# Pressure dependence of NMR proton spin-lattice relaxation times and shear viscosity in liquid water in the temperature range -15-10°C\*

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The NMR proton spin-lattice relaxation times  $T_1$  and shear viscosities have been measured as functions of pressure in the temperature interval -15-10°C. At low temperatures the low pressure boundary of the experiments is ice I, whereas ice V represents the high pressure extreme of our measurements. The initial compression at all temperatures covered in our study results in higher motional freedom of water molecules so that the pressure dependence exhibits a minimum in viscosity and a maximum in  $T_1$ . This is a consequence of significant distortion of the hydrogen bond network due to compression which also seems to weaken the hydrogen bonds. Further compression leads to restricted motional freedom due to increased packing of the molecules. This anomalous behavior of spin-lattice relaxation and shear viscosity with compression is more pronounced at lower temperatures since the hydrogen bond network is better developed at lower temperatures. In agreement with our earlier data covering the 10-90°C temperature range, we find that compression under isothermal conditions distorts the random hydrogen bond network, leading to diminished coupling between the rotational and translational motions of water molecules. The data indicate that the Debye equation describes the relationship between the reorientational correlation time and shear viscosity at constant volume but is not applicable to describe the density effects on water reorientation. In general, pressure and temperature have parallel effects on many dynamic properties at temperatures below 40°C and pressures below 2 kbar, whereas at higher temperatures and pressures their effects are just the opposite. Hard core repulsive interactions become more important than the directional interactions of hydrogen bonding at high compression.

# I. INTRODUCTION

Our earlier high pressure NMR studies<sup>1,2</sup> of liquid water have demonstrated that the most interesting behavior of various transport and relaxation properties with compression occur at temperatures of 10° and 30 °C. Taking advantage of the phase diagram of water as shown in Fig. 1, we decided to measure shear viscosity  $\eta$  and the NMR proton spin-lattice relaxation time  $T_1$  under experimental conditions of P and T denoted by the shaded area in Fig. 1. The temperature range studied was - 15° to 10 °C, and highest pressure was 6 kbar. According to our best knowledge, the measurement of self-diffusion of water to 2380 bar and to -20 °C as reported by Angel *et al.*<sup>4</sup> represents the only other high pressure study of water transport properties at low temperatures. However, there have been numerous experiments dealing with various properties of supercooled water at atmospheric pressure. 5-9

There are several purposes of our study: first, to find whether the anomalous behavior of proton  $T_1$  and shear viscosity with initial compression of liquid water is also present at temperatures below 0 °C; second, to confirm whether the Debye equation is valid under isochoric conditions in this temperature range and whether change in density causes this relationship to fail. Third, by studying  $T_1$  and  $\eta$  under experimental conditions where the extremes at low and high pressures are the ice I and ice V we hope to gain more information about the dynamic structure of water at low temperatures. Another motivation was the finding of our earlier study<sup>1</sup> that compression diminishes the coupling between the rotational and translational motions of water molecules due to changes in the hydrogen bond network. We were interested in whether water exhibits similar behavior at temperatures below 0 °C.

# **II. EXPERIMENTAL**

### A. NMR measurements

The high pressure, pulsed NMR spectrometer used is described elsewhere.<sup>10</sup> The high pressure was generated with Enerpac handpumps and was measured with a Heise bourdon pressure gauge with an estimated accuracy of  $\pm 0.05$  kbar. Pressure was transmitted to the titanium pressure vessel using CS<sub>2</sub> as the pressurizing fluid. The Lauda K-70R Ultra-Kryomat was used to cool the sample via methanol circulating through a jacket surrounding the pressure vessel. The temperature of the sample was measured with a copper/constantan thermocouple placed inside the pressure vessel near the water sample. The sample was kept within  $\pm 0.2$  °C of the nominal temperature.

The spin-lattice relaxation times were measured using the  $180^{\circ}-\tau-90^{\circ}$  sequence to an estimated accuracy of  $\pm 3\%$  with an automated system. The NMR spectrometer was run by a PDP/8 computer which was interfaced with the pulse programmer, Fabritek 1074 computer averager, and the RF transmitter. Optimization of pulse lengths and phase as well as measurement of  $T_1$  was done automatically by the computer as described in detail elsewhere.<sup>11</sup>

### **B.** Viscosity

The viscosity of water was measured using a rolling ball viscometer as described previously.<sup>12</sup> The viscometer was calibrated using the 10 °C, 0-6 kbar data of

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FIG. 1. Phase diagram for  $H_2O$  (Ref. 3). The range of pressures and temperatures of our measurements denoted by shaded area.

