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# The Structure of Liquid Alcohols by Neutron and X-ray Diffraction. III. Liquid Structure of Methanol

Yukio TANAKA,† Norio OHTOMO,† and Kiyoshi ARAKAWA*
*Research Institute of Applied Electricity, Hokkaido University, Sapporo 060*
†*Faculty of Engineering, Hokkaido University, Sapporo 060*
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A structure analysis of neutron and X-ray diffraction data of liquid methanol was performed by applying a general theoretical procedure for the fluid system composed of molecular clusters. The calculated structure factor curves are found to reproduce the essential features of observed ones. It was concluded that in liquid methanol chain clusters consisting of three or four hydrogen-bonded molecules are dominant on the average.

In the preceding neutron diffraction study of methanol[1] the structure of the molecule within liquid was determined. Its geometry was found to be different from that in gaseous phase,[2–4] which occurs from the strong influence of hydrogen-bond formation between molecules. Concerning the intermolecular structure of liquid methanol, however, there is still very few information.[5] Then, we aim here to elucidate the structure of the liquid, further, by applying a general theoretical procedure of analysis for the fluid system composed of molecular clusters, which was proposed recently.[6,7] Thus, we attempt to reproduce below the neutron and X-ray structure factors for comparing those with experimental data[1,5] comprehensively.

## Theoretical Procedure of Analysis

*Theory.* The structure factor for molecular liquids obtained in diffraction experiments (neutron and X-ray) is generally expressed in the following form[8,9]

$$S_{\mathrm{m},\eta}(Q) = N_{\mathrm{m}}^{-1}\{\sum_{\mathrm{n}} f_{\mathrm{n},\eta}\}^{-2}\langle \sum_{\mathrm{p,q}} f_{\mathrm{p},\eta} f_{\mathrm{q},\eta} \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{pq}})\rangle, \qquad \eta = \mathrm{N,X} \quad (1)$$

where p and q denote the p-th and q-th atoms in a sample, n the n-th atom in the molecule, $f_{\mathrm{p},\eta}$, $f_{\mathrm{q},\eta}$, and $f_{\mathrm{n},\eta}$ are the scattering amplitude of atoms p, q, and n, respectively, $\vec{r}_{\mathrm{pq}}$ is the vector between the p-th and q-th atoms, $N_{\mathrm{m}}$ the number of molecules in the sample and $\hbar\vec{Q}$ the momentum transfer. The angular bracket $\langle\cdots\rangle$ means statistical average.

When a liquid is composed of molecular clusters of various sizes including monomers, the structure factor $S_{\mathrm{m}\eta}(Q)$ is given in general by[7]

$$S_{\mathrm{m},\eta}(Q) = \sum_{\nu} \frac{x_{\nu}}{\nu} f_{1}^{\nu}(Q) + \bar{f}_{2\mathrm{U}}(Q)\{S_{\mathrm{c}}(Q)-1\} + \sum_{\nu\geqq 2} \frac{x_{\nu}}{\nu} f_{\mathrm{c}}^{\nu}(Q), \quad (2)$$

where,

$$f_{1}^{\nu}(Q) = \{\sum_{\mathrm{n}} f_{\mathrm{n},\eta}\}^{-2}\{\langle \sum_{l}^{\nu} |\sum_{\mathrm{n}_l} f_{\mathrm{n}_l,\eta} \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}_l})|^2\rangle\}_{\nu}, \quad (3)$$

$$\begin{aligned} f_{\mathrm{c}}^{\nu}(Q) = {} & \{\sum_{\mathrm{n}} f_{\mathrm{n},\eta}\}^{-2}[\langle \sum_{l\neq l'}^{\nu} \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{c}ll'}) \sum_{\mathrm{n}_l,\mathrm{n}_{l'}} f_{\mathrm{n}_l,\eta} f_{\mathrm{n}_{l'},\eta} \\ & \times \exp\{\mathrm{i}\vec{Q}\cdot(-\vec{r}_{\mathrm{cn}_l}+\vec{r}_{\mathrm{cn}_{l'}})\}\rangle - \sum_{l\neq l'}^{\nu} \langle \exp(\mathrm{i}Q\cdot r_{\mathrm{c}ll'})\rangle \\ & \times \langle \sum_{\mathrm{n}_l} f_{\mathrm{n}_l,\eta} \exp(-\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}_l})\rangle \\ & \times \langle \sum_{\mathrm{n}_{l'}} f_{\mathrm{n}_{l'},\eta} \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}_{l'}})\rangle]_{\nu}, \end{aligned} \quad (4)$$

$$S_{\mathrm{c}}(Q) = N_{\mathrm{m}}^{-1}\langle \sum_{i,j} \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{c}ij})\rangle \quad (5)$$

and

$$\bar{f}_{2\mathrm{U}}(Q) = \{\sum_{\mathrm{n}} f_{\mathrm{n},\eta}\}^{-2} \sum_{\nu} \frac{x_{\nu}}{\nu} [\sum_{l}^{\nu} \{\sum_{\mathrm{n}_l} f_{\mathrm{n}_l,\eta} \times \langle \exp(\mathrm{i}\vec{Q}\cdot\vec{r}_{\mathrm{cn}_l})\rangle\}^2]_{\nu}. \quad (6)$$

