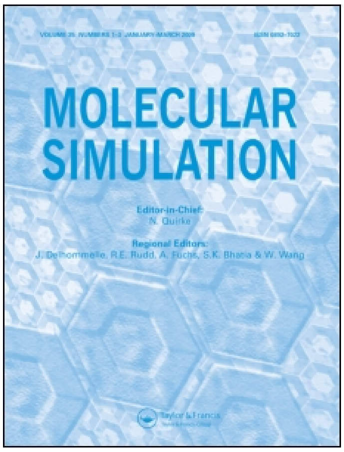

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Angularly Resolved Density Distributions-A Starting Point for Analysis of Liquid Structure

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ANGULARLY RESOLVED DENSITY DISTRIBUTIONS-A STARTING POINT FOR ANALYSIS OF LIQUID STRUCTURE

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We propose that the angular unfolding of atomic density distributions exposes some main features of liquid structure. Examples are the mass and the angular location of major maxima. Such structural features constitute a useful starting point for the analysis of liquid structure. To demonstrate this we have analyzed a molecular dynamics trajectory of an equimolar water-acetonitrile mixture. A new method to characterize the extrema of density distributions is used for the analysis. Using this method we draw some conclusions about different types of hydrogen bonds, their lifetimes, and their associated transition probabilities. We also draw some conclusions about recurrent molecular pair configurations.

Keywords: Liquid structure; spatial distribution function; molecular mixture; molecular dynamics simulation; water; acetonitrile

1 INTRODUCTION

When studying a molecular system, it is sometimes important to understand its spatial structure. In order to describe the structure of a liquid, it is standard practice to define average density distributions of various types [1]. In this work we are primarily concerned with spatial distribution function (SDFs) of the type:

$$g_{AB}(\vec{r}) = \frac{\rho_B(\vec{r}\,|\,\vec{r}_A = 0)}{\rho_B} \tag{1}$$

Here A and B each denotes an atom type, ρ_B denotes the bulk density of type B atoms and, $\rho_B(\vec{r}\,|\,\vec{r}_A = 0)$ is the conditional density of type B atoms at the point $\vec{r}$ as measured in a coordinate system rigidly attached to the molecule containing atom A. The origin of this coordinate system is at the atom A. Casually one may describe this as the average distribution of B atoms an observer riding on an atom of type A would see.

Averaging over all directions of $\vec{r}$ in the definition (1) above yields a radial distribution function (RDF). We denote distribution functions of this type by $g_{AB}(r)$. It is possible to obtain some structural information from radial distribution functions. See Figure 1. One can, for example, find a first shell – and sometimes additional shells – where the local density is considerably above the bulk value. However, the angular averaging removes some information that can be pertinent to the analysis of the spatial structure of liquids. See Svishchev and Kusalik [2] for an example of this. With this work we attempt to show that SDFs, under some circumstances, constitute a more natural starting point for the analysis of spatial structure than RDFs.

We have chosen an equimolar mixture of water (H_2O) and acetonitrile (CH_3CN) to illustrate this approach for several reasons. For one, there is an

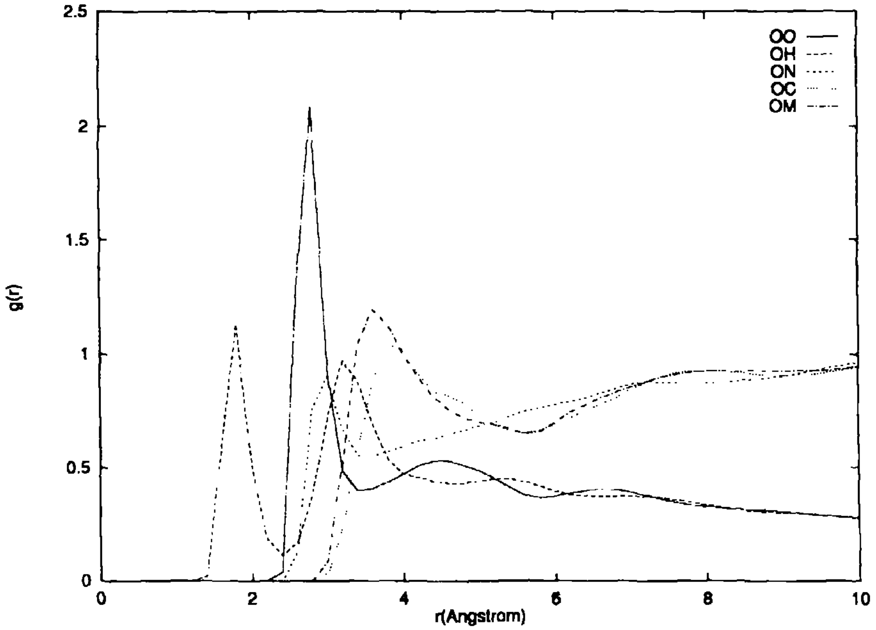

FIGURE 1 The radial distribution functions g_{OO}, g_{OH}, g_{ON}, g_{OC}, and g_{OM} are shown above. g_{OO} and g_{OH} have high peak values (they have been scaled down by a factor 0.25 in this figure), and one can see some signs of a second shell of coordinated atoms in these distributions.

ongoing discussion concerning the micro structure [3] of this mixture. Moreau and Douhéret [4] proposed in 1975 that the mixture has three different types of micro structures depending on the composition. The micro structure has been discussed by Moreau *et al.* [4–6], Easteal *et al.* [7–9], Davis [10, 11], Eaton *et al.* [12], and Hertz and Leiter [13, 14] among others. We have also studied this mixture previously [15] and some questions concerning the micro structure still remain unresolved. Another reason to choose this mixture is the relative simplicity of the molecules: they are small and acetonitrile may be modeled as cylindrically symmetric, see Figure 2. Furthermore, both molecules are strong dipoles, and one can hence anticipate some angular structure in molecular pair correlations.

2 COMPUTATIONAL METHODS

Jorgensen and Briggs [16] have developed a simple three-site potential for acetonitrile. This potential has been shown to describe the structural and thermodynamical properties of pure acetonitrile well, in spite of the fact that the methyl group is treated as a united atom. We have used this potential together with the SPC/E water potential [17]. See Figure 2 for the geometry of the molecules.

Using these potentials we have carried out a molecular dynamics simulation of an NVT-ensemble at 300 K. 128 water molecules were placed together with 128 acetonitrile molecules in a cubic box with side length 24.54 Å.

