Physical Chemistry

Structural properties of liquid *N*-methylformamide

Yu. G. Bushuev[a]* *and S. V. Davletbaeva*[b]

[a]*Ivanovo State University of Chemical Technology,*
7 prosp. F. Engel'sa, 153460 Ivanovo, Russian Federation.
E-mail: bushuev@icti.ivanovo.su
[b]*Institute of Solution Chemistry, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 37 8509

Monte Carlo simulation of liquid *N*-methylformamide was carried out at 298 K. The atom-atom spatial distribution functions, concentrations of closed cycles of H-bonds, radial distribution functions of geometric centers of the cycles, and other characteristics of the system of hydrogen bonds and the network built of the lines connecting neighboring molecules were calculated. The effects of electrostatic and van der Waals interactions as well as molecular conformations on the regularities of mutual arrangement of the molecules were investigated. It was found that open chains of H-bonds dominate over closed cycles. Spatial structure of liquid *N*-methylformamide is determined by packing of the molecules and steric factors and is close to the structure of a random closely packed system of soft spheres.

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

Amides of aliphatic carboxylic acids are of considerable interest for studying intermolecular interactions and peculiarities of the structure ordering of substances in the condensed state. Liquid amides are widely used as organic solvents. Formamide (FA) and *N*-methylformamide (MFA) are characterized by abnormally high static dielectric constants.[1]

Investigation of the properties and energy characteristics of H-bonds formed between carbonyl and amino groups of neighboring MFA molecules is of great importance for an understanding of the specific character of interactions and conformations of biologically active macromolecules. For instance, the amide groups of asparagine and glutamine molecules can form intermolecular H-bonds that are topologically equivalent to the H-bonds in the cyclic FA or MFA dimers.

Experimental studies of liquid amides and solutions based on them[1–3] made it possible to obtain a considerable body of information on the macroscopic properties of the substances. At the same time, the regularities of mutual arrangement and intermolecular interactions have not been adequately studied and the opinions on the subjects are contradictory. Methods of computer simulation are widely used for determining structural properties of the liquids.[4] They make it possible to obtain information on all coordinates and interactions of hundreds of particles in the unit cell using a given potential of intermolecular interactions. However, after obtaining the lists of atomic coordinates, the authors,[4–9] as a rule, restrict themselves to calculations of thermodynamic characteristics, the atom-atom radial distribution functions (RDF), and orientational functions. In conclusion, they establish the presence of correlations in the mutual arrangement of molecules, leaving unexplained the reasons for their origin. In our opinion, it is impossible to establish causal relationships using such an approach.

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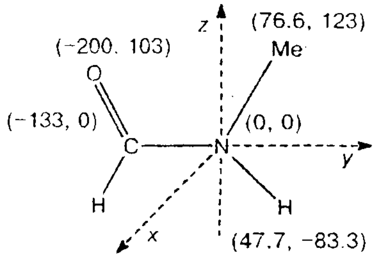
One can succeed in understanding the regularities of the structure of liquid only by studying them at the supramolecular level. This requires calculations of correlation functions defined for objects consisting of molecular aggregates. Hence, the reported data on computer simulation of liquid amides[5—9] are incomplete and their structural properties have not been adequately studied.

Several systems of potential functions were proposed for amide molecules. The OPLS system of the potential functions[5] occupies a particularly important place since it allows one to reproduce many experimental properties of liquid amides. Currently, a major portion of studies carried out by computer simulation is devoted to the development and refinement of the parameters of the potential functions for substances including amides.[7,9] Previously,[7] the parameters of "polarizable intermolecular potential functions" (PIPF) were obtained by fitting the calculated and experimental thermodynamic (and structural) data for neat liquids. The authors pointed to the advantages of the PIPF system for studying polarizability effects in the condensed phase and indicated that thermodynamic and structural characteristics of liquids are virtually independent of the procedure for calculations of intermolecular interactions.

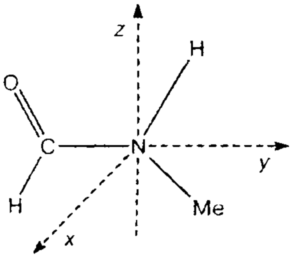
Based on the results of the analysis of the reported data and our studies,[10—15] structural properties of liquids can be divided into those (i) strongly and (ii) weakly dependent on the type of the interaction potential and procedure for simulation. Previously, we have shown that the spatial structure of *N,N*-dimethylformamide (DMF),[12] FA,[14] Me_2CO,[13] MeOH,[10] and solvate shells of ions and neutral particles in MeOH[11] is determined by the type of molecular packing, which is due to universal interactions. The regularities of molecular arrangement in these liquids are determined by the shape of the molecules, whereas their mutual orientation is determined by electrostatic interactions. The distinctions between the known sets of the potential functions are mainly due to the employment of different procedures for calculating the Coulomb interactions rather than the van der Waals interactions. Hence, regularities of the ordering of molecules in liquid can be determined by simulation with simple potential functions.

Striving to develop an adequate model, investigators undertake considerable efforts to derive new potential functions and have to perform necessary calculations on supercomputers because of the complication of the procedure used. However, we believe that the potentialities of the model approach have not been fully utilized. Important information on structural properties of a liquid can be obtained by using the simplest potentials of intermolecular interactions rather than by refining them. In the framework of the models employed, it is possible to determine the properties of liquids or fluids that do not exist in nature, to exclude some types of interactions, and to use the "*reductio ad absurdum*" method. Here, it is pertinent to draw an analogy to the simplified Ising model, which reflects the behavior of many real objects and has been studied for decades by the methods of statistical physics.

Scheme 1



trans-MFA



cis-MFA

The MFA molecule has two stable conformations (*cis* and *trans*, see Scheme 1).

The atomic coordinates (pm) in the (*y*, *z*) plane are given in parentheses. The results of numerous studies[1] show that 90—92 percent of molecules in the liquid phase are in the *trans*-form, despite the relatively small energy difference between the two conformations.[7] It is known[14—16] that the H-bonds formed in liquid FA by *trans*-H atoms strongly differ in their properties from those formed by *cis*-H atoms. The former favor the chain association of the molecules, whereas the latter are responsible for the formation of the spatial network of H-bonds in the condensed states of FA. It was established by X-ray analysis[1] that the model of chain *trans*-association of molecules in liquid MFA does not contradict the experimental results. However, the reasons why this type of structures is formed rather than, *e.g.*, cyclic structures or networks remain unclear. It is to be clarified why the formation of cyclic dimers or other types of associates does not stabilize the *cis*-form of the MFA molecule.

The question can be posed in a wider sense: what are the reasons for the formation of associates consisting of molecules with amide fragments (—CO—NH—)? By retrieving the Cambridge Structural Database (CSD) it was shown[17] that the type of molecular association, similar to that of FA molecules in cyclic dimers, is found only in 202 out of 601 known crystal structures. It is absent in other crystals, notwithstanding the fact that the molecules have amide groups and many of them are biologically active macromolecules. It was established[14] that the probability for the FA molecule to be a constituent of a cyclic dimer decreases by about an order of magnitude on melting. Would the amide-amide cycles exist in melt or in solutions of other substances and what would be their fraction?