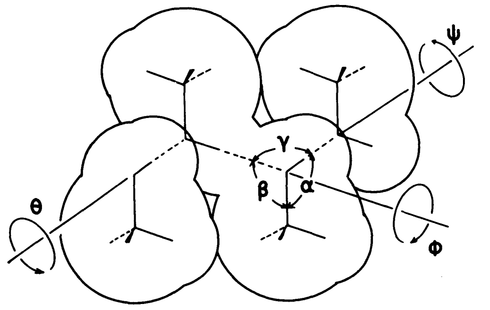
$x_{\nu}=\nu N_{\nu}/N_{\mathrm{m}}$ ($N_{\nu}$; the number of clusters consisting of $\nu$ molecules within the liquid). $l$ and $l'$ denote the molecules within a cluster and, $i$ and $j$ molecules in the sample. $\mathrm{n}_l$ labels the n-th atom in the $l$-th molecule within the cluster. $\vec{r}_{\mathrm{n}_l\mathrm{n}_{l'}}$ denotes the vector distance between atoms $\mathrm{n}_l$ and $\mathrm{n}_{l'}$, $\vec{r}_{\mathrm{n}_l}$ that from the center of molecule $l$ to its n-th atom, $\vec{r}_{\mathrm{c}ll'}$ that between the centers of molecules $l$ and $l'$ and $\vec{r}_{\mathrm{c}ij}$ that between the centers of molecules $i$ and $j$. $f_{1}^{\nu}(Q)$ and $f_{\mathrm{c}}^{\nu}(Q)$ are the intramolecular and intermolecular contribution within the cluster, respectively, and $S_{\mathrm{c}}(Q)$ the molecular center structure factor of liquids. $\sum_{\nu}(x_{\nu}/\nu)f_{1}^{\nu}$ $(=f_{1}(Q))$ is the overall averaged intramolecular contribution in the liquid.

Replacing $f_{\mathrm{n,N}}$ in Eqs. 3, 4, and 6 with the coherent neutron scattering length $b_{\mathrm{n}}$ of atom n, we obtain the neutron structure factor $S_{\mathrm{mN}}(Q)$. In the same way, we obtain the X-ray structure factor $S_{\mathrm{mX}}(Q)$ by replacing the $f_{\mathrm{n,X}}$ with the atomic form factor $f_{\mathrm{n}}(Q)$ of atom n.[9]

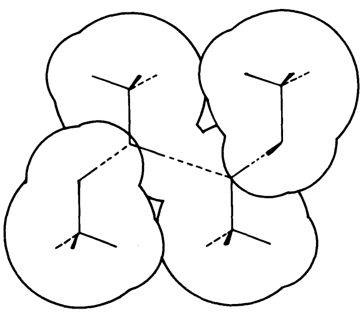
Table 1. The structure of methanol molecule in liquid phase determined by neutron diffraction[1)]

| $r_{CO}$/Å | $r_{OD}$/Å | $r_{CD}$/Å | DCD/degree | COD/degree | Methyl tilt/degree | $\tau$/degree |
|---|---|---|---|---|---|---|
| 1.435 | 0.990 | 1.085 | 109.5 | 109.5 | 0.0 | 15.0 |
| 1.440 | 0.985 | 1.090 | 109.5 | 115.0 | 0.0 | free |

$\tau$ is the dihedral angle concerning the internal rotation of the methyl group: $\tau=0°$ is the model with the staggered conformation.



tetramer I



tetramer II

Fig. 1. The structure of the tetramer models I and II.

*Structural Model of Liquid Methanol and Procedure of Calculation.* According to the theory presented in the preceding item, we can calculate the two structure factors $S_{mX}(Q)$ and $S_{mN}(Q)$. The intramolecular structure of molecules in liquid methanol was determined uniquely in the preceding paper[1)] except the rotational angle of the methyl group: the two models with respect to the angle remain undiscriminated (the fixed angular position and the freely rotating one, Table 1). Then we calculate the $S_{mX}(Q)$ and $S_{mN}(Q)$ for the two intramolecular models in the present study.

