Experimental Report

28/10/2013

Proposal:	**6-02-500**	**Council:**	4/2012

Title: Does the main relaxation process in aqueous systems split in two below some critical temperature?

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Researh Area: Physics

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Samples: (H2O)0.88(LiCl)0.12

Instrument	Req. Days	All. Days	From	To
IN11	7	4	05/12/2012	09/12/2012

Abstract:

The behavior of aqueous systems below critical temperature, Tc (Tc > Tg) can be described by two different scenarios. In the first one, a split of the main relaxation alpha-component occurs at Tc, and, below Tc, besides the main relaxation, there exists an additional "slow" beta-component, sometimes referred to as Johari-Goldstein relaxation. The temperature dependence of this "slow" beta component is suggested to be Arrhenius, unlike the super-Arrhenius temperature dependence of the alpha-component. In the second scenario, the additional relaxation that develops below Tc is not an independent component, but merely an "excess wing" component that follows the temperature dependence of the super-Arrhenius alpha-component. Both scenarios derive support from various experimental results. To resolve this controversy, which has been known and debated for aqueous systems ranging from confined water to hydration water on protein surfaces, we propose to carry out an NSE experiment specifically tailored to the capabilities of the IN11C. The distinct advantage of our aqueous solution system is that it has the same Tc as pure water, yet does not require confinement for supercooling below Tc.

Does the main relaxation process in aqueous systems split in two below some T_c?

E. Mamontov, M. Ohl, P. Fouquet

In order to study water in the normally inaccessible “no man’s land” region, between the homogeneous ice nucleation temperature of ca. 231 K and glassy water crystallization temperature of 150 K (on warming up), confinement in nano-sized pores is usually employed. As the pore size is reduced, the freezing temperature of the confined water progressively decreases. Freezing behavior of confined water differs in details between hydrophilic and hydrophobic matrices, but remains qualitatively unchanged in that in very small pores water freezing can be suppressed altogether.

In principle, water mixed with various substances (e.g., methanol, glycerol, ethylene glycol) can be deeply supercooled without employing nano-confinement. Moreover, the use of deuterated co-solvents may allow probing predominantly the dynamics of the strongly scattering hydrogenated water molecules in the mixture. The disadvantage of this approach is that adding a glass-forming compound changes the important parameters of water, such as, e.g., its glass transition temperature, T_g. That is, the relaxation dynamics of the resulting mixture is not necessarily water-like. On the other hand, we have advocated the use of aqueous solution of lithium chloride in the bulk form to measure the slow dynamics of water molecules by QENS. Uniquely among salts, addition of lithium chloride, even at large concentrations, does not change T_g of water. Furthermore, another important dynamic parameter of water, T_c of ca. 225 K, is not affected either by addition of lithium chloride.

The main goal of this work is to investigate some features of the recently proposed schematic diagram [E. Mamontov and X. Chu, Physical Chemistry Chemical Physics, 2012, 14, 11573-11588; E. Mamontov and M. Ohl, Physical Chemistry Chemical Physics, 2013, 15, 10732-10739] for the relaxation dynamics in water, as shown in Figure 1. In this proposed scenario, if the structural arrest on cooling down is avoided (either for pure water in a tight confinement or water in a bulk-like lithium chloride solution), the relaxation time associated with super-Arrhenius main structural α-relaxation will show a divergence on approaching T_g, which has the same value for pure water and aqueous solutions of LiCl. A secondary relaxation process with rather weak temperature dependence, called β-fast in this notation, splits from the main relaxation at pico-second times, and remains active down to very low temperatures, probably below T_g. Another secondary relaxation process, called β-slow in this notation, splits from the main relaxation at nano-second times.