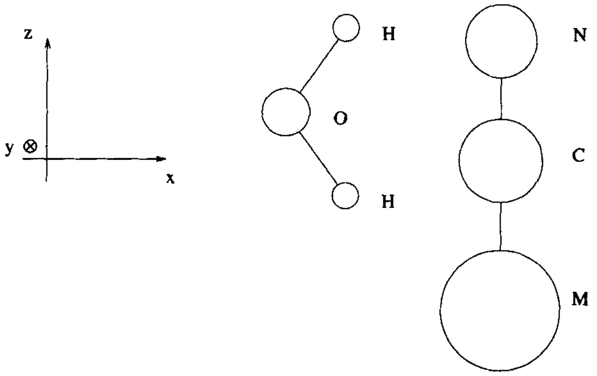

FIGURE 2 The geometries of the water and acetonitrile models are shown in the figure. To the left water with $d_{\mathrm{OH}} = 1$ Å and $HOH = 109.47$. To the right acetonitrile (N = nitrogen, C = carbon, M = methyl group) with $d_{NC} = 1.157$ Å, $d_{CM} = 1.458$ Å, and $d_{NM} = 2.615$ Å. The molecules are oriented so that the axes of their local frames are parallel to the axes of the coordinate system drawn in the figure.

This corresponds to the experimental density of 0.85 g/cm^3 [4]. The temperature was regulated by a Nosé-Hoover thermostat [18]. Details are given in the appendix.

We started this simulation from the final configuration of our previous simulation [15]. The system was first integrated for 0.3 nanoseconds to reach equilibrium and then data was collected during the consecutive 0.2 nanoseconds. The time step was 1 fs. During the data collection period all quantities investigated by us (e.g. the potential energy and the temperature) fluctuated about their mean values as they should.

The structural results which are presented in section 3 bear some characteristics of a phase separation; the high peak value of $g_{OO}(r)$ being one. We have monitored the average OO, CC, and OC distances during the data collection period. The average distances are 10.63 ± 0.14 Å, 11.71 ± 0.03 Å, and 12.23 ± 0.05 Å respectively [21]. The modest non systematic fluctuations about the mean values indicate that we have an equilibrium situation or that we are in a metastable state. We defer further comments to a paper to be published later, and settle here with having noted that the observed characteristics of phase separation seem stationary.

3 RESULTS/DISCUSSION

3.1 Angular Structure of Shells

When resolving the RDF of oxygen around oxygen in angular components by means of an SDF some new features emerge. Compare $g_{OO}(r)$ in Figure 1 and $g_{OO}(\vec{r})$ in Figure 3. The RDF has a sharp peak at $r = 2.8$ Å and a second low and broad peak at $r = 4.5$ Å. Peak values are 8.4 and 2.2 respectively. This can be taken to indicate that there is a well defined primary shell and a diffuse secondary shell of water molecules surrounding the central molecule. From the SDF it is, however, clear that the structure is more complex: The first RDF maximum at $r = 2.8$ Å is resolved into three different maxima: A, B, and C. See Figure 3c. The maxima A and B corresponds to hydrogen bond sites where the water molecule at the center of the coordinate system donates a proton; and the maximum C corresponds to a hydrogen bond site where the water molecule accepts one, two, or even three binding protons. Maxima A and B have the peak value 181 at $r = 2.7$ Å. (See Tab. 1 for a listing of some peak positions and their corresponding peak values). The second RDF maximum consists of at least six different maxima all with peak values above 3. The presence of the six lower

TABLE I Properties of some SDF maxima. Key: *atom pair* tells us which distribution function we are dealing with. g_{low} denotes the cut off used to define the connected volume surrounding the maximum. *maximum position* ($\vec{r}_{\text{max}}$) lists the Cartesian coordinates and the radial coordinate of the point where $g(\vec{r})$ has a local maximum. *maximum height* denotes the value of g at $\vec{r}_{\text{max}}$. *mass* (n) and *center of mass* ($\vec{r}_{\text{com}}$) have their intuitive meanings. (See definitions 2 and 3 for details.) *bulk average* denotes the mass which would have been found in the selected volume, if the conditional density of atoms surrounding the central molecule was equal to the bulk density of the same atoms, see definition 4. σ is an estimate of the spread (standard deviation) of the mass in the volume around its center of mass. ± indicates that the volume surrounds two maxima: one with the + and one with the − coordinate (see Fig. 3). Note that all volumes in this table are connected. All lengths are in Å

atom pair	g_{low}	*maximum position*				*maximum height*	*center of mass*				*mass*	*bulk average*	σ
		x	*y*	*z*	*r*		*x*	*y*	*z*	*r*			
OO	3.3	1.6	0.0	2.2	2.72	181.0	1.6	0.0	2.2	2.81	0.66	0.03	0.7
OO	10.0	1.6	0.0	2.2	2.72	181.0	1.6	0.0	2.2	2.78	0.56	0.02	0.6
OO	3.3	−2.2	±1.6	0.0	2.72	24.5	−2.0	0.0	0.0	2.79	1.21	0.13	2.0
OO	10.0	−2.2	±1.6	0.0	2.72	24.5	−2.2	0.0	0.0	2.76	0.72	0.13	1.7
OO	3.3	3.8	0.0	0.0	3.81	4.2	3.4	0.0	0.0	3.67	0.08	0.02	1.4
ON	1.3	1.8	0.0	2.2	2.84	16.6	1.7	0.0	2.2	2.81	0.15	0.04	0.9
ON	3.3	1.8	0.0	2.2	2.84	16.6	1.7	0.0	2.3	2.93	0.12	0.02	0.7
ON	10.0	1.8	0.0	2.2	2.84	16.6	1.7	0.0	2.3	2.88	0.03	0.002	0.4
OM	1.3	1.0	±3.4	0.0	3.54	3.8	0.2	0.0	0.0	3.83	1.22	0.67	0.3*
OM	2.0	1.0	±3.4	0.0	3.54	3.8	0.16	0.0	0.0	3.65	0.45	0.19	0.2*
OM	2.5	1.0	3.4	0.0	3.54	3.8	1.1	3.3	0.0	3.61	0.07	0.03	1.0
OC	1.3	2.2	0.0	3.2	3.89	3.9	2.3	0.0	3.0	3.86	0.08	0.04	1.1
OC	1.4	1.2	3.6	0.0	3.79	1.9	1.7	3.7	0.0	4.17	0.11	0.07	1.2

*Here we only consider the spread of the mass along the radial direction since the maximum nearly enclose the central molecule.

maxima indicates that sometimes three or even more [26] water molecules are hydrogen bonded to each other, see Figure 3c.

