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Molecular clusters and correlations in water by x-ray and neutron diffraction

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The combined analysis of x-ray- and neutron-diffraction data of liquid water and heavy water exhibits distinct molecular tetrahedral pentamer clusters (in C_{2v} symmetry) in water due to hydrogen bonding. The center structure is derived from the diffraction data and used to evaluate through the model intermolecular partial structures and partial correlations in water. The results are compared with the available experimental and computer-simulated data.

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I. INTRODUCTION

Substantial progress has been made over the past three decades on the detailed structural arrangement of molecules in liquid water by diffraction methods [1–10] and computer-simulation techniques [11–15]. It is now accepted that in water, unlike simple liquids (e.g., argon), hydrogen bonding plays a dominant role in structure and dynamics and significantly contributes to the anomalous characteristics of water in various phases [16]. Amorphous ice, or the "glassy" form of water, has been modeled as possessing a tetrahedral coordinated network [17]. Diffraction studies on normal and supercooled liquid D_2O generally show that the geometric features of the network structure are retained in the dynamic disordered state of the liquid phase and the most dominant local environment of a water molecule in the liquid state at room temperature is, on average, nearly tetrahedral geometry [2]. The question asked, however, is whether the average configuration of nearest neighbors is a regular tetrahedral unit or not. It is in principle possible to examine subtle differences in the molecular conformations in complex hydrogen-bonded liquids by means of difference techniques [18–20], but limitations of the method greatly restrict extraction of useful information in most cases. Because the general method of diffraction analysis is lacking and the true features of complex water-water potential are hardly accessible in present computer-simulation work, the picture remains quite obscure even today. Despite limitations, a number of models of water in liquid state have been proposed over the years [3–7].

Ohtomo, Tokiwano, and Arakawa [7] showed that a combined analysis of x-ray- and neutron-diffraction data suggests the presence of regular tetrahedral pentamer cluster units of liquid water in C_{2v} symmetry and this model appears, to us, to be the best average intermolecular structure of liquid water. In their analysis Ohtomo, Tokiwano, and Arakawa [7] used the center structure given by the x-ray-diffraction analysis of Narten and Levy [3] and computed the neutron molecular-structure factors based on their model. Their results showed that the observed neutron data could be reproduced well in the intermediate wave-vector (Q) region. However, it is to be noted that for distinct (intermolecular) structure function the agreement is not convincing. In their later paper Ohtomo, Tokiwano, and Arakawa [8] employed a mixture model of monomers and regular tetrahedral pentamers and reproduced the neutron molecular-structure factors even at elevated temperatures, but again not so well for the intermolecular term. This is the reason that we find the matter still open to detailed combined analysis via x-ray- and neutron-diffraction data.

Because of the large scattering length of deuterium, we believe that the neutron-diffraction data on deuterated sample would be more suitable to extract intrastructure, as the total-structure function is dominated by the intrastructure term. On the other hand, since the scattering factor of hydrogen is relatively small, the x-ray-diffraction data on a normal sample would be dominated by the intermolecular term (Fig. 1). Since the information for the intermolecular structure is limited to intermediate wave-vector region where the x-ray OH and HH terms contribute substantially, we stress that x-ray data would be quite suitable for the study of the intermolecular structure involving both positional and orientational correlations. The relatively small neutron distinct-structure function is dominated by OD and DD terms [5] and since only the orientational correlation is well defined, it is less useful to extract intermolecular structure. Narten and Levy [3] evaluated directly the intermolecular center-center structure factor (also, equivalently, the OO structure factor) from the x-ray-diffraction data on normal water assuming the molecule to act as a single unit. We have, however, taken up Narten and Levy's x-ray data at 25 °C and evaluated the distinct-structure function using the knowledge of an equally weighted average intrastructure from the neutron data on heavy water [7]. We have then evaluated the intermolecular center-center structure factor through the regular tetrahedral pentamer cluster model in C_{2v} symmetry [7]. The structure evaluated in this way agrees extremely well with Narten and Levy's directly evaluated center structure [3] and this indicates that the proposition is correct. We then show that the model center structure reproduces quite well the total structure function for a number of available neutron-diffraction data. Based on the model, we have evaluated the partial structures and then done

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Fourier inversion to compute the model atom-atom pair-distribution functions. Our results are compared with those of Narten, Thiessen, and Blum [6] and Soper and Phillips [10], and also computer-simulated results [11]. Finally, we have discussed the special features of the network structure exhibited through more sensitive direct-correlation function.

II. THEORY FOR REGULAR MOLECULAR CLUSTERS

The general expression for total structure function $H(Q)$ devoid of a self-term is given by [21]

$$H(Q)=N_m^{-1}M\left\langle \sum_{i,j}\sum_{n_i,n_j} f_{n_i}f_{n_j}\exp(i\mathbf{Q}\cdot\mathbf{r}_{n_in_j})\right\rangle , \tag{1}$$

where N_m is the number of molecules in the sample, f_n's are scattering-length (neutron case) or Q-dependent atomic scattering factors (x-ray case) of the nth nucleus or atom, i and j label molecules in liquid, n_i is the nth nucleus or atom of the ith molecule, $\mathbf{r}_{n_in_j}$ is the corresponding vector distance, and $M=[\sum_n f_n]^{-2}$.

