COMMENTARY

Diverse phases of water molecules confined at nanoscale

Limin Zhou[1] **and Chunlei Wang**[2,*]

[1]Shanghai Synchrotron Radiation Facility, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201204, China

[2]College of Sciences, Shanghai University, Shanghai 200444, China

*Correspondence: Email: wangchunlei1982@shu.edu.cn

Received: November 27, 2023; Accepted: January 31, 2024; Published Online: February 3, 2024; https://doi.org/10.59717/j.xinn-mater.2024.100049

Citation: Zhou L. and Wang C. (2024). Diverse phases of water molecules confined at nanoscale. The Innovation Materials **2(1)**: 100049.

Water possesses a substantial dipole moment and can form hydrogen bonds. In contrast to the bulk phase of liquid water, water molecules in proximity to surfaces exhibit a preference for ordered structures and specific orientations. This preferential alignment with particular hydrogen bond networks of water molecules is dynamically and spatially heterogeneous with the slower dynamics than bulk water. These phenomena primarily arise from confinement at the nanoscale or surface forces, including van der Waals, Coulomb interactions, and even the entropy effect. The unique phase behaviors of water molecules at nanoscale interfaces have significant applications, such as photo-catalysis, electrode materials, and minerals in geology. For

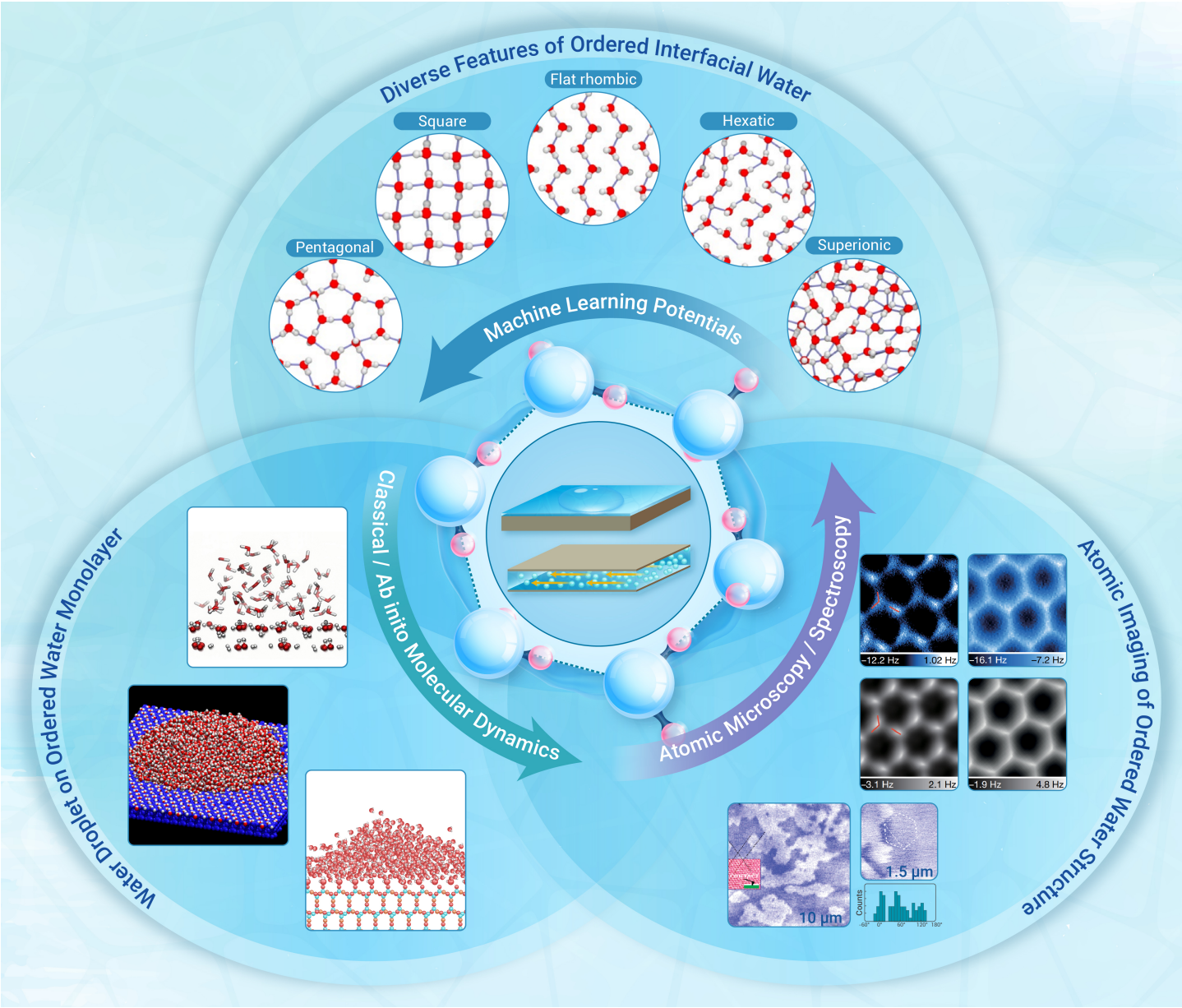

Figure 1. The diverse phase of water molecules has been demonstrated owing to the remarkable advances in both simulation methodology and experimental techniques: machine learning potentials, classical and ab initio molecular dynamics and atomic microscopy and spectroscopy.

instance, the induced ordered phases under confinement exhibit novel wetting behaviors like near frictionless water flow and anomalously low dielectric constant of water in nanochannels.[1] Such properties can be utilized to transport or manipulate water molecules and ions with utmost efficiency and minimal costs. Therefore, the in-depth knowledge of nanoconfined water can be utilized to guide the engineering applications in nanoreactors,

microfluidic device, electrolyte materials, and water desalination.

Remarkable progress has been made in recent years to understand the phase behaviors of nanoconfined water via computational simulations and experiments, as illustrated in Figure 1, the detailed advances will be discussed in below.

