Noncritical Behavior of Density Fluctuations in Supercooled Water

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We have measured the absolute structure factor of liquid water over the wave-number range $0.05 < k < 0.30$ Å^{-1} and temperature range $-34 < T < 25\,°C$ with small-angle x-ray scattering. The correlation lengths of density fluctuations are small and change very little with temperature, suggesting that supercooled water may not be approaching a proposed spinodal point. The increasing density fluctuations with supercooling in water appear to be due to an increasing fraction of water molecules participating in clusters, not an increasing range of correlations.

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Because of its unusual properties, supercooled water has received much attention. With decreasing temperature, anomalous thermodynamic behavior, including rapidly increasing isothermal compressibilities and specific heats [1], is seen, which implies that density fluctuations in the liquid grow. There are several theories which attempt to account for the origin of the enhanced density fluctuations in supercooled water [2–6]. Among them, one of the most widely discussed is the spinodal hypothesis, which suggests that anomalous thermodynamic behavior is associated with an instability, or spinodal, point at $T_s \sim -45\,°C$ [2]. However, experimental evidence distinguishing between theories is still inconclusive. Although the low-wave-number structure factor $S(k)$, which is the Fourier transform of the density-density correlation function in the liquid, is one very important experimental piece of the water puzzle [7], the liquid's weak scattering and broad line shape have led to contradictory results from previous experiments [8–12]. Here we report an absolute measurement of $S(k)$ using synchrotron-based small-angle x-ray scattering from water supercooled down to the lowest temperature possible in bulk samples, $-34\,°C$.

Early small-angle scattering studies of water [8] focused on verifying the thermodynamic relationship between the limit of the structure factor at zero wave number and the isothermal compressibility κ_T:

$$S(k=0) = k_B T n \kappa_T, \qquad (1)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and n is the molecule number density. However Bosio, Teixeira, and Stanley [9] were the first to examine the low-wave-number structure factor of water that is supercooled; they showed that the low-wave-number peak of $S(k)$ grows with decreasing temperature. Because of the limited wave-number range of their experiment, $0.15 \le k \le 1.0$ Å^{-1}, Bosio, Teixeira, and Stanley were not able to observe the detailed line shape at low wave numbers. Howerer, they estimated the correlation

length at their coldest temperature, $-20\,°C$, to be on the order of 8 Å. Subsequently, Michielsen, Bot, and van der Elsken [10] attempted to repeat these measurements but found that after subtraction of the large background due to the glass capillary sample container, no k dependence was seen. In response, Bosio, Teixeria, and Bellissent-Funel [11] used small-angle neutron scattering to corroborate the upturn seen by Bosio, Teixeira, and Stanley [9]. Most recently, Dings, Michielsen, and van der Elsken [12] in a new measurement reported no k dependence for $0.04 \le k \le 0.18$ Å^{-1}, although they did claim a Lorentzian fit to a broader range of k implied a correlation length on the order of 2.5 Å.

Given this history, a few comments are appropriate. The scattering from water is very weak and high incident x-ray beam intensity and/or long accumulation times at each data point are required to give a good signal-to-noise ratio. Background subtraction and cell geometry are important sources of error if not carefully considered. The structure factor varies very slowly with wave number in the accessible temperature range of supercooling. For instance, in the k range of Ref. [12], our measurements show that $S(k)$ varies by only 15% at $-10\,°C$.

The experiments reported here were performed at the X-20C beam line of the National Synchrotron Light Source at Brookhaven National Laboratory and used a high flux multilayer monochromator and a position sensitive detector [13]. The absolute incident beam intensity was monitored with a helium-filled ion chamber and also independently determined by measuring the attenuated direct beam on the diode array detector.

Two different types of sample holders were employed. In the first type, de-ionized and filtered 18 MΩ H_2O samples were held between thin flat Kapton windows, which themselves contributed very little x-ray scattering. The scattering from Kapton windows was approximately 25%–30% of the total scattering at 20° C. These samples could be cooled down to $-20\,°C$ before crystallizing and the structure factor was measured down to 0.05 Å^{-1}. The sample thicknesses were chosen to be near 2 mm (ap-

proximately two absorption lengths of water at the x-ray wavelength used). The second set of water samples was enclosed in sealed 1 mm x-ray capillaries. After annealing [14], some of these could be cooled down to $-34\,°C$ for several minutes without freezing, a significant improvement over water samples in the Kapton sample holder. Raman scattering and density measurements have found no effect of the annealing on the structure of the supercooled liquid [14]. The incident beam was slit down to 0.2 mm, so that the capillaries were effectively flat on the beam's length scale to facilitate the proper subtraction of the sample holder and other "parasitic" scattering. Because of strong glass scattering at low wave numbers in these samples, the water scattering was approximately 9%–25% of the total scattering even at the lowest temperature, $-34\,°C$. However, it could still be reliably extracted. The structure factor in these samples was also measured down to 0.05 Å^{-1}. Although experiments using the two different sample geometries were performed 6 months apart using different slit sizes, they both lead to the same conclusions. Because of their wider temperature range, we will display and discuss results from the capillary samples throughout the remainder of the report.