For liquids composed of molecular clusters, following Ohtomo, Tokiwano, and Arakawa [7], the expression (1) can be separated into two contributions: atom-pair interaction terms within the cluster, i.e., the cluster structure function $H_c^m(Q)$, and the intercluster term, because a liquid can always be regarded virtually as an aggregate of small clusters of various sizes. Thus we have

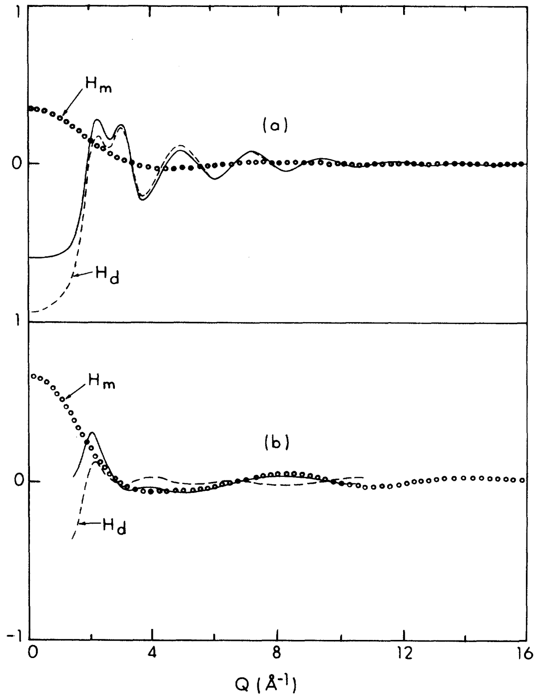

FIG. 1. Diffraction data of water and heavy water at 25 °C. (a) ——, x-ray $H(Q)$ data of Narten and Levy [3]. ○○○, x-ray $H_m(Q)$; — — —, x-ray $H_d(Q)$. (b) ——, Neutron $H(Q)$ data of Ohtomo, Tokiwano, and Arakawa [7]; ○○○, neutron $H_m(Q)$; — — —, neutron $H_d(Q)$.

$$H(Q)=H_c^m(Q)+N_m^{-1}M\left\langle \sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\sum_{l_\alpha,l'_\beta}\sum_{nl_\alpha,nl'_\beta} f_{nl_\alpha}f_{nl'_\beta}\exp(i\mathbf{Q}\cdot\mathbf{r}_{nl_\alpha nl'_\beta})\right\rangle , \tag{2}$$

with

$$H_c^m(Q)=N_m^{-1}M\left\langle \sum_{\substack{\alpha,\beta\\ \alpha=\beta}}\sum_{l_\alpha,l'_\beta}\sum_{nl_\alpha,nl'_\beta} f_{nl_\alpha}f_{nl'_\beta}\exp(i\mathbf{Q}\cdot\mathbf{r}_{nl_\alpha nl'_\beta})\right\rangle ,$$

where α and β denote clusters, l and l' molecules. Denoting $\mathbf{r}_{cl_\alpha l'_\beta}$ the distance from the center of the molecule l_α to that of the molecule l'_β, Eq. (2) takes the form

$$H(Q)=H_c^m(Q)+N_m^{-1}M\left\langle \sum_{\substack{\alpha,\beta\\ \alpha\neq\beta}}\sum_{l_\alpha,l'_\beta}\exp(i\mathbf{Q}\cdot\mathbf{r}_{cl_\alpha l'_\beta})\sum_{nl_\alpha,nl'_\beta} f_{nl_\alpha}f_{nl'_\beta}\exp[i\mathbf{Q}\cdot(\mathbf{r}_{cnl'_\beta}-\mathbf{r}_{cnl_\alpha})]\right\rangle , \tag{3}$$

where $\mathbf{r}_{cnl_\alpha}$ is the distance of the nth nucleus or atom within the cluster α from the center of the molecule l_α.

Considering now the case of identical clusters consisting of N_c molecules and assuming that molecules belonging to different clusters are orientationally uncorrelated (i.e., clusters are uncorrelated [7]) we have

$$H(Q)=H_c^m(Q)+F_{2u}(Q)[S_c(Q)-F_3(Q)-1] , \tag{4}$$

where now

$$H_c^m(Q)=N_m^{-1}M\left\langle \sum_{l,l'}\sum_{nl,nl'} f_{nl}f_{nl'}\exp(i\mathbf{Q}\cdot\mathbf{r}_{nlnl'})\right\rangle$$

as defined,

$$F_{2u}(Q)=M\left[\sum_{nl,nl'} f_n\langle \exp(i\mathbf{Q}\cdot\mathbf{r}_{nlnl'})\rangle\right]^2 ,$$

a form factor representing completely uncorrelated orientational configuration between molecules,

$$S_c(Q)=1+N_m^{-1}\left\langle \sum_{\substack{i,j\\ i\neq j}}\exp(i\mathbf{Q}\cdot\mathbf{r}_{c_{ij}})\right\rangle ,$$

the intermolecular center structure factor of the liquid, and

$$F_3(Q)=N_c^{-1}\left\langle \sum_{\substack{l,l'\\ l\neq l'}}\exp(i\mathbf{Q}\cdot\mathbf{r}_{cll'})\right\rangle ,$$

a structure factor resulting from the molecular-center pairs within the cluster.

