

Supplementary Information

Characterizing the Bifurcating Configuration of Hydrogen Bonding Network in Interfacial Liquid Water and Its Adhesion on Solid Surfaces

Lei Zhao and Jiangtao Cheng*

Department of Mechanical Engineering, Virginia Polytechnic Institute and State University,
Blacksburg, VA 24061, USA

* To whom correspondence should be addressed:

Jiangtao Cheng, Email: chengjt@vt.edu; Tel: +1 (540) 231 4161; Fax: +1 (540) 231 9100

Comparison with SPC/E water model

In our study, all the theoretical analyses were carried out based on the hydrogen bonding within liquid water and Lennard-Jones type solid-liquid interactions without presuming any specific water models. Therefore, our results are supposed to be applicable for other water models as well. However, due to the difference in partial charge distribution, the simulation results are expected to be slightly different for different water models. In this work, we also used SPC/E,^{1,2} i.e., the three-site water model, as a comparison to the TIP4P model.³ Since density undulations and loss of hydrogen bonds have been widely reported in previous studies,⁴⁻⁶ we compare the probability density distribution of Δz and β . The results are shown in Figure S1.

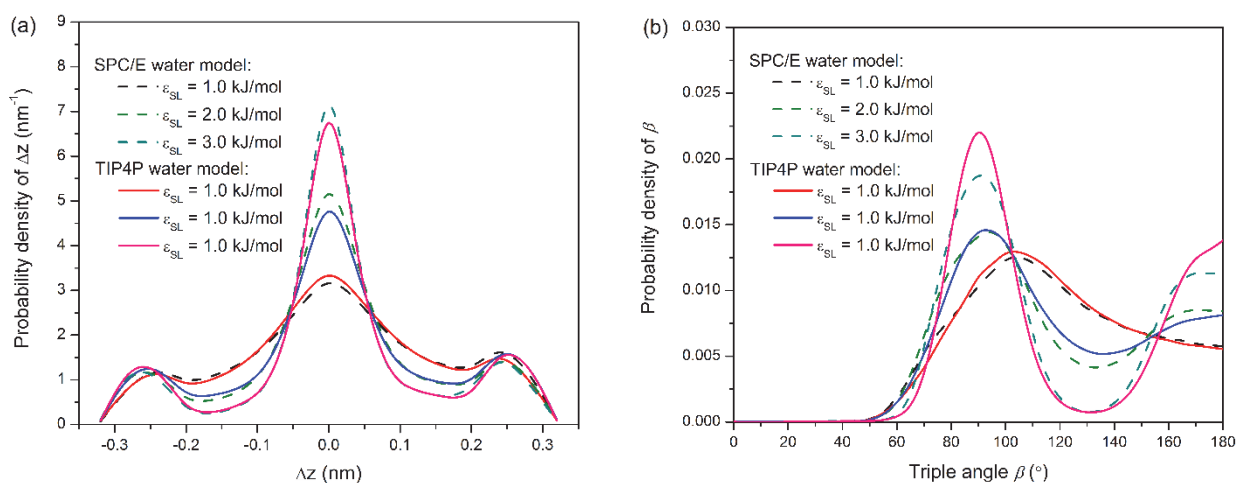


Figure S1. (a) Probability density profiles of Δz for TIP4P water model and SPC/E water model. (b) Probability density profiles of β for TIP4P water model and SPC/E water model. In both figures, results of TIP4P water model are plotted by solid lines and results of SPCE water model are represented by dashed lines.

It is apparent in Figure S1 that the results of SPC/E water model are generally identical to those of TIP4P water model. Based on the density undulations and Figure S1, a bifurcating configuration of SPC/E water close to the solid surface can be concluded as well. Note that the minor shift of profiles in Figure S1 arises from the shift of negative charge center from a virtual site in TIP4P water model to the oxygen atom in SPC/E water model.

Hydrogen bonding in bulk water

In our work, a damped harmonic oscillating function is proposed to predict the density undulations of water at the interface. By fitting our simulation results, the wavelength λ in equation (4) is found to be equal to 0.28 nm. The distance parameters in oxygen-oxygen interaction and solid-water interaction are $\sigma_{OO} = 0.315$ nm and $\sigma_{SL} = 0.298$ nm, which are sufficiently larger than $\lambda = 0.28$ nm. Therefore, the distance between adjacent water sheets is attributed to the optimal distance between oxygen atoms connected by hydrogen bonds. As shown in Figure S2, we computed the probability density distribution of the distance between two oxygen atoms connected by hydrogen bonds R_{OO} in bulk water, where the confining effects of solid surface are absent.

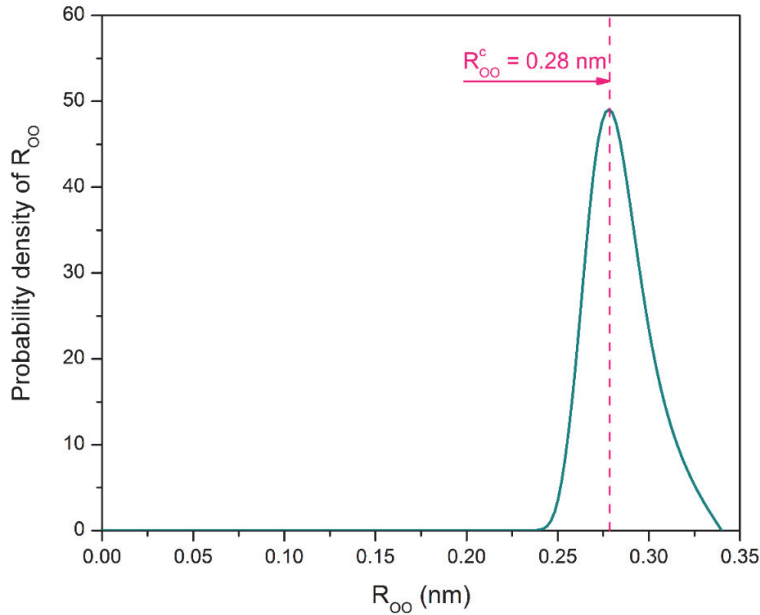


Figure S2. Probability density profile of R_{OO} , the distance between two oxygen atoms connected by hydrogen bonds in bulk water.

Figure S2 shows an optimal value of 0.28 nm for R_{OO} , which is in excellent agreement with wavelength λ . Therefore, the distance between two adjacent water layers is indeed determined by formation of inter-layer hydrogen bonds, rather than solid-water interactions or viscous interactions in the form of Lennard-Jones potential.

References

1. K. Toukan and A. Rahman, *Phys Rev B*, 1985, **31**, 2643-2648.
2. H. J. C. Berendsen, J. R. Grigera and T. P. Straatsma, *J Phys Chem-US*, 1987, **91**, 6269-6271.
3. J. L. F. Abascal and C. Vega, *Journal of Chemical Physics*, 2005, **123**.
4. C. Sendner, D. Horinek, L. Bocquet and R. R. Netz, *Langmuir*, 2009, **25**, 10768-10781.
5. L. Bocquet and E. Charlaix, *Chem Soc Rev*, 2010, **39**, 1073-1095.
6. D. Bratko, C. D. Daub, K. Leung and A. Luzar, *J Am Chem Soc*, 2007, **129**, 2504-2510.