

# A Low-Temperature Crossover in Water Dynamics in an Aqueous LiCl Solution: Diffusion Probed by Neutron Spin–Echo and Nuclear Magnetic Resonance

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Aqueous solutions of lithium chloride are an excellent model system for studying the dynamics of water molecules down to low temperatures without freezing. The apparent dynamic crossover observed in an aqueous solution of LiCl at about 220 to 225 K [Mamontov, JPCB 2009, 113, 14073] is located practically at the same temperature as the crossover found for pure water confined in small hydrophilic pores. This finding suggests a strong similarity of water behavior in these two types of systems. At the same time, studies of solutions allow more effective explorations of the long-range diffusion dynamics, because the water molecules are not confined inside an impenetrable matrix. In contrast to the earlier incoherent quasielastic neutron scattering results obtained for the scattering momentum transfers of  $0.3 \text{ \AA}^{-1} \leq Q \leq 0.9 \text{ \AA}^{-1}$ , our present incoherent neutron spin–echo measurements at a lower  $Q$  of  $0.1 \text{ \AA}^{-1}$  exhibit no apparent crossover in the relaxation times down to 200 K. At the same time, our present nuclear magnetic resonance measurements of the diffusion coefficients clearly show a deviation at the lower temperatures from the non-Arrhenius law obtained at the higher temperatures. Our results are consistent with a scenario in which more than one relaxational component may exist below the temperature of the dynamic crossover in water.

## Introduction

The relaxation dynamics of water molecules exhibit an apparent transition at about 210 to 230 K from high-temperature non-Arrhenius to low-temperature Arrhenius behavior. The origin of this crossover is debated most extensively,<sup>1–12</sup> even though another crossover, between 170 and 200 K, has been also observed in dielectric spectroscopy experiments.<sup>7</sup> A major question that remains unresolved is whether it is the main  $\alpha$ -relaxations that are probed above and below the crossover temperature of  $\approx 220$  K. Inelastic neutron scattering is a powerful tool to distinguish between the localized and long-range dynamic processes through the  $Q$  dependence of the scattering signal. However, confinement of water, either inside nanopores or near surfaces, which is often seen as a prerequisite for studying water dynamics at low temperatures without freezing, makes it difficult to investigate the long-range dynamic processes at low  $Q$  values, where the small-angle scattering from the matrix is dominant. Fortunately, freezing of water can be also avoided in bulk aqueous solutions.<sup>13,14</sup> In particular, aqueous solutions of LiCl exhibit the crossover in the temperature dependence of the relaxation times obtained from incoherent quasielastic neutron scattering (QENS) experiments<sup>13,15</sup> at the same temperature as pure water confined in hydrophilic pores or on surfaces. This

suggests that the same relaxation dynamics of the water molecules are probed in both types of systems. However, the advantage of water solutions is that the  $Q$  dependence of the scattering signal is not affected by confinement, which allows full exploitation of the power of neutron scattering to probe dynamics at various length scales. In this work, we used neutron spin–echo (NSE) to probe the incoherent diffusion dynamics of water molecules in the same 7.6 *m* LiCl aqueous solution with a composition of  $(\text{H}_2\text{O})_{0.88}(\text{LiCl})_{0.12}$ , or  $(\text{LiCl}, 7.3\text{H}_2\text{O})$ , as was studied before by incoherent QENS.<sup>13</sup> Unlike the earlier QENS results obtained at  $0.3 \text{ \AA}^{-1} \leq Q \leq 0.9 \text{ \AA}^{-1}$  that showed the dynamic transition in the relaxation times,<sup>13</sup> the present incoherent NSE experiment performed at  $Q = 0.1 \text{ \AA}^{-1}$  exhibited no apparent crossover in the relaxation times down to 200 K. On the other hand, a crossover was present in the temperature dependence of the diffusion coefficients obtained by NMR. Our observations suggest that more than one main relaxational component likely exist in water below the temperature of the dynamic transition.

## Experimental Section

The  $(\text{LiCl}, 7.3\text{H}_2\text{O})$  solution was prepared using deionized distilled water and anhydrous, ultradry lithium chloride powder (99.995% purity) available commercially from Alfa Aesar.<sup>16</sup> Approximately 20 mg of the solution was transferred into an aluminum pan (Tzero Al Hermetic, diameter 7.4 mm, capacity 60  $\mu\text{L}$ ) and sealed with the appropriate cover. Differential scanning calorimetry (DSC) measurements were performed using a DSC Q2000 from TA Instruments, and the data were treated with the Q Series software, version 3.0.3. The measurement was carried out with the following temperature sequence:

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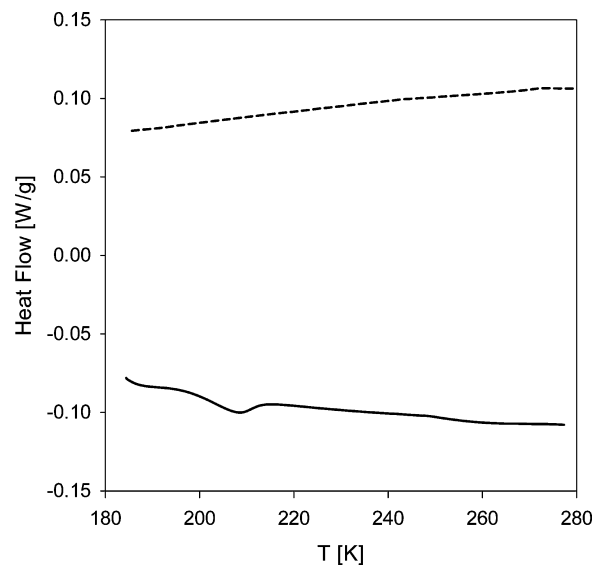
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equilibration at 279 K, cooling ramp from 279 to 183 K at 2 K/min, equilibration at 183 K, and heating ramp from 183 to 277 K at 2 K/min.