A further separation of Eq. (4) gives

$$H(Q)=H_m(Q)+H_c(Q)+F_{2u}(Q)[S_c(Q)-F_3(Q)-1] , \tag{5}$$

where

$$H_m(Q)=M\left\langle \sum_{n} \sum_{\substack{n,n'\\ n\neq n'}} f_n f_{n'} \exp(i\mathbf{Q}\cdot\mathbf{r}_{nn'})\right\rangle$$

is the molecular structure function and

$$H_c(Q)=N_c^{-1}M\left\langle \sum_{\substack{l,l'\\ l\neq l'}} \sum_{nl,nl'} f_{nl} f_{nl'} \exp(i\mathbf{Q}\cdot\mathbf{r}_{nlnl'})\right\rangle$$

is the intermolecular contribution within a cluster. The second and third terms in Eq. (5) combine to form the conventional intermolecular "distinct"-structure function $H_d(Q)$ [21]. Thus we have

$$H_d(Q)=H_c(Q)+F_{2u}(Q)[S_c(Q)-F_3(Q)-1] . \tag{6}$$

The second term in Eq. (6), the intercluster contribution, goes to zero for large Q and so $H_d(Q)\to H_c(Q)$. Equation (6) is thus very useful in identifying a plausible cluster present in the liquid.

We have, in general,

$$\langle \exp(i\mathbf{Q}\cdot\mathbf{r}_{nn'})\rangle = j_0(Qr_{nn'})\exp\left[-\frac{\gamma_{nn'}^2}{2}Q^2\right] ,$$

where $\gamma_{nn'}$ is the root-mean-square (rms) deviation of the local instantaneous atom-atom separation distance $r_{nn'}$ and $j_0(x)=x^{-1}\sin x$. In the specialized case of a regular tetrahedral pentamer model of water in C_{2v} symmetry [7] we have

$$H_m(Q)=2M[2f_O f_z Y_{Oz}(Q)+f_z^2 Y_{zz}(Q)] , \tag{7a}$$

$$F_{2u}(Q)=M[f_O+2f_z Y_{Oz}(Q)]^2 , \tag{7b}$$

$$H_c(Q)=M\sum_{\alpha}\sum_{\beta} f_\alpha f_\beta H_c^{(\alpha\beta)}(Q) . \tag{7c}$$

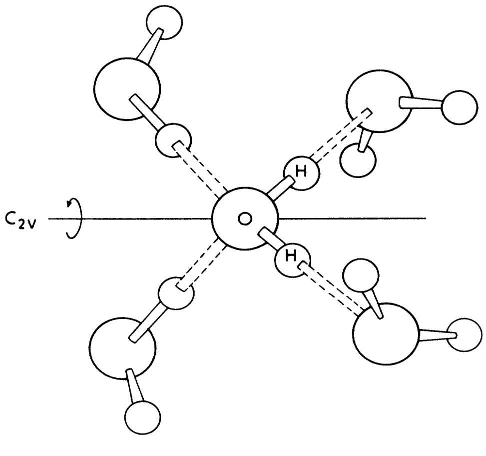

FIG. 2. Regular tetrahedral pentamer cluster model in C_{2v} symmetry of liquid water at 25 °C.

Explicit expressions for $H_c^{(\alpha\beta)}(Q)$ are given in Ref. [7] and hence are not shown. Here z refers to atom D or H and $Y_{nn'}(Q)=\langle \exp(i\mathbf{Q}\cdot\mathbf{r}_{nn'})\rangle$. The model structure is shown in Fig. 2.

III. PARTIAL STRUCTURES AND CORRELATIONS VIA CLUSTER MODEL

The intermolecular distinct-structure function $H_d(Q)$ can be written as [22]

$$H_d(Q)=M\sum_{\alpha}\sum_{\beta} f_\alpha f_\beta H_{\alpha\beta}(Q) , \tag{8}$$

where partial-structure functions $H_{\alpha\beta}(Q)=\rho h_{\alpha\beta}(Q)$ are defined by

$$h_{\alpha\beta}(Q)=\int_0^\infty d\mathbf{r}[g_{\alpha\beta}(r)-1]j_0(Qr) . \tag{9a}$$

The intermolecular atom-atom distribution $g_{\alpha\beta}(r)$ is defined so that $\rho g_{\alpha\beta}(r)d\mathbf{r}$ is the number of β atoms in a volume element $d\mathbf{r}$ at a distance r from an α atom on another molecule in a fluid of bulk number density ρ. $g_{\alpha\beta}(r)$ can be obtained from $h_{\alpha\beta}(Q)$ by Fourier inversion, i.e.,

$$g_{\alpha\beta}(r)=1+\frac{1}{(2\pi)^3}\int_0^\infty h_{\alpha\beta}(Q)j_0(Qr)d\mathbf{Q} . \tag{9b}$$

