Water molecules in action, in real space and time

Water is arguably the most important substance to life. Yet, its properties are shrouded in mystery. For instance, usually liquid becomes denser as it is cooled. But the density of water peaks at 4°C and then decreases. This and other strange behaviors arise in large part because of hydrogen bond which is highly quantum-mechanical in nature. To elucidate such behaviors the traditional axiom in materials science to figure out the structure-property relationship does not help, because a liquid does not have a "structure"; strictly speaking the intensity of elastic neutron or X-ray scattering from a liquid is zero. Instead the snapshot (equal-time) pair-density function (PDF), $g(r)$, is used as the substitute for the "structure". But trying to guess at the dynamics based upon the snapshot structure is like buying stocks knowing only today's stock prices. It does not work.

Atomic dynamics has been described either in terms of collective excitations, such as phonons, or diffusion. Collective dynamics is studied by measuring the dynamic structure factor, $S(Q, E)$, where Q and E are the momentum and energy transfers in scattering, using inelastic neutron or X-ray scattering. Diffusion is measured by quasi-elastic scattering. However, the dynamics in liquid is neither collective nor purely diffusive. Phonons are strongly overdamped due to dynamic disorder, and diffusive motions are highly correlated because liquid is not a gas, but is a condensed matter with strong atomic correlation.

In order to observe such locally correlated dynamics directly we applied the double-Fourier-transformation from Q to r (real space) and E to t (time), to $S(Q, E)$, and obtained the Van Hove function, $G(r, t)$ [1]. The Van Hove function describes the time evolution of the distribution of the atomic distance, $r_{AB}(t) = |\boldsymbol{r}_A(0) - \boldsymbol{r}_B(t)|$, where $\boldsymbol{r}_A(0)$ is the position of the atom A at $t = 0$, and $\boldsymbol{r}_B(t)$ is the position of the atom B at time t. At $t = 0$ it is equal to the snapshot PDF; $G(r, 0) = g(r)$, and $G(r, t)$ describes how the correlations become weaker as t is increased. The Van Hove function was defined in 1954, but nobody used it because it has been difficult to measure it. In order to determine the Van Hove function we have to know $S(Q, E)$ over a wide Q-E space, whereas the inelastic scattering measurements were slow. With a reactor neutron source and a triple-axis-spectrometer it takes a few hours just to get one energy scan at a constant Q.

However, the advent of pulsed neutron source with a two-dimensional detectors for inelastic neutron scattering (INS) [2] and progress in the instrumentation of inelastic X-ray scattering (IXS) [3] made it possible to determine $S(Q, E)$ over a Q-E space wide enough for accurate Fourier-transformation. We used the high-resolution IXS beamline **BL35XU** at the SPring-8 facility to determine $S(Q, E)$ over $1.3\ \text{Å}^{-1} \leq Q \leq 9.5\ \text{Å}^{-1}$ and $-10\ \text{meV} \leq E \leq 100\ \text{meV}$ for water (H_2O) at room

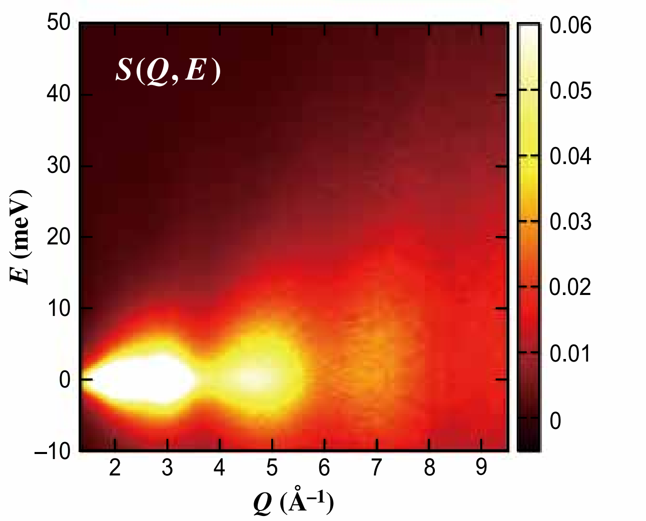

Fig. 1. The dynamic structure factor $S(Q,E)$ of water at room temperature determined by IXS measurement at SPring-8 BL35XU [4].

temperature, as shown in Fig. 1 [4]. We chose IXS to focus on the molecular dynamics, because hydrogen hardly scatters X-ray, so the Van Hove function obtained by IXS is dominated by the oxygen-oxygen, thus inter-molecular, correlations.