DEEP-LEARNING EMPOWERED PHASE SEARCH OF WATER LAYERS

Understanding water behavior at the molecular level is challenged by the high computational costs of molecular simulations and experimental difficulties associated with nanoscale characterization. Artificial intelligence (AI) has emerged as a promising tool for achieving scientific breakthroughs in computer simulations. Recently, a research group at the University of Cambridge combined multiple computational approaches to enable a first-principles-level investigation of monolayer water confined in a hydrophobic two-dimensional channel.[2] An exhaustive structure search under various temperatures and pressures is performed by employing Machine Learning Potentials (MLPs), capitalizing on the accuracy of Quantum Monte Carlo and the computational efficiency of MLPs. Their study revealed unexpectedly diverse and complex phase behaviors of the monolayer water which highly depended on the temperature and the van der Waals force. This approach enabled the exploration of the pressure-temperature phase diagram at first-principles accuracy and recovered all the previously found phases of water monolayers within a few hours on a desktop machine,

Furthermore, machine-learning-based computational results predict an intermediate hexatic phase with van der Waals pressure at 0.5~2 GPa. This new phase has six-fold orientational symmetry, and its enthalpy, diffusion coefficient, and structure change smoothly upon melting, indicating a second-order transition that might be described by the famous Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY) theory. Moreover, at the extremely high pressures beyond 2 GPa and temperatures beyond 350 K, the MLP results revealed that breaking and formation events frequently occurred on the O—H bond of water molecules. This suggests that high-pressure nanoconfinement seems to trigger the superionic behaviour of water molecules under easily accessible conditions. Even without any confinement, there are various simulation evidences of 2-dimensional (2D) ice formation on various surfaces and the dependence of the 2D crystalline structure on the hydrophobicity and morphology of the underlying surface.