For the NSE experiment, the sample was loaded into a flat-plate aluminum container, which was 5 cm tall, 3 cm wide, and 0.025 cm thick. It should be emphasized that H<sub>2</sub>O rather than D<sub>2</sub>O was used for the NSE experiment, so that the same incoherent dynamics could be probed as in the earlier QENS experiment.<sup>13</sup> The NSE measurements were carried out on the NSE spectrometer at the NIST Center for Neutron Research (NCNR).<sup>17</sup> Data have been collected in the temperature range from 270 to 200 K. The incoming beam wavelength,  $\lambda$ , was set to 6 Å with a  $\Delta\lambda/\lambda \approx 15\%$ , allowing the investigation of the time range from  $\approx 7$  ps to 15 ns. For the 210 and 200 K data points, additional measurements using an incoming beam with  $\lambda = 8$  Å were performed, thus allowing to extend the investigated time range to 35 ns. Data have been collected at a single momentum transfer value,  $Q = 4\pi[\sin(2\theta/2)]/\lambda = 0.1$  Å<sup>-1</sup>,  $2\theta$  being the scattering angle. It is well-known that, using a polarized beam, NSE measurements of incoherent dynamics suffer from a reduction to  $1/3$  of the incoherent signal. However, there is no fundamental issue in performing incoherent QENS measurements using NSE, as long as the required counting time can be afforded, as proved by several previous works.<sup>18–22</sup> Still, if both coherent and incoherent dynamics are present at the investigated  $Q$  the separation of the two contributions may be impossible. In the present sample, the observed neutron scattering is overwhelmingly dominated by the incoherent dynamics of the hydrogen atoms in the water molecules, even after the  $1/3$  reduction and at a  $Q$  value as low as  $0.1$  Å<sup>-1</sup>. The main coherent scattering contribution arises from the sample holder, which is not expected to have any temperature dependence in the investigated time range and can be eliminated through a careful subtraction. A polarization analysis of the collected data after subtraction of the can indicates that the remaining signal is incoherent and originates from the (H<sub>2</sub>O)<sub>0.88</sub>(LiCl)<sub>0.12</sub> solution. The measurement of the same sample at  $\approx 10$  K was used as experimentally determined resolution function. The raw data have been reduced to the normalized intermediate scattering function,  $I(Q,t)/I(Q,0)$ , using the software package DAVE.<sup>23</sup> The measured transmission of the 0.025 cm thick (H<sub>2</sub>O)<sub>0.88</sub>(LiCl)<sub>0.12</sub> layer was 0.85, and no multiple scattering corrections were performed.

Diffusion coefficients in the solution were measured by <sup>1</sup>H and <sup>7</sup>Li NMR at Larmor frequencies of 400 and 155.5 MHz, respectively, on a 9.4 T Bruker Avance 400 NMR spectrometer equipped with a  $z$ -gradient probe generating a maximum gradient strength of  $(54.4 \pm 0.3)$  G/cm. <sup>1</sup>H and <sup>7</sup>Li NMR measurements were performed consecutively at descending temperatures from 289.5 to 194.9 K. A temperature equilibration time of 20 min was used between the measurements. The sample temperature was controlled by flowing N<sub>2</sub> gas, evaporated directly from liquid nitrogen reservoir, and heated with a resistance heater in the probe. The actual sample temperature was calibrated using a 100% methanol (Aldrich) sample following standard Bruker procedures. The stimulated echo bipolar pulse-gradient pulse (stebpgp) sequence was used.<sup>24</sup> In this experiment, self-diffusion coefficient  $D$  is determined by varying the gradient strength ( $g$ ) in 16 equal intervals between 2 and 95% of its maximum value. The data were fit to the expression  $S(g) = S(0)\exp[-D(\gamma\delta g)^2(\Delta - \delta/3)]$ . Here  $S(g)$  is the echo intensity at  $g$  and  $S(0)$  the echo intensity in the absence of the gradient pulse, respectively,  $\gamma$  the gyromagnetic ratio of <sup>1</sup>H or <sup>7</sup>Li (as appropriate),  $\delta$  the gradient-pulse length, and  $\Delta$



**Figure 1.** DSC data for (H<sub>2</sub>O)<sub>0.88</sub>(LiCl)<sub>0.12</sub> taken on cooling down (dashed line) and warming up (solid line) at a rate of 2 K/min.

the duration between the two gradient pulses. The diffusion measurement was optimized by adjusting  $\Delta$  and  $\delta$  at each temperature. The parameters  $\Delta$  and  $\delta$  were varied from 0.03 to 0.5 s and 8 to 16 ms, respectively, for <sup>1</sup>H and 0.05 to 2 s and 16 to 18 ms, respectively, for <sup>7</sup>Li as the temperature decreased.

