Physical Chemistry

Structural properties of liquid acetone

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Monte Carlo simulation of liquid acetone was carried out. The effect of electrostatic and van der Waals interactions on the regularities of mutual arrangement of the molecules was studied. Spatial structure of liquid acetone is determined by the molecular shape, repulsive intermolecular interactions, and steric factors and is close to the structure of a random closely packed system of soft spheres. Electrostatic interactions affect only the mutual orientation of the molecules.

Key words: organic solvents, acetone, structure of liquid, intermolecular interactions; computer simulation of liquids, Monte Carlo method.

Investigation of the structure of liquid acetone is of interest both from the viewpoint of the theory of molecular liquids and for practical purposes, since it is widely used as solvent. The Me_2CO molecule has a relatively simple structure and a large dipole moment (2.88 D in the gas phase[1]). It can be assumed that strong electrostatic interactions play an important role in the formation of the spatial structure of the liquid. However, the results of experimental and theoretical studies indicate the absence of tightly bound, long-lived molecular associates.[2–4] It has also been stated[5–7] that the van der Waals interactions have the greatest effect on the spatial structure of liquid acetone.

Currently, methods of computer simulation[8] are successfully used in the studies of liquids. Using the known potential of intermolecular interactions, these methods make it possible to obtain information on the arrangement and interactions of the molecules in a canonical statistical ensemble. Usually, the intramolecular motion of the atoms is ignored in simulations of a liquid and calculations are performed in approximation of the pair additivity of interactions. Hence, the potential used is an effective potential and its parameters are determined by finding the best correspondence between calculated and experimental values.[8,9]

It is the practice to express the energy of interaction between two molecules as the sum of the van der Waals and Coulomb contributions. The first term takes into account sufficiently well known geometric parameters of the molecules. Fitting of the excess electrostatic charges

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and determination of their positions is based on the data on the multipole moments, molecular polarizability, and the results of quantum-chemical calculations. However, the procedure for charge determination is entirely ambiguous.[10] Currently, several sets of essentially different potential functions developed for the simulation of water and liquid organic solvents are known. Thus, investigations dedicated to understanding and estimating the effect of particular types of intermolecular interactions on the structural characteristics of the liquid are timely and favor the development of both the theory of liquid state and optimum procedures for simulation.

Computer simulation of liquid acetone[11] carried out taking into account the molecular polarization revealed no changes in the structural properties as compared to those obtained in the framework of the pair additivity scheme used for the calculations of interactions. Previously,[12—14] we showed that the spatial structure of methanol, DMF, and solvate shells of the ions and uncharged species in MeOH is determined by the way the methyl groups are packed due to universal interactions. The aim of this work was to establish the regularities of the mutual arrangement of the molecules in liquid acetone and to elucidate the role of the van der Waals and electrostatic interactions in the origination of local and global ordering in this system.

Calculation procedure

The simulations were carried out using the standard Monte Carlo method in the NVT ensemble at $N = 125$. The conditions of the computer experiment corresponded to a density of 0.7851 g cm^{-3} and to $T = 298$ K. The Me_2CO molecule has a planar skeleton. The intramolecular C—O and C—CH_3 distances were assumed to be equal to 122.2 and 150.7 pm, respectively, and all angles were assumed to be equal to 120°. These values only slightly differ from those of the structural parameters used previously.[11,15]

The methyl group was considered as a single interacting center. Non-electrostatic interactions were described by the Lennard-Jones (12-6) potentials:

$$U = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6],$$

where ε is the depth of the potential well and σ is the particle diameter. The values of the ε and σ parameters were respectively 85 K and 388 pm (for Me), 52.84 K and 375 pm (for C), and 105.68 K and 296 pm (for O).[11,15] The interactions between oppositely charged centers were calculated according to the Lorentz—Berthelot rule. When determining the contribution of the Coulomb interactions, the following atomic charges were used: -0.502 e (for the O atom), 0.566 e (for the C atom of the carbonyl group), and -0.032 e (for each of the carbon atoms of the Me groups).

The acetone molecules were placed in a cubic cell with an edge length of 2.486 nm. To reduce the influence of surface effects, periodic boundary conditions and spherical cutoff of the potential functions[8] were used. It was assumed that the molecules do not interact at $r_{CC} > 1.243$ nm. A chain of random events of length 34 million configurations was generated. In the simulation of a Lennard-Jones analog of acetone (LJ-Me_2CO), all atomic charges in the initial potential were assumed to be equal to zero. The interaction of particles of the fluid of soft spheres (SS) was described by the Lennard-Jones potential with $\varepsilon = 41.5$ J mol^{-1} and $\sigma = 580$ pm. Since in the last two cases the convergence to average values was attained at a smaller number of steps, 25 and 14 million configurations, respectively, were generated.

Results and Discussion

As was shown by calculations of the energy characteristics of liquid acetone, its average potential energy is -28.69 ± 0.33 kJ mol^{-1}. For LJ-Me_2CO, this value is -22.21 ± 0.25 kJ mol^{-1}. The value obtained in calculations[15] by the method of molecular dynamics at a pressure of 0.28 kbar is -29.4 kJ mol^{-1}. A value of -29.07 ± 0.15 kJ mol^{-1} was obtained by Monte Carlo simulation of acetone[11] under conditions identical to those used in this work. Despite some differences in the procedures and parameters of the potential, the results of our calculations are in good agreement with those of previous studies.

