# Structural properties of liquid *N,N*-dimethylformamide

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Monte-Carlo simulation of liquid *N,N*-dimethylformamide was performed. The influence of electrostatic and van der Waals interactions on regularities of the mutual molecular arrangement was investigated. The spatial structure of liquid DMF is determined by the type of molecular packing and steric factors and is close to a random closely packed system of soft spheres. The electrostatic interactions only affect the mutual orientation of the molecules.

**Key words:** organic solvents, *N,N*-dimethylformamide, structure of liquid; intermolecular interactions; computer simulation of liquids, Monte-Carlo method.

The problem of the dependence of the structure of solvents and solutions on the nature of interparticle interactions has always attracted the attention of researchers. The establishment of relations between properties of the molecules and thermodynamic and structural characteristics of the liquid is one of the fundamental problems of physics of liquid state and physical chemistry of solutions. Despite the fact of applying versatile experimental and theoretical methods for solution of the above problem, many questions concerned with the mutual arrangement of molecules in liquid were not answered even in the case of the simplest systems.

Experimentally obtained information on the structure and intermolecular interactions in the liquid DMF is extremely contradictory. Several authors[1,2] believe that dimerization of the molecules occurs at the expense of the H-bond with participation of the formyl proton of the donor-acceptor N...O bond. The authors of another work inferred that the properties of DMF are defined both by a reactive and weak chemical interactions and that the latter interaction results in the formation of open-chain and cyclic associates.[3]

According to a previously stated belief,[4,5] there are no associates formed due to donor-acceptor and H-bonds in the liquid DMF. Studies of the permittivity of DMF solutions in $CCl_4$ showed that the dimerization constant is close to zero.[6] This indicates a weak self-association of the molecules in pure DMF. The authors of several works dedicated to X-ray studies of DMF[7,8] came to the same conclusion; they found that DMF has a random structure because of the absence of stable molecular associates.

The results of the studies of DMF by NMR spectroscopy and molecular dynamics[9] suggest that the molecules are bonded by the van der Waals interactions with the predominant formation of linear associates since they are more stable than cyclic associates. The tenfold decrease found in the rate of rotation of *trans*-Me groups as compared to that of *cis*-Me groups indicates that the *trans*-Me groups interact more strongly with the environment. Quite the opposite results were obtained in one of the recent investigations:[10] as follows from the analysis of the Raman spectra, about 50% of the molecules are associated into cyclic dimers, while 40% of them form chain associates.

Rigorous calculations performed by the methods of statistical physics are connected with insurmountable difficulties, whereas approximate calculations yield rather limited information on simple liquid systems. A computer simulation based on probability theory and statistical physics makes it possible to obtain information on the structure of the liquid and on the intermolecular interactions in the form of a list of coordinates of the particles and matrices of the energy of pair interactions.

It is common practice to approximate the interactions by using a specially selected set of potential functions and to represent a molecule as a totality of isolated sites (separate atoms or their groups) when performing concrete calculations of molecular systems. For simplicity, the potentials are expressed as a sum of contributions from the van der Waals and electrostatic interactions of the sites.[11]

Among several potentials proposed for the amide molecules, the OPLS system of functions developed by Jorgensen[12] plays an important role. Many experimentally studied properties of liquid DMF are reproduced in the framework of this scheme. It was found that the DMF molecules do not form the H-bonds and the radial distribution function (RDF, $g_{NN}(r)$) of nitrogen atoms has a classical shape and is similar to that for liquid argon. In another publication, the two most probable arrangements of the molecular pair were determined on the basis of calculations of the atom-atom RDFs and two orientational correlation functions.[13]

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Later,[14] thermodynamic properties of liquid DMF and its RDF were found to be independent of the size of the unit cell as well as of the ensemble used in simulations or of the dielectric constant of the reaction field. However, the correlation functions characterizing the mutual orientation of particles are very sensitive to the simulation conditions. In the above-mentioned work,[14] calculations of electrostatic interactions are more complicated and several changes were made in the simulation scheme.