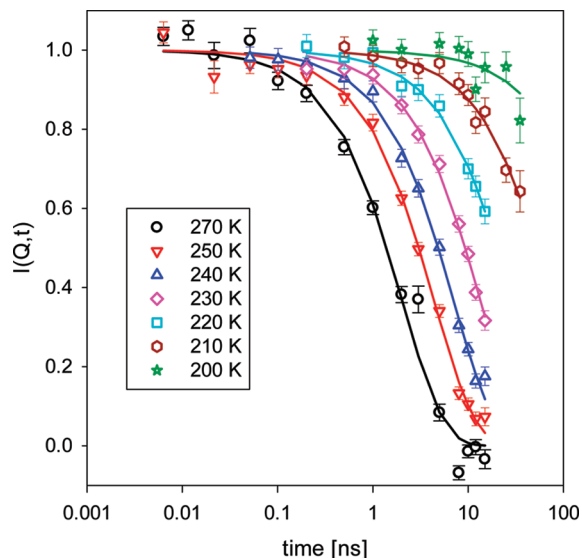
Throughout the paper error bars represent one standard deviation.

## Results and Discussion

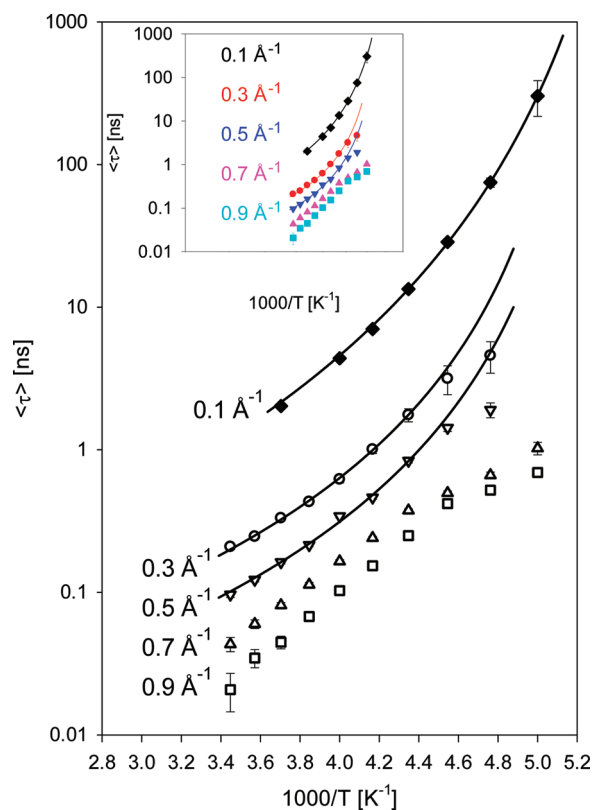
Figure 1 shows the DSC results measured on cooling down (dashed line) and warming up (solid line) at a rate of 2 K/min. Importantly, on cooling down, there are no prominent features in the DSC thermogram in the temperature regions of our NSE and NMR measurements. This suggests that the sample remained in the same state in our measurements, which were carried out on cooling down. On warming up from the glassy state, a peak is present at about 207 K. This is a known peritectic point;<sup>25</sup> a small anomaly in the NSE data was reported at 207 K by Prevel and co-workers,<sup>26</sup> who carried out their measurements on warming up.

The NSE data measured at  $Q = 0.1$  Å<sup>-1</sup> are presented in Figure 2. At all temperatures, the data could be fit well using a single Debye-type relaxation function,  $I(t) = A \exp(-t/\tau)$ , with the value of  $A$  very close to 1. Attempts to introduce an additional elastic background term using functions such as  $I(t) = A \exp(-t/\tau) + B$ , with the parameter  $B$  as a free variable, did not improve the fit quality, and the parameter  $B$  converged to zero or near-zero values. Clearly, the NSE measurement probes the main structural  $\alpha$ -type relaxation, as the fits of the intermediate scattering function decay to zero at sufficiently long Fourier times. This situation, when the character of the  $\alpha$ -type relaxation can be seen unambiguously, is specific to a bulklike solution. For water confined in pores or on surfaces, there is sometimes a residual signal that appears elastic even at the longest Fourier times accessible by NSE, which originates from the molecules in direct contact with the surface.

The relaxation times,  $\tau$ , are plotted in Figure 3 along with the average relaxation times previously measured for the same system at different  $Q$  values on a neutron backscattering spectrometer, BASIS.<sup>13</sup> In this earlier work,<sup>13</sup> a Vogel–Fulcher–Tammann (VFT) law,  $\tau(T) = \tau_0 \exp(-DT_f/(T_0 - T))$  was used to describe the non-Arrhenius temperature dependence of the



**Figure 2.** NSE data (symbols) measured at  $Q = 0.1 \text{ \AA}^{-1}$  and fits (solid lines) with a simple Debye-type relaxation.



