

Structure in liquid methanol from spatial distribution functions

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A structural approach that employs the spatial distribution functions of atoms has been shown recently [J. Chem. Phys. **99**, 3049 (1993)] to greatly improve our understanding of the local structure in liquid water. In the present study we obtain the oxygen–oxygen and oxygen–carbon spatial distribution functions, $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$, respectively, for liquid methanol and use them to characterize its equilibrium structure. For this purpose molecular dynamics simulations with the three-site model of Haughney, Ferrario, and McDonald are carried out at a temperature of 25 °C. Using the spatial distribution functions we demonstrate that the dominant H-bonded structure in this liquid is an open, nonlinear (“zig–zag”) chain of monomers packed spatially in a tetrahedral manner. $g_{OO}(r, \Omega)$ yields an average coordination number of 1.92 which agrees well with results from chain length analysis. There is no evidence in our structural data to support a local planar assembly of oxygen sites. We also observe features in $g_{OO}(r, \Omega)$ which suggest that neighboring H-bonded chains in liquid methanol have a tendency for parallel arrangements.

I. INTRODUCTION

Methanol is widely used in laboratories and industry and is certainly one of the most widely studied molecular liquids. Its physical–chemical properties have been extensively examined both experimentally^{1–5} and theoretically,^{6,7} and in recent years with computer simulations.^{8–11} One focus of these studies has been the structure in the liquid and its implications in dynamical phenomena (in dielectric relaxation,¹¹ etc.). It is now well documented that in the liquid MeOH molecules can form relatively long-lived hydrogen (H-) bonded clusters.^{8,11} Nevertheless, many details concerning molecular association still remain unclear and consequently several different (and frequently conflicting) geometrical models are being used in chemical literature^{6–8,10} to characterize the structure in this common solvent.

Until very recently our understanding of the structure in molecular liquids has relied largely upon radial distribution functions (RDF) of atoms and the abilities of various models for local molecular ordering to reproduce these functions. These one-dimensional RDFs are now routinely available from x-ray diffraction and neutron scattering experiments or from computer simulations, yet they are unable to characterize uniquely the actual local spatial assembly of nonspherical molecules in a liquid.¹² In the case of methanol this ambiguity has led to rather different structural models being proposed. One of these models assumes the dominance of small open chains of sequentially H-bonded MeOH monomers^{7,9,10} in the liquid; both RISM integral equation⁷ and computer simulation^{9,10} studies seem to support this picture. In recent calculations of the total scattering function for liquid methanol Sarkar and Joarder⁶ have used a model consisting of cyclic planar hexamers and have shown that closed clusters of H-bonded molecules can also provide a very good fit to experimental data. They have argued that the heat of fusion of methanol indicates the formation of cyclic, rather than open, clusters in the liquid state.

In recent simulation studies^{12,13} we have demonstrated that greater clarity can be achieved in the structural analysis

of liquids by utilizing pair-distribution functions which span both the radial and angular coordinates of particles, known as the spatial distribution functions (SDF). We have used the spatial distribution function of oxygen atoms, $g_{OO}(r, \Omega)$, to characterize a nontetrahedral (interstitial) coordination in liquid water.¹² Whereas this SDF displays a local pair-density maximum at interstitial separations of about 3.5–3.9 Å confined to a relatively small range of orientations Ω in a local frame, this maximum is lost when the angle-averaged radial distribution function for liquid water, $g_{OO}(r)$, is formed. Earlier studies attempting to identify this local maximum from one-dimensional RDF had led to numerous speculations on water structure.¹⁴ To our knowledge, no one has yet investigated the spatial distribution functions for liquid methanol. Clearly, these functions could be of great value in the analysis of its local structure by providing direct information on the spatial arrangement of MeOH molecules in the liquid state.

In this paper we present the spatial distribution functions, $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$, for liquid methanol at 25 °C and apply them to an analysis of the equilibrium structure in this liquid. These SDFs were calculated in computer simulations with the simple three-site model of Haughney, Ferrario, and McDonald¹⁰ for MeOH. Their model proved to be successful in reproducing various thermodynamic and kinetic properties of liquid methanol. $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$ represent full three-dimensional maps of the local oxygen and carbon density and thus provide an immediate image of the average spatial packing. In general, these direct structural data, which we supplement by an additional search for H-bonded polygons, suggest the formation of open, bent chains of H-bonded molecules as the dominant structure in liquid methanol. The SDFs also appear to indicate a preference for a parallel packing of chains in a bulk liquid where the dominant interactions between the chains are due to $O \cdots CH_3$ contacts.

