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Molecular Dynamics Simulation of Liquid Water

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A molecular dynamics simulation has been performed for a fluid system containing 1000 water molecules confined to a cubical box at mass density 1 g cm^{-3}, where the ST2 type intermolecular potential has been used. Newtonian equations of motion of molecules were solved according to the method of constraints proposed by Ryckaert et al. Atomic radial distribution functions and corresponding partial structure functions at 24 and 93 °C were given and compared with theoretical calculations for the pentamer-monomer mixture model and neutron diffraction data. The agreement among the three was found to be satisfactory on the whole. In order to investigate how profoundly the periodic boundary condition influences upon the calculated values, the difference between the hydrogen-bonding behavior of molecules near the boundary and that of those in the central part of the box was examined into details. The population of hydrogen bonds near the boundary was found to be about 10% lower than that in the central part including about 210 molecules. In addition to these static properties the self-diffusion process was investigated.

The study of the properties of computer model has played a very important role in the development of the theories of liquid. It has been the case in the theories of molecular fluids. With respect to liquid water, such models have provided valuable information[1,2] necessary for constructing theoretical models of the liquid.[3,4] Since the first comprehensive works by Rahman and Stillinger,[1] simulation calculations of liquid water have been performed for various potential models such as ST2, MCY etc.,[5-14] though no decisive results have been obtained until present.

The equilibrium structure of a molecular fluid is described in terms of partial structure functions, $a_{ss'}(Q)$, which is related to atom pair (s,s′) correlations. Recently, we have calculated three partial structure functions, $a_{OO}(Q)$, $a_{OH}(Q)$, and $a_{HH}(Q)$,[15] according to a theoretical calculation procedure[15-17] proposed for obtaining structure factors of a fluid composed of molecular clusters of various sizes. A substantial agreement was found between the calculated and experimental values.

In order to push forward the study of the liquid structure of water further, we have attempted, here, a computer simulation study for the fluid system containing 1000 water molecules. It is straightforward to calculate the partial structure functions $a_{ss'}(Q)$ and others using computer simulation techniques. In this paper we present first the results of partial structure functions obtained from the molecular dynamics simulation. The results are compared with neutron diffraction data[17,18] and our preceding theoretical calculations for the pentamer-monomer mixture model.[15,17] Further discussions on the simulation calculation are given.

Molecular Dynamics Simulations

As a model of liquid water we used the ST2 molecules of Stillinger and Rahman.[2] Molecular dynamics simulations were performed for a system of N=1000 water molecules confined to a cubical box, being subjected to periodic boundary conditions. The mass density was fixed at 1 g cm^{-3}, so that the cube edge length was 31.03 A. In evaluating potentials and forces the interaction between two molecules was neglected when the oxygen-oxygen distance was larger than a cut-off distance r_c. The cut-off was placed at r_c=8.46 A.

Newtonian equations of motion were solved by the method of constraints described by Ryckaert et al.[19] This method was devised originally to deal with the problem of large molecules having internal degrees of freedom, and it has a general applicability. The method of constraints is based on the cartesian equations of motion of individual atoms, being simple to implement. The time increment Δt for numerical integration of the equations of motion was taken to be

$$\Delta t = 1.0 \times 10^{-16}\,\text{s}.$$

To take the molecular dynamics statistical average, we utilized a period of 10000 Δt. Molecular dynamics runs were generated at two distinct temperatures, 24 and 93 °C; they correspond to fixed total energies of $-110\ \varepsilon$ and $-91\ \varepsilon$ respectively, where ε is 0.07575 kcal mol^{-1} (1 cal=4.184 J). The total energy was monitored every 10 steps of Δt, and if it had drifted by $\pm 0.04\ \varepsilon$ (on the average every 500 steps) all velocities were rescaled to recover the initial energy value.

Results and Discussion

Radial Distribution Functions. Figures 1 and 2 show the atomic radial distribution functions $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ obtained from the molecular dynamics runs for the ST2 model for 24 and 93 °C, respectively.

Partial Structure Functions. The partial structure functions $a_{ss'}(Q)$ are related to the atomic radial distribution functions $g_{ss'}(r)$ by the expression

$$a_{ss'}(Q) = 4\pi\rho\int_0^\infty [g_{ss'}(r) - 1]\, r^2 j_0(Qr)\,\mathrm{d}r, \tag{1}$$

where $j_0(x)$=sinx/x, s and s′ label nucleus species, and $Q=|\vec{Q}|$ ($\vec{Q}$: the scattering vector).