Since the exclusion of the Coulomb interactions in liquid acetone increased the internal potential energy only by 23%, one can suggest that the van der Waals interactions play a more important role in the formation of the spatial structure of acetone. Let us consider how a change in the potential affects the functions characterizing the structure of the liquid.

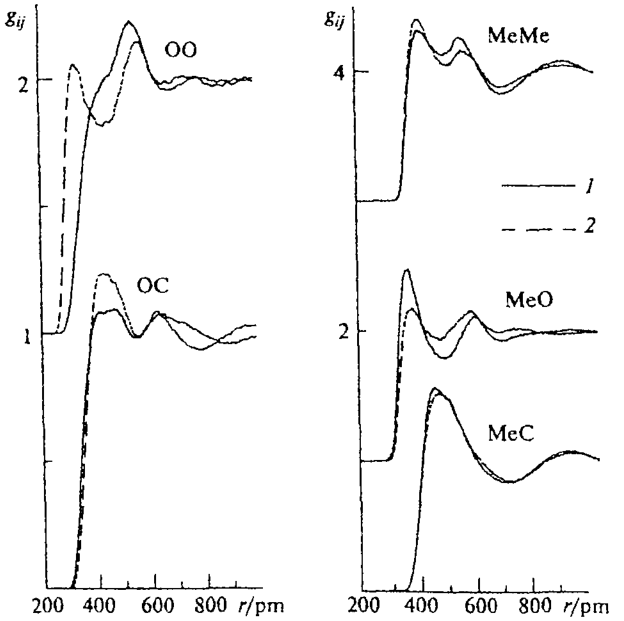

Fig. 1. The atom-atom radial distribution functions, $g_{ij}(r)$ (i,j are the types of the atoms): acetone (*1*) and LJ-Me_2CO (*2*). For clarity, the intervals between the plots along the ordinate axis are enlarged.

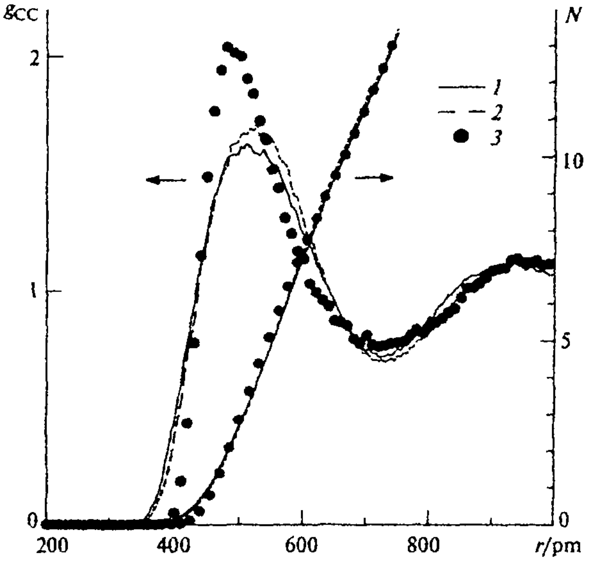

Fig. 2. Radial distribution functions of central carbon atoms, $g_{CC}(r)$, and dependences of the number of particles (N) within the sphere of radius r, $N(r)$: acetone (*1*), LJ-Me_2CO (*2*), and SS system (*3*).

The atom-atom radial distribution functions (RDFs) shown in Figs. 1 and 2 were calculated for acetone and LJ-Me_2CO using the following equation

$$g_{ab}(r) = \rho(r)/\rho = [1/(4\pi r^2\rho)][dN(r)/dr], \qquad (1)$$

where $\rho(r)$ is the local numerical density of atoms of the type b; $dN(r)$ is the number of atoms of the type b in a spherical layer of radius r and thickness dr surrounding a given atom of the type a; and ρ is the average statistical numerical density of atoms of the type b. Good agreement between the above RDFs of the atoms in the acetone molecule and the results obtained previously[11] indicates the correctness of our calculations. The shape of the dependences indicates that the exclusion of Coulomb interactions leads to a substantial change in the g_{OO}, g_{MeO}, and g_{OC} RDFs and has a very little effect on the g_{CC}, g_{MeC}, and g_{MeMe} functions. The strong electrostatic repulsion of oxygen atoms changes the orientation of neighboring molecules; however, the regularities of the spatial arrangement of central C atoms and methyl groups remain unchanged.

As follows from the results of processing of experimental angular dependences of the intensity of neutron and X-ray scattering,[5,6] the weighted sums of atomic correlation functions for liquid acetone $D(r)$ are rather smooth curves with no pronounced peculiarities. With a knowledge of the atom-atom RDFs $g_{ab}(r)$, one can easily calculate the values of $D(r)$ functions from the following equation[6]:

$$D(r) = \sum_{a=1}^{m}\sum_{b=a}^{m}\beta_{ab}g_{ab}(r),$$

where

$$\beta_{ab} = [n_a n_b(2-\delta_{ab})c_a c_b]\Big/\left(\sum_{a=1}^{m} n_a c_a\right)^2. \qquad (2)$$

Here m is the number of different types of atoms in the molecule, n_a is the number of atoms of the type a, δ_{ab} is the Kronecker symbol, and c_a is the Fourier transform of the atomic form factor which, to a first approximation for the X-ray radiation, is equal to the number of electrons in the atom of the type a. Taking into account all the atoms in the acetone molecule, the weights β_{ab} are $\beta_{CC} = 0.3164$, $\beta_{CH} = 0.2109$, $\beta_{OC} = 0.2813$, $\beta_{HH} = 0.0351$, $\beta_{OH} = 0.0938$, and $\beta_{OO} = 0.0625$.