The cluster model of liquid methanol is shown in Fig. 1, where two forms of linear tetramers are given.[10)] Concerning the model, we assumed the chain structure,[11)] *i.e.*, we neglect a branched conformation of clusters. Concerning the associated structure of the liquid, we performed calculation for five classes of liquids which are composed of identical clusters of $\nu$ molecules: The liquid consists of unbonded monomers ($\nu=1$), that of dimers ($\nu=2$), that of trimers ($\nu=3$) and that of tetramers ($\nu=4$, I and II in Fig. 1). The geometry of clusters are characterized by seven structural parameters: the hydrogen-bonded O–O distance $r_{OO}$, the angluar parameters $\alpha$, $\beta$, $\gamma$, $\theta$, $\phi$, and $\psi$. The magnitudes of these parameters were varied in reference to the values tabulated in Table 2. In these cases, Eq. 2 is reduced to the following form,

Table 2. Range of parameters

| Parameter | Range | Interval of variation |
|---|---|---|
| $\nu$ | 1, 2, 3 and 4 (I and II) | |
| $r_{HS}$/Å | 3.40—3.80 | 0.20 |
| $r_{OO}$/Å | 2.75—2.90 | 0.05 |
| $\alpha,\beta,\gamma$/degree | 109.5—120.0 | 10.5 |
| $\theta,\phi,\psi$/degree | 0.0—360.0 | 45.0 |

$r_{HS}$ is the effective hard-sphere diameter of molecules.

$$S_{m\eta}(Q) = \frac{1}{\nu}f_1^\nu(Q) + \bar{f}_{2U}(Q)\{S_c(Q)-1\} + \frac{1}{\nu}f_c^\nu(Q). \tag{9}$$

Especially, for the liquid composed of monomer molecules,

$$S_{m\eta}(Q) = f_1^1(Q) + \bar{f}_{2U}(Q)\{S_c(Q)-1\}, \tag{10}$$

which corresponds to the completely uncorrelated orientation model given by Page and Powles.[9)]

For calculating $S_{mX}(Q)$ and $S_{mN}(Q)$ with Eq. 9, the molecular center structure factor $S_c(Q)$ is required. The distribution of molecular centers in liquid methanol is assumed to be represented by the distribution for hard sphere fluids, and we substitute the structure factor $S_{HS}(Q)$ of hard sphere fluid[12)] (effective hard-sphere diameter, $r_{HS}$) for the $S_c(Q)$.

With respect to the magnitudes of Debye-Waller factors, we assume that the mean-square variation $2\gamma_{n_l n_{l'}}$ is in proportion to the interatomic distance $r_{n_l n_{l'}}$, *i.e.*, $\gamma_{n_l n_{l'}}=1/2D^2_{n_l n_{l'}} r_{n_l n_{l'}}$.[6,7,18)] The values of $D_{n_l n_{l'}}$ assigned are tabulated in Table 3.

## Interpretation of X-ray and Neutron Diffraction Data

*X-Ray and Neutron Data.* Recently, X-ray structure factor data of liquid $CH_3OH$ at 21.5 °C were reported by Magini *et al.*,[5)] which are shown in

Table 3. Root mean-square variation per unit length

| Pair at atoms | $D_{n_t n_t'}$/Å$^{1/2}$ |
|---|---|
| Intramolecular pairs | 0.06 |
| Intermolecular pairs | |
| O···O | 0.06 |
| O···O—C | 0.07 |
| O···O···O | 0.07 |
| Other pairs | 0.15 |
| Intermolecular pairs including hydrogen atoms | |
| D···O | 0.06 |
| D···O—C | 0.07 |
| D···O—D | 0.07 |
| D—O···O | 0.10 |
| Other pairs | 0.20 |
| Between molecular centers | 0.06 |
| Between an atom and its molecular center | 0.06 |

··· means a hydrogen bond.

Fig. 2 by full circles.** As seen in the figure, we can point out several distinctive features: the height and the position of its first peak, the hump at *ca.* $Q$=2.8 Å$^{-1}$, the broad peak at *ca.* 4—6 Å$^{-1}$ and the shoulder at *ca.* $Q$=7.0 Å$^{-1}$. These features suggest the existence of interactions between molecules in the liquid. The neutron structure factor $S_{mN}(Q)$ of liquid $CD_3OD$ at 10.0 °C obtained by authors[1] is given in Fig. 3 by open circles. In the figure, the behavior in the region of the hump ($Q \simeq 4$ Å$^{-1}$) is distinctive as well as that of the first peak. The feature of the hump is due to the superposition of the contributions of intramolecular structure and intermolecular one.[1] Then, in our calculation, the structural model of liquid methanol is required to make a reproduction of these features on both experimental results.

