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Author(s)	Matsumoto, Takaaki
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# Neutron Diffraction Experiment of Liquid Water Using the Electron LINAC

Takaaki MATSUMOTO

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## Abstract

This paper describes a Time-of-Flight neutron diffraction experiment of liquid (heavy) water at room temperature. The experiment was made by using the 45 MeV electron linear accelerator (LINAC) installed at Hokkaido University. From measurements made at scattering angles  $45^\circ$  and  $150^\circ$ , we obtained the structure factor  $S_m(Q)$  of liquid water with the wide range of  $Q$ ;  $0.9$ - $28.3 \text{ \AA}^{-1}$ . A weighted sum function  $D(R)$  of three partial pair distribution functions  $g_{mn}(R)$  was derived by performing the Fourier transformation of  $S_m(Q)$ . In the short distance region of  $D(R)$ , we determined several parameters related to the structure of the water molecule in the liquid state. Furthermore,  $D(R)$  when the long distance region which enabled us to examine the intermolecular structure of liquid water was compared with the Monte Carlo calculations by Watts, there were remarkable differences between them.

## 1. Introduction

The structure of liquid water can be studied by X-ray and neutron diffraction methods. According to Narten and Levy (1971), the X-ray diffraction method gives mainly a partial pair distribution function  $g_{oo}(R)$  of liquid water. On the other hand, the neutron diffraction pattern consists of all three partial pair distribution functions of  $g_{oD}(R)$ ,  $g_{DD}(R)$  and  $g_{oo}(R)$ . Although the contribution of  $g_{oo}(R)$  is small, the hydrogen bonding effects on the orientation of the molecules can be studied well from the functions of  $g_{oD}(R)$  and  $g_{DD}(R)$ . Recently, in several neutron diffraction studies<sup>(2,3,4,5)</sup>, liquid water was measured by neutron diffractometry on nuclear reactors.

This paper describes a neutron diffraction experiment of liquid (heavy) water which was made by a Time-of Flight neutron diffractometry using a pulsed neutron source.<sup>(6)</sup> This diffractometry is very promising for the study of such molecular liquids because it can easily be used to obtain the high  $Q$  measurement and it is free from contaminations of the higher modes of the Bragg reflection on the single crystal monochromator used on nuclear reactors.<sup>(4)</sup>

The 45 MeV electron linear accelerator (LINAC) of Hokkaido University was used as the neutron source. Our previous paper reported the preliminary measurements of liquid water which demonstrate the reliability of our neutron diffractometry.<sup>(6)</sup> The author remeasured liquid water at a scattering angle  $45^\circ$  to obtain better statistical accuracy than

the reference.<sup>(6)</sup> An additional measurement was made at scattering angle  $150^\circ$  which elicited the structure factor with the high  $Q$  up to  $28.3 \text{ \AA}^{-1}$ . In Section 2, the theoretical background for the neutron diffraction method and its application to molecular liquids is described. Section 3 presents the neutron diffraction experiment for liquid water at room temperature. In Section 4, several corrections were carried out on the experimental data to obtain the structure factor  $S_m(Q)$  of liquid water. The Fourier transform of  $S_m(Q)$  derived a weighted sum function  $D(R)$  of the three partial pair distribution functions  $g_{OD}(R)$ ,  $g_{DD}(R)$  and  $g_{OO}(R)$ .

Several parameters related to the structure of the water molecule in the liquid state were determined. Furthermore, in the long distance region,  $D(R)$  enabled us to examine the intermolecular structure, which was then compared with the Monte Carlo calculations by Watts (1974).

## 2. Theoretical Background

Here we present the theoretical background for the neutron diffraction method applied to molecular liquids. The structure factor is written as follows.<sup>(6)</sup>

$$S(Q) = \sum_{ll'} \langle b_l b_{l'} \exp(i\mathbf{Q} \cdot \mathbf{R}_{ll'}) \rangle \quad (1)$$

where  $b_l$ : scattering length of nucleus  $l$

$R_{ll'}$ : distance between nuclei  $l$  and  $l'$ .

