The Structure of Liquid Water by Neutron Scattering

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A comprehensive analysis of the structure of liquid water was performed by combining neutron and X-ray diffraction data. A formula expressing the structure factor of fluids composed of small molecular clusters was obtained and applied to the analysis. In the interpretation of the diffraction data, the tetrahedral pentamer model as an aggregate of the regular tetrahedral pentamers is considered to be the best structure model of liquid water from the excellent agreement between calculated structure factors and experimental data. Some critical discussions about other structure models were made.

Recent diffraction studies of liquid water have brought much valuable information on the structure of the liquid. Among them, the followings are distinguishable: X-ray diffraction studies by Narten and Levy$^{1)}$ and Hajdu *et al.*,$^{2)}$ electron diffraction studies by Kálmán *et al.*,$^{3)}$ and neutron diffraction studies by Page and Powles,$^{4)}$ Narten$^{5)}$ and the authors.$^{6,7)}$ However, the conclusions drawn from the diffraction results by these workers are found to be contradictory to each other. The most important reason for the circumstances is, of course, the "complexity" of the liquid structure of water and the lack of the reasonable general method of analysis for diffraction data by liquids. At the present stage of the development of studies in this field, the combined and comprehensive interpretation of diffraction results$^{8)}$ is strongly required.

Concerning the X-ray studies, observed intensity data agree well with each other in the low Q range (<5 Å^{-1}), though, for large Q, marked discrepancies are found there, for example, between the data reported by Hajdu *et al.*$^{2)}$ and that by Narten *et al.*$^{1,9)}$ In addition, the proposed structure models in those papers are considered to have implausible aspects in several respects: Hajdu's model consists of a fundamentally anisotropic nearest neighbor arrangement of water molecules$^{10)}$ and Narten's earlier model ("interstitial model") in 1967$^{9)}$ has a "largely extended lattice structure."

With respect to the neutron studies, the observed structure factors are found to agree virtually with each other, taking the differences of the experimental method into consideration.$^{6,7)}$ However, the conclusions on the structure model of water are largely inconsistent with each other.$^{4-6)}$ The authors mentioned earlier the cause of the marked discrepancies.$^{6,7)}$ It has turned out that Narten's "near-neighbor model" is physically unacceptable and also that Page and Powles' conclusion disproving all the structure models treated is too severe. We analyzed the neutron data using a "revised watery model," which is a modification of Page and Powles' "watery model." However, the agreement between calculated and experimental structure factors was still insufficient.$^{6,7)}$

Despite these incompatible results, it has become certain through those recent X-ray and neutron diffraction studies that the most dominant local environment of a water molecule within liquid water is nearly tetrahedral on the average. Furthermore, a large amount of information accumulated so far by various experimental$^{11)}$ and theoretical studies$^{12-15)}$ have also ascertained the fact. However, further knowledge on the nearest neighbor coordination shell remains quite undetermined. Concerning the nearest neighbor coordination number, for example, it has been believed to be slightly larger than 4 since the pioneering study by Morgan and Warren, while according to the recent study by Hajdu *et al.*, it is smaller than 4, though slightly.

The major reason for the existence of those contradictory circumstances stated here is supposed to be attributed to the inadequacy of the method of analysis as well as to the experimental difficulties. Thus, we have attempted to perform a combined analysis of the neutron and X-ray diffraction data from various sources including our own, and then to propose a structure model of liquid water. The main purpose of our present analysis is the direct confirmation of the basic structural entities by the combined interpretation of neutron and X-ray diffraction data through the presentation of a new method of analysis. Though the number of the nearest neighbor coordination is believed to be nearly equal to 4, it is not sure whether the average configuration of the nearest neighbor molecules is regular-tetrahedral or not. In another word, it is still a central problem whether the regular tetrahedral pentamer is the primary entity (of course, on the average) or not. This is the most important point as the object of debate with respect to the structure model of liquid water. The details of the present analysis are written in the following.

Neutron and X-Ray Diffraction Data

For the present purpose, we used the X-ray diffraction data of Narten *et al.*$^{1,9)}$ and of Hajdu *et al.*$^{2)}$ As to the neutron diffraction our own data was used.

Neutron Diffraction Data. In addition to the structure factor $S_m(Q)$ data in the low Q region (<10 Å^{-1}),$^{6,7)}$ the factors in the higher Q region (<25 Å^{-1}) were obtained by LINAC-TOF neutron diffraction method.$^{16)}$ Details of the experimental apparatus have been stated in the preceding papers together with the correction and calibration procedures.$^{6,7,16)}$ The neutron structure factor $S_m(Q)$ over a wide range of Q (1—25 Å^{-1}) obtained by combining the low Q data with the higher Q data,$^{17)}$ are shown in Fig. 1. The $S_m(Q)$ data in the low Q region, 1—8 Å^{-1}, agree well with those reported previously, though the slight differences of a main peak at 2 Å^{-1} and a broader

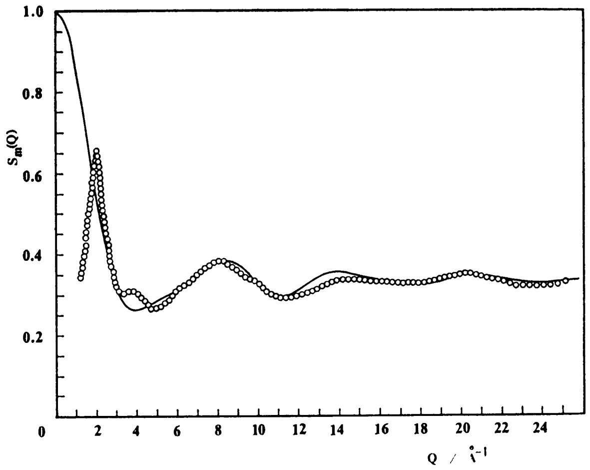

Fig. 1. Observed neutron structure factors $S_m(Q)$ for heavy water at room temperature (15±1 °C), compared with the calculated intramolecular structure factor $S_m^{(1)}(Q)$.
○: $S_m(Q)$ observed ——: $S_m^{(1)}(Q)$ calculated (r_{OD}=0.98 Å, r_{DD}=1.60 Å, and DOD angle=109.5°).