**Figure 3.** Temperature dependence of the relaxation times obtained at various  $Q$  values. Filled symbols: NSE, this work. Open symbols: neutron backscattering spectroscopy (BASIS, SNS, ORNL).<sup>13</sup> Solid lines are power law fits described in the text. Inset: the same data sets on the log–log scale.

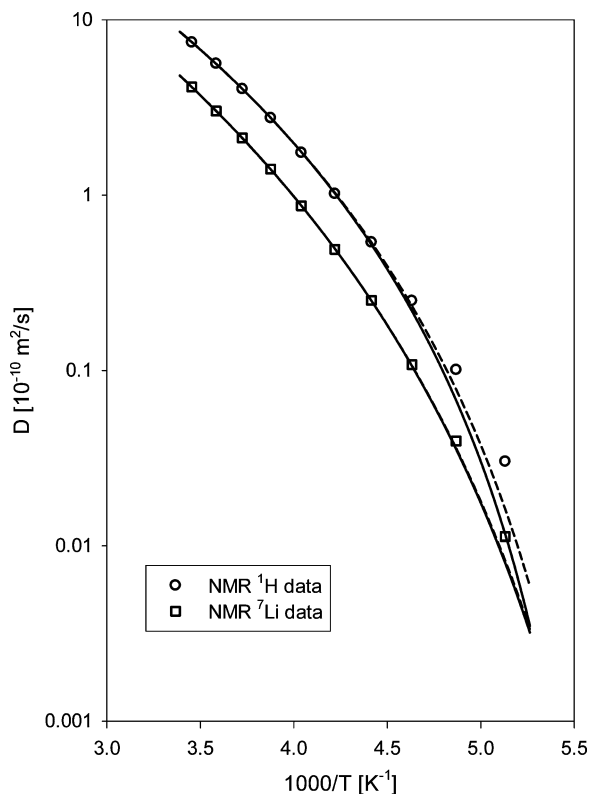
relaxation times at  $Q = 0.3 \text{ \AA}^{-1}$  and  $Q = 0.5 \text{ \AA}^{-1}$ . In the current work, we use fits with a power law:  $\tau(T) = \tau_0(1 - T_0/T)^{-\mu}$ . It is considered<sup>14,26</sup> that a power law better describes non-Arrhenius relaxation temperature dependence in systems similar to  $(\text{H}_2\text{O})_{0.88}(\text{LiCl})_{0.12}$  solution. Similar to the previously obtained<sup>13</sup> results for  $(\text{H}_2\text{O})_{0.88}(\text{LiCl})_{0.12}$ , the high-temperature relaxation times can be described by non-Arrhenius temperature dependence with the following fit parameters:  $\tau_0 = (6.52 \pm 1.89) \text{ ps}$ ,  $T_0 = (189 \pm 5) \text{ K}$ , and  $\mu = (3.245 \pm 0.401)$  for  $Q = 0.3 \text{ \AA}^{-1}$  and  $\tau_0 = (3.41 \pm 3.16) \text{ ps}$ ,  $T_0 = (187 \pm 18) \text{ K}$ , and  $\mu = (3.275$

$\pm 1.339)$  for  $Q = 0.5 \text{ \AA}^{-1}$ . At  $T = 221$  to  $233 \text{ K}$ , there is a crossover from non-Arrhenius to Arrhenius behavior at  $Q = 0.3$  and  $0.5 \text{ \AA}^{-1}$ , whereas at  $Q = 0.7$  and  $0.9 \text{ \AA}^{-1}$  the crossover appears as an intersection of two Arrhenius plots with different activation energies. On the other hand, the relaxation times obtained in the current work from the NSE data at  $Q = 0.1 \text{ \AA}^{-1}$  show no crossover down to the lowest measured temperature of  $200 \text{ K}$ . In the entire measured temperature range of  $270$  to  $200 \text{ K}$ , the NSE data can be fit with a power law with the following parameters:  $\tau_0 = (16.15 \pm 2.68) \text{ ps}$ ,  $T_0 = (176 \pm 1) \text{ K}$ , and  $\mu = (4.629 \pm 0.157)$ . The critical temperature  $T_0$  is close to the value of  $(172 \pm 1) \text{ K}$  previously obtained<sup>26</sup> in a coherent NSE measurement of a  $(\text{LiCl}, 6\text{D}_2\text{O})$  solution at  $Q = 1.9 \text{ \AA}^{-1}$ .

In the past, the crossover in the diffusion dynamics of water was mainly observed in the data measured on neutron backscattering spectrometers with accessible  $Q > 0.2 \text{ \AA}^{-1}$ . The only NSE study known to us where the crossover was observed<sup>27</sup> was performed with confined  $\text{D}_2\text{O}$  at the position of the structural peak at  $Q = 1.67 \text{ \AA}^{-1}$ . To our knowledge, the current work describes the first neutron scattering experiment probing the low-temperature incoherent diffusion dynamics in water at  $Q$  as low as  $0.1 \text{ \AA}^{-1}$ . One reason is that neutron backscattering spectrometers typically cannot access such a low  $Q$  value. Another reason is likely due to the fact that measuring a sizable nonelastic signal at such a low  $Q$  is difficult for confined water, and instead requires a bulk-like system such as an aqueous solution. Does the apparent lack of the crossover in the NSE data at  $Q = 0.1 \text{ \AA}^{-1}$  indicate the discrepancy between neutron backscattering and spin-echo measurements and data analyses, or is it indicative of the real, qualitative difference in the diffusion dynamics measurable at different length scales?

