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# Monte Carlo Calculations for the Structure of Liquid Methanol

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**Abstract**

Monte Carlo Calculations have been made for liquid methanol. Intermolecular potentials used in the calculations consisted of two kinds of potentials: (1) Lennard-Jones potentials which have centers at C and O atoms in the methanol to represent the nonspherical shape of the molecule, and (2) a water-like Coulomb potential to represent the hydrogen bond, respectively.

Partial pair distribution functions $g_{\alpha\beta}(R)$ have been calculated changing the parameters of the Lennard-Jones potentials. A weighted sum function of $g_{\alpha\beta}(R)$, $d_m(R)$, has been compared to the one derived from our previous neutron diffraction experiment[1].

## 1. Introduction

Our previous paper[1] has described Time-of-Flight neutron diffraction measurements for liquid methanol at room temperature, which were performed at the 45 MeV electron LINAC of Hokkaido University. The method used such high energy neutrons efficiently that the measurements in the high momentum transfer ($Q$) region could be easily made. Furthermore, the dynamical effect which becomes a serious problem for light nuclei liquids particularly in the high $Q$ region was successfully corrected. As a result, the structure factor $S(Q)$ of liquid methanol was obtained in the wide range of $Q$, about $1\sim30$ Å$^{-1}$.

In general, the structure factor of molecular liquids can be divided into two parts: the intramolecular part and the intermolecular one. The former which dominates the structure factor in the high $Q$ region enables us to determine the intramolecular structure of molecular liquids. From the latter which becomes significant in the low $Q$ region, on the other hand, it is possible to elicit information related to the intermolecular structure. In our previous paper the intramolecular structure was analyzed using the structure factor in the high $Q$ region. This paper will mainly discuss the intermolecular structure of liquid methanol.

The structure of molecular liquids might be usually more complicated than that of single atomic liquids. In the former the orientational correlation between molecules should be considered in addition to the spatial correlation. Several models which analyze the structure of the molecular liquids have been proposed: for example, the geometrical model,[2] the reference interaction site model (RISM),[3] and the simulational model[4,5]. The first which is alternatively called 'the relaxed lattice

model' is based on a structure of solid state. The randomness characteristic to the liquid state is phenomenologically considered by introducing some adjustable deviations of the interatomic distances.

The second approximates the potential by a hard-core-like one, although the effects of the nonspherical shape of molecules can be well analyzed. On the other hand, the third which consists of the Monte Carlo method[4] and the molecular dynamics method,[5] has the advantage of the fact that it is based on a more realistic intermolecular potential. Many calculations for simple atomic liquids have been made by the simulational models.[4] Several applications have been recently reported to molecular liquids such as nitrogen[6] and benzene[7]. Furthermore liquid water has been extensively calculated by the molecular dynamic method using realistic potentials of the hydrogen bond[8].

In this paper, Monte Carlo calculations were made for liquid (deuterated) methanol. The potentials used in the calculations consisted of two kinds of potentials: (1) Lennard-Jones potentials which have centers at the C and O atoms in the methanol to represent the nonspherical shape of the molecule, and (2) a water-like Coulomb potential to represent the hydrogen bond, respectively. Partial pair distribution functions $g_{\alpha\beta}(R)$ were calculated changing the parameters of the Lennard-Jones potential functions. Moreover, a weighted sum function of $g_{\alpha\beta}(R)$, $d_m(R)$, was compared to the one derived from our previous neutron diffraction experiment.

## 2. Method of Monte Carlo Calculation

### *2. 1 Principle*

We may condider a system of N molecules in the framework of the statistical mechanics of classical mechanical systems. Defining a probability $P(\boldsymbol{R}, \Omega)$ that the system has spatial and orientational configurations of $\boldsymbol{R}=(\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N)$ and $\Omega=(\omega_1, \omega_2, \cdots, \omega_N)$ respectively, the average $\langle f \rangle$ of a function $f(\boldsymbol{R}, \Omega)$ can be represented by the following equation,

$$\langle f \rangle = \int d\boldsymbol{R} d\Omega P(\boldsymbol{R}, \Omega) f(\boldsymbol{R}, \Omega) \Big/ \int d\boldsymbol{R} d\Omega P(\boldsymbol{R}, \Omega) \tag{1}$$

where $P(\boldsymbol{R}, \Omega) = \exp\left\{-U(\boldsymbol{R}, \Omega)/k_B T\right\}$

$U(\boldsymbol{R}, \Omega)$: potential energy of system
$k_B$: Boltzmann constant
$T$: temperature of system.