Using IN11, we have studied the single-particle dynamics of water molecules in a water solution of 7.6 m LiCl, that is, $(H_2O)_{0.88}(LiCl)_{0.12}$. Unlike pure water, the solution remains in the liquid state down to below 200 K; this allowed us to study the temperature evolution of the single-particle dynamics of water molecules. Figure 2 shows the I(Q,t) measured at several Q values at 3 temperature points. Importantly, the logarithmic scaling was used for the y-axis, but not the x-axis; the advantages of such a presentation have been discussed in [E. Mamontov and M. Ohl, Physical Chemistry Chemical Physics, 2013, 15, 10732-10739]. The conclusion that we derive from the data shown in Figure 2 is as follows. The longest Fourier time of ca. 2 ns accessible in the experiment allowed us to measure the component with the I(Q,t) approaching unity in the limit of zero Fourier time and decaying to a finite (non-zero) value at long times, that is, β-slow component in our notation. Thus, the present data set from IN11 will need to be combined with another NSE data set that, by accessing longer Fourier times, captures the structural α-relaxation with the I(Q,t) decaying to zero at long times. The Q-values of the NSE experiments will be matched, so that the combination of the two NSE data sets can be used for studying the Q-dependence of the crossover regime between the initial β-slow and subsequent α-relaxation processes.

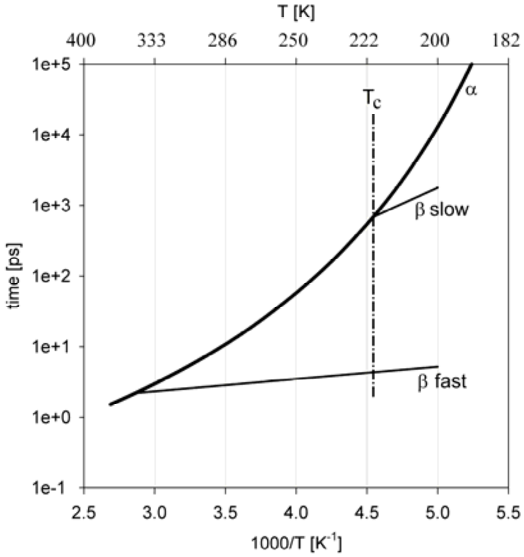

Figure 1. After Mamontov and Chu and Mamontov and Ohl (see the references in the text). Hypothesized schematic phase diagram of the single-particle relaxation dynamics of water if the structural arrest below ca. 228 K can be avoided.

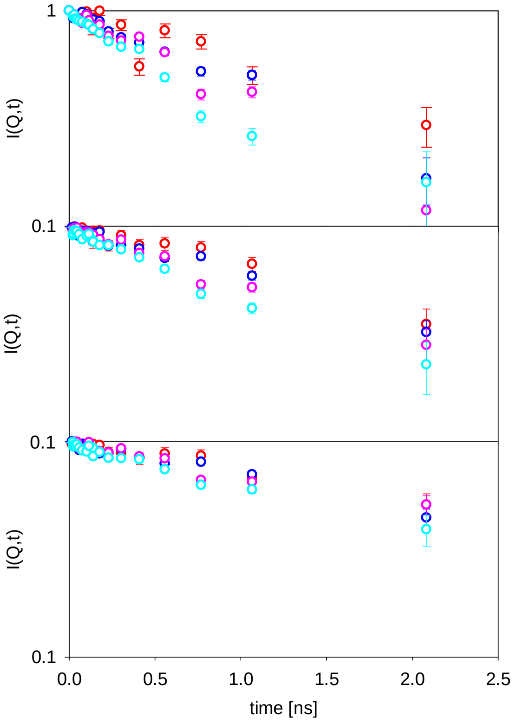

Figure 2. NSE data collected at IN11 from $(H_2O)_{0.88}(LiCl)_{0.12}$. Top: 220 K. Middle: 215 K. Bottom: 210 K. The Q-values are as follows: red 0.62 $Å^{-1}$, blue 0.70 $Å^{-1}$; pink 0.78 $Å^{-1}$; cyan 0.87 $Å^{-1}$.