The remainder of this paper is organized as follows. In Sec. II we outline the simulation procedure used in our study and in Sec. III we summarize the simulation results. Section

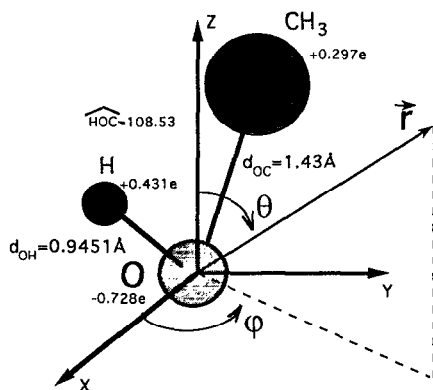


FIG. 1. The principal frame coordinates. Note that the plane of the molecule lies in the XZ plane.

IV is devoted to a discussion of the local structure in liquid methanol. Finally, our conclusions are given in Sec. V.

II. SIMULATION METHODOLOGY

In this article we report results from molecular dynamics (MD) simulations of liquid methanol performed with the effective three-site pair potential of Haughney, Ferrario, and McDonald.¹⁰ This model for the methanol molecule is shown in Fig. 1 where our local frame is also defined. In addition to Coulombic terms due to the charged sites shown in Fig. 1, the interaction between any pair of molecules contains four Lennard-Jones (LJ) terms acting between oxygen and carbon sites: the LJ parameters for like-site interactions are $\epsilon_{\text{LJ}}(\text{OO})=0.7307$ kJ/mol, $\sigma(\text{OO})=3.083$ Å, $\epsilon_{\text{LJ}}(\text{CC})=0.9151$ kJ/mol and $\sigma(\text{CC})=3.861$ Å. To compute LJ interactions for unlike-sites we have used the usual combining rules, $\epsilon_{\text{LJ}}(\text{OC})=[\epsilon_{\text{LJ}}(\text{OO})\epsilon_{\text{LJ}}(\text{CC})]^{1/2}$ and $\sigma(\text{OC})=1/2[\sigma(\text{OO})+\sigma(\text{CC})]$.

MD simulations have been carried with a sample of 108 molecules at a temperature of 25 °C, isothermal conditions being maintained by means of a Gaussian thermostat.¹⁵ We have worked at constant volume using the appropriate experimental density. Test simulations were also conducted with a sample of 256 molecules and no system-size dependence in the spatial distribution functions was detected. In our calculations we have utilized a truncated octahedral geometry for the simulation cell¹⁶ and periodic boundary conditions,¹⁷ the Ewald summation technique^{17,18} being used to evaluate the long-range Coulombic forces. The real space Ewald sum was carried over all nearest images, the Fourier space sum was truncated after the first 395 independent lattice vectors (corresponding to $n^2 \leq 53$), and the value of the unitless convergence parameter, κ , was 6.4. The reaction field contribution due to the surrounding dielectric continuum was obtained from the standard relationship given elsewhere;^{17,18} the dielectric constant of the continuum boundary was taken to be that of real liquid methanol at 25 °C. The Lennard-Jones interactions were truncated spherically at a cutoff of $(\sqrt{3}/4)L$, where L is the length of the cube containing the truncated octahedron, and appropriate tail corrections added. A fourth order Gear algorithm¹⁹ and a time

TABLE I. Basic simulation results for liquid methanol at 25 °C obtained with sample of 108 molecules.

| | |
|------------------------------------|-----------------|
| $\langle U_Q \rangle$ (kJ/mol) | -29.6 ± 0.1 |
| $\langle U \rangle$ (kJ/mol) | -35.2 ± 0.1 |
| ϵ | 31.5 ± 4.0 |
| D (10^5 cm ² /s) | 1.92 ± 0.04 |
| D_x (10^5 cm ² /s) | 1.80 |
| D_y (10^5 cm ² /s) | 2.14 |
| D_z (10^5 cm ² /s) | 1.83 |

step of 8 fs were used to integrate our equations of motion in which the rotational degrees of freedom were represented using quaternions.¹⁷ The system was equilibrated for approximately 200 ps and averages were collected over two subsequent 1 ns runs.