In our previous publications,[15,16] we showed that the spatial structure of methanol and that of the solvate shells of the ions and neutral particles in MeOH is defined by the type of packing of methyl groups, which is dictated by universal interactions. The DMF molecule has a more complicated shape with no spherical symmetry, and does not form stable intermolecular bonds. It should be expected that in this case the van der Waals interactions would also play a key role in the formation of spatial supramolecular structure. To confirm this assumption, we decided to successively simplify the initial potential.

The aim of this work was to establish the regularities of the mutual arrangement of the molecules in liquid DMF, to elucidate the role of the van der Waals and electrostatic interactions in the formation of local and global order in the arrangement and orientation of the molecules. Several independent models were considered. In the first variant, the interactions were described using the OPLS potential. In the second variant, all electrostatic interactions were excluded from the above potential. In the third variant, the fluid of soft spheres (SS) was studied. The parameters of the interactions were specially fitted. Contrary to our preceding studies of DMF, we employed a procedure for determination of topological properties of networks of bonds in addition to the analysis of correlation functions; this made it possible to draw a conclusion on the supramolecular structure of the liquid.[15,16]

## Calculation Procedure

The simulations were performed using a standard Monte-Carlo method in the *NVT* ensemble at $N = 125$. The conditions of the computer experiment corresponded to a density of 0.9443 g cm$^{-3}$ and to $T = 298$ K. Periodic boundary conditions and spherical cutoff of the potential functions were used. The molecular structure and intermolecular interactions were given as a system of the OPLS potential functions[12—14] with the following atomic charges: −0.5, −0.57, 0.5 (on the O, N, and C atoms, respectively), and 0.285 (on each of the two carbon atoms of the Me groups). A chain of random events of length 27 million configurations was generated, which is comparable with the chain lengths in the models (5 to 50 million configurations) recently published by Jorgensen.[14] In the simulation of a Lennard—Jones analog of DMF (LJ-DMF), all atomic charges in the OPLS potential were assumed to be equal to zero. The interaction of particles of the SS fluid was described by the Lennard—Jones potential with $\varepsilon = 16.72$ J mol$^{-1}$ and $\sigma = 800$ pm. Since in these cases the convergence to average values was attained at a smaller number of steps, only ~4 million configurations were generated. The main energetic and structural parameters of liquid DMF we calculated are in good agreement with the results of previous investigations,[12—14] which is evidence of the correctness of the calculations performed.

## Results and Discussion

Calculations of energetic characteristics of liquid DMF showed that its average potential energy is equal to −43.8 kJ mol$^{-1}$, while the energy level of LJ-DMF lies 15 kJ mol$^{-1}$ higher. Hence, electrostatic interactions account for ~34% of energy. It can be assumed that the van der Waals interactions play a more important role. Let us consider how this fact affects the functions characterizing the spatial and orientational structure of the liquid.

The DMF molecule consists of five atoms, which intensely scatter X-ray radiation. Fifteen atom-atom functions contribute to the combined RDF obtained as a result of processing the experimental data. In a number of the simplest cases, the neutron diffraction studies make it possible to determine some orientational correlation functions; however, they cannot yield exhaustive information on the complete set of the atom-atom RDFs. Therefore, the published information on the spatial structure of DMF and other organic solvents is scarce. At the same time, one can easily determine RDFs using the lists of atomic coordinates obtained by computer simulation. However, it is impossible to say with confidence something on the spatial structure of DMF without invoking additional assumptions even in the case when the complete set of functions is known.

