

**Communications: The fractional Stokes–Einstein equation: Application to water**

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## Communications: The fractional Stokes–Einstein equation: Application to water

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Previously [K. R. Harris, J. Chem. Phys. **131**, 054503 (2009)] it was shown that both real and model liquids fit the fractional form of the Stokes–Einstein relation [fractional Stokes–Einstein (FSE)] over extended ranges of temperature and density. For example, the self-diffusion coefficient and viscosity of the Lennard-Jones fluid fit the relation  $(D/T)=(1/\eta)^t$  with  $t=(0.921\pm0.003)$  and a range of molecular and ionic liquids for which high pressure data are available behave similarly, with  $t$  values between 0.79 and 1. At atmospheric pressure, normal and heavy water were also found to fit FSE from 238 to 363 K and from 242 to 328 K, respectively, but with distinct transitions in the supercooled region at about 258 and 265 K, respectively, from  $t=0.94$  (high temperature) to 0.67 (low temperature). Here the recent self-diffusion data of Yoshida *et al.* [J. Chem. Phys. **129**, 214501 (2008)] for the saturation line are used to extend the high temperature fit to FSE to 623 K for both isotopomers. The FSE transition temperature in bulk water can be contrasted with much lower values reported in the literature for confined water. © 2010 American Institute of Physics.  
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It was previously demonstrated that the fractional Stokes–Einstein relation or FSE relation,  $(D/T)\propto\eta^{-t}$ , can well correlate viscosity ( $\eta$ ) and self-diffusion coefficient ( $D$ ) data for both model and real liquids over extended ranges of temperature, pressure, and density.<sup>1</sup> Water was shown to fit the FSE well only at atmospheric pressure, but there was a large change in the exponent  $t$  from 0.94 to 0.68 in the upper supercooled region at about 258 K (265 K for D<sub>2</sub>O). Here the result for water is supplemented with new data at temperatures between the normal boiling point and close to the critical region.

The upper temperature limits of the best available diffusion data were 363 K for H<sub>2</sub>O and 328 K for D<sub>2</sub>O.<sup>1</sup> It is now possible to extend these limits considerably using the recent NMR self-diffusion results of Yoshida *et al.*<sup>2</sup> which extend along the saturation line ( $303<T/K<623$ ) and the oscillating disk viscometer results of Kestin *et al.*,<sup>3</sup> ( $298<T/K<493$ ). The self-diffusion coefficients have an uncertainty of  $(\pm1\text{--}\pm5)\%$ , increasing with increasing temperature,<sup>4</sup> and the viscosities have an uncertainty of  $\pm0.5\%$ , [although the H<sub>2</sub>O data fit the most recent IAPWS correlation somewhat better, to  $\pm0.24\%$  (Ref. 5)].

Figure 1 shows that FSE can be extended to the upper temperature limit of the Kestin viscosity data sets (493 K) with essentially the same slope as determined previously for both H<sub>2</sub>O ( $258<T/K<393$ ) and D<sub>2</sub>O ( $265<T/K<328$ ). Further extension to the limits of the diffusion data [623 K,  $0.96 T_c(\text{H}_2\text{O})$  or  $0.97 T_c(\text{D}_2\text{O})$ ] is made possible by employing the IAPWS viscosity correlations for H<sub>2</sub>O (Ref. 5) and D<sub>2</sub>O,<sup>6</sup> which both have uncertainties of  $\pm2\%$  in this region. At 623 K, the vapor pressure of water is 16.5 MPa;<sup>7</sup>

despite the change in pressure along the saturation line, its effects on the two transport properties are small compared to those of temperature, as is known from high pressure measurements in this high temperature region.<sup>8,9</sup> For H<sub>2</sub>O,  $t$  is a constant ( $0.943\pm0.003$ ) for  $258<T/K<623$ ; for D<sub>2</sub>O,  $t=(0.956\pm0.005)$  in the range  $265<T/K<623$ . The standard deviations of the fits are 2.1% and 3.3% respectively, which compare well with the means of the standard deviations of the diffusion data given by Yoshida *et al.*,<sup>2</sup> 1.9% and 4.5%, respectively.