Angular decomposition of the nitrogen around oxygen RDF, see Figures 1 and 4, again reveals a new structure. In Figure 4 one can see that the two highest maxima are, as in the case of the oxygen-oxygen distribu-

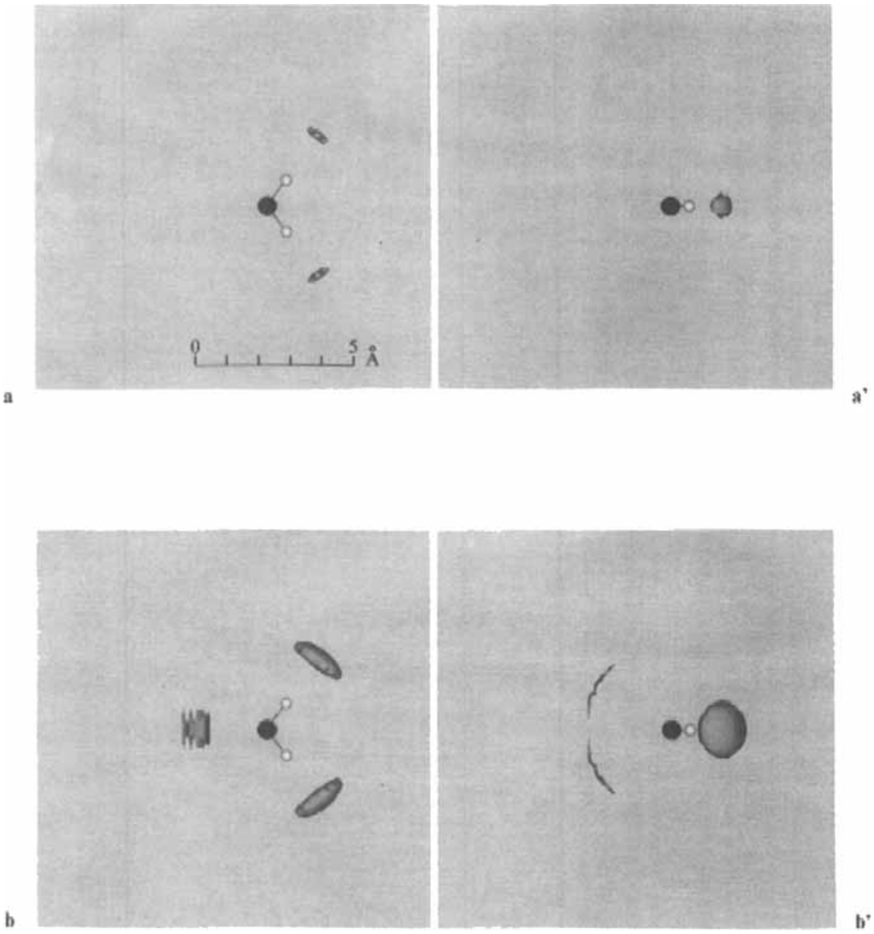

FIGURE 3 Six isosurfaces defined by $g_{OO} = 100, 20, 3.3, 2, 0.5, 0.2$ are shown in (a)–(f). In (a')–(f') another projection of the same surfaces is shown. The surfaces in figures (e)–(f) and (e')–(f') are have been sliced open by the planes $y = 0$ and $z = 0$ respectively. A, B and C in figure (c) gives names to the primary maxima which correspond to hydrogen bond sites. At A and B the central water molecule is donating a proton, and at C it is accepting one, two, or three protons. In (a) the length scale common to (a)–(d) and (a')–(d') is indicated. In (e) the length scale common to (e)–(f) and (e')–(f') is indicated.

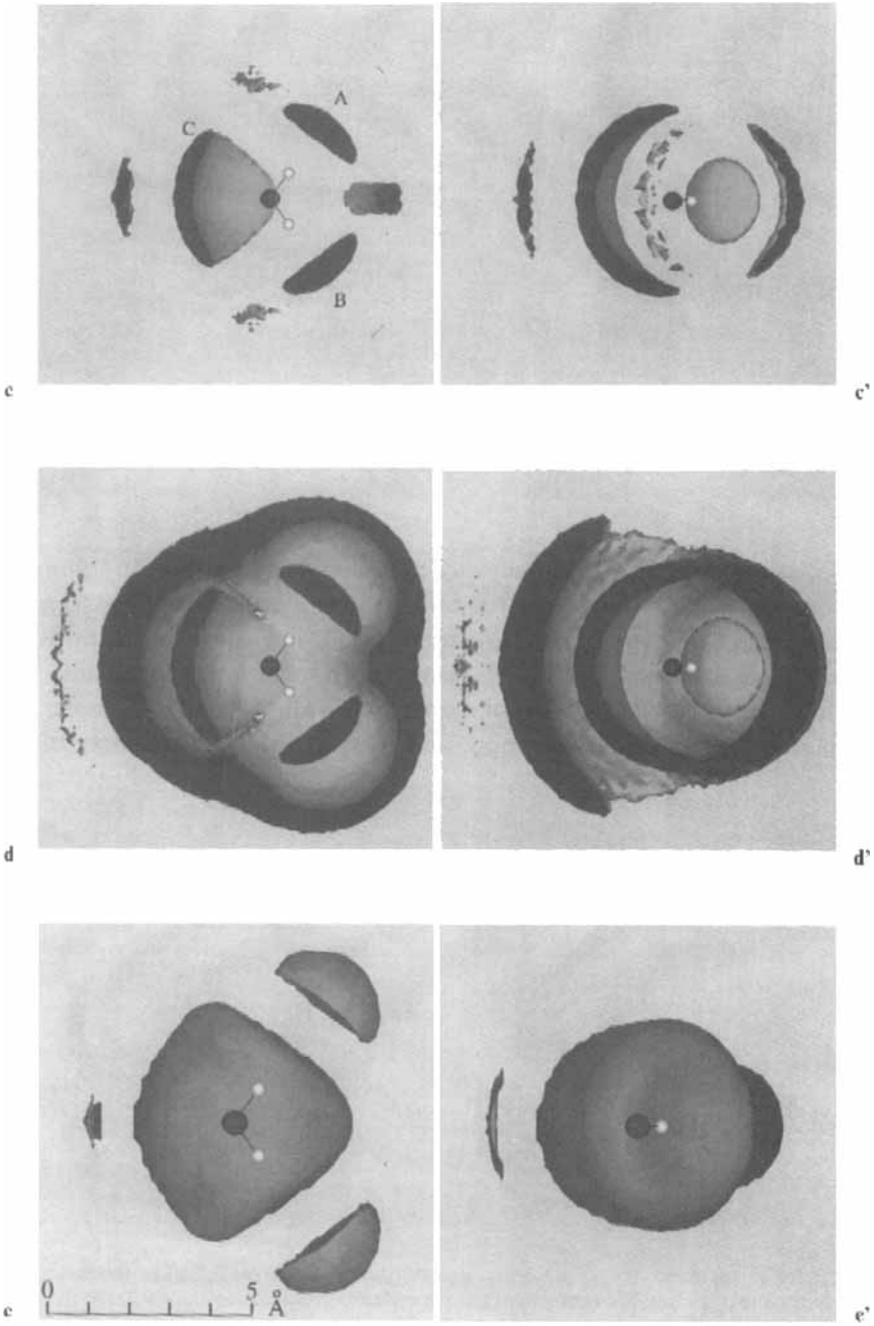

FIGURE 3 (Continued).