Our procedure for calculating spatial distribution functions has been discussed in detail in our previous work with liquid water.¹² In our implementation the angular coordinates of the separation vector are defined by $\Omega \equiv \{\theta, \varphi\}$, where θ is the angle between the median of the COH angle (the local Z axis) and the separation-vector \mathbf{r} , and φ is the angle between the principal X axis and the projection of \mathbf{r} onto the XY plane (see Fig. 1). We remark that the lower symmetry of the MeOH molecule results in a doubling of the numerical data required to represent the full SDFs from liquid methanol relative to liquid water (given the same numerical grid used for the local frame decomposition).

III. BASIC SIMULATION RESULTS

Simulation results for select thermodynamic properties, including the average Coulombic energy, $\langle U_Q \rangle$, and the average configurational energy, $\langle U \rangle$, the static dielectric constant, ϵ , the mean self-diffusion coefficient, D , and its principal (orthogonal) components for liquid methanol are given in Table I for a 108 molecule sample at 25 °C. The usual RDFs, $g_{\text{OO}}(r)$ and $g_{\text{OC}}(r)$, can be found in Fig. 2. Where comparison is possible these quantities are in a good agreement with previous calculations.¹⁰

The spatial distribution functions $g_{\text{OO}}(r, \Omega)$ and $g_{\text{OC}}(r, \Omega)$ for liquid methanol at 25 °C are shown, respectively, in Figs. 3 and 4 where explicit dependencies upon the interatomic separations r and the angles θ are considered for selected values of the angular variable φ . The angles θ and φ are defined as in Fig. 1. In Figs. 3(a) and 4(a) “slices” of $g_{\text{OO}}(r, \Omega)$ and $g_{\text{OC}}(r, \Omega)$ for $\varphi=0$ deg are plotted. These slices reflect those pair correlations in the plane of the MeOH molecule which have positive X coordinates. The most prominent feature in Fig. 3(a) is the peak due to the oxygen sites of the first H-bond accepting neighbors. In Figs. 3(b) and 4(b) we give $g_{\text{OO}}(r, \Omega)$ and $g_{\text{OC}}(r, \Omega)$ for $\varphi=90$ deg (i.e., O···O and O···C correlations in directions perpendicular to the plane of the MeOH molecule). Finally, in Figs. 3(c) and 4(c) slices of $g_{\text{OO}}(r, \Omega)$ and $g_{\text{OC}}(r, \Omega)$ for $\varphi=180$ deg are presented, reflecting pair correlations in the plane of the molecule but now in the negative X direction. These figures are particularly convenient if we wish to visualize the local structure in the vicinity of a methyl group. Clearly, $g_{\text{OO}}(r,$

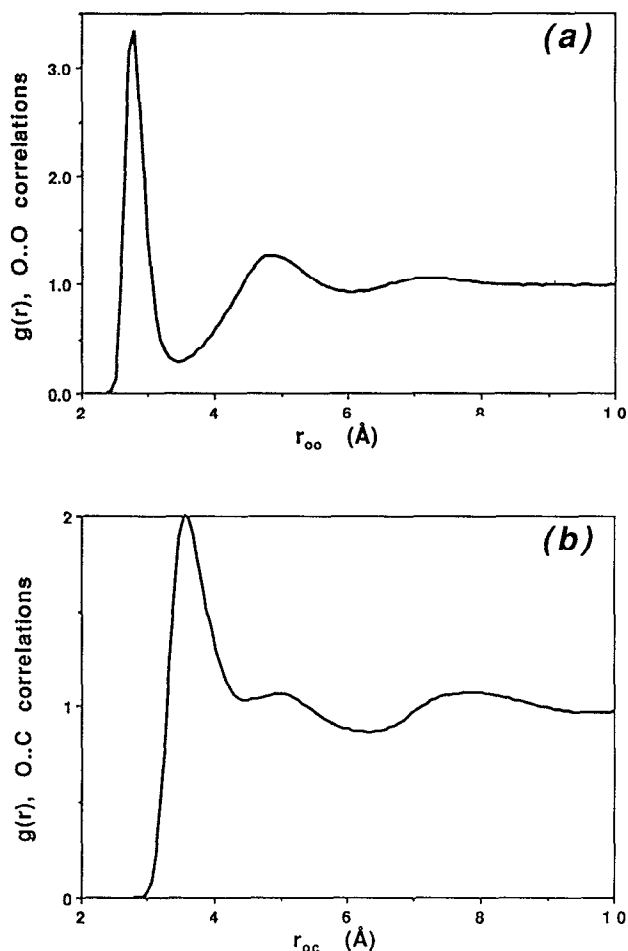


FIG. 2. The radial (angle-averaged) distribution functions for liquid methanol at 25 °C. (a) $g_{OO}(r)$, (b) $g_{OC}(r)$.

