COLLECTIVE DYNAMICS OF SUPERCRITICAL WATER

Supercritical water (SCW) is a fluid above the critical point (T_c = 647 K, P_c = 22.1 MPa, ρ_c = 0.322 g·cm^{-3}) of water, and its physicochemical properties, such as density, dielectric constant, and ionic product (= [H$^+$][OH$^-$]), vary continuously from gas-like to liquid-like properties as functions of temperature and pressure. For example, the dielectric constants of SCW are in a range of 3 ~ 30, comparable to those of hexane (1.8) and methanol (32.6), and thus SCW can dissolve organic compounds that are not soluble in ambient water. The ionic product of water increases from 1×10^{-14} (mol/dm^3)^2 under ambient conditions to a maximum of 1×10^{-11} (mol/dm^3)^2 at 34.5 MPa and ~573 K, i.e., ~30 times higher in hydrogen ion concentration in the latter thermodynamic state. Owing to its unique properties, SCW has recently drawn much attention as a medium for use in various reactions, such as decomposition of hazardous chlorinated organic compounds like dioxin and PCB and organic syntheses without acid catalysts, and production of nanometer scale metal oxides used as industrial materials. The unique properties of SCW should arise from the nature of hydrogen bonding that depends on pressure and temperature, and thus it is essential to investigate the structure and dynamic properties of hydrogen bonding in SCW as functions of temperature and pressure to understand the properties of SCW to enable the development of supercritical water technology.

In the present experiment, inelastic X-ray scattering (IXS) measurements were made using a high-resolution spectrometer installed at beamline **BL35XU** [1] on water from ambient to supercritical conditions to investigate the collective dynamics of water as a function of density. Sample water was inserted into a specially designed high-temperature and high-pressure cell made of Inconel 625 with single-crystal diamond windows (1 mm in thickness and 5 mm in diameter). The IXS measurements were carried out at eight Q values from 1.3 to 10.7 nm^{-1}, and a typical energy scan was in the range of ±40 meV.

Typical IXS spectra of water obtained at various temperatures and pressures are shown in Fig. 1 as a function of density. In ambient water (ρ = 0.997 g·cm^{-3}), the excitations are observed as shoulders on both sides of the central quasielastic peak, in good agreement with the literature data [2]. It is interesting to see that with decreasing density the shoulders corresponding to the inelastic excitation rapidly shift to the lower energies and merge into the central quasielastic peak. The observed spectra were analyzed by using a generalized Langevin formalism [3] convoluted with a resolution function, which was measured separately with a Plexiglas sample, to obtain the dynamic structure factor, $S(Q,\omega)$. The best-fitted values denoted by solid lines are compared with the observed ones denoted by open circles in Fig. 1.

The $S(Q,\omega)$ thus obtained was used to obtain the energy of the inelastic excitation, ω_1, of water as a function of density (Fig. 2) through the corresponding longitudinal current-current correlation function. The dashed lines show the hydrodynamic adiabatic velocity of sound of water in the corresponding thermodynamic states. In ambient water, the magnitude of the positive deviation of the high frequency inelastic excitations is almost 100% from the hydrodynamic values, as also reported in ref. [2]. One of the most interesting findings is the peculiar tendency of the positive deviation that gradually
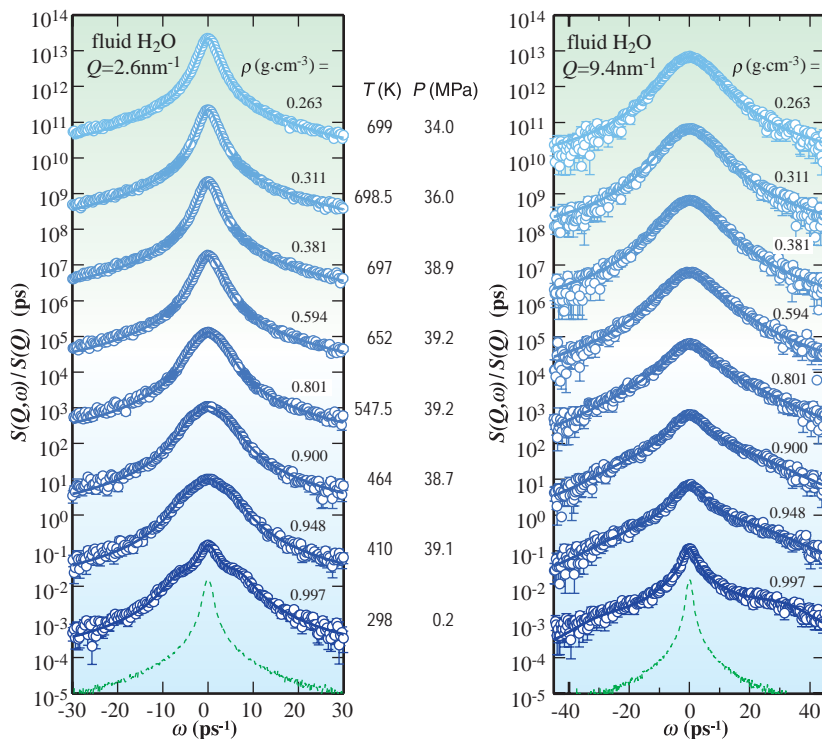