$S(Q)$  of the molecular liquid is divided into two parts, i. e.,

$$\begin{aligned} S(Q) &= S^{\text{inc}}(Q) + S^{\text{coh}}(Q) \\ &= \sum_n N_n (\bar{b}_n^2 - \bar{b}_n^2) + N_m (\sum_\alpha \bar{b}_\alpha)^2 S_m(Q) \end{aligned} \quad (2)$$

where

$$S_m(Q) = S^{\text{coh}}(Q) / N_m (\sum_\alpha \bar{b}_\alpha)^2$$

$N_n$ : number of nuclei of species  $n$  in sample

$N_m$ : number of molecules in sample

and the summation  $\alpha$  extends over all the nuclei in the single molecule. Alternately, the structure factor  $S(Q)$  can be presented by the partial pair distribution functions  $g_{mn'}(R)$ :

$$\begin{aligned} S(Q) &= \sum_n N_n [\bar{b}_n^2 + \bar{b}_n^2 (\frac{N_n}{V}) \int d\mathbf{R} e^{i\mathbf{Q} \cdot \mathbf{R}} \{g_{nn}(R) - 1\}] \\ &\quad + \sum_{n \neq n'} \frac{N_n N_{n'}}{V} \bar{b}_n \bar{b}_{n'} \int d\mathbf{R} e^{i\mathbf{Q} \cdot \mathbf{R}} \{g_{nn'}(R) - 1\} \end{aligned} \quad (3)$$

where  $V$ : volume of sample.

From Egs. (2) and (3), we obtain the following equation,

$$\begin{aligned} i(Q) &\equiv S_m(Q) \cdot (\sum_\alpha \bar{b}_\alpha)^2 / \sum_\alpha \bar{b}_\alpha^2 - 1 \\ &= \frac{\rho}{\sum_\alpha \bar{b}_\alpha^2} [\sum_n \nu_n \bar{b}_n^2 \int d\mathbf{R} e^{i\mathbf{Q} \cdot \mathbf{R}} \{g_{nn}(R) - 1\} \\ &\quad + \sum_{n \neq n'} \nu_n \nu_{n'} \bar{b}_n \bar{b}_{n'} \int d\mathbf{R} e^{i\mathbf{Q} \cdot \mathbf{R}} \{g_{nn'}(R) - 1\}] \end{aligned} \quad (4)$$

where  $\nu_n = N_n/N_m$  : number of nuclei of species  $n$  in molecule

$\rho = N_m/V$  : number density of molecule.

The Fourier transformation of  $i(Q)$  gives the weighted sum function  $d(R)$  of the partial pair distribution functions in real space,

$$\begin{aligned} d(R) &= \frac{2}{\pi} \int_0^\infty dQ Q \sin QR \cdot i(Q) \\ &= \frac{4\pi R \rho}{\sum_\alpha \bar{b}_\alpha^2} \left[ \sum_n \nu_n^2 \bar{b}_\alpha^2 \{g_{nn}(R) - 1\} + \sum_{n \neq n'} \nu_n \nu_{n'} \bar{b}_n \bar{b}_{n'} \{g_{nn'}(R) - 1\} \right] \end{aligned} \quad (5)$$

and alternately,

$$\begin{aligned} D(R) &\equiv \frac{\sum_\alpha \bar{b}_\alpha^2}{\epsilon} \frac{d(R)}{4\pi R \rho} + 1 \\ &= \frac{\sum_\alpha \bar{b}_\alpha^2}{\epsilon} \left[ \sum_n \nu_n^2 \bar{b}_n^2 g_{nn}(R) + \sum_{n \neq n'} \nu_n \nu_{n'} \bar{b}_n \bar{b}_{n'} g_{nn'}(R) \right] \end{aligned} \quad (6)$$

where

$$\epsilon = \sum_{nn'} \nu_n \nu_{n'} \bar{b}_n \bar{b}_{n'}$$

In the case of liquid heavy water, Eq. (6) can be explicitly written by three partial pair distribution functions as follows:

$$D(R) = 0.486 g_{DD}(R) + 0.423 g_{OD}(R) + 0.091 g_{OO}(R) \quad (7)$$

Eq. (7) indicates that the function  $D(R)$  is mainly determined from the functions of  $g_{OD}(R)$  and  $g_{DD}(R)$ , which may contain useful information concerning the hydrogen bonding effects on the orientation of the molecules. It appears that the weighted sum function  $D(R)$  in Eq. (7) is useful for examining any model calculation for liquid water.