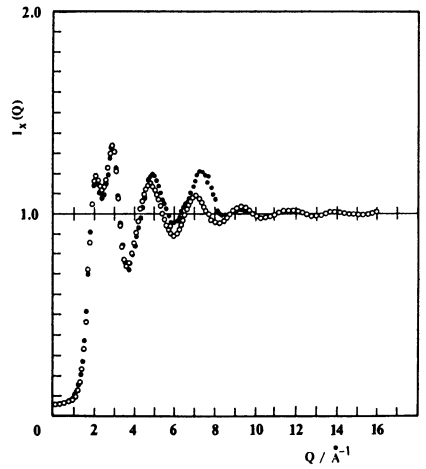

Fig. 2. Observed X-ray intensity function $I_x(Q)$.
○: $I_x(Q)$ by Narten *et al.* (20 °C),[1,9] ●: $I_x(Q)$ by Hajdu *et al.* (25 °C).[2]

peak at *ca.* 8 Å^{-1} are observed.[6,7] It is noticeable that the $S_m(Q)$ data for D_2O obtained by the authors at LINAC are found to agree virtually with Page and Powles' and Narten' data at reactor, taking the experimental uncertainities as well as the small difference in temperature into consideration. The reproducibility of the neutron data in the low Q region is thus confirmed with sufficient accuracy.

X-Ray Diffraction Data. Many X-ray diffraction data of liquid water have been reported. Among them, the data of Narten *et al.*[1,9] and those of Hajdu *et al.*[2] are available for the present purpose. "Molecular" modified intensity functions given in those papers are shown in Fig. 2. The two data are found in good agreement with each other in the low Q range, though marked discrepancies are observed in the higher Q range ($Q \gtrsim 5$ Å^{-1}).

Theoretical Procedures of Analysis

Coherent Neutron Structure Factor. The coherent neutron scattering cross-section $(d\sigma/d\Omega)_{coh}$ is given in the static approximation by

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh} = N_m \Sigma^2 S_m(Q), \tag{1}$$

where $\Sigma = \sum_n b_n$. Equation 1 defines the coherent neutron structure factor $S_m(Q)$ for molecular liquid.[4] N_m is the number of molecules in the sample and b_n the scattering length of nucleus n. $\sum$ is over all the nuclei in the molecule. $\vec{Q}(=\vec{k}_0-\vec{k}_s)$ is the scattering vector and $|\vec{Q}|=Q=(4\pi/\lambda)\sin\theta$, where $\vec{k}_0$ and $\vec{k}_s$ are the incident and scattered wave vectors, respectively.

In this study we attempt to determine the best structure model of water for the interpretation of its diffraction data. For that purpose, we will give here a general expression of $S_m(Q)$ for liquid which can be regarded as an aggregate of small clusters composed of molecules. The derivation of the $S_m(Q)$ is as in the following.

Structure Factor $S_m(Q)$ for Fluids Composed of Molecular Clusters. The coherent neutron structure factor $S_m(Q)$ in Eq. 1 is given in general by

$$S_m(Q) = N_m^{-1}\Sigma^{-2}\langle\sum_{i\neq j}\sum_{n_i,n_j} b_{n_i}b_{n_j}\exp(i\vec{Q}\cdot\vec{r}_{n_in_j})\rangle, \tag{2}$$

where i and j label molecules in a liquid and n_i denotes the n-th nucleus in the molecule i. $\vec{r}_{n_in_j}$ is the vector distance between the nuclei n_i and n_j, and b_{n_i} the scattering length of nucleus n_i. We sum over all the scatterers in the N_m molecules in the system.

Then, in the right hand side of Eq. 2, the separation of the contribution of atom-pair interactions within the clusters from the "inter-cluster" contribution is permitted in general, because a liquid can always be regarded virtually as an aggregate of small clusters of various sizes. We have

$$S_m(Q) = f_1^c(Q) + N_m^{-1}\Sigma^{-2}\langle\sum_{\alpha\neq\beta}\sum_{l_\alpha,l_\beta}\sum_{n_{l\alpha},n_{l\beta}} b_{n_{l\alpha}}b_{n_{l\beta}}\exp(i\vec{Q}\cdot\vec{r}_{n_{l\alpha}n_{l\beta}})\rangle \tag{3}$$

and

$$f_1^c(Q) = N_m^{-1}\Sigma^{-2}\langle\sum_{\alpha}\sum_{l_\alpha,l'_\alpha}\sum_{n_{l\alpha},n_{l'\alpha}} b_{n_{l\alpha}}b_{n_{l'\alpha}}\exp(i\vec{Q}\cdot\vec{r}_{n_{l\alpha}n_{l'\alpha}})\rangle, \tag{4}$$

where l and l′ label molecules within a given cluster, and l_α denotes the l-th molecule in the cluster α. The transformation of Eq. 2 to Eq. 3 is only mathematical and it should be noted that the two equations are physically identical.