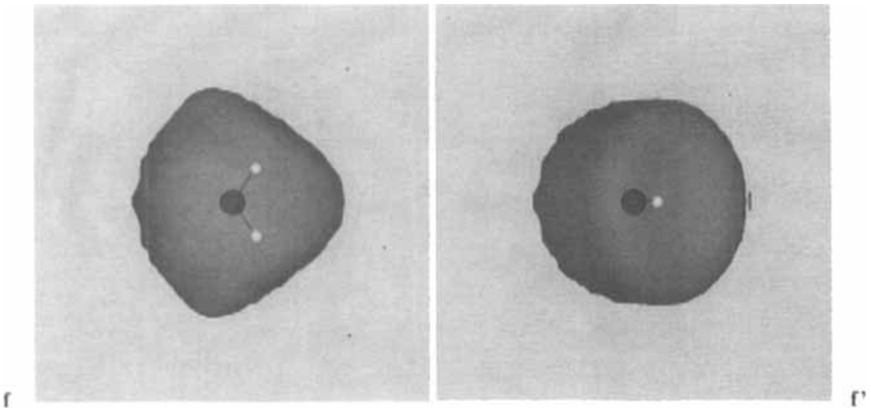

FIGURE 3 (Continued).

tion, at the position where the water molecule donates a proton to form a hydrogen bond. Since acetonitrile cannot donate any protons, we have no maximum of the type C as in Figure 3c. This is one cause of the low RDF peak at $r = 2.9$ Å ($g_{ON}(2.9) = 0.9$). There are no other nitrogen maxima.

In order to get an overview of the near structure around a molecule one can study the position, sharpness, and mass of the major maxima of the

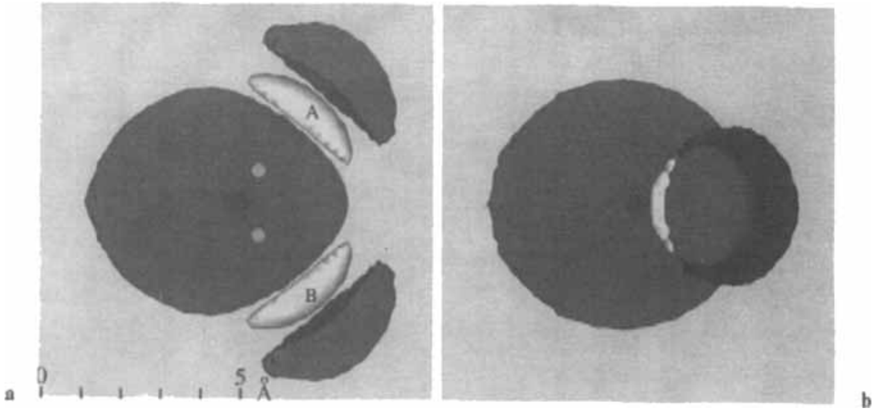

FIGURE 4 (a) shows the xz-projection and (b) shows the xy-projection of the isosurfaces $g_{ON} = 0.2$ and $g_{ON} = 1.3$. The transparent grayish surface corresponds to $g_{ON} = 0.2$, and the white (or light grey) surface corresponds to $g_{ON} = 1.3$. The white maxima are labeled A and B, and correspond to hydrogen bond sites where the central water molecule donates a proton to form a hydrogen bond.

SDFs. Figure 5 shows the major maxima of different atomic specie around a water molecule. The relative sharpness of the oxygen and nitrogen maxima is due to hydrogen bond formation. The more spread out shape of the methyl maxima, and its angular position, indicates that the methyl end usually approaches water from directions, which are not occupied by oxygen or nitrogen atoms.

When simulating it is usually difficult to decide how well the simulations reflect the true physical system. Radial distribution functions computed from MD simulations can, in some cases, be compared directly with experimental data from neutron or X-ray scattering [27–29], and at some level of

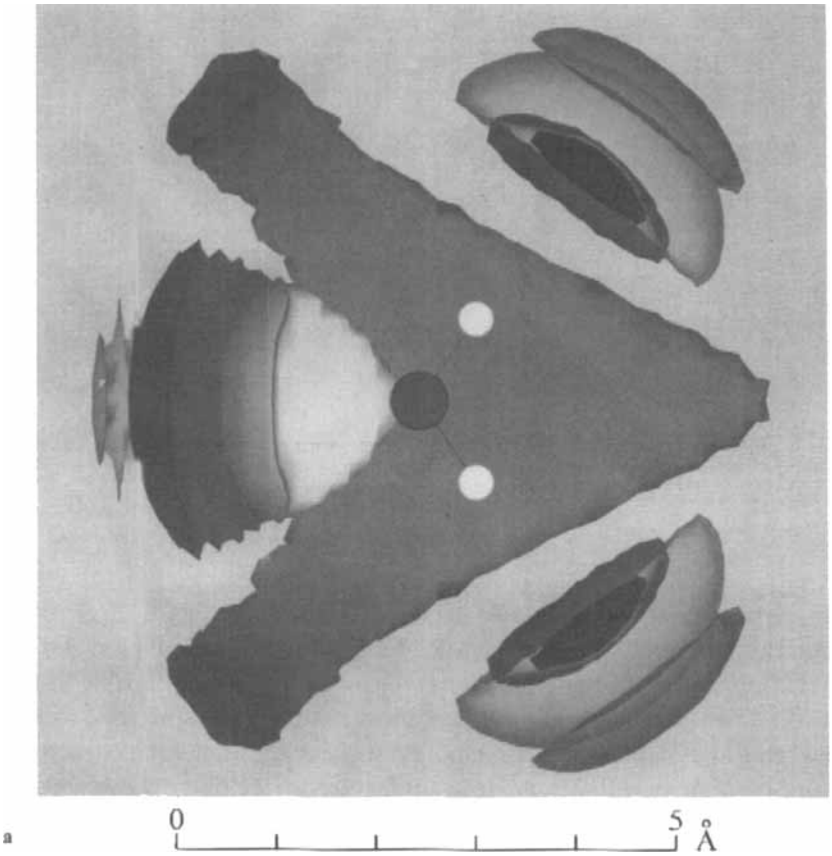

FIGURE 5 The isosurfaces $g_{OO} = 10$ (red), $g_{OH} = 6$ (yellow), $g_{ON} = 8$ (blue), $g_{OC} = 2$ (green), $g_{OM} = 2$ (magenta) are shown in this figure. The inside of a surface is somewhat darker than the outside. (a) shows the projection onto the xz-plane and (b) shows the xy-projection. (a) and (b) have been sliced open by the planes $y = 0$ and $z = 0$ respectively. (See Color Plate III).