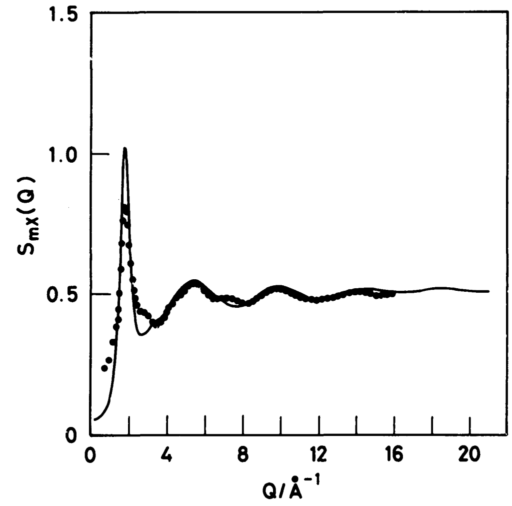


Fig. 2. Comparison between the calculated $S_{mX}(Q)$ for the unbonded monomer model and the observed X-ray structure factor $S_{mX}(Q)$.
——: Calculated $S_{mX}(Q)$ for the model with freely rotating methyl group,†† ●: observed $S_{mX}(Q)$. Observed data was transformed from the interference function $I(Q)$ by Magini et al.[5] by using the relation,[9]

$$S_{mX}(Q)=N_m^{-1}\{\sum_n f_n(Q)\}^{-2}I(Q).$$

††Concerning the rotation angle of the methyl group, there is no difference between the calculated $S_{mX}(Q)$ results for the two models (Table 1).

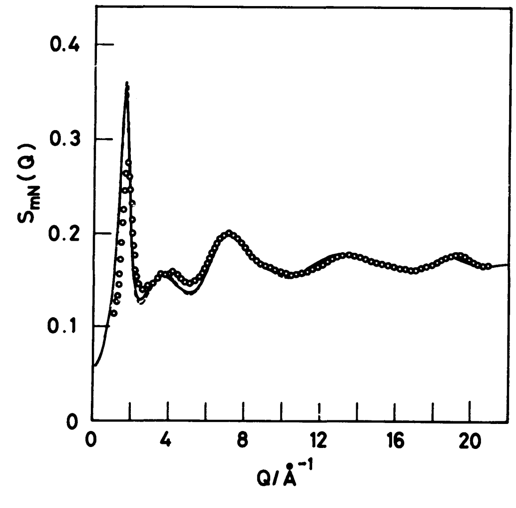


Fig. 3. Comparison between the calculated $S_{mN}(Q)$ curves for the unbonded monomer models and the observed neutron structure factor $S_{mN}(Q)$.
——: Calculated $S_{mN}(Q)$ for the model with freely rotating methyl group (Table 1), ----: calculated $S_{mN}(Q)$ for the model with fixed methyl group (Table 1), ○: observed $S_{mN}(Q)$.[1]

*Unbonded Monomer Model of Liquid Methanol.* For the present purpose, we first calculated the X-ray and neutron structure factors for the liquid model consisting of unbonded monomers by using Eq. 10. The $S_{mX}(Q)$ and $S_{mN}(Q)$ curves obtained with $r_{HS}$=3.60 Å are compared with the X-ray and neutron diffraction results in Figs. 2 and 3, respectively. As clearly seen in these figures, the calculated curves can reproduce the fundamental behaviors of the experimental data, though discrepancies still remain in its detailed behavior. This means the dominance of the liquid structure as a randomly packed state of effective hard spheres, and shows the availability of the hard-sphere expression[12] for the molecular center distribution adopted in the present calculation.

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** Quite recently, Narten and Habenschuss have reported and X-ray diffraction study on liquid alcohols (*J. Chem. Phys.* **80**, 3387 (1984)). Their data is found substantially in agreement with that of Magini *et al.*, and concerning the intramolecular structure of methanol, they assignied a quite identical value of the C-O distance with that of Magini *et al.*

