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The Structure and Dynamics of Amorphous and Crystalline Phases of Ice

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Abstract

The structures of the high and low-density amorphous phases of ice are studied using several techniques. The diffraction patterns of high and low density amorphous ice are analyzed using reverse Monte Carlo methods and compared with molecular dynamics simulations of these phases. The spectra of crystalline and amorphous phases of ice obtained by Raman and incoherent inelastic neutron scattering are analyzed to yield structural features for comparison with the results of molecular dynamics and Reverse Monte Carlo analysis. The structural details obtained indicate that there are significant differences between the structure of liquid water and the amorphous phases of ice.

Introduction

The structure of liquid water at low temperatures and high pressure has been a subject of significant research since the discovery of the high-density amorphous (HDA) phase of ice Ih\(^1\). Since HDA ice was obtained at a pressure close to the extrapolated melting curve of ice, it was suggested that it may have a structure similar to dense water. Upon annealing, HDA ice transforms into a low density form (LDA) with a distinct phase boundary.\(^2,3\) Extrapolation of thermodynamic data along the HDA-LDA ices coexistence line into the liquid region led to a hypothesis of the existence of a second critical point for water and the speculation that liquid water is a mixture of two distinct structures with different densities.\(^4\)

In this paper, a reverse Monte Carlo analysis of diffraction data is carried out for the structures of HDA and LDA ice in order to compare it with the structure of quenched liquid water obtained by molecular dynamics simulations. The vibrational spectra of ice Ih, LDA ice and quenched water obtained using incoherent inelastic neutron scattering and Raman spectroscopy are used to compare structural details of amorphous and crystalline forms of ice by examining the vibrational modes of water molecules in these materials.

Experimental and Computational Details

RMC analyses\(^5,6\) were performed on the experimental structure factors obtained from neutron diffraction experiments on fully deuterated (D\(_2\)O) samples. Since the structural model produced by RMC may not be unique, to avoid biasing the RMC analysis, two initial structural models constructed from liquid water and ice Ih were used. For the ice Ih starting configuration, a model system in a rectangular cell with a zero dipole moment consisting of 1562 water molecules was constructed. The water simulation cell was prepared by performing a MD calculation on 1152 water molecules at 300 K employing the TIP4P potential.\(^7\) The geometrical constraints applied to the water molecule in the RMC analysis are that the O-D bond must be shorter or equal to 1.1 Å and the D-D distance is less than 1.59 Å. The corrections to the experimental neutron diffraction data used for the RMC analysis have been described in detail.\(^8\) The radial distribution function for oxygen atoms and the O–O–O angle distribution are also obtained from molecular dynamics simulations on a 216 and 512 water molecule samples quenched to 100 K that employed the NCCFLEX polarizable water potential.\(^8\)

The samples of HDA were prepared by pressurizing ice Ih to 14 GPa at 77 K. The apparatus used has been described previously.\(^8,10\) The was no evidence of crystalline impurities that have been identified as ice XII\(^11\). The reasons for the appearance of ice XII or other crystalline impurities is currently under investigation and has not been clearly understood. The samples were contained in liquid nitrogen during release of pressure and sample manipulation, and then mounted in a cell of planar geometry (75 mm by 100 mm) with a thickness of about 1–2 mm for the neutron measurements. Samples were maintained at 15 K for the neutron scattering measurements. After data was collected on this sample, it was annealed at 120 K for 10 min to transform it to low-density amorphous ice (LDA) and cooled back to 15 K for measurements. The sample was then annealed at 150 K to first form ice Ic and then at 240 K to produce ice Ih. Hyperquenched water (HWQ) was prepared by rapid cooling (10\(^8\) K/s) of 3 micron diameter water droplets as described in Ref. 12.

