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Enhanced density fluctuations in water analyzed by neutron scattering

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As a result of the unusual temperature dependence of the isothermal compressibility of water at low temperature, the structure factor increases with decreasing momentum transfer, below 0.5 A^{-1}. We confirm this behavior with a neutron scattering experiment performed at different temperatures and in isochoric conditions. Neutron scattering conditions allow the obtaining of data almost free of the container contribution. The experimental result is in agreement with the theory describing the hydrogen-bond network of water at low temperature.

Density fluctuations in molecular liquids far from the critical point are normally of small amplitude. Their small-angle scattering is consequently rather weak and essentially independent of the momentum transfer.

The zero-angle scattering of a one-component liquid is given by $S(0)=k_BT\rho\chi_T$, where ρ is the number density and χ_T the isothermal compressibility. The existence of enhanced density fluctuations can be probed by the angular wave vector Q dependence of the scattered intensity in the range where those fluctuations take place.

The isothermal compressibility of pure water has a nontrivial temperature dependence. In contrast with other molecular liquids, it shows a minimum around 46 °C (52 °C for D_2O) and increases sharply with decreasing temperature.[1] As a consequence, $S(0)$ has a minimum too, around 0 °C, and the scattering law at low Q changes with temperature in an unusual way.

We presented in a previous paper[2] the results for the structure factor $S(Q)$ obtained by x-ray scattering in a Q range extending from 0.15 to 1.0 Å^{-1}. Enhanced density fluctuations are clearly present at low temperatures and can be analyzed within the classical Ornstein-Zernike theory and give a temperature-dependent correlation length ξ. At -20 °C, ξ was estimated around 8 Å, a value in agreement with the theoretical description of supercooled water[3] and with computer molecular dynamic simulations based on ST2 potential.[4]

More recently, another determination of the low-Q x-ray scattering from supercooled water has been published in the Q range extending from 0.05 to 0.5 Å^{-1}.[5] This work performed with synchrotron radiation does not agree with our previous work and, moreover, gives values for $S(0)$ smaller than those predicted by thermodynamics.

The determination of the Q dependence of the structure factor of water is difficult because it is relatively small even at low temperature and implies extremely good experimental conditions. In particular, the contribution due to the container must be small. On the other hand, all contamination of water must be avoided because even small amounts of impurities strongly decrease the isothermal compressibility at low temperature[6] and suppress the Q dependence of $S(Q)$[2].

Neutron scattering is certainly the more suitable method to avoid these problems. Namely, one can use a very large amount of pure D_2O and the vanadium container has essentially negligible and incoherent scattering. Moreover, absolute calibration is possible and comparisons with theory more reliable.

The interesting Q region concerned by the anomalous behavior of liquid water is an intermediate Q range, technically speaking. It is then more appropriate to use a diffraction instrument at large wavelength than a high-resolution small-angle diffractometer. Experiments were performed in the spectrometer 7C2 of the Laboratoire Léon Brillouin. The instrument is equipped with a multidetector containing 640 cells covering an angle of 128°. We used an incident wavelength equal to 1.106 Å. The sample was a cylindrical vanadium container (diameter of 8 mm, height of 50 mm, thickness of 0.1 mm) containing about 2 g of pure D_2O. Experiments were performed at 5°, 18°, and 75 °C with the sample maintained inside an evacuated tank. We did not perform experiments in the