Let us consider first what happens to the RDF if all electrostatic interactions are excluded. Of the nine functions shown in Figs. 1 and 2, four functions remain

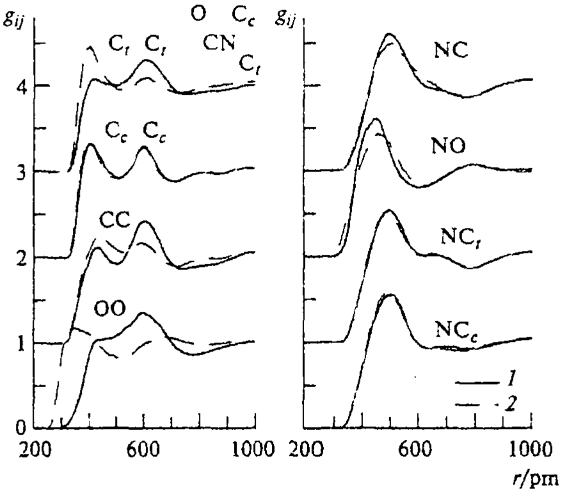

**Fig. 1.** The atom-atom RDFs, $g_{ij}(r)$ ($i$, $j$ are the type of the atom): DMF (*1*) and LJ-DMF (*2*). For clarity, the intervals between the plots along the ordinate axis are enlarged.

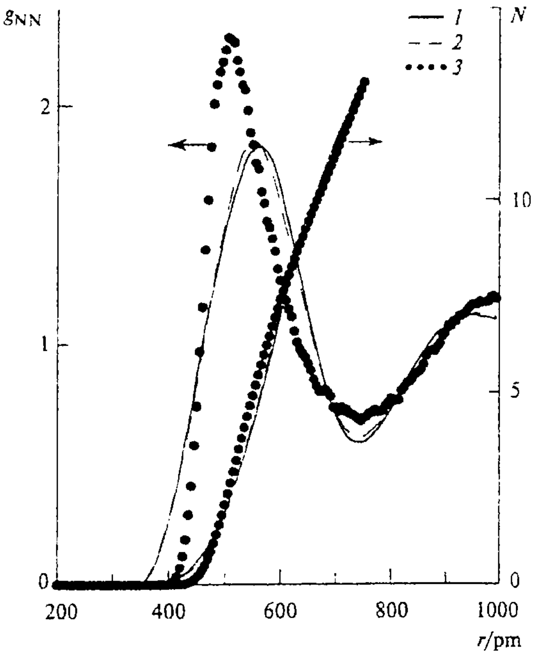

**Fig. 2.** RDFs of nitrogen atoms, $g_{NN}(r)$, and dependences of the number of particles within the sphere of radius *r*, *N*(*r*): DMF (*1*); LJ-DMF (*2*), and the SS fluid (*3*).

nearly unchanged whereas two functions ($g_{OO}$ and $g_{C_tC_t}$) undergo considerable transformations. On the basis of the behavior of the functions one can only draw apparent conclusions on both the structure of liquid DMF and its changes, since a set of configurations of the molecular pair rather than its certain configuration corresponds to each maximum of the functions. The functions reach their extrema at different interatomic distances. The summation of the functions results in leveling of nearly all individual features.[7,8]

To unambiguously describe the mutual arrangement of two DMF molecules, six coordinates should be given (for instance, the radius vector and three Euler's angles). The spatial and orientational *D*-structure of DMF can be completely characterized by a correlation function of six variables. However, we cannot investigate such objects for certain obvious reasons. Functions of three variables are much simpler but less informative. They can be depicted on plane using specially developed software, as was done for water and methanol in several publications.[17,18] We further simplified the problem by considering the distribution of molecules in two layers, one parallel and the other perpendicular to the molecular plane (each of the layers was 400 pm thick). In both cases, the N—C bond of the central molecule was in the middle between cutting planes.

As is known, the RDF, by definition, is equal to the ratio of the local numerical density of particles in a spherical layer of thickness d*r* to the average volume density (ρ) of the liquid. By analogy, let us define the atom-atom correlation function of three variables as

$$g_{ab}(x, y, z) = [\mathrm{d}N_{ab}(x, y, z)/\mathrm{d}x\mathrm{d}y\mathrm{d}z]/\rho,$$

where $\mathrm{d}N_{ab}$ is the number of particles of type *b* in the volume element d*x*d*y*d*z* at a distance *r*(*x*, *y*, *z*) from a particle of type *a*. By fixing one of the coordinates we get a function of two variables. Let us assume that the N atom is in the origin and the molecule lies in the *yz* plane.