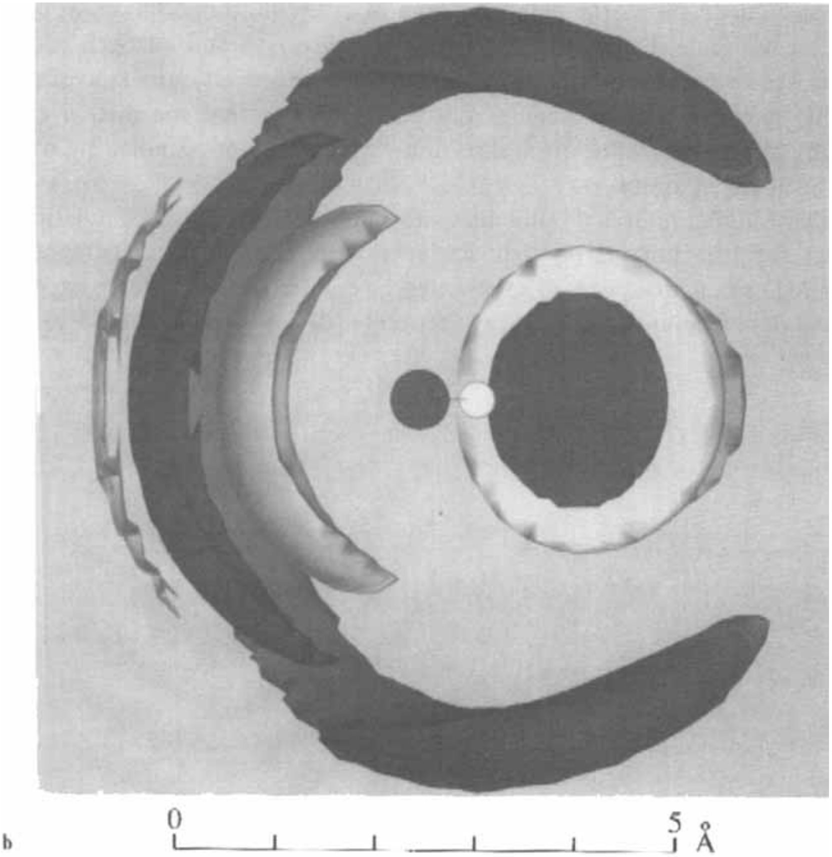

FIGURE 5 (Continued).

detail experimental and simulated RDFs disagree. Attempts to draw conclusions about liquid structure from RDFs generated by simulation should be based on aspects of these functions which can be deemed reliable in the light of known experimental and theoretical results. The same is of course true when using SDFs as a starting point for the analysis of liquid structure. It is our point of view that some relevant features of the micro structure can be discerned more clearly from simulations when beginning from SDFs instead of RDFs. The angular locations of major maxima and the existence of some secondary maxima are examples of such features. In the following subsections we give examples of how SDFs can be used as a starting point for analysis of micro structure in a liquid mixture.

3.2 Characterization of SDF Extrema

In order to understand the significance of an SDF maximum, one can characterize it in several ways. Here we discuss one way to characterize two of the major maxima of $g_{OO}(\vec{r})$ and $g_{ON}(\vec{r})$. These maxima are marked by A and B in Figures 3c and 4a. Now, the idea is to define a connected volume such that whenever there is an oxygen or a nitrogen atom inside the volume, then it can be considered to be hydrogen bonded to the central water molecule. Consider the maximum A of $g_{OO}(\vec{r})$ for example. Corresponding to this hydrogen bond position we define the volume $V_{OO}(A)=\{\vec{r}\,|\,g_{OO}(\vec{r})\geqslant g_{\text{low}}\}$. Note that the points close to B in Figure 3c, which satisfy $g_{OO}(\vec{r})\geqslant g_{\text{low}}$, are not part of $V_{OO}(A)$: they belong to $V_{OO}(B)$. One can estimate the average number (or mass) of oxygen atoms in the volume $V_{OO}(A)$ by:

$$n_{OO}(A)=\rho_O\int_{V_{OO}(A)} g_{OO}(\vec{r})\,dV \tag{2}$$

The gradient of $g_{OO}(\vec{r})$ is rather steep at the surface defined by $g_{OO}(\vec{r})=3.3$ and the mass inside the $V_{OO}(A)$ maximum is therefore relatively insensitive to the precise value of g_{low}, as long as g_{low} is close to 3.3. The same is true for $V_{ON}(A)$ when g_{low} is about 1.3. If one chooses a too low g_{low} then regions which cannot be considered as hydrogen bond sites are included in the volume. The volumes $V_{OO}(A)$ and $V_{ON}(A)$ are small and overlap largely. It is therefore unlikely that two or more atoms will reside in either of them simultaneously. One can thus interpret $n_{OO}(A)$ as the probability of finding an oxygen atom in the maximum, or – equivalently – as the fraction of time which the hydrogen bond site is occupied. In Table I this average number, n, and some other characteristics of some maxima are listed. The values of $n_{OO}(A)$ and $n_{ON}(A)$ are 0.66 and 0.15 respectively. (If only the first 0.1 ns of the simulation are used to compute $n_{OO}(A)$ and $n_{ON}(A)$ then one obtains 0.65 and 0.16 respectively. If the last 0.1 ns are used then one obtains 0.66 and 0.14 respectively.)

In addition to the mass one can define the center of mass, $\vec{r}_{\text{com}}$, and the bulk average, n_{bulk}, corresponding to the volume $V_{OO}(A)$:

$$\vec{r}_{\text{com}}(A)=\frac{\rho_O\int_{V_{OO}(A)} g_{OO}(\vec{r})\,\vec{r}\,dV}{\rho_O\int_{V_{OO}(A)} g_{OO}(\vec{r})\,dV} \tag{3}$$

$$n_{\text{bulk}}(A)=\rho_O\int_{V_{OO}(A)} dV \tag{4}$$

The center of mass is useful to understand where the maximum is located and n_{bulk} estimates the mass which would be found in the volume assuming bulk density. When deciding if a maximum such as $V_{OO}(A)$ can be thought of as a privileged position for a certain atom type, then the ratio $n_{OO}(A)/n_{\text{bulk}}(A)$ can be useful.

