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Dynamics in supercritical fluid water

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Abstract. Recently we have developed a new microwave spectroscopy technique in the frequency range up to 40 GHz and measured the dielectric relaxation time for supercritical water and heavy water. The dielectric relaxation time τ_D in both liquid H₂O and D₂O decreases rapidly with increasing temperature and jumps to a large value at the liquid–gas transition. The relaxation time of D₂O is longer than that of H₂O in the liquid state, and the difference becomes smaller with decreasing density in the gaseous state. Based upon the observation that the dielectric relaxation time becomes fairly long in the dilute limit, we propose that the dielectric relaxation in the gaseous state is governed by the binary collision of molecules. In the liquid state, on the other hand, the contribution of the molecules that are incorporated in the hydrogen-bond network to the dielectric relaxation should be taken into account. The relation between τ_D and the viscosity, as well as the relation between τ_D and the diffusion constant, are also discussed in the whole fluid phase.

1. Introduction

Water is one of the most intensively studied liquids but it still remains one of the most complicated liquids. This is mainly due to the existence of the hydrogen-bond network. The local structure of ambient water is considered to be similar to that of ice, in which each molecule is tetrahedrally coordinated to other molecules via hydrogen bonding [1] (see figure 1). When the temperature is raised, liquid water is changed into vapour with large heat of vaporization. In the dilute vapour phase the molecule is isolated and the hydrogen bond is of little importance. Therefore, it is expected in principle that the transition from hydrogen-bonded state to non-hydrogen-bonded state should occur when the water is transformed from an ambient liquid to the dilute vapour passing through the supercritical condition. The transformation may be somewhat similar to the metal–nonmetal transition in expanded fluid metals [2] in the sense that the interaction among the constituent particles changes with thermodynamic variables (see figure 2). At this stage the existence of hydrogen bonds in supercritical water seems to be accepted by many authors [3–5]. However, this does not necessarily mean that the hydrogen-bond network survives in supercritical water. Studies on the low frequency dynamics are crucial for understanding the hydrogen-bond network.

The dielectric relaxation is one of the most fundamental properties that characterize the dynamics of water, because each water molecule has an electric dipole moment. Although tremendous efforts have been devoted to studying the dielectric relaxation of water [6–9], the mechanism is still controversial. In the Debye model the dielectric relaxation time τ_D is thought to reflect a single-molecule reorientation process [10]. Bagchi and Chandra [11] proposed, however, that the calculated complex dielectric constant $\varepsilon(\omega)$ exhibits strongly

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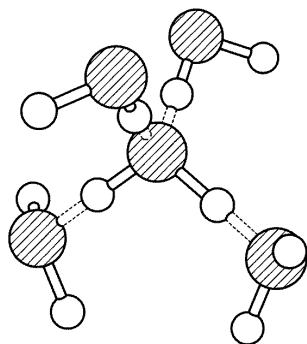


Figure 1. The local structure of ice, in which each molecule is tetrahedrally coordinated to other molecules via hydrogen bonding [1].

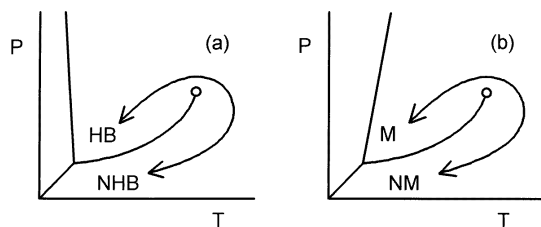


Figure 2. A possible transformation from the hydrogen-bonded to non-hydrogen-bonded states (a) and the metal–nonmetal transition in expanded fluid metal (b) are schematically shown on the pressure–temperature plane.

non-Debye behaviour if only the orientational mechanism of polarization relaxation is considered, and that simple Debye behaviour is recovered when the translational contribution to polarization relaxation is significant. In a percolation model, on the other hand, the motion of a water molecule depends on the number of hydrogen bonds by which the molecule is constrained and only less constrained molecules are relevant to the dielectric relaxation [12].

