

## Structural and dynamical properties of water under high temperatures and pressures revealed by combining first principles molecular dynamics simulations and *in situ* X-ray diffraction experiments

Although liquid water is one of the most abundant materials on earth and one of the most familiar to all of us, the present understanding of liquid water that exhibits various anomalous properties around ambient conditions is still far from satisfactory. Recently, it is found that water also exists in the Earth's interior in the form of hydrous minerals; it plays crucial roles, e.g., in the formation of magma etc. Hence, water is certainly vital for the global environment. A joint research team of the Quantum Beam Science Directorate of JAEA has successfully studied fluid water at multi-extreme conditions of pressures ( $\sim 1$  GPa) and temperatures ( $> 700$  K) corresponding to the Earth's interior at a depth  $\sim 30$  km, by

both advanced first principles molecular dynamics simulations [1] and *in situ* X-ray diffraction experiments [1,2]. Thus we gained a novel insight into water under such multi-extreme conditions.

*In situ* X-ray diffraction experiments of fluid water under high temperatures and pressures were conducted at beamline **BL14B1**, where the cubic-type multianvil press is installed as shown in Fig. 1. On the other hand, first principles molecular dynamics simulations for fluid water at almost the same temperature-pressure conditions as the experimental ones were performed using supercomputer facilities of JAEA. Figure 2 compares the theoretical radial distribution functions  $g_{XY}(r)$  in isochore conditions of

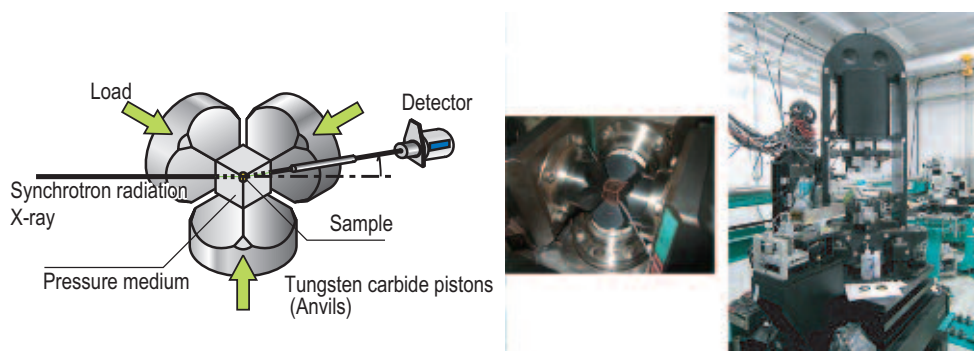


Fig. 1. Apparatus for high temperature and pressure X-ray diffraction experiment. Schematic view (left) and photograph (right) of the cubic-type multianvil press installed at BL14B1, where the present diffraction experiment was conducted.

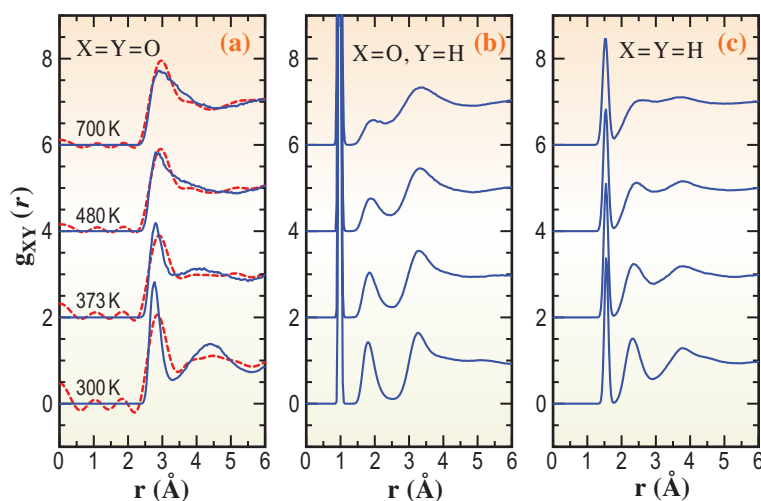


Fig. 2. Comparison of theoretical and experimental radial distribution functions. Radial distribution functions (a)  $g_{OO}(r)$ , (b)  $g_{OH}(r)$ , and (c)  $g_{HH}(r)$  for  $1.0 \text{ g/cm}^3$  obtained from our first principles molecular dynamics simulation and *in situ* X-ray diffraction experiment are shown as solid and dashed lines, respectively. For clarity, the vertical axis for data of different temperatures is shifted up.