Ω) and $g_{OC}(r, \Omega)$ provide a great deal more detailed information on the local structure in liquid methanol than the usual RDFs, $g_{OO}(r)$ and $g_{OC}(r)$.

IV. STRUCTURE IN LIQUID METHANOL

The differences in the molecular structures of MeOH and H₂O give rise to very different local structures in their liquids. Although strong directionally dependent electrostatic forces act between molecules in both liquids, in liquid methanol the steric bulk of the methyl group does not allow MeOH molecules to form the continuous three-dimensional H-bonded network peculiar to liquid water.^{12,14} As mentioned above, both open chain^{9,10} and ring cluster⁶ models have been shown to be consistent with available RDFs¹⁻³ for methanol. To provide further insights into the local structure in liquid methanol we now consider in detail the features in $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$.

Our analysis begins with the oxygen–oxygen spatial distribution function shown at different values of the angular coordinate φ in Fig. 3. Peaks due to the first, second, and third (sequential) neighbors have been identified as 1, 2, and 3, respectively. As we might expect, the dominant feature in $g_{OO}(r, \Omega)$ for liquid methanol is an extremely sharp peak due to the first H-bond accepting neighbors which can be seen in

Fig. 3(a) at separations of about 2.8 Å and at angles θ around 54°. The distribution of H-bond donors, which is found in Fig. 3 at the same separations but at large θ , is broader. These two nearest-neighbor peaks are well-defined and integration yields an average coordination number of 1.92 in our model liquid. It is important to point out that our integration of the first maximum in the angle-averaged radial distribution function $g_{OO}(r)$ yields a somewhat larger value of 2.01 for an average coordination number. (Virtually the same coordination number has been reported earlier by Jorgensen for a very similar model for liquid methanol⁹). Although the difference between the coordination numbers from $g_{OO}(r, \Omega)$ and those from $g_{OO}(r)$ appears to be rather small, it nevertheless has significant structural implications. Indeed, a coordination number of 2.0 would support the model of Sarkar and Joarder⁶ (of cyclic clusters) or the model of infinite chains of monomers, while a coordination number less than two suggests the formation of finite chains, in accord with the previous observations of Haughney, Ferrario, and McDonald,¹⁰ as well as others workers.^{7,9} Our estimate of 1.92 for the average coordination number in liquid methanol is slightly larger than the average number of H-bonded neighbors, 1.87, given by Haughney, Ferrario, and McDonald.¹⁰ This small discrepancy arises because their geometric criterion of H bonding is not entirely consistent with our criterion based on knowledge of the full spatial distribution of nearest neighbors. In particular, they regard two MeOH molecules as being H bonded if their O...O separation is less than 3.5 Å and their OH...O angle is less than 30°. It follows from the present data that, in fact, H-bonded neighbors [those which are part of the two first distinct maxima in the SDF $g_{OO}(r, \Omega)$] can be found at separations as large as 4.0 Å for certain directions Ω in the local frame.

We now shift our discussion to the more remote neighbors in liquid methanol structure where two distinct classes of neighbors apparently exist. The first class of neighbors are molecules which appear to belong to the same chain as the central (principal) molecule giving rise to the features denoted as 2 and 3 in Figs. 3(a) and 3(b). The second class of neighbors are those molecules which appear to belong to another, closely packed chain. The presence of these molecules is apparent in Fig. 3(c) as a rather wide ridge in $g_{OO}(r, \Omega)$ at separations of about 5.2 Å spanning the entire range of angles θ . We recall that Fig. 3(c) contains the $\varphi=180$ deg slice of $g_{OO}(r, \Omega)$, the local structure on the methyl “side” of the molecule. To help clarify this packing pattern further, we have plotted in Fig. 5 a full three-dimensional local density map for oxygen atoms. In Fig. 5 the isosurfaces reflect an oxygen density of 1.5 times that of the bulk at 25 °C. Both nearest and more distant (second) chain partners can be clearly seen, as well as molecules in neighboring chains. The latter are manifest in Fig. 5 as the broad cap centered over the methyl group of the central molecule and the small archtype feature nearby.