It is remarkable that the empirical FSE equation is able to fit the water self-diffusion and viscosity data over nearly the whole of the saturation line together with the upper end of the supercooled region, a temperature range of some 365 K, to within 25 K of the critical temperature. The reliability of the self-diffusion and viscosity data in this region is extremely good (Table I). The self-diffusion data sets are mainly NMR spin-echo results based on calibrations traceable to the values determined by Mills in the range of 274–318 K from tracer diffusion values for tritium and deuterium labeled water (HTO and HDO) in water, which have precisions of  $\pm0.1\%$ – $0.2\%$ .<sup>10</sup> The viscosity data set is consistent with the recent recommendations of IAPWS which are based on a critical analysis of data sets for water published between 1914 and 2007.<sup>5</sup> The Kestin data set<sup>3</sup> was chosen as it is specific to the saturation line and is more precise than the IAPWS recommendations.

The low temperature data which define the transition temperatures are fewer in number. These extend to 238 K for H<sub>2</sub>O and to 242 K for D<sub>2</sub>O. The self-diffusion data sets are those of Price and co-workers [H<sub>2</sub>O (Ref. 11) and D<sub>2</sub>O (Ref. 12)], who avoided freezing with 130  $\mu\text{m}$  capillaries; the viscosity data sets employed are those of Ossipov and

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TABLE I. Experimental data sets.

H <sub>2</sub> O, Self-diffusion				H <sub>2</sub> O, viscosity			
T range (K)	Technique	Precision (%)	Reference	T range (K)	Technique	Precision (%)	Reference
274–318	Radiotracer diaphragm cell; <sup>a</sup> interferometry	±0.2	10	253–383	Critical literature analysis	± 1	5
277–333	Spin-echo NMR <sup>b</sup>	±1	21	264–273	Capillary	±0.5	22
298–363	Radiotracer diaphragm cell <sup>a</sup>	±1	23	254–273	Capillary	±0.3	24
238–298	Spin-echo NMR	±1	11	265–313	Capillary	±0.3	25
288–329	Spin-echo NMR	±1	26	238–273	Capillary	±3	13
303–623	Spin-echo NMR	±1.9 (mean)	2	298–492	Oscillating disc	±0.5	3
D <sub>2</sub> O, self-diffusion				D <sub>2</sub> O, viscosity			
T range (K)	Technique	Precision (%)	Reference	T range (K)	Technique	Precision (%)	Reference
278–318	Radiotracer diaphragm cell; <sup>a</sup> interferometry	±0.2	10	277–643	Critical literature analysis	±1–2	6
281–328	Radiotracer diaphragm cell <sup>a</sup>	±2	27	242–273	Capillary	±3	13
244–298	Spin-echo NMR	±2	12	298–492	Oscillating disc	±0.5	3
303–623	Spin-echo NMR	±4.5 (mean)	2				

<sup>a</sup>Calibrated using absolute interferometric results for aqueous KCl.

<sup>b</sup>All spin-echo NMR measurements rely on calibrations based on Mills's data (Ref. 10), Ref. 21 also employed cross-checks with benzene.

co-workers,<sup>13</sup> who used 1  $\mu\text{m}$  capillaries. However consistent  $t$  values are obtained for the two isotopomers, 0.668, and, as noted in our original paper, the transition temperature difference is consistent with the thermal offset noted by Robinson and co-workers<sup>14</sup> for the two transport properties.<sup>15</sup> The transition temperatures are rather higher than other estimates that have been used to support arguments for dynamic heterogeneities in supercooled water.<sup>16–20</sup>

Chen *et al.*<sup>16</sup> reported a fragile-to-strong crossover temperature of 225 K for light water based on NMR self-diffusion measurements on confined samples a few nanometers in cross-section and on QENS spectra. The Stokes–Einstein relation was written in the form  $D \approx \tau^{-\varepsilon}$ , where  $\tau$  is a translational relaxation time derived from the QENS experiments. In the fragile (higher temperature) region above 225 K, the exponent  $\varepsilon$  derived was 0.74 and in the strong region (lower temperature) it was 0.67. However the actual