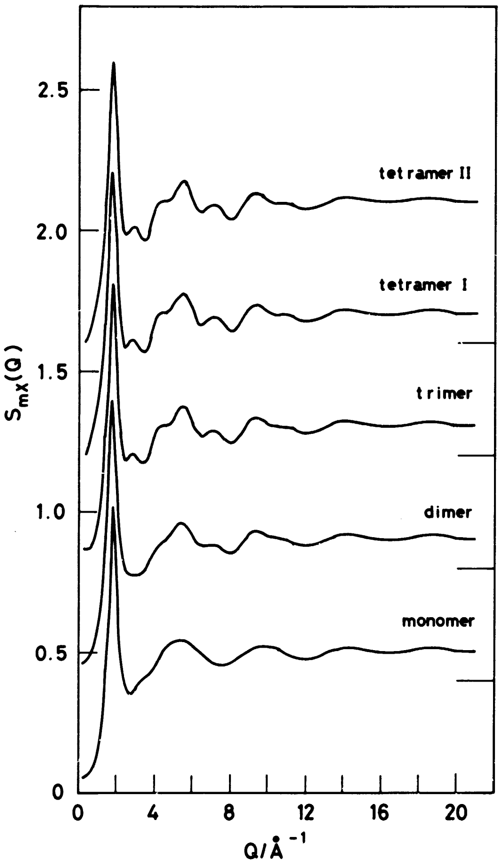

Fig. 4. The calculated $S_{mX}(Q)$ curves for five models.

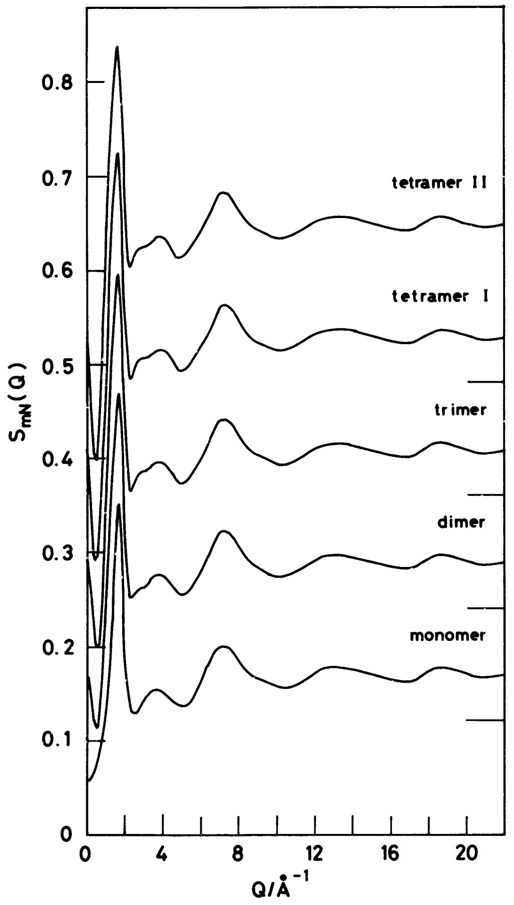

Fig. 5. The calculated $S_{mN}(Q)$ curves for five models with freely rotating methyl group.

*The Best Fit Cluster Model.* In Figs. 2 and 3 the discrepancies between the calculated curves and the observed data are seen in the intermediate $Q$ region, 2.3—8.0 Å$^{-1}$ for the X-ray result and 2.5—5.8 Å$^{-1}$ for the neutron result. To explain these features, the calculations of $S_{mX}(Q)$ and $S_{mN}(Q)$ are required for the models of the liquid consisting of molecular culsters. The orientational configuration of the nearest neighbor molecules within liquid methanol is obtained from the combination of the X-ray and the neutron results.

We calculated the $S_{mX}(Q)$ and $S_{mN}(Q)$ for dimer fluid, trimer fluid and tetramer fluids (I and II) and the calculated curves are shown in Figs. 4 and 5. The geometrical parameters of the cluster model are determined as follows: $r_{OO}$=2.85 Å, $\alpha=\beta=\gamma=109.5°$, $\theta=\phi=\psi=0.0°$ and hard sphere diameter $r_{HS}$=3.6 Å ($\xi$= 0.363, $\xi$; packing fraction), which all are found to be identical for each oligomer fluid. As clearly seen in these figures, the characteristic features observed in the intermediate $Q$ region (the hump at 2.8 Å$^{-1}$, the shoulder at *ca.* 4 Å$^{-1}$ and that at 7.0 Å$^{-1}$ in the X-ray curve and the hump at *ca.* 4 Å$^{-1}$ in the neutron curve) are well-reproduced in the calculated curves for the trimer and tetramer models. Thus, we conclude that the liquid structure of methanol is regarded as the aggregates of the molecular clusters consisting of three or four linearly hydrogen-bonded molecules. The calculated curves of X-ray and neutron structure factors for trimer fluid are compared with the diffraction data in Figs. 6 and 7, respectively. Concerning the fitness of the calculated curves with the observed ones, we can not discriminate, which of the trimer and tetramer is better. In Fig. 7, the curves for the two models of the methyl-group rotation (freely rotating model and fixed one)[1] are shown.

