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Studies of Liquid Water by Computer Simulations. III. Dynamical Properties of a 2-D Model

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Molecular dynamics simulations of a water-like system are performed at many temperatures and densities. A 2-dimensional model of water is used for the system with 144 molecules in a square cell. The calculated self-diffusion coeffcient and the dipole direction relaxation time are in good agreement with the observed values in a wide temperature-pressure plane. Cross correlation function of displacement and local orientational order parameter are computed by the time-averaged configurations, where the average of period is several times longer than the velocity correlation time. The cross correlation is observed even in the third neighbor pairs, which proves the existence of hydrogen-bonded local structure. The lifetime of this local structure is about 2×10 ps at low temperatures and low density, where density maximum is known. The lifetime of the unstable species with a rather high energy is found to be about 0.5—2 ps at low temperatures and low density.

In the first paper of this series,[1] it was shown that a simple 2-D model of water can reproduce main features of the thermodynamical behavior observed in real water over a wide region of the liquid state. In the present article, we shall study dynamical properties of 2-D water by molecular dynamics (MD) simulations.

By MD method, Rahman and Stillinger and others[2] studied static and dynamic properties of liquid water. However, a systematic study is not yet performed on the density dependence of the dynamical properties of liquid water. For this reason, we are going to perform MD simulations at many temperatures and densities. The dipole direction relaxation time and the self-diffusion coefficient will be calculated as a function of temperature and density. The effects of compression on these quantities which are in good agreement with experimental data[3,4] will be discussed. The present paper also deals with the lifetime of the local structure in liquid water which is not examined so far. Because water molecules perform oscillatory motion within the framework of hydrogen-bonded local structure, the configuration is averaged over a period longer than the correlation time of velocity. The lifetime of the local structure will be calculated by two methods, the cross correlation function of displacement and the local orientational order parameter. The dynamics of the unstable molecule which is not well bound in the hydrogen-bonded cluster will be also studied. The concentration of the unstable species will be obtained as a function of temperature and pressure and will be compared with the results of the two-state model analysis of real water.[5]

Molecular Dynamics Method

Classical mechanics describes the time evolution of our 2-D water system. The Hamiltonian H for N rigid rotor molecules consists of kinetic energy for translational and rotational motions, plus interaction potential energy.

$$H = \frac{1}{2}\sum_{i=1}^{N}(mv_i^2+I\dot{\varphi}^2) + \sum_{(ij)} U(\boldsymbol{R}_{ij}, \varphi_i, \varphi_j). \tag{1}$$

The linear and angular velocities are denoted by v and $\dot{\varphi}$.

The pair potential U consists of a Lennard-Jones potential and an anisotropic potential U_{anis} multiplied by a switching function S:

$$U(\boldsymbol{R}_{12}, \varphi_1, \varphi_2) = 4\varepsilon\left[\left(\frac{\sigma}{R_{12}}\right)^{12} - \left(\frac{\sigma}{R_{12}}\right)^{6}\right] + S(R_{12}; R_1, \mathrm{R}_2, R_3)\, U_{\mathrm{anis}}(\boldsymbol{R}_{12}, \varphi_1, \varphi_2), \tag{2}$$

where R_{12} denotes the distance between two molecules 1 and 2 and φ_1 and φ_2 the orientations of the respective molecules. The switching function S cuts down the anisotropic potential for $R_{12}<R_1$ and for $R_{12}>R_3$. The details are shown in Ref. 1.

The mass of the molecule m is 18 in units of atomic weight and the moment of inertia I is $3.34\times10^{-46}\,\mathrm{g\,m^2}$. For simplicity, the center of mass is assumed to be the center of the molecule (see Fig. 2 of Ref. 1).

We shall use the following reduced units.[1] The energy E is measured in units of $\varepsilon_0=24.68\,\mathrm{kJ/mol}$, ($-\varepsilon_0$ is the absolute minimum of the pair potential energy, *i.e.* ε_0 is the hydrogen bond energy), the length in units of $R_0=27.6$ nm and area per molecule A in units of R_0^2. Pressure P is measured in units of ε_0/R_0^2. (If we replace R_0^2 by R_0^3, new reduced units can be applied to the three-dimensional real water. Such reductions of units are of course only a convention, and therefore one should be satisfied with semiquantitative comparisons between the 2 D model and real water). Temperature T is measured in units of ε_0/R, where R is the gas constant which is not shown explicitly hereafter. As for the time units we use three kinds of units:

1) **Time unit for rotation**

$$t_0^{\mathrm{ROT}} = (I/\varepsilon_0)^{1/2} = 2.86 \times 10^{-14}\,\mathrm{s},$$

2) **Time unit for translation** (3)

$$t_0^{\mathrm{TR}} = (mR_0^2/\varepsilon_0)^{1/2} = 2.37 \times 10^{-13}\,\mathrm{s},$$

3) **and real time scale s.**

Our system consists of 144 molecules in a square unit cell with periodic boundary condition. The coupled dynamical equations are numerically integrated[6] with time increment

$$\Delta t = 0.870 \times 10^{-15}\,\mathrm{s} = 0.304\, t_0^{\mathrm{ROT}}. \tag{4}$$

The total energy is conserved within 0.01% after 24000 steps, or 21 ps. At low temperatures and low density, a long run (30000 steps or 78ps) with time increment

2.6×10^{-15} s is performed to obtain the long (20 ps) lifetime of the local structure.

At a given density the 144 molecules are placed initially within the periodic cell at random positions, with random orientations, and with no translational or rotational velocities. After some steps, the kinetic energies are reduced to decrease the temperature. This reduction was repeatedly performed to obtain several low temperature samples. In our standard run, 3000 steps are spent for the aging of the system. After this interval, the subsequent period of 30000 steps, or 26 ps is the period over which the molecular dynamics' statistical averages are calculated. Simulations are performed at about 90 state points. The static properties (energy, pressure, radial distribution function and others) thus calculated are in good agreement with the results of our Monte Carlo simulations.[1]

Kinetic Properties

A couple of dynamical quantities are calculated in a way similar to Rahman and Stillinger's method.[2] As these results are only the 2-D version of their results, in the first place only a part of these will be shown briefly in the low density region (area per molecule $A=0.957$ R_0^2), where thermodynamic quantities of 2-D water show interesting aspects like real liquid water under normal pressure. After that, the dipole direction relaxation time and the self-diffusion coefficient will be discussed.

The velocity autocorrelation function at temperature $T=0.18\ \varepsilon_0$, area per molecule $A=0.957\ R_0^2$ crosses the horizontal axis at 0.05 ps and shows several oscillations. The Fourier spectrum has a peak at 3×10^{13} s^{-1} with half-full-width 6×10^{13} s^{-1}. The angular velocity correlation function crosses the horizontal axis at 0.02 ps. The Fourier spectrum has a peak at 9×10^{13} s^{-1}, with half-full-width 6×10^{13} s^{-1}. These frequencies correspond to the observed ν_L and ν_T.[7] These functions show clearly that there exists an oscillatory motion of water molecules at low temperatures.

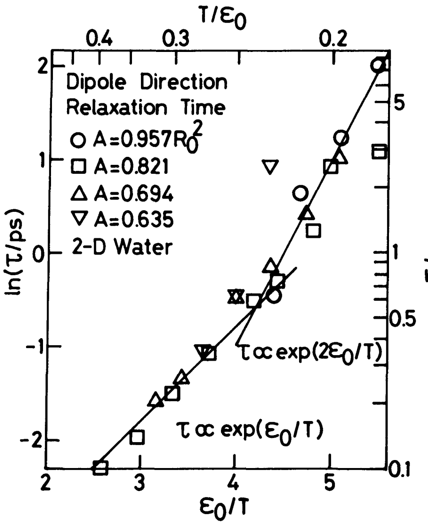

Fig. 1. The dipole direction relaxation time τ is plotted against the inverse of temperature $1/T$ at four densities.

The molecular dipole direction relaxation time τ is shown in Fig. 1 at four densities. This time constant at low densities and low temperatures has the comparable value to the measured dielectric relaxation time.[3,7] The relaxation time in the case where $A=0.821\ R_0^2$ is shorter than that in the case of low density ($A=0.957\ R_0^2$) at low temperatures $T\lesssim0.24\ \varepsilon_0$. This effect of compression is compared with the experiments on the dielectric relaxation under high pressure,[3] qualitatively. Figure 1 also shows that the temperature dependence of the dipole direction relaxation time τ is roughly written as $\tau\propto\exp(2\ \varepsilon_0/T)$ at low temperatures ($T\lesssim0.24\ \varepsilon_0$) and as $\tau\propto\exp(\varepsilon_0/T)$ at high temperatures ($T\gtrsim0.24\ \varepsilon_0$), where ε_0 is the hydrogen bond energy. The temperature dependence at low temperatures seems too steep, compared with the observed results on real water.[7]