We used NMR measurements of the diffusion coefficients to verify the presence of the dynamic crossover in  $(\text{H}_2\text{O})_{0.88}(\text{LiCl})_{0.12}$ . As one can see in Figure 4, the temperature dependence for both  $^1\text{H}$  and  $^7\text{Li}$  diffusion coefficients does show a deviation from power law fits,  $D(T) = D_0(1 - T_0/T)^\mu$ , at low temperatures. This holds regardless of the number of data points used in the fits. An attempt to fit all the temperature points with a power law (dashed lines in Figure 4) clearly shows a deviation for the lowest 3 points for the  $^1\text{H}$  data and 2 points for the  $^7\text{Li}$  data. Power law fits that exclude these low-temperature data points (solid lines in Figure 4) yield the following parameters:  $D_0 = (657 \pm 60) \times 10^{-10} \text{ m}^2/\text{s}$ ,  $T_0 = (174 \pm 3) \text{ K}$ , and  $\mu = (4.853 \pm 0.220)$  for  $^1\text{H}$  and  $D_0 = (745 \pm 37) \times 10^{-10} \text{ m}^2/\text{s}$ ,  $T_0 = (164 \pm 2) \text{ K}$ , and  $\mu = (6.213 \pm 0.145)$  for  $^7\text{Li}$ . For the  $^1\text{H}$  diffusion coefficient, a deviation from a power law fit is evident at  $T = 216 \text{ K}$ , well above the peritectic point at  $T = 207 \text{ K}$ . This indicates that breaking the power law at low temperatures is not related to crossing the peritectic point. This is in agreement with the DSC data discussed above that suggest that the state of the system does change at  $207 \text{ K}$  on warming up, but not on cooling down. Interestingly, the ratio of the crossover temperature,  $T_c$ , to the singularity temperature,  $T_0$ , remains constant for different diffusion components:  $(T_c/T_0) = (216 \text{ K}/174 \text{ K}) = 1.24$  for the  $^1\text{H}$  data and  $(T_c/T_0) = (205 \text{ K}/164 \text{ K}) = 1.25$  for the  $^7\text{Li}$  data. Furthermore, the ratio remains approximately the same for the QENS data obtained at different  $Q$  values:  $(T_c/T_0) = (225 \text{ K}/189 \text{ K}) = 1.19$  at  $Q = 0.3 \text{ \AA}^{-1}$  and  $(T_c/T_0) = (222 \text{ K}/187 \text{ K}) = 1.19$  at  $Q = 0.5 \text{ \AA}^{-1}$ . This ratio is remarkably close to the commonly accepted ratio of the crossover and glass transition temperatures,  $(T_c/T_g) = 1.2$ , for the “universal” dynamic transition observed experimentally in



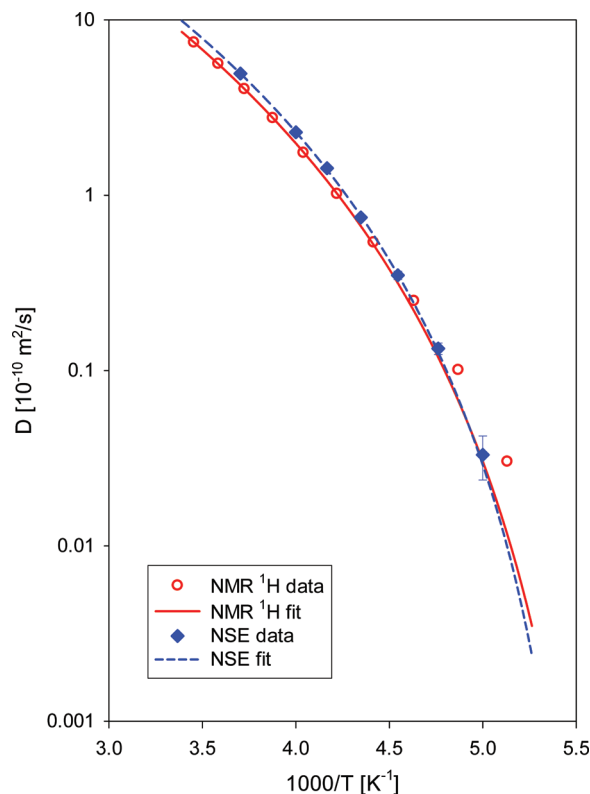


**Figure 4.** Temperature dependence of the diffusion coefficients obtained from the NMR data. Dashed lines: power law fits using all data points as described in the text. Solid lines: power law fits that exclude the low temperature data points as described in the text.

many glass forming systems, even though some variations of ( $T_c/T_g$ ) have been tabulated.<sup>28</sup>

