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Dings, J.; Michielsen, J.C.F.; Vanderelsken, J.

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Equilibrium and nonequilibrium contributions to x-ray scattering from supercooled water

J. Dings, J. C. F. Michielsen, and J. van der Elken

*Laboratorium voor Fysische Chemie, Universiteit van Amsterdam, Nieuwe Achtergracht 127,
NL-1018 WS Amsterdam, The Netherlands*

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Percolation theory for supercooled water predicts an enhanced intensity in the low- q range of the spectrum. In small-angle x-ray measurements on water in the $|q|$ range $0.4\text{--}1.8\text{ nm}^{-1}$ and the temperature range $273\text{--}253\text{ K}$, no enhanced intensity could be measured. The spectra just follow the normal equilibrium thermodynamic behavior. A nonequilibrium enhanced intensity is observed in the spectra of supercooled water in vertically mounted capillaries in the $|q|$ range below 0.3 nm^{-1} . This intensity is due to convection in the capillaries.

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The generally accepted picture of liquid water is one in which the molecules constitute a macroscopic hydrogen-bonded network. A refined model is based on connectivity concepts as used in correlated-site percolation theory [1]. This theory gives a very satisfactory interpretation of the unusual low-temperature behavior of liquid water, in particular, for temperatures below the normal melting point down to the singularity temperature presumed to be 228 K [2]. In this model the spatial positions of water molecules with four hydrogen bonds intact are highly correlated, thus giving rise to domains of low density. This has raised the question whether the strong density fluctuations as manifested by the increasing compressibility with decreasing temperature are associated with the existence of such domains. One might expect a structure factor $S(q)$ of a Lorentzian shape $S(q) \approx (q^2 + \xi^{-2})^{-1}$, with q the wave vector and ξ the correlation length of the density fluctuations diverging towards 228 K . However, such anomalous fluctuations will be superimposed on the normal fluctuations and the amplitude of a Lorentzian contribution may be small and difficult to detect, the more so as the singularity temperature of 228 K cannot be obtained in large-size samples of supercooled water [3]. Nevertheless, there remains the question whether there is any part in the structure factor that depends on the degree of supercooling and that shows a wave-vector dependence in the low- q region. Efforts to answer this question have led to conflicting results. Bosio *et al.* [4] reported the measurement of $S(q)$ by small-angle x-ray scattering performed with a diffractometer and a conventional x-ray source. The range of the scattering vector $|q|$ was from 1.5 to 9.0 nm^{-1} . The data showed that the structure factor of supercooled water at 253 K has a minimum around $|q|=5\text{ nm}^{-1}$ and steadily increases by 20% for wave vectors down to 1.5 nm^{-1} . Michielsen *et al.* [5] later reported on an attempt to verify this result using synchrotron radiation and a geometry that allowed the measurement of $S(q)$ over the vector range $0.5\text{--}5\text{ nm}^{-1}$. Analysis of the data and of the errors involved resulted in the conclusion that there was no demonstrable q dependence in the accessible q -vector range. Furthermore, it appeared that the scattering level decreased with decreasing temperature, and since the value of the struc-

ture factor at $|q|=0$ is known to increase with decreasing temperature, this implied that there must be a strong increase of the value of $S(q)$ at $|q|$ values lower than 0.25 nm^{-1} .

To find the cause of such unsatisfactory discrepancy we ventured to repeat the experiments under improved experimental conditions. The small-angle x-ray-scattering measurements were performed at the Synchrotron Radiation Source at Daresbury, U.K. The intensity of the photon beam is in the order of 10^{11} photons per sec with a photon wavelength of 0.15 nm . The monochromatic beam in our experiments had a width of 4 mm and a height of 0.5 mm . The absorbency in the cell and the total intensity of the photon beam during the experiments were monitored by two ionization-type detectors. One was placed in front of the sample cell and the other one behind the sample cell. The scattering intensity was measured by a quadrant detector. The sensitivity of this detector is at least a factor of 10^6 better than the sensitivity of the linear detector used in our previous experiments [5] leading to an improvement of the signal-to-noise ratio of at least 3 orders of magnitude. The distance between the sample cell and detector was 450 cm , the accessible wave-vector range was from 0.1 to 2 nm^{-1} . Wet collagen was used to calibrate the wave-vector scale. The water samples were contained in capillaries made from Lindemann glass. These capillaries were heated in a carbon mould and deformed in such a way that an approximately rectangular cross section was formed. The two flattened surfaces were $5 \times 20\text{ mm}^2$. That allowed us to place the capillaries both in a vertical and in a horizontal position in the photon beam. The optical path length was $1 \pm 0.05\text{ mm}$ and the wall thickness $0.01 \pm 0.004\text{ mm}$. The cooling of the samples was achieved by cooling a silver block—surrounding the sample to minimize temperature gradients—by Peltier elements via heat pipes. The water used in the experiments was carefully cleaned, double distilled, deionized, and filtered through a $0.1\text{-}\mu\text{m}$ membrane filter. After degassing, the water was distilled in a carefully cleaned glass container, which was sealed off after filling and was only opened immediately before the experiment when the water was put into the capillary via a syringe.