The self-diffusion coefficient D is calculated from the mean-square displacement. In Fig. 2, D is shown as a function of T and P. The region between two dashed lines corresponds to liquid state. At low temperature ($T=0.18\varepsilon_0$), D is almost constant in spite of compression, thus D shows anomalous behavior similar to the observed one.[4] Figure 3 shows that the temperature dependence of D at constant density is well approximated to be $D\propto\exp(-\varepsilon_0/T)$. This depend-

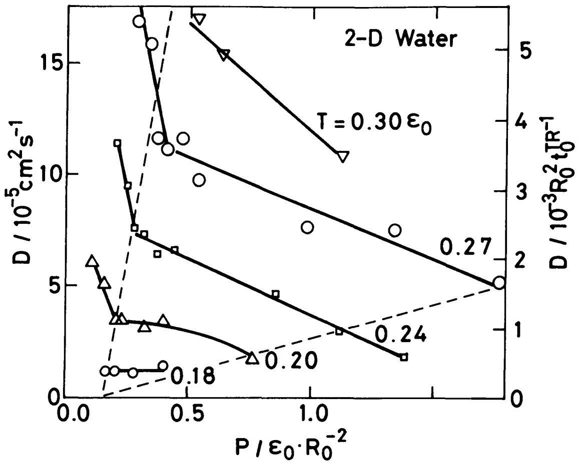

Fig 2. The self-diffusion coefficient D *vs.* pressure P plots are shown. Values of the temperature are indicated next to each curve. The region between two dashed lines corresponds to the liquid state.

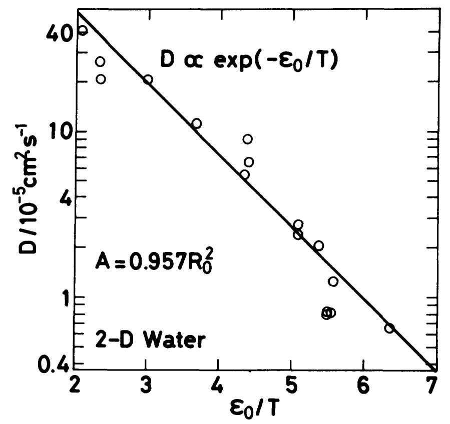

Fig. 3. Plot of D *vs.* $1/T$ at $A=0.957\ R_0^2$.

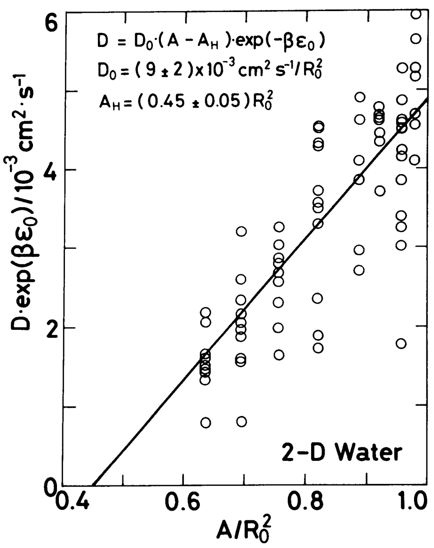

Fig. 4. Plot of $D\ \exp(\varepsilon_0/T)$ *vs.* area per molecule A.

ence is comparable with experimental results on real water.[7] The density dependence is shown in Fig. 4. From Figs. 3 and 4 the temperature-density dependence of D is summarized as follows;

$$\begin{aligned} D &= D_0\,(A-A_{\mathrm{H}})\exp\,(-\varepsilon_0/T), \\ D_0 &= (9\pm2)\times10^{-3}\,\mathrm{cm^2\,s^{-1}}\,R_0^{-2}, \\ A_{\mathrm{H}} &= (0.45\pm0.05)\,R_0^2, \end{aligned} \tag{5}$$

although there are some deviations especially at low temperatures. It is worthwhile to notice that the value of constant A_{H} is close to the area of the high density ice (0.50 R_0^2) and A-A_{H} means the area of hole in liquid water.