## Discussion

*Molecular Center Distribution.* In the present calculation, we assumed that the molecular center distribution in liquid methanol can be represented by the distribution in hard-sphere fluids and we substituted the $S_{HS}(Q)$ for the term $S_c(Q)$ in Eqs. 9 and 10. As mentioned in the preceding section, the features of the X-ray and neutron diffraction data were reproduced by the theoretical curves calculated under this assumption (Figs. 2—7). Especially, it is emphasized that the fundamental behaviors of diffraction data were explained by the use of the model of monomer fluid (Figs. 2 and 3). These facts mean the adequacy of

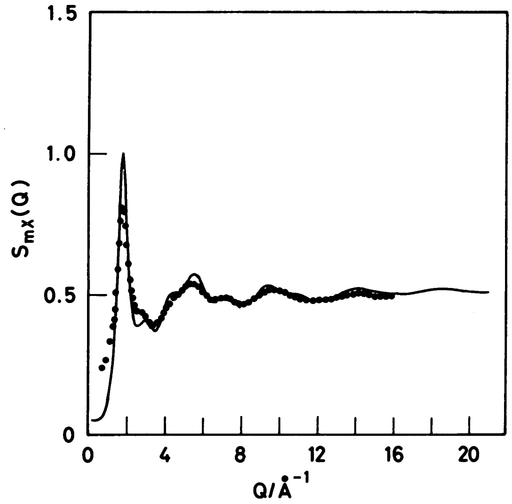

Fig. 6. Comparison between the calculated $S_{\mathrm{mX}}(Q)$ for the trimer model and the observed X-ray structure factor $S_{\mathrm{mX}}(Q)$.
——: Calculated $S_{\mathrm{mX}}(Q)$, ●: observed $S_{\mathrm{mN}}(Q)$.5)

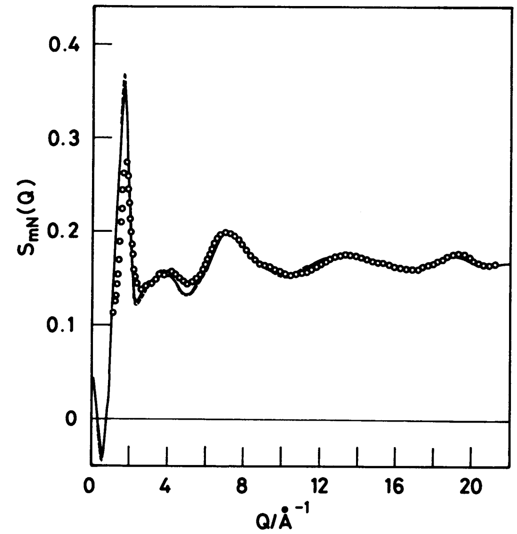

Fig. 7. Comparison between the calculated $S_{\mathrm{mN}}(Q)$ for the trimer models and the observed neutron structure factor $S_{\mathrm{mN}}(Q)$.
——: Calculated $S_{\mathrm{mN}}(Q)$ for the model with freely rotating methyl group, ----: calculated $S_{\mathrm{mN}}(Q)$ for the model with fixed methyl group, ○: observed $S_{\mathrm{mN}}(Q)$.1)

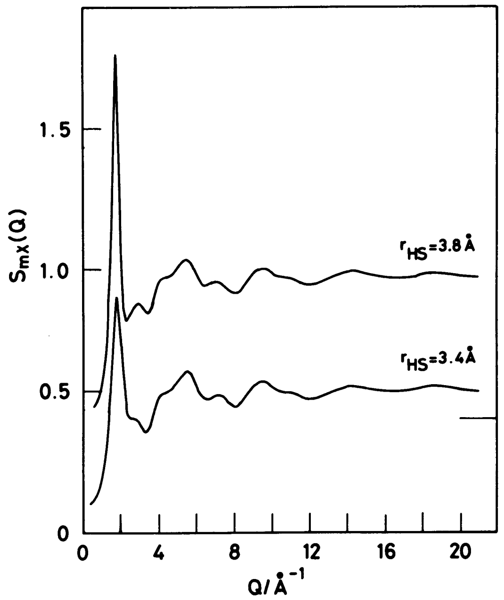

Fig. 8. The calculated $S_{\mathrm{mX}}(Q)$ curves for the trimer models with $r_{\mathrm{HS}}=3.4$Å and 3.8Å.