Stokes–Einstein plot from this paper (their Fig. 1) shows a transition closer to 240 K. A later paper<sup>18</sup> from the same group, apparently based on a reworking of the same data, gives a higher crossover temperature of 290 K and exponents of 1 and 0.6. Still more recent work<sup>20</sup> reverts to the lower temperature, with exponents dependent on the degree of confinement. The capillary work was regarded as “quasi-one-dimensional,” experiments on protein surface water as “quasi-two-dimensional,” and water in methanol solution as “quasi-three-dimensional.” Molecular dynamics studies<sup>17</sup> on the SPE/C water model have yielded a transition from normal to FSE behavior at low temperatures. A fragile-to-strong crossover temperature of 225 K was also reported by Banerjee and co-workers.<sup>19</sup> This was based on rotational correlation times derived from the electron spin resonance spectroscopy (ESR) of a free-radical probe molecule (1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine or tempol) in supercooled water, with samples approximately 100  $\mu\text{m}$  in cross-section. Using estimates of the viscosity in this region, the Stokes–Einstein plot (their Fig. 5) shows a transition at approximately 240 K. In each of these examples, the transition is taken as evidence for dynamic heterogeneity at low temperatures.<sup>20</sup>

The transition temperatures and FSE slopes listed in this summary appear to depend on the technique employed, the method of data analysis, and the parameters used to approximate the self-diffusion coefficient and the viscosity where measurements were indirect. What is clear from the bulk-property data used in the analysis of this paper is that (a) water isotopomers show FSE over a wide range of temperature from 238 to 693 K; (b) there is a transition temperature between low and high temperature FSE behaviors at about 258 K for light water and 265 K for heavy water; (c) the slopes for the two isotopomers are almost identical within experimental error in both temperature regions, being 0.94–0.95 in the high temperature region and 0.67 on the lower.

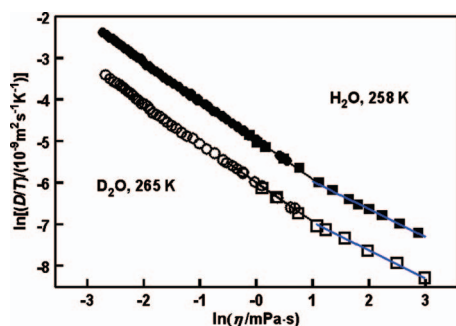


FIG. 1. FSE plot for water and heavy water at atmospheric pressure, showing transition from high (black lines) to low temperature (blue lines) behavior. The transition temperatures are shown on the figure. D<sub>2</sub>O lines are offset by  $-1$  for clarity. For H<sub>2</sub>O,  $623 \geq T/\text{K} \geq 274$ ,  $\ln[(D/T)/(10^{-9} \text{ m}^2 \text{ s}^{-1})] = -0.9429 \ln(\eta/\text{mPa s}) - 4.9767$ ;  $273 \geq T/\text{K} \geq 238$ ,  $\ln[(D/T)/(10^{-9} \text{ m}^2 \text{ s}^{-1})] = -0.6684 \ln(\eta/\text{mPa s}) - 5.2971$ ; for D<sub>2</sub>O,  $623 \geq T/\text{K} \geq 278$  K,  $\ln[(D/T)/(10^{-9} \text{ m}^2 \text{ s}^{-1})] = -0.9558 \ln(\eta/\text{mPa s}) - 5.0073$ ;  $277 \geq T/\text{K} \geq 242$ ,  $\ln[(D/T)/(10^{-9} \text{ m}^2 \text{ s}^{-1})] = -0.6677 \ln(\eta/\text{mPa s}) - 5.2935$ . Symbols: ● and ■—H<sub>2</sub>O; ○ and □—D<sub>2</sub>O.

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