes in the M layer of the film with thickness 1.1 nm.

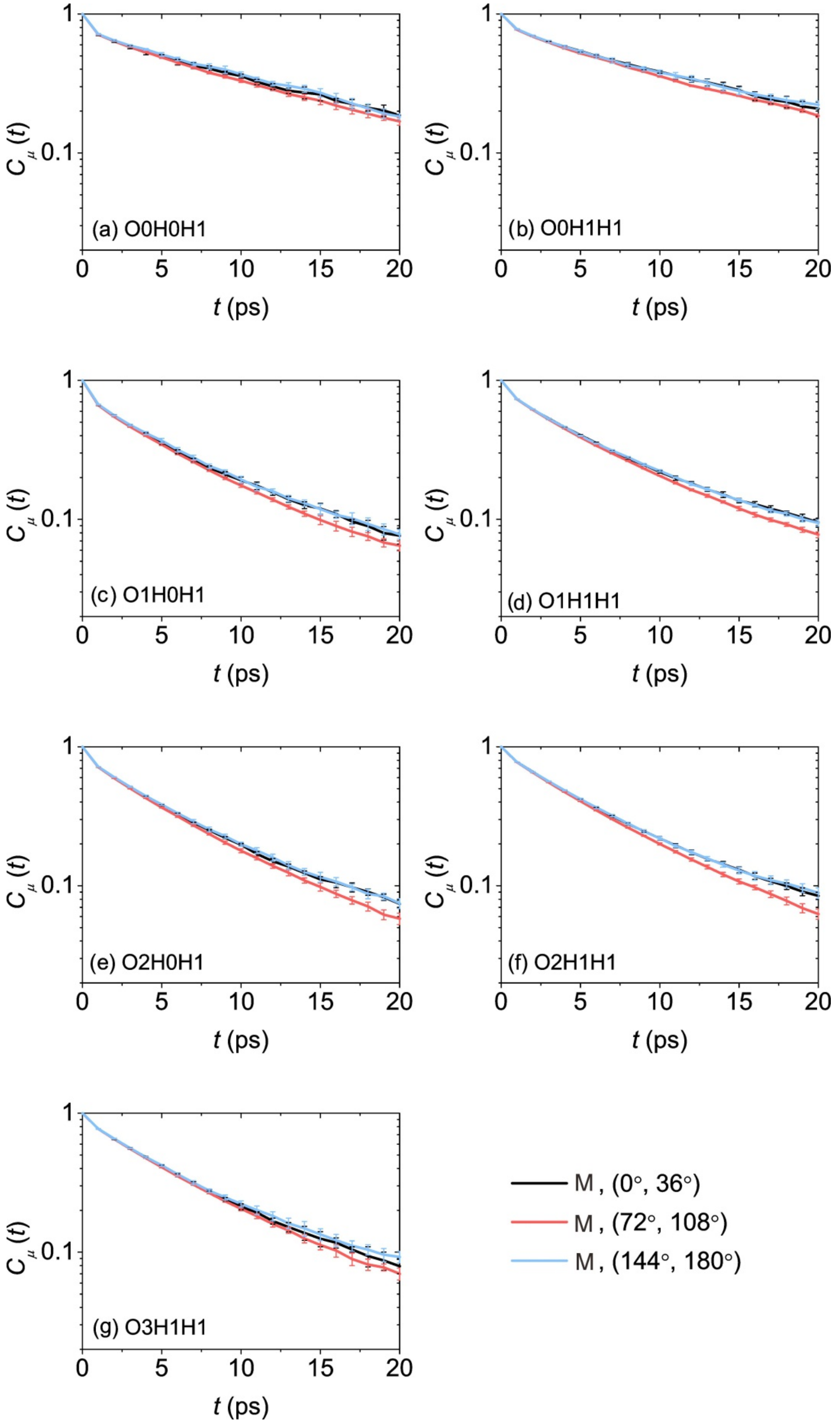

Fig. S9. The dependences of $C_\mu(t)$ on initial tilt angles of water with different coordination modes in the M layer of the film with thickness 2.1 nm.

H. Reorientational dynamics of water from the pure water slab

$C_\mu(t)$ for water of different coordination modes from the pure water slab in the semilogarithmic coordination system are almost parallel to each other after 1 ps (Fig. S10). The difference in $C_\mu(t)$ before 1 ps is due to the libration motion of water.[6] It implies that except libration motion, bulk-like water exhibits independent reorientational dynamics on local coordination environment, consistent with a previous study on the hydrogen bond dynamics of bulk water.[7]

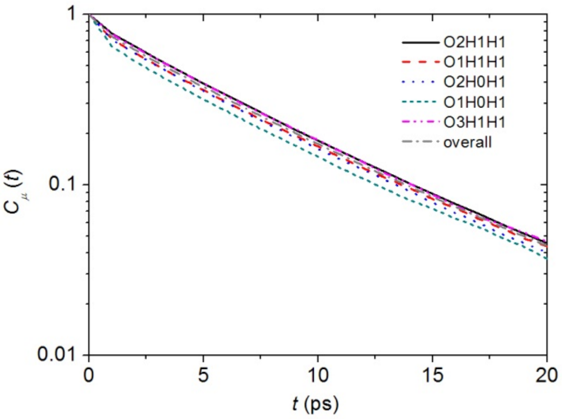

Fig. S10. $C_\mu(t)$ for water of different coordination modes from the pure water slab. The overall $C_\mu(t)$ is also shown in the figure.

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