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# A Molecular Dynamical Study of the Mutual Diffusion Coefficient and Cooperative Motion in a 2-Dimensional Aqueous Solution

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Constant-temperature constant-pressure molecular dynamics simulations of a two-dimensional aqueous solution-like system are performed at many temperatures under a constant pressure. The total number of molecules in the system is 576, and the mole fraction of the solute is 0.5. The mutual diffusion coefficient, the kinetic diffusion coefficient, and the velocity correlation between different molecules are thus obtained. The reduced kinetic diffusion coefficient has a maximum at an intermediate temperature under a constant pressure. This feature is consistent with the temperature dependence of the mean-square-concentration fluctuations. The lifetime of the local structure is estimated from the cross-correlation function of displacement, which is computed from the time-averaged configurations, where the average period is several times longer than the velocity-autocorrelation time. The correlation length of the local concentration fluctuations is obtained and compared with the snapshots of the configurations at several temperatures. The dynamical properties are qualitatively in agreement with those of an alcohol-water mixture.

Local fluctuations of concentration afford information which is useful for understanding the mixing of liquids from a molecular point of view.[1] In order to discuss the state of mixing from a dynamical standpoint, the lifetime of local structures should be taken into account.[1] For these reasons, quasi-elastic light scattering, NMR, and Rayleigh–Brillouin scattering experiments are performed in order to determine the mean-square-concentration fluctuations, the mutual diffusion coefficients, and the correlation length.[1–25] In such studies, solutions with a lower critical solution temperature are often examined because many thermodynamical quantities of such solutions show a prominent temperature- and concentration-dependence. Binary mixtures of an alcohol and water are typical examples. For the present, it is difficult to simulale such systems with a sufficient number of molecules by either the Monte Carlo or molecular dynamics (MD) method using realistic models at many temperatures and concentrations for a systematic study, although some works have been published reporting on work at a few temperatures and concentrations.[26–29]

In a previous paper,[30] a Monte Carlo study of a 2-dimensional (2-D) aqueous solution-like system was carried out by making use of the 2-D water-like model.[31] This solution model was designed to simulate binary mixtures of an alcohol and water. This is suitable for the systematic Monte Carlo calculation and molecular dynamics of solutions. The mean-square-concentration fluctuation was calculated as a function of the temperature, the density and the concentration. The mean-square-concentration fluctuation has a maximum at an intermediate temperature. This feature is similar to those of solutions with upper and lower critical solution temperatures.[30] The concentration dependence of the thermodynamic properties at low temperatures is qualitatively in agreement with that of an alcohol–water mixture.[30] We perform molecular dynamical calculations on the same model in this work.

The purpose of the present study is to see dynamical properties of a system where the concentration fluctuates to a considerable extent and to obtain the mutual diffusion coefficient, the velocity correlation between different molecules, and the lifetime of the local structure.

We adopt the 2-dimensional (2-D) aqueous solution-like model.[30] The solvent is a 2-D water-like model, which reproduces the well-known anomalous behavior of liquid water.[31,32] The water-solute interaction is anisotropic. The solute–solute interaction is assumed to be of the Lennard–Jones type for the sake of simplicity.

The merits of low dimensions are as follows. (i) We can save computing time and memory size. This point is important because we are going to perform many simulations at various temperatures. (ii) The linear dimension of the basic cell in the simulation is larger than that of a three-dimensional cell (3-D) ($576=24^2\simeq 8.3^3$) provided that the total number of molecules is fixed. Thus, the effect of the periodic boundary condition would be smaller in the case of 2-D than that in the 3-D calculation with the same number of molecules. Despite theoretical predictions that transport coefficients in a 2-D system will diverge, a computer simulation of a small system can be used to study the transport properties.[33] The shortcoming of our simulation on a 2-D solution is that there are no experimental results on any 2-D aqueous-like solution and that our results must, therefore, be qualitatively compared with experimental results; we shall use reduced units.[31]

The constant-temperature and constant-pressure MD(T-P-MD) method is used, because this method is more convenient for obtaining the temperature dependence of the system. By T-P-MD, the mutual diffusion coefficient $D$[35,36] is calculated for the system with 576 molecules in a square cell. As the mean-square-concentration fluctuation of the system has a maximum around $x_s=0.5$ ($x_s$ is the mole fraction of the solute),[30] the mole fraction of the solute is 0.5 in this work. The kinetic diffusion coefficient, $L$, is derived from the mutual diffusion coefficient $D$ and the mean-square-concentration fluctuation. We want here to discuss the temperaure dependence of the kinetic diffusion coefficient $L$. The kinetic diffusion coefficient $L$ includes the $L_0$ term, which equals $L$ when the velocity correlation between different molecules can be neglected. As this term $L_0$ also depends on the temperature, the temperature dependence of $L$ will be discussed by means of the reduced quantities $L/L_0$. Its temperature dependence will be qualitatively compared with that in an alcohol–water mixture.[21]