In the Monte Carlo calculation, $\langle f \rangle$ might be obtained by a sequence of the Markov chains, in which the appearence of configurations is approximated to be proportional to the probability $P(\boldsymbol{R}, \Omega)$[4]. Equation (1) is written as follows:

$$\langle f \rangle \cong \frac{1}{s_n} \sum_{s=1}^{s_n} f\left(\boldsymbol{R}(s), \Omega(s)\right) \tag{2}$$

where $\boldsymbol{R}(s)$ and $\Omega(s)$ represent the spatial and the orientational configurations at

the step $s$, respectively. This Markov chain can be obtained in the following sequence.

(1) One molecule $n$ is selected at random among the $N$ molecules, *i. e.*,

$$n = \mathrm{Int}\,(N \cdot RN_1) \tag{3}$$

where $RN_i$: random number $0 < RN_i < 1$ $i = 1, 2, \cdots$
$\mathrm{Int}\,(x)$: integer of $x$.

(2) The $n$-th molecule is translationally moved at random, *i. e.*,

$$\begin{cases} x'_n = x_n(s) + \delta \cdot (1 - 2\,RN_2) \\ y'_n = y_n(s) + \delta \cdot (1 - 2\,RN_3) \\ z'_n = z_n(s) + \delta \cdot (1 - 2\,RN_4) \end{cases} \tag{4}$$

where $\delta$: maximum of translational displacement.

(3) The $n$-th molecule is rotated at random, *i. e.*,

$$\theta'_{ln} = \theta_{ln}(s) + \delta\theta \cdot (1 - 2\,RN_5) \tag{5}$$

where $\delta\theta$: maximum of rotational angle.

In Eq. (5) the rotational axis is also selected at random according to

$$\begin{cases} 1 > RN_6 \geq 2/3 & : \quad l = x \\ 2/3 > RN_6 \geq 1/3 & : \quad l = y \\ 1/3 > RN_6 > 0 & : \quad l = z\,. \end{cases} \tag{6}$$

(4) The difference of the potential energy is calculated between the moved and the unmoved systems,

$$\begin{aligned} dU = U\big(\boldsymbol{r}_1(s), \boldsymbol{r}_2(s), \cdots, \boldsymbol{r}'_n, \cdots, \boldsymbol{r}_N(s);\ \boldsymbol{\omega}_1(s), \boldsymbol{\omega}_2(s), \cdots \boldsymbol{\omega}'_n, \cdots, \boldsymbol{\omega}_N(s)\big) - \\ - U\big(\boldsymbol{r}_1(s), \boldsymbol{r}_2(s), \cdots, \boldsymbol{r}_n(s), \cdots, \boldsymbol{r}_N(s);\ \boldsymbol{\omega}_1(s), \boldsymbol{\omega}_2(s), \cdots, \boldsymbol{\omega}_n(s), \cdots, \boldsymbol{\omega}_N(s)\big)\,. \end{aligned} \tag{7}$$

(5) The new configuration is accepted depending on a quantity $\eta = \exp(-dU/k_BT)$, *i. e.*,

$$\begin{cases} \text{(i)} \quad dU < 0: & \boldsymbol{r}_n(s+1) = \boldsymbol{r}'_n,\ \boldsymbol{\omega}_n(s+1) = \boldsymbol{\omega}'_n \\ \text{(ii)} \quad dU \geq 0: & \begin{cases} \eta \geq RN_7: & \boldsymbol{r}_n(s+1) = \boldsymbol{r}'_n,\ \boldsymbol{\omega}_n(s+1) = \boldsymbol{\omega}'_n \\ \eta < RN_7: & \boldsymbol{r}_n(s+1) = \boldsymbol{r}_n(s),\ \boldsymbol{\omega}_n(s+1) = \boldsymbol{\omega}_n(s) \end{cases} \end{cases} \tag{8}$$

whereas the other molecules remain unchanged.