The plots of the atom-atom correlation functions for DMF and LJ-DMF are shown in Figs. 3 and 4. The spatial structure of LJ-DMF is dictated by temperature and the type of molecular packing. A nearly complete coincidence of functions $g_{NN}(0, y, z)$ in both systems (see Fig. 3) can be noted. In the plane of each molecule, the six most probable areas for location of the N atoms of neighboring molecules are seen. This number of neighbors in the layer is also characteristic of the closest packing of spheres.

Judging by the behavior of functions $g_{NC}$ and $g_{NO}$, the spatial distributions of the C and O atoms in DMF and those in the LJ-DMF differ substantially. In the first case, because of electrostatic interactions the O atoms of neighboring molecules tend to approach the methyl groups, but not to come closer to the O atom of the central molecule. The local density of the C and O atoms increases near methyl groups (mostly near the *trans*-Me groups). Therefore, the decrease in the rate of rotation of the *trans*-Me group (as compared to that of the *cis*-Me group) determined by NMR spectroscopy[9] is explained by stronger interaction of the *trans*-Me group with neighboring molecules.

Since the choice of the central molecule is arbitrary and only the statistically averaged picture is studied, it can be concluded that the methyl groups are in the area where the O atom is located. This results in a small increase in the local density of the N atoms in this area seen on the $g_{NN}$ plot.

Let us consider the behavior of the $g_{ij}(x, y, 0)$ functions obtained through cutting the volume by planes perpendicular to the molecular plane (see Fig. 4). The distributions for the N atoms in DMF and LJ-DMF ($g_{NN}$) are nearly identical, whereas they appreciably differ for the C and O atoms ($g_{NC}$, $g_{NO}$). Thus, the mutual orientation of neighboring molecules in these systems is different despite the fact that the central atoms are arranged identically. The distributions of particles located above and below the molecular plane are identical due to the symmetry of the cross-cut.

As follows from Figs. 3 and 4, the local density of the C and O atoms appreciably increases in the areas of the methyl groups of DMF in the case of two mutually perpendicular cross-cuts. Therefore, the neighboring molecules are capable of executing large-amplitude low-frequency rotation-vibration motions in different planes with respect to the N atom of the central molecule. It is