Let us use $\vec{r}_{cl_\alpha l_\beta}$ to denote the vector distance from the center of the molecule l_α to that of the molecule l_β. Since $\vec{r}_{n_{l\alpha}n_{l\beta}}=\vec{r}_{cl_\alpha l_\beta}-\vec{r}_{cn_{l\alpha}}+\vec{r}_{cn_{l\beta}}$ where $\vec{r}_{cn_{l\alpha}}$ is the vector distance from the center of the molecule l_α to its n-th nucleus within the cluster α, Eq. 3 is written as

$$S_m(Q) = f_1^c(Q) + N_m^{-1}\Sigma^{-2}\langle\sum_{\alpha\neq\beta}\sum_{l_\alpha,l_\beta}\exp(i\vec{Q}\cdot\vec{r}_{cl_\alpha l_\beta}) \times \sum_{n_{l\alpha},n_{l\beta}} b_{n_{l\alpha}}b_{n_{l\beta}}\exp[i\vec{Q}\cdot(-\vec{r}_{cn_{l\alpha}}+\vec{r}_{cn_{l\beta}})]\rangle. \tag{5}$$

Equation 5 is quite general, and we now consider the case of a system consisting of identical clusters, each of which is composed of N_c molecules. Further, we assume that $\vec{r}_{\mathrm{cn}1\alpha}$, $\vec{r}_{\mathrm{cn}1\beta}$, and $\vec{r}_{\mathrm{cl}\alpha 1\beta}$ are all stasistically independent. That is, the molecules belonging to different clusters are assumed to be orientationally-uncorrelated. Then, Eq. 5 becomes

$$\begin{aligned} S_{\mathrm{m}}(Q) &= f_1^{\mathrm{c}}(Q) + N_{\mathrm{m}}^{-1}\Sigma^{-2}\langle\sum_{\alpha\neq\beta}\sum_{1_\alpha,1_\beta}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cl}_\alpha \mathrm{l}_\beta})\rangle \\ &\quad\times[\sum_{\mathrm{n}} b_{\mathrm{n}}\langle\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}})\rangle]^2, \\ &= f_1^{\mathrm{c}}(Q) + \Sigma^{-2}[\sum_{\mathrm{n}} b_{\mathrm{n}}\langle\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}})\rangle]^2 N_{\mathrm{m}}^{-1} \\ &\quad\times[\langle\sum_{\mathrm{i}\neq\mathrm{j}}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cij}})\rangle \\ &\quad-\frac{N_{\mathrm{m}}}{N_{\mathrm{c}}}\langle\sum_{\mathrm{l}\neq\mathrm{l}'}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cll}'})\rangle], \end{aligned} \tag{6}$$

where $\vec{r}_{\mathrm{cn}}$ is the vector distance from the center of a molecule to its n-th nucleus.

Thus, we can write the $S_{\mathrm{m}}(Q)$ as in the form,

$$S_{\mathrm{m}}(Q) = f_1^{\mathrm{c}}(Q) + f_{2\mathrm{U}}(Q)[S_{\mathrm{C}}(Q) - f_3(Q) - 1], \tag{7}$$

$$f_1^{\mathrm{c}}(Q) = \Sigma^{-2}N_{\mathrm{c}}^{-1}\langle\sum_{\mathrm{l},\mathrm{l}'}\sum_{\mathrm{n_l},\mathrm{n_l}'} b_{\mathrm{n_l}}b_{\mathrm{n_l}'}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{n_l n_l}'})\rangle, \tag{8}$$

$$f_{2\mathrm{U}}(Q) = \Sigma^{-2}[\sum_{\mathrm{n}} b_{\mathrm{n}}\langle\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}})\rangle]^2, \tag{9}$$

$$S_{\mathrm{C}}(Q) = 1 + N_{\mathrm{m}}^{-1}\langle\sum_{\mathrm{i}\neq\mathrm{j}}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cij}})\rangle, \tag{10}$$

and

$$f_3(Q) = N_{\mathrm{c}}^{-1}\langle\sum_{\mathrm{l}\neq\mathrm{l}'}\exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cll}'})\rangle, \tag{11}$$

where $f_1^{\mathrm{c}}(Q)$ is the contribution of atom-pairs within the cluster, $S_{\mathrm{C}}(Q)$ the molecular-centers structure factor of the liquid, $f_3(Q)$ a factor resulting from the molecular-center pairs within the cluster, and $f_{2\mathrm{U}}(Q)$ a factor resulting from the completely uncorrelated orientational configuration between molecules.

In the following of this section the formula for the analysis of diffraction data will be given according to the theoretical procedure described above to examine structure models of liquid water.

Regular Tetrahedral Pentamer Model. We will give here the $S_{\mathrm{m}}(Q)$ for the regular tetrahedral pentamer model where the structural unit as the basic entity of liquid water is the regular tetrahedral pentamer. In the model water is considered to be an aggregate of the pentamers on the average which are packed to give the density of 1 g/cm³. The central oxygen atom in the pentamer is tetrahedrally surrounded by four oxygen atoms at the corners of a regular tetrahedron, each pair of the central and peripheral oxygens being connected by a straight hydrogen bond (Fig. 3).

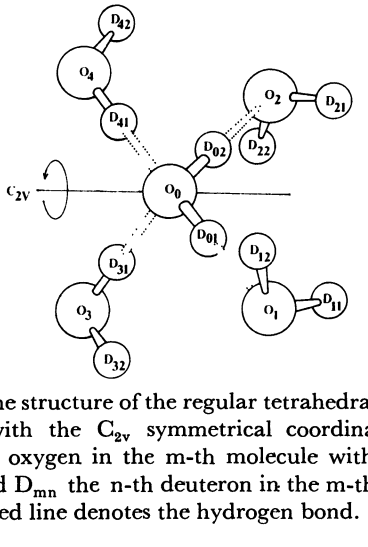

Fig. 3. The structure of the regular tetrahedral pentamer model with the C_{2v} symmetrical coordination. O_m indicates oxygen in the m-th molecule with the pentamer and D_{mn} the n-th deuteron in the m-th molecule. The dotted line denotes the hydrogen bond.