In order to estimate the lifetime of the local structure, the cross-correlation function of translation will be studied using the time-averaged positions of molecules, where the average period is several times longer than the velocity-autocorrelation time.[32] From the analysis of the cross-correlation of translation, the size of the "moving unit" will also be estimated; the "moving unit" is a group of molecules which move together for a time much longer than the velocity-autocorrelation time.[1] This size will be compared with the static correlation lenght of the local-concentration fluctuations. It will be shown that these are consistent with the snapshots of the configurations at several temperatures.

## Molecular Dynamics Method

The 2-D model of an aqueous solution-like system was described in the previous paper.[30] The constant-temperature constant-pressure MD method was shown in another paper.[32] Therefore, the model and the MD method will be described only briefly here.

The pair potential $U_{AB}$ between molecules A and B is given as follows (the suffixes A and B will be used to express water or a solute, unless otherwise stated):

$$U_{WW} = U_{LJ}^{WW}(R_{WW}) + U_{ANISO}^{WW}(R_{WW}, \varphi_{W1}, \varphi_{W2}), \tag{1}$$

$$U_{WS} = U_{LJ}^{WS}(R_{WS}) + U_{ANISO}^{WS}(R_{WS}, \varphi_{W}, \varphi_{S}), \tag{2}$$

$$U_{SS} = U_{LJ}^{SS}(R_{SS}). \tag{3}$$

Here, $U_{WW}$ is the water–water interaction energy,[31] $R_{AB}$ denotes the distance between two molecules A and B, and $\varphi_A$ and $\varphi_B$, the orientation of the respective molecules, as is shown in Fig. 1 in Ref. 30. The first terms in Eqs. 1—3 $U_{LJ}^{AB}(R_{AB})$ are the Lennard–Jones potential functions. The parameter of these functions and the anisotropic interaction between water and a solute $U_{ANISO}^{WS}$ are given in Ref. 30.

The mass $M_A$ and the moment of inertia $I_A$ of the A molecule are assumed as follows for the sake of simplicity:

$$M_W = M_S = 18 \text{ (in units of atomic weight)} \tag{4}$$

$$I_W = I_S = 3.34 \times 10^{-44}\,\text{gm}^2. \tag{5}$$

We use the following reduced units.[31] The energy $E$ is measured in units of $\varepsilon_0 = 24.68$ kJ mol$^{-1}$, ($-\varepsilon_0$ is the absolute minimum of the pair potential energy $U_{WW}$); the temperature in units of $\varepsilon_0/k_B$ ($k_B$ is the Boltzmann constant,) and the length, in units of $R_0 = 0.276$ nm which is the hydrogen-bond length in $U_{WW}$. The pressure $P$ is measured in units of $\varepsilon_0/R_0^2$.

The T-P-MD simulations of the system mentioned above[30] are performed at many temperatures under a constant pressure ($P = 0.17\ \varepsilon_0/R_0^2$). This value of the pressure is a representative one in the 2-D aqueous solution.[30] The system consists of 576 molecules in a square unit cell with the periodic boundary condition. The mole fraction of the solute $x_S$ is 0.5 in this work, since a solution with this concentration is interesting because of the large mean-square-concentration fluctuation.[30] The dynamical equations are integrated with the time increment:

$$\Delta t = 0.435 \times 10^{-15}\,\text{s} \tag{6}$$

by the predictor-corrector method. In our standard run, 60000 steps are spent for the aging of the system. After this, the 60000-step run is performed twice a least; from these runs the statistical averages are obtained.

