

Temperature Dependence of the Self-Diffusion of Supercooled Heavy Water to 244 K

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The translational diffusion coefficients of supercooled heavy water ($^2\text{H}_2\text{O}$) at atmospheric pressure were examined using pulsed-gradient spin-echo NMR diffusion measurements down to 244 K. At this temperature the diffusion coefficient was $1.67 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The temperature dependence of the $^2\text{H}_2\text{O}$ diffusion was distinctly non-Arrhenius. It was found that the temperature dependence of the diffusion could be modeled almost equally well by both Vogel–Tamman–Fulcher and fractional power law relationships. However, at the lowest temperatures the fractional power law equation appeared to be slightly better at describing the data.

Introduction

The anomalous behavior of water in the supercooled state is poorly understood (e.g., see refs 1–7), and a number of theories have been put forward to explain this behavior, including the stability limit conjecture^{8–10} and the existence of high and low density phases of supercooled water.^{11,12} Recently, using ^1H pulsed-gradient spin-echo (PGSE) NMR measurements,^{13–15} we measured the translational diffusion (also known as self-diffusion or intradiffusion) coefficients¹⁶ of supercooled $^1\text{H}_2\text{O}$ down to 238 K at ambient pressure.¹⁷ To further clarify the behavior of supercooled water and to allow comparison with our recent data for supercooled water, here we present the results for supercooled $^2\text{H}_2\text{O}$ down to 244 K. Previous studies of the diffusion coefficient of $^2\text{H}_2\text{O}$ have generally been at elevated pressures and above supercooling by NMR measurements^{18–20} and other techniques (e.g., see refs 21–23). In addition to the problems of studying water in a metastable state,¹ ^2H PGSE NMR diffusion measurements of supercooled $^2\text{H}_2\text{O}$ are much more technically demanding than the ^1H PGSE NMR measurements of $^1\text{H}_2\text{O}$ due to ^2H having a much shorter spin-spin relaxation time and only 1% of the sensitivity of protons. Moreover, by virtue of its lower gyromagnetic ratio, ^2H PGSE diffusion measurements require much larger applied magnetic field gradients.

Materials and Methods

Fine capillaries (0.13 mm i.d.) containing filtered 99.9% $^2\text{H}_2\text{O}$ were prepared in a manner similar to that described in ref 17. For the NMR measurements, five of these capillaries and a capillary containing absolute methanol for accurate temperature determination of the $^2\text{H}_2\text{O}$ capillaries were placed into a 5 mm NMR tube.

^2H PGSE NMR experiments were performed at 46.07 MHz using an inverse probe with a z-axis shielded magnetic field gradient coil. The strength of the gradient had been previously

calibrated using water.¹⁷ The sample temperature was calibrated using the temperature dependent chemical shift difference of the methanol resonances, and the temperature uncertainty was estimated to be ± 0.2 K at most. Similar cooling rates and temperature equilibration delays were used as in our previous study.¹⁷

The Hahn spin-echo pulse sequence containing a “square” magnetic field gradient pulse in each τ period was used for the translational diffusion measurements. For a single diffusing species, the normalized echo signal attenuation, E , is related to the experimental parameters and the self-diffusion coefficient, D , by^{14,24}

$$E = \exp\left(-\gamma^2 g^2 D \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right) \quad (1)$$

where γ is the gyromagnetic ratio, g is the magnitude, δ is the duration of the gradient pulses, and Δ is the separation between the leading edges of the gradient pulses. Regression of eq 1 onto the spin-echo attenuation data based on the integrals of the ^2H resonance using nonlinear least squares regression based on the Levenberg–Marquardt²⁵ algorithm provided estimates of the diffusion coefficients and associated error margin.

Diffusion was measured along the long axis of the capillaries (i.e., the direction of the gradient), thereby avoiding any possibility of restricted diffusion effects.^{14,26} Any surface effects at the capillary walls on the observed diffusion coefficient should be negligible due to the relatively large radius of the capillary, which means that the fraction of water molecules perturbed by the capillary surface is negligible.

Nonlinear regression analysis of the temperature dependence of the diffusion behavior (see below) was performed using the nonlinear least-squares fitter of Origin ver. 6.0 (Microcal, MA), which is based on the Levenberg–Marquardt algorithm. In each regression the diffusion coefficients measured in the present study were weighted with the respective errors determined from regressing eq 1 onto the PGSE data.

Results and Discussion

The measured $^2\text{H}_2\text{O}$ self-diffusion coefficients determined are tabulated in Table 1 and plotted in Arrhenius form in Figure 1.