The minima of spatial distribution functions is another feature which can be used to understand liquid structure. An upper cut off, g_{up}, is used to define a volume $\{\vec{r}\,|\,g_{OO}(\vec{r}) \leqslant g_{\text{up}}\}$ surrounding the minimum. The properties of some minima are listed in Table II. Figure 4 shows the main minimum and the main maxima of $g_{ON}(\vec{r})$. The short distance between some points of the surfaces indicates large gradients.

3.3 Hydrogen Bond Lifetimes

Using the volumes surrounding the primary maxima (A and B) of $g_{OO}(\vec{r})$ and the two corresponding maxima of $g_{ON}(\vec{r})$ one can look at hydrogen bond lifetimes and transition probabilities. Let us make the following definitions: Each water molecule can donate two protons (proton α and proton β) to form hydrogen bonds. The proton α is considered to participate in a hydrogen bond to an oxygen atom if there is an oxygen atom in the volume $V_{OO}(A) = \{\vec{r}\,|\,g_{OO}(\vec{r}) \geqslant 3.3\}$. Similarly, if there is a nitrogen atom in the volume $V_{ON}(A) = \{\vec{r}\,|\,g_{ON}(\vec{r}) \geqslant 1.3\}$, then the proton α is considered to participate in a hydrogen bond to a nitrogen atom. The proton β and the maxima $V_{OO}(B)$ and $V_{ON}(B)$ are treated analogously. Now we define the

TABLE II In this table are the *volume* (Å^3), the *center of mass* (Å), the *mass* (dimensionless), and the *bulk average* (dimensionless) of the central minima listed. See the caption of Table I for definitions of these quantities. Note that only the x coordinate and the radial distance of the maximum is given, since the y and z coordinates are zero by symmetry. Two different upper cut off values, g_{up}, have been used to define the volumes. The volumes need not be connected, see Figures 3e and 4

atom pair	g_{up}	*volume*	*center of mass*		*mass*	*bulk average*
			x	r		
OO	0.1	70	0.8	2.6	0.003	0.61
OO	0.2	73	0.3	2.6	0.007	0.63
OH	0.1	35	0.8	2.1	0.005	0.60
OH	0.2	38	0.7	2.2	0.015	0.66
ON	0.1	115	0.5	3.6	0.014	1.00
ON	0.2	144	0.7	3.7	0.051	1.25
OC	0.1	132	0.8	3.7	0.011	1.14
OC	0.2	163	1.5	4.2	0.052	1.41
OM	0.1	157	1.5	3.6	0.016	1.32
OM	0.2	174	1.5	3.8	0.043	1.51

lifetime, τ, of a hydrogen bond as the length of the time period which begins when a proton binds to a new oxygen or nitrogen atom, and which ends when another oxygen or nitrogen atom replaces the original atom binding to the proton. The hydrogen bond is not considered as terminated just because nothing binds to the proton. This definition has the advantage of yielding lifetimes which are rather independent of the precise choice of the g_{low} value. However, the lifetime defined in this way contain a time period when the proton site is empty. This time is probably short since the masses of the *OO* and *ON* maxima are 0.66 and 0.15 respectively. Hence every site should be occupied about 81 percent of the time. In Figure 6 the distributions of lifetimes are shown. The average lifetimes are:

$$\tau_{HO} = 2.88 \pm 0.07 \text{ ps}$$

$$\tau_{HN} = 1.58 \pm 0.03 \text{ ps}$$

From MD-simulations, Rapaport [30] have estimated the average hydrogen bond lifetime in water to lie between 1 and 10 ps. Our estimated τ_{HO} lies in this interval. Rapaport uses the pair interaction energy to define hydro-

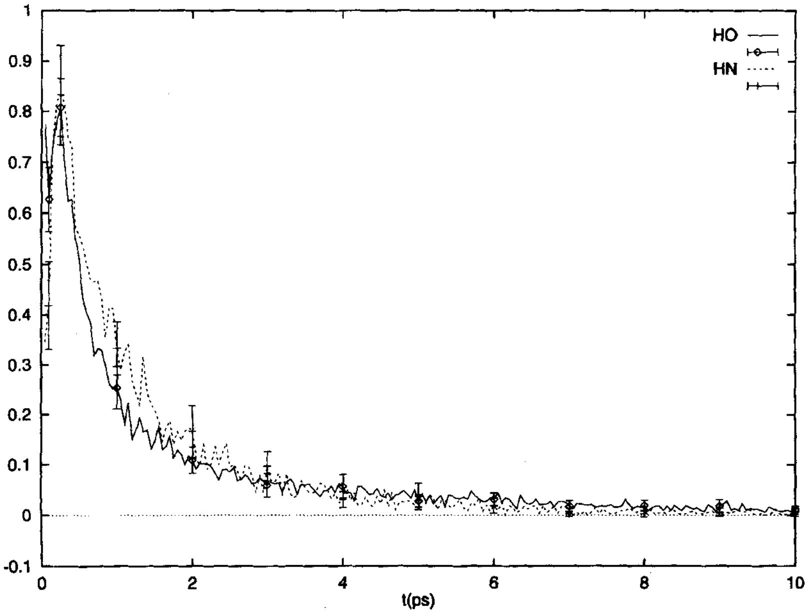

FIGURE 6 The curves marked by HO and HN are the normalized distributions of lifetimes of hydrogen-oxygen and hydrogen-nitrogen bonds respectively. Corresponding to each curve have some 95 percent confidence intervals been drawn to indicate the uncertainty in the values. The average lifetimes are $\tau_{HO} = 2.88 \pm 0.07$ ps and $\tau_{HN} = 1.58 \pm 0.03$ ps.

gen bonds and he points out that how one defines hydrogen bonds is somewhat arbitrary. The obtained lifetimes depend on the definition chosen.

