



# Characteristic features of water dynamics in restricted geometries investigated with quasi-elastic neutron scattering



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## ABSTRACT

Understanding the molecular behavior of water in spatially restricted environments is key to better understanding its role in many biological, chemical and geological processes. Here we examine the translational diffusion of water confined to a variety of substrates, from flat surfaces to nanoporous media, in the context of a recently proposed universal scaling law (Chiavazzo 2014) [1]. Using over a dozen previous neutron scattering results, we test the validity of this law, evaluating separately the influence of the hydration amount, and the effects of the size and morphology of the confining medium. Additionally, we investigate the effects of changing instrument resolutions and fitting models on the applicability of this law. Finally, we perform quasi-elastic neutron scattering measurements on water confined inside nanoporous silica to further evaluate this predictive law, in the temperature range  $250 \leq T \leq 290$  K.

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## 1. Introduction

Although water has been at the center of considerable research efforts over the years [1–5], its peculiar but important thermophysical properties are far from being fully understood. Compared to non-hydrogen bonded liquids, water behaves in some respect more like a solid due to its strong hydrogen bond network and exhibits key properties relevant to many biological, chemical and technological processes like unusually large specific heat, high melting point, and large surface tension. Understanding how water molecules behave in various spatially restricted environments is of key scientific importance in geophysics, biological physics and many other research areas. For this reason, the diffusive motions of water molecules nanoscopically confined in materials like porous silica have been widely investigated using a variety of probes including neutron scattering [6–9,9–12], dielectric spectroscopy [2] and NMR [13–15]. These studies have revealed a clear retardation of the water diffusion compared to the bulk phase, which becomes increasingly pronounced as the restrictive dimension or the temperature decreases. However, the difference in size, geometry and morphology of the pores, the instrumentation used, and the various analysis methods have often introduced ambiguity in

the interpretation or reconciliation of the results. These issues can be overcome by conducting experiments in which only one experimental parameter (temperature, pore size, morphology, etc.) is changed at a time. This ideal approach would require years of planning and measurements to complete with neutron scattering, because of the limited availability of the neutron sources. Alternatively, it may be convenient to examine the influence of each variable separately by using existing measurements performed over many decades by different research groups.

In this article, we thus present a survey of previous quasi-elastic neutron scattering (QENS) measurements of water diffusion, examined in the context of a predictive scaling law for water transport, recently proposed by Chiavazzo et al. [1]. Our aim is to look for identifiable trends or features in the water dynamics under given confinement conditions. Using over a dozen QENS results, we test the validity of this law, evaluating separately the effects of variable hydration, changing confinement size and dimensionality. This scaling depends primarily on a single parameter  $\theta$ , the ratio between the average number of water molecules that are most influenced by the surface or pore walls and the total number of water molecules under confinement. This parameter can also be related to the fractional volume occupied by these molecules compared to the total volume available. This geometry-dependent parameter tends to be smaller for systems with large confining volume or small curvature at higher coverages. Based on the aforementioned model, the translational diffusion coefficient  $D_r$  of confined water, which is typically measured with neutrons, can

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be conveniently expressed at any temperature  $T$  above the bulk water nucleation temperature as,

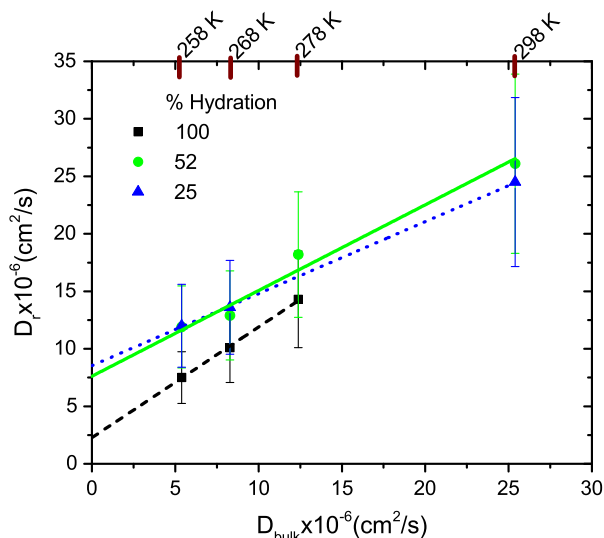
$$D_r(T) = \theta D_c + (1 - \theta) D_{bulk}(T). \tag{1}$$

Here  $D_{bulk}(T)$  represents the bulk water translational diffusion at temperature  $T$  and  $D_c$  the temperature independent translational diffusion coefficient of the water molecules that are solely affected by the walls. In practice,  $D_{bulk}(T)$  can be obtained from the literature [16], and  $D_c$  and  $\theta$  are specific to the confining sample and its geometrical characteristics. Because Eq. (1) assumes that  $\theta$  and  $D_c$  do not change significantly with temperature, its validity can only be verified over temperature ranges where water does not experience phase changes, and for which  $D_c$  and  $\theta$  indeed remain constant on average. Our empirical observation is that Eq. (1) could be reliably verified for water confined in a number of confining media at temperatures between  $\sim 250$  K and room temperature. The low limit is set by the homogeneous nucleation temperature of bulk water ( $T_H \approx 230 - 235$  K) and the high limit by the accessible energy window of the neutron instrument (approximately around 300 K for most existing high energy backscattering spectrometers).