The aim of this work is to establish the regularities of mutual arrangement of molecules in liquid MFA and to elucidate the role of the van der Waals and electrostatic interactions in increasing the local and global ordering in the arrangement and orientation of the molecules. To solve the problem posed and to answer the questions formulated, we carried out a series of simulations. The models of the liquid in which all molecules have either *trans*- or *cis*-conformation (*trans*-MFA and *cis*-MFA, respectively) were studied separately. To clarify the role of universal interactions, we excluded ("switched off") all electrostatic interactions in the *trans*-MFA model, thus obtaining the LJ-MFA model. Comparative analysis of supramolecular structures of the above-mentioned models was carried out by comparing the corresponding results with the data of simulation of the fluid of soft spheres (SS) with specially chosen interaction parameters. The arrangement of the molecules in the above-mentioned models was also compared with that found in a system of random closely packed solid spheres.[18]

Calculation procedure

Calculations were carried out by the standard Monte Carlo method[4] in the *NVT*-ensemble at $N = 125$. The conditions of the computer experiment corresponded to a density of 0.998 g cm^{-3} and to $T = 298$ K. The edge length of the cubic unit cell was 2307 pm. Periodic boundary conditions and spherical cutoff of the potential functions were used. The molecular geometry and intermolecular interactions were chosen in accord with the OPLS system of the potential functions.[5–7] The energy of universal nonelectrostatic interactions of molecules was calculated using the Lennard-Jones potentials, while calculations of the Coulomb energy (specific interactions) were carried out taking into account the distribution of excess charges on the i, j atoms.

$$E = \sum_{i,j} (q_i q_j / r_{ij} + A_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^{6}),$$

$$A_{ii} = 4\varepsilon_i \sigma_i^{12},\ C_{ii} = 4\varepsilon_i \sigma_i^{6},\ A_{ij} = (A_{ii}A_{jj})^{0.5},\ C_{ij} = (C_{ii}C_{jj})^{0.5}$$

The following corresponding parameters (ε/J mol^{-1}, σ/pm, q/e) for N (711, 325, −0.57) and O (879, 296, −0.5) atoms and for the Me (711, 380, 0.2) and CH (481, 380, 0.5) groups were used. The *trans*-conformation is more stable. The energy difference between the two states of the molecule is 11.7 kJ mol^{-1}.[7] According to the reported data,[1] most of the molecules in the liquid phase are in *trans*-form. Simulation[7] carried out using the potential functions describing torsional motions of the molecules showed that conformational transitions are rare. In this work, the molecules were assumed to be rigid. In each simulation a chain of random events of length $\sim 30 \cdot 10^6$ configurations was generated, which is comparable with the chain lengths in recent publications[6,7] dealing with simulation of amides (from $5 \cdot 10^6$ to $50 \cdot 10^6$ (Ref. 6) and $4 \cdot 10^6$ (Ref. 7) configurations).

Simulation of the Lennard-Jones analog of *trans*-MFA (the LJ-MFA model) was carried out assuming that all atomic charges in the initial potential are equal to zero. The interaction of the particles in the SS fluid was described by the Lennard-Jones potential with the parameters $\varepsilon = 41.8$ J mol^{-1} and $\sigma = 560$ pm. Since in the last two cases the convergence to average values was attained at a smaller number of steps, $\sim 15 \cdot 10^6$ configurations were generated. The calculations were carried out on a personal computer. The values of the main energy and structural parameters of liquid MFA determined in this work are in good agreement with the results of previous studies,[7] which indicates the correctness of our calculations.

Results and Discussion

The results of calculations of energy characteristics for different models of liquid MFA are shown in Table 1. The average potential energy (E) is minimum for the *trans*-MFA model and is in good agreement with that obtained from experimental data on the vaporization enthalpy of the liquid (−54.6 kJ mol^{-1}).[7] The contribution of the van der Waals interactions to the energy is ~38%. In all cases, the $E_{\rm vdw}$ values are close despite the more than twofold variation of E values. Strong electrostatic interactions in *trans*-MFA destabilize the structure characteristic of LJ-MFA, which manifests itself in a 14% increase in the $E_{\rm vdw}$ values. Electrostatic interactions make the major contribution to the internal energy of liquid MFA. It can be assumed that the van der Waals interactions play the more important role in the formation of spatially ordered arrangement of the molecules in the liquid.

Radial distribution functions (RDF) characterize the short-range order in the liquid. Out of nine atom-atom RDF (Figs. 1 and 2), five remain virtually unchanged on exclusion ("switching off") electrostatic interactions, whereas the shapes of four RDF ($g_{\rm CO}$, $g_{\rm OO}$, $g_{\rm OMe}$, $g_{\rm NO}$) are essentially changed. The formation of intermolecular H-bonds results in reorientations of the molecules and affects the behavior of the RDF of O atoms. Slight variations in the behavior of the $g_{\rm CMe}$, $g_{\rm CC}$, $g_{\rm NC}$, and $g_{\rm NN}$ RDF are observed on going from *trans*-MFA to *cis*-MFA, whereas other RDF change to a greater extent.

Table 1. Average potential internal energies (E) and energies of the van der Waals interactions ($E_{\rm vdw}$) for the different MFA models

Model	E	$E_{\rm vdw}$
	kJ mol^{-1}	
trans-MFA	−54.33±0.03	−20.44±0.03
cis-MFA	−47.44±0.03	−21.95±0.03
LJ-MFA	−23.87±0.02	−23.87±0.02

Note. Listed are errors at a 95% confidence level.

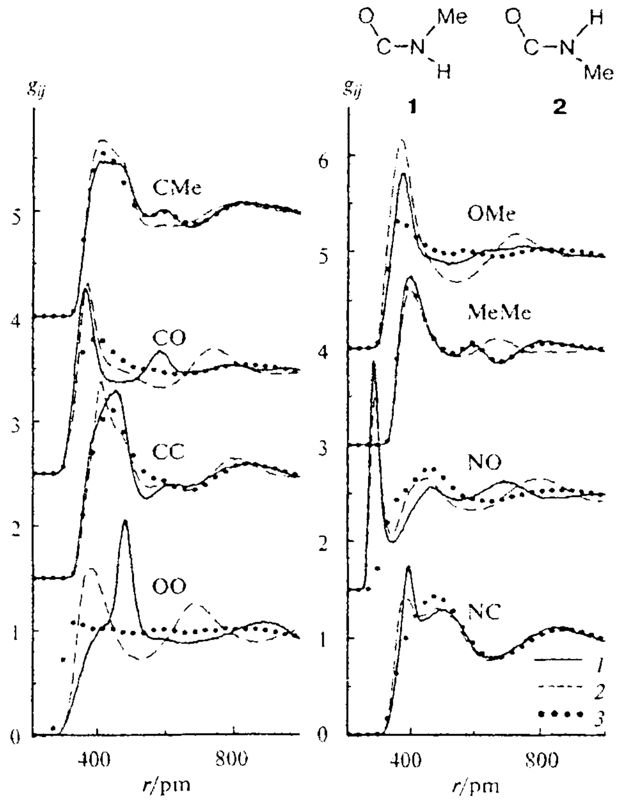


Fig. 1. Radial distribution functions of the atoms of MFA molecules ($g_{ij}(r)$, where *i*, *j* is the type of the atom): *1*, *trans*-MFA; *2*, *cis*-MFA; and *3*, LJ-MFA. For clarity, the intervals between the plots along the ordinate axis are enlarged.