Since the methyl group in the model we accepted is considered as a single center, it is impossible to directly estimate the g_{CH}, g_{OH}, and g_{HH} RDFs, *i.e.*, the functions making substantial contributions to the integrated characteristic. As was expected, the simulation[6] of the behavior of these functions showed that they have no structural peculiarities in the whole range of interatomic distances. The g_{CH}, g_{OH}, and g_{HH} functions make the greatest contributions to the $D(r)$ values only at small r, when they increase from zero to unity.

We have considered two procedures for calculation of X-ray correlation functions $D(r)$. In the first case, the scattering of radiation by hydrogen atoms was ignored and it was assumed that the molecule consists of three C atoms and one O atom. Then the corresponding weights (see Eq. (2)) are

$$\beta_{CC} = 0.4793,\ \beta_{OO} = 0.0947,\ \beta_{OC} = 0.426.$$

In the second case, the methyl groups were assumed to have 9 electrons on each of the orbitals centered on C atoms. The $D(r)$ function was calculated using the following equation:

$$D(r) = 0.3164g_{MeMe}(r) + 0.0352g_{CC}(r) + 0.0625g_{OO}(r) +$$
$$+ 0.2109g_{MeC}(r) + 0.2813g_{MeO}(r) + 0.0938g_{OC}(r). \qquad (3)$$

The calculations showed that the results obtained by both procedures are similar qualitatively, though there are slight quantitative differences.

The $D(r)$ curves calculated for acetone and LJ-Me_2CO using Eq. (3) and the experimental dependence[6] are shown in Fig. 3. Taking into account that the procedure for the processing of primary experimental data is ambiguous[16] and that the accepted procedure of the Fourier transform over the finite space introduces large errors, one should not pay particular attention to the amplitude of the $D(r)$ function and its high-frequency oscillations. Distinctions between the experimental and calculated dependence are to a great extent associated with incorrect pattern of the spatial distribution of H atoms.

Two important conclusions can be drawn based on the behavior of the $D(r)$ curves. First, the results of computer simulation, for the most part, adequately re-

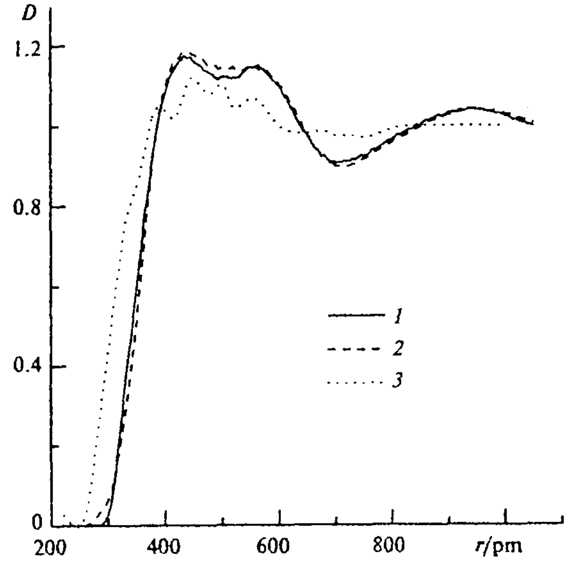

Fig. 3. Weighted sums of atomic radial distribution functions, $D(r)$: acetone (*1*, calculations using Eq. (3)), LJ-Me_2CO (*2*, calculations using Eq. (3)), and experimental data[6] obtained using X-ray scattering (*3*).

flect the regularities of the arrangement of the atoms of liquid acetone molecules. Second, summation of strongly different atom-atom RDFs of acetone and LJ-Me_2CO results in virtually coinciding $D(r)$ functions. The reason for such a coincidence is associated with the fact that the β_{OO} coefficient in all variants considered is relatively small and the increase in the $g_{OO}(r)$ RDF at $r < 400$ pm observed on going from acetone to LJ-Me_2CO is compensated for by the decrease in the $g_{MeO}(r)$ function in the same range of distances (see Fig. 1).

The solution of the problem of reconstruction of the atom-atom RDFs using the experimental $D(r)$ curve is fraught with significant difficulties. It is impossible to determine the behavior of particular atom-atom RDFs from X-ray data. As was shown above, even if the $g_{OO}(r)$ and $g_{MeO}(r)$ functions change substantially, the observed $D(r)$ variations lie within the limits of experimental or calculation errors. The contribution of the $g_{OO}(r)$ function is very small also for neutron scattering. In particular, the ratio of the β_{OO}/β_{HH} coefficients is 0.02.[6]

Thus, it is impossible to establish the regularities of the arrangement of O atoms and, hence, the mutual orientations of the molecules of liquid acetone using only the available experimental data. The results of computer simulation unambiguously indicate the compensation of structural peculiarities of the atom-atom RDFs in the calculations of pair correlation function $D(r)$ not only in the case of liquid acetone, but also for a model with a substantially changed Coulomb term of the potential. Within the limits of experimental error, the integrated curve can be divided by several procedures. Therefore the conclusions on the orientational structure of acetone[6] based entirely on the available data of X-ray and neutron diffraction studies are doubtful. Since the regularities of the spatial arrangement of the molecules are weakly dependent on the peculiarities of calculations of electrostatic interactions, it is not surprising that the inclusion of polarization effects[11] has no effect on the behavior of the atom-atom RDFs of acetone, which confirms the validity of our conclusions.