UNDISTURBED MEASUREMENT OF WATER MONOLAYERS AT INTERFACES

In experiments, scanning tunneling microscopy (STM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are the most popular techniques to probe interfacial molecules, including water molecules, with atomic resolutions. However, due to the presence of high-energy electrons and potential disturbances caused by the tip, utilization of high-resolution TEM and STM may result in interference with the edge structure. To minimize disruption, non-contact AFM with its ultrahigh flexibility of the tip apex and weak higher-order electrostatic force becomes a promising choice. Recently, by combining STM and AFM imaging using qPlus-based tips, Ma et al. have found the armchair-type edges coexist with the zigzag edges observed in 2D hexagonal crystals.[3] Furthermore, the intermediate edge structures of a 2D bilayer ice island on Au(111) were identified when freezing these samples during growth. X-ray spectroscopy is another effective tool to study the structure of water, but it is still not highly surface-specific. The vibrational sum-frequency generation (VSFG) spectroscope has been proven to be a sensitive and efficient tool to study surface water. Highly ordered water structures on typical metal oxides, such as TiO_2, have been identified via combining sum-frequency techniques and molecular dynamics simulation. The ordered water bilayer here on the TiO_2 exhibited hydrophobic-like properties same as the previously proposed "ordered water monolayer that does not completely wet water", where a water droplet actually stood on a water monolayer.[4] More recent ab initio molecular dynamics simulations reveal that hydrophobicity can be mediated by order-water layer at hydrophilic water/rare-earth oxide interfaces,[5] which further broaden our knowledge on the origins of hydrophobic effects.

UNSOLVED QUESTIONS AND FUTURE DIRECTIONS

During the past decades, considerable efforts in experiments and theoretical studies have been made to unveil the diverse phases of water molecules confined at the nanoscale. However, how these ordered water structures on the solid surfaces affect the surface properties, such as the catalysis, non-fouling, electric potential and gas formation remain largely unexplored. For example, whether the ordered water hydrogen bonds network affects the water transport efficiency through the covalent organic framework channels and the lubrication strategy of hydrogen is still an open question in terms of the applications. Another example is the so-called electric double layer (EDL) which is usually induced to describe the charged surfaces within the aqueous electrolyte solution. However, the classical theory neglecting the interfacial molecular water structures is still unable to precisely describe the observed phenomenon under assumptions, such as no ion-ion correlations and the homogeneous dielectric continuum of water.

The rapidly evolving artificial intelligence has opened a whole new era in the study of water structure under confinement. When embracing the accurate and robust machine learning framework and other neural network potentials, one is expected to explore the behaviors of water molecules at various solid surfaces as well as their dynamics during chemical reactions, which are nearly impossible to achieve via ab initio molecular dynamics. The technological advancement in microscopy and spectroscopy with atomistic resolution offers us direct tools to verify the diverse phases of water under nanoscale confinement as predicted by computational results. As illustrated in Figure 1, by combining these newly evolved machine learning concepts with advanced techniques, together with the accumulation of knowledge from classical molecular simulations, enormous progress will be achieved in understanding the structure, phase, and dynamics of interfacial water under confinement within complex process like photolysis of water on TiO_2 surfaces, ice-formation on solids, electrochemical double-layer structure at charged electrodes, and so on. More efforts should be made in future research with the consideration of multiple phases of water molecules at the nanoscale.

REFERENCES

1. Fumagalli, L., Esfandiar, A., Fabregas, R., et al. (2018) Anomalously low dielectric constant of confined water. Science **360**:1339-1342. DOI:10.1126/science.aat4191.
2. Kapil, V., Schran, C., Zen, A., et al. (2022) The first-principles phase diagram of monolayer nanoconfined water. Nature **609**: 512-516. DOI: 10.1038/s41586-022-05036-x.
3. Ma, R., Cao, D., Zhu, C., et al. (2020) Atomic imaging of the edge structure and growth of a two-dimensional hexagonal ice. Nature **577**: 60-63. DOI: 10.1038/s41586-019-1853-4.
4. Qu, M., Huang, G., Liu, X., et al. (2022) Room temperature bilayer water structures on a rutile TiO_2(110) surface: hydrophobic or hydrophilic? Chem. Sci. **13**:10546-10554. DOI: 10.1039/D2SC02047E.
5. Agosta, L., Arismendi-Arrieta, D., Dzugutov, M., et al. (2023) Origin of the hydrophobic behaviour of hydrophilic CeO_2. Angew. Chem. Int. Ed. **62**: e202303910. DOI: 10.1002/anie.202303910.

FUNDING AND ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (12022508, 12005284, 12074394). The funders had no role in study design, data collection and analysis, decision to publish or preparation of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.