Thus it has been shown that the MD simulation of 2-D model can reproduce the main anomalous dynamical behavior of liquid water. On the basis of these results, the lifetime of the hydrogen-bonded cluster will be obtained in the next section.

Lifetime of Hydrogen-bonded Local Structure

Time Averaged Configuration. An oscillatory motion of water molecule is seen at low temperatures and densities as shown in the preceding section. Therefore, we use the time averaged configuration in this section in order to obtain the lifetime of hydrogen bonded local structure. The configuration is averaged over a period of 0.13 ps. This means that we study the vibrationally averaged structure (V-structure) of liquid water as discussed by Eisenberg and Kauzmann.[7,8]

Cross Correlation of Displacement. In the V-structure it is expected that the molecules in the same hydrogen-bonded cluster move to nearly the same direction on average. On the basis of this idea, we are going to calculate the cross correlation of displacement.

The position r_i of molecule i at time $t=0$ is denoted as r_i^0, and the displacement of molecule i is $r_i-r_i^0$. Figure 5 shows the cross correlation of displacement of molecule i and j $<(r_i-r_i^0)\cdot(r_j-r_j^0)>$ at low temperatures and low density with the following condition at $t=0$. As the low density ice type network of hydrogen bond is the square lattice in our model,[1] the molecular distance R_{ij} at $t=0$ is classified as follows;

$$\begin{aligned} &0.85\,R_0 < R_{ij} < 1.23\,R_0 \quad (\textit{i.e.}\ R_{ij}-R_0), \\ &1.23\,R_0 < R_{ij} < 1.71\,R_0 \quad (\textit{i.e.}\ R_{ij}-2^{1/2}R_0), \\ &1.71\,R_0 < R_{ij} < 2.41\,R_0 \quad (\textit{i.e.}\ R_{ij}-2R_0), \\ \text{or}\ &2.41\,R_0 < R_{ij} < 2.91\,R_0 \quad (\textit{i.e.}\ R_{ij}-2^{3/2}R_0). \end{aligned} \tag{6}$$

It should be noticed that the linear part of cross correlation function ($R_{ij}-R_0$ at $t=0$) extends up to 2× 10 ps. The value of tangent of this linear part is as large as about 30% of that in the

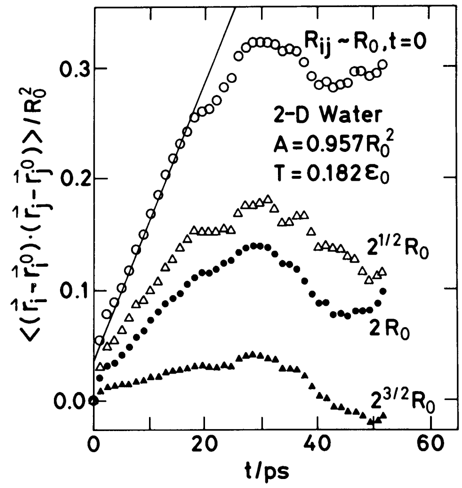

Fig. 5. The cross correlation functions $<(r_i-r_i^0)\cdot(r_j-r_j^0)>$. The initial conditions in the statistics are indicated in the figure.

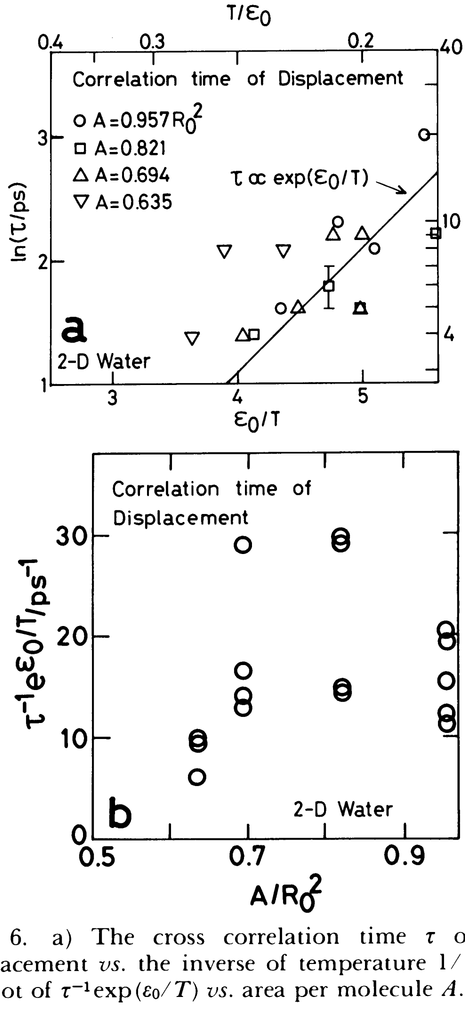

Fig. 6. a) The cross correlation time τ of displacement *vs.* the inverse of temperature $1/T$. b) Plot of $\tau^{-1}\exp(\varepsilon_0/T)$ *vs.* area per molecule A.