Recently we have developed microwave spectroscopy that can be applied to study dielectric relaxation of various fluids under high temperature and pressure in the frequency range up to 40 GHz [13]. By utilizing this new technique we have measured the static dielectric constant and the dielectric relaxation time in water and heavy water in the whole fluid phase [13–15]. This experimental information enables us to discuss the dynamics of water in a completely different way: we study first the motion of isolated water molecule in the gaseous state and proceed to more complicated cooperative dynamics in the liquid state.

In the present paper we will give a brief review of our recent works on the dielectric properties of supercritical water and heavy water [13–15]. This paper is composed as follows. In the next section we describe the microwave spectroscopy at high temperatures and pressures. In section 3 representative results of the dielectric relaxation time are shown and in section 4 we try to give a simple but comprehensive explanation for the relaxation mechanisms. Then we compare the relaxation time with the viscosity and the self-diffusion constant in section 5.

2. Microwave spectroscopy at high temperatures and pressures

Time domain reflectometry (TDR) is an established microwave spectroscopy in ambient conditions [16]. However, since this method requires several reference measurements, it is difficult to apply TDR to study the dielectric properties under high temperature and high

pressure. Recently we have modified the transmission line method so that it can be applied to extreme conditions [13].

The experimental apparatus for dielectric measurements of supercritical water and heavy water is schematically shown in figure 3. The sample cell has the shape of a coaxial cable in which platinum was used as the conducting material and quartz as the insulating material. The sample was introduced as the dielectric material in place of the quartz in the middle part of the cell. The sample cell was placed in an internally heated high pressure vessel pressurized by Ar gas. Both ends of the sample cell were connected to high pressure electrodes through which microwave signals were introduced from the outside of the high pressure vessel. A network analyser (Wiltron 37269A) was used as both the generator and the receiver of microwaves in the frequency range from 40 MHz to 40 GHz. The S -matrix, which consists of four complex S -parameters S_{ij} , can be measured directly by the network analyser. The suffixes of the S -parameters specify the input and output ports of the device under test (DUT), and S_{11} and S_{22} correspond to the complex reflection rates and S_{21} and S_{12} the complex transmission rates.

Since the present DUT consists of the sample cell and high pressure electrodes, the S -matrix of the DUT can be expressed by cascade connections of individual S -matrices [17]:

$$S = S^{E1} * S^{Q1} * S^{sample} * S^{Q2} * S^{E2} \quad (1)$$

where the suffixes E and Q denote the high pressure electrodes and the quartz parts and the symbol $*$ denotes the operation of cascade connection. Except for S^{sample} , the individual S -matrices can be measured or calculated in advance. S^{sample} is related to the complex dielectric constant $\varepsilon(\omega)$ through the characteristic impedance and the propagation constant of the coaxial transmission line. For water and heavy water we have assumed the Debye relaxation process in the whole density range [18]:

$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon(0) - \varepsilon_{\infty}}{1 + i\omega\tau_D} \quad (2)$$

where τ_D is the dielectric relaxation time and ε_{∞} the dielectric constant at high frequencies beyond the microwave region. In equation (2), we used the value of $\varepsilon(0)$ which was obtained in our experiments [13–15] and proved to be reproduced by the Uematsu–Franck formula [19]. As for ε_{∞} , we have assumed 5.6 for H₂O at 25 °C [6] and 4.8 for D₂O [20], and it decreases rapidly with temperature and approaches unity near 200 °C for both H₂O and D₂O. Then taking τ_D as a fitting parameter, we have minimized

$$R = \sum_i (\log |S_{21}^{cal}(\omega_i)| - \log |S_{21}^{exp}(\omega_i)|)^2 \quad (3)$$

by a nonlinear least squares fitting method. Here $S_{21}^{cal}(\omega_i)$ is the calculated S_{21} at ω_i , and $S_{21}^{exp}(\omega_i)$ is the experimental S_{21} at ω_i .