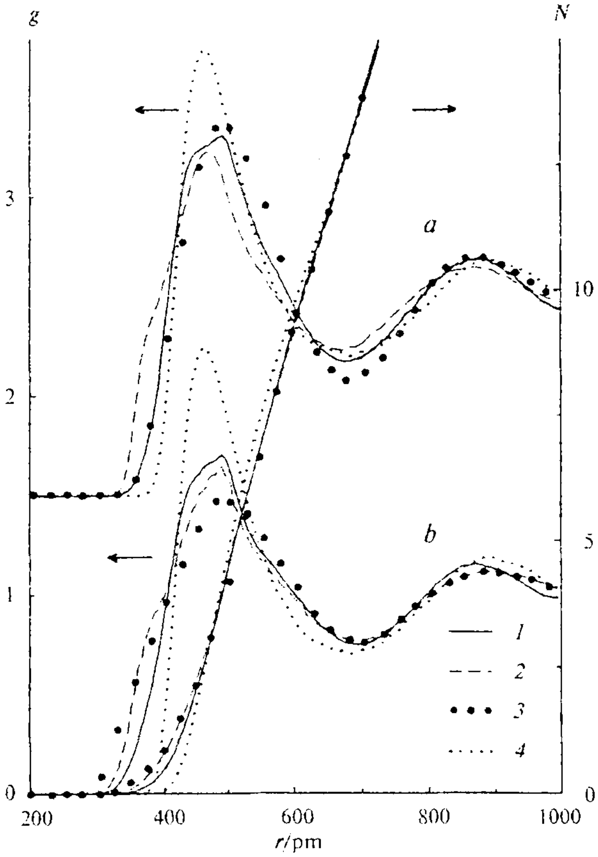


Fig. 2. Radial distribution functions of the centers of mass of the molecules $g_{mm}(r)$ (*a*) and of nitrogen atoms $g_{NN}(r)$ (*b*); dependences of the number of particles in a sphere of radius *r* (*N*(*r*)) on *r*. *1*, *trans*-MFA; *2*, *cis*-MFA; *3*, LJ-MFA; and *4*, SS. For clarity, the intervals between the plots along the ordinate axis are enlarged.

The g_{mm} functions shown in Fig. 2, *a* characterize the mutual spatial arrangement of the centers of mass of the molecules. For different MFA models the distinctions between corresponding g_{mm} functions are small and the functions behave as the RDF of the atoms in the SS model. From the plot of the dependence of the number of particles (*N*(*r*)) in the sphere of radius *r* it follows that the first coordination sphere of each molecule contains ~12 neighbors.

The same number is characteristic of the system of random closely packed solid spheres.[18] Parameters of the Lennard-Jones potential used for description of the interactions in the SS fluid were chosen from similarity considerations of the g_{mm} functions in the MFA models to the RDF of particles in the SS model. Since we were interested in obtaining a qualitative picture only, no problem was posed of rigorous mathematical optimization of the parameters. The patterns of the *N*(*r*) dependence for the four systems are identical. These peculiarities of the behavior of the $g_{mm}(r)$ and *N*(*r*) functions suggest that common regularities of the molecular packing in liquids manifest themselves in all cases.

Knowing the $g_{ij}(r)$ atom-atom RDF, it is possible to calculate the *D*(*r*) function using the formula[19]

$$D(r) = \sum_{i=1}^{m}\sum_{j=i}^{m} b_{ij} g_{ij}(r), \qquad (1)$$

$$b_{ij} = [n_i n_j (2 - \delta_{ij}) c_i c_j]/(\sum_{i=1}^{m} n_i c_i)^2.$$

Where *m* is the number of different types of atoms in the molecule, n_i, n_j is the number of atoms of type *i* and *j*; $\delta_{i,j}$ is the Kronecker symbol, and c_i is the Fourier transform of the atom form factor for X-ray radiation (to a first approximation, it is equal to the number of electrons in the atom of type *i*).

The function *D*(*r*) is obtained by processing experimental data on angular dependence of the intensity of coherent neutron or X-ray radiation scattering. Hence one can compare the experimental and calculated curves. Since the Me and CH groups are considered as single interacting centers in the initial model potential, the c_i coefficients were assumed to be $c_{Me} = 9$, $c_{CH} = 7$, and $c_{NH} = 8$. Using formulas (1), we get for the *D*(*r*) function

$$\begin{aligned} D(r) = {} & 0.0791\, g_{\mathrm{MeMe}}(r) + 0.141\, g_{\mathrm{NMe}}(r) + \\ & + 0.123\, g_{\mathrm{CMe}}(r) + 0.141\, g_{\mathrm{OMe}}(r) + \\ & + 0.0625\, g_{\mathrm{NN}}(r) + 0.109\, g_{\mathrm{NC}}(r) + \\ & + 0.125\, g_{\mathrm{NO}}(r) + 0.0479\, g_{\mathrm{CC}}(r) + \\ & + 0.109\, g_{\mathrm{CO}}(r) + 0.0625\, g_{\mathrm{OO}}(r). \end{aligned} \qquad (2)$$

The plots of the $D(r)$ functions are shown in Fig. 3. The inclusion of electrostatic intermolecular interactions changes the shape of the curve for the LJ-MFA model, namely, a peak at $r = 280$ pm and weak oscillations in the region 400—600 pm appear. The former peculiarity is associated with the maximum of the g_{NO} function, while the latter is explained by the behavior of the functions characterizing the distribution of O atoms in the MFA models.

More pronounced distinctions are observed between the $D(r)$ functions determined for the *trans*- and *cis*-MFA models. The lack of data on the intensities of X-ray scattering allows only qualitative comparison of calculated and experimental[1] $D(r)$ curves. Taking into account inevitable experimental errors and distinctions between accepted procedures for processing of initial data, the behavior of the curves suggests that the properties of real liquid are better reproduced in the framework of the *trans*-MFA model. At the same time, two liquids characterized by (i) the same shape of molecules and (ii) strongly different intermolecular interactions can hardly be experimentally distinguished in any range of distances except for a narrow range $r < 300$ pm. Knowing the shape of the $D(r)$ curve, one can draw only trivial conclusions concerning the structure of liquid MFA and its changes. The atom-atom functions reach extrema at different interatomic distances. Summation using formula (1) smoothes almost all peculiarities. Moreover, it is well known that a large number of feasible mutual arrangements of molecules corresponds to each maximum of the functions. The available information is obviously insufficient to interpret the behavior of the $D(r)$ curve at the molecular level.

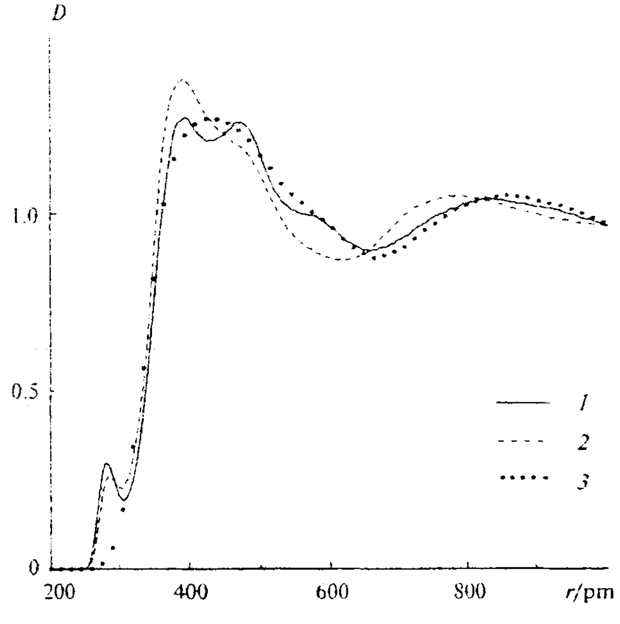


Fig. 3. Atomic density distribution functions ($D(r)$) calculated using formula (2): *1*, *trans*-MFA; *2*, *cis*-MFA; and *3*, LJ-MFA.