In this case, Eq. 7 becomes

$$S_{\mathrm{m}}(Q) = S_{\mathrm{m}}^{\mathrm{p}}(Q) + f_{2\mathrm{U}}(Q)[\{S_{\mathrm{C}}(Q) - S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)\} - 1], \tag{12}$$

where the intra-pentamer contribution $S_{\mathrm{m}}^{\mathrm{p}}(Q)(\equiv f_1^{\mathrm{c}}(Q))$ is[18]

$$\begin{aligned} S_{\mathrm{m}}^{\mathrm{p}}(Q) &= S_{\mathrm{m}}^{(1)}(Q) + 0.092S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q) + 0.422S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q) \\ &\quad + 0.486S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q), \end{aligned} \tag{13}$$

and

$$f_{2\mathrm{U}}(Q) = \Sigma^{-2}[b_{\mathrm{o}} + 2b_{\mathrm{D}}Y_{\mathrm{OD}}(Q)]^2. \tag{14}$$

$S_{\mathrm{m}}^{(1)}(Q)$ is the intramolecular contribution and the $S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)$ $(\equiv f_3(Q)^{19)})$, $S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q)$, and $S_{\mathrm{m.p}}^{)\mathrm{DD})}(Q)$ are the intra-pentamer part of the contributions of the O–O, O–D, and D–D pairs, respectively. $Y_{\mathrm{nn}'}(Q) = j_0(Qr_{\mathrm{nn}'})\exp(-\gamma_{\mathrm{nn}'}Q^2)$, where $j_0(\chi) = \sin\chi/\chi$, $r_{\mathrm{nn}'}$ is the distance between the n-th and n′-th nuclei, and $2\gamma_{\mathrm{nn}'}$ the mean-square variation to the distance $r_{\mathrm{nn}'}$. Thus, we can calculate the $S_{\mathrm{m}}(Q)$ by using Eq. 12. Each term in Eqs. 12 and 13 will be specified in the following.

The $S_{\mathrm{m}}^{(1)}(Q)$ for heavy water molecules is

$$S_{\mathrm{m}}^{(1)}(Q) = \Sigma^{-2}[b_{\mathrm{O}}^2 + 2b_{\mathrm{D}}^2 + 4b_{\mathrm{O}}b_{\mathrm{D}}Y_{\mathrm{OD}}(Q) + 2b_{\mathrm{D}}^2Y_{\mathrm{DD}}(Q)]. \tag{15}$$

For the regular tetrahedral pentamer model as shown in Fig. 3 the $S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)$ becomes

$$S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q) = \frac{4}{5}[2Y_{\mathrm{OO}}(Q) + 3Y_{\mathrm{O_1O_2}}(Q)]. \tag{16}$$

In order to obtain the expression of the $S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q)$ and $S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q)$, we consider two extreme cases with respect to the orientation of the peripheral molecules within the pentamer: the one orientation where deuterium atoms of those molecules are located in the positions of the C_{2v} symmetry (Fig. 3) and the other orientation where the peripheral molecules are rotating freely around the axis on a straight line joining the central and peripheral oxygens.

Thus, for the C_{2v} symmetry cluster the contributions of the intra-pentamer O–D and D–D pairs, $S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q)$ and $S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q)$, become

$$\begin{aligned} S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q) &= \frac{1}{5}[2Y_{\mathrm{O_1D_{01}}}(Q) + 3\{Y_{\mathrm{O_1D_{31}}}(Q) + Y_{\mathrm{O_1D_{21}}}(Q)\} \\ &\quad + 6\{Y_{\mathrm{O_0D_{11}}}(Q) + Y_{\mathrm{O_1D_{22}}}(Q)\}] \end{aligned} \tag{17}$$

and

$$\begin{aligned} S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q) &= \frac{1}{5}\Big[\frac{1}{2}\{Y_{\mathrm{D_{31}D_{41}}}(Q) + Y_{\mathrm{D_{11}D_{21}}}(Q)\} \\ &\quad + Y_{\mathrm{D_{11}D_{42}}}(Q) + Y_{\mathrm{D_{12}D_{22}}}(Q) + Y_{\mathrm{D_{12}D_{41}}}(Q) \\ &\quad + 2\{Y_{\mathrm{D_{01}D_{21}}}(Q) + Y_{\mathrm{D_{01}D_{22}}}(Q)\} \\ &\quad + 4\{Y_{\mathrm{D_{01}D_{11}}}(Q) + Y_{\mathrm{D_{11}D_{31}}}(Q) + Y_{\mathrm{D_{11}D_{32}}}(Q)\}\Big], \end{aligned} \tag{18}$$

respectively. For the model with freely rotating peripheral molecules, we assumed that the positions of six deuterons at a larger distance within the peripheral molecules are reduced approximately to the positions of peripheral oxygens on the average. Then, the $S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q)$ and $S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q)$ can be written as

$$S_{\mathrm{m.p}}^{(\mathrm{OD})}(Q) = \frac{1}{5}[2Y_{\mathrm{O_1D_{21}}}(Q)+3Y_{\mathrm{O_1D_{31}}}(Q)+6Y_{\mathrm{O_2D_{11}}}(Q) +9Y_{\mathrm{O_1O_2}}(Q)] \tag{19}$$

and

$$S_{\mathrm{m.p}}^{(\mathrm{DD})}(Q) = \frac{1}{10}[Y_{\mathrm{D_{31}D_{41}}}(Q)+8Y_{\mathrm{O_2D_{11}}}(Q)+10Y_{\mathrm{O_1D_{31}}}(Q) +3Y_{\mathrm{O_1O_2}}(Q)], \tag{20}$$

respectively.