Harlow.<sup>13</sup> The viscosities have an estimated accuracy of  $\pm 2\%$ .

# C. Sample preparation

Samples of distilled deionized water were degassed in quartz tubes by the freeze-pump-thaw technique. The liquid was then loaded into the Pyrex tube-stainless steel bellows sample cell in an oxygen-free argon glove box.

# III. RESULTS AND DISCUSSION

The experimental shear viscosities and proton spinlattice relaxation times are given in Table I. The results of shear viscosity measurements are shown in Fig. 2. The  $\eta$  values of water at 2.2 °C reported by Bett and Cappi<sup>14</sup> are included in Fig. 2 as a check of the accuracy of our  $\eta$  vs pressure dependence. Their values appear between our 0° and 5° C values, and the agreement is excellent. Hindman<sup>7</sup> used a double exponential form of a rate expression to fit the measured viscosities in H<sub>2</sub>O by various authors. Since points below 0 °C represent supercooled data, we have plotted them as 1 bar values. They are in good agreement with extrapolated values of our measurement of individual isotherms. It is interesting to note that Bruges and Gibson's<sup>15</sup> expression which correlated viscosity vs pressure data above 0° C can be successfully used to predict viscosities at temperatures below 0 °C. Our experimental viscosities agree well with those calculated by the correlation equations as given by Bruges and Gibson. One finds agreement at  $0^{\circ}$  and  $-5^{\circ}$ C to within 1%; at -10 °C, 2%; and at -15 °C, 3% Since the equation is based on viscosities at temperatures

above 0 °C, it is not surprising that the deviation of predicted values from the experimental ones increases with decreasing temperature.

The spin-lattice relaxation times of  $H_2O$  are shown in Fig. 3. The low temperature, supercooled values measured by Hindman *et al.*<sup>6</sup> are shown on the plot as 1 bar points. They agree very well with our measure-

TABLE I. Experimental shear viscosities and spin-lattice relaxation times  $T_1$  in liquid water.<sup>a</sup>

t (° C)	P (kbar)	$ ho  (g/cm^3)^b$	η (cP)	$T_1$ (sec)
10°	0.001	1.000	1.30	2.35
	1	1.042	1.27	2.52
	1.22	1.050	1.27	2.55
	2	1.078	1.29	2.59
	2.79	1.100	1.34	2.58
	3	1.106	1.36	2.57
	4	1,131	1.46	2.48
1 1 X 1 X 1	4.83	1.150	1.58	2.40
	5	1.154	1.60	2.38
	6	I all served for date	1.77	
5°	0.001	1.001	1.53	2.00
	1	1.043	1.44	2.21
	1.19	1.050	1.44	2,23
	2	1.079	1.46	2.27
	2.75	1.100	1.51	2,23
	3	1.107	1.54	2.22
	4	1,133	1.67	2.14
	4.77	1,150	1.78	2.07
	5	1,155	1.83	2.04
	6		2.03	
	1011 103		2.00	
0°	0.001	1.000	(1.80)°	(1.69)
	1	1.044	1.64	1.92
	1.17	1.050	1.64	1.93
	2	1.080	1.65	1.96
	2.69	1.100	1.72	1.93
	3	1.109	1.76	1.92
	4	1.135	1.90	1.84
	4.68	1,150	2.02	1.77
	5151509	1.157	2.09	1.74
	6	all block (D' OL a	2.31	a libert a stage of
-5°	1	1.045	1.91	1.61
	1.14	1.050	1.91	1.63
	2	1.081	1.92	1.68
	2.63	1.100	1.98	1.66
	3	1,111	2.03	1.64
	4	1.137	2.21	1.55
	4.57	1.150	2.35	1.49
	5	1.160	2.45	1.44
-10°	1 (21)	(1.046)	2.29	(1.36)
	1.11	1.050	2.27	(1.38)
	2	1.083	2.26	1.45
	2.55	1.100	2.33	1.43
	3	1.114	2.43	1.40
	4	1.140	2.68	1.29
	4.38	1.150	(2.80)	(1.24)
-15°	1	(1.047)	(2,77)	(1.08)
	1.08	(1,050)	(2.75)	(1.09)
	2	1.085	2.71	1,18
	2.48	1,100	2,80	1.18
	3	1.116	2,96	1.14

<sup>a</sup>Values obtained by best-fit of experimental data. <sup>b</sup>Reference 24.