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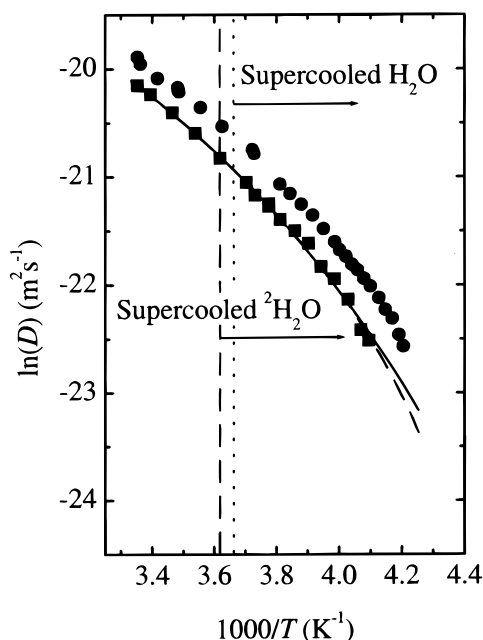


Figure 1. Arrhenius plot of the diffusion coefficients of the present $^2\text{H}_2\text{O}$ (■) results and previous $^1\text{H}_2\text{O}$ (●) results.¹⁷ The results of regressing the VTF (—) and FPL equation (---) onto the $^2\text{H}_2\text{O}$ data are also shown. The parameters for $^1\text{H}_2\text{O}$ are $D_0 = 4.00 \pm 0.87 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, $B = 371 \pm 45 \text{ K}$, and $T_0 = 169.7 \pm 6.1 \text{ K}$ for the VTF equation; for the FPL equation $D_0 = 7.66 \pm 0.24 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $T_S = 219.2 \pm 2.6 \text{ K}$, and $\gamma = 1.74 \pm 0.10$.¹⁷

TABLE 1: Measured Values of the Self-Diffusion Coefficient of $^2\text{H}_2\text{O}$

$T \text{ (K)}$	$D (\times 10^{-9} \text{ m}^2 \text{ s}^{-1})^a$
298.25	1.768 ± 0.004
294.6	1.631 ± 0.004
288.7	1.378 ± 0.004
282.6	1.138 ± 0.005
276.4	0.902 ± 0.003
270.1	0.721 ± 0.006
268.1	0.641 ± 0.005
264.9	0.593 ± 0.004^b
264.9	0.578 ± 0.004^c
262.3	0.512 ± 0.005
259.1	0.461 ± 0.008
256.2	0.410 ± 0.008
253.6	0.331 ± 0.007
250.9	0.296 ± 0.008
248.2	0.244 ± 0.007
245.7	0.184 ± 0.008
244.2	0.167 ± 0.004

^a The errors represent the 80% confidence limit from Monte Carlo simulations.²⁸ ^{b,c} Two different values of Δ (200 and 300 ms, respectively) were used to confirm Fickian diffusion.

We found that above 244 K, our data was well described by an empirical Vogel–Tamman–Fulcher (VTF)-type relationship,

$$D = D_0 \exp\{-B/(T - T_0)\} \quad (2)$$

where T is temperature and T_0 , D_0 , and B are fitting constants. Regression of eq 2 onto the data (see Figure 1) gave the following estimates, $D_0 = 5.30 \pm 0.42 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, $B = 456 \pm 19 \text{ K}$, and $T_0 = 164.0 \pm 2.3 \text{ K}$. A dynamic scaling behavior (i.e., fractional power law (FPL)) of the form²⁷

$$D = D_0 T^{1/2} \left(\frac{T}{T_S} - 1 \right)^\gamma \quad (3)$$

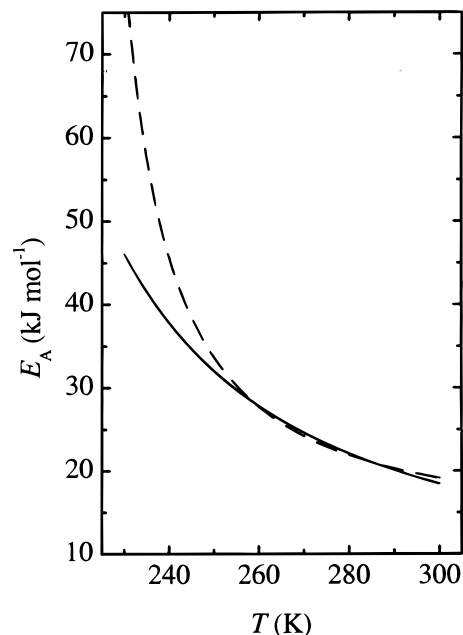


Figure 2. Plot of the E_A for the diffusion of $^2\text{H}_2\text{O}$ according to the differential of the VTF equation (—) and the FPL equation (---).