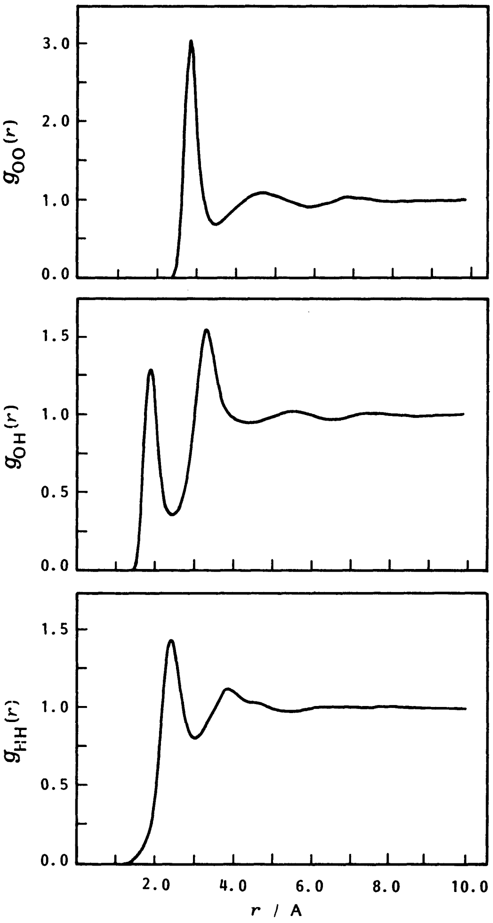

Fig. 1. Radial distribution functions at 24°C.

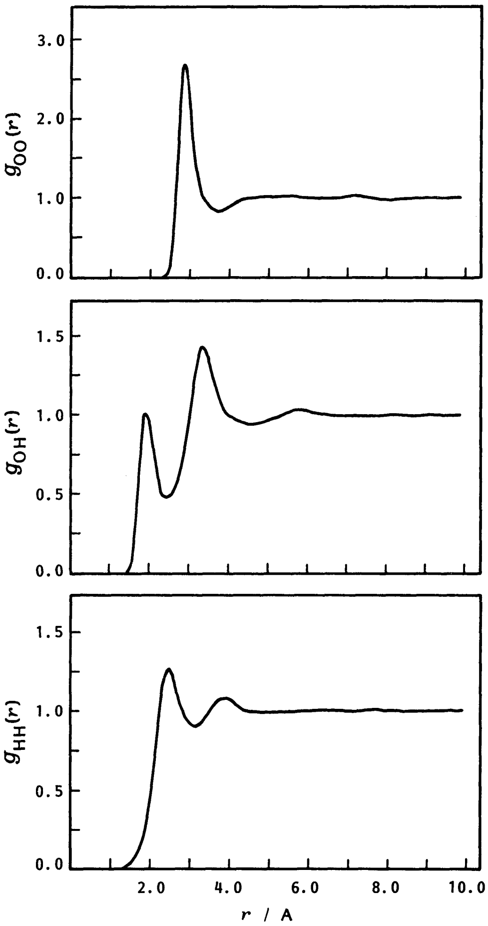

Fig. 2. Radial distribution functions at 93°C.

Now, we can calculate the partial structure functions $a_{ss'}(Q)$ for the ST2 model by using the molecular dynamics results of $g_{ss'}(r)$ given in Figs. 1 and 2. The calculated $a_{OO}(Q)$, $a_{OH}(Q)$, and $a_{HH}(Q)$ functions for 24 °C are shown in Figs. 3—5, respectively, and are compared with the corresponding neutron diffraction data of Thiessen and Narten[18] as well as with the preceding theoretical calculations for the pentamer-monomer mixture model.[15] The agreement among those three is satisfactory on the whole.

We calculated the total coherent neutron structure factor $S_m(Q)$ by using the three partial structure functions $a_{ss'}(Q)$ given in Figs. 3—5. The structure factor $S_m(Q)$ is defined as a sum of partial structure factors $S_{ss'}(Q)$[15]

$$S_m(Q) = (b_O + 2b_H)^{-2}[b_O^2 S_{OO}(Q) + 4b_O b_H S_{OH}(Q) + 4b_H^2 S_{HH}(Q)], \qquad (2)$$

where b_s is the coherent scattering length of nucleus s, and

$$S_{OO}(Q) = 1 + a_{OO}(Q),$$
$$S_{OH}(Q) = a_{OH}(Q) + Y_{OH}(Q),$$
$$S_{HH}(Q) = (1/2) + a_{HH}(Q) + (1/2)Y_{HH}(Q).$$