The scattering patterns were normalized to an absolute differential cross section using the measured incident beam intensity. The empty capillary scattering was then carefully subtracted from the total scattering and normalized water structure factors were calculated from the observed differential cross sections. Figure 1 shows the normalized structure factors at 0, -23, and $-34\,°C$. The larger error bars at low wave numbers reflect the increased uncertainty associated with the removal of the capillary holder scattering there. As expected, the structure factor increases with decreasing temperature, indicative of the growing amplitude of density fluctuations.
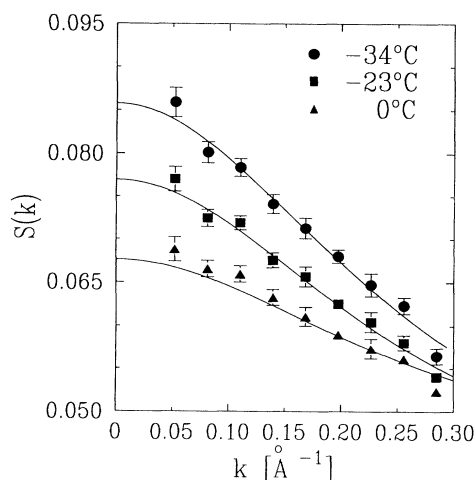

FIG. 1. Measured structure factors of H_2O at three different temperatures. Lines are fits by Eq. (2).

The lines in Fig. 1 are fits of the measured structure factors to the Ornstein-Zernicke Lorentzian form characteristic of a system approaching a spinodal or a critical point [15]:

$$S(k) = S^n(k) + S^a(k) = S^n(k) + C\frac{k_BT}{k_c^2 + k^2}. \qquad (2)$$

Here $S^n(k)$ and $S^a(k)$ are the "normal" and "anomalous" components of the structure factor, respectively. The latter is associated with the critical fluctuations. The correlation length of the fluctuations is $\xi(T) = k_c^{-1}$. Most liquids show no sign of an instability point at low temperatures and $S(k)$ is then relatively constant in the low-wave-number regime. We have investigated several forms for $S^n(k)$ in our fits. For the fits shown in Fig. 1, the $S^n(k)$ were assumed to be k independent with values calculated from the normal isothermal compressibility [$\kappa_T^n(T)$] measurements of D'Arrigo and Paparelli [16]. The normal component varies from 0.047 at $25\,°C$ to 0.033 at $-34\,°C$. The fit correlation lengths range from roughly 3.6 to 3.8 Å for temperatures between 25 and $-34\,°C$. Other reasonable assumptions for the shape of $S^n(k)$ (e.g., a Percus-Yevick form [17]) yield equivalent results. If no normal component is assumed in the fit, the correlation lengths are much smaller—from 2.0 to 2.8 Å, in good agreement with Dings, Michielsen, and van der Elsken [12].

If there is a spinodal or a critical point nearby, $\xi(T)$ should diverge as it is approached. Within the mean-field approximation, the correlation length would diverge with temperature as a power law when the spinodal or critical point is approached:

$$\xi(T) = \xi_0 \epsilon^{-\nu}, \qquad (3)$$

where $\epsilon = (T - T_s)/T_s$ is the reduced temperature, ξ_0 is a constant comparable to the length of interactions in the system, and $\nu = \frac{1}{4}$ for a spinodal point [18,19] and $\frac{1}{2}$ for a critical point [15]. In contrast, measurements in Fig. 2 show that there is no significant increase of ξ. For comparison, the calculated correlation lengths according to Eq. (4) with $\nu = \frac{1}{4}$ are also shown (assuming a spinodal temperature $T_s = -45\,°C$ and $\xi_0 = 2.5$ Å evaluated from our measured correlation length at $0\,°C$). It can be seen that the calculated correlation lengths increase rapidly at low temperatures, contrary to what is observed.

As shown in Fig. 3, values of $\kappa_T(T)$ calculated from the extrapolated $S(k=0)$ values of Fig. 1 display the same upward curvature with decreasing temperature as published $\kappa_T(T)$ measurements [18,20]. We know of no published values of the compressibility at the lowest temperatures examined here. However, while the error bars on the $S(k=0)$ values measured here are relatively large, they systematically fall below the extrapolated values of the divergent fit of Ref. [18] at the lower temperatures. Agreement with the extrapolation of Ref. [20] is better.

