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Investigation of phase transfer properties of light and heavy water by means of energy selective neutron imaging

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ABSTRACT

We report an investigation of the phase transitions between water and ice using neutron imaging as a research tool. Because of the high scattering cross section of hydrogen for slow neutrons, very small amounts of water can easily be quantified by this technique. However, it is not easy to determine the aggregate state (liquid or solid) if the sample does not have a well defined size, as might happen in the case of water produced in PEM fuel cells. It is important to be able to judge the state of the water (or ice), particularly when it is not easily accessible or hidden by the surrounding structure.

The neutron interaction properties of the two aggregates (water and ice) were investigated in dynamic series, in which light water and heavy water were frozen under controlled conditions; transmission images were taken continuously during the phase transition. In addition to the expected density reduction of the ice, some other features were also observed in the images, causing the derived neutron transmission data to differ from the tabulated nuclear data.

Energy-selective experiments with thermally stabilized water (+10 °C) and ice (−10 °C) showed different interaction behaviors for the two aggregates in the neutron wavelength range of 2–6 Å. We found clear differences in the absolute values of the attenuation cross-sections and the slopes of their energy dependencies. This result might be used in the future as a criterion to distinguish between the aggregate states in arbitrary water or ice assemblies.

1. Introduction

Water is a common material in nature, and it is well understood in principle. When clean water is cooled to 0 °C or below at normal pressure, the phase transition to ice occurs. This transition is accompanied by a volume expansion produced by the formation of crystals, which occupy more space than the liquid water before freezing. From the literature, the density reduction is known to be approximately 10% [1]. This abrupt density change is more significant than the water density variations around the point of anomaly (+4°).

The observation of hidden water inside opaque objects is possible with the help of neutrons, for which the spatial and time resolution depends on the specific experimental setup.

Water plays an essential role in Polymer Electrolyte Membrane PEM fuel cells because their conductivity and gas transport properties are strongly influenced by their moisture distribution. Perhaps the most prominent future application of PEM fuel cells is their possible use as an alternative energy source in cars.

If the usage of fuel cells in temperature ranges near the freezing point is envisaged, their behavior must be studied in greater detail. In particular, the phase transition from water to ice and back should be investigated non-invasively during fuel cell operation [2].

In this study, neutron imaging was used as a research method for this purpose. Neutrons provide high sensitivity in water detection and quantification, even through thick layers of optically opaque materials (e.g., metals).

We performed two different investigations:

1. In the first investigation, the temperature was changed from +25 °C to −30 °C and the phase transition was monitored in-situ. Transmission images were taken continuously over the full temperature range, and the effective attenuation was derived, characterizing not only the density variation but also the neutron scattering behavior. This study was conducted for both light water (H_2O) and heavy water (D_2O).
2. In the second investigation, ice and water were investigated individually at fixed temperatures of −10 °C and +10 °C, respectively; the neutron energy was changed over the wavelength range from 2 Å to 6 Å using the energy selective imaging mode. A comparison was drawn via the attenuation coefficients, showing their dependency on the neutron energy.

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The aim of both experiments was to clearly determine whether it is possible to detect the phase transition between water and ice and, if it is detectable, how it can be detected with neutrons. From the available neutron database, there is a strong indication that a difference in the microscopic cross-sections for either ice or water is only visible in the cold neutron energy range, with an increasing tendency towards lower energies (see Fig. 1).

2. Experimental setup

The two parts of this study were performed at two different neutron imaging beam lines: CONRAD at HZB [2] and ICON at PSI [3]. The principle of the experimental setup remained the same: the neutron beam was transmitted by the object, and it was observed with a two-dimensional neutron detector (a highly sensitive 16-bit CCD camera observing the light excitation on a scintillation screen); see Fig. 2. The image data were used (after dark current corrections and intensity normalization) for the direct quantification of the sample properties, the density in particular.

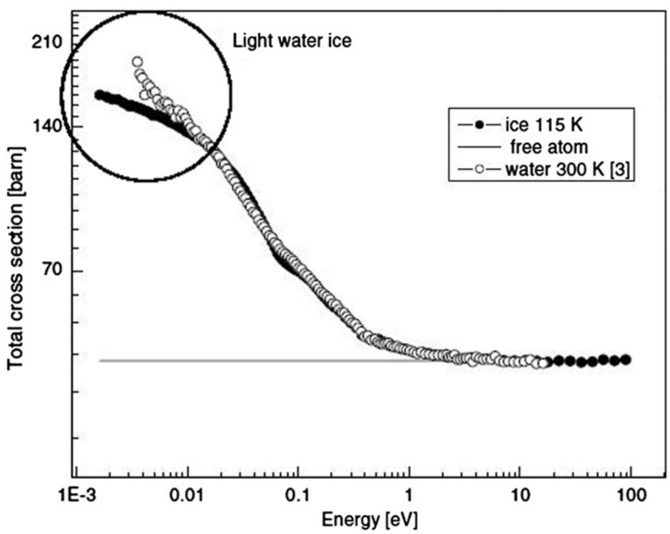

Fig. 1. Cross-section data for water/ice in the cold range according to [1].