The $Y_{ss'}(Q)$ is generally approximated by

$$Y_{ss'}(Q) = j_0(Qr_{ss'})\exp(-\gamma_{ss'}Q^2),$$

where $r_{ss'}$ is the distance between the s and s′ nuclei, and $(2\gamma_{ss'})^{1/2}$ the rms variation to the distance $r_{ss'}$. Figure 6 shows the calculated $S_m(Q)$ curve, together with the corresponding observed data[17] and the previous result for the pentamer-monomer mixture model.[17] As seen in Fig. 6, the present values are in good agreement with the observed data as well as with the ones for the pentamer-monomer mixture model.

Here, the $a_{OH}(Q)$ and $a_{HH}(Q)$ curves, shown in Figs. 4 and 5 respectively, are of particularly interest. First, taking account of experimental difficulties in determining partial structure functions, it can be said that the present $a_{OH}(Q)$ and $a_{HH}(Q)$ curves essentially reproduce the corresponding observed data, and also that the agreement between the $a_{OH}(Q)$ and $a_{HH}(Q)$ curves for the ST2 model and the pentamer-monomer mixture model is remarkably good on the whole. These results seem to show the effectiveness of the pentamer-monomer mixture model for describing the equilibrium structure of liquid water. The ST2 model has a strong tendency for water molecules to form tetrahedrally-coordinated structures. The dominance of a tetrahedral configuration as the local environment around a molecule on the average is essential for liquid water.

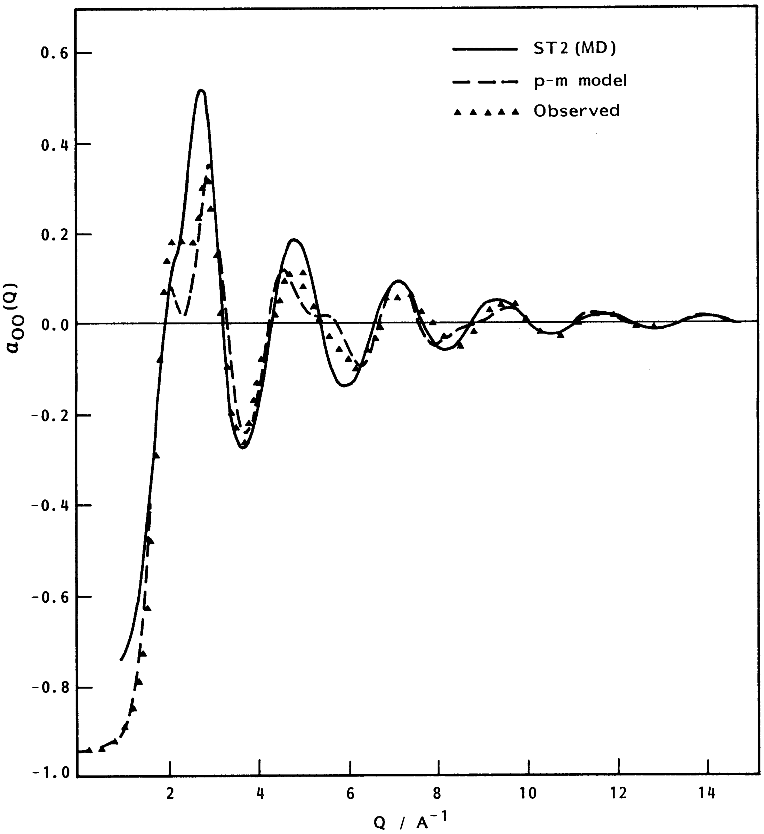

Fig. 3. O-O structure function $a_{OO}(Q)$ at 24°C in comparison with the observed data[18] and the calculated ones for pentamer-monomer mixture model (p-m model).[15]