The atom-atom RDFs contain very little information on the spatial structure of organic liquids with a complex molecular structure. To unambiguously describe the mutual arrangement of two DMF molecules, six coordinates should be given (*e.g.*, the radius vector and three Euler's angles). The spatial and orientational *D*-structure of a liquid can be completely characterized by a correlation function of six variables. However, we cannot investigate such objects for certain 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.[16–18] We still further simplified the problem by considering the distribution of molecules in three layers, one parallel and two perpendicular to the molecular plane.

By analogy with the RDF definition (see Eq. (1)), let us define a generalized atom-atom correlation function of three variables as the ratio

$$g_{ab}(x,y,z) = \rho(\mathbf{r}_{ab})/\rho, \tag{4}$$

where $\mathbf{r}_{ab}(x,y,z)$ is the vector connecting an atom of the type *a* to the center of an elementary volume of an arbitrary shape into which an atom of the type *b* of the other molecule falls, and $\rho(r)$ is the local numerical density of atoms of the type *b* in the elementary volume. By fixing one of the coordinates we get a function of two variables, which can be depicted on plane by contour lines. We assumed that the C atom of a given Me_2CO molecule is in the origin and the molecular plane coincides with the *xy* plane. The local densities were determined in elementary volumes of the shape of a rectangular parallelepiped 400 pm in height and 15 pm in length of square base edge.

The generalized correlation functions characterizing the spatial distributions of C atoms in the three mutually perpendicular planes are shown in Fig. 4. As for the atom-atom RDFs, slight deviations between the dependences calculated for liquid acetone and for LJ-Me_2CO are observed in this case. The shape of the plots in the region of short intermolecular distances is determined by geometric parameters of the molecule. The points of the most probable location of C atoms are in the "hollows" on the van der Waals surface of the central molecule. A tendency for the local density of C atoms to increase in the vicinity of the methyl groups should be pointed out.