In order to evaluate partial structures through the cluster model we assume that $H_{\alpha\beta}(Q)$ is given by terms involving α-β interactions from $H_c(Q)$ and $F_{2u}(Q)$ of Eq. (6). Thus

$$H_{\alpha\beta}(Q)=H_c^{(\alpha\beta)}(Q)+F_{2u}^{(\alpha\beta)}(Q)[S_c(Q)-F_3(Q)-1] . \tag{10}$$

The procedure is similar to the one used by Orton [23]. In our case $S_c(Q)=1+H_{OO}(Q)$, since oxygen can be supposed to be at the center. The center-center radial-distribution function (CRDF) $g_c(r)$ and the center-center direct-correlation function (CDCF) $C_c(r)$ are given by

$$g_c(r)=1+\frac{1}{(2\pi)^3\rho}\int_0^\infty [S_c(Q)-1]j_0(Qr_{cc})d\mathbf{Q} , \tag{11a}$$

$$C_c(r)=\frac{1}{(2\pi)^3\rho}\int_0^\infty \{[S_c(Q)-1]/S_c(Q)\}j_0(Qr_{cc})d\mathbf{Q} . \tag{11b}$$

The evaluation of function $C_c(r)$ is important because the function is short ranged like the effective-pair potential.

IV. EVALUATION OF CENTER STRUCTURE AND TESTING THE MODEL

The best intraparameters from neutron-diffraction data [7] and the corresponding rms variation γ's from spectroscopic data [24] are shown in Table I. In Fig. 1(a) we have shown the x-ray structure function $H(Q)$ of liquid water at 25 °C extracted from Narten and Levy's data [3] together with the molecular-structure function $H_m(Q)$ and the distinct-structure function $H_d(Q)$. $H_m(Q)$ is based on the neutron-diffraction analysis [7] of the best intrastructure of the water molecule. The $H(Q)$ data of Hajdu, Lengyel, and Pálinkás [4] agree more or less with

TABLE I. Intra- and intermolecular parameters and rms variations. Asterisk denotes corresponding to best fitting of model $H_c(Q)$ and $H_d(Q)$ from experimental data.

Bond	r (Å)	γ (Å)
OH	0.98	0.0663
HH	1.60	0.1149
OH · · · O	2.85*	0.1453*
	∠H—O—H = 109.5°	

the Narten and Levy [3] data except that the data of Ref. [4] shows undue large values in the high-Q region. From Fig. 1(a) it is clear that the $H(Q)$ function is dominated by the intermolecular term $H_d(Q)$. To the contrary, the neutron $H(Q)$ [5,7] function is dominated by the intracontribution $H_m(Q)$ [Fig. 1(b)]. The intermolecular term $H_d(Q)$ for the neutron case is also shown. In general, the neutron $H_d(Q)$ function is much smaller in magnitude than the x-ray $H_d(Q)$ function and further, in the high-Q region, the neutron $H_d(Q)$ is less reliable due to a lack of consistency among the various sets of neutron data available [5,7,8]. The structure of the regular tetrahedral pentamer in C_{2v} symmetry (Fig. 2) is characterized by a single parameter—the intermolecular O—O distance which, in our case, is an adjustable parameter. The intermolecular rms variation γ is assumed to be proportional to the corresponding bond distance and taken to be 0.051 Å per 1 Å of bond distance (corresponding to the best fit) and this is used throughout the present calculation. Please note that Ohtomo, Tokiwano, and Arakawa used 0.06 Å per 1 Å of bond distance quite empirically. The calculated $H_c(Q)$ based on the model is compared with $H_d(Q)$ for both x-ray and neutron cases and shown in Fig. 3. The best agreement in both cases is obtained by a standard χ^2-fitting routine [19,20] and it corresponds to an intermolecular O—O distance of 2.85 Å. The agreement in the case of x-ray data is very good, except for the low-Q region. The difference in the low-Q region is attributed to the presence of an intercluster term which has yet to be accounted for. There is some overall agreement for neutron data too, but the agreement is obviously less conclusive. The disagreement in the neutron case is not difficult to understand. The neutron $H_d(Q)$ function of D_2O is dominated by OD and DD terms which specify orientational correlations of water molecules. The x-ray $H_d(Q)$ function of H_2O is, however, dominated by the OO term, which specifies the positional correlation among water molecules. As we have pointed out earlier, that information about intermolecular correlations is restricted to intermediate-Q range only and in this region both OH and HH, and OH in particular, contribute substantially, we feel that the intermolecular orientational correlations are also included adequately in the x-ray $H_d(Q)$ function. Hence intermolecular information regarding plausible hydrogen-bonded clustering