### 3. Experiment

The measurements were made using the Time-of-Flight neutron diffractometry on the 45 MeV electron LINAC of Hokkaido University.

The details of the equipment are presented in the reference<sup>(6)</sup>. The neutron path lengths were 693 cm and 23 cm for the incident and the scattered neutrons respectively. Liquid heavy water ( $D$ : 99.75 %) prepared by Merck Company was kept in a cylindrical container (10 mm $\phi$  x 100 mm) of vanadium sheet (0.025 mm thickness). A series of measurements was made at room temperature for the following cases: (1) a copper polycrystalline plate for calibrating the scale of  $Q$ ; (2) a vanadium rod (10 mm $\phi$ ) for calculating the distortions caused by the energy dependence of the neutron source and the detector; (3) a sample of liquid heavy water; and (4) the vanadium container for the background counts.

Figures 1 and 2 show the time-dependent neutron diffraction patterns at scattering angles 45° and 150° respectively. The former was remeasured in order to obtain better statistical accuracy. The measurements for the background counts and the vanadium rod are also compared in the figures. The counts for the vanadium rod were normalized in the short flight time region.

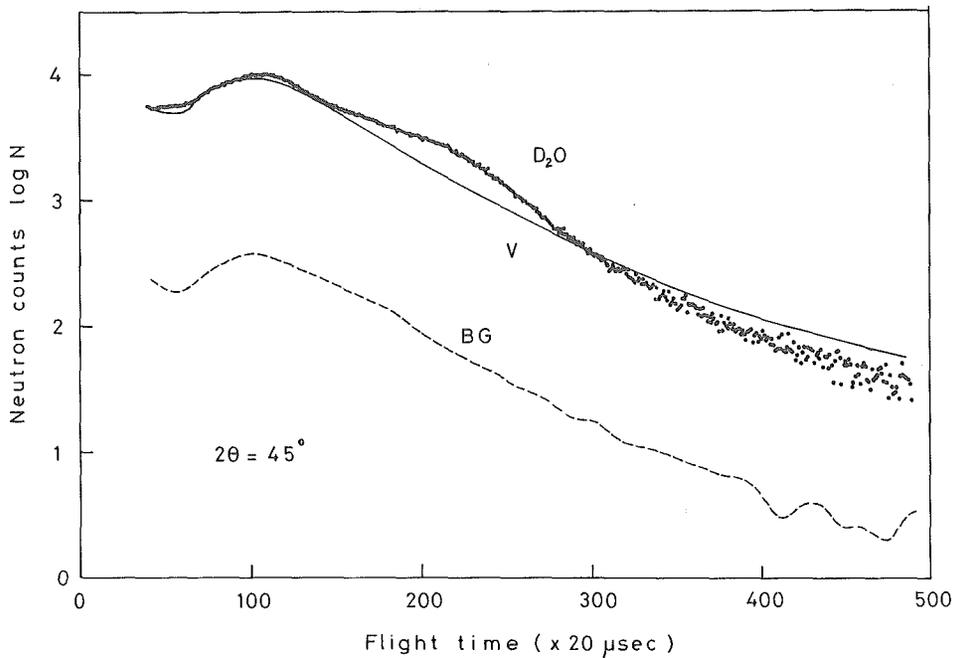


Fig. 1 Time dependent neutron diffraction pattern at  $2\theta = 45^\circ$

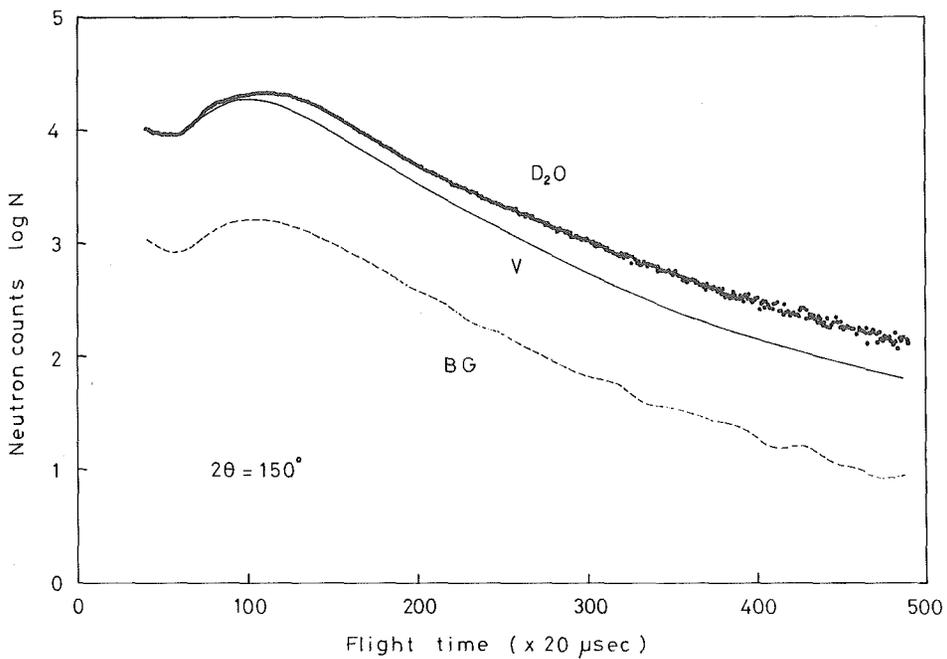


Fig. 2 Time dependent neutron diffraction pattern at  $2\theta = 150^\circ$

## 4. Results and Discussion

### 4.1 Data Reduction

After transforming the diffraction patterns in the time space to the  $Q$  space, several corrections were made to obtain the structure factor.

