Enhanced Density Fluctuations in Supercooled H_2O, D_2O, and Ethanol-Water Solutions: Evidence from Small-Angle X-Ray Scattering

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The static structure factor $S(q)$ for H_2O was measured by x-ray scattering for 0.15 Å^{-1} $< q < 1$ Å^{-1} and for 253 K$< T < 348$ K. The low-temperature data show a surprising increase of $S(q)$ with decreasing q, which can be fitted with a Lorentzian whose width corresponds to density fluctuations with a length scale that increases to about 8 Å as T is decreased to 253 K. The anomaly is more pronounced in D_2O, while small amounts of the hydrogen-bonding impurity ethanol decrease the anomaly.

The structure factor $S(q)$ of a one-component fluid is, by definition, proportional to the Fourier transform of the density-density correlation function $g(r)$. For simple fluids, $S(q)$ has a pronounced peak at roughly 2 Å^{-1}, corresponding to the fact that $g(r)$ has a characteristic maximum at roughly the nearest-neighbor separation.[1] Near the critical point, $S(q)$ has a pronounced increase about $q = 0$, which can often be approximated with a Lorentzian function,[1]

$$S(q) \sim [q^2 + \xi^{-2}]^{-1}, \tag{1}$$

where ξ is interpreted by Ornstein-Zernike theory as the correlation length and is a measure of the characteristic length scale of the density fluctuations.

Recent experimental and theoretical work on liquid water suggests that increased density fluctuations may *also* be present at low temperatures, especially for $T < T_m$, the normal melting temperature.[2-4] However, no indications of a $q = 0$ peak in $S(q)$ have been reported.[5] In this work we present new measurements of $S(q)$ using small-angle x-ray scattering from samples of H_2O, D_2O, and H_2O with a hydrogen-bonding "impurity." These data provide the first *microscopic* probe of density fluctuations that *increase* as T decreases (below T_m) for any fluid.

The samples were contained in Lindemann glass tubes (wall thickness 0.01 mm) filled by Mossop's method[6] to obtain the maximum degree of super-

cooling. The 1 mm i.d. of the tubes limited our data to $T > 253$ K for H_2O ($T_m = 273$ K) and $T > 256$ K for D_2O ($T_m = 277$ K). The H_2O was bidistilled, deionized, and filtered; its electrical resistivity was about 15×10^6 Ω cm. The D_2O (NMR spectroscopy quality) was 99.75% pure. Sealed Lindemann tubes were inserted in a Cu chamber provided with an Al-covered Mylar film (0.01 mm thick), and placed in a cryostat.[7] A Pt resistor was the sensing element to regulate T, which was controlled to ± 0.1 K; gradients in the sample of ± 0.5 K were measured at T_m by using x-ray diffraction. The intensity $I(q)$ was measured with a modified diffractometer described previously.[7] Monochromatization of the Cu $K\alpha$ radiation was achieved by a bent LiF monochromator in the diffracted beam, in conjunction with a scintillation detector and a pulse-height discriminator in the detecting circuit. The incident beam (whose divergence was reduced to 0.001 rad by a 0.3-mm entrance slit) and the emergent beam were contained in two evacuated guides. The momentum transfer vector q was varied from 0.15 to 1.00 Å^{-1} in constant steps of 0.04 Å^{-1}. With few exceptions, $I(q)$ was measured with a fixed-count method: The time required to accumulate 15×800 x-ray pulses was recorded from fifteen runs carried out over the q range. Typical data are presented in Fig. 1.