3. Dielectric relaxation time

The dielectric relaxation time τ_D for H₂O is shown in figure 4 as a function of temperature at various pressures below and above the critical pressure of 22.1 MPa [13]. In the liquid state τ_D decreases rapidly with increasing temperature irrespective of pressure. The present data at low temperatures are in good agreement with previous results [6–9]. It should be noted that τ_D jumps to a larger value at the boiling point. In the gaseous state τ_D is strongly pressure dependent and exhibits positive temperature dependence. In contrast to the isobaric temperature dependence, τ_D at constant densities shows small and negative temperature dependence when the density is below the critical one ($=0.32 \text{ g cm}^{-3}$). The

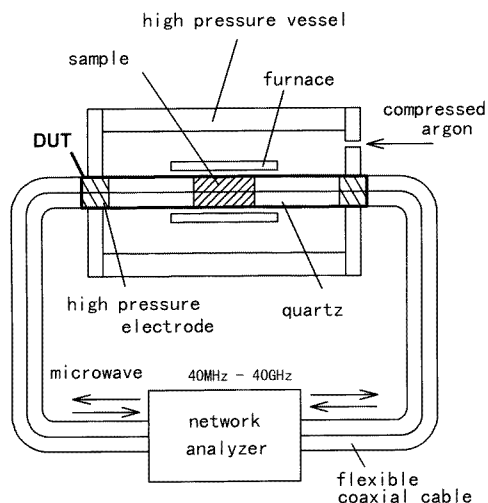


Figure 3. Schematic view of the experimental apparatus for the dielectric measurements of supercritical water and heavy water.

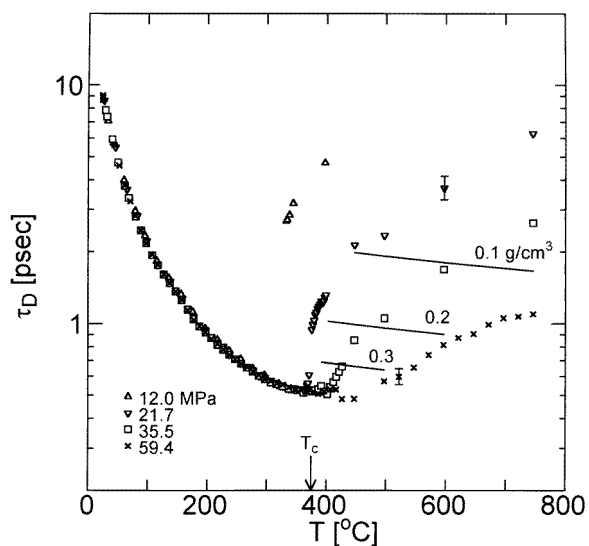


Figure 4. The dielectric relaxation time τ_D for H_2O is shown as a function of temperature at various pressures below and above the critical pressure of 22.1 MPa [13]. The lines denote the temperature dependence of τ_D at constant densities.

lines denote the temperature dependence of τ_D at 0.1, 0.2 and 0.3 g cm^{-3} . It is concluded from these results that the most relevant parameter determining τ_D is the temperature at lower temperatures or higher densities and it is the density at higher temperatures or lower densities [13].

A quantitative comparison between H_2O and D_2O is made in figure 5, where τ_D at constant temperatures are plotted as a function of number density by various symbols for H_2O and by solid and dotted lines for D_2O [13, 14]. The mass density of H_2O , $d(\text{H}_2\text{O})$, is indicated on the upper abscissa. As the density of H_2O decreases from 1 to 0.7 g cm^{-3} ,