We first calibrated the axis of  $Q$  using the diffraction peaks of a polycrystalline copper plate in which the effect for the emission time was corrected using interpolated data measured by Fluharty et al.<sup>(9)</sup> There was a 1 % agreement between the neutron and X-ray diffraction methods used to determine the  $Q$  values for several fundamental Bragg reflections for copper. Next, we corrected the effects of the neutron absorption in the sample and the vanadium. Figure 3 shows the corrected ratio  $R(2\theta, Q)$  of the neutron diffraction pattern of the sample to vanadium at a scattering angle of  $150^\circ$ .

The value of  $R(2\theta, Q)$  slowly decreased in the high  $Q$  region due to the dynamic effect which was caused mainly by deuterium nuclei. The dynamical effect was corrected separately for the high and the low  $Q$  regions.<sup>(10)</sup> In the high  $Q$  region, the ratio  $R(2\theta, Q)$  at  $2\theta = 150^\circ$  was fitted by the least square method to Eq. (14) in Matsumoto's reference, where, for simplicity, the third term at the right hand side was neglected. On the other hand, the low  $Q$  region data which was measured at  $2\theta = 45^\circ$  was corrected by Eq. (18) in the same reference. Figure 4 shows the resulting structure factor  $i(Q)$  of liquid heavy water in which the measurements at scattering angles of  $45^\circ$  and  $150^\circ$  were connected at  $Q = 9.0 \text{ \AA}^{-1}$ . The agreement between the data from both measurements was satisfactory in the neighbourhood of the connecting point. In addition, we carried out the Fourier transformation of  $i(Q)$  to obtain the function  $d(R)$  by Eq. (5), in which we used the Lorch modification function:<sup>(11)</sup>

$$M(Q) = \sin(\pi Q/Q_{\max})/(\pi Q/Q_{\max}) \quad (8)$$

where  $Q_{\max}$ : maximum of  $Q$ .