### 2. 2 *Intermolecular Potential*

Methanol is a nonspherical and polar molecule. In order to analyze the effect of these complicated properties on the liquid structure, we used an intermolecular potential function which consisted of two kinds of potentials.

One potential was the Lennard-Jones potential function written by the following equation,

$$U_{LJ}(R) = 4\varepsilon\left\{(\sigma/R)^{12} - (\sigma/R)^{6}\right\}. \tag{9}$$

The nonspherical shape of the methanol molecule was approximately represented by the two Lennard-Jones potentials whose centers were located at the $C$ and $O$ atoms in the molecule. We assumed the following relations between these parameters,[9]

$$\begin{cases} \varepsilon_{CO} = (\varepsilon_{CC} \cdot \varepsilon_{OO})^{1/2} \\ \sigma_{CO} = (\sigma_{CC} + \sigma_{OO})/2 \end{cases} \tag{10}$$

where $\varepsilon_{CO}$ represents the parameter $\varepsilon$ when the spherical parts of the two molecules whose centers are located at the $C$ and $O$ atoms interact with each other. The other notations have the same meaning. As standard values of the parameters, we determined the following values,

$$\begin{cases} \varepsilon_{CC} = 2.047 \times 10^{-4}\ \text{erg}, & \sigma_{CC} = 3.817\ \text{Å} \\ \varepsilon_{OO} = 4.914 \times 10^{-14}\ \text{erg}, & \sigma_{OO} = 2.725\ \text{Å}. \end{cases} \tag{11}$$

Herein, the parameters for the $C-C$ interaction were obtained from the second Virial coefficient of methane,[9] and for the $O-O$ interaction from the Rowlinson's model for liquid water,[10] respectively. From Eqs. (10) and (11), we obtained

$$\begin{cases} \varepsilon_{CO} = 3.172 \times 10^{-14}\ \text{erg} \\ \sigma_{CO} = 3.271\ \text{Å}. \end{cases} \tag{12}$$

The other potential, the Coulomb interaction due to the dipole moment $U_{el}$, was represented by a water-like potential proposed by Rowlinson[10]. In the hydrogen bond, one positive charge $q_3 = 0.3245\,e$ was located at the $D$ atom and two negative charges $q_1 = q_2 = 0.1622\,e$ at the distance $\delta = 0.2539$ Å from the $O$ atom, respectively. The intensity of the charges was determined from the measurement of the dipole moment 1.62 D for liquid methanol[11]. Figure 1 shows the arrangement of the charges.

In the practical calculations, several calculational techniques were applied to save calculation time and to obtain good performanance.

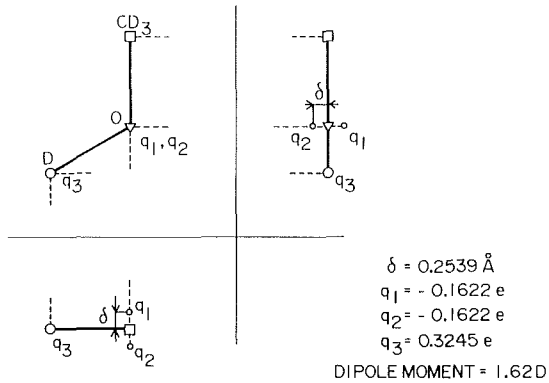


**Fig. 1.** Arrangement of charges.

First, a switch function $S_W(R)$, which should be multiplied to the Coulomb potential, was used to avoid any unordinary approach between the charges with opposite signs,[12]

$$S_W(R)=\begin{cases} 0 & \text{for} \quad 0<R\leq R_1 \\ \dfrac{(R-R_1)^2(3R_2-R_1-2R)}{(R_2-R_1)^3} & \text{for} \quad R_1<R\leq R_2 \\ 1 & \text{for} \quad R_2<R \end{cases} \tag{13}$$

where $R_1=2.0$ Å and $R_2=3.0$ Å were used. Second, we introduced a cutoff distance $R_C$, beyond which the interaction between the molecules is negligible.