The features evident in the three-dimensional oxygen density map (see Fig. 5) indicate that H-bonded chains in liquid methanol are nonlinear; the positions of maxima for distant-chain neighbors and the broad H-bond donor distribution imply a “zig-zag” coordination with an obvious ten-

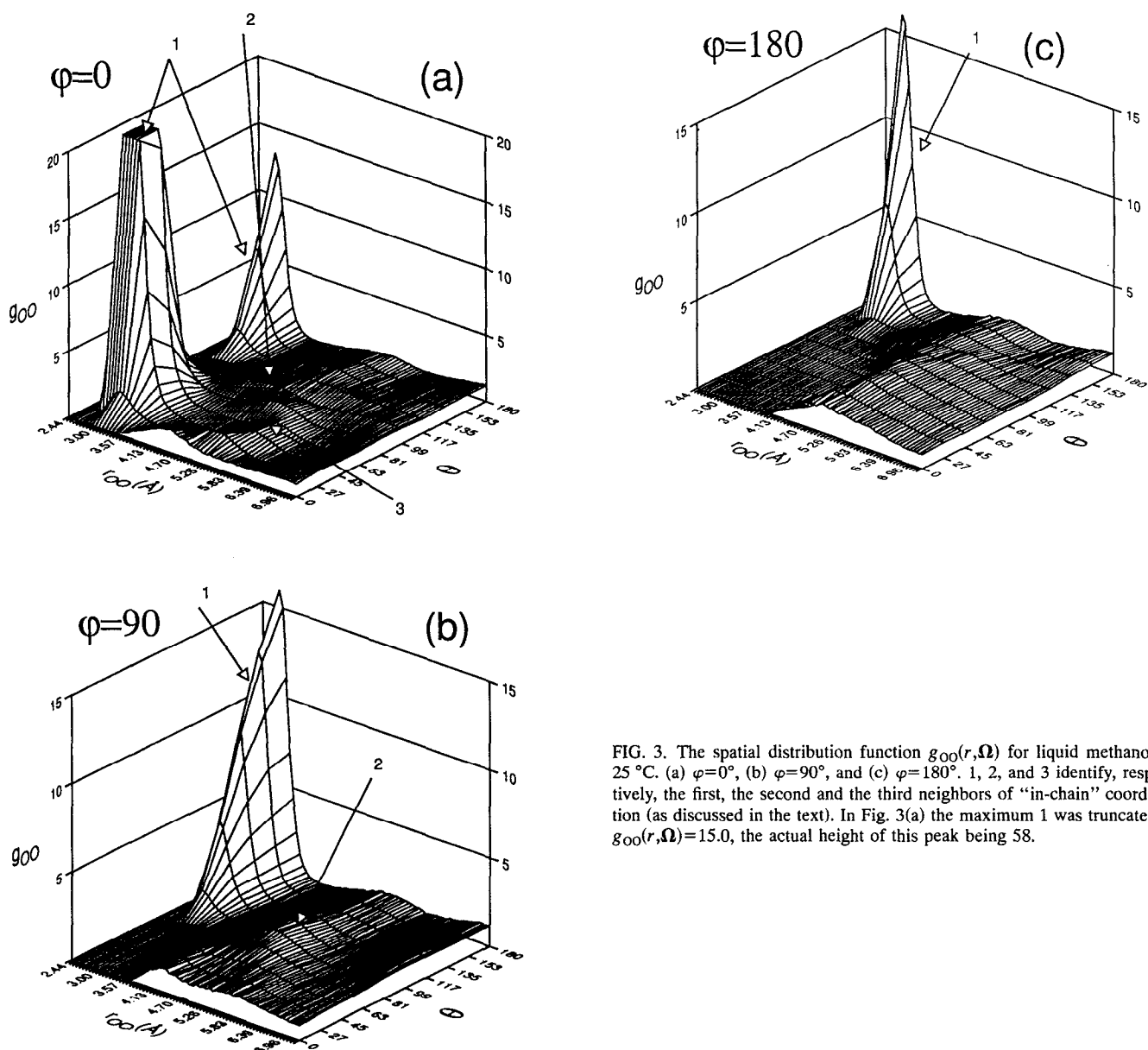


FIG. 3. The spatial distribution function $g_{00}(r, \Omega)$ for liquid methanol at 25 °C. (a) $\varphi=0^\circ$, (b) $\varphi=90^\circ$, and (c) $\varphi=180^\circ$. 1, 2, and 3 identify, respectively, the first, the second and the third neighbors of "in-chain" coordination (as discussed in the text). In Fig. 3(a) the maximum 1 was truncated at $g_{00}(r, \Omega)=15.0$, the actual height of this peak being 58.