The resulting function  $d(R)$  is shown in Fig. 5. The very low  $Q$  data was compensated for by a theoretical value at  $Q=0$ , which hardly contributed to the structure factor.

### 4.2 Intramolecular Structure

In the real distance space, we were able to determine several parameters relating to the structure of the water molecule in the liquid state. The distances of O-D and D-D in the molecule were derived from the peaks in function  $d(R)$  from which the angle DOD was determined. On the other hand, the rms variation  $\Delta R_{OD}$  for the O-D distance was also obtained in the real space by the following method. The observed width  $\Delta R_{obs}$  of the corresponding peak at about  $1 \text{ \AA}$  could be observed by combining  $\Delta R_{OD}$  and the resolutional width induced in the Fourier transformation, i. e.,

$$(\Delta R_{obs})^2 = (\Delta R_{OD})^2 + c/Q_{\max}^2 \quad (9)$$

where  $c$ : constant. Figure 6 shows the dependence of  $(\Delta R_{obs})^2$  on  $Q_{\max}^{-2}$ , in which  $\Delta R_{OD}$  was obtained by the least square extrapolation. Table 1 summarizes the values of the parameters for the structure of the water molecule in the liquid state. The obtained values were then compared with those from other studies where the values were derived in the  $Q$  space

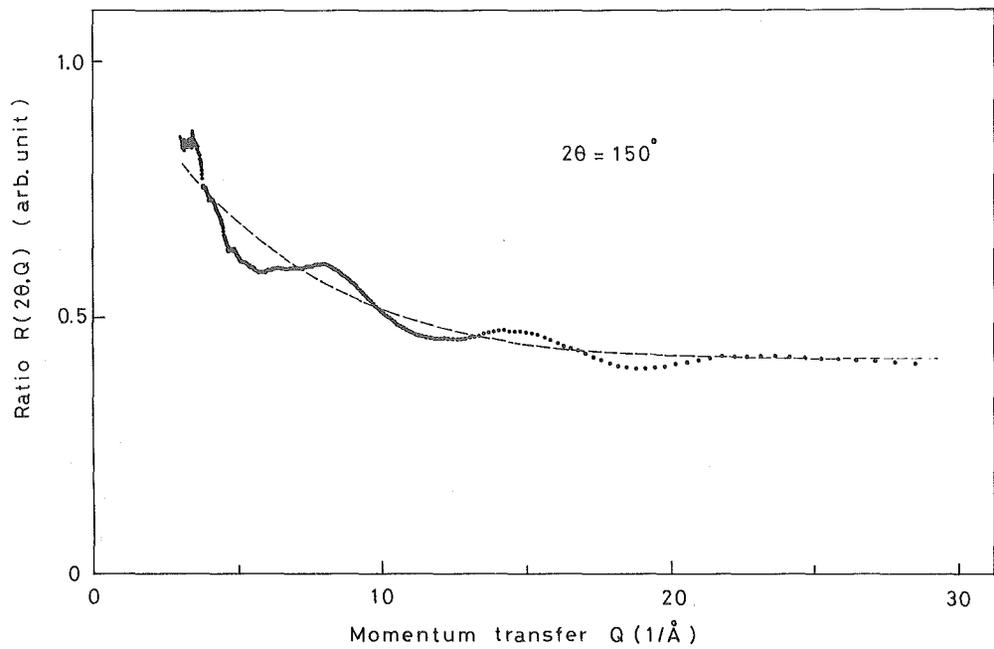
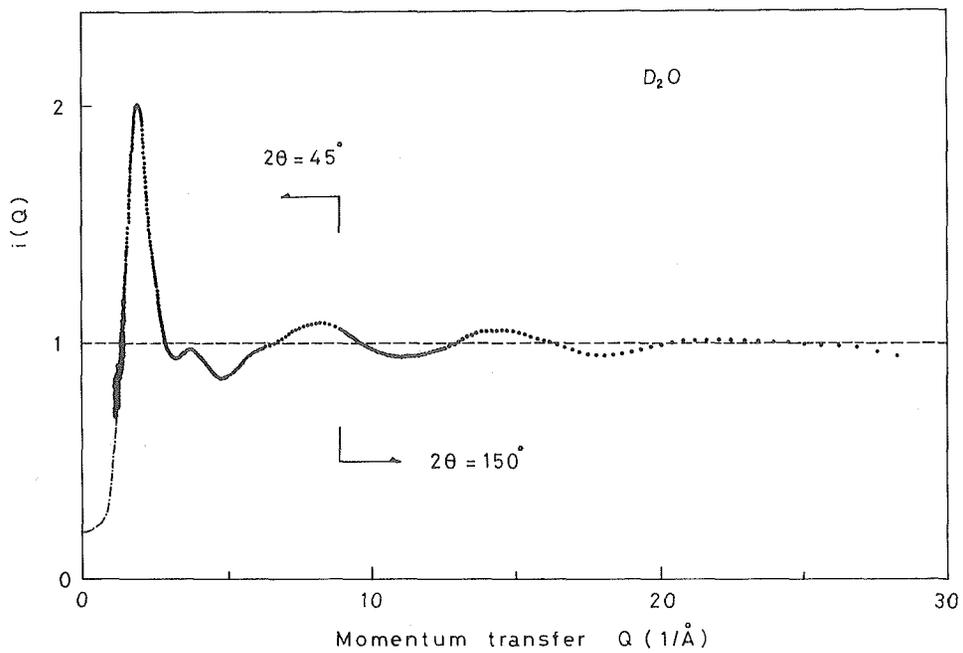
Fig. 3 Ratio of water to vanadium at  $2\theta = 150^\circ$ 