Therefore the cutoff function $h(R)$, which should be multiplied by both the potential functions, was written as follows:

$$h(R_C-R)=\begin{cases} 1 & \text{for} \quad R\leq R_C \\ 0 & \text{otherwise}. \end{cases} \tag{14}$$

A periodical boundary condition was last set in order to compensate the calculation for the large distance correlations. Twenty-six cells having the same molecular configuration were located around the basic cell mentioned above.

The position of the $n$-th molecule in the boundary cells were written as follows:

$$\boldsymbol{r}_n(\nu)=\boldsymbol{r}_n+L\nu \tag{15}$$

where $L$ is the length of the cubic cell and $\nu=(\nu_x, \nu_y, \nu_z)$ represents a set of the integers $\nu_x$, $\nu_y$ and $\nu_z$ which take either of $-1$, 0 and 1.

From Eqs. (9) to (15), the potential energy of system was summarized in the following equation,

$$\begin{aligned} U=\sum_{\nu}\sum_{i,j=1}^{N}\Bigg\{ & \sum_{\alpha,\beta=C,O}\frac{1}{2}U_{LJ}\left(|\boldsymbol{R}_{ij}+\boldsymbol{r}_{\alpha\beta}+L\nu|\right)h\left(R_{CLJ}-|\boldsymbol{R}_{ij}+\boldsymbol{r}_{\alpha\beta}+L\nu|\right) \\ & +\sum_{q,q'=1}^{3}\frac{1}{2}U_{el}\left(|\boldsymbol{R}_{ij}+\boldsymbol{r}_{qq'}+L\nu|\right)S_W\left(|\boldsymbol{R}_{ij}+\boldsymbol{r}_{qq'}+L\nu|\right) \\ & h\left(R_{Cel}-|\boldsymbol{R}_{ij}+\boldsymbol{r}_{qq'}+L\nu|\right)\Bigg\} \end{aligned} \tag{16}$$

where $R_{CLJ}=6$ Å and $R_{Cel}=10$ Å were used respectively.

### 2.3. *Functions $g_{\alpha\beta}(R)$ and $d_m(R)$*

The partial pair distribution function $g_{\alpha\beta}(R)$ can be obtained calculating the distance $R$ between the nuclei of $\alpha$ and $\beta$ kinds in all the accepted molecular configurations. The function $g_{\alpha\beta}(R)$ is, in the following manner, related with the molecular structure factor $S(Q)$ which can be derived from the neutron diffraction experiment. We define a function $d(R)$ as the Fourier transform of $S(Q)$,

$$d(R)=\frac{2}{\pi}\int_0^{\infty}dQQ\sin QR\left\{\frac{(\sum_{\alpha}\bar{b}_{\alpha})^2}{\sum_{\alpha}b_{\alpha}^{\,2}}S(Q)-1\right\}. \tag{17}$$

The function $d(R)$ can be divided into two terms the same as $S(Q)=F_1(Q)+D_m(Q)$ (Eq. (4-1) in Ref. 1),

$$d(R)=f_1(R)+d_m(R)\,. \tag{18}$$

Therefore the following relations are obtained,

$$f_1(R)=\frac{2}{\pi}\int_0^\infty dQQ\sin QR\left\{\frac{(\sum_\alpha \bar{b}_\alpha)^2}{\sum_\alpha \bar{b}_\alpha{}^2}F_1(Q)-1\right\} \tag{19}$$

and

$$\begin{aligned} d_m(R)&=\frac{2}{\pi}\int_0^\infty dQQ\sin QR\left\{\frac{(\sum_\alpha \bar{b}_\alpha)^2}{\sum_\alpha \bar{b}_\alpha{}^2}D_m(Q)\right\} \\ &=\frac{\rho}{\sum_\alpha \bar{b}_\alpha{}^2}\sum_{\alpha\beta}\bar{b}_\alpha\bar{b}_\beta 4\pi R\left\{g_{\alpha\beta}(R)-1\right\} \end{aligned} \tag{20}$$

where $\rho$: number density of molecules. After the function $F_1(Q)$ is determined in the high $Q$ region of $S(q)$ where $D_m(Q)\to 0$, the weighted sum function of $g_{\alpha\beta}(R)$, $d_m(R)$, is available for analyzing the intermolecular structure of molecular liquids.