<sup>c</sup>Values in parentheses denote extrapolated values.



FIG. 2. Pressure dependence of shear viscosity in H<sub>2</sub>O. X denotes values from Ref. 14.  $\Delta$  denotes values from Ref. 7. Dotted lines denote phase boundaries (ice I and ice V).

ments<sup>1</sup> above 0  $^{\circ}$ C, and those below the freezing point fall on the isotherms when they are extrapolated into the supercooled region. Previous pressure measurements<sup>1</sup> at 10  $^{\circ}$ C are also plotted. They agree with the new data within 3%, which is about the error of our measurements.

The anomalous pressure dependence of shear viscosity and  $T_1$  in  $H_2O$  is clearly seen from Figs. 2 and 3. The isotherms of both viscosity and proton  $T_1$  have low pressure slopes which are opposite in sign to those found for normal liquids. It can also be seen that at lower temperatures the magnitude of these slopes increases.

Earlier work<sup>1</sup> has shown that  $(\partial T_1/\partial P)_{P=0} = 0$  at about 30 °C. At 10 °C the maximum in the curve is at about 2.2 kbar. This trend might be expected to continue as the temperature is decreased to -15 °C. However, it



FIG. 3. Pressure dependence of the proton spin-lattice relaxation time  $T_1$  in  $H_2O$ . X denotes values obtained in our earlier study (Ref. 1).  $\Delta$  denotes values from Ref. 6. Dotted lines denote phase boundaries (ice *I* and ice *V*).

can be seen from Fig. 3 that the maximum falls between 1.9 and 2.2 kbar and there is no apparent temperature trend. This means that the position of the maximum must change rather sharply for it to be at 30 °C and 1 bar. Similarly Bett and Cappi<sup>14</sup> have found that the minimum in the viscosity vs pressure curve at 33.5 °C is at 1 bar. At 10 °C the minimum was found to be at about 1.1 kbar. Our data show that the minimum moves up to 1.6 kbar at -15 °C. The positions of the maxima and minima are listed in Table II. It is interesting that the positions of the extremes in the viscosity and the relaxation are not at the same pressures and do not have the same temperature dependences. The discussion which follows will show they need not have the same behavior.

The analysis of the proton relaxation data follows the procedure used and discussed in our earlier study<sup>1</sup> of  $H_2O$  in the 10 °C to 90 °C temperature range. As pointed out in detail, <sup>1</sup> the data analysis involves several assumptions but enables one to reach qualitative conclusions about the effects of density and temperature on the dynamic behavior of water.

Since spin-rotation interactions are small<sup>16</sup> at temperatures below 100 °C,  $H_2O$  relaxes primarily by dipole-dipole interaction, which is composed of interand intramolecular terms

$$\left(\frac{1}{T_1}\right)_{\text{observed}} = \left(\frac{1}{T_1}\right)_{\text{inter}} + \left(\frac{1}{T_1}\right)_{\text{intra}}.$$
 (1)

The intra term can be related to the correlation time  $\tau_{\theta}$  by

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_{\theta} \quad , \tag{2}$$

where r is the distance between the protons in the water molecule, and  $\gamma$  is the magnetogyric ratio of the proton.  $\tau_{\theta}$  can be related to the viscosity by the modified Debye equation:

$$\tau_{\theta} = \frac{4}{3} \pi \frac{a^3 \eta}{kT} \kappa \quad , \tag{3}$$

where  $\frac{4}{3}\pi a^3$  is the volume of the molecule,  $\eta$  is the viscosity,  $\kappa$  is the parameter introduced by McClung and Kivelson<sup>17</sup> (see discussion in our earlier study).<sup>1</sup> Equations (2) and (3) can be combined to give the dependence of  $(1/T_1)_{intra}$  on  $\eta/T$ .

Hubbard<sup>18</sup> has derived the following equation, which

TABLE II. PVT conditions for shear viscosity minimum and  $T_1$  maximum.