Finally, for the $S_{\mathrm{C}}(Q)$ required in the calculation of the inter-pentamer contribution (the second term in the right hand side of Eq. 12), we can use the observed X-ray intensity data assuming the molecular center to be at the oxygen nucleus.

Interpretation of Experimental Data

We calculated first the total neutron structure factor $S_{\mathrm{m}}(Q)$ for the tetrahedral pentamer model using Eqs. 12—20, compared the calculated curves with the experimental data.

Calculation of the $S_{\mathrm{m}}^{\mathrm{p}}(Q)$. The intra-pentamer contribution $S_{\mathrm{m}}^{\mathrm{p}}(Q)$ (the first term of Eq. 12) was calculated by using Eq. 15 together with Eqs. 16—20, and the curves obtained at each stage of the calculations were compared with the corresponding experimental data.

The intramolecular contribution $S_{\mathrm{m}}^{(1)}(Q)$ calculated by use of Eq. 15 are shown in Fig. 4 for four possible cases assumed for the intramolecular structure: (1) the intramolecular oxygen-to-deuteron distance $r_{\mathrm{OD}}=0.96$ Å and the deuteron-to-deuteron distance $r_{\mathrm{DD}}=1.52$ Å, corresponding to the molecule in the vapor when all the DOD angle is 104.5°, (2) $r_{\mathrm{OD}}=1.01$ Å and $r_{\mathrm{DD}}=1.65$ Å, corresponding to the molecule in heavy ice-I when all the DOD angle is 109.5°, (3) the earlier "revised watery model,"[6,7,16] and (4) the equally weighted average values, $r_{\mathrm{OD}}=0.98$ Å and $r_{\mathrm{DD}}=1.60$ Å, when all the DOD angle is taken to be 109.5°. The $S_{\mathrm{m}}^{(1)}(Q)$ calculated for the case (3) is found to be quite identical with that for the case (4) over all range of Q. For the calculated curves (Fig. 4) in comparison with the observed data (Fig. 1), the best fit curve with observed $S_{\mathrm{m}}(Q)$ for the larger Q region ($Q \gtrsim 6$ Å^{-1}) is obtained in the cases (3) and (4). The calculated $S_{\mathrm{m}}^{(1)}(Q)$ curve for the case (4) is indicated in Fig. 1. Then, in the analysis of diffraction data in the following sections, we shall use the values of the case (4) for intramolecular parameters.

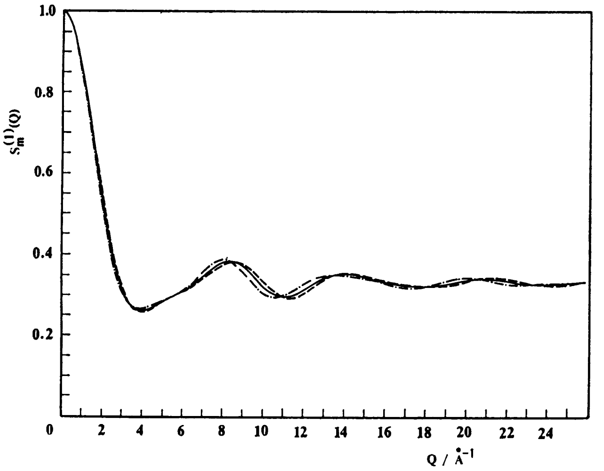

Fig. 4. Calculated intramolecular structure factor $S_{\mathrm{m}}^{(1)}(Q)$ for heavy water.

——: $S_{\mathrm{m}}^{(1)}(Q)$ for the averaged intramolecular parameters ($r_{\mathrm{OD}}=0.98$ Å, $r_{\mathrm{DD}}=1.60$ Å, and DOD angle=109.5°) and that for the revised watery model,[6,7] ($\varepsilon=0.0047$), ------: $S_{\mathrm{m}}^{(1)}(Q)$ for the vapor molecule ($r_{\mathrm{OD}}=0.96$ Å, $r_{\mathrm{DD}}=1.52$ Å, and DOD angle=104.5°), ($\varepsilon=0.0057$), –·–·–: $S_{\mathrm{m}}^{(1)}(Q)$ for the heavy ice-I molecule ($r_{\mathrm{OD}}=1.01$ Å, $r_{\mathrm{DD}}=1.65$ Å, and DOD angle=109.5°), ($\varepsilon=0.0061$). ε is a measure for indicating the deviations of $S_{\mathrm{m}}^{(1)}(Q)$ from the experimental data, and it is expressed as[16]

$$\varepsilon = \{\sum_{i=1}^{N}[S_{\mathrm{m}}(Q_i)_{\mathrm{obsd}} - S_{\mathrm{m}}^{(1)}(Q_i)^2]\}^{1/2}/\sum_{i=1}^{N}[S_{\mathrm{m}}(Q_i)_{\mathrm{obsd}}],$$

where N is the number of data points in the fitting range of Q, 8—25 Å^{-1}.

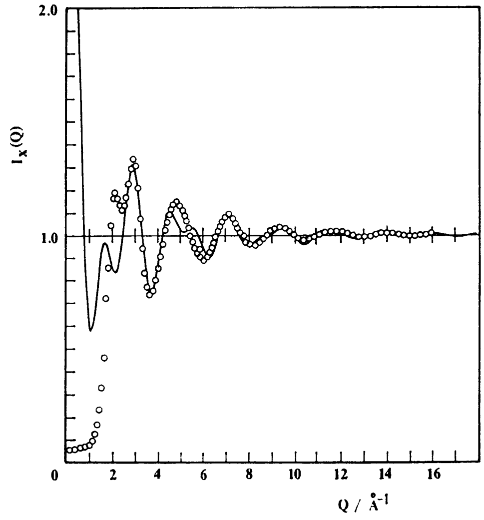

Fig. 5. The comparison between the calculated $[1+S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)]$ and the observed X-ray intensity function $I_{\mathrm{x}}(Q)$.