1.00 g/cm<sup>3</sup> computed from the molecular dynamics simulations with our experimental ones. Both the theoretical and experimental results show that with raising temperature the second peak of the oxygen-oxygen radial distribution function  $g_{OO}(r)$  located for ambient water at  $\sim 4.5$  Å (bottom of Fig. 2(a)) represents an inward shift, which ends up merging the first and second peaks, thus leading to the increase in coordination number up to 12-14. Moreover, close examination of the coordination structure of water produced in the simulations reveals that with increasing temperature the tetrahedral coordination characteristic of ambient water tends to be diminished from 373 K and finally it is completely collapsed at high temperatures of  $\sim 700$  K, although the intermolecular peak of  $g_{OH}(r)$  which can be traced back to hydrogen bonds is still visible at around 1.8 Å as shown in Fig. 2(b).

The apparent inconsistency of the collapsed tetrahedral coordination with intact hydrogen bonds yet inferred at high temperatures turns out to be reconciled by unusual dynamical properties of high-temperature water. Our simulations show that high-temperature water under pressure exhibits a characteristic structure of simple liquids, resulting from anomalously fast rotational motions, which are found to be typically two orders of magnitude faster than in ambient water irrespective of density as shown in Fig. 3.

Our conclusions derived from a series of systematic studies via first principles molecular dynamics combined with *in situ* X-ray diffraction

are summarized schematically in Fig. 4. The crossover is found to occur from hydrogen-bonded to simple-liquid-like liquids by raising temperature within molecular liquid phase at around 400-500 K. The resulting high-temperature water is characterized by very rapid molecular reorientation, which is hardly affected by compression, contrary to molecular diffusion, which is found to be much more easily quenched.

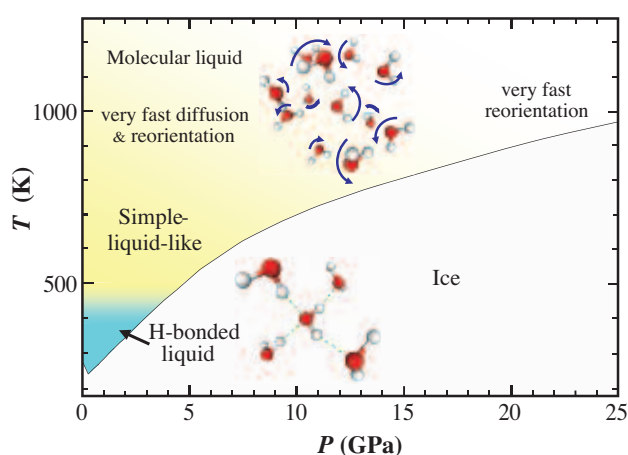


Fig. 4. Schematic  $P$ - $T$  phase diagram of water representing the crossover between hydrogen-bonded and simple-liquid-like liquids in molecular liquid phase. Typical structures of water under high temperature-pressure and ambient conditions are shown at the top and bottom of the figure, respectively.

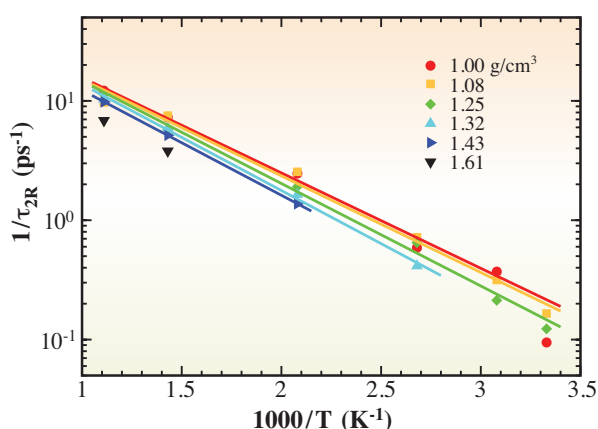


Fig. 3. Temperature dependence of rotational correlation time  $\tau_{2R}$  estimated for various densities from first principles molecular dynamics simulations. High-temperature water under pressure exhibits anomalously fast rotational motions, which are suggested to be typically two orders of magnitude faster than in ambient water irrespective of density.

Takashi Ikeda\* and Yoshinori Katayama

SPring-8/JAEA

\*E-mail: tiked@spring8.or.jp

#### References

- [1] T. Ikeda, Y. Katayama, H. Saitoh and K. Aoki: *J. Chem. Phys.* **132** (2010) 121102.
- [2] Y. Katayama, T. Hattori, H. Saitoh, T. Ikeda, K. Aoki, H. Fukui and K. Funakoshi: *Phys. Rev. B* **81** (2010) 014109.