The constant-temperature MD mehod by Nosé[34] is used, combined with the constant-pressure MD method of Andersen.[37] Some things special to these methods has heen described elsewhere.[32]

## Mutual Diffusion Coefficient

In a binary liquid system there are three diffusion coefficients, viz. the two self diffusion coefficients and the mutual diffusion coefficient. The former are calculated from the mean-square displacement or from the velocity autocorrelation[35] in the MD simulation. The latter is interesting in solutions with local concentration fluctuations.[1] The mutual diffusion coefficient can be obtained from the mean-square displacement of the center of mass of all water molecules $\langle R_{WCM}(t)^2 \rangle$ as follows:[35]

$$D = \frac{Q}{4Nc_W c_S}\left[\left(\frac{M_W}{M_S}\right)c_W + c_S\right]^2 \lim_{t\to\infty} \frac{\partial}{\partial t}\langle R_{WCM}(t)^2\rangle, \tag{7}$$

where $c_A$ is the concentration (number density) of the species A, the velocity of the center of the mass of the system is fixed as 0, $N$ is the total number of molecules in the system and $M_A$ is the mass of the species A. The quantity $Q$ is often called the thermodynamic factor and is defined as:

$$Q = \frac{x_W x_S}{N\langle(\Delta x)^2\rangle}, \tag{8}$$

where $x_A$ is the mole fraction of the species A and where $\langle(\Delta x)^2\rangle$ is the mean-square-concentration fluctuation.[30] The mean-square-concentration fluc-

Table 1. Thermodynamic and Transport Properties of the 2-D Aqueous Solution Using Micro Canonical MD and Constant-Temperature Constant-Pressure MD

| | Micro canonical MD | | | T-P-MD | | |
|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Av. | Run 1 | Run 2 | Av. |
| $T/\varepsilon_0 k_B^{-1}$ | 0.230 | 0.231 | 0.230 | 0.229 | 0.229 | 0.229 |
| $P/\varepsilon_0 R_0^{-2}$ | 0.130 | 0.137 | 0.134 | 0.131 | 0.131 | 0.131 |
| $A/NR_0^2$ | 1.296 | 1.296 | 1.296 | 1.302 | 1.332 | 1.317 |
| $E/N\varepsilon_0$ | −0.605 | −0.608 | −0.606 | −0.601 | −0.592 | −0.596 |
| $N\langle(\Delta x)^2\rangle$ | 1.19 | 1.29 | 1.24 | 1.36 | 1.35 | 1.36 |
| $D_W/10^{-7}\,\mathrm{m^2\,s^{-1}}$ | 0.355 | 0.313 | 0.334 | 0.319 | 0.341 | 0.330 |
| $D_S/10^{-7}\,\mathrm{m^2\,s^{-1}}$ | 0.311 | 0.337 | 0.324 | 0.348 | 0.417 | 0.383 |
| $D/10^{-7}\,\mathrm{m^2\,s^{-1}}$ | 0.204 | 0.156 | 0.180 | 0.211 | 0.137 | 0.174 |

$T$ is the temperature, $P$ is the pressure, $A$ is the total area of the system, $E$ is the potential energy, $\langle(\Delta x)^2\rangle$ is the mean square concentration fluctuation, $D_W$ and $D_S$ are the self diffusion coefficients of the water and the solute, and $D$ is the mutual diffusion coefficient. The mole fraction of solute $x_S=0.5$, the total number of molecules in the system $N=576$.

tuation is calculated using the radial-distribution function.[30]

Although it has been proved that the sufficient averages of the static quantities are the same in micro canonical MD and in T-P-MD,[34,38] nothing is known about the mutual diffusion coefficient. For this reason, typical examples of calculations in the two methods are compared in Table 1. The results are not very different from each other for the micro canonical MD and T-P-MD.

As the mutual diffuion coefficient $D$ has the thermodynamic factor $Q$, the kinetic diffusion coefficient $L$ is more directly related to velocity correlation functions between different molecules:[39]

$$D = QL, \tag{9}$$

with:

$$L = L_0 + x_W x_S(D_{WW}+D_{SS}-2D_{WS}) \tag{10}$$

$$L_0 = x_S D_W + x_W D_S, \tag{11}$$

$$D_{AB} = \frac{N}{2}\int_0^\infty \langle \boldsymbol{v}_{Ai}(t)\cdot\boldsymbol{v}_{Bj}(0)\rangle \mathrm{d}t, \qquad (i \neq j) \tag{12}$$

where $v_{Ai}$ is the velocity of an $i$-th molecule of the species A. $D_A$ is the self-diffusion coefficient of the species A. By the use of Eq. 10, the trend of the cooperative translation in the binary mixture can be seen from the comparison of $L$ with $L_0$, because the second term in Eq. 10 comes from the velocity correlations between different molecules. At the same time, we would like to discuss the temperature dependence of $L$ by means of the reduced quantity $L/L_0$ since the first term $L_0$ in Eq. 10 also depends on the temperature. The temperature dependence of $L/L_0$ is shown in Fig. 1. The reduced kinetic diffusion coefficient $L/L_0$ has a maximum value around $T=0.24$ $\varepsilon_0/k_B$. The mean-square-concentration fluctuation also has a maximum value around the same temperaure (Fig. 7 in Ref. 30). The second point to be mentioned about Fig. 1 is that the value of $L/L_0$ is larger than 1.