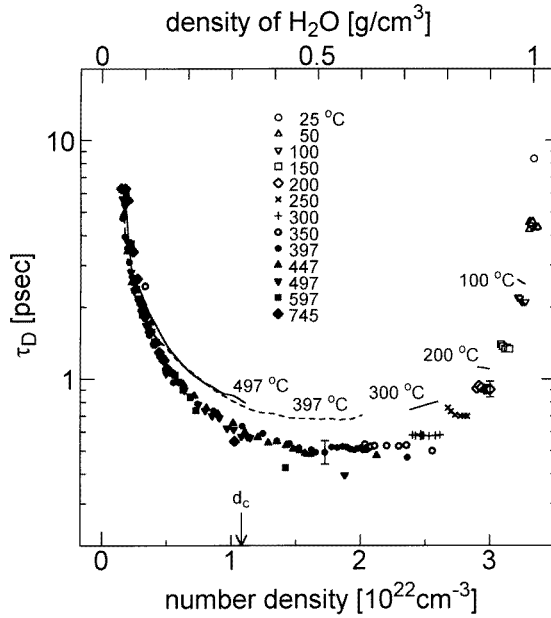


Figure 5. Comparison of τ_D between H_2O and D_2O . The various symbols denote τ_D for H_2O at constant temperatures as a function of number density and the solid and dotted lines τ_D for D_2O [13, 14].

τ_D decreases rapidly. Then, passing through a broad minimum, τ_D begins to increase near 0.4 g cm^{-3} . It is known that in ambient conditions τ_D for D_2O , $\tau_D(\text{D}_2\text{O})$, is larger than that for H_2O , $\tau_D(\text{H}_2\text{O})$, and their ratio $\tau_D(\text{D}_2\text{O})/\tau_D(\text{H}_2\text{O})$ is about 1.25 [20]. The present measurements reveal that this ratio is nearly conserved in the whole liquid state. When the density is further decreased, $\tau_D(\text{D}_2\text{O})/\tau_D(\text{H}_2\text{O})$ begins to decrease and reaches unity around 0.1 g cm^{-3} .

4. Relaxation mechanism

Since the dielectric relaxation time of isolated dipolar particles should be very short, our result that τ_D increases with decreasing density in the dilute limit is rather unexpected. This evidence implies that, when the dielectric properties are discussed, water molecules cannot be treated as a point dipolar particle and the internal rotational degree of freedom should be taken into account. We suppose that the applied electric field can hardly change the thermal motion of water molecules as far as they are rotating with large angular momentum. This is similar to our common experience that a rapidly spinning top remains standing against the gravity. Indeed the rotational energy of the water molecule is by far larger than the electrostatic energy of the dipole moment in our experiments. It is expected, however, that the dipole moment may obey the change of the applied field when the molecules lose angular momentum owing to collisions with other molecules.

Based upon a simple model where a water molecule is regarded as a hard sphere with the diameter of r_{eff} , the binary collision time τ_{col} of dilute gas is given by

$$\tau_{col} = \frac{1}{4n\pi r_{eff}^2} \sqrt{\frac{m\pi}{k_B T}} \quad (4)$$

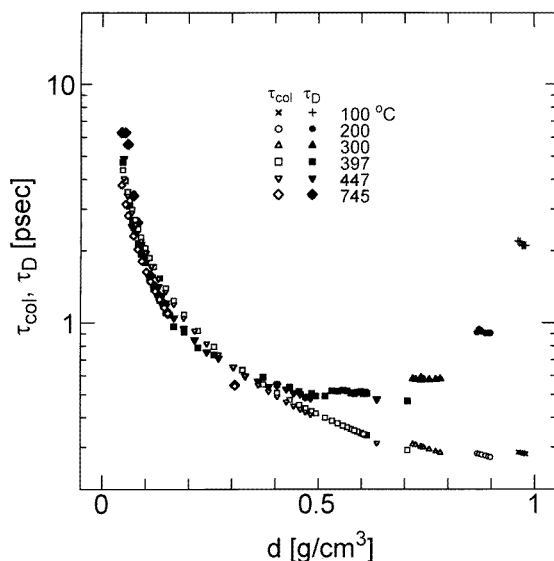


Figure 6. The calculated τ_{col} is shown by the open symbols as a function of density and compared with the observed τ_D for H₂O denoted by the closed symbols.