Using the lists of atomic coordinates obtained by computer simulation, it is possible to define another group of functions[12—15] which characterize structural properties of the liquid in more detail. Six coordinates, *e.g.*, the radius vector **r** and three Euler angles, should be given to unambiguously describe the mutual arrangement of two MFA molecules. Using a correlation function of six variables, a complete description of the spatial and orientational *D*-structure of the liquid can be obtained. However, such objects can hardly be studied because of some clearly seen reasons. We simplified the problem and investigated the distribution of the molecules in two layers, one parallel and one perpendicular to the molecular plane, of thickness 400 pm each. 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 dr to the average volume density of the liquid (ρ). By analogy, let us define the generalized 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 dN_{ab} is the number of particles of type b in the volume element dxdydz 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. The accepted orientations of axes of the system of coordinates with respect to the central molecule is shown in Scheme 1.

The maps of the generalized atom-atom correlation functions for three models of liquid MFA are shown in Figs. 4 and 5. For the *trans*- and *cis*-MFA models, the atomic density distribution in spherical layers in the regions of short intermolecular distances is highly nonuniform. Obviously, the averaging over spherical layers, which is a step of the calculation procedure for the atom-atom RDF, smoothes many peculiarities of the arrangement of molecules and prevents detailed studies of the spatial structure of the liquid. The atomic density distribution in the LJ-MFA model is more uniform. The shape of the contours resembles the shape of the molecule (see Figs. 4, *b* and 4, *e*). Slight distinctions between the $g_{\mathrm{NN}}(r)$ functions (see Fig. 2, *b*) do not reflect the specific anisotropic character of spatial distribution of the atoms. The formation of intermolecular H-bonds results in the appearance of well-defined areas of increased density of N and O atoms (see Figs. 4 and 5, respectively) near the O and H atoms of the central molecule. For the *trans*-MFA model, the character of distributions indicates the formation of chain structures, whereas the formation of cyclic dimers as well as linear

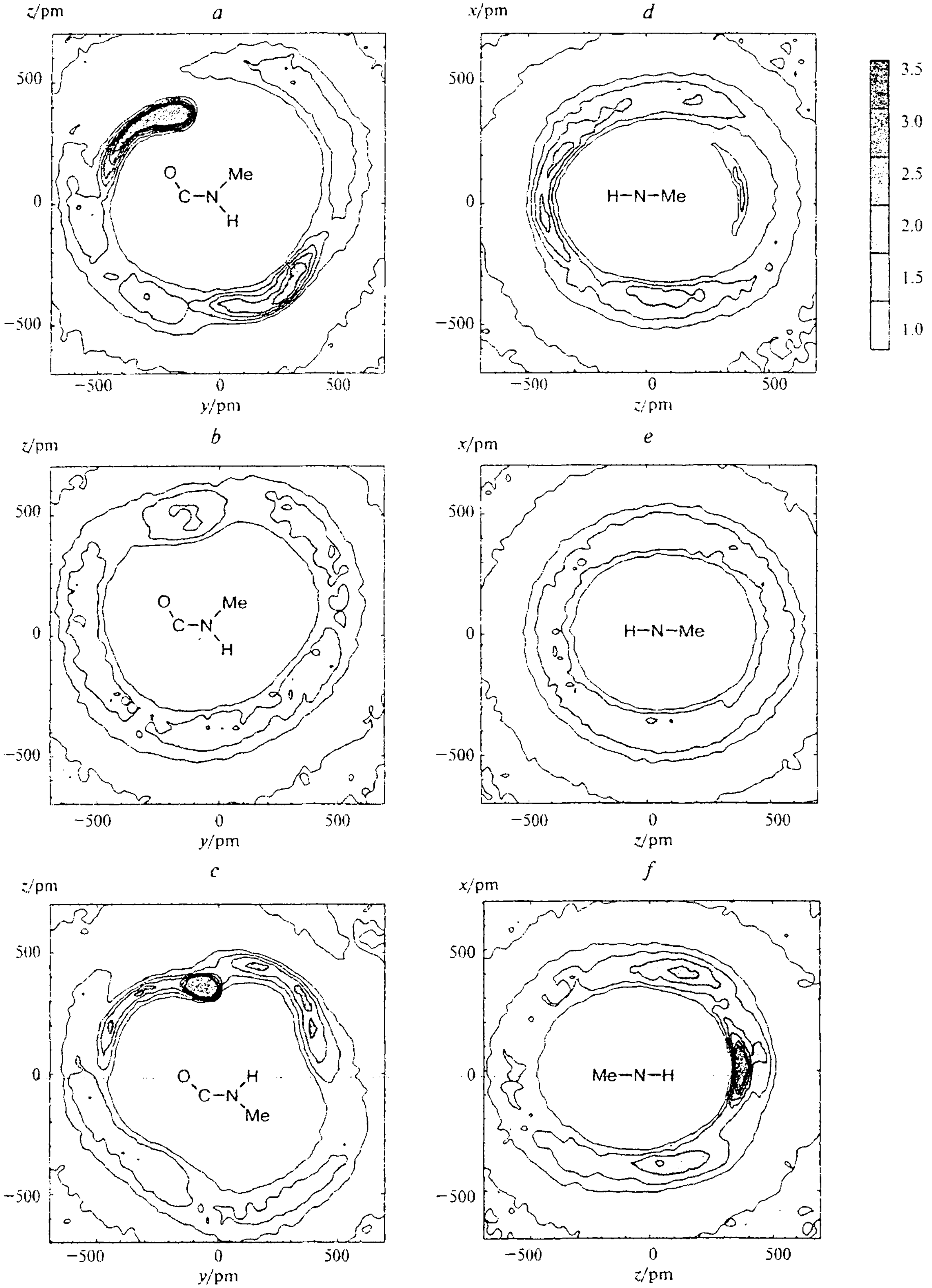


Fig. 4. Generalized spatial distribution functions of the N atoms ($g_{NN}(x, y, z)$): *trans*-MFA (*a, d*); LJ-MFA (*b, e*); and *cis*-MFA (*c, f*).