It is well known that some difficulties arise in correcting the raw data for smearing by the collimation system,[8] the container scattering and
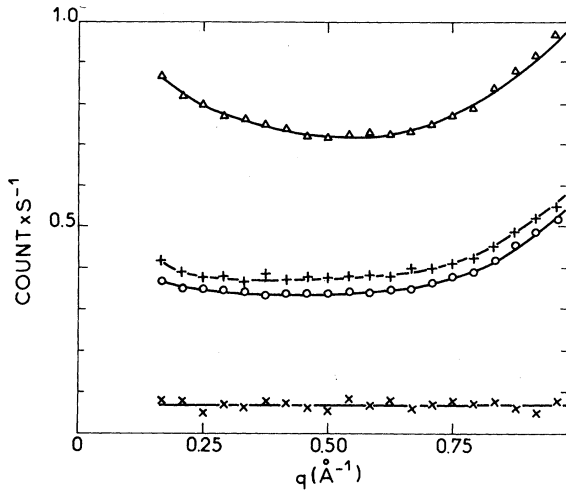
FIG. 1. Observed scattering intensity $I(q)$: Crosses, background; plusses, empty container; circles, H_2O in the ice I_h phase at $T = 253$ K; and triangles, typical data (H_2O at 253 K).
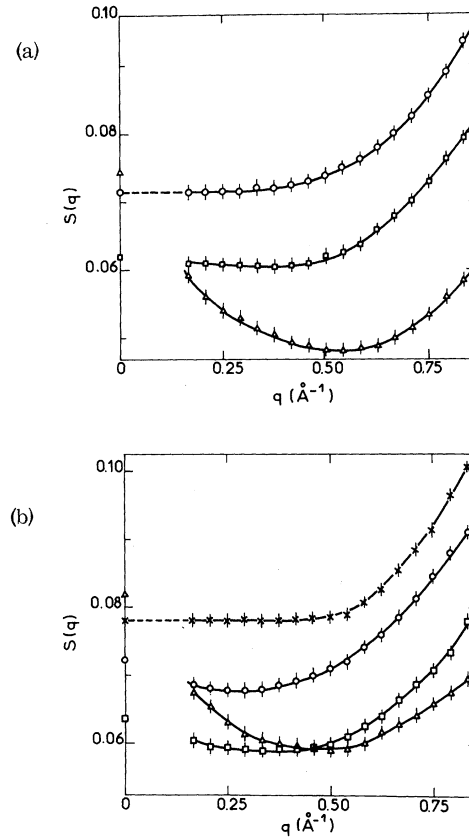

FIG. 2. $S(q)$ for (a) H_2O and (b) D_2O at several different temperatures: Crosses, 363 K; circles, 348 K; squares, 298 K; and triangles, 253 K. The error bars are estimates based on the dispersion observed from measurements on three different samples. The points at $q = 0$ are obtained from Eq. (2) and K_T data of Ref. 3.

absorption, and the multiple scattering[9] before determining the absolute intensity calibration factor.[10] These complications did not arise here, since we are concerned with the T dependence of $I(q)$. Nevertheless, the slit-size corrections might be neglected, taking into account the diffractometer geometry and the q range. The container contribution was eliminated by subtracting from the total intensity the scattering from the frozen sample. We have thus assumed that the thermal diffuse scattering from ice is either negligible, or at least is roughly constant in the q range explored. This assumption is confirmed by the fact that the difference between the scattering from the empty Lindemann glass tube and from the crystalline sample (Fig. 1) is only attributable to the absorption of ice, and is found to be negligible. Multiple scattering, contributing a few percent of the excess intensity in the forward direction,[5,11] has been assumed small for $q > 0.25$ Å^{-1}. Finally, $I(q)$ was corrected with the use of the molecular structure factor of Narten and Levy.[12]

The normalization factor was determined by extrapolating, to zero angle, the high-T data where $I(q)$ seems to be sufficiently flat to coincide with $I(0)$ predicted from the relation

$$S(q = 0) = RT\rho K_T. \tag{2}$$

Here R is the gas constant, ρ the mass density, and K_T the isothermal compressibility. The calibration factors for H_2O and D_2O were found to be in the same ratio as their densities — a good

check.

$S(q)$ thereby obtained is plotted for H_2O in Fig. 2(a), and for D_2O in Fig. 2(b). Note that the H_2O data for $T = 253$ K display a clear minimum at 0.53 Å^{-1} and cross the $T = 298$ K curve at 0.15 Å^{-1}. In D_2O the anomaly is more pronounced, with even the $T = 348$ K data indicating the presence of a minimum (for this reason, data at $T = 363$ K are also shown). Figure 3 shows the effect of small concentrations of the hydrogen-bonding impurity C_2H_5OH on the $T = 253$ K data. It is clear that the minimum becomes less pronounced with increasing ethanol concentration, and almost disappears for 5.8 mol% C_2H_5OH.