where m is the mass of the molecule and n the number density [21]. In figure 6 the calculated τ_{col} is plotted by open symbols as a function of density and compared with the observed τ_D for H₂O denoted by closed symbols. Here we have used $r_{eff} = 0.96 \text{ \AA}$, which is suitable for the size of molecule because it is the intra-molecular O–H distance. It should be noted that the density dependence of τ_{col} strikingly coincides with τ_D when the density is lower than d_c . Not only the density dependence but also the temperature dependence of τ_D can be reproduced by τ_{col} [15]. Furthermore, this model is consistent with the observed mass dependence. Therefore, it is concluded that the dielectric relaxation of water and heavy water is governed by the binary collision.

At high densities τ_D exhibits remarkable upward deviation from τ_{col} . This deviation should be associated with the existence of hydrogen bonding. A natural extension of the dielectric relaxation mechanism from the gaseous to the liquid state may be to add the contribution of those molecules that are incorporated in the hydrogen-bond network. Let the relaxation time of free molecules be τ_0 ($= \tau_{col}$) and that of bound molecules τ_1 . Then the complex dielectric constant $\varepsilon(\omega)$ is given as follows [22]:

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A}{1 + i\omega\tau_0} + \frac{B}{1 + i\omega\tau_1}. \quad (5)$$

Here A is proportional to the number of molecules that are initially free and reoriented by changing the applied field, and B is proportional to the number of molecules that are initially bound in the hydrogen-bond network and then reoriented. Since $\varepsilon(0) = \varepsilon_\infty + A + B$ for $\omega = 0$, A and B are rewritten as

$$A = f_0[\varepsilon(0) - \varepsilon_\infty] \quad (6a)$$

and

$$B = (1 - f_0)[\varepsilon(0) - \varepsilon_\infty] \quad (6b)$$

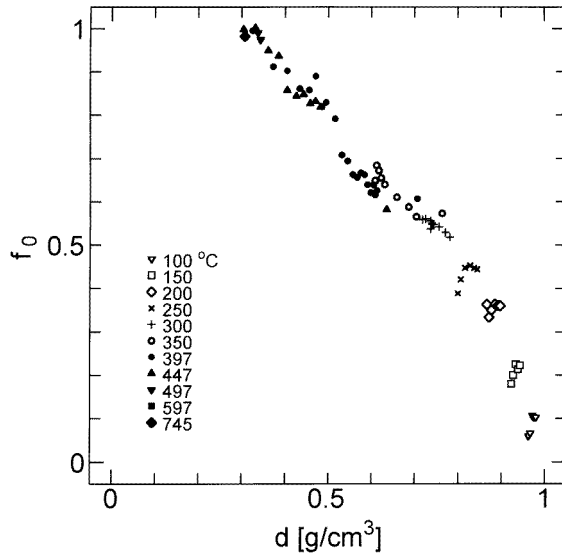


Figure 7. The fraction of free molecules f_0 is plotted as a function of density.

where f_0 is the fraction of free molecules:

$$f_0 = \frac{A}{A + B}. \quad (7)$$

It is expected that τ_1 is longer than τ_0 , because the free molecules are more easily reoriented than the bound molecules. We assume that the time difference $\tau_B (= \tau_1 - \tau_0)$ may be regarded as the time for the bound molecule to escape from the hydrogen-bond network. Then τ_B may be expressed as

$$\tau_B(T) = \langle \tau_{lib} \rangle \exp(\Delta H / k_B T) \quad (8)$$

where $\langle \tau_{lib} \rangle$ is the inverse of the mean librational frequency and ΔH is the hydrogen bond enthalpy. Here we adopt $\langle \tau_{lib} \rangle = 0.067$ ps and $\Delta H = 2.53$ kcal mol⁻¹, which are estimated from Raman scattering measurements up to supercritical conditions by Carey and Korenowski [23]. The parameter f_0 can be determined from

$$\tau_D = f_0 \tau_0 + (1 - f_0) \tau_1 = \tau_0 + (1 - f_0) \tau_B. \quad (9)$$

The resulting f_0 , which is plotted as a function of density in figure 7, exhibits a very reasonable trend that f_0 starts to deviate from unity near d_c and becomes zero near 1 g cm^{-3} . It may be interesting to compare the fraction of bound molecules, $1 - f_0$, with the number of hydrogen bonds per molecule divided by four which has been estimated from static measurements such as neutron diffraction [24] and NMR [25] measurements. We have found that the agreement among these quantities is fairly good at densities above 0.6 g cm^{-3} .