dency to sequent tetrahedral packing. A similar conclusion has also been reached in the experimental work of Magini, Paschina, and Piccaluga.² There is no evidence in this map to suggest planar assemblies of oxygen sites, and hence we would conclude that the structural model of Sarkar and Joarder⁶ which relies on planar hexagonal rings is not realistic, at least for the present system. In addition, we have performed an explicit search for possible ring closures to provide further structural information for liquid methanol. We have used a polygon search algorithm similar to that described by Motakabbir and Berkowitz²⁰ in their work with liquid water. However, our implementation employs a criterion of H bonding in liquid methanol based on the oxygen-oxygen SDF, in particular, we have regarded two MeOH molecules as being H bonded if their O...O separations and their angular coordinates fall within the first H bond accepting maximum of $g_{00}(r, \Omega)$. During this search the incidences of both open chains and rings were monitored. In general, open chains were found to predominate. The average chain

length was approximately 10–12 monomers which, if we assume negligible ring closures, agrees well with the average coordination number of 1.92 derived above from $g_{00}(r, \Omega)$. A small number of three and four member rings was identified, incorporating around 5% of all H-bonded molecules in the system. Yet, careful examination reveals that many of these rings are due to self-crossing of chains (a small ring with a long tail).

The three-dimensional map shown in Fig. 5 enables us not only to clarify the coordination of H-bonded monomers within the same chain, it also provides insights into the packing pattern of the chains themselves in the bulk liquid. The broad cap of oxygen sites over the methyl group, representing the OC...O correlations from neighboring chains, has its maximum at $\varphi=180$ deg and $\theta \approx 54$ deg. The average separation for these sites is approximately 5.2 Å. The small archetype feature evident in Fig. 5, representing the nearest O...O interchain contacts, has its maximum at about $\theta=0$ deg (over a small range of angles φ) and at separations of