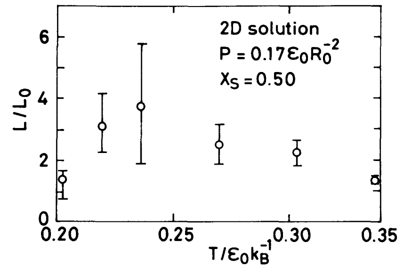

Fig. 1. Plot of the reduced kinetic diffusion coefficient $L/L_0$ vs. temperature $T$, at $P=0.17$ $\varepsilon_0/R_0^2$, $x_S=0.5$.

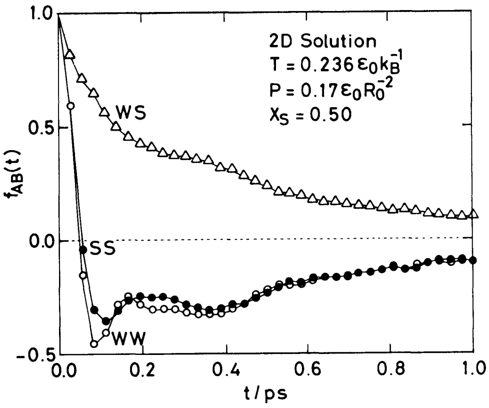

Fig. 2. The correlation function of velocity $f_{AB}(t)$ vs. time $t$. $T=0.236$ $\varepsilon_0/k_B$, $P=0.17$ $\varepsilon_0/R_0^2$, $x_S=0.5$.

The experimental values in a binary solution of $t$-butyl alcohol and water are as follows: $L/L_0=$ about 2 at 24 °C and about 5 at 63 °C.[21] The order of magnitude of $L/L_0$ shown in Fig. 1 is comparable to the experimental results.[21] The temperature dependence below about 0.24 $\varepsilon_0/k_B$ in Fig. 1 is qualitatively in agreement with such results.[21]

As the value of $L/L_0$ is larger than 1, the general tendency for the same species to move in the same direction is seen in this solution. In order to see this more directly, the correlation functions of velocities between the different molecules are shown in Fig. 2. The correlation functions of velocities $f_{AB}$ $(t)$ are defined as follows:

$$f_{AB}(t) = \frac{\langle \boldsymbol{v}_{Ai}(t)\cdot \boldsymbol{v}_{Bj}(0)\rangle}{\langle \boldsymbol{v}_{Ai}(0)\cdot \boldsymbol{v}_{Bj}(0)\rangle}, \qquad (i \neq j). \tag{13}$$

The normalization constants at temperature $T$=0.236 $\varepsilon_0/k_B$ are given below:

$$\left.\begin{aligned} \langle \boldsymbol{v}_{Wi}(0)\cdot \boldsymbol{v}_{Wj}(0)\rangle &= -0.7 \times 10^6\,\mathrm{m^2\,s^{-2}}, \\ \langle \boldsymbol{v}_{Wi}(0)\cdot \boldsymbol{v}_{Sj}(0)\rangle &= -0.8 \times 10^6\,\mathrm{m^2\,s^{-2}}, \\ \langle \boldsymbol{v}_{Si}(0)\cdot \boldsymbol{v}_{Sj}(0)\rangle &= -0.7 \times 10^6\,\mathrm{m^2\,s^{-2}}. \end{aligned}\right\} \tag{14}$$

From Eqs. 12—14 and Fig. 2 it may be seen that $D_{WW}$ and $D_{SS}$ are positive, while $D_{WS}$ is negative. The tendency mentioned above for the same species generally to move in the same direction may be seen again in Fig. 2.

There are two time constants in the correlation functions in Fig. 2. They are 0.05 ps and 1 ps. As these time constants are derived from all the pairs in the system they are not adequate for an examination of the lifetime of the local structure. For this reason, the lifetime will be studied in a different way in the next section.