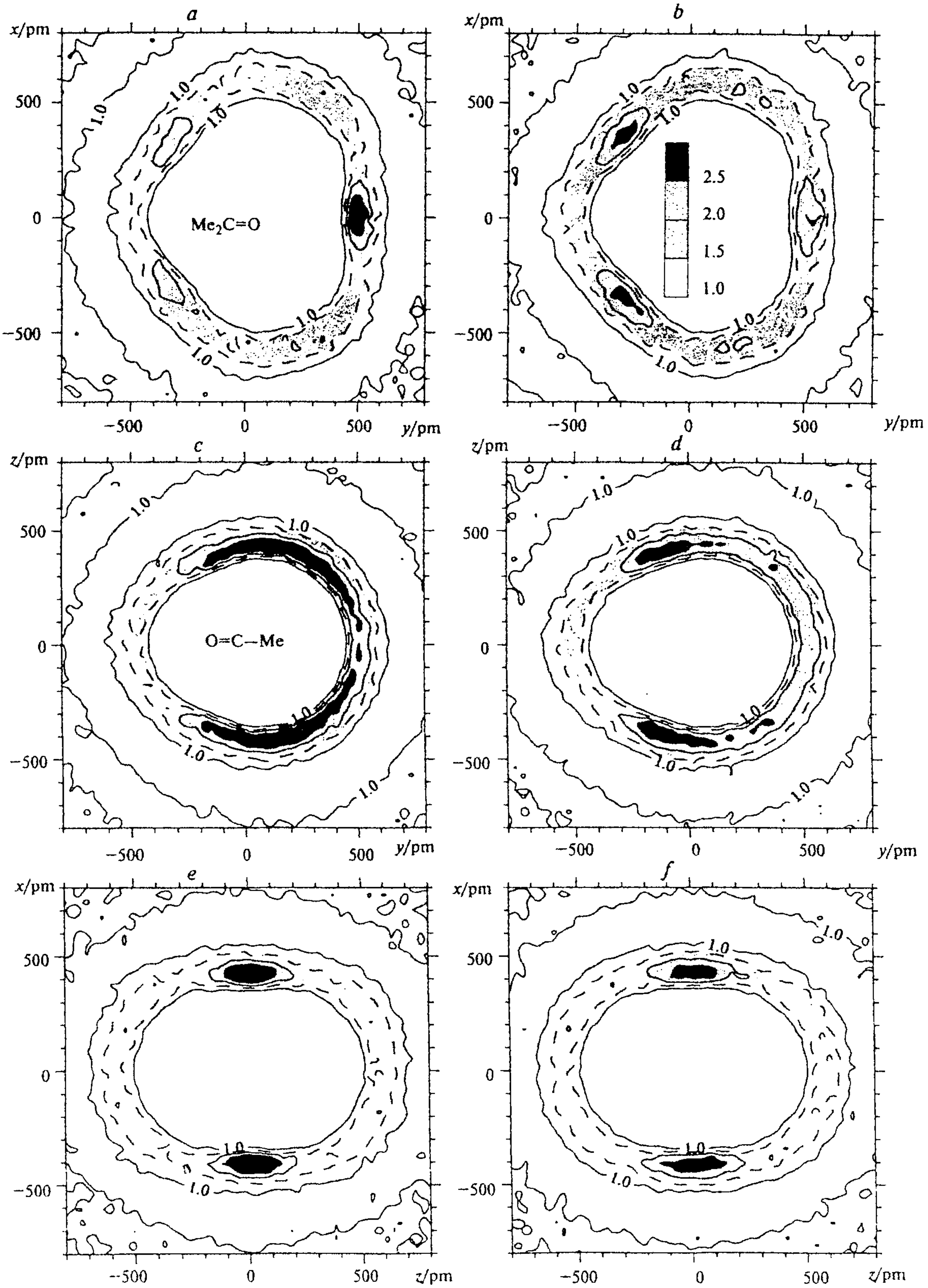

Fig. 4. Generalized correlation functions of spatial distribution of central carbon atoms, $g_{CC}(x,y,z)$ (see Eq. (4)): acetone (*a*, *c*, *e*), and LJ-Me$_2$CO (*b*, *d*, *f*).

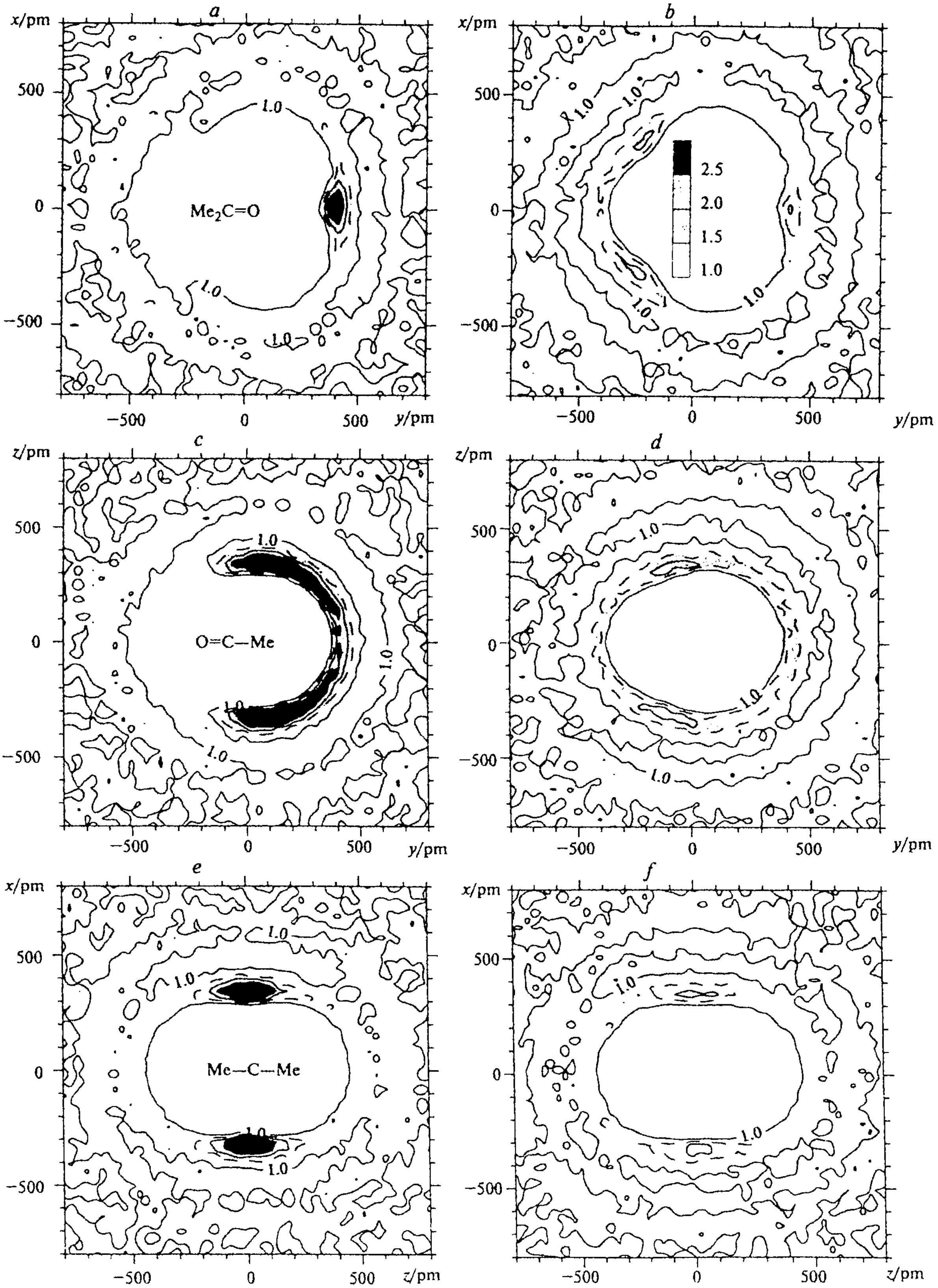

Fig. 5. Generalized correlation functions of spatial distribution of oxygen atoms relative to carbon atoms, $g_{CO}(x,y,z)$ (see Eq. (4)): acetone (*a*, *c*, *e*) and LJ-Me_2CO (*b*, *d*, *f*).

