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Small-angle x-ray scattering from supercooled water

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The structure factor of supercooled water was determined at the small-angle x-ray scattering facilities at the Daresbury Synchrotron for $0.50 \text{ nm}^{-1} < q < 5.0 \text{ nm}^{-1}$ and for $247 \text{ K} < T < 274 \text{ K}$. In this temperature range the scattered intensity decreases with decreasing temperature. Interpreting our results in terms of an additional Ornstein-Zernike-like contribution at $q=0$, we report an upper limit to the width of the associated Lorentzian. This width is at variance with earlier results. Our results support the separation of thermodynamic quantities into a normal and an anomalous part.

Isothermal compressibility is among the thermodynamic properties of liquid water that behave anomalously at low temperatures; in particular, below the normal melting point.¹ The compressibility increases strongly with decreasing temperature and the approximate exponential dependence suggests a divergence around 228 K and an associated transition point,² although the actual liquid always freezes long before that temperature is reached. Such a divergence in the compressibility implies an enhancement of the density fluctuations and hence an increase of the structure factor $S(q)$ over a finite wave-vector range. The observed increase of $S(q)$ at $q=0$ may be caused by the growth of a Lorentzian contribution of which the width is given by the correlation length in the Ornstein-Zernike theory. The determination of the q dependence of the structure factor around $q=0$ would therefore give us a measure of the length scale of the density fluctuations. The temperature dependence of this correlation length might furthermore provide us with values for exponents indicative of the nature of the transition.

Bosio *et al.*³ reported the first venture at determining $S(q)$ at low q by a small-angle x-ray scattering. The data that were obtained in the q range of $1.5\text{--}10 \text{ nm}^{-1}$, showed that for supercooled water at 253 K the structure factor has a minimum around $q = 5 \text{ nm}^{-1}$ and steadily increases by 20% for wave vectors to 1.5 nm^{-1} . If one assumes that this increase is caused by the wing of a Lorentzian, one can extrapolate to the $S(q)$ value at $q=0$, deduced from the compressibility. The width of the Lorentzian thus obtained indicates a correlation length of only 0.8 nm. This rather intriguing result induced us to repeat and extend the x-ray scattering experiments. The use of synchrotron radiation should allow us to improve the accuracy and to extend the q range. Knowledge of the precise temperature dependence of the structure factor could yield interesting additional information.

We performed our experiments at the Synchrotron Radiation Source in Daresbury, U.K. A germanium crystal acts as a monochromator to select photons with a wave-

length of 0.150 nm. The dimensions of the monochromated beam are typically a width of 5 mm and a height of 0.5 mm. An ionization chamber is used to monitor the total intensity of the beam during the collection of a spectrum. Behind the sample cell a camera is placed, containing a beam stop to block the direct beam. The camera has been vacuum pumped to reduce air scattering. The position-sensitive detector at the end of the experimental setup can be placed at various distances from the sample. In our experiments we used 0.75 and 1.50 m. The detector is subdivided into small sections that are electronically connected to the 512 channels wherein the digitalized signal is stored.

Our design of the sample cell was especially chosen to minimize temperature gradients to obtain maximum supercooling of the sample.⁴ Flat glass capillaries were mounted in a silver container that could be placed in a copper holder. The holder was cooled by Peltier elements. The complete sample cell was placed in a polystyrene cover for temperature isolation. Lindemann glass capillaries of 2.0 mm outer diameter were flattened by heating them in a carbon mold. The water used was distilled, deionized, and filtered by a Millipore $0.1 \mu\text{m}$ membrane filter and degassed. After this treatment the water was put into a glass container that was sealed off, only to be opened again just before the scattering experiment, when the water was introduced into one of the capillaries.

Figure 1 shows an example of the wave-vector dependence of the scattered x-ray intensity. The strong increase below $q=0.5 \text{ nm}^{-1}$ is caused by the glass capillary and puts a limit to the wave-vector range over which the scattering by water can be determined. At all temperatures between 274 and 247 K there is virtually no q dependence in the range between 0.5 and 5.0 nm^{-1} . With the intensity in arbitrary units as $I = (c \pm \Delta c) + (m \pm \Delta m)q$ an error analysis given typically $c = 3.11 \times 10^{-3}$ arb. units, $\Delta c = 0.16 \times 10^{-3}$ arb. units, $m = -1.76 \times 10^{-5}$ arb. units nm, and $\Delta m = 4.70 \times 10^{-5}$ arb. units nm. These values are for the lowest temperature, 247 K, but only c is weakly temperature dependent, as can be seen from Fig. 2. Its decrease with decreasing temperature

FIG. 1. Examples of experimental data after correction for the detector response: $\times$, capillary filled with water at 247 K; $\square$, empty capillary; ∇ , water at 247 K.

was established from several series of measurements as $0.48\% \text{ K}^{-1}$.

If one accepts the values of the parameter c as being proportional to the values of the structure factor in the q range between 0.5 and 5.0 nm^{-1} , one can combine the values at different temperatures with compressibility data, as in Fig. 3.

FIG. 2. Difference of scattered intensity of water at 274 and at 247 K, illustrating the lack of temperature dependence in the dispersion of $S(q)$. The experimental results of Ref. 3 suggest that the difference in intensity would become zero at about 1.0 nm^{-1} .

FIG. 3. Structure factor $S(q)$ as a function of temperature. Solid line; thermodynamical limit, calculated according to $S(0) = RT\rho\chi_T$ using values from Ref. 8; $\bullet$, experimental values presented in this study.

On the basis of a percolation model for supercooled water,^{5,6} it is customary to separate the derivative thermodynamic quantities, such as the isothermal compressibility χ , into a "normal" component χ_{nor} and an anomalous component. Experimentally one has made such a separation by extrapolation from high-temperature data or from binary solution data.^{7,8} Although our setup only allows for $S(q)$ data in arbitrary units and a quantitative conclusion can therefore not be given, the relative temperature dependence of the parameter c is approximately the same as the presumed relative temperature dependence of the normal component of the compressibility. It is seen in Fig. 3 that the assumption that the quantity $RT\rho\chi_{\text{nor}}$ is equal to the value of the structure factor at small but finite wave vectors, in the range of several nm^{-1} , leads to a consistent picture. This may be taken as a support of the physical soundness of the division into a normal part and an anomalous part of the compressibility and that x-ray scattering data do provide us in a straightforward way with the temperature dependence of the normal component.

The possibility of an intensity contribution from a Lorentzian centered at $q = 0$ is severely limited by our experimental findings. Accepting the maximum possible (negative) slope, determined by the values of m and Δm , one can estimate the maximum width of a Lorentzian with a height compatible with the known macroscopic compressibility. Such a width could not be more than 0.25 nm^{-1} and the associated correlation length not less than 4 nm . Here is a discrepancy with the results published by Bosio *et al.*³ An explanation may be found in the difference in experimental circumstances.⁹ The use of synchrotron radiation as a source does away with the troublesome procedure of desmearing, among other things.

Finally, we remark that a Lorentzian contribution to the structure factor with a width of less than 0.25 nm^{-1} would not influence the values found for the scattering intensity at $q = 0.5 \text{ nm}^{-1}$ to any measurable extent. This justifies the use of the values of the parameters c as proportional to the values of the structure factor between 0.5 and 5.0 nm^{-1} .

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