The neutron incoherent inelastic scattering (INS) measurements were performed using the High-Resolution Medium Energy Chopper Spectrometer (HRMECS) at the Intense Pulsed Neutron Source of Argonne National Laboratory. Incident neutron energies (E\(_i\)) of 300 and 600 meV were employed to cover the energy regions of both the librational and internal stretching vibrations with good resolution. The energy resolution ΔE/E₀ (ΔE = full-width-at-half maximum) was approximately 3 % at the upper end of the neutron-energy-loss spectrum. The low scattering angles (<20°) result in a relatively low wave-vector transfer Q (~3 and ~8 Å\(^{-1}\)) at energy transfers of 80 and 450 meV, respectively, for the high incident energies E\(_i\) used in this study. The Doppler broadening of the vibrational peaks was therefore minimized.

Results and Discussion

The structure factor S(q) (Fig. 1) of HDA and the oxygen atom radial distribution function (O-O r.d.f.) (Fig. 2) derived from two different starting structures in the RMC analysis are
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very similar and differ significantly from the ice Ih precursor. The solid and dotted lines are for results using crystalline ice Ih and water starting configurations, respectively. Inspection of the structural model for HDA ice obtained from the RMC calculations shows packing of oxygen atoms into the interstitial voids of the ice Ih structure. This is characterized by the peak at ~3.2 Å in the O–O r.d.f. and the broad deviation from the ideal tetrahedral angle and significant additional low-angle contribution to the O–O–O distribution (Fig. 5). This HDA ice structure agrees with an earlier MD calculation that showed that additional O atoms were forced into the first-neighbor coordination sphere in a collapsed ice structure. There are

at 6.3 Å. To make a meaningful comparison with HDA ice, the experimental structure has to be compared to quenched water at a density of 1.17 gm/cm³. This is done in Fig. 5 where the O–O–O distribution from the RMC analysis is compared with the results of the molecular dynamics simulations performed here using the NCC potential.

A similar analysis has been performed on LDA and, as in the case of HDA, the structure factor was fit well by the RMC analysis (Fig. 3). The RMC fit (Fig. 4) for the O–O r.d.f. shows differences depending on the starting configuration (Fig. 4). The resulting fit of the O–O–O angle distribution is shown in Fig. 6 and compared with the results of a molecular dynamics simulations on water quenched at 1 bar to 100 K. It is clear that in this case there are also differences between LDA and quenched water. It appears from the RMC analysis that LDA is similar to a relaxed form of HDA. Further work on this is currently in progress using x-ray data.
The comparison of the inelastic incoherent neutron spectra of HDA, LDA, ice Ih and quenched liquid water is shown in Figure 7 and 8. It is clear from the spectra in both the region of the librational vibrations of water molecules and for internal modes of water molecules that the hydrogen bond strengths, as reflected in the onset and peak energies of the bands, show differences between the amorphous and crystalline phases. The energies of the librational bands in the energy range 55 –135 meV are sensitive to the hydrogen bond strengths the restrict rotation of water molecules in the material. The lower onset and mean energy for HDA band indicates that the hydrogen bond strengths in this material are weaker than for the other LDA, quenched water, and Ice Ih. This is also indicated in the high energy region and is consistent with data obtained in this region for Raman spectra obtained on dilute solutions of H2O in D2O.

The peak and onset energies in the Raman and IINS spectra are to a good approximation related to the average O – H – O hydrogen bond lengths in these materials and therefore show that the hydrogen bond lengths in HDA are somewhat longer than in the other phases. It is also clear that LDA has mean hydrogen bond strengths that are similar to Ice Ih and differ from quenched water. Thus, it appears from these measurements that LDA is not structurally identical to quenched liquid water and may not be a good model for this material. It also has been clearly shown that the mechanism for the formation of HDA is due to a mechanical instability in the ice lattice.

Conclusion
The relationship between quenched water, HDA, LDA, and ice Ih has been investigated using IINS, RMC analysis, and molecular dynamics simulations. The results indicate that there
are distinct differences between liquid water and the amorphous phases and support the results of previous calculations and suggestions regarding the structure of HDA. This raises the question whether there is a thermodynamic connection between the amorphous phases made by pressurization and subsequent annealing and whether these phases should be used to support the hypothesis that two forms of liquid water may exist at low temperatures. This very interesting idea will certainly require further research.

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