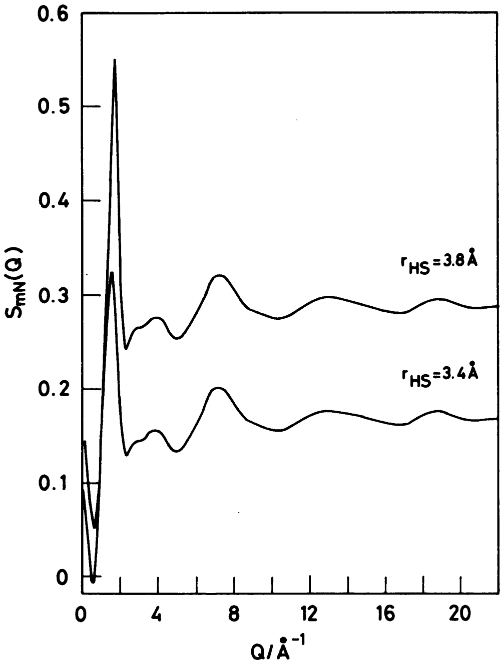

Fig. 9. The calculated $S_{\mathrm{mN}}(Q)$ curves for the trimer models with $r_{\mathrm{HS}}=3.4$Å and 3.8Å (freely rotating methyl group).

the assumption, and we can conclude that the liquid structure of methanol is expressed by the randomly-packed hard-sphere model as a rough approximation.

Concerning the hard sphere diameter as the effective size of molecules, we performed the calculation of X-ray and neutron structure factors, $S_{\mathrm{mX}}(Q)$ and $S_{\mathrm{mN}}(Q)$, for various magnitude of $r_{\mathrm{HS}}$. When the $r_{\mathrm{HS}}$ increases, the height of the first peak increases rapidly as seen in Figs. 8 and 9. In the case of $r_{\mathrm{HS}}=3.4$ Å ($\xi=0.306$), the $S_{\mathrm{mX}}(Q)$ curve in Fig. 8 shows improved agreement with the X-ray diffraction data, but, the first peak position of the $S_{\mathrm{mN}}(Q)$ curve in Fig. 9 shifts to lower $Q$ side and disagrees with the neutron diffraction data (Fig. 7). On the other hand, in the case of $r_{\mathrm{HS}}=3.8$ Å ($\xi=0.427$), the heights of the first

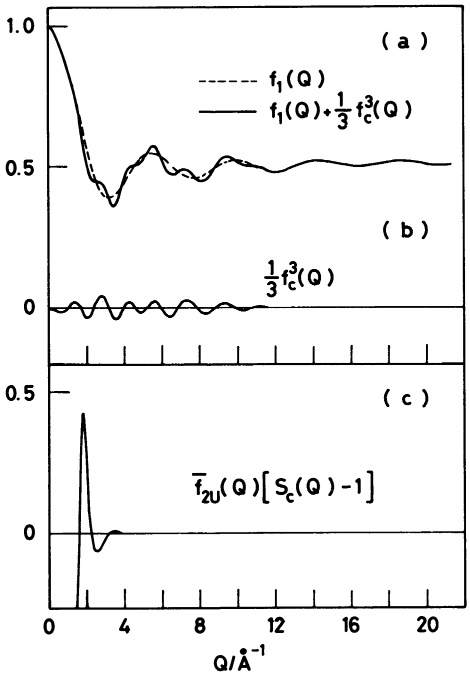

Fig. 10. Contribution of (a) $f_1(Q)$ $(=\frac{1}{3}f_1^3(Q))$ and $f_1(Q)+\frac{1}{3}f_c^3(Q)$, (b) $\frac{1}{3}f_c^3(Q)$ and (c) $\bar{f}_{2U}(Q)$ $\{S_c(Q)-1\}$ to the total $S_{mX}(Q)$ for the trimer model.

peaks of the $S_{mX}(Q)$ and $S_{mN}(Q)$ curves are too high compared with experimental results. The hard sphere diameter is thus determined to be 3.6 Å ($\xi$= 0.363) at room temperature. Formerly, in crystals, Tauer and Lipscomb[11] gave the value of 3.88 Å for the methyl-methyl-interchain distances at −110 °C and 3.64 Å at −160 °C, and Wertz and Krue reported the value of 3.8 Å in the liquid state by X-ray diffraction.[13] Pettitt and Rossky showed the value of 3.9 Å for the distance as the result of the recent RISM calculation.[14] Concerning the packing fraction, there is no systematic studies for molecular fluids and only the cases of liquid alkali metals are available. According to the results, the packing fraction of liquid metals is about 0.45 near the melting point,[12,15] and decreases rapidly as the temperature increases.[16] Then, since the melting point of methanol is far below the room temperature, −94 °C for $CH_3OH$ and −98 °C for $CD_3OD$, the present result that $\xi$=0.363 ($r_{HS}$=3.6 Å) at room temperature is acceptable. The value $r_{HS}$=3.6 Å is thus considered to be reasonable.