The generalized correlation functions of the distribution of the O atoms relative to the C atoms of the central molecule are shown in Fig. 5. In this case the distinctions between the systems are clearly seen. LJ-Me_2CO is characterized by a more uniform spatial distribution of the atoms and by increased probability of location of O atoms in "hollows" on the van der Waals surface of the central molecule. For liquid acetone, the region of maximum density of distribution of O atoms lies near the methyl groups and, as in the case of distribution of C atoms, the bounding contour has a toroidal shape. On the average, the O atom is ~100 pm closer to the methyl groups than the C atom. Against the background of relatively uniform distribution of O atoms at $r_{CO} > 500$ pm, statistical errors of calculations of the functions result in an appreciable distortion of the shape of the contours in Fig. 5.

The positions of the local density maxima in Fig. 4, *a* ($x = 0$, $y \approx 500$ pm) and Fig. 5, *a* ($x = 0$ pm, $y \approx 400$ pm) differ by about the length of the C—O bond. It can be concluded that in this spatial region the dipole moments of neighboring molecules are oriented according to the "head-to-tail" type. Such an arrangement is illustrated in Fig. 6 for molecules *1* and *2* and to a lesser extent for molecules *4* and *1*. It should be noted that both orientational and the van der Waals interactions favor this arrangement (see Figs. 4, *b* and 5, *b*).

Strong attraction between the C and O atoms of neighboring molecules leads to the appearance of rotation-vibration motions of molecule *3*, predominantly in the *yz* plane (see Fig. 6). In this case the orientation of molecular planes changes from antiparallel to the perpendicular and the shifted parallel one. Such processes are confirmed by Fig. 4, *c* and Fig. 5, *c* from which it follows that the interatomic O...C distances are, as a rule, 100 pm shorter than the C...C distances. The contours bounding the region of increased density in Fig. 4, *c* are extended towards the negative *y* values.

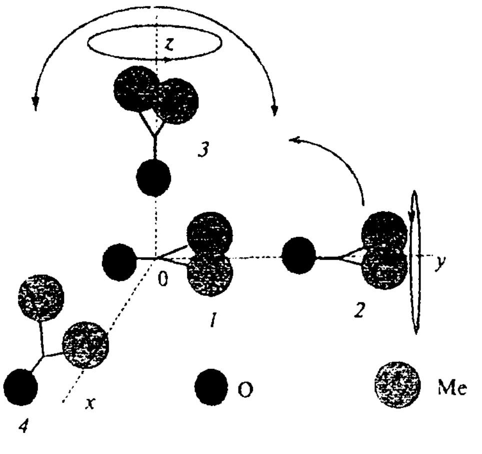

Fig. 6. Scheme of spatial arrangement of acetone molecules (*1—4*, see text), corresponding to the areas of maxima of the $g_{CC}(x,y,z)$ and $g_{CO}(x,y,z)$ functions.

Ways of the mutual arrangement of the molecules in liquid acetone have been discussed previously.[6,11] The authors of Ref. 6 have concluded that the perpendicular orientation of the O—C bonds (or the dipole moments) of neighboring molecules dominates and that the spatial structure of acetone is stabilized due to a weak C—H...O interaction. The authors of Ref. 11 have pointed to the presence of molecules with antiparallel orientation of dipole moments. The analysis of generalized correlation functions unambiguously indicates that all possible molecular orientations that can be observed equiprobably are present in liquid acetone. There is no obvious predominance of two or three particular molecular configurations over others. The most probable arrangement of five acetone molecules found previously[6] using experimental $D(r)$ functions has little in common with the configurations of both the instantaneous (*I*) and vibrational-averaged *V*-structure of liquid. It cannot describe all types of mutual ordering of the molecules in the first coordination sphere that can be determined from the position of the minimum of the g_{CC} function (see Fig. 2).

The potentials of intermolecular interactions used in the methods of computer simulation are derived taking into account both the results of quantum-chemical calculations and experimental data on the structure and properties of the molecule and the substance. The set of potential functions includes several parameters on which the results of simulation can be dependent. Peculiarities of the charge distribution affect mutual orientations of the molecules in the liquid. The results obtained for the acetone molecule using the available procedures for the determination of excess charges on the atoms differ from each other more than by a factor of 2.[10] In those cases when steric factors have the major effect on the regularities of the molecular ordering, the spatial structure of liquid depends primarily on strong short-range interactions and molecular packing. The repulsive term of the potential is determined less arbitrarily. Hence, basic structural characteristics of a liquid are well reproduced by methods of computer simulation.

The atom-atom RDFs play an important role in the structural studies of liquids; however, they cannot describe all regularities of the spatial ordering of the molecules. At best, one can determine the probabilities of observation of different configurations within the first coordination shell of the molecule (short-range order). In principle, it is impossible to establish the regularities of the arrangement of the groups consisting of several molecules constituting the elements of the supramolecular structure using the atom-atom RDFs.