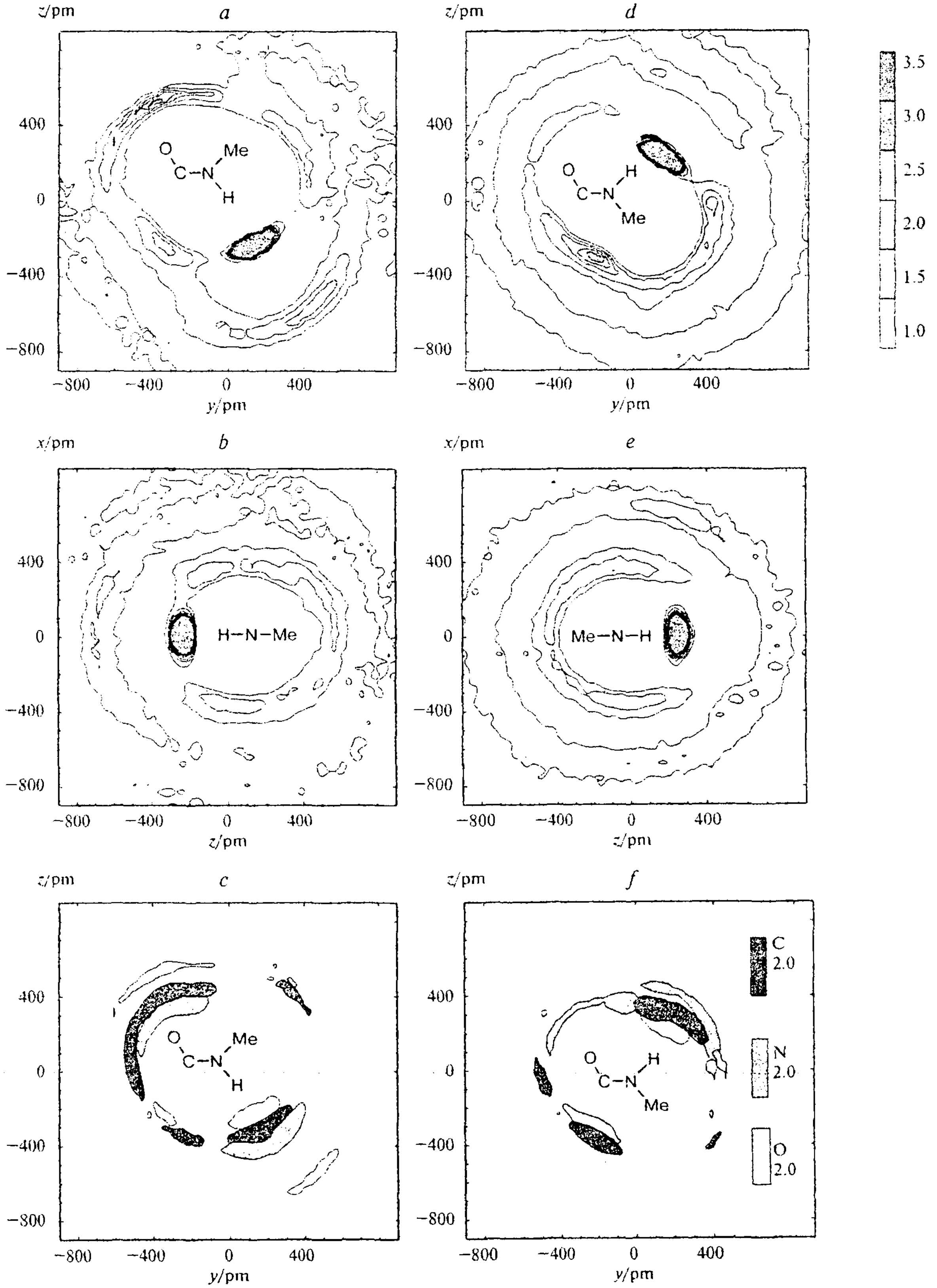


Fig. 5. Generalized spatial distribution functions of atoms ($g_{NO}(x, y, z)$): *trans*-MFA (*a*, *b*); *cis*-MFA (*d*, *e*); the functions obtained by superposition of regions of increased density of N, C, and O atoms (*c*, *f*).

association of the molecules is observed for the *cis*-MFA model.

The areas of increased density of O atoms near the H atom of the amino group (see Fig. 5, *b* and Fig. 5, *e*) are localized near the plane of the central molecule, which indicates essentially linear configuration of the H-bonds (N—H...O—C). Linearity of bonds also manifests itself in a strict order (O, C, N) in which the atoms of neighboring molecules follow (see Fig. 5, *c* and Fig. 5, *f*). However, correlations in the mutual arrangement of the molecules become much weaker already for the second sphere neighbors. For *cis*-MFA, directionality of the bonds is more pronounced. In this case the area of increased density of N atoms at $x \approx 0$, $z \approx 350$ pm (see Fig. 4, *f*) is more clearly seen and has a smaller size than the area at $x \approx 0$, $z \approx -350$ pm (see Fig. 4, *d*). Actually, the molecules in a cyclic dimer are bonded by two H-bonds, which explains the greater planarity of such associates.

Therefore, knowing the atom-atom RDF, it is impossible to establish the regularities of the arrangement of MFA molecules even at short intermolecular distances where the RDF display clearly seen peculiarities. This statement is all the more valid for $D(r)$ functions obtained in experimental studies of angular dependences of the amplitudes of coherent X-ray or neutron scattering. Analysis of their behavior revealed[1] only that the model of chain association of MFA molecules does not contradict experimental results. Generalized correlation functions contain much more information on the mutual arrangement of molecules in the liquid. They make it possible to determine the type of the arrangement and orientation of the molecules; however, this can be done only in the region of short intermolecular distances.

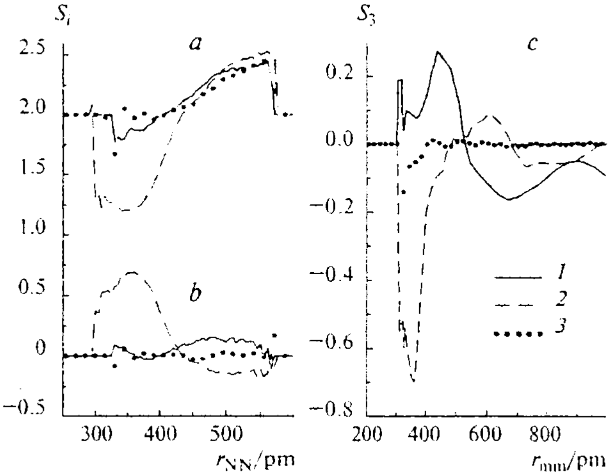


Fig. 6. Orientational correlation functions ($S_i(r)$) calculated using formula (3): *a*, $S_1(r_{NN})$; *b*, $S_2(r_{NN})$ (where r_{NN} is the distance between the N atoms of H-bonded molecules); and *c*, $S_3(r_{mm})$ (where r_{mm} is the distance between the centers of mass of the molecules); *trans*-MFA (*1*), *cis*-MFA (*2*), and LJ-MFA (*3*). For clarity, the intervals between the plots *a* and *b* along the ordinate axis are enlarged.

In simplified form, information on mutual orientations of the molecules is obtained from calculations of orientational correlation functions, *e.g.*, dependences of average cosines of the angles between the vectors tied to the proper systems of molecular coordinates:

$$S_i(r) = \langle \cos \alpha_i(r) \rangle, \qquad (3)$$

where brackets denote averaging over the ensemble. We determined the behavior of the functions S_1 and S_2 that respectively characterize correlations between the directions of the N—Me bonds and between the planes of the nearest neighboring molecules participating in the formation of H-bonds ($r_{OH} < 250$ pm). The dipole-dipole correlation function S_3 is determined by mutual orientations of the dipole moments of the molecules.

The curves characterizing correlations in the orientation of MFA molecules are shown in Fig. 6. The behavior of S_i functions is specific to each mode. Strong correlations at short intermolecular distances for the *cis*-MFA model are due to the formation of cyclic dimers. In fact, the molecular planes are nearly coplanar ($S_2 > 0$), while the dipole moments and N—Me bonds are oppositely directed ($S_3 < 0$ and $S_1 < 0$, respectively). The peculiarity of the behavior of the g_{mm} function (see Fig. 2, *a*) at $r < 400$ pm becomes clear. The molecules in cyclic dimers are arranged at shorter distances. The formation of linear associates in the *trans*-MFA model manifests itself in preferential parallel orientation of the dipole moments of the molecules at $r_{mm} < 600$ pm ($S_3 > 0$). For the LJ-MFA model, the behavior of the $S_i(r)$ functions is determined by molecular packing only. Mention may be made that neighboring molecules are randomly oriented ($S_i \approx 0$) except for a weak correlation between the directions of the N—Me bonds at $r_{NN} > 450$ pm.

Taking into account that (i) the energy of the van der Waals interactions depends only slightly on the strength of electrostatic interactions between the molecules in liquid MFA and (ii) their spatial arrangement is determined by packing factors, the inclusion of an external electric field should result in appreciable reorientation of the molecules. Hence two conclusions can be drawn. First, liquid MFA should have a high dielectric constant. Second, the dipole-dipole correlation function should be strongly dependent on the conditions of computer simulation and on the presence of the external field. In fact, the dielectric constants of the representatives of the FA homologous series are abnormally high (*e.g.*, 111 for FA (at 20 °C), 182.4 for MFA, and 178.2 for *N*-methylacetamide)[1] compared to those of other liquids. The smaller value for FA is explained by the presence of both the spatial network of H-bonds, which is responsible for decrease in the rotational mobility of the molecules, and cyclic dimers with antiparallel orientation of the dipole moments. Previously,[6] it was established that the results of calculations of the dielectric characteristics of liquid FA depend on the conditions of simulation and on the presence or absence of an external field.