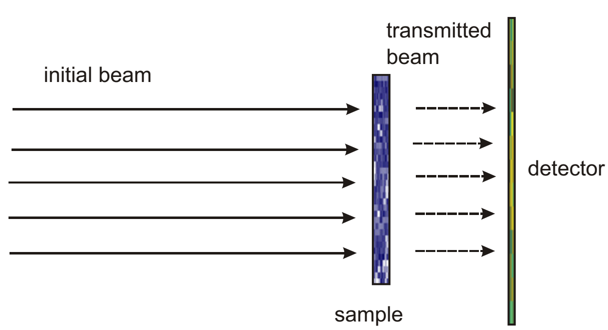

Fig. 2. Simplified experimental arrangement during the transmission measurements of the flat water/ice samples.

The temperature of the setup was changed by applying a cold gas jet of nitrogen above the sample, while the temperature was measured precisely inside the sample with a thermocouple. The individual image was directly attributed to the temperature during acquisition.

In the second run, the samples were kept completely stable and the nominal temperatures were monitored inside a box around the setup.

The data analysis is based on the following considerations. Assuming a plate type arrangement of the water/ice setup, the neutron transmission can be calculated (in the first order and assuming the validity of Lambert's law) as follows:

$$I = I_0 \cdot e^{-\Sigma \cdot z} \quad (1)$$

where I_0 describes the initial beam intensity, I is the beam intensity after interaction with the sample and z is the sample thickness in beam direction. Because flat samples (constant d) were measured, the intensities are calculated as the mean values of the entire sample across the beam.

The attenuation coefficient Σ is directly related to the density ρ of the water (N is the nuclear density, L is Avogadro's constant, M is the molecular mass, m is the sample mass, and V is the sample volume):

$$\Sigma = N \cdot \sigma = \frac{\rho \cdot L}{M} \cdot \sigma = \frac{m \cdot L}{V \cdot M} \cdot \sigma \quad (2)$$

Knowing z to be constant across the sample allows us to derive the attenuation coefficient Σ, where I and I_0 represent the pixel values for the sample and the "open beam" images, respectively.

$$\Sigma = \ln\left(\frac{I_0}{I}\right) \Big/ z \quad (3)$$

During the phase transition from liquid water to ice, the well-known crystallization is accompanied by a volume expansion and an equivalent density reduction of approximately 10%.

For our first experiment, the particular behavior of the sample is essential for the interpretation of the image data (whether there is a uniform expansion in all directions or a hindered expansion into only the free space at the top of the Al container). In the first case, the new sample thickness must be considered ($z_{ICE} > z_{WATER}$), and the exact Σ values must be derived according to (3). This requirement holds under the verified conditions of no mass loss during the measurements.

Fortunately, the transmission image data already contains information about the change in volume (increasing area of the water/ice zone in the beam direction), as shown in Fig. 3 for the liquid and solid phases. If the expected volume change is caused

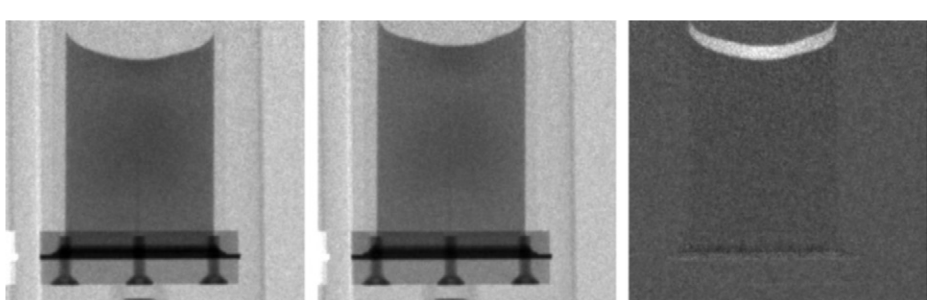

Fig. 3. Transmission neutron images of the water and ice assembly; the referenced third image is shown to visualize the volume change.