	Pressure (bar)				
t (° C)	$\eta$ (minimum)	T <sub>1</sub> (maximum)			
10	$1.0 \pm 0.1$	$2.2 \pm 0.2$			
5	1.2	2.0			
0	1.4	1.9			
-5	1.5	2.1			
-10	1.6	2.0			
-15	1.6	2.2			

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relates  $(1/T_1)_{inter}$  to the diffusion coefficient D

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{N\pi\gamma^4\hbar^2}{5aD} \left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 + \dots\right], \quad (4)$$

where N is the number density of the nuclei, a is the hydrodynamic radius, and b is the distance of the nucleus from the center of the molecule.

The modified Stokes-Einstein equation relates D and viscosity  $\eta$ :

$$D = \frac{kT}{C\pi a\eta} \quad . \tag{5}$$

The coefficient C can take on values of 6 or 4 for the hydrodynamic stick or slip limits, respectively. It has been found<sup>2</sup> that water more closely obeys the stick limit as would be expected considering the extent of hydrogen bonding. We will, therefore, assume that C = 6 and combine Eqs. (4) and (5), which will give the dependence of  $(1/T_1)_{inter}$  on  $\eta/T$ . If Eqs. (1)-(5) are all combined, the relationship between  $T_1$ ,  $\eta$ ,  $\rho$ , and T will be obtained:

$$\left(\frac{1}{T_1}\right)_{H} = (c'\rho + c\kappa)\eta/T \quad , \tag{6}$$

where

5k

$$c = \left(\frac{3\gamma^{4}\hbar^{2}}{2r^{6}}\right) \left(\frac{4\pi a^{3}}{3k}\right) , \qquad (6'a)$$

$$c' = \frac{6\pi^{2}\gamma^{4}\hbar^{2}}{2r^{6}} \left[1 + 0.233\left(\frac{b}{2}\right)^{2} + 0.15\left(\frac{b}{2}\right)^{4} + \frac{N_{0}}{2r^{6}}\right] N_{0} s \qquad (6'b)$$

\al

M

where  $N_0$  is Avagadro's number, M is the molecular weight, and s is the number of spins per molecule. If it is assumed that a, b, and r do not change with temperature and density, then both c and c' will not depend on T and  $\rho$ . We use the following values: a=1.38 Å, b=0.92 Å, r=1.52 Å.

If  $\kappa$  depends only on density, a plot of  $(1/T_1)_{\rm H} \text{ vs } \eta/T$ at constant density would yield a straight line through the origin. The plot in Fig. 4 shows that this is indeed



FIG. 4. Dependence of the observed proton relaxation rate  $(1/T_1)_H$  upon  $\eta/T$  in H<sub>2</sub>O at several constant densities.

TABLE III. Density dependence of pa	arameter ĸ.
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$\rho(g/cm^3)$	1.00	1.05	1.10	1.15	1.20
к	0.93	0.81	0.65	0.58	0.47

the case. The standard deviation of the slope of the best fit straight lines is at most 1.4%. We have used 30° and 90° data from our earlier work<sup>1</sup> to increase the range of temperature used on the plot and to show the marked difference in isothermal behavior of  $(1/T_1)_H$  at temperatures above ~30 °C. The dramatic curvature of the isotherms from  $10^{\circ}$  to  $-15^{\circ}$ C shows the differing pressure dependence of the extrema of viscosity and relaxation. A minimum in the viscosity will be at the extreme left-hand part of the isotherm; whereas, a maximum in the  $T_1$  will occur at the lowest point. Depending upon the curvature of the isotherm, these two points might be at different pressures (see Table II). If our assumptions are valid (see Ref. 1), the data suggest that  $\kappa$  is independent of temperature within experimental error and depends only on density, as shown in Table III.