Methods of statistical geometry are widely used for analyzing the structure of liquids.[19–22] The space of a disordered system is partitioned into the Voronoi polyhedra or Delaunay simplices.[23] The mathematical rigor and uniqueness should be considered as merits of the above methods. However, the procedure for constructing the Voronoi polyhedra and analyzing their geometric characteristics is rather complicated, whereas a variety of shapes is characteristic of the polyhedra obtained. It has been pointed out[20] that hundreds of topological types of the polyhedra can be distinguished in the bulk of the liquid. Statistical distribution of their geometric characteristics can be strongly affected by periodic boundary conditions used in the computer simulation. The procedure for partitioning the space into the Delaunay simplices also suffers from drawbacks. In the three-dimensional space, the simplices are topologically equivalent tetrahedra. The primitivity of their shape drastically restricts the set of possible structural characteristics.

A method[12–14,19] based on constructing a network of "bonds" and analyzing its topological properties is more preferable and illustrative (though less rigorous) for qualitative description of the supramolecular structure of a liquid. Being the elements of the supramolecular structure, closed cycles of "bonds" contain small number of vertices, which simplifies calculations and reduces errors due to the peculiarities of the simulation procedure used.

The C atom in the Me_2CO molecule is located near the center of gravity. As follows from the plot of the $N(r)$ dependence (see Fig. 2), there are, on the average, ~12 neighboring molecules in the first coordination sphere of each acetone molecule (r = 715 pm). This number is characteristic of a random closely packed system of hard spheres. We found the parameters of the Lennard-Jones potential, which describes the interactions between the SS species, from the behavior of the $g_{CC}(r)$ function of acetone. Since we were interested only in a qualitative picture, rigorous mathematical optimization of these parameters 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 acetone, it is necessary to calculate the functions characterizing the mutual arrangement of objects consisting of several molecules. When C atoms of neighboring molecules are connected by lines, a network of "bonds" is formed, in which closed cycles (elements of supramolecular structure) can be singled out. After having determined the arithmetic mean of the coordinates of the C 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.

Six acetone molecules nearest to the central molecule in a randomly chosen configuration obtained from the simulation are shown in Fig. 7. They lie in the same layer, whereas the molecules located above and below the plane of the layer are not shown. It can be concluded that a hexagonal packing is characteristic of this arrangement of the molecules. There are closed cycles in a network built of the lines connecting neighboring molecules. Triangles are the main structural elements. A tetragonal cycle can consist of two triangular cycles sharing a common side.

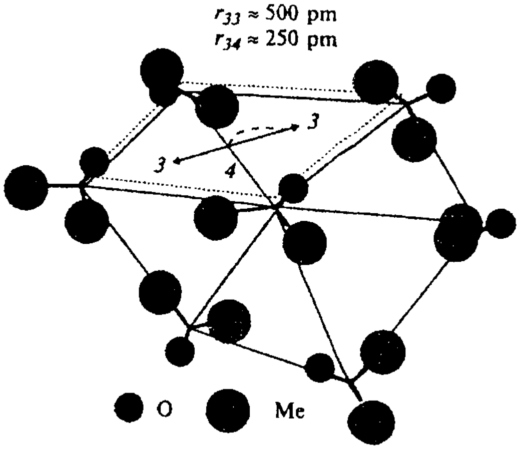

Fig. 7. Mutual arrangement of neighboring acetone molecules in the same layer in the configuration obtained by the Monte Carlo method. Molecules lying above and under the plane layer are not shown.

By analogy with the atom-atom RDFs (see Eq. (1)) 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 dr at a distance r from a 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 the networks constructed for the three liquids. We connected by lines the C atoms or spheres arranged at a distance shorter than 571 pm for acetone and LJ-Me_2CO and shorter than 565 pm in the SS fluid. The average number of bonds per molecule was six 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 value of the connectedness parameter result in a 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 the 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 = 1.28, 1.28, and 1.25; c_4 = 2.02, 2.15, and 2.19; c_5 = 1.97, 2.15, and 2.25; c_6 = 4.66, 5.04, and 5.30 for acetone, LJ-Me_2CO and 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.