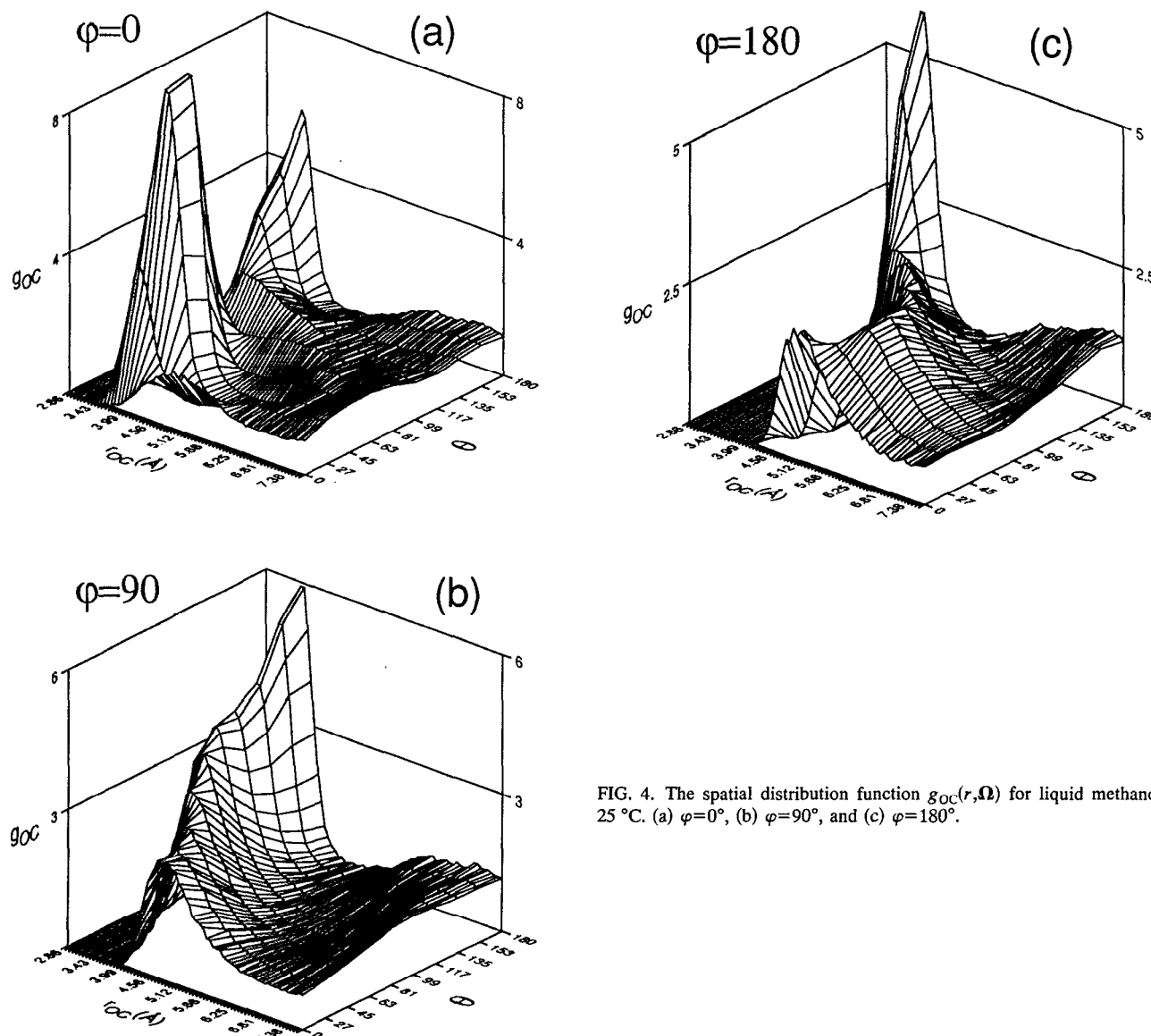


FIG. 4. The spatial distribution function $g_{OC}(r, \Omega)$ for liquid methanol at 25 °C. (a) $\varphi=0^\circ$, (b) $\varphi=90^\circ$, and (c) $\varphi=180^\circ$.

about 4.6 Å. These coordinates suggest that H-bonded chains in liquid methanol have a tendency for parallel arrangements, similar to that observed in the solid state.²¹ At the same time, the repeat distances for the interchain oxygen–oxygen correlations in the liquid state (~ 4.6 and ~ 5.2 Å) appear to be smaller than the corresponding repeat distances measured for the solid state, ~ 4.7 and ~ 5.5 Å, respectively.²¹ The apparent existence of a tight parallel local assembly in the liquid is perhaps not surprising since it is favored energetically by the electrostatic $O \cdots CH_3$ interactions which help to stabilize this structure in the solid. We point out that the oxygen–oxygen distributions for the interchain neighbors in liquid methanol are very broad which of course indicates much greater variation in the possible arrangements of chains in the liquid state in comparison with their solid packing.

We now shift our focus of attention to the spatial distribution of carbon sites as represented in Fig. 4 by the oxygen–carbon SDF $g_{OC}(r, \Omega)$. The most prominent feature in this SDF is a sharp peak with a maximum at separations of about 3.9 Å and θ of about 54 deg for $\varphi=0$ deg [see Fig. 4(a)]. This peak reflects the distribution of carbon atoms of

the nearest H-bonded (or chain) neighbors (these molecules also being evident as an extremely sharp peak in $g_{OO}(r, \Omega)$ at approximately the same angles). In order to provide further insights we have plotted the corresponding three-dimensional local density map for carbon atoms in Fig. 6, where the isosurfaces reflect a carbon density of 2.8 times that of the bulk liquid. Intrachain oxygen–carbon correlations are clearly demonstrated in Fig. 6. The small cap over the hydrogen site of the central molecule reflects carbon atoms in H-bond accepting neighbors, while the diffuse bananalike feature at the bottom is largely due to H-bond donor molecules.

The spatial picture of the short-range order in methanol emerging from Figs. 5 and 6 provides a natural explanation for some subtle features of the local molecular diffusion in this liquid. As can be seen in Table I, the principal components of the translational self-diffusion coefficient for liquid methanol are relatively close in value, unlike those for liquid water. The Y component, which measures the out-of-plane diffusive motion, is approximately 1.2 times larger than the X and Z components. This dynamical behavior is consistent

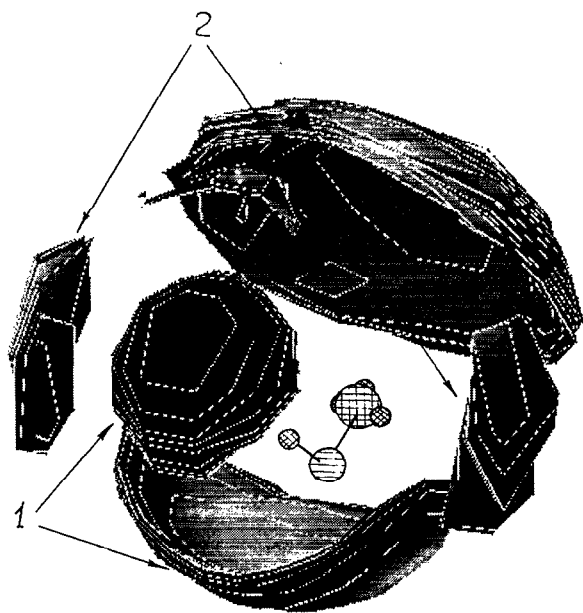


FIG. 5. A three-dimensional map of local oxygen density in liquid methanol at 25 °C. The isosurface for $g_{OO}(r, \Omega)=1.5$ is shown. The central molecule has been included to define the local frame. 1 and 2 are as in Fig. 3.