○: Observed $I_{\mathrm{x}}(Q)$ by Narten *et al.*,[1,9] ——: calculated $[1+S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)]$ for the regular tetrahedral pentamer model.

The $S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)$ was calculated by using Eq. 16. The value of distance r_{OO} for the hydrogen-bonded O–D···O was taken to be 2.85 Å from various sources,[1,2,5,9,12,15,20,21] and the O–O–O angle was taken to be the tetrahedral angle (109.5°). The factor $S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)$ is also known from X-ray diffraction. The X-ray diffraction pattern is almost completely determined by oxygen-oxygen pairs only. Then, the calculated values of $[1+S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)]$ for the model proposed can be compared with the X-ray data. The function $[1+S_{\mathrm{m.p}}^{(\mathrm{OO})}(Q)]$ calculated from Eq. 16 is shown in Fig. 5 together with the total experimental data. The calculated curve is in agreement with the data of Narten *et al.* on the whole, except for the deviation in the first peak at 2.1 Å^{-1} and that in the range of $Q=4.5$—6 Å^{-1}. The main contribution

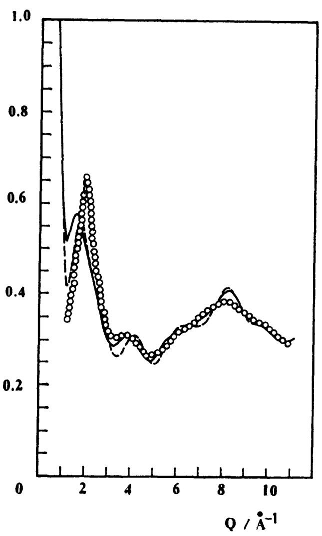

Fig. 6. The comparison between the calculated $S_{\rm m}^{\rm P}(Q)$ for the regular tetrahedral pentamer model and the observed neutron structure factor $S_{\rm m}(Q)$.
○: Observed $S_{\rm m}(Q)$, ——: calculated $S_{\rm m}^{\rm P}(Q)$ for the C_{2v} symmetry structure, ------: calculated $S_{\rm m}^{\rm P}(Q)$ for the freely rotating structure.

to the diffraction data at low Q region ($Q \lesssim 2$ Å^{-1}) comes from the long range interactions of molecules and so the contribution from the interaction pairs between pentamers is expected to recover the deviation of the first peak. Then, the result of the analysis of X-ray data suggests the essential effectiveness of the regular tetrahedral pentamer model.

In order to obtain the $S_{\rm m}^{\rm P}(Q)$, the calculation of $S_{\rm m.p}^{\rm (OD)}(Q)$ and $S_{\rm m.p}^{\rm (DD)}(Q)$ as the intra-pentamer contribution is required further, and we performed it for the C_{2v} symmetry model by using Eqs. 17 and 18, and also for the freely rotating model by using Eqs. 19 and 20. The $S_{\rm m}^{\rm P}(Q)$ thus obtained are shown in Fig. 6 together with the total experimental data. As clearly seen in Fig. 6, the curve for the freely rotating model is slightly deviated from that for the C_{2v} symmetry model, but, except for the first peak region ($Q \lesssim 3$ Å^{-1}) which is attributed to the long range (inter-pentamer) interactions of molecules, the agreement between the two calculated $S_{\rm m}^{\rm P}(Q)$ curves and the experimental data is essentially satisfactory. The comparison between the calculated $S_{\rm m}^{\rm P}(Q)$ and the observed total $S_{\rm m}(Q)$ shows that the structure factor of liquid water is well-reproduced by the $S_{\rm m}^{\rm P}(Q)$ only except for the lower Q region ($Q \lesssim 3$ Å^{-1}), that is, $S_{\rm m}(Q) \simeq S_{\rm m}^{\rm P}(Q)$ for $Q \gtrsim 3$ Å^{-1}.

Calculation of the Total Structure Factor $S_{\rm m}(Q)$. In the calculated values shown in Figs. 5 and 6 the contribution from the inter-pentamer atomic pairs (the second term in Eq. 12) is not contained. In order to estimate that contribution, we calculated the second term $f_{2\rm U}(Q)[S_{\rm C}(Q) - S_{\rm m.p}^{\rm (OO)}(Q) - 1]$ using Eqs. 14 and 16 for the $f_{2\rm U}(Q)$ and $S_{\rm m.p}^{\rm (OO)}(Q)$ together with the observed X-ray intensity data for the $S_{\rm C}(Q)$. Its values are shown in Fig. 7 as a dash-dot line. As seen in Fig. 7, the inter-cluster term contributes only in the lower Q region, $Q \lesssim 3$ Å^{-1}.

The total $S_{\rm m}(Q)$ curves thus calculated as the sum of all terms described in the preceding items by using Eq. 12 together with Eqs. 13—20 for the two orientational arrangements (the C_{2v} symmetry model and the freely rotating model) are shown in Fig. 7 in comparison with the observed $S_{\rm m}(Q)$. The agreements between the calculated curves and the scattering data are excellent on the whole, though the detailed shape of $S_{\rm m}(Q)$ is less well-reproduced for the freely rotating model compared with the C_{2v} model. The result suggests that the extent of orientational correlation of liquid water lies between these two extremes.