## 3. Results and Discussion

### *3. 1. Calculational Conditions*

We made the Monte Carlo calculations of liquid methanol for five cases of the potentials having different parameters in the Lennard-Jones potential. Among them a standard case was assigned to the parameters mentioned in Sec. 2, in which the set of parameters $\varepsilon$ and $\sigma$ were represented by $\varepsilon_0$ and $\sigma_0$, respectively. The other four cases were taken for combinations of the parameters of $\varepsilon$ and $\sigma$ which deviated by $\pm 10\%$ from the standard values $\varepsilon_0$ and $\sigma_0$.

The flow of the calculation is shown in Fig. 2. A cubic cell which contained 27 molecules was taken as a basic cell, and the dimension of the cell was determined to be such that the number density of molecules might consist of the experimental value $1.471\times 10^{22}\ n/\mathrm{cm}^3$. The intermolecular structure of methanol which was determened in our previous neutron diffraction study was used, in which the methyl group was approximated to be freely rotating.

Before the intermolecular structure was calculated from many molecular configurations, preliminary calculations were made : starting from the initial temperature of 2097 K, the system was cooled down by 300 K per 200 step configurations to arrive at 297 K. Additional warming-up calculations were continued until the system satisfactorily approached to the equilibrium state : this reguried a calculation of 7000 steps. The intrinsic calculation of 6000 steps wes performed to obtain the equilibrium state configurations of liquid methanol. Throughout the calculations, the parameters of $\delta=0.2$ Å and $\delta\theta=10°$ were used respectively.