with the spatial pair-density maps shown in Fig. 5 and 6. In particular, Fig. 5 suggests that MeOH molecules “see” more empty space in out-of-plane directions and it is the corresponding Y component of the self-diffusion coefficient that has the largest value. At the same time, the close proximity of H-bonded chains in liquid methanol helps to explain the relatively small directional anisotropy exhibited by the local translational diffusion. By contrast, in liquid water (with its continuous three-dimensional network of H bonds) there can

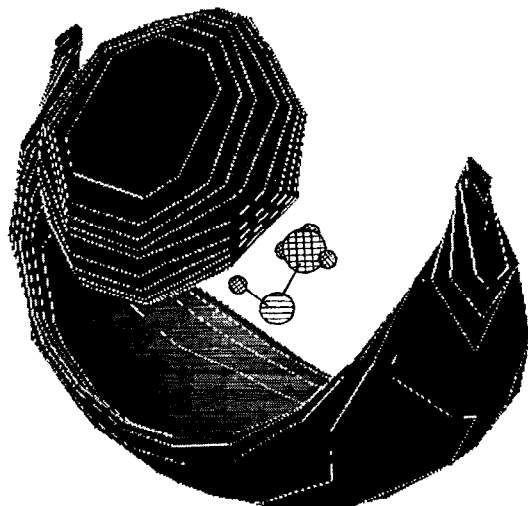


FIG. 6. A three-dimensional map of local carbon density in liquid methanol at 25 °C. The isosurface for $g_{OC}(r, \Omega)=2.8$ is shown. The central molecule has been included to define the local frame.

be a twofold difference in the principal components of the translational self-diffusion coefficient.^{22,23}

V. CONCLUSIONS

In this article we have reported results from MD simulations of liquid methanol at room temperature performed with the three-site model of Haughney, Ferrario, and McDonald.¹⁰ We have determined spatial distribution functions for the oxygen–oxygen and oxygen–carbon correlations, namely, $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$, and have used these to characterize the equilibrium structure in this liquid. One of our principal aims has been to demonstrate that a structural analysis based on SDFs (rather than on radial distribution functions) can greatly improve our understanding of the local structure in molecular liquids.

Using the SDF $g_{OO}(r, \Omega)$, we have analyzed in detail the structural implications of H bonding in liquid methanol. In particular, we have argued that the dominant H-bonded structure in this liquid is an open, nonlinear chain of monomers with approximately tetrahedral coordination of sequent oxygen sites. Although this coordination has been suggested in previous studies,^{2,7} $g_{OO}(r, \Omega)$ and the corresponding three-dimensional map of local oxygen density have enabled us to visualize directly this pattern. Integration of the first two maxima in $g_{OO}(r, \Omega)$ due to nearest neighbors yields an average coordination number of 1.92 in liquid methanol which agrees well with the results from a chain length analysis. No evidence has been found in our structural data to support a planar assembly of oxygen sites or the formation of hexagonal rings as suggested recently by Sarkar and Joarder.⁶

The SDFs $g_{OO}(r, \Omega)$ and $g_{OC}(r, \Omega)$ have helped to clarify not only the coordination of sequentially H-bonded monomers, they have also provided insights into the packing pattern of chains in the bulk liquid. H-bonded chains in liquid methanol appear to prefer a local parallel arrangement, similar to the structures found in the solid state. We suggest that $O \cdots CH_3$ interactions are important when considering neighboring H-bonded chains in liquid methanol. Our structural data were also useful in identifying connections between the local structure and the local translational diffusion of MeOH molecules in the liquid.

Note added in proof. The insights into the local structure provided by SDF can also help explain other dynamical behaviors of molecular liquids. For example, given that the peak due to nearest H-bond accepting neighbors is in fact sharper in methanol than in water, it is then not surprising that the orientational time-correlation function for O–H bonds should exhibit a more pronounced librational feature in the former (see Fig. 2 of Ref. 24).

ACKNOWLEDGMENT

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