Figure 4 can be qualitatively understood in terms of a simple physical picture based on the changes in the random hydrogen bond network. As is clear from Fig. 1 and Figs. 2 and 3, ice I and the high pressure ice V represent the boundaries of our experiments. The important structural features of ice V are the distorted hydrogen bonds and the closer approach between non-hydrogen-bonded neighbors. As Eisenberg and Kauzmann<sup>3</sup> pointed out, such features permit relatively high densities without necessitating the complete rupture of hydrogen bonds. By compressing liquid water in the temperature range studied, we gradually go from an open structure with optimal tetrahedral order toward a more compact arrangement where non-hydrogenbonded neighbors are in repulsive contact and where hydrogen bonds are distorted. The net result is that compression leads to distortion of hydrogen bonds and thus weakens them. From Fig. 4 we see that the slopes of  $(1/T_1)_{\rm H}$  vs  $\eta/T$  lines decrease with increasing density. This indicates that the coupling between rotational and translational motions, as characterized qualitatively by changing parameter  $\kappa$ , is decreasing with increasing density at constant temperature. The fact that at constant density the  $(1/T_1)_{\rm H}$  vs  $\eta/T$  plots are straight lines suggests that thermal agitation at constant volume obviously affects reorientation and shear viscosity to the same extent, i.e., the increase in temperature causes viscosity  $\eta$  and the reorientational correlation time to decrease proportionately. This finding agrees with results of dielectric and NMR relaxation studies which reported that reorientation of water at 1 bar can be described by the Debye equation (see discussion in Ref. 19). However, it is not surprising that the Debye equation fails to describe the effects of compression because of the change in the coupling between the rotational and translational motions of water with density. It should be emphasized that  $\kappa$  for molecular liquids is usually in the range  $\sim 0.1-0.3$ . If one considers only the molecular shape of a water molecule and neglects

TABLE IV. Activation energies at constant pressure for shear viscosity in  $H_2O$ .

$E_{p}\pm 0.5$ (kcal/mole) Temperature interval (° C)					
P (kbar)	10,5	5,0	0,-5	-5,-10	-10,-15
0 mil as	5.1	5.1	(5.4) <sup>a</sup>	(5.8)	(6.1)
1	4.0	4.1	4.6	5.0	5.1
2	3.8	3.9	4.3	4.9	4.9
3	3.9	3.9	4.3	5.1	5.3
4	4.0	4.0	4.4	5.7	
5	4.2	4.2	4.7	ial inconse	(index (d))

<sup>a</sup>Parentheses denote extrapolated values from the supercooled region.

any effects of hydrogen bonding, one estimates<sup>20</sup>  $\kappa$  for water in the range 0.01-0.1. Therefore, if water at higher density is behaving more like a normal liquid, it is not surprising to find a decrease of  $\kappa$  with compression since the shape of the molecule is becoming relatively more important.

It is well-known that many dynamic processes in water exhibit a non-Arrhenius temperature dependence. In our earlier relaxation studies<sup>1,19</sup> of compressed water in the temperature range 10 °C to 90 °C and our diffusion study<sup>2</sup> of  $D_2O$  from 10 °C to 200 °C, we have shown that the activation energies for relaxation, self-diffusion, and shear viscosity decrease with increasing density. Since the non-Arrhenius behavior is very pronounced at temperatures below 10 °C, we calculated approximate activation energies for each temperature interval at which we carried out our measurements. The activation energies at constant pressure  $E_{\star}$  and constant density  $E_v$  for shear viscosity are given in Tables IV and V. In spite of the fact that the  $E_{v}$  and  $E_{v}$ are subject to relatively large error  $(\pm 0.5 \text{ kcal/mole})$ because of the calculation procedure using only one pair of  $\eta$  values at two temperatures, one can nevertheless detect some trends with temperature and pressure. As expected, both  $E_{p}$  and  $E_{v}$  will increase with decreasing temperature and go through a slight minimum at pressures of about 2 kbar or densities  $\sim 1.050-1.075$  g/cm<sup>3</sup>. Above these pressures and/or densities there is again a rise in the activation energies. This observation is in agreement with expectation because the increase of density first distorts the random hydrogen bond network leading to a minimum in viscosity, but further compression again increases  $E_p$  and  $E_v$  due to increased repulsive core interactions. After all, in normal molecular liquids compression leads to an increase in the magnitude of activation energies for various dynamic properties. Our findings are in agreement with the results of molecular dynamics calculations on compressed water by Stillinger and Rahman.<sup>21</sup> Another observation worth mentioning is the comparable magnitude of  $E_{p}$  and  $E_{v}$ under the same experimental conditions. In this way water differs from the behavior of normal molecular liquids, where we usually find  $E_p \simeq 2E_v$ .