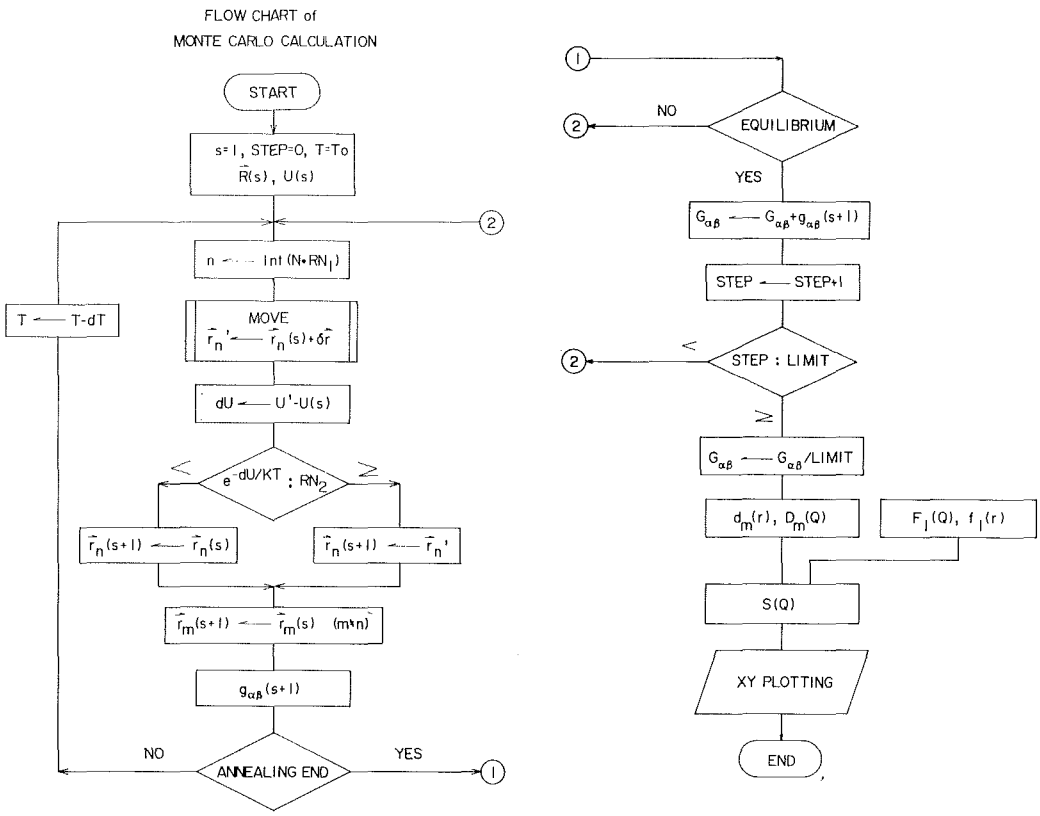


**Fig. 2.** Flow of calculation.

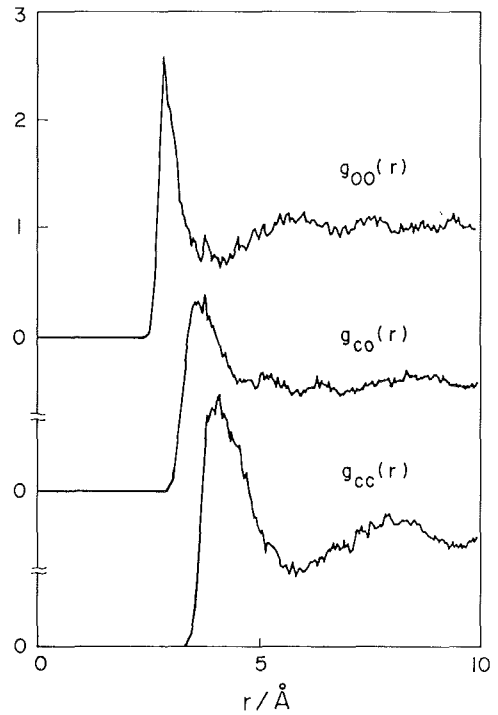


**Fig. 3.** Partial pair distribution function $g_{\alpha\beta}(R)$.

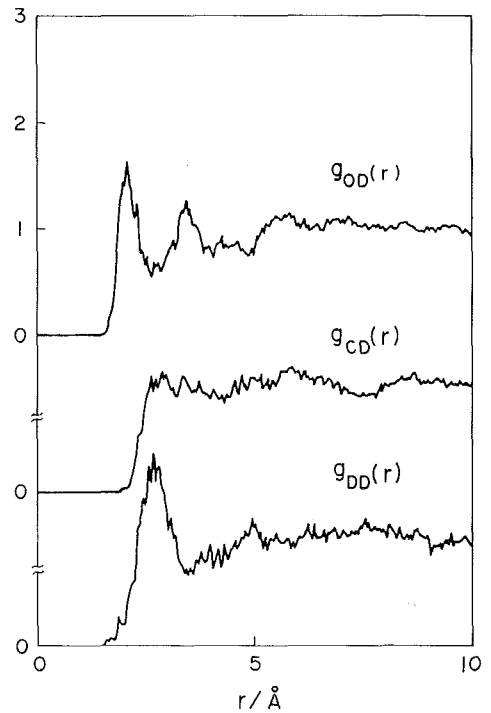


**Fig. 4.** Partial pair distribution function $g_{\alpha\beta}(R)$.

### 3. 2. *Partial Pair Distribution Functions* $g_{\alpha\beta}(R)$

The calculational results of the partial pair distribution functions $g_{\alpha\beta}(R)$ are shown in Fig. 3 to 5 for the case of the standard potential with the parameters of $\varepsilon_0$ and $\sigma_0$.

In order to classify hydrogens located at different positions in the molecule, the deuterium in the methyl group was denoted by $D_M$ and the one in the hydroxyl group by $D$, respectively.

The functions $g_{OO}(R)$, $g_{CO}(R)$ and $g_{CC}(R)$ had a first well-resolved peak, whose position was correspondingly in good agreement with the value obtained by the $X$-ray diffraction method[13].

The first peak observed in $g_{OO}(R)$ was particularly sharp and excited. It was caused by the existence of the hydrogen bond. The effect of the hydrogen bond also remarkably appeared in the function $g_{OD}(R)$ which had two well-resolved peaks located at 2.0 Å and 3.4 Å. However, it was noticable that the function $g_{CD}(R)$ had no well-resolved peak. These calculational results suggested that there might exist molecular configurations which allow fairly free rotation of the neighboring molecule around the axis of the hydrogen bound. On the other hand, the functions $g_{\alpha\beta}(R)$ containing the deuterium located in methyl group $D_M$ showed no well-resolved peak. This was due to the model used for the single molecule which approximated the free internal rotation of the methyl group. The position of the first peak observed in $g_{\alpha\beta}(R)$ was summarized in Table 1.