Any complex system (almost all objects considered in statistical physics) can be studied at different structural levels. Unfortunately, no unambiguous definition of the concept "structure" has been commonly accepted by investigators of the liquid state of matter as yet. Actually, the term structure is used in reference to (i) a particular arrangement of particles in space[20,21]; (ii) a list of coordinates of all particles and regularities of their arrangement[22]; (iii) a characteristic set of correlation functions[23]; and (iv) a statistical ordering of interacting atom-molecule particles in elementary volume under given conditions.[24] Numerous analogous definitions are known. For instance, the *I*-, *V*-, *D*-,[25] proper, and hidden structures are considered. Each definition characterizes an aspect of a complex phenomenon. We believe that it is necessary to use a generalized definition of structure, based on the concepts formulated in a general theory of systems, where each object is considered as a system.

By definition,[26] an object-system (OS) is a composition, or unity, composed of "primary" elements m belonging to set $\{M_{OS}\}$ chosen for reasons a belonging to set $\{A_{OS}\}$ using relations (in particular, interactions) r of set $\{R_{OS}\}$ taking into account restrictions imposed by conditions z belonging to set $\{Z_{OS}\}$. The set $\{A_{OS}\}$ belongs to universe $\{U\}$. The sets $\{Z_{OS}\}$; $\{Z_{OS}\}$ and $\{R_{OS}\}$; $\{Z_{OS}\}$ or $\{R_{OS}\}$ and $\{A_{OS}\}$ can be empty or contain one, two, ..., infinite number of identical or different elements. Such a formulation made it possible[26] to study and classify systems using powerful mathematical tools. According to the definition, separation of a particular system in the object under study requires that the elements and relations between them be chosen by using certain specific reasons.

By *structure* is meant a totality of stable relations (bonds) of an object responsible for retention of main properties of the object subjected to various external and internal changes. In statistical physics, establishment of stable relations always requires averaging over time or ensemble. By choosing a mutual arrangement of atoms (elements of a system) in a liquid as a system relation we can characterize the spatial structure of the liquid by a set of the atom-atom correlation functions. If the molecules and their mutual orientations are respectively chosen as system elements and relations between them, then the orientational structure of the system is described using another set of correlation functions, in particular, the S_i functions (see Fig. 7). It is reasonable that an infinite number of systems can be distinguished in such a complex object as liquid by changing either elements or relations between them.

In experimental studies of liquids, the type of a system is given by the method employed and procedure used for initial data processing. It is not surprising that the same solute can be considered either as "structure maker" or as "structure breaker" toward the solvent, depending on the method of investigation employed. Each experimental method reveals specific elements in the object and relations between them. Particular types of correlations and stable relations can be strengthened, whereas other types can be weakened.

Methods of computer simulation make it possible to obtain exhaustive information on all coordinates and interactions between the molecules in a model liquid. However, in most cases the authors restrict themselves to calculations of thermodynamic characteristics, atom-atom RDF, orientational and autocorrelation functions, and statistical properties of a system of H-bonds (if they exist) only. Atoms or molecules are usually chosen as structural elements. The limitations and drawbacks of such an approach have been mentioned above to some extent.

Quite different regularities can be established by choosing molecular aggregates or objects built of them as system elements. The former can be clusters and associates with particular composition or topology, or networks of bonds, while the latter can be the Delaunay simplices or Voronoi polyhedra.[27,28] Previously,[13] the advantages and drawbacks of using the methods of statistical geometry have been reported. The method based on constructing the networks of "bonds" in the object under study[10—15] is preferable for description of the supramolecular structure of a liquid. Ensemble-average statistical and topological properties of the network are stable relations and, hence, characterize the supramolecular structure of liquid.

The MFA molecules can form intermolecular H-bonds. By choosing a totality of H-bonds as a structural element and by considering the parameters characterizing its connectivity and topological properties, as well as the spatial arrangement of H-bonds, as relations we construct a new supramolecular object, namely, a system of H-bonds, which can be considered as a graph in three-dimensional space. Two MFA molecules were assumed to be linked by an H-bond if the distance between the O atom of one molecule and an H atom of the amino group of the other molecule did not exceed 250 pm. The average number of bonds per molecule is called the connectivity parameter *n*. The *n* values for *trans*- and *cis*-MFA are 1.89 and 1.79, respectively.

The results of calculations of concentrations of the molecules forming *m* bonds with the neighbors (A_m) are listed below.

Model	A_0	A_1	A_2	A_3	A_4
trans-MFA	0.9	17.4	73.4	8.2	0.1
cis-MFA	3.9	27.7	54.5	13.5	0.4

Both models are characterized by small numbers of monomers and molecules that form four bonds. Large A_2 values and small A_3 values indicate the formation of weakly branched chains of bonds in the *trans*-MFA system. The distribution of the molecules over types for the *cis*-MFA system is more uniform. Other types of molecular association should also be present in addition to chain association.

Considering the system of H-bonds, we can also define and count new structural elements, namely, closed

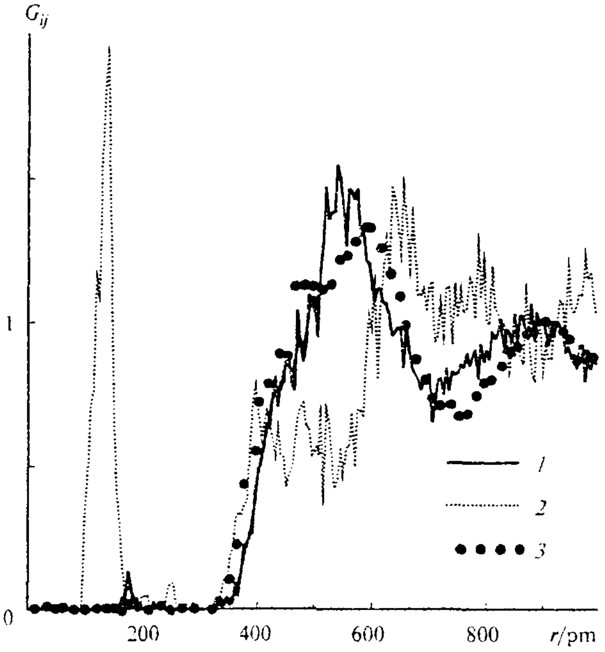


Fig. 7. Radial distribution functions of geometric centers of closed cycles in the networks of H-bonds ($G_{ij}(r)$, where i, j is the number of vertices in the cycle): *1*, *cis*-MFA (i,j = 22); *2*, *cis*-MFA (i,j = 23); and *3*, FA (i,j = 22).

cycles of bonds. A *cycle* is any closed sequence connecting adjacent vertices of a graph. The ratios of the concentrations of cycles with different numbers of vertices and the functions characterizing correlations in the spatial arrangement of cycles are the most important topological characteristics of a system. The results of calculations show that no cyclic polymers (from dimers up to heptamers) are formed in the system of H-bonds of *trans*-MFA. No closed chains of bonds are formed. A different picture is observed for *cis*-MFA. On the average, 12.6±0.1 cyclic dimers, 1.77±0.07 trimers, 0.86±0.05 tetramers, and 0.06±0.01 pentamers per 100 molecules are formed in this system. Liquid MFA consists of molecules that are mainly in *trans*-form. The fact that its viscosity is half that of liquid FA ($1.65 \cdot 10^{-3}$ *vs.* $3.3 \cdot 10^{-3}$ Pa s, respectively)[29] is explained by the fact that the system of H-bonds consists of weakly branched chains and no spatial network is formed.