## Lifetime of the Local Structure

In this section, we will estimate the lifetime of the local structure due to fluctuations in the concentration. An oscillatory motion of water molecules is seen at low temperatures and densities, as is shown in Ref. 32. Therefore, we use the time-averaged configuration in order to obtain the lifetime of the local structure.[32] The configuration is averaged over a period of 0.13 ps which is several times longer than the velocity autocorrelation time. We calculate the cross-correlation of displacement as in the case of the estimation of the lifetime of the hydrogen-bonded local structure in 2D water.[32] When the position $\boldsymbol{r}_i$ of $i$-th molecule at time $t$=0 is denoted as $\boldsymbol{r}_i^0$, the displacement of the molecule i is $\boldsymbol{r}_i-\boldsymbol{r}_i^0$. Figure 3 shows the cross-correlation of the displacement of the molecules i and j $\langle(\boldsymbol{r}_i-\boldsymbol{r}_i^0)\cdot(\boldsymbol{r}_j-\boldsymbol{r}_j^0)\rangle$ where the following conditions, with the molecular distance $R_{ij}$ set at $t$=0:

$$\left.\begin{aligned} 1.5R_0<R_{ij}(0)<2.5R_0 &\quad (\text{i.e. } R_{ij}(0)\text{—}2R_0), \\ 3.5R_0<R_{ij}(0)<4.5R_0 &\quad (\text{i.e. } R_{ij}(0)\text{—}4R_0), \\ 5.5R_0<R_{ij}(0)<6.5R_0 &\quad (\text{i.e. } R_{ij}(0)\text{—}6R_0). \end{aligned}\right\} \tag{15}$$

The linear part of the cross-correlation function extends up to 3×10 ps in the case of $R_{ij}(0)$—$2R_0$. The tangent of this linear part is about 25% as large as that in the case of $i$=$j$. Thus, this figure shows that the molecules i and j with $R_{ij}$—$2R_0$ at $t$=0 move collectively in nearly the same direction over a period of about 3×10 ps.

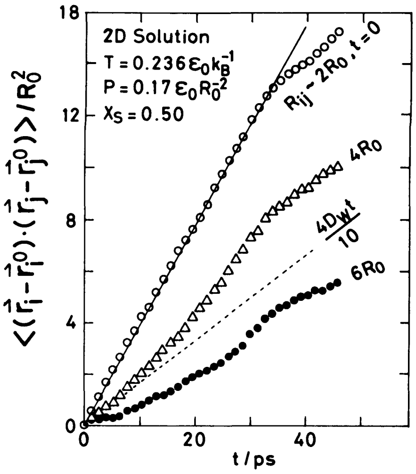

Fig. 3. The cross correlation function $\langle(\boldsymbol{r}_i-\boldsymbol{r}_i^0)\cdot(\boldsymbol{r}_j-\boldsymbol{r}_j^0)\rangle$ vs. time $t$. The initial conditions in statistics are indicated in the figure. $T$=0.236 $\varepsilon_0/k_B$, $P$=0.17 $\varepsilon_0/R_0^2$, $x_S$=0.5.

As the molecular distance at $t$=0 increases, the cross-correlation decreases, as is shown in Fig. 3. We tentatively use one-tenth of the correlation in the case of $i$=$j$ (the dotted line in Fig. 3) as the criterion to determine whether or not the cross-correlation is sufficiently large. By this criterion, we see that the correlation length of translation is about $4R_0$ in Fig. 3.

The cross-correlation time and the length of the solute–solute pair are about the same as those of the water–water pair at $T$=0.236 and 0.270 $\varepsilon_0/k_B$. At low temperatures, the length of the MD run was not enough to determine the correlation length. The temperature dependence of the cross-correlation time $\tau$ and length $\xi_{\mathrm{trans}}$ are as follows:

$$\left.\begin{aligned} \tau(T=0.202\,\varepsilon_0/k_B) &= 9 \times 10\,\text{ps}, \quad \text{run length}=131\,\text{ps}, \\ \tau(T=0.236\,\varepsilon_0/k_B) &= 3 \times 10\,\text{ps}, \quad \xi_{\mathrm{trans}}=4R_0, \\ &\qquad\qquad \text{run length}=131\,\text{ps}, \\ \tau(T=0.270\,\varepsilon_0/k_B) &= 4\,\text{ps}, \quad \xi_{\mathrm{trans}}=3R_0, \\ &\qquad\qquad \text{run length}=104\,\text{ps}, \end{aligned}\right\} \tag{16}$$

where the length of the MD run used in the analysis is also shown. The value of the correlation time at $T$=0.202 $\varepsilon_0/k_B$ listed above is only a tentative one, because the MD run was not long enough to determine such a long correlation time (9×10 ps).