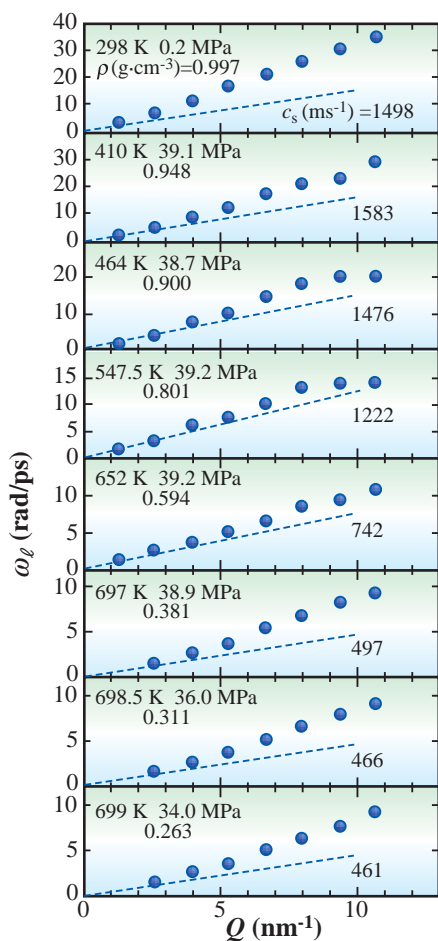Fig. 1. Typical IXS spectra of water at various densities and at Q = 2.6 and 9.4 nm^{-1}.

Fig. 2. *Q*-dependence of energy of inelastic excitation w1 of water at various densities.

decreases from ρ = 0.997 to 0.801 g·cm^{-3} in the subcritical state and then increases again up to ρ = 0.263 g·cm^{-3} in the supercritical state with a minimum at ρ = 0.801 g·cm^{-3}. Another characteristic to note is that the positive deviation of the inelastic excitation from the hydrodynamic data is not linear against *Q*, but appears to change with two different behaviors in the range of *Q* < ~ 5 nm^{-1} and *Q* > ~ 5 nm^{-1}.

In order to quantify the behavior, the apparent velocity of sound, which can be defined as $c_Q = \omega_1/Q$, was calculated at *Q* = 2.6 (open circles) and 9.4 nm^{-1} (solid circles) and the obtained results are shown in Fig. 3 together with the hydrodynamic velocity of sound c_s (dashed lines). Apparently, the ratios of c_Q / c_s rapidly decrease with lowering density and approach to unity at ~0.8 g·cm^{-3}. In the supercritical state, however, the c_Q /c_s ratios at *Q* = 9.4 nm^{-1} increase with decreasing density and reach a value of ~80% for the positive deviation near the critical density of 0.32 g·cm^{-3}, whereas those at *Q* = 2.6 nm^{-1} are practically independent of density. It should be noted that large density fluctuations occur near the critical point, which

probably reflects the present finding of a large positive deviation of sound velocity.

In conclusion, IXS experiments on sub- and supercritical water were performed to investigate the collective dynamics of water over a wide range of densities. Analysis of the IXS data by using a generalized Langevin formalism has shown that a high apparent sound velocity of water decreases from ~3000 m·s^{-1} in ambient water at ρ = 0.997 g·cm^{-3} to a hydrodynamic value of ~1100 m·s^{-1} at ρ = 0.801 g·cm^{-3} and that in the supercritical regime a positive deviation of sound velocity from the hydrodynamic velocity of sound gradually evolves when the density approaches the critical value, probably reflecting large density fluctuations in supercritical water [4].
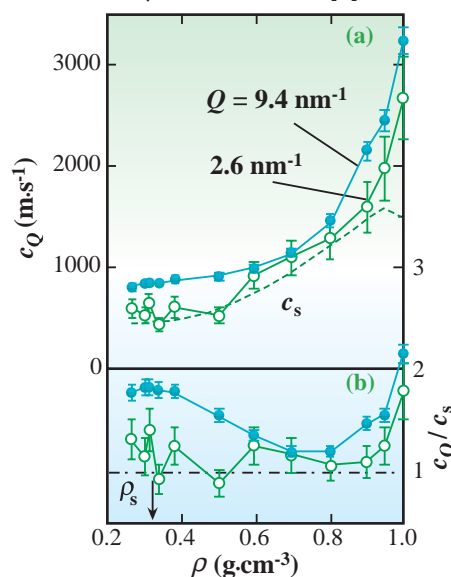
(a) Density dependence of apparent sound velocity c_Q of water as a function of density at *Q* = 2.6 (open circles) and 9.4 (solid circles) nm^{-1} and the hydrodynamic values c_s (dashed line), (b) Density dependence of the ratio of c_Q / c_s.

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