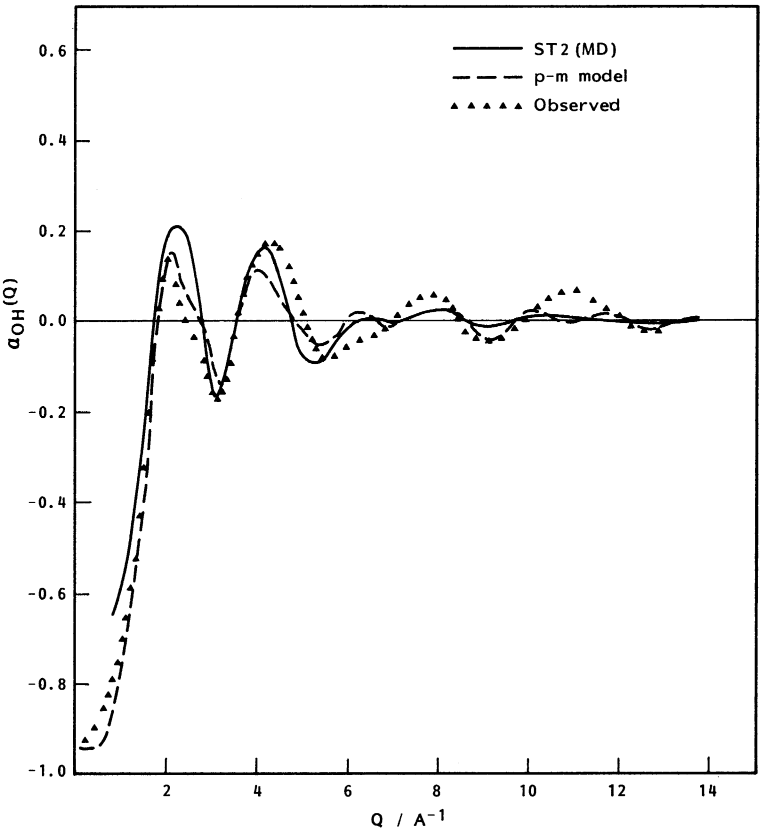

Fig. 4. O-H structure function $a_{OH}(Q)$ at 24°C in comparison with the observed data[18] and the calculated ones for pentamer-monomer mixture model.[15]

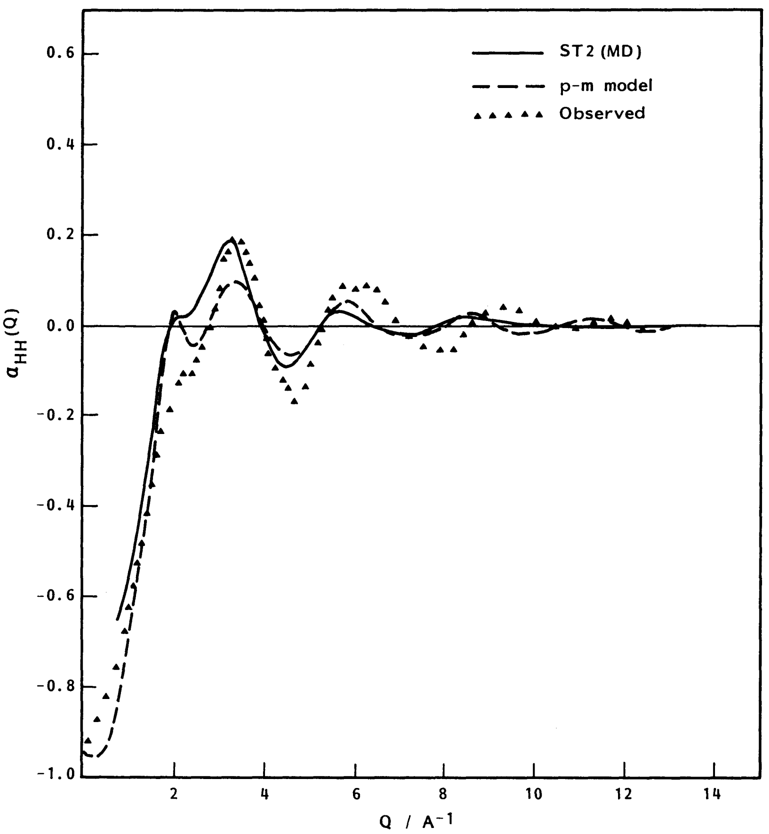

Fig. 5. H-H structure function $a_{HH}(Q)$ at 24°C in comparison with the observed data[18] and the calculated ones for pentamer-monomer mixture model.[15]