## Correlation Length of Concentration Fluctuation

In the preceding section, the cross-correlation length of translation was estimated. Now we are going to obtain the static correlation length of the local fluctuation of concentration.

There are many definitions of the correlation length in a solution.[25] We define the following function using radial-distribution functions:

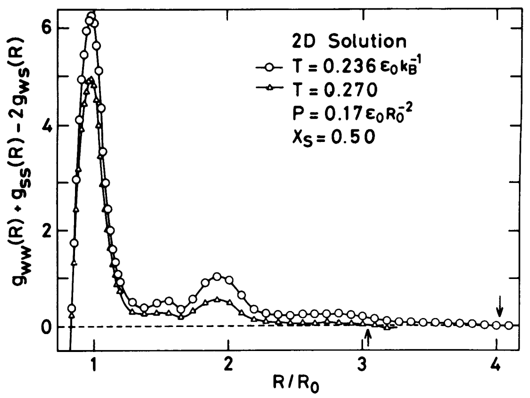

Fig. 4. The distribution function $\Delta g(R)$ defined in Eq. 17, at $T$=0.236 and 0.270 $\varepsilon_0/k_B$, $P$=0.17 $\varepsilon_0/R_0^2$, $x_S$=0.5.

$$\Delta g(R) = g_{WW}(R) + g_{SS}(R) - 2g_{WS}(R) \tag{17}$$

because the integration of this function with respect to the molecular distance $R$ is proportional to the excess mean-square fluctuation in the concentration (cf. Eqs. 2.12, 2.19 in Ref. 30):

$$N\langle(\Delta x)^2\rangle = x_W x_S + \frac{N}{\langle A\rangle}(x_W x_S)^2 \int_0^\infty \Delta g(R) \mathrm{d}^2 R, \tag{18}$$

where $A$ is the total area of the system.

This function $\Delta g(R)$ is plotted at $T$=0.236 and 0.270 $\varepsilon_0/k_B$ in Fig. 4. At the point shown by an arrow, the function is 0. As the function $\Delta g(R)$ is positive in the $0.8R_0<R<4R_0$ range at $T$=0.236 $\varepsilon_0/k_B$, we can see that, in this case, the same species have a tendency to gather in the region where the molecular distance is less than $4R_0$. This length $4R_0$ is identified with the static correlation length of the local-concentration fluctuation in this work. The correlation length at $T$=0.270 $\varepsilon_0/k_B$ is $3R_0$. It was difficult to estimate the correlation length at low temperatures by this method because the radial-distribution functions oscillate frequently with a large amplitude (cf. Fig. 18 in Ref. 30).

In order to confirm the correlation length mentioned above, typical configurations at several temperatures are shown in Fig. 5. Circles with a rectangular indication are water molecules; circles without a rectangular indication mean solutes. The stable pair with a pair energy larger than 0.55 $\varepsilon_0$ is connected by a straight line.

There are many water-rich regions and solute-rich regions at $T$=0.236 $\varepsilon_0/k_B$, and the characteristic radius of these regions is about $4R_0$. The radius of these regions at $T$=0.270 $\varepsilon_0/k_B$ is seen as about $3R_0$. These values are in agreement with the correlation length determined by $\Delta g(R)$. The radius of the water-rich region at a low temperature ($T$=0.202 $\varepsilon_0/k_B$) is read as 5±1 $R_0$ while that of the solute-rich region is about 3±1 $R_0$.