It is customary to analyze low-temperature data on water by separating functions into two components, a normal component and an anomalous component.[3,13-15] Hence we write[16] $S = S^N + S^A$, where, from Eq. (2), S^N ($= RT\rho^N K_T^N$) is assumed
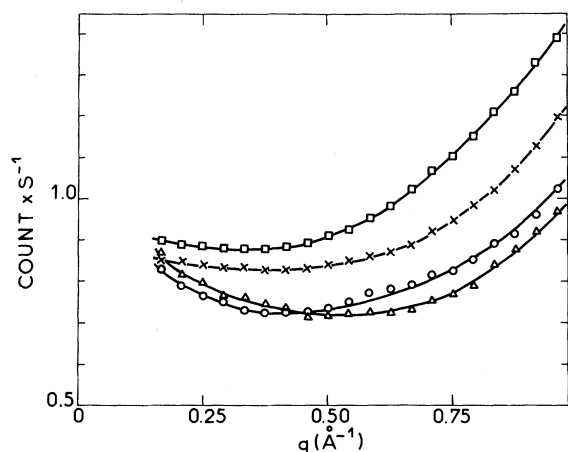
FIG. 3. Effect of small concentrations of a hydrogen-bonding "impurity" on $I(q)$ at $T = 253$ K: Triangles, pure water; circles, 1.7; crosses, 3.5; and squares, 5.8 mol% C_2H_5OH.

to be roughly independent of q for small q, consistent with the behavior for other fluids and the high-T data on H_2O. Using values of K_T^N reported elsewhere,[3] we find that S^A is remarkably well described by Eq. (1). Moreover, we find that ξ is roughly 8 Å at $T = 253$ K for H_2O, is somewhat larger for D_2O, and becomes dramatically smaller when hydrogen-bonding impurity is introduced.

The presence of such density fluctuations is not entirely unexpected in low-temperature water, because of recent theoretical conjectures.[3-4] Whether the system is tending toward a "spinodal" (as suggested in Ref. 3) or a "percolation threshold" (as suggested in Ref. 4) cannot be completely resolved by the present data, since both possibilities are consistent with an increase in ξ as T decreases.[17] However, our data do rule out the oft-discussed "iceberg clusters" appearing in a "sea" of dissociated liquid.[2]

In conclusion, we have found a surprising increase in $S(q)$ with decreasing q in pure H_2O and D_2O at low temperature. Moreover, the data are described by a Lorentzian with a half-width corresponding to density fluctuations with a length scale ξ that increases to about 8 Å as T is decreased to 253 K, consistent with very recent calculations on hydrogen-bond networks in liquid water.[18,4]

We wish to acknowledge extremely stimulating discussions with A. Geiger, technical assistance from O. Conde, and support from the U. S. Office of Naval Research, the National Science Foundation, and Le Centre National de la Recherche

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[1]See, e.g., P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967); H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, New York, 1981), 2nd ed.

[2]A recent and comprehensive review of the anomalies displayed by water at low temperatures is given by C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1981), Vol. 7.

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[4]H. E. Stanley and J. Teixeira, J. Chem. Phys. 73, 3404 (1980); H. E. Stanley, J. Phys. A 12, L329 (1979). The picture presented by two of us there is that liquid water is a macroscopic hydrogen bonded network, as expected from continuum models of water. Tiny "patches" of this network, perhaps those in which all bonds are intact, are of lower density than the rest of the network and hence give rise to anomalous density fluctuations. Moreover, this previous work predicts that small quantities of a hydrogen-bonding impurity should significantly decrease the characteristic size of these low-density "patches," and thereby reduce the density fluctuations. Thus the data presented in this paper are consistent with these earlier predictions.

[5]Previous measurements of $S(q)$ in water did not attain extremely low q or extremely low T; see, e.g., R. W. Hendricks, P. G. Mardon, and L. B. Schaffer, J. Chem. Phys. 61, 319 (1974), and references therein.