In order to examine the validity of the above mentioned simple model, we have put the estimated values of τ_0 , τ_1 , f_0 etc into the equation (5) and confirmed that $\varepsilon(\omega)$ calculated in this way can reproduce the experimental transmission spectrum in the temperature range above 100°C . In addition we have also confirmed that the present $\varepsilon(\omega)$ near 100°C is in fairly good agreement with that obtained recently by THz reflection spectroscopy [26]. However, our simple model cannot be applied to ambient water below 100°C , for which τ_D exceeds τ_B estimated by equation (8). This discrepancy may be reconciled by considering

the possibility that at relatively low temperatures the molecule once separated from the hydrogen-bond network could be trapped again by the network because the molecule does not have sufficient kinetic energy to escape from it. In such a case the average value of τ_B would be enhanced by a factor $1/p$, here p being the escape probability from the hydrogen-bond network, and τ_B would have a broad distribution [15].

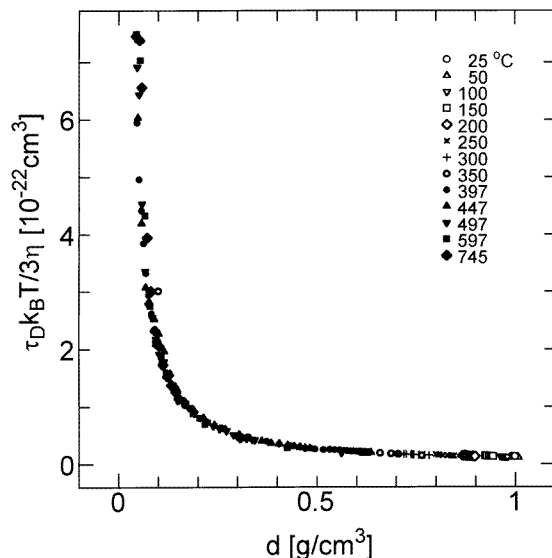


Figure 8. The effective volume expressed as $\tau_D k_B T / 3\eta$ is plotted as a function of density at various temperatures [13].

5. Viscosity and self-diffusion

It is known that the dielectric relaxation time τ_D of water under atmospheric pressure is approximately proportional to η/T and also to $1/D$, here η being the shear viscosity and D the self-diffusion coefficient [27, 28]. In the Debye model [22], a spherical molecule having an electric dipole moment is immersed in fluid with shear viscosity η and the orientation of the dipole moment is changed by the applied electric field with relaxation time τ_D . In this case, τ_D is given by

$$\tau_D = \frac{4\pi\eta a^3}{k_B T} \quad (10)$$

where a is the radius of the molecule and k_B is the Boltzmann constant. Then the effective volume per molecule, $V_{eff} = (4\pi/3)a^3$, is expressed as $\tau_D k_B T / 3\eta$. In figure 8 V_{eff} at various temperatures is plotted as a function of density [13]. At relatively high densities V_{eff} does not change so much with density, which is compatible with the proportionality of τ_D to η/T at 1 atm. However, when the density is lowered, V_{eff} rises abruptly and approaches the molecular volume $V_m = m/d$. It should be noted that all the data points in a very wide temperature range fall on a single curve. This means that $\tau_D k_B T / 3\eta$ is approximately scaled by the density, though the Debye model has no longer its original meaning in the gaseous state.