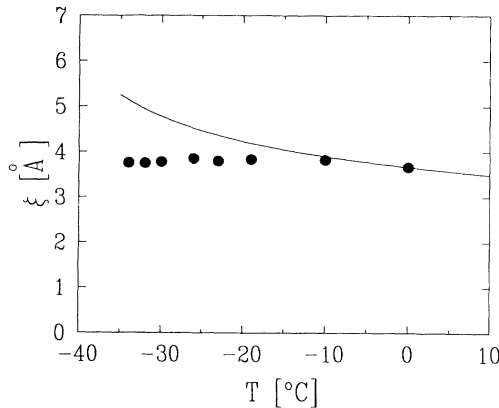The contrasting behavior of κ_T and ξ—the former in-

FIG. 2. Correlation lengths at different temperatures obtained by fitting the structure factors by Eq. (2). The line is calculated from Eq. (3) with $T_s = -46\,°C$ and $\xi_0 = 2.5$ Å.

FIG. 3. Comparison between previous measurements of κ_T and values calculated from extrapolations of the measured $S(k)$ to $k = 0$.

creasing rapidly with decreasing temperature and the latter remaining constant in the same range—has important implications for the nature of supercooled water. If the properties of water were dominated by a neighboring spinodal or critical point, increases in κ_T and ξ should be coupled. The Ornstein-Zernicke correlation function predicts $\xi^2 \sim \kappa_T$. Our results contradict such a relationship and question whether the properties of supercooled water can be associated with either a spinodal point [2] or a critical point separating amorphous phases [6].

What then is the cause of the anomalies in supercooled water? Although our experiments do not definitively resolve this issue, they do put strong restrictions on future structural models.

Several models attribute the growing compressibility of the liquid to density fluctuations between regions that are "liquidlike" and those that have a local structure similar to that of hexagonal ice [4]. Gaussian fits to the measured structure factors yield a cluster radius of gyration [21] of $R_g \approx 5$ Å independent of temperature. However, the strength of scattering from such small clusters is too small to account for the experimental scattering intensity if we assume a reasonable independent cluster population and density difference between the clusters and the matrix.

These considerations naturally lead to the examination of models in which clusters are connected. Stanley and Teixeira [3] have suggested one such model in which fourfold-bonded regions in water are similar to polychromatic correlated-site percolation clusters. An interesting consequence of this model is that, since it incorporates only nearest-neighbor correlations, the width of the resulting $S(k)$ peak is essentially independent of the bond probability. This implies that even though the hydrogen bonding density increases with supercooling, the measured correlation length would be roughly independent of temperature, in agreement with our experimental results. However, the magnitude of $S(k)$ predict-
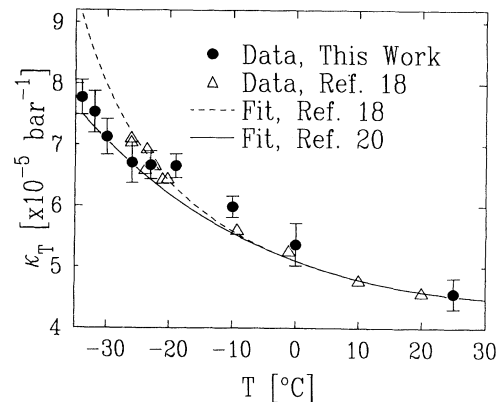
ed by this model is too small to account for the observed $S(k)$ and compressibility values by approximately a factor of 5. Moreover, the experimental radius of gyration above suggests that correlations in water extend beyond nearest neighbors. Models seeking to explain the anomalous behavior of water based upon connected clusters with the density of hexagonal ice must therefore incorporate stronger correlations than exist in the simple polychromatic percolation approach.

Several workers have pointed to the possible existence of "clathratelike" polyhedra and cages in liquid water [5]. These polyhedra typically have cavity radii of ~ 2.5 Å and hence overall radii, including the water molecules that make up the polyhedra, of 5-6 Å. Also, because of the high contrast between low density clathratelike structures and the liquidlike matrix in water, far fewer clusters would be required to give the observed structure factor peak than in the case of the higher density hexagonal ice clusters. Thus the clathrate polyhedra picture is not inconsistent with our measurements.

In conclusion, we have measured the absolute structure factor of supercooled water down to $-34\,°C$, corresponding to a reduced temperature of 0.05 with respect to the proposed spinodal point. This is currently the lowest temperature of supercooling possible with bulk samples. Although the experimental structure factors display an upturn at low wave numbers which grows with decreasing temperature, the fit correlation lengths are small and relatively constant with supercooling. This is at odds with what is expected if water is approaching a spinodal point. Thus it appears that the increasing density fluctuations with supercooling in water are associated not with increasing correlation lengths, but rather with an increasing fraction of water molecules participating in clusters.

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