where γ is a fitting parameter and T_S represents a low temperature limit where D extrapolates to zero was also regressed onto the data (see Figure 1) and appears to provide a slightly better fit to the data at lower temperatures ($T < 250 \text{ K}$) than does the VTF equation. This power law behavior constitutes the grounds for the stability limit conjecture, which, assuming a true singularity at T_S , predicts that there is no continuity of states between the liquid and solid states.^{8–10} The parameters of best fit are given by $D_0 = 7.38 \pm 0.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $T_S = 219.3 \pm 1.0 \text{ K}$, and $\gamma = 1.93 \pm 0.03$. Interestingly, the value of T_S is almost identical to the value obtained for H_2O (219.2 K) in our previous diffusion study (see Figure 1).¹⁷ The slightly better fit of the FPL than the VTF equation to the data at low temperatures, as was also found for supercooled $^1\text{H}_2\text{O}$ diffusion measurements, mediates against the diffusion behavior in the supercooled regime being described by the VTF equation. Finally, we note that the ratio of the $^1\text{H}_2\text{O}$ diffusion coefficient divided by the $^2\text{H}_2\text{O}$ diffusion coefficient increases with decreasing temperature (i.e., 1.3 at 298 K and 1.65 at 244 K).

By taking the derivative of eqs 2 and 3, we were able to obtain the apparent activation energy (E_A) for the diffusive process; see Figure 2. E_A increases with decreasing temperature and at 245 K the value of E_A determined from the VTF equation is 34.7 kJ mol^{-1} ($8.3 \text{ kcal mol}^{-1}$) and 38.5 kJ mol^{-1} ($9.2 \text{ kcal mol}^{-1}$) from the FPL equation. As the temperature decreases, the estimates of E_A given by the two equations diverge significantly and at 240 K the value of E_A determined from the VTF equation is 37.8 kJ mol^{-1} ($9.0 \text{ kcal mol}^{-1}$) and 45.6 kJ mol^{-1} ($10.9 \text{ kcal mol}^{-1}$) from the FPL equation. As a comparison, the activation energy for H_2O at 240 K derived from the VTF equation exceeds 36 kJ mol^{-1} ($8.6 \text{ kcal mol}^{-1}$) or 41 kJ mol^{-1} ($9.8 \text{ kcal mol}^{-1}$) if determined from the FPL equation.¹⁷

Previously published $^2\text{H}_2\text{O}$ diffusion data, in addition to our present data, together with the results of regressing the VTF and FPL equations are plotted in Figure 3. It is clear that the FPL law provides a better fit to the data than does the VTF equation at lower temperatures. Interestingly, it was concluded in a recent study³ using molecular dynamics simulations that the T_S implied by the FPL may be associated with a temperature of structural arrest due to the cage effect that appears in deeply

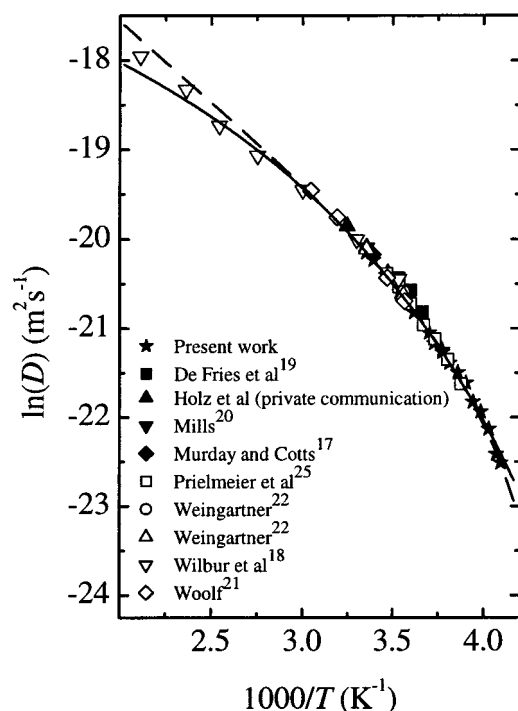


Figure 3. Arrhenius plot of ambient pressure $^2\text{H}_2\text{O}$ diffusion data. The parameters of best fit for the VTF equation (—) are $D_0 = 6.52 \pm 0.42 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, $B = 505 \pm 16 \text{ K}$, and $T_0 = 158.1 \pm 1.9 \text{ K}$; for the FPL equation (---) $D_0 = 7.20 \pm 0.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $T_S = 223.3 \pm 0.7 \text{ K}$, and $\gamma = 1.78 \pm 0.02$. If the regression is performed omitting the data from Wilbur et al.¹⁹ and Prielmeier et al.,²⁷ the parameters of best fit for the VTF equation are $D_0 = 5.38 \pm 0.42 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, $B = 459 \pm 18 \text{ K}$, and $T_0 = 163.6 \pm 2.3 \text{ K}$; for the FPL equation $D_0 = 7.38 \pm 0.05 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $T_S = 219.3 \pm 1.0 \text{ K}$, and $\gamma = 1.93 \pm 0.03$. In performing the regressions, it was assumed that the diffusion coefficients from the literature had errors of 5%.

supercooled liquids close to their mode-coupling theory glass transition temperature. This would obviate the requirement for thermodynamic instability to explain the anomalous behavior of supercooled water near T_S .

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