Fig. 4 Structure factor of water

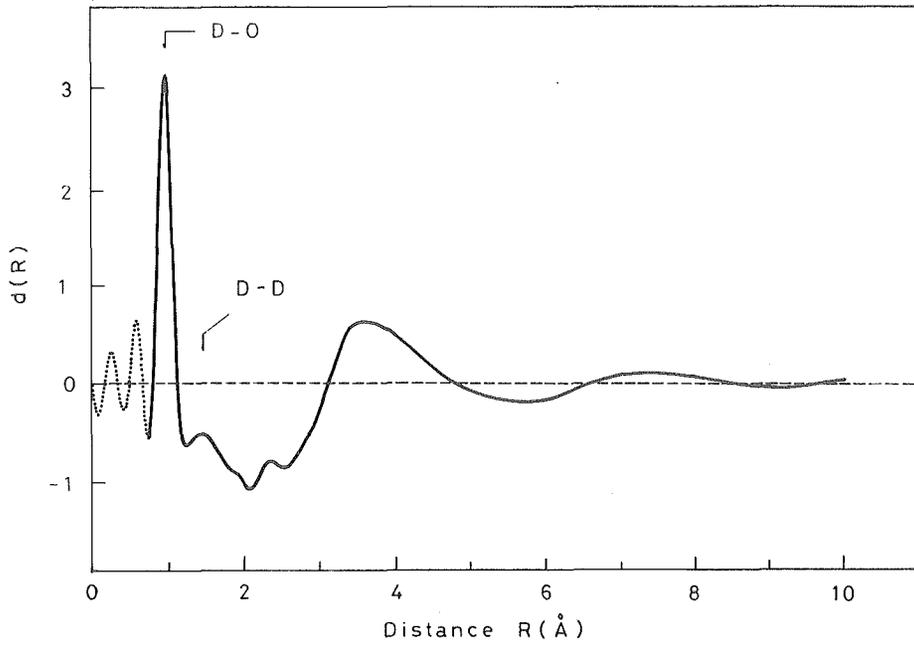


Fig. 5 Function  $d(R)$

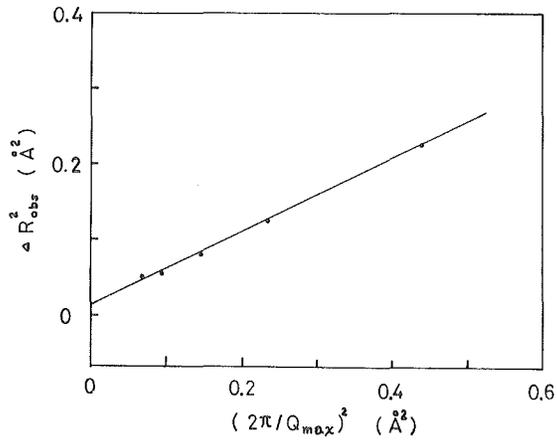


Fig. 6 Half width of O-D peak

Tab. 1 Parameters for structure of water molecule

	$R_{OD}$ (Å)	$R_{DD}$ (Å)	$\angle DOD$ ( $^{\circ}$ )	$\Delta R_{OD}$ (Å)	$\Delta R_{DD}$ (Å)	$\Delta(\angle DOD)$ ( $^{\circ}$ )
Walford et al. (Ref. 5)	0.98	1.56	105.5	—	—	—
Narten (Ref. 3)	0.934	1.53	109	0.138	0.24	15
This work	0.948	1.56	110.7	0.115	—	—

by fitting function  $S_m(Q)$  to the experimental data. The determination of the parameter values was more direct in this method as it could be made in the real distance space.

### 4.3 Intermolecular Structure

Narten (1972) tried to obtain the partial pair distribution functions from two independent experiments using X-ray and neutron diffraction methods. In principle, three independent experiments are necessary, if we desire to derive three partial pair distribution functions of liquid water separately. Therefore, Narten introduced an assumption for the orientation of the molecules in the liquid state which influenced, to some