One may also count the number of transitions that occur on a given site. Let $n_{O\to O}$ denote the number of times that an oxygen atom replaces another oxygen atom per proton site and ps. Let, analogously, $n_{O\to N}$ denote the number of times that a nitrogen atom replaces an oxygen atom and so on. From the simulation we obtain:

$$n_{O\to O}=0.21\pm 0.01\ \mathrm{ps}^{-1}$$

$$n_{O\to N}=0.053\pm 0.002\ \mathrm{ps}^{-1}$$

$$n_{N\to O}=0.053\pm 0.002\ \mathrm{ps}^{-1}$$

$$n_{N\to N}=0.085\pm 0.002\ \mathrm{ps}^{-1}$$

Dividing the number of transitions per site and ps by the masses of the corresponding maxima, gives an estimate of the average transition probability, π, per occupied proton site and ps:

$$\pi_{O\to O}=0.32\ \mathrm{ps}^{-1}$$

$$\pi_{O\to N}=0.081\ \mathrm{ps}^{-1}$$

$$\pi_{N\to O}=0.36\ \mathrm{ps}^{-1}$$

$$\pi_{N\to N}=0.57\ \mathrm{ps}^{-1}$$

For clarity: $\pi_{O\to O}=n_{O\to O}/n_{OO}(A), \pi_{O\to N}=n_{O\to N}/n_{ON}(A)$, and so on. It is perhaps interesting to note that $\pi_{N\to N}$ is greater than $\pi_{N\to O}$ which indicates that nitrogen atoms usually replace nitrogen atoms on hydrogen bond sites. $\pi_{O\to O}$ is greater than $\pi_{O\to N}$.

3.4 Relative Orientations of Molecules

It is probably not uncommon to have some frequently recurrent pair configurations in mixtures of polar molecules. A first step towards a characterization of the micro structure can be to look for configurations of this type. One may do this for example by studying the SDFs of various atomic specie around a central molecule. It is likely that some traces of recurrent configurations can be seen in the relative positions of the maxima in the SDFs, if such configurations are present. We give one example of this below.

Combining the distributions $g_{ON}(\vec{r})$, $g_{OC}(\vec{r})$, and $g_{OM}(\vec{r})$ suggests that acetonitrile molecules which are hydrogen bonded to a water molecule have a tendency to align their $\vec{r}_{NM}$ vectors parallel to the $\vec{r}_{OH}$ vector of the central water molecule, see Figure 7. The distances between the maxima of $g_{ON}(\vec{r})$,

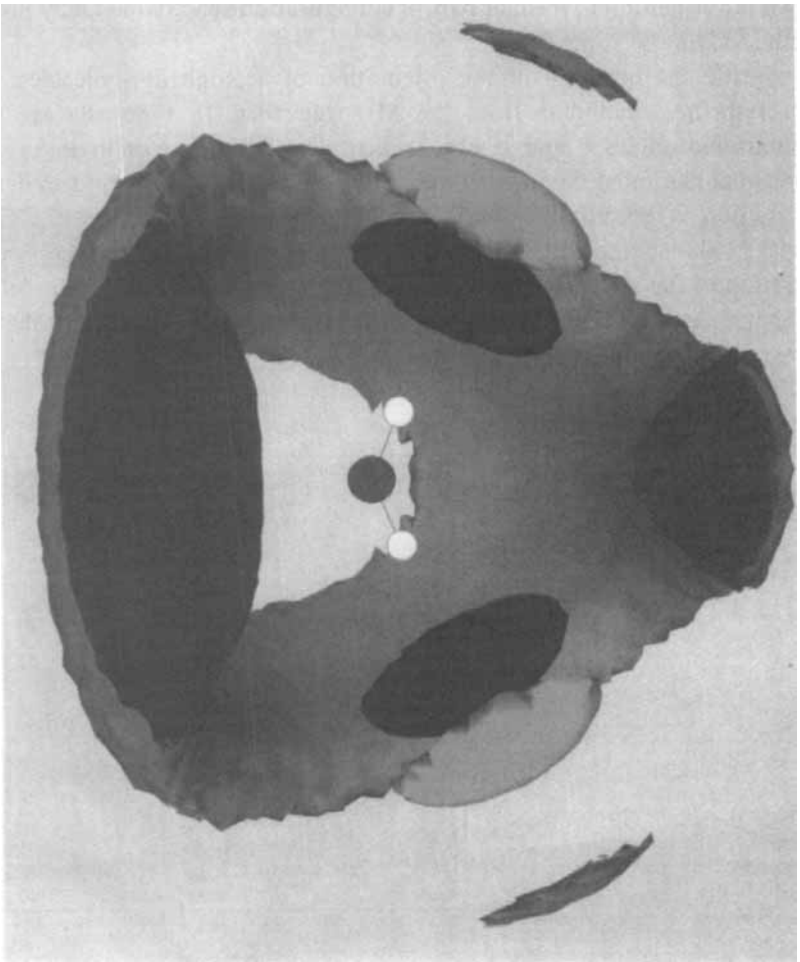

FIGURE 7 Three different isosurfaces are shown: $g_{ON} = 2.5$ (blue), $g_{OC} = 2$ (green), and $g_{OM} = 1.15$ (magenta). Part of the g_{OM} surface have been removed so that one can see the central water molecule. If one moves from one of the hydrogens in the direction of the $\vec{r}_{OH}$, then one encounters the three maxima: g_{ON}, g_{OC}, and g_{OM} in the given order. This can indicate that acetonitrile molecules which hydrogen bond to water molecules often have their $\vec{r}_{NM}$ vectors aligned parallel to the $\vec{r}_{OH}$ vector. (See Color Plate IV).

$g_{OC}(\vec{r})$, and $g_{OM}(\vec{r})$ are approximately: $d_{NC} = 1.1$ Å, $d_{CM} = 1.6$ Å and $d_{NM} = 2.6$ Å. This can be compared with the fixed distances in the acetonitrile molecule: $d_{NC} = 1.157$ Å, $d_{CM} = 1.458$ Å, and $d_{NM} = 2.615$ Å. Since the maxima of the different distributions (ON, OC, and OM) need not be correlated, one can not be certain that any acetonitrile molecules have their $\vec{r}_{NM}$ vectors oriented parallel to the $\vec{r}_{OH}$ vector, although this conclusion seem probable. The main virtue of the SDFs is, in this case, that they have drawn our attention to a small part of configuration space which may prove worth studying in some detail.

To settle the question of the orientation of acetonitrile molecules, we extract the required data from the MD-trajectory. In Figure 8a are the orientational angles θ and ϕ are defined. The contour plot in Figure 8b shows that the most common θ value is close to $52.5 \pm 0.7°$, and that the distribution is essentially invariant under rotation around the $\vec{r}_{OH}$ axis. However, the spatial angle decreases with θ and the most common configuration of the water-acetonitrile pair is the one which has $\vec{r}_{NM}$ parallel to $\vec{r}_{OH}$ as indicated by the SDFs. This configuration is about twice as probable as one of the configurations with $\theta = 52.5°$.