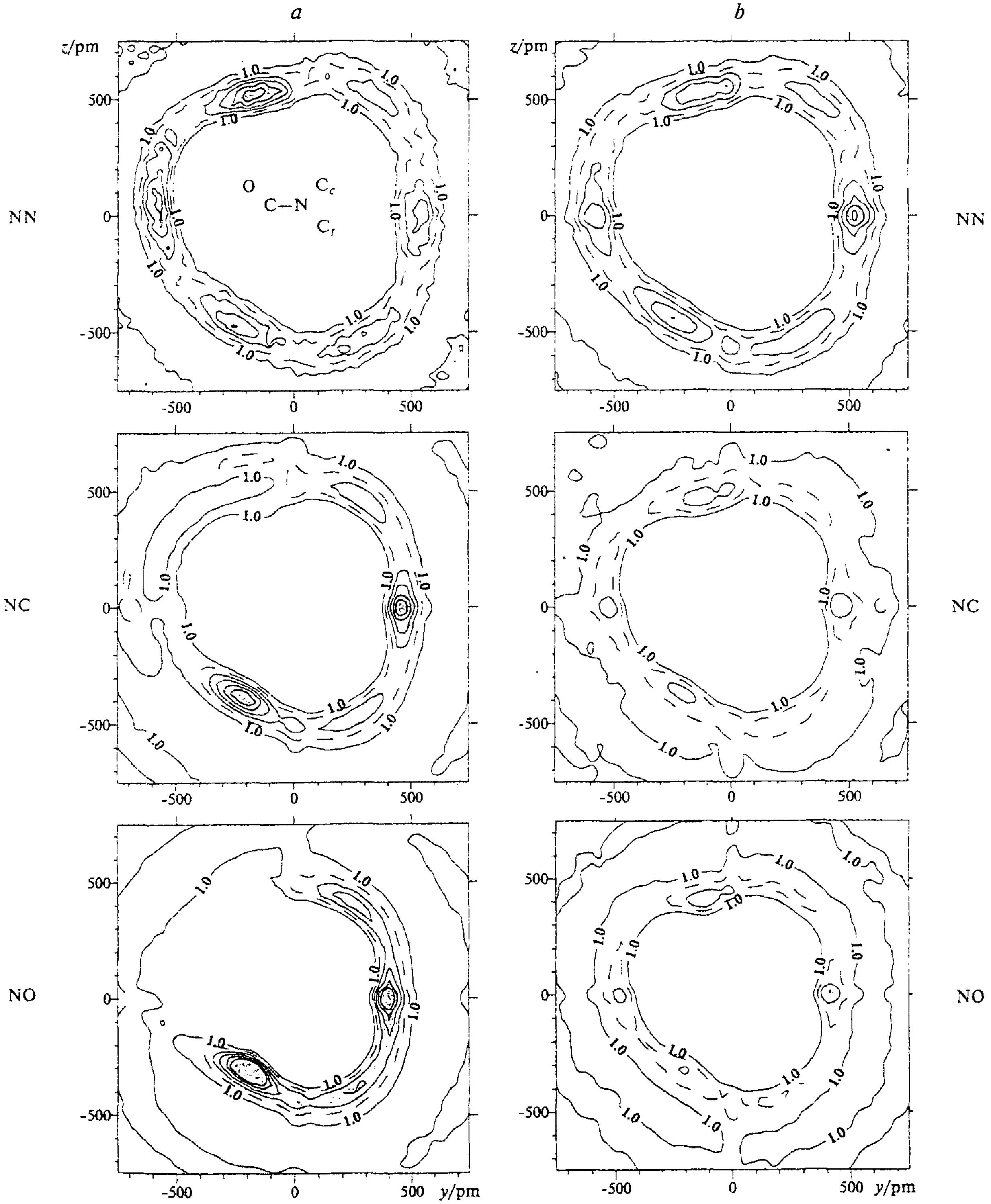

Fig. 3. Correlation functions of distribution of the atoms in the space, $g_{ij}(0, y, z)$, ($i$, $j$ are the type of the atom), for DMF (*a*) and LJ-DMF (*b*). The local density in shaded areas is more than twice as large as the average density. The contour lines are traced with an interval of 0.5.

not surprising that their orientations will be changed considerably in the case of applying an external field or varying the conditions of simulation.[14] The states are more stable if a neighboring molecule lies on the van der