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[17]Experiments of this sort could distinguish the two possibilities provided data could be obtained at still

lower temperatures (e.g., by using a synchrotron radiation source). It would be particularly interesting if the data were to indicate a maximum in $\xi(T)$, consistent with the recently observed maxima in the adiabatic compressibility [see, e.g., Ref. 15, and E. Trinh and R. E. Apfel, J. Chem. Phys. 72, 6731 (1980)], as such behavior could rule out the spinodal possibility.

[18]A. Geiger et al., to be published.

Buckling Reconstruction on Laser-Annealed Si(111) Surfaces

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Angle-integrated photoemission and low-energy electron-diffraction studies of laser-annealed Si(111) surfaces show that a buckled reconstruction takes place upon laser quenching. No long-range order exists but a short-range 2×1 reconstruction is present.

There is much interest in laser-annealed Si(111) surfaces,[1-3] because of the apparently perfect regrowth of the surface layer (no reconstruction)[1] and of the cleanness of the surface after laser annealing.[4] If the top layer is a simple termination of the bulk, then theoretical models[5] for a perfect, unreconstructed Si(111) surface ought to predict the surface electronic structure. However, if the top layer is disordered,[6] then evidence of this disorder should be reflected in the surface density of states as measured by photoemission spectroscopy. In this Letter, we report a photoemission study of laser-annealed Si(111) surfaces. Our results clearly show that the peak in the surface state density is not located in the band gap as expected for a relaxed unreconstructed surface layer,[7] but instead, the surface states peak ~0.5 eV below the top of the valence band. The opening of a gap[8] in the dangling-bond density of surface states upon laser annealing is attributed to a buckling of the surface atoms. Low-energy electron-diffraction (LEED) studies of flat and stepped Si(111) surfaces show the presence of very weak half-order spots, after laser annealing, consistent with a buckled (2×1)-like reconstruction. The weakness and diffusivity of the half-order spots for the flat Si(111) surface suggests a lack of long-range order in the top silicon layer.

The photoemission LEED chamber used a double-pass cylindrical-mirror analyzer (CMA)[9] with 0.25 eV energy resolution and a resonance lamp radiation at 11.7 eV (Ar), 16.8 eV (Ne), or 21.2 eV (He), incident at an angle 70° measured from the sample normal. The n-type Si(111) samples ($\rho \sim 1\ \Omega$ cm) were cleaned by argon sputtering (1 kV, 10 μA/cm^2 for 3 h) followed by thermal annealing at 1000 °C by resistive heating. The

LEED pattern obtained after such a treatment was a very sharp 7×7. In all cases, Auger analysis revealed that less than 1% of an impurity monolayer was present at the surface. The laser was a Q-switched Nd-doped yttrium aluminum garnet laser (1.064 μm) equipped with a frequency doubler. A typical Q-switched pulse gave ~0.4±0.2 J/cm^2 at 5320 Å in a 10-nsec pulse as estimated from the threshold for order-disorder transition of the 7×7 LEED pattern at 0.2 J/cm^2 and 1130 K.[10,11] Refracting prisms eliminated the 1.06-μm radiation from the optical path. To uniformly laser anneal the sample over the complete 2×0.6 cm^2 area, ~600 shots were fired at a rate of 10 shots/sec while the sample was slowly translated in front of the beam. After laser annealing, the LEED pattern was recorded on polaroid film and angular intensity profiles recorded with a Vidicon camera interfaced to a minicomputer.[9]

The photoemission results are summarized in Fig. 1. In order to match the bulk feature[12] at −4.8 eV the photoemission spectra for the laser-annealed surfaces had to be shifted by −0.15 eV, thus shifting their Fermi energy by the same amount. This shift is due to a change in band bending,[13] similar in sign and magnitude to that occurring for the Si(111)-(2×1) surface.[14,15] The main feature characterizing the laser-annealed spectra is a strong dangling-bond surface peak located at −0.85 eV below E_F. Note that the strength of the mostly p_z-like surface states in the 0−1-eV region is greatly reduced because of the acceptance angle of the CMA (42°± 6° with respect to the normal).[16] The back-bond states located at −2 and −8 eV are suppressed and enhanced, respectively, for laser-annealed surfaces as shown in Fig. 1.