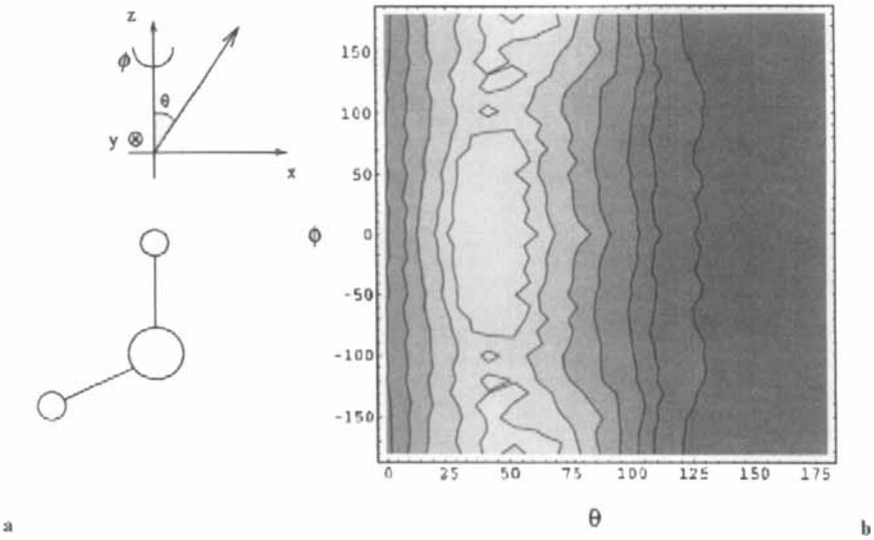

FIGURE 8 (a) Definition of the angels θ and ϕ. The fat arrow, parallel to $\vec{e}_{NM}$, represents the acetonitrile molecule. cos $\theta = \vec{e}_z\, \vec{e}_{NM}$ and tan $\phi = \vec{e}_{NM}\vec{e}_y / \vec{e}_{NM}\vec{e}_x$. (b) The distribution of orientations of the vector $\vec{r}_{NM}$. The maximum of the distribution is normalized to one, and the values of the distribution on the contours are: 0.9, 0.8, 0.6, 0.4, 0.2, 0.1, and 0.01. The average value of θ is $52.5 \pm 0.7°$.

4 CONCLUSION

A pair of rigid molecules has, in general, a 6-dimensional configuration space. This space is large, and it can be cumbersome to compute the full 6-dimensional distribution. Spatial distribution functions (or combinations of them) often show some signs of frequently recurrent pair configurations, and may be used to identify parts of configuration space that are worth studying in detail. An example is the orientation of acetonitrile molecules interacting with water molecules through hydrogen bonds.

It is also possible to study some aspects of liquid dynamics using structural features exposed by SDFs. We have only looked at different types of hydrogen bonds, their lifetimes, and their associated transition probabilities. One can easily imagine a more extensive study; concerning, for example, the dynamics of bond rearrangement.

Care is needed when drawing conclusions about liquid micro structure from simulations since current potential models are imperfect. This is especially true for liquid mixtures. With this work we have attempted to show that some features of the micro structure – which are difficult to discover from RDFs – are clearly exposed by SDFs. Examples of such features are the angular location and the mass of major maxima. We have also attempted to demonstrate that this type of structural features constitutes a useful starting point for the analysis of micro structure and dynamics.

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APPENDIX

The translational equations of motion for the center of mass movement were integrated using the Verlet leap-frog algorithm [19] and the rotational motion was treated by Fincham's quaternion based leap-frog algorithm [20]. Periodic boundary conditions have been applied together with the minimum image convention [19]. Long-ranged coulombic interactions were evaluated using the Ewald summation technique, and the Lorentz-Berthelot combination rules have been used to compute the Lennard-Jones parameters between all types of sites [19]. The parameters of the potential models are shown in Table III.

We have estimated the standard deviation of some of the quantities presented in this work by partitioning the simulation time into 20 intervals. Each quantity has been computed for each interval and the standard deviation of the mean value has been estimated assuming that the values obtained from different intervals can be regarded as independent.

The self-diffusion coefficient, *D*, and the potential energy have been computed from the simulation to investigate if the chosen potentials give reasonable results for experimentally accessible quantities. *D* was estimated from the mean square displacement to 0.17 ± 0.01 Å^2/ps for water and to 0.19 ± 0.02 Å^2/ps for acetonitrile. An experimental NMR-study [14] of the equimolar mixture gives 0.30 and 0.325 Å^2/ps for water and acetonitrile respectively. The potential energy per molecule is estimated from our simulation to -37.15 ± 0.03 kJ/mol which can be compared with the experimental energies values of -41.4 kJ/mol for pure water [17] and -31.0 kJ/mol for pure acetonitrile [22, 23].

To obtain the SDFs, the space around each atom is divided into a 100 × 100 × 100 mesh of cubic boxes. The mesh is, at each time step, centered at the selected atom and the principal axes of the mesh is chosen to coincide with those of the molecule to which the atom belong. For each

TABLE III Potential parameters of the SPC/E water and Jorgensen's acetonitrile model

		$\varepsilon(kJ/mol)$	$\rho(\AA)$	$q(e)$
water	O	0.6502	3.1656	−0.8476
	H	–*	–*	0.4238
acetonitrile	N	0.711	3.200	−0.43
	C	0.628	3.650	0.28
	M	0.866	3.775	0.15

*There is no Lennard-Jones potential associated with the hydrogen atoms.

atom the number of other atoms in the various boxes were counted at each time step. A double average over time and all similar atom pairs [24] is used to construct the SDFs. Formally we may describe this procedure by

$$g_{AB}(i,j,k) = \frac{\langle \frac{1}{N_A} \sum_{n_A=1}^{N_A} \sum_{n_B=1}^{N_B} I_{ijk}(R_{n_A}^{A}(\vec{r}_{n_B}^{\,B} - \vec{r}_{n_A}^{\,A})) \rangle}{\rho_B l^3} \tag{5}$$

where i, j, and k index the various boxes in the mesh, N_A denotes the number of atoms of type A, n_A is an index running from 1 to N_A, $\vec{r}_{n_A}^{\,A}$ is the position vector of the atom numbered n_A of the type A in the lab frame, and $R_{n_A}^{A}$ is the rotational transformation from the lab frame to the local frame of atom n_A. I_{jkl} is an indicator function taking the value 1 for $\vec{r} \in [l(i-1/2), l(i+1/2)) \times [l(j-1/2), l(j+1/2)) \times [l(k-1/2), l(k+1/2))$ and the value 0 elsewhere. l (0.2 Å) is the side-length of the boxes. The angular brackets denote time average.

The simulation was carried out on a Fujitsu VX machine at the Center for Parallel Computers at the Royal Institute of Technology using a modified version of McMoldyn [25].