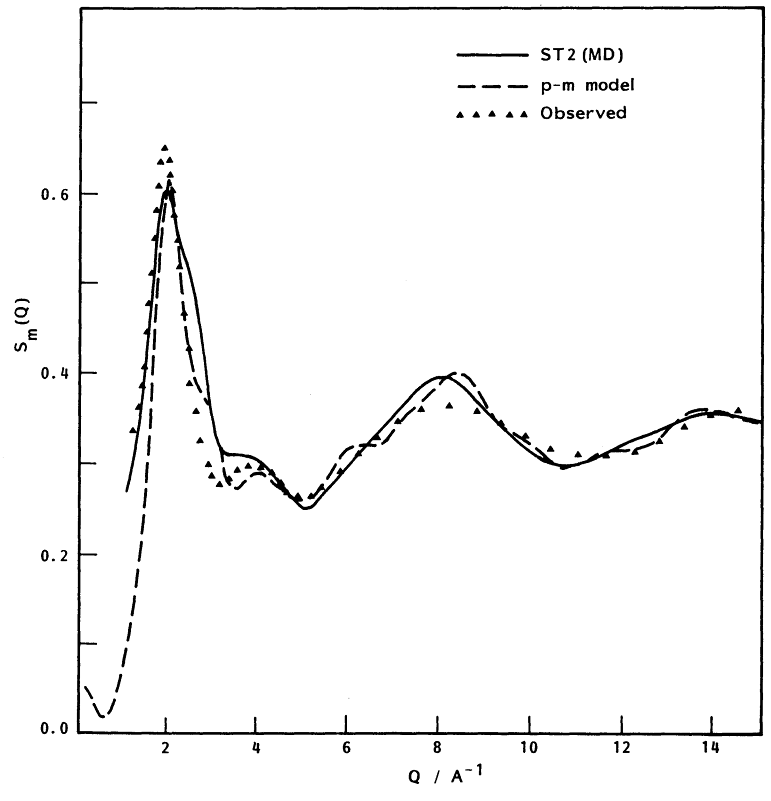

Fig. 6. Coherent neutron structure factor $S_m(Q)$ at 24°C in comparison with the observed data[17] and the calculated ones for pentamer-monomer mixture model.[17]

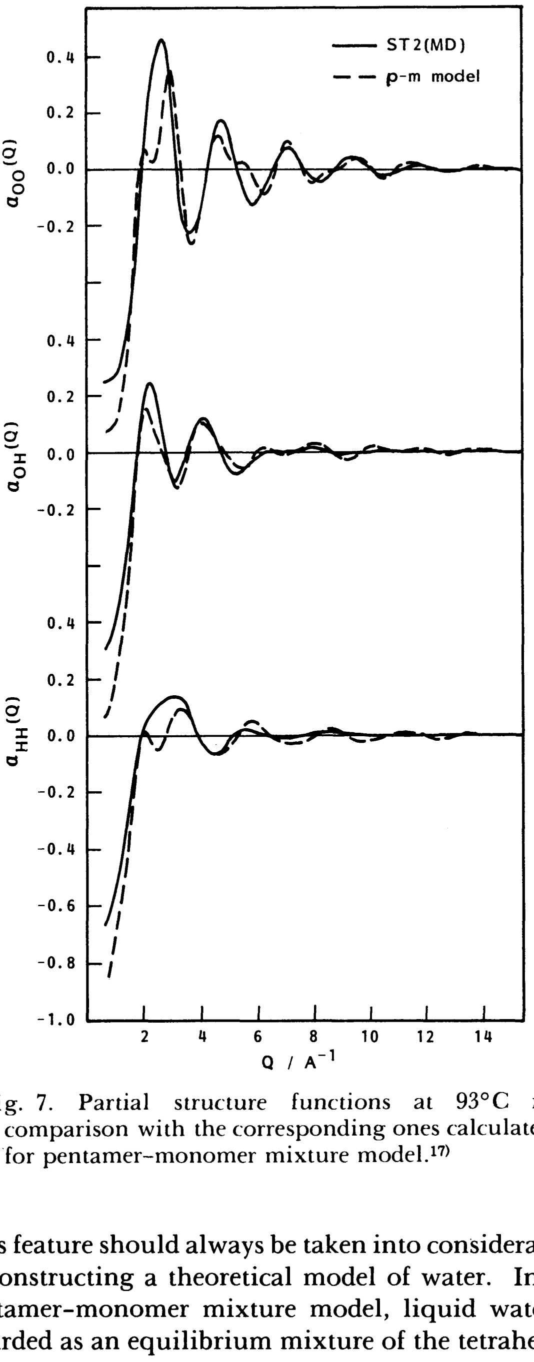

Fig. 7. Partial structure functions at 93°C in comparison with the corresponding ones calculated for pentamer-monomer mixture model.[17]

This feature should always be taken into consideration in constructing a theoretical model of water. In the pentamer-monomer mixture model, liquid water is regarded as an equilibrium mixture of the tetrahedral hydrogen-bonded pentamers and the non-hydrogen-bonded monomers.[3,17] The present results show that the pentamer-monomer mixture model can describe the overall structural properties of liquid water.

