

**The Influence of Force Field on the Structure and Dynamics of
Water Confined in ZIF-8 from Atomistic Simulations**

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1. Elastic Constants

Table S1. Elastic constants computed from different force fields. All values in GPa.

	C11	C12	C13	C22	C33	C44	C55	C66
ZHEN G	11.13	7.69	7.40	11.36	12.46	2.63	3.48	2.96
ZHAN G	9.68	7.86	7.96	10.16	9.68	0.79	0.89	0.96
WU	9.81	7.82	7.69	9.808	9.73	0.65	0.52	0.56
DÜRHH OLT	8.68	5.81	6.42	8.68	9.84	0.69	0.69	0.26
WENG	7.23	4.81	4.75	6.8	6.69	0.94	1.14	0.95
DR	28.76	17.17	17.33	29.10	28.85	4.40	4.06	4.39
DD	27.73	16.84	17.22	28.83	28.44	4.26	4.07	4.10

2. Swing Angle Distribution

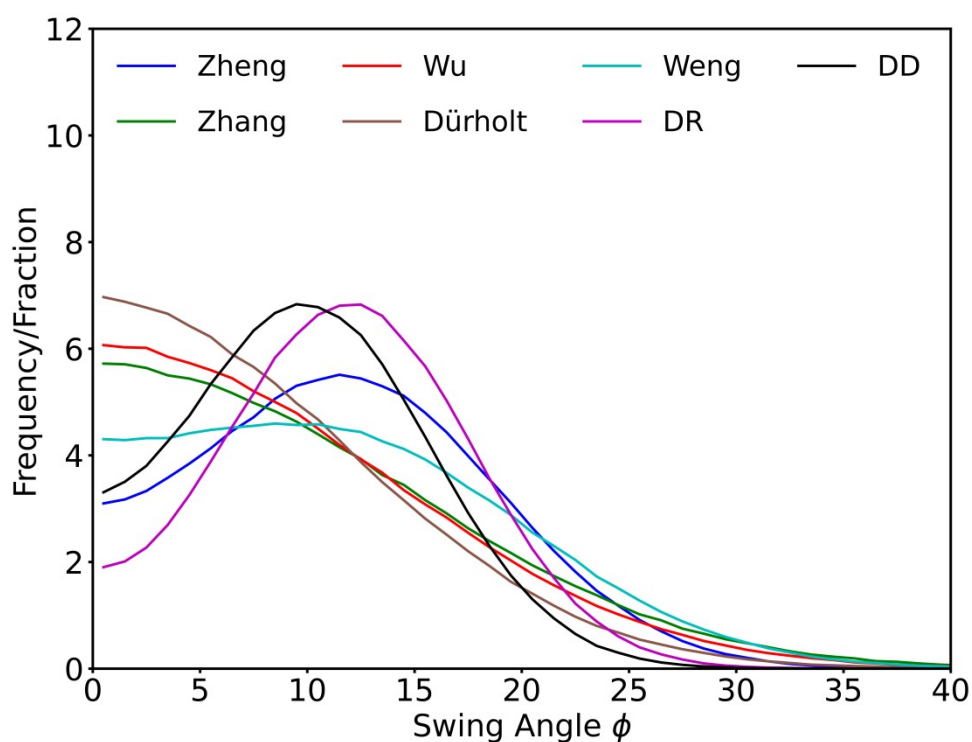


Figure S1. Swing angle distribution for empty ZIF-8 with various force fields.

3. Hydrogen-Bonding State

It is common to define the hydrogen bond between a donor and an acceptor on the basis of energetic and/or geometric criteria [1]. In this case, geometric criteria are utilized for defining hydrogen bond: two water molecules are considered hydrogen-bonded only if the interoxygen distance is less than 3.5 Å, simultaneously the hydrogen-accept oxygen distance is less than 2.45 Å, and the accept oxygen-donor oxygen-hydrogen (OOH) angle being less than 30° [2]. Figure S2 illustrates the hydrogen-bonding state of confined water, including a comparison with the corresponding result for bulk water. Here, hydrogen-bonding state refers to the number of hydrogen bonds formed by each water molecule. While bulk water is predominantly composed of molecules that form 3 or 4 hydrogen bonds, confined water tends to form 2 or 3 hydrogen bonds. Consequently, the average hydrogen bond number per water molecule under confinement is smaller than that of bulk water (3.51). Thus, nanoscale confinement inhibits the formation of the typical tetrahedral structure [2] observed in bulk water, leading to the aggregation of molecules. This observation is consistent with the local structural changes of confined water, characterized by tetrahedral order parameter and asphericity.