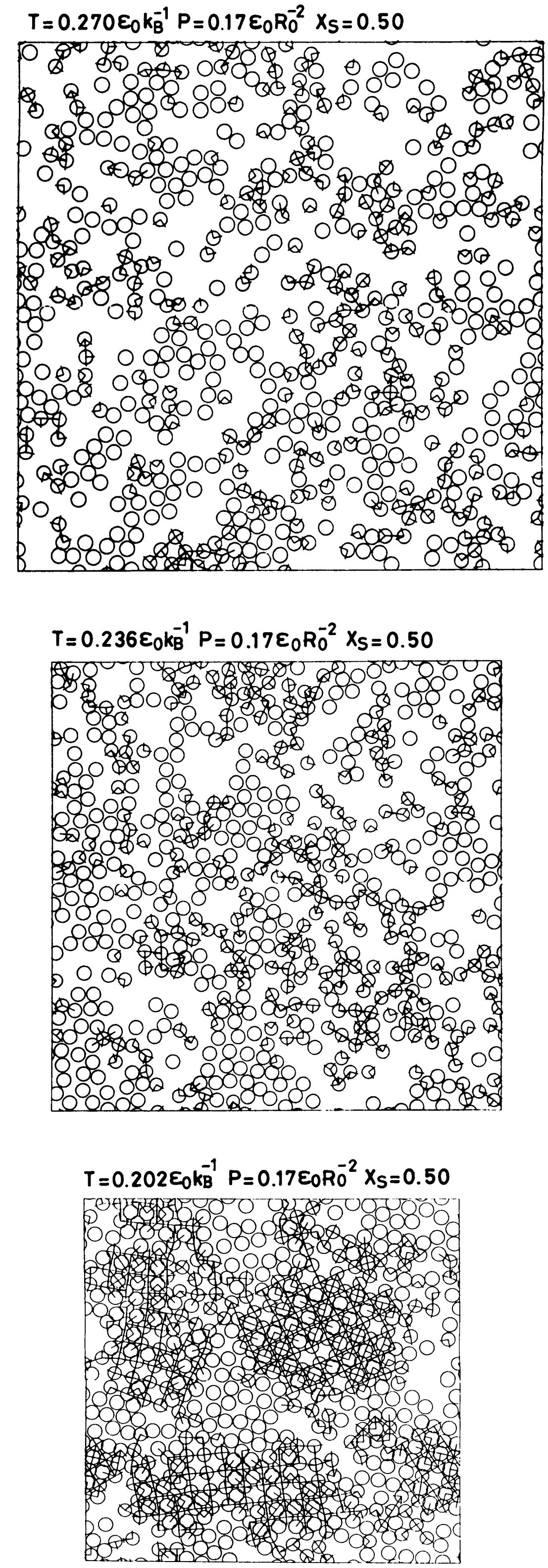

Fig. 5. Some examples of configurations. Circles with a rectangular indication are water molecules, where the diameter is the Lennard-Jones parameter $\sigma_{WW}$ (=0.212 nm). Circles without a rectangular indication mean solute and the diameter is $\sigma_{SS}$(=0.228 nm). The stable pair with bond energy larger than 0.55 $\varepsilon_0$ is connected by a straight line. $P$=0.17 $\varepsilon_0/R_0^2$, $x_S$=0.5.

Although the present model is too simple, let us compare the correlation length obtained with that in the real system, as we have no experimental results on any 2-D aqueous-like solution. The correlation length observed in a 2-butoxyethanol–water mixture at 23 °C is about 2 nm.[25] The order of magnitude of our correlation length ($5R_0 \simeq 1$ nm) is in agreement with such an experimental result.[25]

A few configurations are shown in Fig. 5 because it is easier to see some examples of configurations in a 2-D solution than in a 3-D solution. However, it should be noted that the configurations shown in Fig. 5 are special, as they depend on the model assumed. The present model has a tendency toward phase separation at an intermediate temperature (around $T=0.236\ \varepsilon_0/k_0$) This feature is seen by the temperature dependences of the mean-square-concentration fluctuation, the reduced kinetic diffusion coefficient, and the free energy.[30] The temperature dependence of the mean-square-concentration fluctuation is as follows:

$$\left.\begin{aligned} N\langle(\Delta x)^2\rangle &= 0.55 \pm 0.05, & T &= 0.202\ \varepsilon_0/k_\mathrm{B}, \\ N\langle(\Delta x)^2\rangle &= 1.3 \pm 0.3, & T &= 0.236\ \varepsilon_0/k_\mathrm{B}, \\ N\langle(\Delta x)^2\rangle &= 0.67 \pm 0.08, & T &= 0.270\ \varepsilon_0/k_\mathrm{B}, \end{aligned}\right\} \qquad (19)$$

where pressure $P=0.17\ \varepsilon_0/R_0^2$.

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### References

1) T. Kato, N. Ito, and T. Fujiyama *Bull. Chem. Soc. Jpn.*, **53**, 2167 (1980).

2) D. W. McCall and D. C. Douglass *J. Phys. Chem.*, **71**, 987 (1967).

3) D. G. Miller, *Faraday Discuss. Chem. Soc.*, **64**, 295 (1977).

4) D. G. Miller, *J. Phys. Chem.*, **85**, 1137 (1981).