Seeing further details, some discrepancies are found for the $a_{OO}(Q)$ curves shown in Fig. 3; a double peak appears in the observed curve around Q=2.5 A^{-1}, but for the ST2 curve at 24 °C the double peak is quite less impressive and the right peak is too high. The similar situation was seen in the simulated X-ray scattering intensity curves due to Rahman and Stillinger for the BNS potential system at 34.3 °C.[1] An improvement is considered to be achieved by allowing the simulations to incorporate the nonrigidity of water molecules.[5,14]

In Fig. 7 the molecular dynamics $a_{ss'}(Q)$ curves for the ST2 system at 93 °C are given in comparison with the calculated curves for the pentamer-monomer mixture model. In Fig. 8 the $S_m(Q)$ curve for the ST2 system at 93 °C is shown, together with neutron diffraction data.[17]

Effects of the Periodic Boundary Conditions on Distributions of Hydrogen Bonds. In a molecular dynamics simulation of liquid systems, a periodic boundary condition is required in order to minimize surface effects, and the influences of artificial correlations imposed by the condition have been believed to be satisfactorily small for substantially large cells. For hydrogen-bonded fluids like water, however, there is a possibility that the periodicity condition affects the aspect of "hydrogen bonding" between molecules. In the following we examine the effects of the periodic boundary condition on distributions of hydrogen bonds.

In measuring the degree of hydrogen bonding, we follow a guideline due to Rahman and Stillinger.[1] If the interaction energy for a given pair of molecules lies below an assigned negative cut-off energy V_{HB}, the pair is hydrogen bonded and if their interaction equals or exceeds V_{HB}, they are not hydrogen bonded.

In order to see the degree of hydrogen bonding near the surface of the box, we classify molecules into two groups, and calculate separately the distributions of hydrogen bonds for each group;

group I: $0.2L<x_j,\ y_j,\ z_j<0.8L$

group II: $x_j,\ y_j,\ z_j<0.2L$ and $x_j,\ y_j,\ z_j>0.8L$

where L is the edge length of the cubic box and x_j, y_j, and z_j are the center of mass cartesian coordinates of molecule j.

In Fig. 9 we show the distributions of hydrogen bonds thus obtained for five different values of V_{HB}. These were determined by averaging over a period of 1000 Δt. From the comparison between the histograms for group I (about 210 molecules in the central part of the box) and those of group II (about 790 molecules near the surface), it is seen that the mean of the distribution for group II clearly shifts to lower numbers of hydrogen bonds. The population of hydrogen bonds which are destroyed near the surface is estimated roughly to be 10%. The cause of lowering of the degree of hydrogen bonding in group II is supposed as in the following. The periodic boundary condition clearly constrains the freedom of the molecules in motion near the surface of the box on the whole. This constraint subjected to the condition, probably that with respect to the rotationary degree of freedom of molecules, is considered resultantly to shift the degree of hydrogen bonding in group II to a lower magnitude than that in group I. Thus, it can be said that in the present simulation the molecules in group I (about 210 molecules) as the inner part resemble more exactly to the real water. In order to avoid such effects due to the