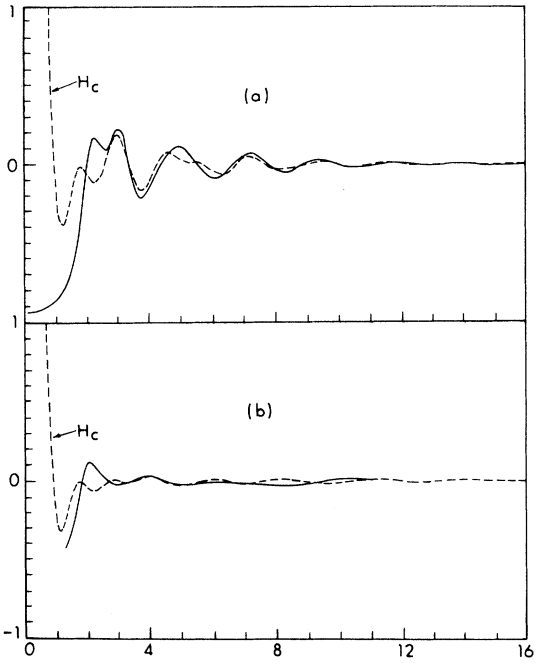

FIG. 3. The $H_c(Q)$ best fit to $H_d(Q)$ data. (a) ——, x-ray $H_d(Q)$ data of Ref. [3]; — — —, x-ray $H_c(Q)$ on the model. (b) ——, neutron $H_d(Q)$ data of Ref. [7]; — — —, neutron $H_c(Q)$ on the model.

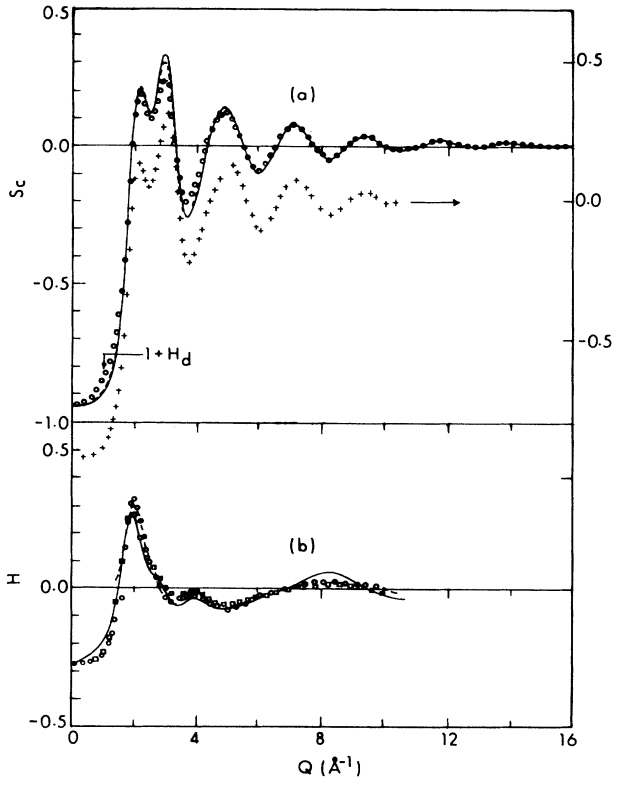

FIG. 4. (a) ——, center structure factor from the model; — — —, center structure factor (x-ray OO) of Ref. [3]; ○○○, $1+H_d(Q)$ of x-ray data (from Ref. [3]); + + +, center structure factor of D_2O at 11.2 °C (from Ref. [9]). (b) Neutron $H(Q)$ of heavy water at 25 °C. ——, from the model; — — —, Ohtomo, Tokiwano, and Arakawa [7]; ○○○, Narten [5]; □□□, Page and Powles [5].

would be more precisely defined in the x-ray $H_d(Q)$ function. Thus the agreement in Fig. 3(a) is guiding evidence to the proposition that the regular tetrahedral pentamer in C_{2v} symmetry is a good model structure of water. Also it is generally true that the neutron $H_d(Q)$ function [Fig. 3(b)] is less useful in testing any plausible clustering model in the liquid.

We then use the x-ray $H_d(Q)$ data to extract $S_c(Q)$ through Eq. (6) based on the tetrahedral pentamer model in C_{2v} and the result is shown in Fig. 4(a). Narten and Levy's [3] directly evaluated $S_c(Q)$ (which is also an OO structure factor because oxygen is at the center) is also shown. The two agree extremely well all throughout and this supports the proposed cluster model very well. We also show the function $1+H_d(Q)$ in Fig. 4(a); its difference with $S_c(Q)$ indicates the presence of OH and HH partial contributions. Bosio, Chen, and Teixeira [9] studied the isochoric temperature differentials of heavy water through x-ray diffraction. Their tabulated results for $S_c(Q)$ at 11.2 °C generally agree with our model data except at the first peak, but the cause of this disagreement is not very clear. In order to test the model further, we have used the model $S_c(Q)$ to reproduce the neutron $H(Q)$ function through Eq. (5) for a number of neutron data on D_2O [5,7] and H_2O-D_2O mixtures [6]. For H_2O-D_2O mixtures, scattering lengths used at various concentrations are those given in Ref. [6]. The comparison in Figs. 4(b) and 5 show that the present average model of liquid water is quite satisfactory. The large discrepancy in Fig. 5(d) is because the mixture is almost like pure water and with hydrogen possessing a very large incoherent scattering, the experimental data have somewhat limited accuracy. In spite of the disagreement, we see that the general feature is well produced. The reason for disagreement of the model in Fig. 4(b) with different data sets is not very clear, but still the general shape is satisfactory.

