Water Dynamics in Controlled Pore Silica Glasses

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Abstract. Water in porous silica glass is a suitable system for investigating the effect of confinement on translational diffusion. These systems are important because of their relevance in catalytic and separation processes. Here quasi-elastic neutron scattering experiments at room-temperature on water-filled-controlled-pore glasses with radius of 15, 24 and 32 Å, are presented and analyzed using the random-jump diffusion model. Both the average residence time and the mean jump distance increase with decreasing pore radius.

1. INTRODUCTION

No liquid has been as extensively studied as water. Experiments using techniques such as Raman, infrared absorption, inelastic and quasi-elastic neutron scattering, x-ray and computer molecular-dynamics (MD) simulations have been performed in the supercooled regime, where the effects due to hydrogen bonding are dominant [1]. Analysis of the dynamical behavior demonstrates that hydrogen bonds play a crucial role in water [2]. However, of recent interest is understanding modifications to its bulk behavior when water is placed in a confined geometry [3]. This situation occurs in a large variety of important contexts such as mining, corrosion inhibition, enzymatic activity, and functions of membranes and food conservation. In addition, the structure and dynamical properties of confined water have been considerably studied due to their relevance in the understanding of chemical reactions in catalysis and separation process in micropores such as vycor glass, silica gel and nafion.

Investigations of the dynamics of water molecule confined in different geometries reveal a slowing down of the translational motion compared to bulk water [4]. Recent MD simulations on TIP4P water confined in cylindrical pore built inside a SiO₂ glass indicate that the H-bond distribution through the pore is strongly distorted and that a number of non H-bonded (interstitial) neighboring molecules must be present [5]. This suggests that the main effect of confinement is to disturb the orientational arrangement of molecules to such an extent that a continuous network of bonds is not favored up to distances from the interface of the order of 8 Å. The MD results are in qualitative agreement with experimental findings on water confined in Vycor glass [6]. Two factors are to be considered in the case of confined water: (1) the effects of hydrophilic and hydrophobic surfaces on interfacial water and (2) how the dynamics of the hydrogen bond network changes due to the volume of confinement. Water in porous silica glass is a suitable system for investigating the effect of confinement on the translational diffusion. In this paper quasi-elastic (QE) neutron scattering experiments at room temperature on water-filled controlled-pore glasses (CPG) with radius of 15, 24 and 32 Å are reported. CPG is a total porous borosilicate glass with a very narrow size distribution about a mean radius.

2. EXPERIMENTAL

The QE experiments were performed using the time-of-flight spectrometer QENS at the Intense Pulsed Neutron Source at Argonne National Laboratory. Unique constant-energy focusing of the graphite analyzer crystal arrays provides high resolution (~90 μeV) for quasi-elastic and low-energy inelastic scattering, while maintaining high data rates. Three spectra were recorded for each angular setting of the spectrometer corresponding to three different momentum transfers, Q . Data from up to four settings of the instrument were analyzed corresponding to $0.57 \text{ Å}^{-1} < Q < 2.54 \text{ Å}^{-1}$. Data were

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collected at room temperature from water-filled controlled-pore glasses (CPG) with radius of 15, 24, and 32 Å contained in an aluminum sample cell. Backgrounds were initially collected from the dry glass samples. The glass was then immersed into water, allowed to fill, and subsequently weighed. The samples were approximately cylindrical in shape with an average radius of approximately 3 mm. Table I gives the amount of absorbed water in each case along with the empty sample mass.

Table I – Samples size and amount of absorbed water.

Pore radius	Empty glass (g)	H ₂ O (g)	% of absorbed H ₂ O
15 Å	3.14	0.53	14
24 Å	2.28	0.62	21
32 Å	0.53	0.24	31

The detector efficiencies were normalized to a vanadium scan. Fig. 1 shows the spectrum for a water droplet of 24 Å radius and momentum transfers of 0.80 and 2.35 Å⁻¹. The solid fits to the data include an elastic contribution (dashed curve) from the sample cell and glass, and a broadened contribution from the mobile water in the sample. It was necessary to allow the elastic intensity to vary as a fitting parameter. It varied in strength from approximately 0.5 of the empty cell signal at low Q to the measured intensity at high Q . We attribute the attenuation of this signal to multiple scattering and self-shielding effects upon the addition of water to the samples.

Figure 1 - QENS spectrum for water contained in a porous glass of 24 Å radius and momentum transfers of 0.80 and 2.35 Å⁻¹ as indicated. The heavy solid line is the full fit to the data and includes a constant background term, an elastic term (dashed curve) from the sample cell and glass, and a broadened term (light solid line) from the mobile water.

Figure 2 – QENS spectra of the 24 Å sample. Solid curves are fits to the data using the model described in Eqs. 1-4 with the addition of an elastic term used to describe the scattering from the glass and the aluminum sample can.