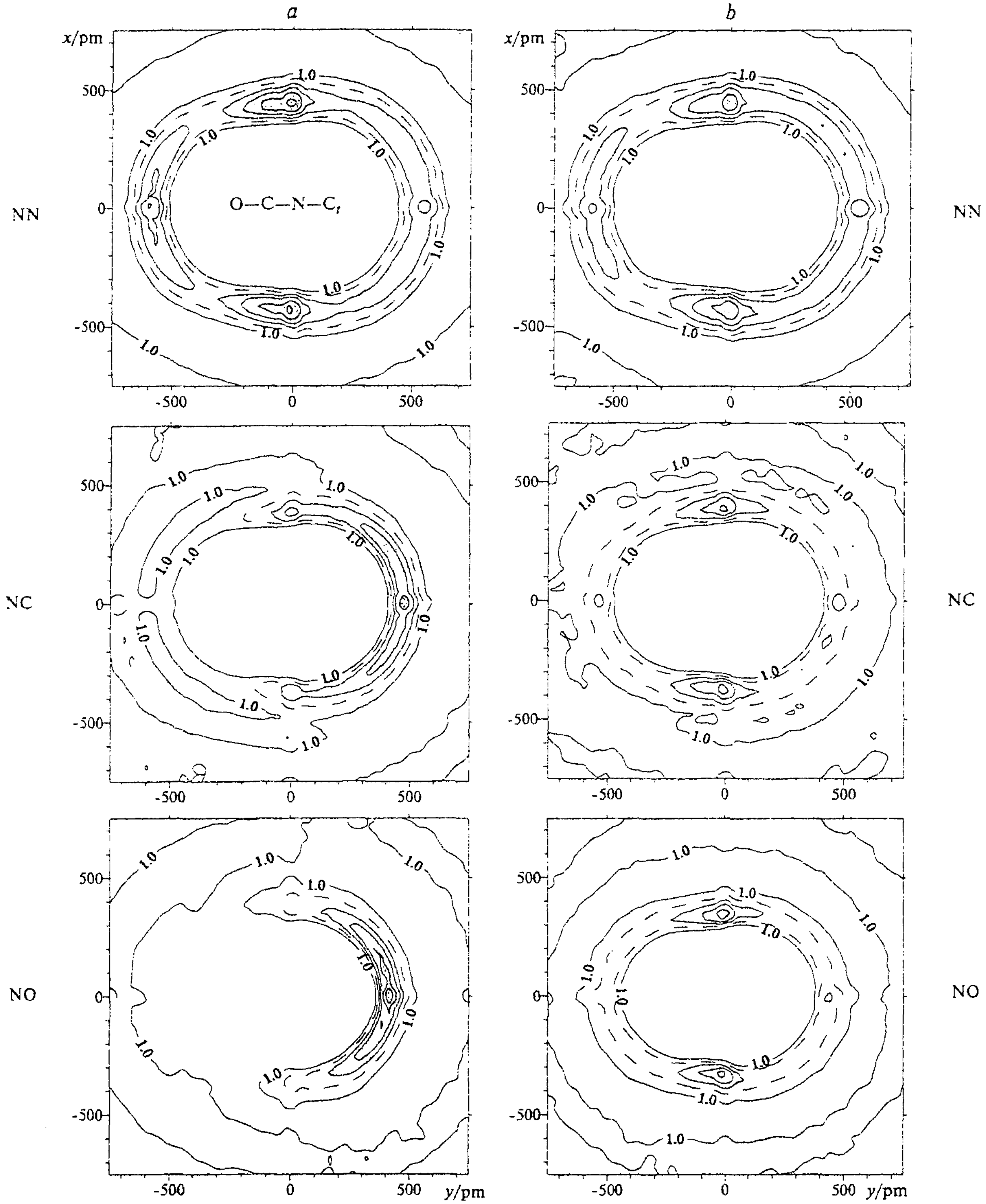

**Fig. 4.** Correlation functions of distribution of the atoms in the space, $g_{ij}$ (*x*, *y*, 0), for DMF (*a*) and LJ-DMF (*b*) (for explanations, see Fig. 3).

Waals surface in the notch between the methyl groups or in that between the *trans*-Me group and the carbonyl C atom of the central molecule. It can be admitted that chain associates with participation of the Me groups of one molecule and the O atom of the other molecule are formed. However, their structure is very labile.

The density of atoms increases in the sequence N, C, and O as $y$ increases on the three plots in Fig. 4. This fact indicates the presence of a certain fraction of coplanar molecules with preferred antiparallel orientation in DMF.

The N atom lies near the center of gravity of the DMF molecule. As follows from the shape of the curve of the $g_{NN}(r)$ RDF and the plot of the dependence of the number of particles ($N$) within the sphere of radius $r$ on $r$ (see Fig. 2), about 12 neighbors are contained, on the average, in the first coordination sphere of each DMF molecule. This number is also characteristic of a random closely packed system of hard spheres. We found the parameters of the Lennard—Jones potential, which describes the SS interactions, from the behavior of the $g_{NN}(r)$ function of DMF. Since we were interested only in a qualitative picture, rigorous mathematical optimization of parameters of the potential was not performed. The shape of the curves of the $N(r)$ dependences for all three systems is identical.