The $G_{ij}(r)$ RDF shown in Fig. 7 characterize the mutual spatial arrangement of geometric centers of the cycles of H-bonds. The center of each cycle of type i (i is the number of molecules constituting the cycle) was calculated as the arithmetic mean of the coordinates of N atoms. For the system of points obtained, the positions of peaks of the RDF calculated correspond to the most probable intercycle distances. Since the concentrations of cycles at $i > 3$ are low, statistical errors of calculations of the RDF appreciably increase; therefore, only two functions are shown in Fig. 7. The shape of the curves indicates that the cycles are nonuniformly distributed in space.

Previously,[14—16] analogous dependences were obtained and discussed in the studies of structural properties of liquid FA. Marked similarity in the behavior of the G_{22} functions for the models of two liquids (*cis*-MFA and FA) indicates the action of common factors determining the supramolecular structural organization. The presence of the Me group in *cis*-MFA insignificantly affects the regularities of mutual spatial arrangement of cyclic dimers. The shape of the G_{22} curve for the FA model is explained by retention in the liquid phase of fragments of the network of H-bonds characteristic of the FA crystal.[14] On the other hand, the inverse proposition is also true, namely, the parameters of the unit cell of FA are determined by mutual packing of cyclic dimers, whereas the bonds formed with participation of *trans*-H atoms are of little importance.

The average energy of each *cis*-bond in the *cis*-MFA dimer and in a chain associate is −23 and −26.1 kJ mol^{-1}, respectively. In a cyclic dimer, the molecules are linked by two H-bonds, which is energetically favorable. However, the number of dimers and, moreover, other cycles in the system of H-bonds is small. It should be noted that, on the average, the number of cyclic dimers in the networks of H-bonds of liquid FA[14,15] and its mixtures with DMF[16] also does not exceed 10—12 per 100 molecules and varies only slightly on both strengthening of *cis*-bonds in FA and on addition of DMF to FA. This system relation is highly stable toward external influence. This raises the question of what are the reasons for the small number of cycles in the system of H-bonds in MFA. Why are only chain (*trans*-MFA), open-chain branched (*cis*-MFA), or network (FA) structures realized preferably in spite of various feasible types of molecular associates?

To answer these questions, we studied the properties of the networks consisting of lines connecting the nearest N atoms of neighboring molecules. One more supramolecular system, namely, the network of "bonds" of the nearest neighbors, was constructed in the object under study. Its properties depend on the connectivity parameter; therefore the criterion for a "bond" was chosen assuming that $n \approx 6$ for all models because too large an n value dramatically reduces the performance of calculations, whereas too small a value of the connectivity parameter increases the statistical error. The

Table 2. Concentrations of closed cycles of bonds in the network of nearest neighbors

Model	n	C_3	C_4	C_5	C_6
trans-MFA	6.05	1.29	2.10	2.05	4.76
cis-MFA	6.05	1.58	2.81	2.87	6.12
LJ-MFA	6.04	1.46	2.52	2.46	5.59
SS	6.04	1.21	2.17	2.26	5.41

Note: n is the average number of bonds per molecule, C_i is the number of cycles per molecule, and i is the number of vertices in the cycle.

results of our studies show that the choice of the network has a little effect on the regularities of the formation of supramolecular structure at a qualitative level. The N atoms or spheres connected by lines were separated by less than 532 pm (for the *t*-MFA and *cis*-MFA models), by 537 pm (for the LJ-MFA model), and by 522 pm for the SS fluid.

The results of calculations of the concentrations of closed cycles are presented in Table 2. It may be deduced that the properties of the networks (with respect to this parameter) are fairly close. The network for the *cis*-MFA model differs from that for the SS model to the greatest extent. Hence, in this case the molecular packing intrinsic in simple liquids is more pronouncedly distorted. This conclusion is also confirmed by the behavior of the $G_{ij}(r)$ RDF of the centers of cycles; their plots are presented in Fig. 8.

The $G_{ij}(r)$ functions have a complex shape, which indicates a rather high correlation in the mutual spatial arrangement of cycles in the network of bonds of nearest neighbors. The functions reach extrema at certain points. The positions of peaks can be correlated (Table 3) with the distances between the centers of cycles (intercycle distances) in polyhedra or in their fragments shown in Fig. 9. Geometric figures *1*—*5* are characteristic of a random closely packed system of solid spheres[18] and figure *6* reflects salient features of the closest hexagonal packing of spheres. Considering each figure as a graph with an edge length of 470 pm, we calculated the distances between geometric centers of the cycles.

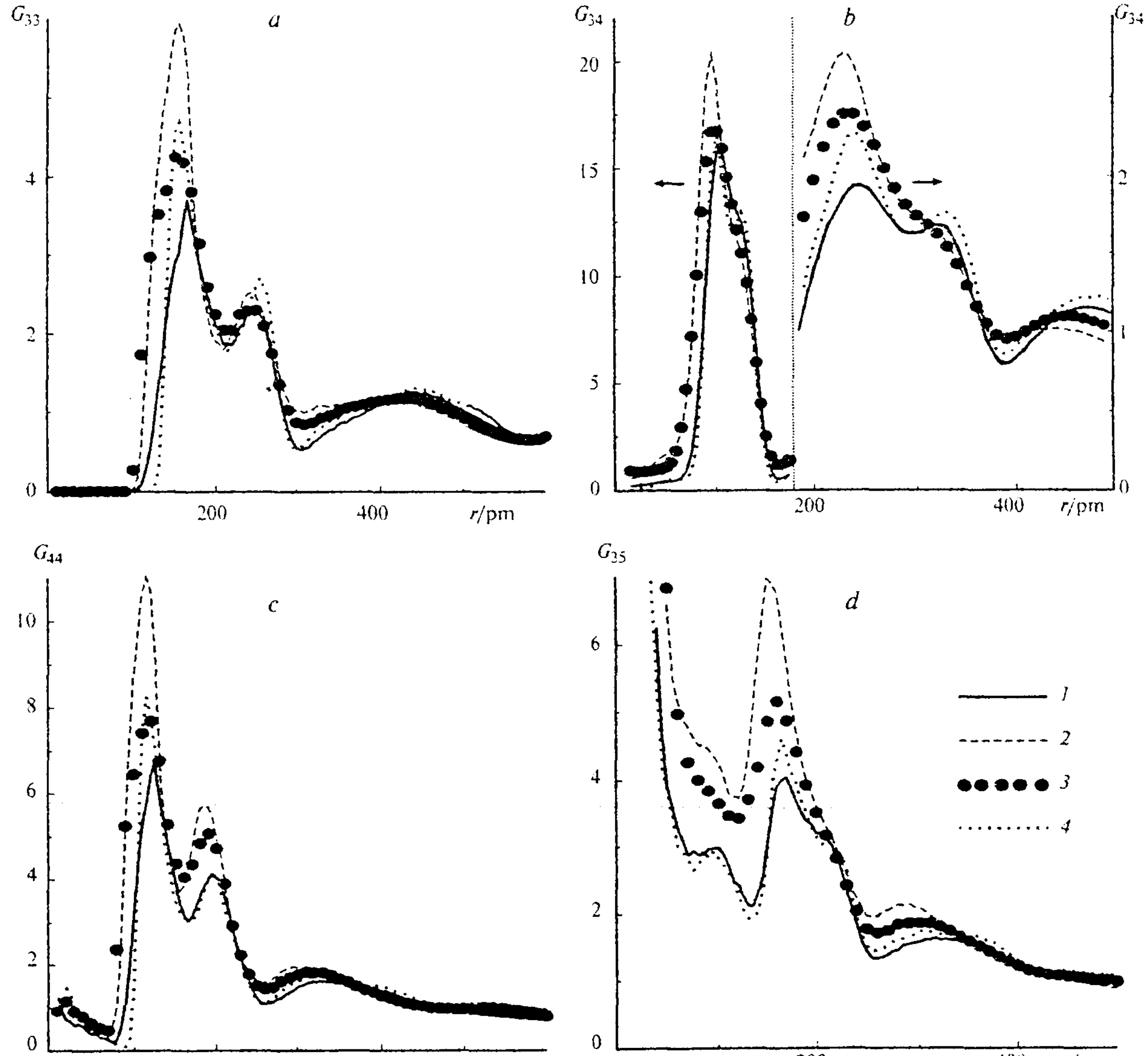


Fig. 8. Radial distribution functions of geometric centers of closed cycles of bonds in the networks of nearest neighbors ($G_{ij}(r)$, where *i*, *j* is the number of vertices in the cycle): *1*, *trans*-MFA; *2*, *cis*-MFA; *3*, LJ-MFA; and *4*, SS.