5) D. G. Miller, J. A. Rard, L. B. Eppstein, and J. G. Albright, *J. Phys. Chem.*, **88**, 5739 (1984).

6) H. G. Hertz, *Ber Bunsenges. Phys Chem.*, **81**, 656 (1977).

7) H. G. Hertz and R. J. Mills, *J. Phys. Chem.*, **82**, 952 (1978).

8) A Geiger, H. G. Hertz, and R. J. Mills, *J. Solution Chem.*, **10**, 83 (1981).

9) H. J. Schonert, *J. Phy. Chem.*, **88**, 3359 (1984).

10) L. A. Woolf, *J. Phys. Chem.*, **82**, 959 (1978).

11) L. A. Woolf and K. R. Harris, *J. Chem. Soc., Faraday Trans. I*, **74**, 933 (1978).

12) D. C. Douglass and H. L. Frisch, *J. Phys. Chem.*, **73**, 3039 (1969).

13) R. Mills and H. G. Hertz, *J. Phys. Chem.*, **84**, 220 (1980).

14) H. L. Freedman and R. Mills, *J. Solution Chem.*, **10**, 395 (1981).

15) T. Kato, S. Hyodo, and T. Fujiyama, *J. Phys. Chem.*, **82**, 1010 (1978).

16) K. Iwasaki and T. Fujiyama, *J. Phys. Chem.*, **83**, 463 (1979).

17) T. Kato, K. Yano, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 53 (1980).

18) T. Kato, T. Nakanishi, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **53**, 2173 (1980).

19) N. Ito, K. Saito, T, Kato, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **54** 991 (1981).

20) T. Kato, M. Yudasaka, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **54**, 1632 (1981).

21) N. Ito, T. Kato, and T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **54**, 2573 (1981).

22) T. Kato, T. Fujiyama, and H. Nomura, *Bull. Chem. Soc. Jpn.*, **55**, 3368 (1982).

23) N. Ito, T. Fujiyama, and Y. Udagawa, *Bull. Chem. Soc. Jpn.*, **56**, 379 (1983).

24) N. Ito and T. Kato, *J. Phys. Chem.*, **88**, 801 (1984); T. Kato, *ibid.*, **88**, 1248 (1984)

25) T. Kato, *J. Phys. Chem.*, **89**, 5750 (1985).

26) G. Alagona and A. Tani, *J. Chem. Phys.*, **74**, 3980 (1981); *Chem. Phys. Lett.*, **87**, 337 (1982).

27) S. Okazaki, K. Nakanishi, and H. Touhara, *J. Chem. Phys.*, **78**, 454 (1983).

28) K. Nakanishi, K. Ikari, S. Okazaki, and H. Touhara, *J. Chem. Phys.*, **80**, 1656 (1984); S. Okazaki, H. Touhara, and K. Nakanishi, *J. Chem. Phys.*, **81**, 890 (1984).

29) H. Tanaka, K. Nakanishi, and H. Touhara, *J. Chem. Phys.*, **81**, 4065 (1984).

30) Y. Kataoka, *J. Chem. Phys.*, **80**, 4470 (1984).

31) K. Okazaki, S. Nosé, Y. Kataoka, and T. Yamamoto, *J. Chem. Phys.*, **75**, 5864 (1981).

32) Y. Kataoka, *Bull. Chem. Soc. Jpn.*, **57**, 1522 (1984); **59**, 1425 (1986).

33) W. G. Hoover, W. T. Ashurst, and R. J. Olness, *J. Chem, Phys.*, **60**, 4043 (1974); D. J. Evans, *Phys. Rev.*, **A22**, 290 (1980); T. E. Wainwright, B. J. Alder, and D. M. Gass, *Phys. Rev.*, **A4**, 233 (1971); S. Toxvaerd, *Mol. Phys.*, **29**, 373 (1975).

34) S. Nosé, *Mol. Phys.*, **52**, 255 (1984); *J. Chem. Phys.*, **81**, 511 (1984).

35) D. L. Jolly and R. J. Bearman, *Mol. Phys.*, **41**, 137 (1980).

36) M. Schoen and C. Hoheisel, *Mol. Phys.*, **52**, 33 (1984); **52**, 1029 (1984).

37) H. C. Andersen, *J. Chem. Phys.*, **72**, 2384 (1980).

38) D. Brown and J. H. R. Clarke, *Mol. Phys.*, **51**, 1243 (1984).

39) See Eq. 35 in Ref. 2 or Eq. 10 in Ref. 25.