As shown in Fig. 1 $S(Q,E)$ of water is totally dominated by the quasi-elastic scattering (QEXS). Phonons are there (27 meV at 1.3 $Å^{-1}$), but are all but invisible in this intensity scale, because they are overdamped and their spectral density is quite low. The QEXS intensity is nearly featureless and is it hard to figure out what information it can provide.

However, once $S(Q,E)$ is converted to the Van Hove function as shown in Fig. 2, it conveys rich information regarding the local dynamics. In Fig. 2 the intensity around $r=0$ is due to self-correlation. At $t=0$ the nearest neighbor peak is seen at 2.8 Å and the second and third peaks at 4.5 and 6.8 Å. Surprisingly the first and the second peaks come closer and appear to merge as t increases. It means that as soon as the neighbor molecule goes away the second neighbor comes in to take its place, because water molecules want to maintain its four neighbors environment. Water molecules do not do random walk, but their footsteps are highly correlated.

From this result we were able to determine the time it takes for one nearest neighbor of a molecule to go away by cutting the hydrogen bond. This time, τ_{LC}, was found to be equal to the Maxwell relaxation time, $\tau_M = \eta/G_\infty$, where η is viscosity and G_∞ is the high-frequency shear modulus. τ_M is the time-scale which characterizes the time-dependent mechanical response of liquid. Earlier we have shown that $\tau_M=\tau_{LC}$ through computer simulation [5]. This work provides the first experimental confirmation of this prediction, and proves that the origin of viscosity in liquid is the excitation in the local topology of atomic connectivity network [5].

This work demonstrated that local atomic and molecular dynamics can be directly studied by IXS. We are now examining how addition of salt and other ionic compounds will modify the local dynamics in water. This work opens up a huge new field of study for local dynamics in liquid and other soft matter, impacting soft-matter physics, chemistry, and possibly biology and even medical sciences.

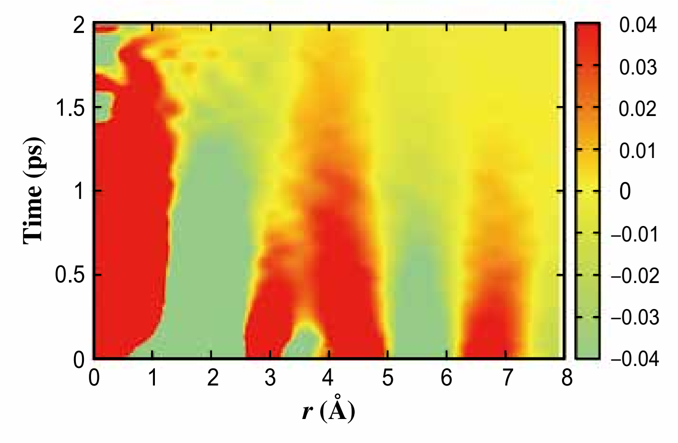

Fig. 2. The Van Hove function of water at room temperature determined by the IXS measurement [4].

Takeshi Egami[a,b]

[a] Shull-Wollan Center – Joint Institute for Neutron Sciences, University of Tennessee and Oak Ridge National Lab., USA
[b] Department of Physics and Astronomy, University of Tennessee, USA

Email: egami@utk.edu

References

[1] L. Van Hove: Phys. Rev. **95** (1954) 249.
[2] T.E. Mason *et al.*: Physica B **385-386** (2006) 955.
[3] A.Q.R. Baron *et al.*: J. Phys. Chem. Solids **61** (2000) 461.
[4] *T. Iwashita, B. Wu, W.R. Chen, S. Tsutsui, A.Q.R. Baron and T. Egami: Science Adv.* ***3*** *(2017) e1603079.*
[5] T. Iwashita *et al.*: Phys. Rev. Lett. **110** (2013) 205504.