3. QUASI-ELASTIC NEUTRON SCATTERING OF WATER IN CONFINED SPACES: METHOD OF ANALYSIS

The simplest analytical model to describe the diffusion of the water molecules assumes decoupled translational and rotational motions [7]. The decoupling is necessary in order to have a tractable model, suitable for fitting to the data as given below.

$$S_m(Q, \omega) = e^{-\langle u^2 \rangle Q^2 / 3} T(Q, \omega) \otimes R(Q, \omega) \quad (1)$$

where ω is the energy transfer, $\langle u^2 \rangle$ the Debye-Waller factor, $T(Q, \omega)$ denotes the contribution from the translational motion of the molecule and $R(Q, \omega)$ the contribution for the low-frequency rotational motion. The particles are assumed to diffuse uniformly on a sphere of radius a , with a rotational time constant τ_r . For a random rotational motion $R(Q, \omega)$ is given by [8]:

$$R(Q, \omega) = j_0^2(Qa)\delta(Qa) + \frac{1}{\pi} \sum_{l=1}^{\infty} (2l+1) j_l^2(Qa) \frac{l(l+1)D_r}{(l(l+1)D_r)^2 + \omega^2} \quad (2)$$

where a is taken as the O-H distance in a water molecule (0.98 Å), D_r is the rotational diffusion constant and j_l are the spherical Bessel functions. The rotational diffusion is characterized by a relaxation time $\tau_r = 1/6D_r$.

$T(Q, \omega)$ is a Lorentzian curve with a half-width at half maximum (hwhm) $\Gamma(Q)$:

$$T(Q, \omega) = \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + \omega^2} \quad (3)$$

$\Gamma(Q)$ is given by the unbounded medium expression for typical jump diffusion as:

$$\Gamma(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0} \text{ and } D_t = \frac{L^2}{6\tau_0} \quad (4)$$

where τ_0 is the average residence time between jumps and D_t is the translational diffusion constant.

4. RESULTS AND DISCUSSION

The experimental results have been analyzed by two procedures. In the first, the translational Lorentzian was constrained to the behavior dictated by Eq. 4. In addition, it was found necessary to constrain the value of the rotational diffusion constant, D_r . Previous work observed very little change at room temperature in D_r for water in porous glass [4]. Consequently, the value of D_r was held fixed at that observed for a bulk water sample at 300K. The quality of the resulting fit is illustrated in Fig. 2 (as noted above it was necessary to allow the intensity of the elastic term to vary). The values of the fitting parameters are recorded in Table II along with the results obtained for bulk water.

The line-width $\Gamma(Q)$ was then allowed to vary independently at each Q -value, again with τ_r fixed at the observed value for bulk water. Fig. 3 shows $\Gamma(Q)$ obtained for each sample as a function of momentum transfer with fixed τ_r . The solid lines were calculated using the fitted values of D_t and τ_r given in Table II. The excellent agreement illustrates the applicability of the random jump diffusion model to the translational motion for the confined water.

Table II – Parameters extracted from fits to the QENS spectra using the model described in Eqs. 1-4. The value of the rotational diffusion constant was held fixed at that observed for the bulk water sample. The value of L is determined from the fitted parameters using Eq. 4.

Pore radius	L (Å)	τ_0 (10^{-12} sec)	D_t (10^{-5} cm ² /sec)	τ_r (10^{-12} sec)	$\langle u^2 \rangle^{1/2}$
15Å	3.39 ± 0.18	6.4 ± 0.4	3.0 ± 0.3	1.07 (fixed)	0.36 ± 0.1
24Å	2.47 ± 0.07	4.4 ± 0.1	2.3 ± 0.1	1.07 (fixed)	0.17 ± 0.02
32Å	1.60 ± 0.05	1.67 ± 0.07	2.6 ± 0.1	1.07 (fixed)	0.24 ± 0.02
Bulk water	1.53 ± 0.06	1.6 ± 0.1	2.49 ± 0.07	1.07 ± 0.08	0.56 ± 0.01

In this paper we have described the diffusion of water molecules in a porous hydrophilic borosilicate glass in terms of a simple model. The Q dependence of the narrow quasi-elastic line width can be described by a jump diffusion model, consistent with previous observations of water

diffusion in porous media. It is clear from Table II that while the residence time for jump diffusion (τ_0) shows a slowing down with decreasing pore radius the values upon confinement, the values of D_j are very similar to that of bulk water. The most significant result of this study is illustrated in Fig. 4. The mean residence time shows a marked dependence on the pore radius, what is consistent with previous measurements of water in porous media. It is also consistent with a previous study of water diffusion in the interior of reverse micelles and on biopolymers [9]. As in these studies, we attribute this behavior to deviations in structure from the ideal hydrogen-bonded network. New QE neutron scattering studies are being planned as a function of temperature to understand the behavior of water in CPG at supercooled temperatures. In particular, it will be interesting to note if any zoning of water occurs in this system with preferential-freezing-of-the-water-motion-in-molecules-closest-to-the-pore surface.

Figure 3 – The hwhm of the translational Lorentzian $\Gamma_L(Q)$ of Eq. (3) as a function of Q^2 . The solid lines are determined using the jump diffusion model with the values given in Table II.

Figure 4 – Dependence of the mean residence time, τ_0 , on the pore radius. The dashed line is the value observed for bulk water.

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