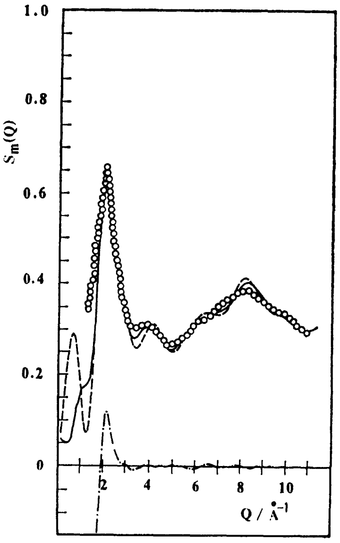

Fig. 7. The comparison between the calculated $S_{\rm m}(Q)$ for the regular tetrahedral pentamer model and the observed neutron structure factor $S_{\rm m}(Q)$.
○: Observed $S_{\rm m}(Q)$, ——: calculated $S_{\rm m}(Q)$ for the C_{2v} symmetry structure, ------: calculated $S_{\rm m}(Q)$ for the freely rotating structure, —·—·—: $f_{2\rm U}(Q)$-$[S_{\rm C}(Q) - S_{\rm m.p}^{\rm (OO)}(Q) - 1]$.

We see that the behavior of the curve near 4 Å^{-1} is essential for the adequacy of the model as stated in Page and Powles' paper.[4] From this point of view, it is noticeable that the agreement with respect to the bump at *ca.* 4 Å^{-1} is achieved satisfactorily without any adjustable parameters. Especially, in addition to this agreement concerning the bump at *ca.* 4 Å^{-1}, the excellent agreement with respect to the first peak justifies the assumption that liquid water is composed of the aggregate of the regular tetrahedral pentamers on the average. Thus, we can conclude from the present result that the regular tetrahedral pentamer model is considered to be one of the best structure models of liquid water.

Discussion

Comparison with the Page and Powles' Analysis.[4] Page and Powles' analysis of the neutron diffraction data of liquid heavy water has a marked feature in which the orientational correlation between molecules is separated from the positional one between molecular centers. This separation is exact when there is no orientational correlation for any intermolecular distances (the completely uncorrelated orientation model), and then, the structure factor $S_m(Q)$ becomes

$$S_m(Q) = f_1(Q) + f_{2U}(Q)[S_C(Q)-1], \tag{21}$$

where

$$f_1(Q) = \Sigma^{-2}\langle|\sum_n b_n \exp(i\vec{Q}\cdot\vec{r}_{cn})|^2\rangle. \tag{22}$$

$f_1(Q)$ is identical with $S^m_{(1)}(Q)$ in the present paper. On the other hand, Eq. 12 is rewritten as follows,

$$\begin{aligned} S_m(Q) = {} & S_m^{(1)}(Q) + f_{2U}(Q)[S_C(Q)-1] \\ & + [S_m^p(Q) - S_m^{(1)}(Q) - f_{2U}(Q)S_{m.p}^{(OO)}(Q)]. \end{aligned} \tag{23}$$

The third term in Eq. 23 clearly originates from the orientational correlation of molecules within the clusters (see Appendix).

From the comparison of Eq. 23 with Eq. 21, the feature of our present analysis can be understood. The most important point is the presence of additional terms in Eq. 23 resulting from the pentamer structure. The terms vanish for the completely-uncorrelated orientation model and then Eq. 23 reduces to Eq. 21.

In another extreme of Page and Powles' treatment, that is, for the completely-correlated orientation model (Eq. 7 in Ref. 4), the $S_m(Q)$ was expressed as

$$S_m(Q) = f_1(Q) + f_{2C}(Q)[S_C(Q)-1]. \tag{24}$$

The orientational correlation between molecules was introduced through the replacement of $f_{2U}(Q)$ by $f_{2C}(Q)$. This is compared with the feature in our model that the third term in Eq. 23 expresses directly the correlated-orientation effect between molecules within clusters. Page and Powles' assumption of complete correlated orientation which is independent of the distance apart is, however, too severe in principle. In the analysis carried out by Page and Powles, they could not succeed to reproduce the bump at 4 Å^{-1} in the $S_m(Q)$ curve calculated, and they rejected all the model treated in their paper. The most important reason for their failure is considered to lie in their procedure of analysis.

Interstitial Model. We examine the "interstitial model," which consists of the regular tetrahedral pentamers and non-hydrogen-bonded monomers, where the positions of its monomer oxygens are restricted to the four triad axes of the regular tetrahedron formed by pentamer oxygens. Then, one tetrahedral pentamer plus N_i monomers ($N_i \lesssim 4$) is regarded as the basic structure unit of this model.

The X-ray intensity function $I_x^{in}(Q)$ which corresponds to $[1+f_3(Q)]$ in Eq. 7 becomes

$$\begin{aligned} I_x^{in}(Q) = {} & 1 + S_{m.p}^{(OO)}(Q) + \frac{1}{(N_c+N_i)}[2(N_i-1)Y_{O_iO_2}(Q) \\ & + 2N_i\{Y_{O_iO_3}(Q) + Y_{O_iO_1}(Q) + Y_{O_iO_4}(Q)\}], \\ & [N_i = 1, 2, 3, \text{and } 4) \end{aligned} \tag{25}$$

where N_c is the number of molecules within a cluster, being taken to be 5 for the pentamer. O_i denotes the oxygen atom of the interstitial molecules. The number of interstitial molecules N_i per pentamer is considered to be not larger than one practically.[11,22] Then, for the present purposes, it is sufficient for us to take into consideration the following two cases only: $N_i=1$ and 2. The calculated $I_x^{in}(Q)$ curves are shown in Fig. 8 in comparison with the experimental data. The two $I_x^{in}(Q)$ curves deviate appreciably from the experimental data, and thus, the interstitial model should be rejected.