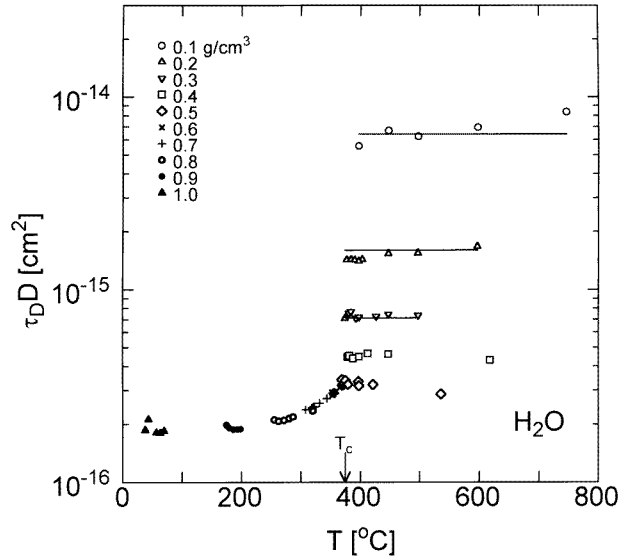


Figure 9. The product of the dielectric relaxation time and self-diffusion constant is plotted at various densities as a function of temperature. The solid lines denote $0.006/(n\pi r_{eff}^2)^2$ for 0.1, 0.2 and 0.3 g cm^{-3} .

The self-diffusion coefficient D_0 of dilute gas consisting of spherical molecules having the radius r_{eff} is described as [21],

$$D_0 = \frac{2}{3} \frac{1}{n\pi r_{eff}^2} \sqrt{\frac{k_B T}{\pi m}}. \quad (11)$$

Lamb *et al* [29] measured the self-diffusion coefficient D_{H_2O} in compressed vapour and expressed it as $D_{H_2O} = gD_0$, where the factor g is inversely proportional to a collision integral and is independent of temperature and density. Then it is expected that the product $\tau_D D_{H_2O}$ is nearly proportional to $1/d^2$ and independent of T at low densities. In figure 9 $\tau_D D_{H_2O}$ are shown at various densities as a function of temperature. In the gaseous state $\tau_D D_{H_2O}$ is nearly temperature independent and scaled with the square of density. The solid lines denote $0.006/(n\pi r_{eff}^2)^2$ for 0.1, 0.2 and 0.3 g cm^{-3} . In the liquid state, on the other hand, the product $\tau_D D_{H_2O}$ is nearly independent of both temperature and pressure at densities above 0.8 g cm^{-3} . Quasi-elastic neutron scattering experiments [30] suggest that the jump diffusion takes place in low temperature water, which is consistent with the suggested enhancement of τ_B .

6. Summary

We have developed a new microwave spectroscopy technique in the frequency range up to 40 GHz that can be applied to measure the dielectric relaxation in various fluids at high temperatures and pressures. By utilizing this technique we have measured the dielectric relaxation time for supercritical water and heavy water. The dielectric relaxation time τ_D decreases rapidly with increasing temperature and jumps to a large value on the liquid–gas transition for both liquid H_2O and D_2O . The relaxation time of D_2O is longer than that of

H₂O in the liquid state, while the difference becomes smaller with decreasing density in the gaseous state. Based upon the observation that the dielectric relaxation time increases with decreasing density in the gaseous state, we have proposed that the dielectric relaxation in the dilute limit is governed by the binary collision of molecules. We have extended the dielectric relaxation mechanism to the liquid state by taking into account the contribution of bound molecules that are incorporated in the hydrogen-bond network. The comparison between τ_D and η/T shows that $\tau_D k_B T / 3\eta$ is approximately scaled by density, and the comparison between τ_D and D shows that $\tau_D D_{H_2O}$ is nearly proportional to $1/d^2$ in the gaseous state and rather insensitive to both temperature and density in the liquid state. It should be emphasized that studies under extreme conditions promote a better understanding of the properties under ambient conditions in the case of water.

Acknowledgments

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