This article is organized as follows. Sections 2–4 evaluate respectively the influence of hydration, confinement size, and morphology on the scaling transport law described above. We then discuss the importance of hydrophilicity/hydrophobicity as well as the impact of varying instrument resolution and data modeling on this law in Sections 5 and 6. In Section 7, we use exact geometrical models to better quantify water adsorption based on surface morphology and hydration amount. Section 8 examines in details the pore size dependence of water dynamics in folded mesoporous silica (FSM) materials, with cylindrical pores. Our final remarks are presented in Section 9.

## 2. Hydration dependence

Here we investigate the applicability of Eq. (1) under varying hydration conditions. The goal is to look for systematic evolution or patterns in the characteristic variables  $\theta$  and  $D_c$  as the hydration level, defined here as the fractional mass of water uptake per mass of sample,  $h = m_{water}/m_{sample}$ , is increased for a given substrate. Although this so-defined hydration parameter  $h$  does not necessarily correspond to the filling ratio  $V_{fill}/V$ , where  $V_{fill}$  and  $V$  are respectively the filled volume and the total confining volume, it can be used to estimate it, provided the sample characteristics (such as porosity, geometry, density) and water layer densities are known. For example, using the dry density of Vycor glass of 1.45 g/cc and the porosity of 28% and a layer-by-layer filling of the 50 Å cylindrical pore of Vycor at constant density, Bellissent-Funel et al. [17] estimated full pore filling to correspond to 100% water uptake,  $\sim 3-4$  layers of water on the internal surface to 52% hydration, and a monolayer to 25% hydration. Using the  $D_r$  reported by Bellissent-Funel and co-workers as a starting example, we plot them in Fig. 1 as a function of  $D_{bulk}(T)$  reported by Teixeira et al. [16]. The  $D_r(T)$  values are for water in porous 50 Å Vycor at respective hydration levels of (weight %) 25%, 52% and 100%. These plots allow us to extract the corresponding  $\theta$  and  $D_c$ , based on the intercept and slope of the fits (solid lines). Using imposed constraints  $0 \leq \theta \leq 100\%$  and  $0 \leq D_c \leq D_{bulk}$ , the validity of the scaling expression above can be tested. We find in the case of Vycor that  $D_c$  increases with increasing hydration level  $h$  while  $\theta$  follows the opposite trend. This observation is also true for water in a number of other systems such as protein, zeolite and hydrothermal clay, as indicated in Table 1 and can be generalized. We will return to this point in Section 4.



**Fig. 1.** Hydration dependence (measured as weight %) of water diffusion  $D_r$  vs  $D_{bulk}$  in porous Vycor glass (50 Å average pore dimension). Data points correspond to hydration level of 25% (blue triangle), 52% (green circles) and 100% (black squares). The lines are fits of Eq. (1) to the data Refs. [16,17]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Table 1**  
Best fit parameters of Eq. (1) using reported  $D_r$  values from selected materials [17–20] as a function of increasing water uptake  $h$  (weight %).  $h$  can be used to estimate the filling fraction, given the sample density, porosity, the confinement geometry and dimension.

Sample	$h = m_{water}/m_{sample}$ (%)	$\theta$ (%)	$D_c$ ( $10^{-6}\text{cm}^2/\text{s}$ )
Vycor [17]	25	37	22.7
	52	25	29.8
	100	4	59.4
Zeolite [18]	22	86	0.09
	28	85	0.95
Hydrothermal clay [19]	10	78	2.36
	30	4	75.3
Lysozyme [20]	35	77	–
	45	54	–

## 3. Confinement size

While it is generally well established that tighter confinement leads to slower dynamics, it is not clear how variable confinement dimension would affect the parameters in Eq. (1). We thus examine the validity of the scaling relation using data from the well-characterized silica system MCM-41 with variable pore sizes, as previously investigated by Takahara et al. [21] on the MIBEMOL spectrometer at the Laboratoire Léon Brillouin (France). We verified that the law can indeed be applied, yielding in general a  $\theta$  that decreases with increasing pore size (or looser confinement), and a  $D_c$  that increases, as exemplified by Fig. 2. For a given system, the lower limit of this range appears to be set by the neutron instrument used, yielding much lower values with the higher energy resolution spectrometers. The dependency of  $\theta$  and  $D_c$  on pore size found in MCM-41 is consistently similar across all the systems we examined. It is the case for the activated carbon fibers [22] for example and for many other porous media, as listed in Table 2. We conclude that this trend with size is thus a generic feature of confined water.

In one of particular cases examined, that of the fully hydrated MCM-41 [23] measured on the HFBS instrument, we have not been able to extract meaningful  $D_c$  and  $\theta$  values. This exception

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