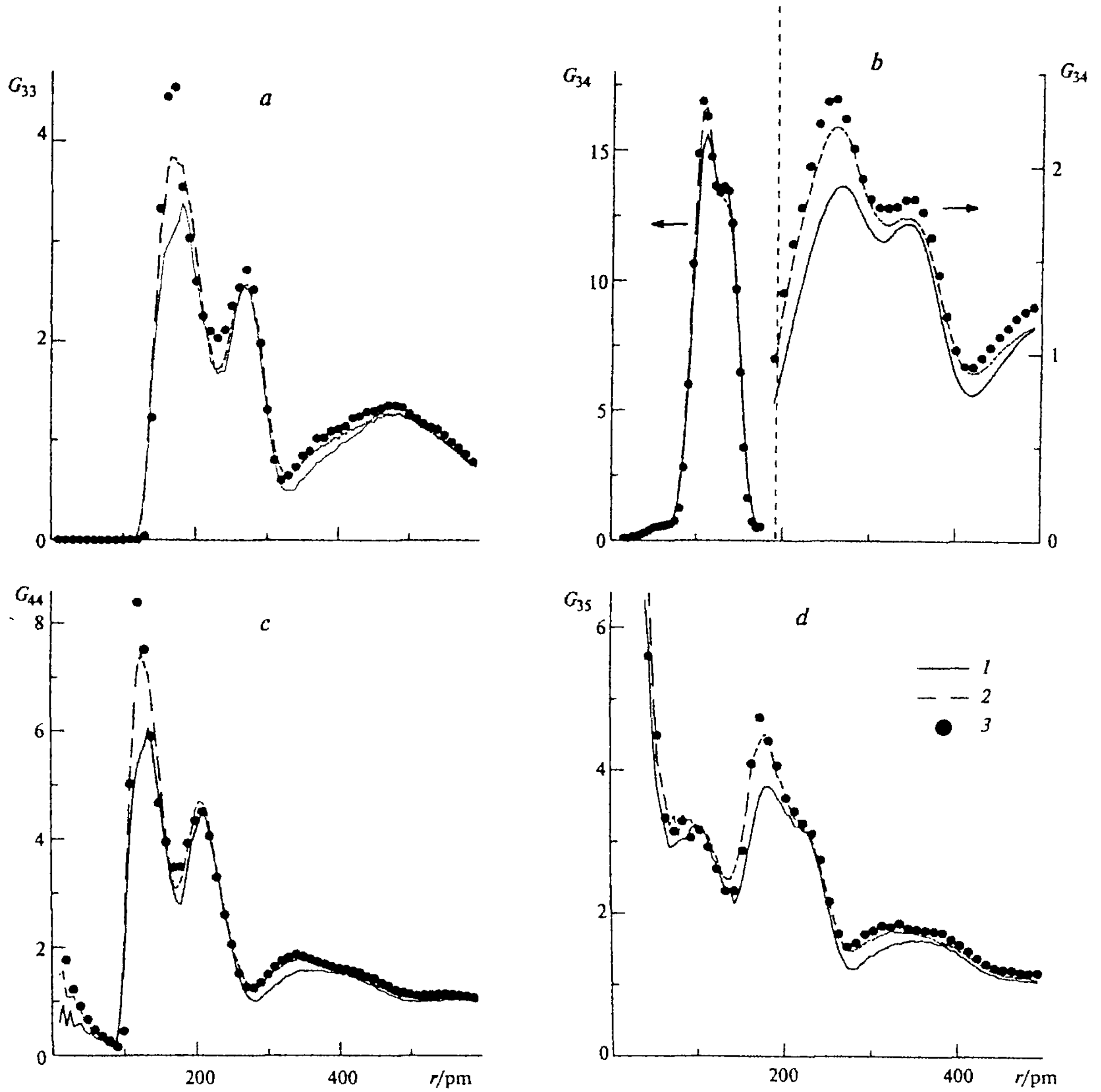

Fig. 8. Radial distribution functions of geometric centers of the closed cycles of "bonds" in the networks of nearest neighbors, $G_{ij}(r)$ (i,j are the numbers of vertices in the cycle); ij = 33 (*a*), 34 (*b*), 44 (*c*), and 35 (*d*): acetone (*1*), LJ-Me$_2$CO (*2*), and SS system (*3*).

The plots of several RDFs of geometric centers of the cycles are shown in Fig. 8. Minimum differences are observed for the functions calculated for acetone and LJ-Me$_2$CO; 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 sufficiently small. Previously,[12,14] we obtained analogous results for methanol and DMF. It was shown that the positions of maxima of the RDFs of the centers of the cycles correspond to the intercycle distances in five types of polyhedra of which the network of "bonds" of a random closely packed system of hard spheres[19] (tetrahedron, octahedron, trigonal biprism, antiprism, and a tetragonal dodecahedron) is built. A continuous spectrum 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. The identical behavior of the functions for three liquids indicates the existence of general principles of the formation of supramolecular structures and is direct evidence for the determining role of the molecular shape and packing factors in the formation of spatial structure at short and long intermolecular distances.

Thus, a broad spectrum of values for the parameters of mutual arrangement and orientation of neighboring molecules is characteristic of the local environment of the acetone molecules in the liquid phase. Steric factors and molecular shape determine the regularities of their spatial arrangement, whereas electrostatic interactions mainly affect their orientation. In addition to other possible configurations, there also exist configurations with antiparallel, parallel, and perpendicular orientations of the vectors of the dipole moments of neighboring molecules in liquid acetone. Chain association of the molecules according to the "head-to-tail" type is favored by both packing factors and the Coulomb interactions. It is impossible to describe the spatial structure of liquid acetone using two or three characteristic configurations of the molecular pair.

Not only local but also spatial supramolecular structure of liquid acetone (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 the potentials 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. The degree of violation of the spatial ordering in liquid acetone upon solvation of the molecules and ions is likely determined first of all by correspondence between the size of the dissolved particle and the structure of the solvent. Effect of the electrostatic field of the ion should manifest itself as changes in the orientations nearest environment of acetone molecules. When there is no need to determine the properties strongly dependent on the mutual orientation of the acetone molecules, a simpler system (LJ-Me_2CO or SS system) 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 acetone will also be valid for other organic solvents.

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