V. INTERMOLECULAR ATOM-ATOM PARTIALS AND FURTHER CONFIRMATION

To explore the model further we have obtained partial-structure functions using Eq. (10) and these are shown in Fig. 6. Thiessen and Narten [6] used their four sets of neutron data on a H_2O and D_2O mixture (Fig. 5) to extract partial structures by a least-squares method. The agreement with our model calculations is reasonable, except a distinct peak in our model at about 2 Å^{-1} in place of a hump in experimental HH partial structure. The accuracy of Thiessen-Narten partial structures is difficult to assess because these were derived from experiments with very low signal-to-noise ratio [6], although

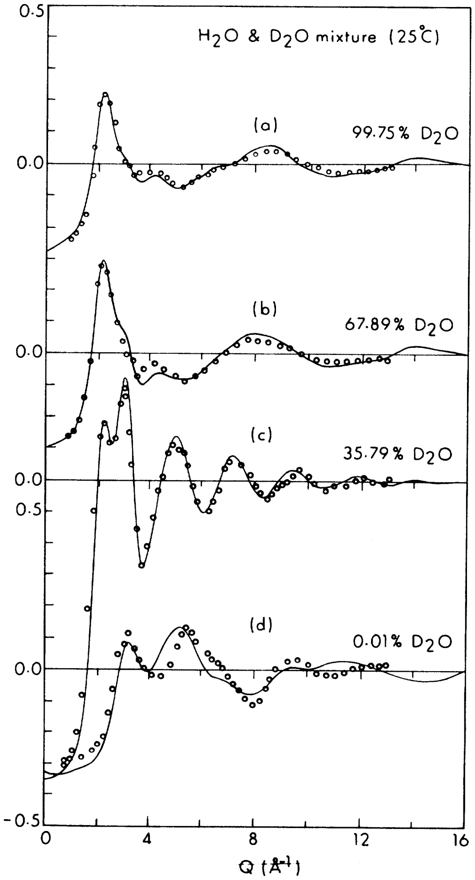

FIG. 5. Neutron $H(Q)$ of H_2O and D_2O mixture at 25 °C. ——, model; ○○○, Thiessen and Narten data [6]. (a) 99.75% D_2O, (b) 67.89% D_2O, (c) 35.79% D_2O, and (d) 0.01% D_2O.

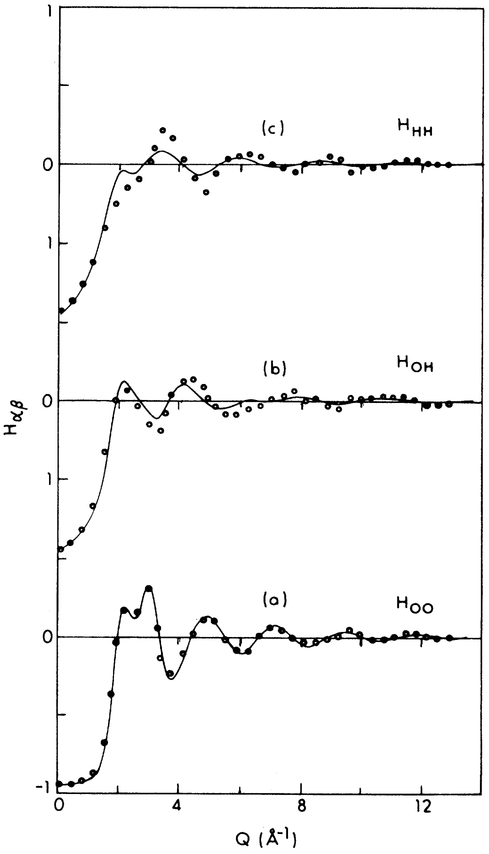

FIG. 6. Partial structure functions $H_{\alpha\beta}(Q)$ of water at 25 °C, ——, model; ○○○, Thiessen and Narten results [6]. (a) $H_{OO}(Q)$, (b) $H_{OH}(Q)$, and (c) $H_{HH}(Q)$.

the authors claimed all possible consistency checks. The more recent work on water partial structures is due to Soper and Phillips [10], who use a new subtraction method of analysis for their neutron data on light and heavy water. Results for time-of-flight (TOF) and reactor data differed to some extent despite good general agreement between the two, and no evidence [25] whatsoever existed as to the failure of the subtraction method. The general shape and peak positions of partial structures obtained from two sets of data agree well with the present results, except OH peak heights, which differ considerably.