case of $i=j$. Thus this figure shows that molecules i and j with R_{ij}—R_0 at $t=0$ move collectively in a period of about 2×10 ps to nearly the same direction.

One can see cross correlation of the displacement in the cases of R_{ij}—$2^{1/2}R_0$ and $2R_0$ which is negligible in the case of more distant pair R_{ij}—$2^{3/2}R_0$. In other words cross correlation of displacement is seen even in the third neighbor pair. Figure 6 shows the temperature and density dependence of the cross correlation time τ of displacement. In Fig. 6(a), we see that the cross correlation time τ depends on temperature T as $\tau \propto \exp(\varepsilon_0/T)$ on average, where ε_0 is the energy of hydrogen bond. This temperature dependence seems reasonable (*cf.* Fig. 3). For this reason, a quantity $\tau^{-1}\exp(\varepsilon_0/T)$ is plotted against the area per molecule A in Fig. 6(b) in order to obtain the density dependence of τ. This figure shows that the cross correlation time τ at first becomes shorter due to compression from the normal density, then it becomes longer if 2-D water is compressed to the density close to that of high density ice.[1)]

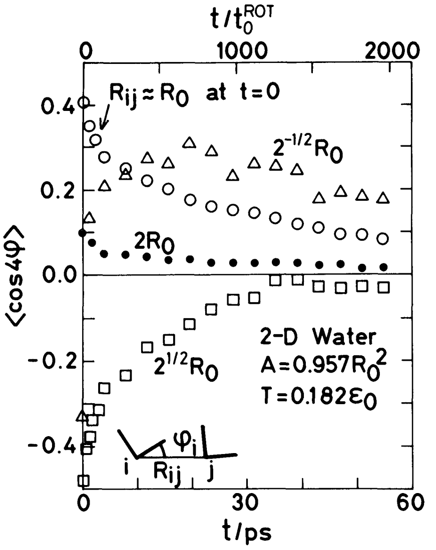

Fig. 7. Plot of $\langle\cos 4\varphi\rangle$ *vs.* time t. The initial conditions in the statistics are indicated in the figure.

Local Orientational Order Parameter. We performed many calculations to confirm the above lifetime by other methods. One of them will be shown in this section. The rotational motion, too, will be studied here.

At low temperatures water molecule has local orientational order due to the hydrogen bond. The angle φ_i is the orientation of the molecule i measured from the vector $\boldsymbol{R}_{ij}$ (see Fig. 2 in Ref. 1). The average $\langle\cos 4\varphi\rangle$ is used to examine the local orientational order, as shown in Fig. 7. In the case of low density ice at 0K (Fig. 5 in Ref. 1), this order parameter has the following values:

$$\langle\cos 4\varphi\rangle = 1, \qquad R_{ij} = R_0,\ 2R_0,$$
$$\langle\cos 4\varphi\rangle = -1, \qquad R_{ij} = 2^{1/2}R_0. \qquad (7)$$

One can see the local orientational order in the first neighbor (R_{ij}—R_0) and the second neighbor pair (R_{ij}—$2^{1/2}R_0$). The half-life period of $\langle\cos 4\varphi\rangle$ (orientational relaxation time) is 15 ps in the case of R_{ij}—R_0. This value is in good agreement with that of the cross correlation time of displacement.