FIG. 1. $S^{q=0}$ as function of the temperature. The points are the experimental data (with error bars). The dotted line is the calculated equilibrium thermodynamic structure factor.

It was clear from the earlier experiments that the procedure to properly subtract the scattering by the empty glass capillary from the total scattering is very crucial since the scattering from water is a small difference of two large quantities that have a pronounced q dependence caused by the scattering of the glass capillary. Straightforward subtraction of the scattering by an empty capillary is not necessarily correct. The comparison of the scattering of a filled and an empty capillary inevitably implies an interference with the position of the capillary in the beam. A difference of the thickness of the scattering glass of only $6 \mu\text{m}$, with an absorption coefficient of glass of about 30 mm^{-1} , might easily give variations in the scattering by the glass of 20%. To circumvent this difficulty, we chose to follow a slightly different approach. We required the $S(q)$ in the $|q|$ range $1\text{--}2 \text{ nm}^{-1}$ to be q independent for $T=293 \text{ K}$. To achieve this, one has to allow for a weight factor for each empty glass capillary, varying from 1.0 to 1.2 for different capillaries. This requirement of the q independence is supported by the results of earlier measurements of the scattering of water at 293 K [6] where the use of mica windows precluded the vitiating effect of scattering by glass. For each

FIG. 2. X-ray-scattering intensity as function of scattering vector and temperature, after subtraction of the scattering intensity of the sample at 277 K . The arrow at 260 K indicates the run at which the sample froze. The sample was contained in a *vertically* placed capillary.

FIG. 3. The same as Fig. 2 for a *horizontally* placed capillary.

set of runs with a given capillary at successive lower temperatures, the weight factor thus obtained at 293 K was used throughout. None of the spectra obtained in this way showed any $|q|$ dependence between 0.4 and 1.8 nm^{-1} . The values of $S(q)$ in this $|q|$ range thus obtained for different temperatures are shown in Fig. 1 together with the values of $[S(q)]_{q=0}$ obtained from compressibility data. As can be seen, the method leads to a complete consistency between the two sets of data. One therefore has to conclude that the value of $[S(q)]_{q=0}$ is already reached at $|q|$ values as high as 1.8 nm^{-1} for all temperatures down to 253 K . To fit a Lorentzian within the experimental errors would require a full width at half maximum larger than 4 nm^{-1} , the corresponding correlation length of 0.25 nm obviously has no physical meaning in the percolation model.

The origin of the sharp increase of the scattering intensity at $|q|$ values lower than 0.03 nm^{-1} becomes clear when we subtract from the scattering of water at a given temperature the scattering from the capillary with water at 277 K , the temperature of the density maximum. The

FIG. 4. The temperature dependence of the extrapolated difference scattering intensity for $|q|=0$ from a vertical placed capillary vs the absolute value of the expansion coefficient of supercooled and normal water.

result for a vertically mounted capillary is shown in Fig. 2. The effect is absent in a horizontally mounted capillary (Fig. 3). Clearly the strong increase of the scattering by water with decreasing temperatures at wave numbers smaller than 0.03 nm^{-1} is a nonequilibrium effect. From Fig. 4 it emerges that the excess scattering is correlated with the value of the thermal expansion coefficient. Considering the Rayleigh number for the system, one can estimate that a temperature difference of 0.10 K over a vertically mounted capillary is enough to surpass the critical value $Ra^c \approx 700$ if the system temperature is about 3°C above or below the temperature of the density maximum at 277 K. We therefore assign the temperature-dependent excess scattering at small wave numbers as caused by convection in the system. Such scattering is not necessarily caused by the density fluctuations but rather by the fluctuations in the Reynolds stress tensor. The spectrum would be given by the pressure spectrum

$$\Pi(q) = \frac{1}{8\pi^2} \int E(q') E(|\mathbf{q} - \mathbf{q}'|) \frac{\sin^4 \theta}{(|\mathbf{q} - \mathbf{q}'|)^4} dq',$$

where $E(q)$ is the energy spectrum and θ is the angle between the wave vectors $\mathbf{q}$ and $\mathbf{q}'$ of the associated fluctuations [7]. The wave vectors in the region of observation are far beyond any microscale and, moreover, so large

that the form of $\Pi(q)$ is determined by the form of the energy spectrum $E(q)$ in that wave-vector region.

On the other hand, density fluctuations at small wave vectors may be enhanced by convection by a variety of mechanisms. Coupling through the density-dependent viscosity between shear flow and density fluctuations might occur, analogous with the effects in polymer solutions [8,9]. Considering the relatively low Reynolds numbers, it is, however, clear that the $\mathbf{q}$ -vector range where we measure the effect is well in the dissipative range. Local temperature gradients caused by the convection may give rise to an enhancement of the structure factor as proposed by Kirkpatrick and Cohen [10]. The measured $\mathbf{q}$ -vector dependence does not allow a decisive conclusion about the applicable mechanism, it is approximating an algebraic decay with power -2 .

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