extent, his results of the partial pair distribution functions. Here the weighted sum function  $D(R)$  was compared with the model calculation which can be derived from the partial pair distribution functions.

The weighted sum function  $D(R)$  was calculated by Eq. (6) from  $d(R)$  in order to examine the intermolecular structure of the liquid water. The function  $D(R)$  is shown in Figs. 7 and 8, in which the contribution of the intramolecular structure was subtracted. The function  $D(R)$  was then compared with the Monte Carlo calculations made by Watts.<sup>(7)</sup> In his calculations, the interaction potential between water molecules consisted of two parts: the spherical molecule was presented by a Lennard-Jones (12, 6) function and by the effect of hydrogen bonding, which was obtained by setting one negative and two positive charges respectively. The parameters are those suggested by the Rowlinson (1951) and Ben-Naim and Stillinger (1972) models.

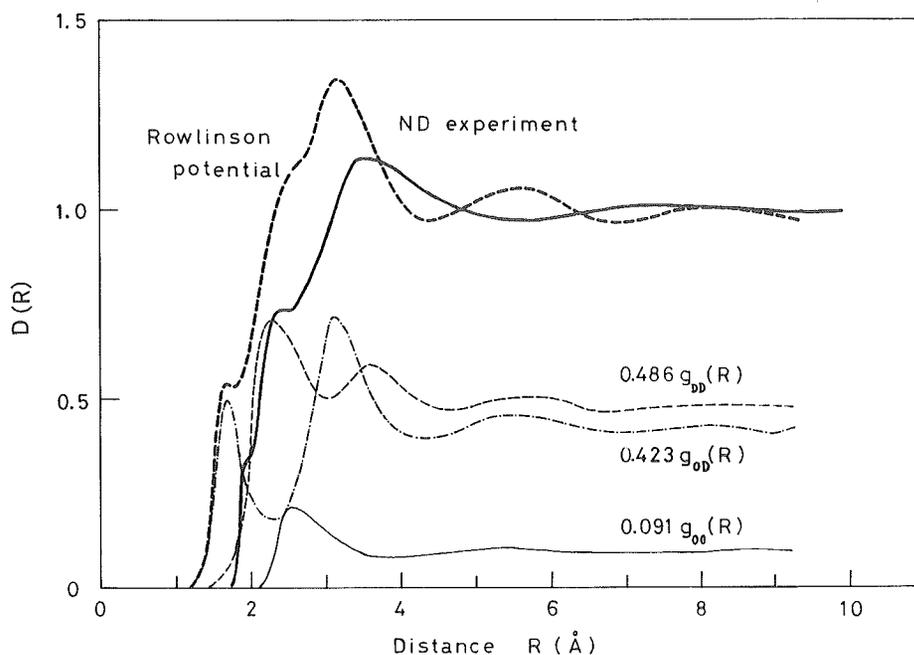


Fig. 7 Comparison of intermolecular structure between experiment and Monte Carlo calculation with Rowlinson potential