The density dependence of orientational relaxation time is shown in Fig. 8. Figure 8(a) shows that the temperature dependence of the orientational relaxation time τ is written as $\tau \propto \exp(2\varepsilon_0/T)$ at low temperatures ($T \lesssim 0.24\varepsilon_0$) (*cf.* Fig. 1). As for the density dependence, the cross correlation time of displacement and the relaxation time of $\langle\cos 4\varphi\rangle$ has a similar behavior as that shown in Figs. 6(b) and 8(b). Figures 1, 6, and 8 indicate that the initial effect of pressure increase (at low temperatures and low pressure) leads to increased fluidity, known to be true in the case of real water.[3,4)]

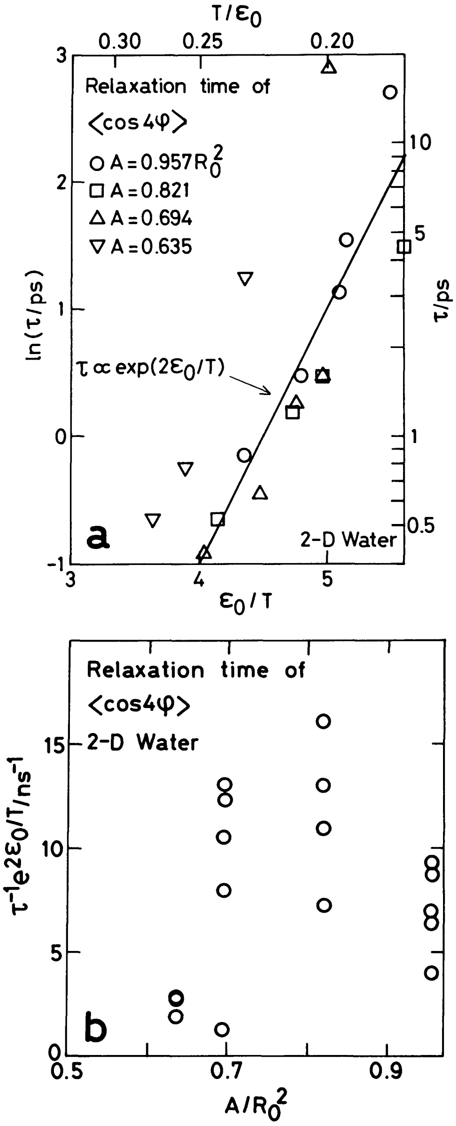

Fig. 8. a) The orientational relaxation time τ of $\langle\cos 4\varphi\rangle$ *vs.* the inverse of temperature $1/T$. b) Plot of $\tau^{-1}\exp(2\varepsilon_0/T)$ *vs.* area per molecule A.

Dynamics of Unstable Species

In the preceding section it was described that molecules with the oscillatory motion are stable and are located in the hydrogen-bonded cluster. This section is devoted to the dynamics of the unstable species. On the contrary to the preceding section, the time averaged configuration is not used here.

The binding energy (BE) is defined as follows:

$$\mathrm{BE}_i = \frac{1}{2}\sum_j U_{ij} \qquad (8)$$

In liquid water the distribution of BE is as wide as shown in Fig. 9 in Ref. 1.[9)] The BE of the molecule with one hydrogen bond is about 0.5 ε_0. The molecule with more than one hydrogen bond may be called stable species. Thus, we call this molecule unstable species if the following condition is fulfilled:

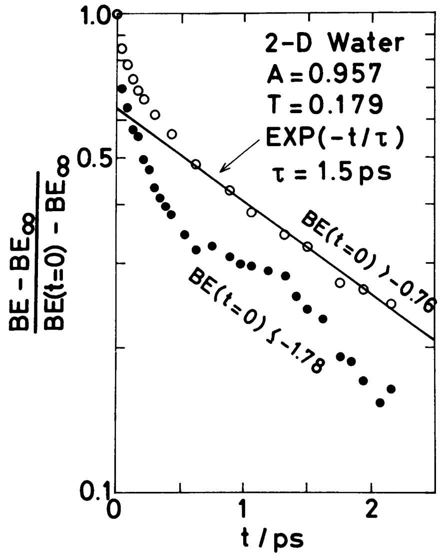

Fig. 9. The relaxation of the binding energy.

$$\mathrm{BE} > -0.76\,\varepsilon_0. \tag{9}$$

The relaxation of BE for unstable species is shown in Fig. 9. Here, the molecules are classified according to Eq. (9), where BE is taken to be the value at $t=0$. The deviation of BE from its equilibrium value relaxes to 0.5 times the deviation at initial condition at about $t=0.5$ ps (short term) and then decays as a function exp(-t/τ), $\tau=1.5$ ps (long term) ($A=0.957$ R_0^2, $T=0.179$ ε_0). The long term of relaxation time of BE is shown as a function of temperature and density in Fig. 10. It can be seen that this relaxation time τ does not depend strongly on density and that its temperature dependence is written as $\tau \propto \exp(\varepsilon_0/T)$.