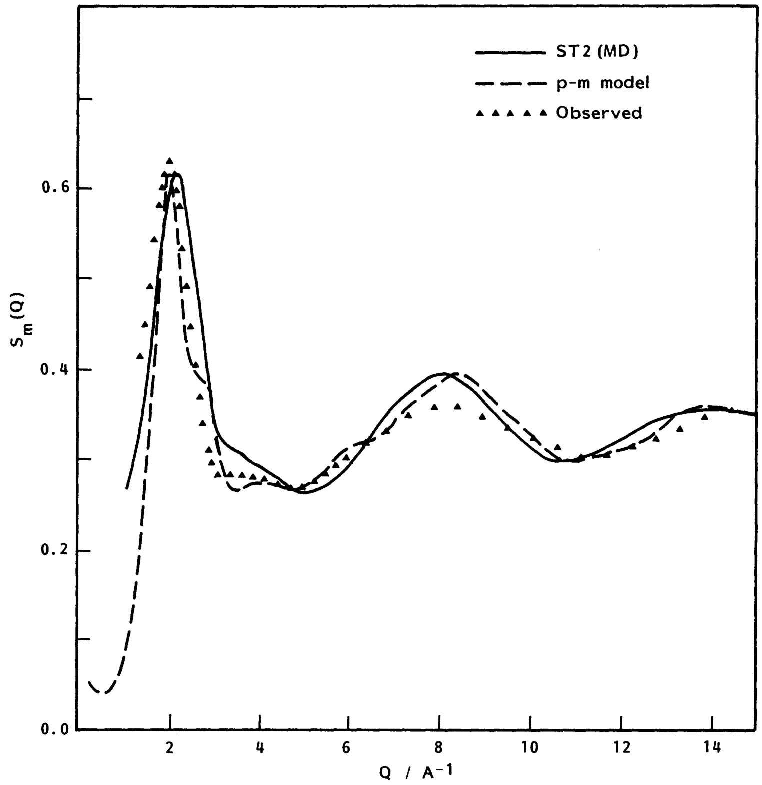

Fig. 8. Coherent neutron structure factor $S_m(Q)$ at 93°C in comparison with the observed data[17] and the calculated ones for pentamer-monomer mixture model.[17]

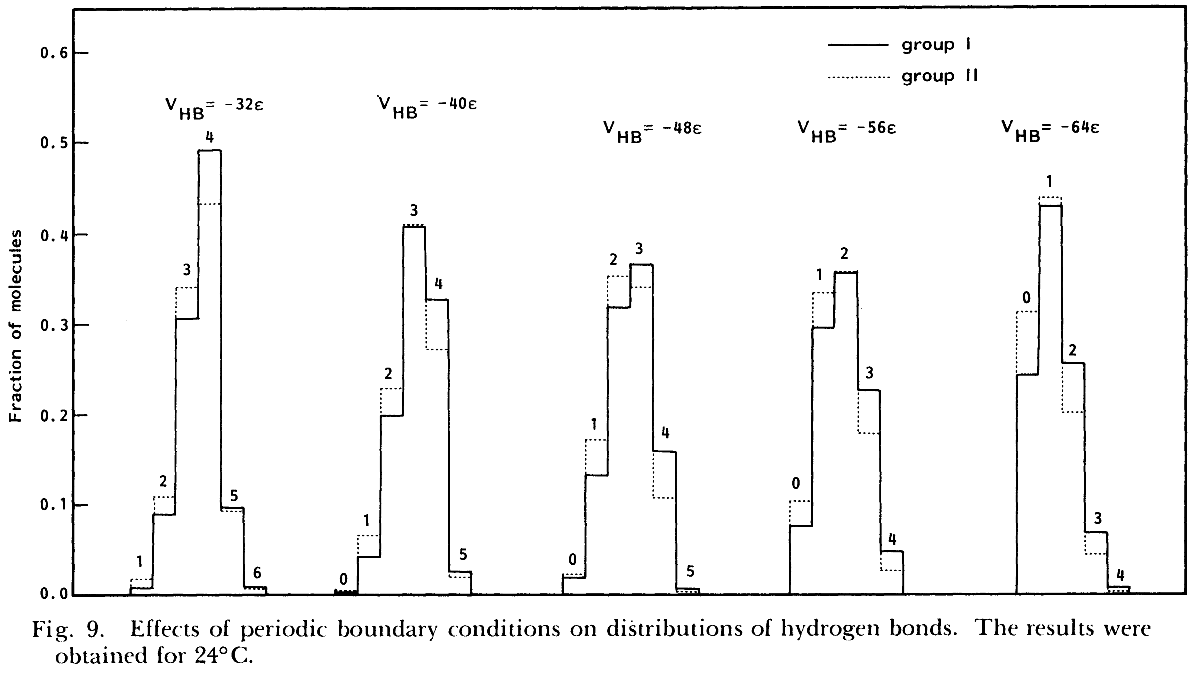

Fig. 9. Effects of periodic boundary conditions on distributions of hydrogen bonds. The results were obtained for 24°C.

periodic boundary conditions in a simulation of liquid water, the total number of molecules is desired to be as large as in the present simulation.