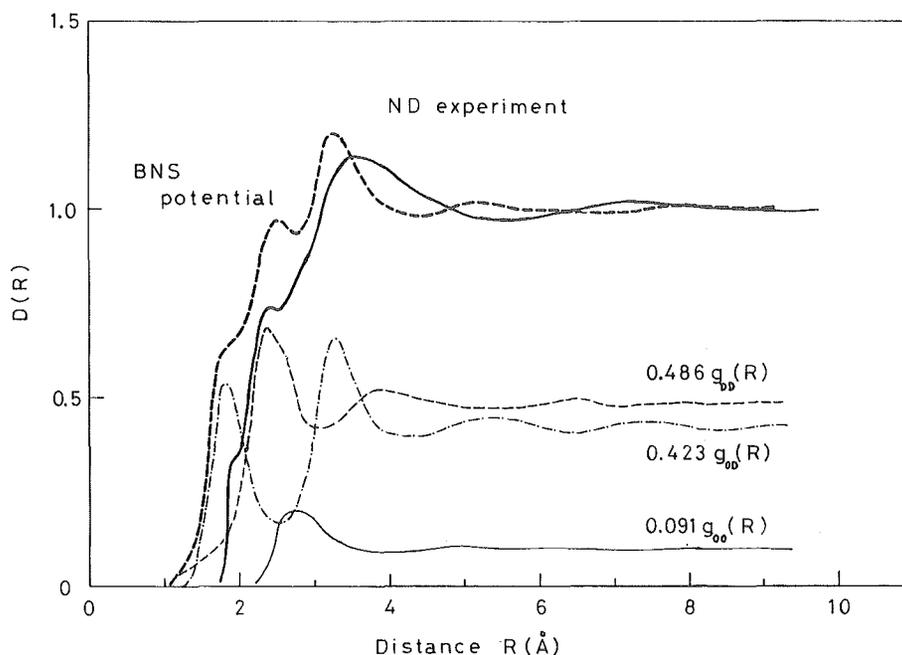


Fig. 8 Comparison of intermolecular structure between experiment and Monte Carlo calculation with BNS potential

Figures 7 and 8 demonstrate that the agreement is fairly poor, especially in the long distance region (larger than about 4 Å). In the short distance region, however, the resembling features are observable whereas the absolute values of  $D(R)$  differ to some extent. The tetrahedral structure of liquid water appears approximately at peaks 1.8 Å and 3.2 Å in the calculated function  $g_{OD}(R)$  and at about peak 2.2 Å in  $g_{DB}(R)$  respectively. These corresponding peaks were also observed in the neutron diffraction experiment.

## 5. Conclusion

Herein we have presented the neutron diffraction experiment of liquid heavy water. The Time-of-Flight neutron diffractometry on the electron LINAC yielded a structure factor with a wide range of  $Q$ ; 0.9-28.3 Å<sup>-1</sup>. The dynamical effect was successfully treated by the correction method proposed by the author.

We determined several parameters concerning the structure of water molecule in the liquid state. As the determination was made in the real space, the values of the parameters may be more accurate than those derived in the  $Q$  space. For the intermolecular structure of liquid water, the weighted sum function  $D(R)$  was compared with the Monte Carlo calculations by Watts in which the potentials of Rowlinson and Ben-Naim and Stillinger were used. There was generally poor agreement between the experiment and the calculations, especially in the long distance region. However, in the short distance region, the peaks reflected the tetrahedral structure of liquid water. It appears that a more accurate potential function is required to reduce the discrepancy between the experiment and

calculation. At the same time, we proved the weighted sum function  $D(R)$  to be useful for examining model calculations for liquid water.

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