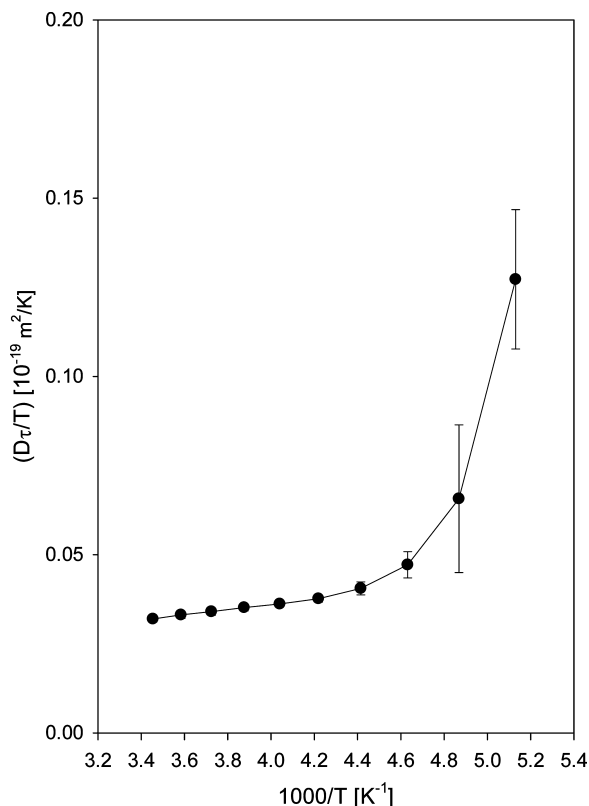
The diffusion coefficients can be independently evaluated from the NSE data, where, in the low- $Q$  limit,  $DQ^2 = 1/\tau$ . Figure 5 shows a comparison of the NSE diffusion coefficient calculated from the relaxation times obtained at  $Q = 0.1 \text{ \AA}^{-1}$  with the  $^1\text{H}$  NMR data. Clearly, the NSE and  $^1\text{H}$  NMR measurements probe the same dynamic component. The data overlap reasonably well at higher temperatures but show some pronounced decoupling below the dynamic crossover point. The NSE data keep following the power law dependence that can be extrapolated from the high-temperature NSE and NMR data. On the contrary, the actual NMR-obtained diffusion coefficient shows substantial increase with respect to the values predicted from the extrapolation of the high-temperature data. There is clear decoupling between the main relaxation times measured by NSE and the macroscopic diffusion coefficient measured by NMR. Indeed, using fit extrapolation of the NSE relaxation times,  $\tau$ , to the set of temperature points used in the NMR measurement, we have calculated the value of  $D\tau/T$ , as plotted in Figure 6. Since the main structural relaxation time,  $\tau$ , is proportional to the system viscosity,  $\eta$ , the Stokes–Einstein relation between the self-diffusion coefficient and viscosity,  $D \propto T/\eta$ , predicts that  $D\tau/T = \text{constant}$ . Despite the relatively large error bars in the low-temperature data in Figure 6 driven by the uncertainty in the  $\tau$  values experimentally determined from the NSE data, it is clear that the Stokes–Einstein relation breaks down below the dynamic crossover temperature. This effect has been observed in the past for confined water.<sup>14,29</sup>

As was suggested in the previous neutron scattering study of water dynamics in a LiCl solution,<sup>13</sup> a NSE experiment at  $Q$  values lower than those attainable with QENS would help in



**Figure 5.** Comparison of the diffusion coefficient from the  $^1\text{H}$  NMR and NSE experiments. The NSE data are fit with a power law, whereas the  $^1\text{H}$  NMR data exhibit a deviation from a power law fit at low temperatures.

determining whether the dynamic crossover in  $(\text{H}_2\text{O})_{0.88}(\text{LiCl})_{0.12}$  represents the breakdown in the temperature dependence of the main  $\alpha$ -relaxation of water in the solution. On the basis of the results of the current study, the answer seems to be negative. The main relaxation component continues to follow a non-Arrhenius power law below  $T_c$ , as evidenced by the data collected at low  $Q$  that show no dynamic crossover. At higher  $Q$ , the crossover marks the temperature below which a localized component with apparently Arrhenius temperature dependence splits from the main component. It is this localized component that is likely observed in QENS measurements, whereas the relaxation times of the main component become too long for the experimental resolution. The localized character of the component observed in QENS experiment below  $T_c$  is evident from the nonvanishing elastic scattering, which is  $Q$  dependent.<sup>13</sup> On the other hand, there is no elastic scattering in the present NSE data collected at low  $Q$ , which indicates that the measured process is not localized. The spatial localization for the faster process that splits from the main component below  $T_c$  can be estimated as  $2\pi/Q_c \approx 30 \text{ \AA}$ , if  $Q_c = 0.2 \text{ \AA}^{-1}$  is taken between the  $Q$  values where there is only the main component present ( $Q = 0.1 \text{ \AA}^{-1}$  in the NSE data), and the secondary component becomes measurable ( $Q = 0.3 \text{ \AA}^{-1}$  in the QENS data<sup>13</sup>). The presence of  $Q_c$  in our system is somewhat analogous to the results obtained for polymers. In particular, in 1–4 polybutadiene, below 220 to 230 K a secondary, faster relaxation component was found to split from the main relaxation component in the measurements performed above certain  $Q$  value (beyond the first structural peak).<sup>30–32</sup> There the faster component was classified as  $\beta$ -relaxation, or Johari–Goldstein process,<sup>33</sup> commonly found in polymers. It is not clear whether or not the faster relaxation component in the dynamics of the water molecules is of the same character. One difference is the