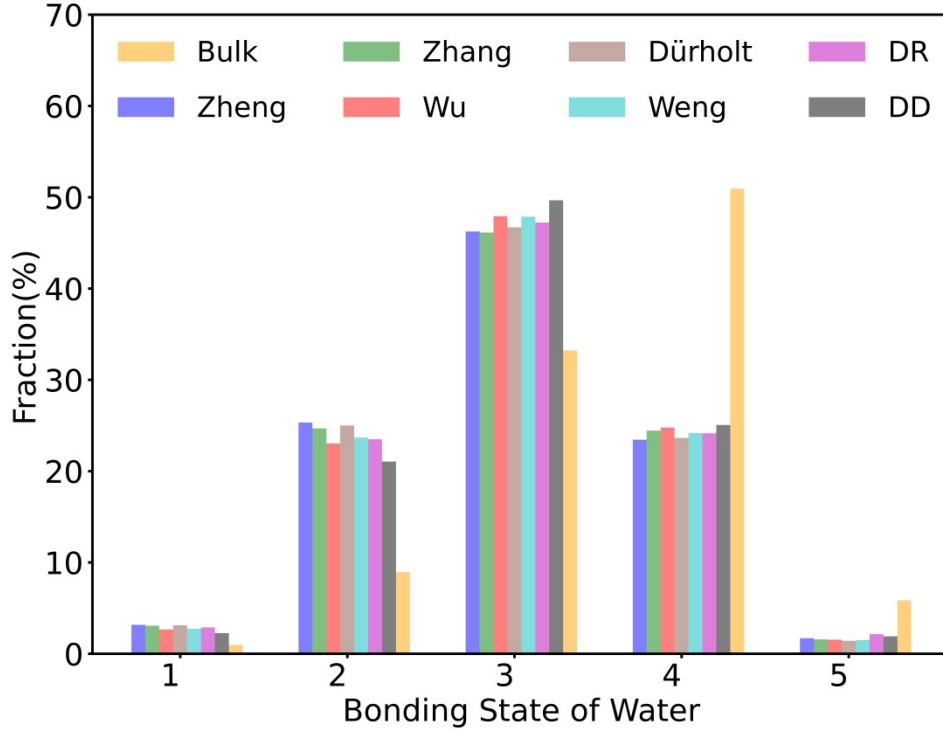


Figure S2. Histogram of hydrogen-bonding state of bulk water and confined water for various force fields.

4. Velocity-velocity autocorrelation function of oxygen atoms

The rigidity of the environment can also be assessed by examining the normalized velocity-velocity autocorrelation function (VACF) [3] of water oxygen:

$$\text{VACF} = \frac{\langle v_i(0) \cdot v_i(t) \rangle}{\langle v_i(0) \cdot v_i(0) \rangle}$$

where v denotes the velocity of oxygen atom in water. Figure S3 shows a comparison of the normalized VACF for water oxygen under confinement and in bulk. The presence of minimum in the VACF profile indicates the “cage effect” experienced by the tagged particle, meaning it takes some time for the particle to escape from the cage formed by its surrounding neighbors [4]. Therefore, it is highly related to the first minimum of the slope in MSD. The oscillatory behavior and features of the first minimum in the VACF

profile can therefore be utilized to investigate the interaction between the tagged particle and its surrounding cage [4]. It is important to note that all force fields results in a deeper minimum, a direct consequence of more rigid environment [5]. Moreover, the minima for DR and DD force fields are notably deeper compared to the other force fields. This observation further emphasizes the importance of framework flexibility as a critical factor influencing the rigidity of the environment for water dynamics.

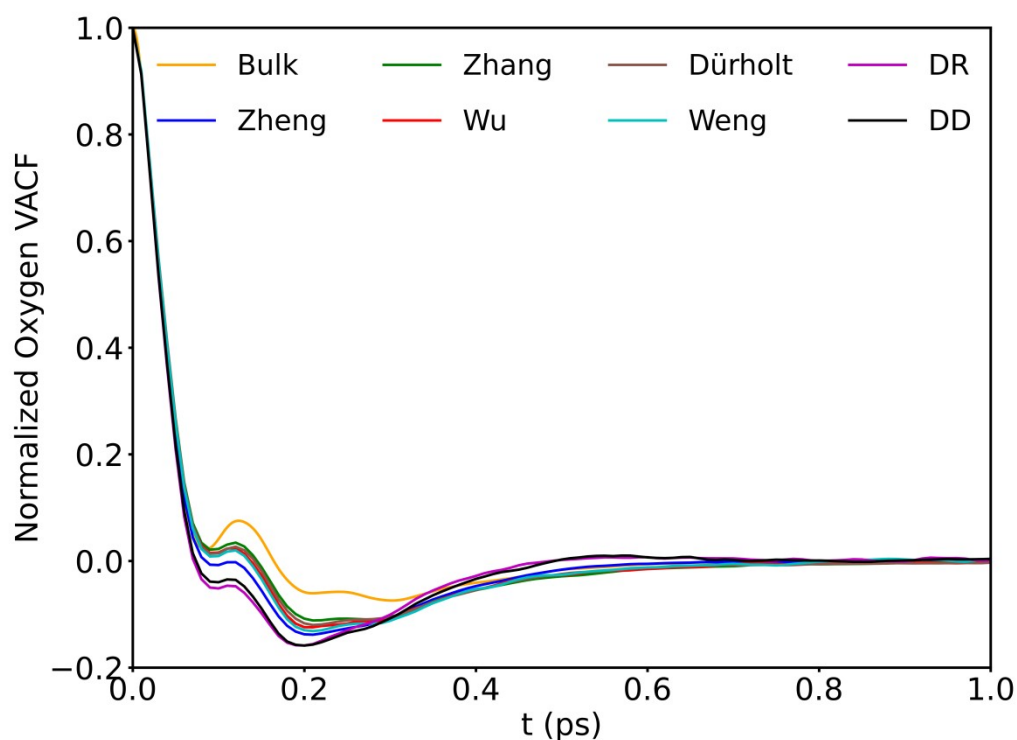


Figure S3. Velocity-velocity autocorrelation function of oxygen atoms in confined water for various force fields. For comparison, the corresponding result in pure water is also shown.

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2. D. R. Nutt and J. C. Smith, *J. Am. Chem. Soc.* 2008, **130**, 13066-13073.
3. D. V. Zlenko, *Biophysics* 2012, **57**, 127.

4. D. D. Tommaso, M. Prakash, T. Lemaire, M. Lewerenz, N. H. D. Leeuw and S. Naili, *Crystals*, 2017, **7**, 57.

5. S. Pal, S. Balasubramanian and B. Bagchi, *Phys. Rev. E*, 2003, **67**, 061502.