To describe the supramolecular spatial structure of liquid DMF, it is necessary to calculate the functions characterizing the mutual arrangement of objects consisting of several molecules. When N atoms of neighboring molecules are connected by lines, a network of bonds is formed, in which closed cycles (elements of

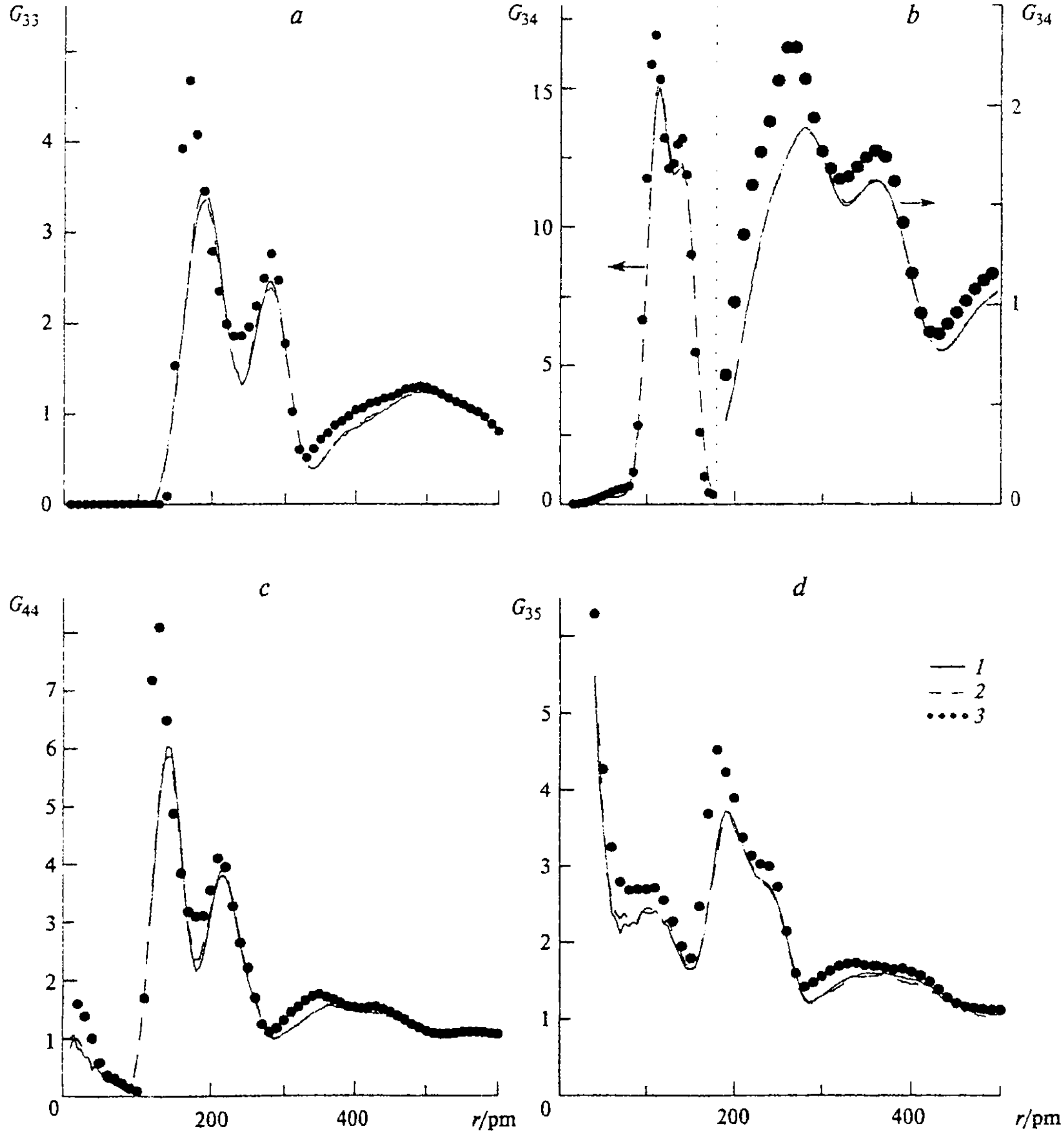

**Fig. 5.** RDFs of geometric centers of the closed cycles of bonds in the networks of nearest neighbors, $G_{ij}(r)$ ($i$, $j$ are the numbers of vertices in the cycle); $ij$ = 33 (*a*), 34 (*b*), 44 (*c*), and 35 (*d*): DMF (*1*), LJ-DMF (*2*), and SS (*3*).