Speedy and Angell<sup>8</sup> have recently shown that many physical properties of water at atmospheric pressure can be correlated by an expression<sup>22</sup>

$$X = A(T/T_{s} - 1)^{\gamma} , (7)$$

where X is the physical property, A and  $\gamma$  are constants, and  $T_s$  is the temperature of a thermodynamic singularity. Their atmospheric pressure data extend for some properties into the supercooled region. It is interesting to note that an expression of this form describes well our shear viscosity and proton  $T_1$  data from -15 °C to 90 °C over the range of pressures measured. The temperature  $T_s \cong 228$  °K obtained by fitting our experimental data agrees with the value reported by Angell *et al.*<sup>23</sup> Further work dealing with the applicability of Eq. (7) on other data including also self-diffusion and deuteron  $T_1$  data in compressed liquid heavy water at low temperatures is in progress in our laboratory.

# IV. CONCLUSIONS

The anomalous behavior of shear viscosity and proton spin-lattice relaxation time,  $T_1$ , with initial compression of liquid water at temperatures below approximately 40 °C becomes more pronounced at temperatures below 0 °C. The fact that extremes of our pressure range at each temperature correspond to ice I and high pressure ice V enables us to draw some general conclusions about the dynamic structure of water under these experimental conditions. The main difference between the ice I and ice V are the decreased distance of closest non-hydrogen-bonded neighbors and the distortion of hydrogen bond angles. One can expect that the initial compression first distorts hydrogen bonds and thus weakens them, and therefore reorientation of water molecules will be facilitated under these conditions. Needless to say that the same is true for the behavior of shear viscosity. Only above density of approximately 1.075 g/cm<sup>3</sup> further compression will hinder molecular motions due to increased packing and stronger short-range repulsive interactions. This picture of the compression effects on water is in agreement with the results of molecular dynamics calculations by Stillinger and Rahman.<sup>21</sup>

A general picture of the effects of temperature and pressure on dynamic properties can be illustrated by Fig. 5, which shows the effect of pressure and temperature on shear viscosity in water in the tempera-

TABLE V. Activation energies at constant volume for shear viscosity in  $H_2O$ .

Density $\rho (g/cm^3)$		Te	E <sub>v</sub> ±0.5 kc mperature	0.5 kcal/mole rature interval (°C)		
	10,5	5,0	0,-5	-5,-10	-10, -15	
1.000	5.2	4.9	(5.4) <sup>a</sup>	(5.9)	(6.0)	
1.025	4.6	4.0	4.5	6.1	5.7	
1.050	4.0	3.9	4.5	4.9	5.2	
1.075	3.9	3.5	4.3	4.6	4.9	
1.100	3.8	3.9	4.1	4.6	5.0	
1.125	4.2	3.8	4.0	4.9	5.3	
1.150	3.8	3.8	4.5	4.9		

<sup>a</sup>Parentheses denote extrapolated values from the supercooled region.



FIG. 5. Shear viscosity relief map as a function of temperature and pressure in liquid H<sub>2</sub>O.

ture range - 15 °C to 100 °C. We emphasize that analogous figures exhibiting maxima or minima can be constructed for the proton  $T_1$ , self-diffusion, chemical shift in H<sub>2</sub>O, and self-diffusion, shear viscosity, and deuteron relaxation in  $D_2O$ . The important finding of general validity which is clear from Fig. 5 is that both temperature and pressure have a parallel effect on the dynamic structure of water-both P and T increase molecular motional freedom at low temperatures and pressures. On the other hand, above ~2 kbar and at temperatures above ~40 °C, pressure and temperature exhibit just the opposite effect on dynamic properties, as is the case for normal liquids. It is quite understandable that compression of a normal liquid slows down the motional processes due to increased packing and stronger repulsive interactions. One may conclude that at high temperatures and high compression, behavior of water resembles that of normal molecular liquids.

In our earlier study<sup>1</sup> of H<sub>2</sub>O, we proposed that compression changes the coupling between the rotational and translational motions of water molecules and that the Debye equation fails to describe the effects of density on reorientational motions. Using the same procedure for analysis of our experimental data at temperatures below 10 °C we arrive at the same conclusions. It is interesting to find that even at lower temperatures the  $(1/T_1)_H$  vs  $\eta/T$  plots are linear in an isochoric experiment. In summary, the results indicate that increasing the density of liquid water has two effects. It causes (a) the temperature independent coupling between translation and rotation to decrease, presumably until it is limited by the shape of the molecule and (b) an initial increase of rotational and translational motions until the effects of molecular packing become important. Detailed analysis of the self-diffusion data and deuteron relaxation in liquid heavy water under comparable experimental conditions will be published shortly.

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