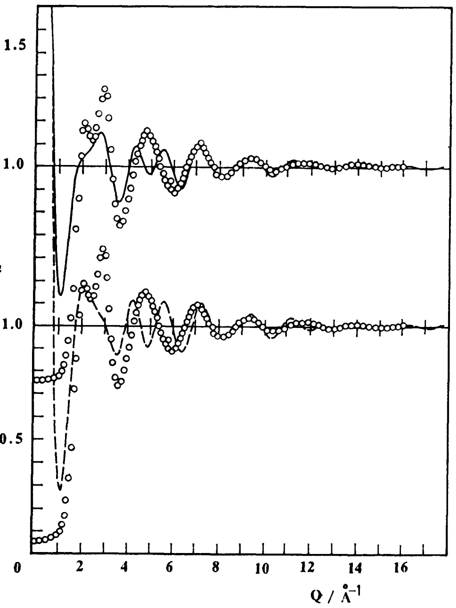

Fig. 8. The comparison between the calculated $I_x^{in}(Q)$ for the interstitial model with variation of the number of interstitial molecules N_j and the observed X-ray intensity function $I_x(Q)$.
○: Observed $I_x(Q)$ by Narten *et al.*,[1,9] ——: calculated $I_x^{in}(Q)$ ($N_i=1$), ------: calculated $I_x^{in}(Q)$ ($N_i=2$).

Comment on Narten's Near-neighbor Model. The authors pointed out formerly that Narten's later model (the "near-neighbor model") was physically unacceptable despite its success in the calculation of $QS_m(Q)$ curves because several unplausible parameters were used.[6] Here, we discuss the defect of Narten's model in comparison with the present analysis.

Narten's near-neighbor model consists of a tetrahedral arrangement of molecules around a central molecule and a continuum region outside of the discrete near-neighbor structure.[5] In the calculation of $S_m(Q)$ by this model, the contribution of atomic pairs at various distances from a central molecule were summed up, where the molecule was taken as the origin. Accordingly, the contribution of the atomic pairs between the peripheral molecules within the discrete structure, for example, is not contained substantially in the calculation of the contribution of the discrete structure. In this respect, Narten's model differs from our tetrahedral model essentially. As the result, the curve calculated from the discrete structure only is found to deviate largely from the observed data. Thus, there appears an intensive contribution from the continuum region beyond a distance r_c taken as a measure of the extent of the discrete structure as described in his paper,[23,24] and the latter contribution is found to play a dominant role for the overall agreement between the calculated $S_m(Q)$ and the observed data by using r_c as a disposable parameter.

According to the same procedures as described in Narten's paper,[5,23] we calculated $S_m(Q)$ using quite identical parameters except for the value of r_c, its magnitude being not specified in those papers.[5,23] As reported previously by the authors,[6] a practically complete fit of the calculated $S_m(Q)$ curve with the observed data was obtained for the assignment of $r_c = 3$ Å. For values larger than 3 Å a good fit was not obtained. Thus, in the analysis using Narten's near-neighbor model, the fitness of the calculated curve with the observed data is influenced decisively by the assignment of the value r_c.[6,25] Narten stated later in his review[24] that "the contribution of longer distances can be estimated as arising from a uniform distance distribution starting at r_c, the radius of sphere of volume $(N+1)/\rho_0$, ρ_0 being the bulk density of liquid water. Using Eq. 7 (in his review; Ref. 24) and adjusting by least squares the distance r_0 and the mean-square variations in both r_0 and r_c, we find that a value of $N=4.4$ gives the best agreement with the experimental curves for water at all temperatures." According to this description the magnitude of r_c is given to be about 3 Å from the relation: $(N+1)/\rho_0=(4\pi/3)r_c^3$ using $N=4.4$. Considering from the size of the discrete structure, however, the magnitude of $r_c=3$ Å is clearly too small and physically unacceptable, of course.

Thus, from all the consideration described above Narten's model should be said to be implausible physically in spite of its successful appearance.

Concluding Remarks

A general expression of the neutron structure factor for liquid regarded as an aggregate of small molecular clusters was obtained. The equations derived are widely applicable to liquids for analyzing diffraction data under due assumptions. We applied it to water and obtained the following conclusions:

1) The regular tetrahedral pentamer model is the best as a structure model of water in interpreting neutron diffraction data combined with X-ray results,

2) The interstitial model composed of tetrahedral pentamers and unbonded monomers is rejected because of the large deviations of calculated curves from experimental data,

3) Narten's near-neighbor model can not be accepted, because it is impossible to obtain calculated structure factor fitted with experimental data without assigning unreasonable value to its main disposable parameter r_c,

4) Page and Powles' (completely-correlated) orientation model has turned out to bring a too severe restriction with respect to orientational correlation compared with the authors' model which is considered to be the main reason of the deviation of their calculated curves from experimental data.

Appendix

In the right hand side of Eq. 6, we can separate the intramolecular terms from the intermolecular contributions. Then, Eq. 6 becomes

$$S_m(Q) = f_1(Q) + f_{2U}(Q)[S_C(Q)-1]$$
$$+\Sigma^{-2}N_c^{-1}\{\langle\sum_{l\neq l'}\exp(\vec{r}_{cll'})\sum_{n_l,n_{l'}}b_{n_l}b_{n_{l'}}\exp[i\vec{Q}\cdot(\vec{r}_{cn_l}-\vec{r}_{cn_{l'}})]\rangle$$
$$-\langle\sum_{l\neq l'}\exp(i\vec{Q}\cdot\vec{r}_{cll'})\rangle[\sum_{n}b_n\langle\exp(i\vec{Q}\cdot\vec{r}_{cn})\rangle]^2\}.$$

The third term in Eq. 23 corresponds to the last term of this equation which means the orientational correlations of molecules within the clusters.

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