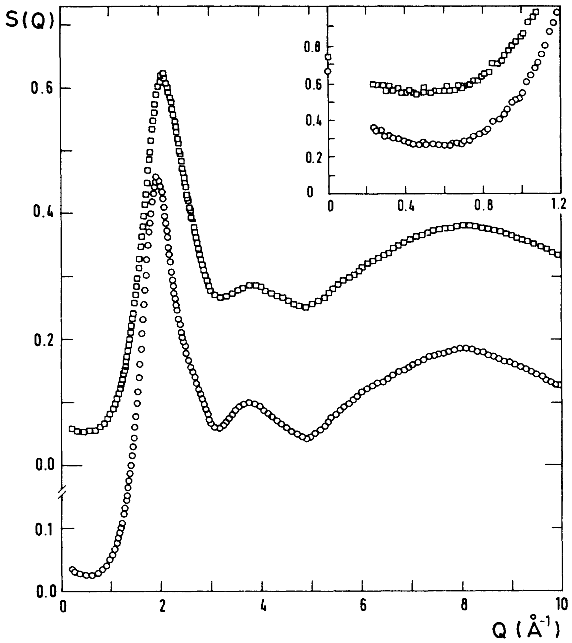

FIG. 1. Structure factor of water at 5 °C (circles) and 75 °C (squares) in absolute units. Inset: Structure factor of water at small wave-vector transfer, at 5 and 75 °C. Note the decrease of $S(Q)$ with increasing Q, at low temperature.

supercooled region, because the effect we wanted to observe is already clearly present at temperatures above the melting point and the large size of the sample makes supercooling difficult. In other experiments we used capillaries, samples, or emulsions to avoid bulk nucleation,[7] but in the present experiment we want to remove all the possible contributions which eventually would mask the effect we want to observe. The data reduction was performed according to the usual procedure; after background and empty-cell subtraction the spectra were corrected for absorption, multiple scattering, and inelasticity effects. The reduced scattered intensity was put on an absolute scale by means of a vanadium standard (having the same dimensions as the sample), vanadium giving rise to completely incoherent scattering.

Figure 1 shows the structure factor at 5 and 75 °C, as determined in the whole Q range covered by the instrument. The inset shows the low-Q region more in detail and gives the calculated values of $S(Q)$. One clearly observes the increase of $S(Q)$ with decreasing Q, the anomaly being more pronounced at 5 °C. The absolute scale enables the determination of a small correlation length, of the order of 6 Å, within the same hypothesis used before for the treatment of the "normal" contribution to the compressibility.[2]

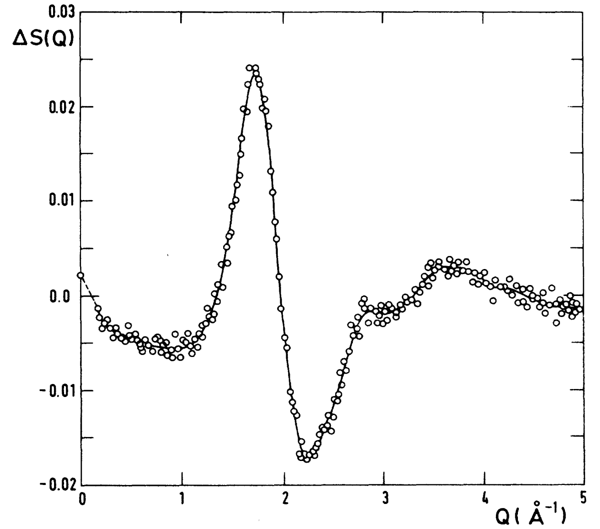

FIG. 2. Difference $\Delta S(Q)$ between the structure factor of water at 5 °C and at 18 °C, two isochoric temperatures. The Q dependence of $\Delta S(Q)$ shows that the observed effect is independent of density corrections.

In order to definitively test if our result could be disturbed by other effects or, eventually, density corrections, we took two spectra obtained at 5 and 18 °C. These two temperatures correspond to the same density for D_2O, each one being on opposite sides of the maximum of the density versus temperature curve. The two experiments correspond then to isochoric conditions and their difference is certainly not affected by density dependent corrections. Figure 2 shows this difference and again despite the small temperature variations, the increase of $S(Q)$ with decreasing Q is clearly seen because the enhanced density fluctuations are larger at 5 °C than at 18 °C.

We conclude that the anomalous low-Q dependence of the structure factor of low-temperature water can be well observed under convenient experimental conditions. Our result confirms our previous analysis and supports the theoretical description and the simulation of the hydrogen-bond network of water.

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