TABLE 1. Position of first peak in $g_{\alpha\beta}(R)$

| TYPE | $CD_3OD$ (this paper) | $CH_3OH$ (ref. 13) |
|---|---|---|
| O D | 2.0, 3.4 Å | |
| D D | 2.7 Å | |
| O O | 2.9 Å | 2.7 Å |
| C O | 3.7 Å | 3.8, 4.4 Å |
| C C | 4.2 Å | |

Watts made calculations of liquid water using the Monte Carlo method[14]. It might be interesting to compar our results with his calculations, because both the calculations were based on the same Rowlinson's interaction potential for the hydrogen bond. In the function $g_{OD}(R)$, Watts also observed two well-resolved peaks which were caused by the hydrogen bond in liquid water. The peaks resulted from our calculations were broader and less excited than the one by Watts. This was due to the fact that the methanol molecule has only one hydrogen bond and, instead of the second hydrogen bond in water molecule, has a fairly large atomic group (the methyl group).

### 3. 3. *Comparison with Neutron Diffraction Experiment*

The function $d_m(R)$ was calculated using Eq. (20) from the functions $g_{\alpha\beta}(R)$ which were mentioned in Sec. 3. 2. Figure 6 compares the functions $d_m(r)$ for the different values of Lennard-Jones potential. It is indicated that although the function $d_m(R)$ hardly depends on the parameter of $\varepsilon$ in this deviation range, the amplitude of the correlational oscillation in $d_m(R)$, as well as the peak position,

changes significantly due to the $\pm 10\%$ deviation of the parameter $\sigma$.

In order to compare the calculational results with our neutron experiment,[1] the function $d(R)$ was calculated by Eq. (18). Here in the intramolecular function $f_1(R)$ was obtained by Eq. (19) using $F_1(Q)$ which was calculated in our previous study[1]. The function $d(R)$ derived from the neutron diffraction experiment is compared with the Monte Carlo calculation in Fig. 7 : the calculation was shown for the standard case.

In the experimental $d(R)$, small ripples appeared at $Q \gtrsim 3$ Å$^{-1}$ due to the truncation of $Q$ in the Fourier transform of Eq. (17). Since the ripples were clearly discriminated from the correlational oscillation, the final function $d(R)$ was obtained applying an appropriate method of smoothing. In the low $Q$ region less than 0.8 Å$^{-1}$, on the other hand, two small ghost peaks appeared due to some unknown systematical error. As these peaks were rejected physically, a theoretical value was shown by a broken line to compensate these low $Q$ region. The experimental function $d(R)$ could be reproduced satisfactorily by the Monte Carlo calculation. The best agreement was achieved for the case of the potential with the standard values of parameters $\varepsilon_0$ and $\sigma_0$.