*Hydrogen-bonded Structure in Liquid Methanol.* In order to elucidate further the structure factors we examined the ingredients of the $S_{mX}(Q)$ and $S_{mN}(Q)$ for the trimer, by considering the terms in Eq. 9 and gave the terms in Figs. 10 and 11. In the higher $Q$ region, the structure factor curve is practically composed of the $f_1(Q)$ term only.[17] On the other hand, the first peak is mainly composed of the sum of the curve $f_1(Q)$ and the curve $\bar{f}_{2U}(Q)\{S_c(Q)-1\}$. The sum of these curves corresponds to the $S_{mX}(Q)$ and $S_{mN}(Q)$ for monomer fluids. As seen in the figures, the shoulders and the hump for the $S_{mX}(Q)$ curve are originated from the term $1/3f_c^3(Q)$, which reflects the hydrogen-bonded structures within the cluster. The influence of the factor $1/3f_c^3(Q)$ appears mainly in the lower $Q$ region. It is noticeable that the term $1/3f_c^3(Q)$ contributes to the total structure factor in a different way for $S_{mX}(Q)$ and $S_{mN}(Q)$. In the case of X-ray, its contribution remains up to 10—11 Å$^{-1}$ (Fig. 10(b)). On the other hand in the case of neutron, it disappears virtually beyond the range of $Q$, 6—7 Å$^{-1}$ (Fig. 11(b)).[1] The same trend is seen in the term $\bar{f}_{2U}(Q)\{S_c(Q)-1\}$ for each case (Figs. 10(c) and 11(c)).

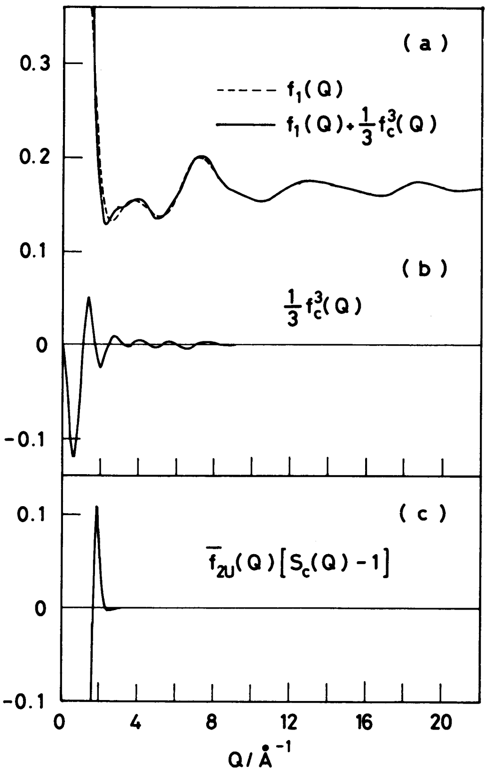

Fig. 11. Contribution of (a) $f_1(Q)$ $(=\frac{1}{3}f_1^3(Q))$ and $f_1(Q)+\frac{1}{3}f_c^3(Q)$, (b) $\frac{1}{3}f_c^3(Q)$ and (c) $\bar{f}_{2U}(Q)\{S_c(Q)-1\}$ to the total $S_{mN}(Q)$ for the trimer model with freely rotating methyl group.

Concering the hydrogen-bonded O-O distance $r_{OO}$ which gives a criterion for the strength of hydrogen bonds as well as the O-D (or O-H) distance in liquid phase, no significant changes occur in calculated $S_{mX}(Q)$ and $S_{mN}(Q)$ curves when its magnitude is varied from 2.75 to 2.90 Å. Then, we assigned the value of $r_{OO}$ to be 2.85 Å, which is identical with the value in the tetrahedral pentamer cluster in water.[6,7,18] Magini *et al.*[5] showed the value of 2.8 Å for the O-O distance by X-ray diffraction study. As the result of the Monte Carlo simulations for liquid methanol at 25 °C, Jorgensen gave the value of 2.8 Å for the distance.[19] The present value is consistent with these values.

In the present study, we performed a structure analysis of X-ray and neutron diffraction data for methanol as an associated liquid by using a newly-proposed structure factor formula. The complete elucidation of the liquid structure of methanol is still left for future studies, of course, and we obtained here a chain-cluster model to represent its fundamental features approximately. The liquid methanol is thus considered as an aggregate of chain clusters consisting of three or four molecules linked with hydrogen bonds on the average.

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