We have also Fourier inverted partial structures to evaluate the atom-atom RDF's and these are shown in Fig. 7. This is a crucial and sensitive test for the model. Results for Narten, Thiessen, and Blum [6] based on Thiessen-Narten partial structure and also those for more recent works of Soper and Phillips [10] (from reactor data) are shown for comparison. Except for a very large OH and larger HH first peaks, results of Narten, Thiessen, and Blum agree fairly well. The agreement with the Soper-Phillips data is much better, except for small discrepancies in the first peak heights and HH peak position. Keeping in mind that there were small differences in the results for TOF and reactor data [25], the agreement is quite satisfactory. For both the Narten and Soper data the peak positions occur almost in agreement with the present results. Probably the latest work on H_2O-D_2O mixture is due to Dore [26]. The author avoided the measurements near the cancellation point ($\langle b_{\text{H-D}} \rangle = 0$) and used mixtures containing small quantities of hydrogen. The published $g_{\text{OH}}(r)$ and $g_{\text{HH}}(r)$ curves show good agreement with our curves. Our results also agree very well with the molecular-dynamics simulation results of Stillinger and Rahman [11]. More recent computer simulation of Impey, Klein, and McDonald [12] on Matsuoka-Clementi-Yoshimine water-water potential produced more or less similar results at room temperature. Results of Monte Carlo simulation based on Jorgensen's transferable intermolecular potential [13] also agree in general with our results, though beyond the first peak the simulated $g_{\text{OO}}(r)$ smooths out to one very quickly, unlike the values observed experimentally or in our case. Anyway, the comparison made is enough to indicate that the present average model is quite satisfactory. One might ask, however, as to how sensitive the RDF curves are to the choice of any specific model. It is, therefore, relevant to mention that only a small deviation from the average structure is enough to change the RDF curves significantly. For example, for a slightly different model than the present one, tetrahedral pentamer with freely rotating peripheral molecules, $g_{\text{OO}}(r)$ does not change as expected, $g_{\text{OH}}(r)$ shows changes only beyond the second peak, but $g_{\text{HH}}(r)$ changes drastically in the first peak height and position. Changes in the DCF are much more pronounced (Fig. 8).

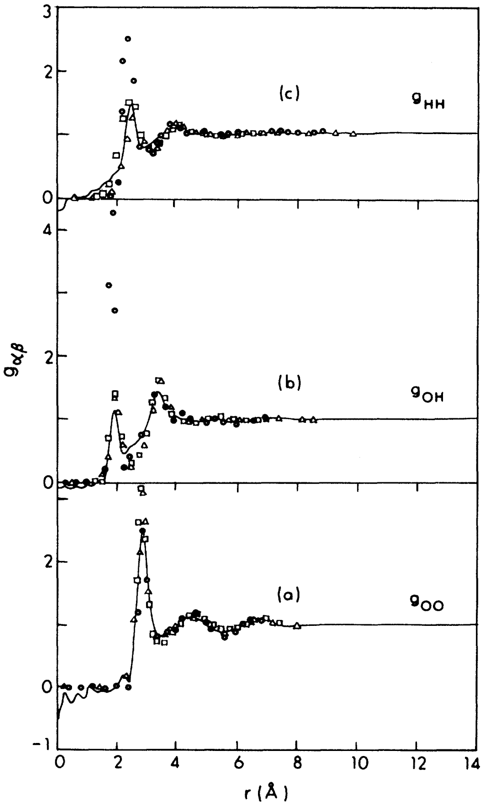

FIG. 7. Atom-atom RDF's of water at 25 °C. ——, model; ○○○, Narten, Thiessen, and Blum [6] results, □□□, computer simulated results [11]; △△△, Soper and Phillips (from Ref. [10]). (a) $g_{\text{OO}}(r)$, (b) $g_{\text{OH}}(r)$, and (c) $g_{\text{HH}}(r)$.

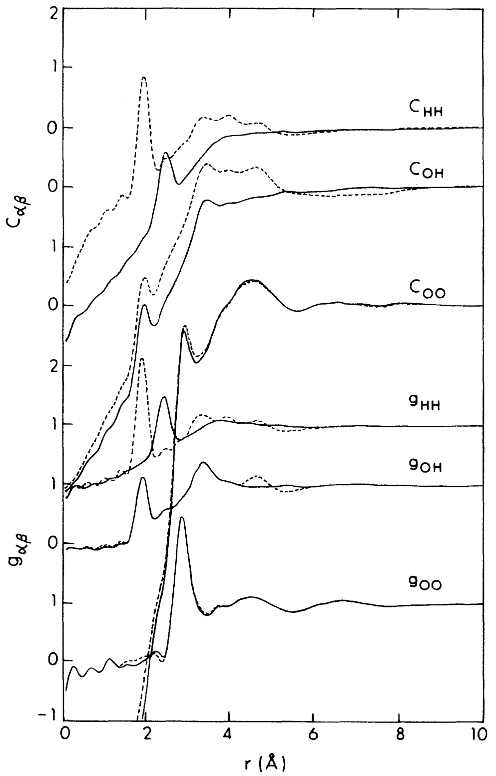

FIG. 8. $g_{\alpha\beta}(r)$ and $C_{\alpha\beta}(r)$ for two different regular tetrahedral pentamer models of water at 25 °C showing model sensitivity. ——, with C_{2v} symmetry; — — —, with freely rotating peripheral molecules.