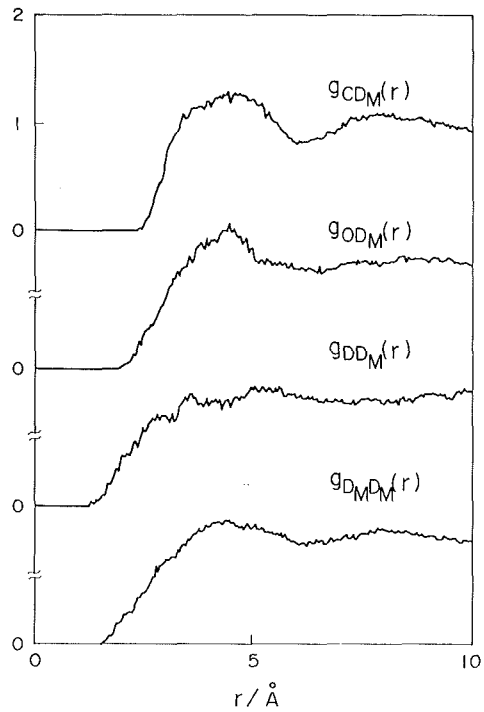


**Fig. 5.** Partial pair distribution function $g_{\alpha\beta}(R)$.

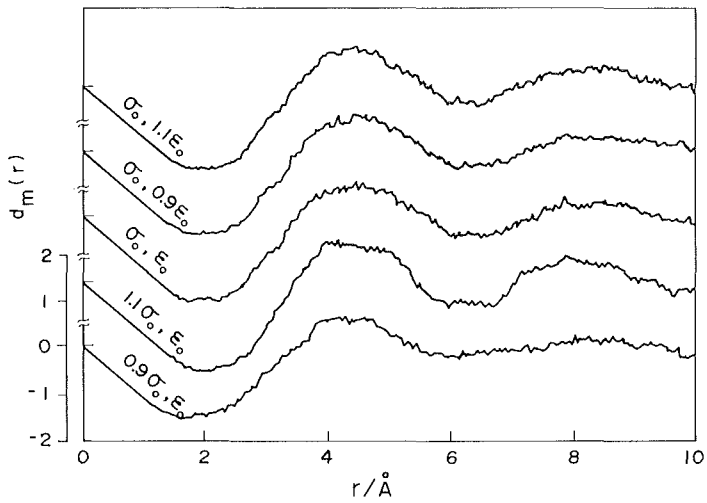


**Fig. 6.** Comparison of calculated $d_m(R)$.

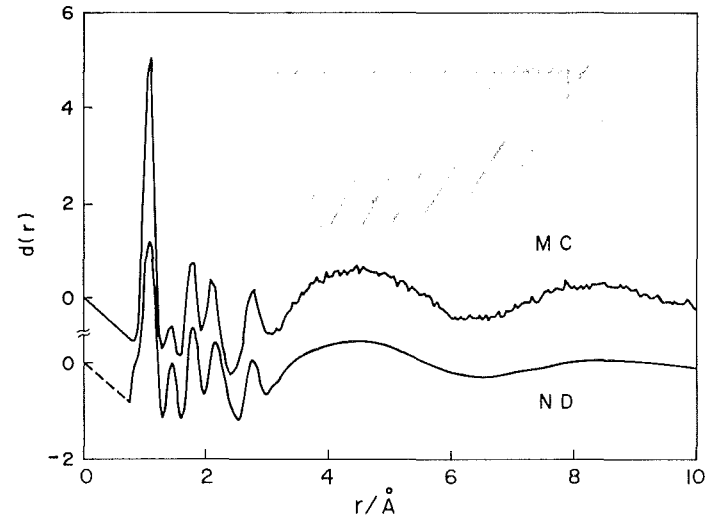


**Fig. 7.** Comparison of experimental and calculated $d(R)$.

## 4. Conclusion

In this paper Monte Carlo calculations were made for liquid (deuterated) methanol. Intermolecular potentials used in the calculations consisted of two kinds of potentials: (1) Lennard-Jones potentials which have centers at the *C* and *O* atoms in the methanol to represent the nonspherical shape of the molecule, and (2) a water-like Coulomb potential to represent the hydrogen bond, respectively. The partial pair distribution functions $g_{\alpha\beta}(R)$ and the function $d_m(R)$ were obtained for five cases: changing parameters of the Lennard-Jones potential whilst the Coulomb potential remained unchanged.

As the result of that the function $d(R)$ was compared with our previous neutron diffraction study,[1] the calculation was confirmed to reproduce the experimantal function $d(R)$ satisfactorily well. It is concluded that the potential function which was proposed by the authors is appropriate for calculating the intermolecular structure of liquid methanol.

In the functions $g_{\alpha\beta}(R)$ which could be obtained from the decomposition of $d_m(R)$, the effect of the hydrogen bound was clearly investigated on the intermolecular structure of liquid methanol. Compared with liquid water, it is noticable that $g_{CD}(R)$ has no well-resolved peaks, and suggested that molecular configurations which allow fairly free rotation of the neighboring molecule around the axis of the hydrogen bond might exist in the liquid methanol.

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