The velocity autocorrelation functions

$$f^{TR}(t) = \frac{\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(\mathrm{o})\rangle}{\langle \boldsymbol{v}(\mathrm{o})\cdot\boldsymbol{v}(\mathrm{o})\rangle}, \tag{10}$$

of both species are shown in Fig. 11. Dynamical properties are different in two species. The behavior of $f^{TR}(t)$ for the unstable species is very similar to that of liquid Ar.[10] The unstable species has a larger self-diffusion coefficient than the stable one.

The concentration x of the unstable species is shown as a function of T and P in Fig. 12. This figure is similar to the results of the mixture model by Konda and Yamamoto.[5]

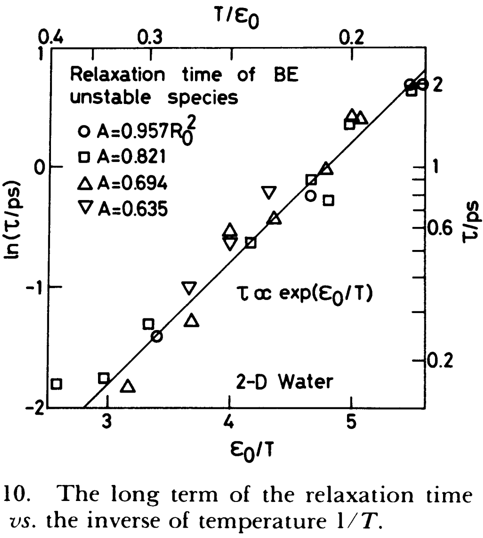

Fig. 10. The long term of the relaxation time τ of BE *vs.* the inverse of temperature $1/T$.

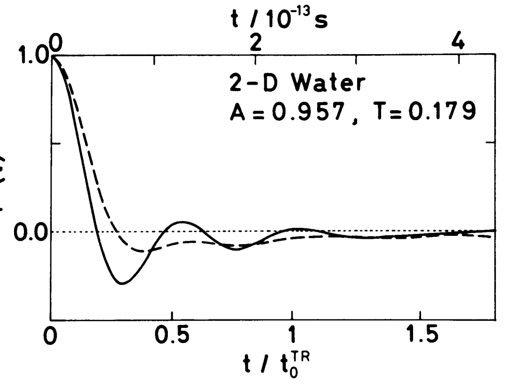

Fig. 11. The velocity autocorrelation functions. The dashed curve corresponds to the unstable species and the solid one corresponds to the stable species.

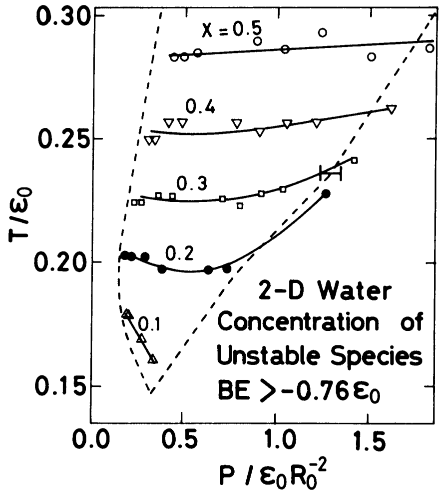

Fig. 12. The concentration of the unstable species is shown in P–T plane.

In this section, the relaxation of BE is calculated and it turned out that the short term of relaxation is about 0.5 ps and the long term one, about 1.5 ps. Therefore, classification like Eq. (9) is meaningfull in observations where the time scale in not longer than several ps. Such classification may be usefull in understanding of the anomalous behavior of liquid water, like the simple two-state model.

Concluding Remarks

The vibrationally-averaged structure (V-structure) of liquid water was discussed by Eisenberg and Kauzmann.[7,8] In the present article the size and lifetime of the vibrationally-averaged local structure in 2-D water are obtained to be about 13 molecules (as far as third neighbors) and about 2×10 ps by observing time scale of 0.13 ps at low temperatures and low density, where the density maximum is known.

The oscillatory motion of water molecule has a time constant of about 0.02—0.05 ps. The relaxation time of dipolemoment of the water molecule is about 5 ps. The binding energy relaxes with decay constants of about 0.5—1.5 ps.

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