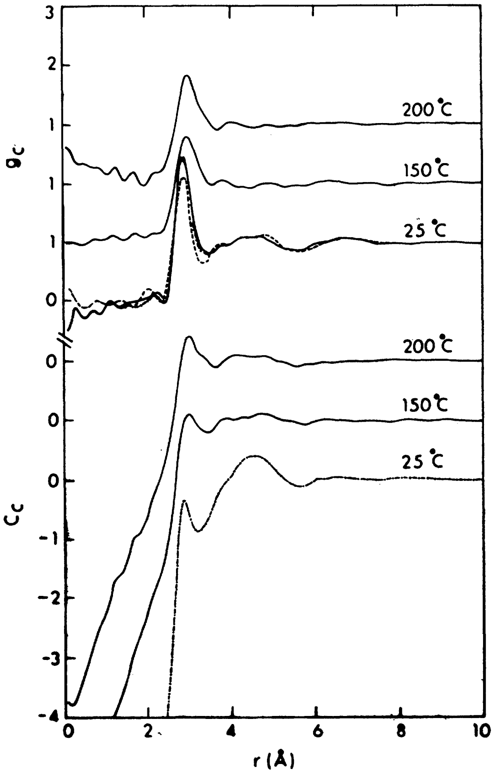

FIG. 9. $g_c(r)$ and $C_c(r)$ of water. ——, Narten and Levy (x-ray OO) of Ref. [3]; —·—·—·, from Narten $H_d(Q)$ data through the model at 25 °C; — — — Bosio, Chen, and Teixeira D_2O data at 11.2 °C (Ref. [9]).

The general feature of all RDF curves is that these are very short ranged. The $g_{OO}(r)$ is, however, relatively longer ranged and this indicates that beyond about 4 Å the positional correlation rather than orientational correlation exists. The information about clustering of molecules is restricted to the lower-Q region and so precise information about it is obtainable from x-ray data. It is also to be noted that the total real-space neutron distribution function obtained from the model $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$ also agrees well with the observed neutron results [27].

In our case too, $g_c(r)$ is equivalent to $g_{OO}(r)$ and both $g_c(r)$ and $C_c(r)$ [computed using Eq. (11b)] are shown in Fig. 9. Like simple liquids $g_c(r)$ has oscillations for large r, but unlike them (e.g., argon) $g_c(r)$ drops down to one very quickly. The $g_c(r)$ of Narten and Levy [3] and Bosio, Chen, Teixeira [9] are shown. The disagreement with the data of Bosio, Chen, and Teixeira (D_2O at 11.2 °C) is not very clear. $C_c(r)$ has, unlike simple liquids, several peaks and it has a range comparable with that of $g_c(r)$. The first peaks in $g_c(r)$ and $C_c(r)$ correspond to about $r = 2.85$ Å, the first intermolecular OO distance. The occurrence of a major peak at about $r = 4.5$ Å in the $C_c(r)$ curve indicates the presence of strong clustering correlations among the neighboring molecules. The existence of two peaks in DCF is quite unusual in simple liquids [28] and this feature in $C_c(r)$, we believe, is an indication of hydrogen-bonded clustering of the water structure. The discussion via $C_c(r)$ is more relevant and useful in the sense that $C_c(r)$ is intimately related to the center effective-pair potential. $C_c(r)$ is also a more sensitive function to the variations in low-Q structural data than $g_c(r)$ where the information about long-range correlations of the liquid lies. Evidently the center effective-pair potential will be complex in nature, probably exhibiting two distinct minima very uncommon in simple liquids but frequently occurring in systems showing effects of long-range, many-body terms [29]. It is probably more complex than the one currently used in most computer-simulation work. We have, however, good reason to believe that these bonding features will gradually vanish as the temperature is raised. In order to explore this point we have shown both $g_c(r)$ and $C_c(r)$ extracted from Narten's $S_c(Q)$ data for two higher temperatures 150 and 200 °C. In both $g_c(r)$ and $C_c(r)$ the second-neighbor peak gradually smears out while the first $C_c(r)$ peak shoots up and becomes more prominent, very similar to a peak found in simple liquids [28]. Thus the changes in $g_c(r)$ and $C_c(r)$ evidently suggest the disruption or at least nonlinearity of the hydrogen bonds at higher temperature, but the weak existence of the second peak ensures that the tetrahedral network still survives. There is now considerable evidence of hydrogen-bond disruptions and change in relative orientations of neighboring molecules at higher temperature [26,30]. The liquid is, however, nonsimple in the sense that significant oscillations exist in $C_c(r)$ at large r. We are presently trying to incorporate these features into the model at elevated temperatures. The present method of combined analysis of x-ray- and neutron-diffraction data is also useful in defining the cluster model of liquid methanol at room temperature [31].

VI. CONCLUDING REMARKS

The regular cluster model for water at room temperature, proposed by Ohtomo, Tokiwano, and Arakawa has been tested thoroughly via the x-ray- and neutron-diffraction data available in the literature. The study yields the following significant points.

(i) The regular tetrahedral pentamer cluster in C_{2v} symmetry is a good average cluster model for liquid water at room temperature.

(ii) Orientational correlations hardly extend beyond the second neighbor. Even the positional correlation is short ranged compared to simple liquids.

(iii) The two major peaks in CDCF, one negative and the other positive, are features of molecular-cluster formation. This also suggests a complex nature of average intermolecular pair interaction for water molecules at room temperature.

(iv) The method is quite general and is applicable to other systems which might exhibit distinct clusters in liquid phase.

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