supramolecular structure) can be singled out. After having determined the arithmetic mean of the coordinates of the nitrogen atoms of the molecules forming the cycle, we can find its geometric center. Let us create sets of points for each type of the cycles in the bulk of the liquid using the same procedure. By analogy with the atom-atom RDFs, let us calculate the RDFs of geometric centers of the closed cycles of bonds ($G_{ij}(r)$), which are equal to the ratio of the local density of points in a spherical layer of thickness d$r$ at a distance $r$ from the fixed point to the average density. In this case, the index number corresponds to the number of vertices in the cycles, for which the correlation is sought. These functions characterize topological properties of the network of bonds and, hence, the supramolecular spatial structure of the liquid.

Let us compare the properties of networks constructed for the three liquids. We connected by lines the N atoms or spheres arranged at a distance shorter than 582, 581, and 570 pm for DMF, LJ-DMF, and the SS fluid, respectively. The average number of bonds per molecule was 5.98 in all three cases. The equality of the connectedness parameters made it possible to compare the properties of networks at the same value of the most important topological characteristic. Very large or very small values of the connectedness parameter result in a sharp retardation of the calculation process or in an increase in the statistical error. As has been shown in several works, the choice of this value has little effect on the qualitative picture reflecting regularities of the formation of supramolecular structure.

The following values of the concentrations of closed cycles were obtained for the networks of bonds of three liquids: $c_3$ = 1.12, 1.15, and 1.17; $c_4$ = 1.82, 1.86, and 2.07; $c_5$ = 1.92, 1.84, and 2.13 for DMF, LJ-DMF, and the SS fluid, respectively. (In this case, the concentration is expressed through the average number of cycles per molecule.) It can be concluded that the networks exhibit similar dependences of their properties on this parameter. Several functions of radial distributions of geometric centers of the cycles are shown in Fig. 5. Minimum differences are observed for the functions calculated for DMF and LJ-DMF; however, it can be argued that the differences between the functions calculated for the SS fluid and the corresponding functions of the two other systems are also small.

Previously,[15,16] similar results have been obtained for methanol. It was shown that the positions of maxima of the RDF of the centers of the cycles coincide with the intercycle distances in five type of polyhedra of which the network of bonds of a random closely packed system of hard spheres is built.[19] A continuous spectrum of intercycle distances rather than a set of their fixed values determined by the particle size is observed in the SS system closest to the system of hard spheres. Identical behavior of the functions in the three liquids indicates the existence of general principles of the formation of supramolecular structures.

Thus, several conclusions can be drawn. A broad spectrum of values for the parameters of mutual arrangement and orientation of neighboring molecules is characteristic of the local environment of the DMF molecule in the liquid phase. Steric factors and molecular shape determine the regularities of spatial arrangement of the molecules, whereas electrostatic interactions mainly affect their orientation. Existence of the chain associates formed by the Me groups of one molecule and the O atom of the other molecule can be admitted. There also exists a certain fraction of coplanar molecules with antiparallel orientation. However, it is impossible to describe the structure of DMF using two or three characteristic configurations of the molecular pair.

Not only local but also spatial supramolecular structure of liquid DMF (which is close to the structure of random closely packed system of soft spheres or, to a lesser extent, to that of hard spheres) is determined by steric factors, the shape of the molecules, and the type of their packing.

Complication of the potential functions due to the introduction of intramolecular motions and polarization and more complicated procedures for taking into account the long-range interactions affect mainly the mutual orientations of the molecules. When there is no need to determine the properties strongly dependent on the mutual orientation of the DMF molecules, a simpler system (LJ-DMF or the SS fluid) can be used as a model solvent. We believe that the above conclusions concerning the effect of electrostatic and non-electrostatic interactions on the structure of liquid DMF will also be valid for other organic solvents.

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