**Figure 6.** Temperature dependence of  $D\tau/T$ , where  $D$  is the  $^1\text{H}$  NMR diffusion coefficient,  $\tau$  the relaxation time from NSE measurements, and  $T$  the temperature. The Stokes–Einstein relation predicts that  $D\tau/T$  should be a temperature-independent constant.

value of  $Q_c$ , which is lower by an order of magnitude in water compared to 1–4 polybutadiene. The NSE measurements of 1–4 polybutadiene are sensitive predominantly to the coherent dynamics, whereas in the current experiment the incoherent dynamics of water molecules have been explored, and the  $Q_c$  appears to be well below the first structural peak. The low value of the  $Q_c$  indicating the spatial localization of the fast process on the 30 Å length scale is puzzling. It is not obvious how such a relatively large distance is compatible with any localized process, which usually describes the faster relaxation component. Given the fact that the faster component observed in our measurements is likely responsible for the increase in the long-range diffusion coefficient above the value predicted by the main component, the origin of the fast component in the dynamics of water molecules may differ from that of the regular, highly localized fast component in glass-forming systems. There is a possibility that the fast component in water may be indicative of the presence of heterogeneities on the nanometer length scale. The relationship between the dynamic crossover in water and dynamic heterogeneities has been recently explored using neutron scattering and molecular dynamics simulations.<sup>34–36</sup> Even more recently, an experimental report of heterogeneities in water on the ~1 nm length scale has generated much interest and debate.<sup>37</sup> Because of the  $Q$ -dependent relaxation times observed below  $T_c$ , it appears that the faster relaxation observed in the QENS experiment<sup>13</sup> represents some kind of translational dynamics, albeit spatially localized on the length scale of  $2\pi/Q_c$ . Furthermore, these localized translational dynamics contribute to the enhanced transport properties, resulting in the self-diffusion which is faster than one would expect from the main relaxation component. Therefore, the presence of dynamic heterogeneities on the nanometer length scale may be consistent with the development of the faster relaxation component.

There are some results available in the literature which, while lacking the spatial resolution capabilities provided by the  $Q$ -dependence of the neutron scattering signal, are consistent with our observation of the relaxation component split below  $T_c$ . For instance, dielectric spectroscopy studies of aqueous solutions of ethylene glycol oligomers<sup>38</sup> and *n*-propylene glycol<sup>39</sup> revealed the split of the faster component referred to as  $\beta$ -relaxation from the main  $\alpha$ -relaxation below  $T_c$ , the value of which was dependent on the solution composition. The change in  $T_c$  is commonly observed when a solution of water with another glass-forming component is studied. On the other hand, adding LiCl to water does not seem to affect the  $T_c$ , which remains the same as  $T_c$  of pure water confined in hydrophilic environments, regardless of the LiCl concentration.<sup>13,15</sup> Brillouin scattering experiments on (LiCl,6H<sub>2</sub>O) in various energy ranges revealed the split of the  $\beta$ -relaxation from the main  $\alpha$ -relaxation below ~215 K<sup>40</sup> and ~220 K.<sup>41</sup> Because experimental techniques such as dielectric spectroscopy cannot pinpoint the exact mechanism of the measured relaxations, this faster relaxation component is often described as a process due to the reorientation of the water molecules. However, from neutron scattering measurements it is well known that reorientation of individual water molecules (so-called rotational diffusion component) takes place on the picosecond time scale in ambient and supercooled water and is usually too fast for dielectric spectroscopy measurements. In particular, it was demonstrated<sup>42</sup> that even in hydration water, which experiences a higher degree of confinement compared to bulk solutions, the reorientational, or rotational component, remains relatively fast (on the time scale of the tens of pico-seconds) down to at least 195 K. This is well below the dynamic crossover temperature, which manifests itself in the much slower (nanosecond time scale) dynamics. Moreover, within the classical decoupling approximation for the translational and rotational dynamics of water,<sup>43</sup> using the exact Sears expansion<sup>44</sup> for separating the  $Q$  and  $t$  dependence of the rotational dynamics, at  $Q$  values  $\leq 0.5 \text{ \AA}^{-1}$ , the incoherent QENS spectra are dominated (>90%) by the center-of-mass motion of the water molecules. Although the decoupling approximation for the translational and rotational dynamics of water has been shown to be less accurate at low temperatures,<sup>45–47</sup> it is still valid to assume that for the  $Q$  range investigated in this and previous works on the dynamic crossover the center-of-mass dynamics of the water molecules is probed. On this basis, we contend that, despite its spatial localization on the nanometer length scale, the faster component in water below  $T_c$  possesses some characteristics of translational diffusion, as opposed to a purely reorientational process.