Table 3. Positions of maxima for the G_{ij} RDF of geometric centers of cycles for MFA models and intercycle distances (r_{ij}/pm) in geometric figures shown in Fig. 10

G_{33}	r_{33}	G_{44}	r_{44}	G_{34}	r_{34}	G_{35}	r_{35}
155	$\underline{157}^{1}$	115	$\underline{115}^{2}$	100	$\underline{96}^{1}$, 119^{2}, $127^{4,5}$, 136^{6}	90	$\underline{109}$
255	226^{2}, 244^{4}, $\underline{254}^{5}$, 272^{6}	195	$168^{2,4}$, $\underline{190}^{5}$, $235^{3,6}$, 293^{4}	240	191^{2}, $\underline{229}^{2}$, 271^{3}, 281^{4}	165	$\underline{165}^{2}$, 196^{3} 208^{5}
445	411^{5}, $470^{3,6}$	320	$\underline{308}^{4,5}$	330	299^{4}, $\underline{308}^{5}$, 360^{6}, $376^{4,5}$	300	$\underline{285}^{3,4,5}$, 335^{4}
				485	$\underline{482}^{4}$, $\underline{490}^{6}$		

Note. The superscript denotes the number of the geometric figure; the distances closest to positions of the RDF maxima are underlined.

No fixed intercycle distances are observed for the SS model (the closest to the random closely packed system of solid spheres); their values form a continuous spectrum. Identical behavior of the functions for all models indicates the existence of some general principles of the formation of supramolecular structures. High correlation between the intercycle distances in the networks of the nearest neighbors of the models studied and those in the system of closely packed spheres (see Table 3) makes it possible to argue that the principle of a close packing of molecules in liquids is common for all systems.

The fragments of randomly chosen configurations obtained by computer simulation and reproducing salient features of the arrangement of the molecules in the monomolecular layer are shown in Fig. 10. *trans*-MFA is characterized by packing close to a hexagonal one; this is typical of the closest-packed systems. Orientation of the molecules favors the formation of chains of H-bonds. Despite the presence of strong specific intermolecular interactions, universal van der Waals interactions have a determining effect on the structural organization of the liquid. Chain association of the molecules does not contradict the principle of a close packing. On the contrary, a cyclic dimer formed by *cis*-MFA molecules is a defect of the network of nearest neighbors of a random closely packed system (see Fig. 10, *b*). It breaks typical structural elements.

The behavior of the parameters characterizing structural properties of *cis*-MFA indicates more pronounced deviations from regularities of the structure of the system of random closely packed solid spheres or the SS fluid. In this case the structure of the system of H-bonds corresponds to that of the network of the nearest neighbors to a lesser extent and, as a consequence, the number of H-bonds and closed cycles that formed is less than would be expected. The internal energy of the liquid increases. The calculations were carried out for the *NVT*-ensemble at a fixed density of the substance. Hence the external pressure in the *cis*-MFA model is unknown. If such a liquid were to exist, it should likely have a lower density. Domination of the *trans*-conformation over the *cis*-conformation observed in liquid MFA is due to not only the lower energy of the former,

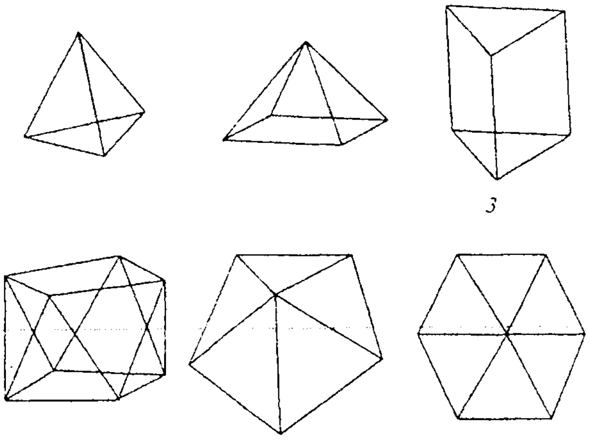


Fig. 9. Geometric figures characterizing salient features of molecular arrangement in a random closely packed system of solid spheres: *1*, tetrahedron; *2*, semioctahedron; *3*, trigonal prism; *4*, antiprism; *5*, a fragment of tetragonal dodecadeltohedron; and *6*, fragment that reflects salient features of the closest packing of spheres.

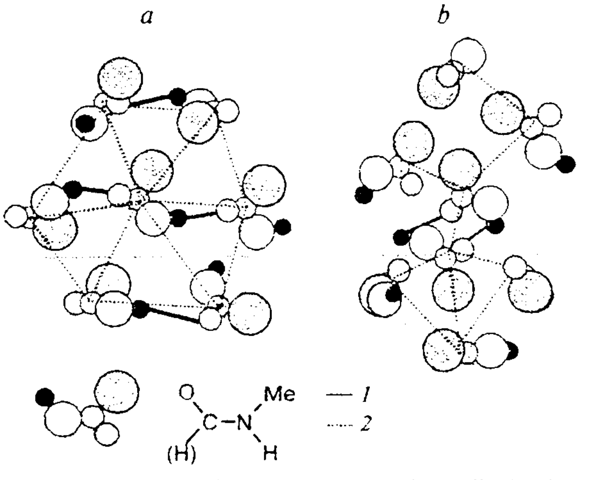


Fig. 10. Schemes of molecular arrangement in the liquid phase of *trans*-MFA (*a*) and *cis*-MFA (*b*) in the monomolecular layer. *1*, H-bond; and *2*, a bond in the network of nearest neighbors.

but also to the effect of packing factors and to complementarity of the structure of the network of H-bonds and that of the network of nearest neighbors. These reasons also explain the presence of the spatial network of H-bonds in liquid FA.

Thus, with a knowledge of structural properties of liquid MFA determined at the molecular level only, it is impossible to establish the main regularities of mutual arrangement and orientation of the molecules even at short intermolecular distances. The system-structural approach allows one to define in the object under study a virtually infinite number of systems that have structure. Consideration of the network of H-bonds and that of the nearest neighbors shows that structural properties of liquid MFA are mainly due to universal interactions and packing. Specific electrostatic interactions can be considered as perturbation affecting mutual orientation of the molecules. Regularities of the formation of spatial ordering of molecules in a liquid can be understood only by studying the liquid at the supramolecular level. Topological properties of the system of H-bonds are first of all determined by correspondence to the properties of the network of nearest neighbors. Linear weakly branched open chains of H-bonds are complementary to this network and, hence, only they are formed in liquid MFA. It can be assumed that progress in understanding of both structural properties of liquids and salient features of the condensed state of matter will be determined by the degree to which supramolecular structures are studied.

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