Self-Diffusion Process. The normalized velocity autocorrelation function for the molecular center of mass motion is given by

$$\psi(t) = <\frac{1}{N}\sum_{j}^{N}\vec{v}_j(0)\vec{v}_j(t)>/<\frac{1}{N}\sum_{j}^{N}\vec{v}_j(0)^2>, \qquad (3)$$

where $\vec{v}_j$ is the center of mass velocity for molecule j. Figure 10 gives the normalized velocity autocorrelation function $\psi(t)$ at 24°C, including the simulation

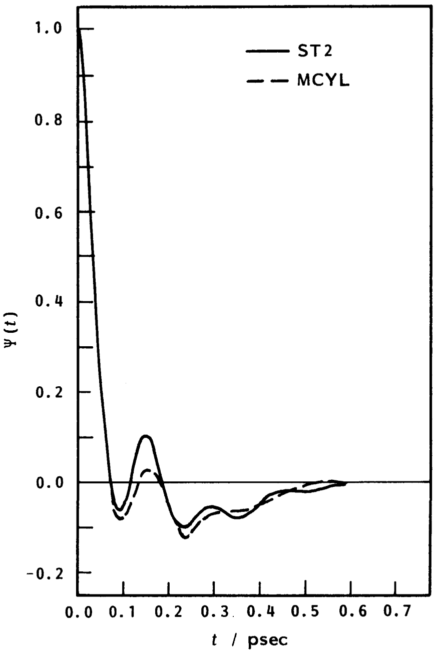

Fig.10. Velocity autocorrelation function for the molecular center of mass motion at 24°C in comparison with the ones for MCYL model given by Lie and Clementi.[14]

calculation of Lie and Clementi for the MCYL model at 27 °C.[14] The present result is consistent with the results of Stillinger and Rahman's simulations[2] expected at the corresponding temperature. Then, we find that the curves for the ST2 and MCYL models substantially resemble each other on the whole, although a more pronounced oscillatory behavior after the first negative region appears in the ST2 curve.

The self-diffusion coefficient D can be calculated by means of a Green-Kubo relation. Using the $\psi(t)$ curve given in Fig. 10, we obtain 2.8×10^{-5} $\mathrm{cm}^2\,\mathrm{s}^{-1}$ for the ST2 model at 24 °C. This value is consistent with the results of Stillinger and Rahman extrapolated at the corresponding temperature.

References

1) A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **55**, 3336 (1971).

2) F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, **60**, 1545 (1974).

3) K. Arakawa, K. Tokiwano, and K. Kojima, *Bull. Chem. Soc. Jpn.*, **50**, 65 (1977).

4) B. R. Lentz, A. T. Hagler, and H. A. Scheraga, *J. Phys. Chem.*, **78**, 1531 (1974).

5) A. Rahman, F. H. Stillinger, and H. L. Lemberg, *J. Chem. Phys.*, **63**, 5223 (1975); F. H. Stillinger and A. Rahman, *J. Chem. Phys.*, **68**, 666 (1978).

6) M. Rao, C. S. Pangali, and B. J. Berne, *Mol. Phys.*, **37**, 1773 (1979).

7) R. O. Watts, *Mol. Phys.*, **28**, 1069 (1974).

8) G. C. Lie, E. Clementi, and M. Yoshimine, *J. Chem. Phys.*, **64**, 2314 (1976).

9) J. C. Owicki and H. A. Scheraga, *J. Am. Chem. Soc.*, **99**, 7403 (1977).

10) J. R. McDonald and M. L. Klein, *J. Chem. Phys.*, **68**, 4875 (1978); R. W. Impey, M. L. Klein, and J. R. McDonald, *J. Chem. Phys.*, **74**, 647 (1981).

11) D. C. Rapaport and H. A. Scheraga, *Chem. Phys. Lett.*, **78**, 491 (1981).

12) G. Jancso, P. Bopp, and K. Heinzinger, *Chem. Phys.*, **85**, 377 (1984).

13) W. L. Jorgensen, J. Chandrasekhar, J. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.*, **79**, 926 (1983).

14) G. C. Lie and E. Clementi, *Phys. Rev. A*, **33**, 2679 (1986).

15) N. Ohtomo, K. Tokiwano, and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **57**, 329 (1984).

16) N. Ohtomo, K. Tokiwano, and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **54**, 1802 (1981).

17) N. Ohtomo, K. Tokiwano, and K. Arakawa, *Bull. Chem. Soc. Jpn.*, **55**, 2788 (1982).

18) W. E. Thiessen and A. H. Narten, *J. Chem. Phys.*, **77**, 2656 (1982).

19) J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, *J. Comput. Phys.*, **23**, 327 (1977); G. Ciccotti, M. Ferrario, and J. P. Ryckaert, *Mol. Phys.*, **47**, 1253 (1982).