We cannot reach a definitive conclusion about the nature of the faster relaxation below  $T_c$  in the dynamics of water molecules. Whether it is a generic  $\beta$ -relaxation process such as Johari–Goldstein relaxation commonly found in glass-forming systems, or a process specific to the properties of water, remains unknown. If the latter is true, the presence of  $T_c$  can be either related to the existence of the two liquid phases and a possible critical point in bulk water or be a more common phenomenon originating from hydrogen bonding. In any case, the current results suggest that the experimental QENS studies that involve pure hydration water (on various types of surfaces) may be sensitive to the dynamics of the faster component below  $T_c$ , while the main component quickly exits the experimentally accessible QENS resolution window. It was shown<sup>48</sup> that, in order for the non-Arrhenius relaxation and the dynamic crossover to be present, the hydration level should exceed one mobile layer of water; that is, the system of surface water needs to be

sufficiently bulklike. Thus, it is likely that the relaxation mechanism measurable on the nanosecond time scale below  $T_c$  is essentially the same for water in bulk solutions and hydration water on hydrophilic or partially hydrophilic surfaces. This is also suggested by the similarity of  $T_c$  in bulk solutions and surface water.

Furthermore, the dynamic crossovers in pure confined water had been previously discussed in the framework of the idea of  $\alpha$ - and  $\beta$ -relaxation processes merging above the crossover temperature. Such merging was proposed as an explanation of the crossover detected by broadband dielectric spectroscopy between 170 and 200 K.<sup>7</sup> Since the relaxation time at the temperature of this crossover was on the micro- to millisecond time scale, this crossover is beyond the dynamic range of a neutron scattering experiment by many orders of magnitude. Another crossover, at much shorter relaxation times, measured in the same dielectric spectroscopy experiment at about 225 K showed an excellent overlap with the QENS data.<sup>7</sup> This crossover was proposed to originate from the split of the “universal” dielectric process due to the motions of defects that lead to the fast long-range proton diffusivity which does not require translational motions of the molecules in the system. This interpretation of the fast component is in agreement with QENS and <sup>1</sup>H NMR data that are sensitive to proton diffusivity. However, in the current study we observed the low-temperature decoupling from the main relaxation of not only the <sup>1</sup>H NMR diffusion, but also the <sup>7</sup>Li NMR diffusion (Figure 4). This suggests that the fast component may be related to the translational motions of the molecules, not just the protons.

It is natural to assume that pure bulk water, if it could be studied below the homogeneous nucleation temperature, would also exhibit a crossover near  $T_c$ . In fact, a transition from the high-temperature  $\alpha$ -relaxation regime to the low-temperature  $\beta$ -relaxation regime has been proposed for bulk water;<sup>49,50</sup> this scenario basically agrees with our present conclusions except that we have not observed the disappearance of the  $\alpha$ -relaxation below  $T_c$ . Instead, this component remains observable if one uses an experimental technique capable of probing relaxation times much longer than those accessible using QENS. In this regard, a recent QENS study<sup>51</sup> of protein hydration water that found no sign of the dynamic crossover in the data measured at  $Q = 1.0 \text{ \AA}^{-1}$  yielded some surprising results. Instead of the Arrhenius-type dynamic component below  $T_c$ , the data analysis yielded a single super-Arrhenius component both above and below  $T_c$ , even though the relaxation times extracted from the data analysis below  $T_c$  were orders of magnitude outside the experiment resolution. The conclusion was that there is no time-scale independent transition in hydration water. While this may be true for the dynamics of hydrated proteins,<sup>51,52</sup> the presence of an Arrhenius-type relaxation component in the protein hydration water below  $T_c$  with the relaxation times within QENS experimental resolution (unlike for the  $\alpha$ -relaxation relaxation component) was found in dielectric spectroscopy experiments.<sup>53</sup> We believe that there exists a sufficient body of evidence for a time-scale independent dynamic crossover in supercooled water, whether confined in pores or on surfaces, or in solutions.

## Conclusion

We have found that NSE measurements of the incoherent relaxation dynamics of the water molecules in a LiCl aqueous solution at a low  $Q$  of  $0.1 \text{ \AA}^{-1}$  yield a non-Arrhenius relaxation time dependence originating from the main structural relaxation in the studied temperature range of 270 to 200 K. On the other hand, the NMR measurements of the diffusion coefficient in

the same system have demonstrated the breakdown of the non-Arrhenius temperature dependence, at 216 and 207 K for <sup>1</sup>H and <sup>7</sup>Li, respectively. This breakdown is qualitatively similar to the crossover in the relaxation times previously obtained in an incoherent QENS experiment on the same system at  $Q \geq 0.3 \text{ \AA}^{-1}$ . Our results suggest that below a certain temperature (about 220 K) in water there exist more than one relaxation component of translational character. One is the main structural relaxation component with non-Arrhenius temperature dependence, which should be measurable at any  $Q$  value, given a sufficient experimental resolution. The other is a faster, secondary relaxation component with Arrhenius temperature dependence, which is distinguishable from the main component below the temperature of the dynamics crossover. This component is spatially localized and, as such, is measurable only above certain value of  $Q$ . This component is accessible with a typical resolution and  $Q$ -range of QENS experiments. Whether the faster component is a generic  $\beta$ -relaxation process commonly found in glass-forming systems or a process specific to the properties of water remains unknown. However, we believe that this fast component is universally present below the dynamic crossover temperature in water, whether confined in pores or on surfaces, or in solutions. Compared to confined water, the advantage of the bulklike aqueous solution as a model system for neutron scattering studies is that the scattering at low  $Q$  values can be measured, which allows probing the length scale associated with the fast relaxation component. This length scale appears to be on the order of a nanometer.

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