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SPATIAL CORRELATIONS OF INTERATOMIC VOIDS IN MOLECULAR LIQUIDS STUDIED USING DELAUNAY SIMPLICES

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Pair correlation functions are calculated for interatomic voids determined using Delaunay simplices. Various modifications of these functions are suggested in relation to the problem formulated. In the simplest case, this correlator is a conventional radial distribution function $g(r)$, but its calculation employs the centers of voids, but not the centers of atoms. For analysis of nonuniform systems, it is suggested that a "weighted" radial distribution function be used, where pair distances are taken with weights that depend on the volume of the voids. To study structural differences between molecular liquids (e.g., alkane isomers) we use the partial radial distribution functions that take into account only relatively "wide" voids. The ion–void distance distribution functions define voids in the hydration shells of ions an aqueous salts.

Keywords: structure of a liquid, free volume, Delaunay simplices, interatomic voids, radial distribution function.

INTRODUCTION

Investigation of interatomic voids is of interest to researchers in many fields of science. In liquids, free volume determines diffusion and self-diffusion of atoms and molecules. In solids, the structure of voids bears direct relationship to diffusion of impurities and material strength. The spatial distribution and connectivity of voids dictate passive diffusion of small neutral particles in lipid membranes and accessibility of functional groups in globular proteins. Moreover, investigation of intermolecular voids makes it possible to rationalize and define the structure of molecular systems. Indeed, voids reflect that aspect of structure which is not simply related to the arrangement of atoms as they are because the interatomic void is defined by an atomic group (a quadruple in the simplest case). This approach is well known in crystallography where the motifs of crystal structures are more vividly represented in terms of interatomic voids. For example, the difference between the closest crystal structures of fcc and hcp can easily be seen from the arrangement of the tetrahedral and octahedral voids [1, 2]. For disordered systems, this is a relatively new problem [3-6]. Here we have the problem of quantitative determination of interatomic voids solved by using the Voronoi–Delaunay method [7-10].

The geometrical principles of the Voronoi–Delaunay method are well known. Voronoi's classical (for atoms of the same size) partitioning has long been in use [9, 10]. In recent years, the method was generalized to atoms of different dimensions [10-12]. The key notion employed for our purposes is the Voronoi region, defined as a region of space around an atom whose all points are closer to the surface of the given atom than to the surfaces of other atoms in the system. If all atoms

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have the same radius, the region is a classical Voronoi polyhedron defined with respect to the centers of spheres. In the general case, the Voronoi regions are more complex in shape, but they also fill the entire space without gaps or overlaps. The edges and vertices of all Voronoi regions in the atomic system under study form a connected net — Voronoi net. By construction this net lies "deep" between system's atoms and is therefore a convenient tool for investigating voids [10-13]. The apex of the Voronoi region (Voronoi net) is the center of an empty sphere inscribed between the nearest four atoms. Thus each vertex defines the site of the simplest (simplicial) void in the system. The quadruple of atoms defines a Delaunay simplex — the simplest figure in 3D space. Thus for our model, we calculate the Voronoi net using the coordinates of the centers of atoms (set *A*) and their radii (*Ra*). If atoms differ in dimensions, the calculation demands a special algorithm. We use our universal algorithm that can work with systems of identical and different atoms [13, 14]. For purposes of this work we employ the coordinates of the net nodes (*D*), the radii of inscribed spheres (*Ri*), and free volumes of Delaunay simplices (*Ve*).

RADIAL DISTRIBUTION FUNCTION OF VOIDS

The radial distribution function of atoms (RDF) or the pair correlation function $g(r)$ is well known in condensed state physics. It defines the probability of occurrence of an atom at a distance r from the given atom. For dense liquids and amorphous phases, this function demonstrates a clear-cut first peak at distances r comparable to the atomic diameters and oscillations decaying at increasing distances r (Fig. 1*a*). The atoms of the first peak form the first coordination sphere. Further oscillations that can be seen within a wide range point to "extended" structural correlations whose nature and behavior differ between systems [4, 6]. Figure 1 shows the function $(g(r) - 1)r$ used in diffraction theory of liquids; long-range oscillations are more distinct than on the $g(r)$.

In addition to the set of coordinates of the centers of atoms *A*, we have a set of coordinates of the centers of elementary voids *D*. Thus by analogy with the conventional atom-atom RDF, one can calculate the same function for set *D*, i.e., RDF for voids [4-6, 15]. This function is shown in Fig. 1*b* for the same system of disordered spherical atoms. Note that the curves look very similar — oscillations decay at approximately the same rate and have the same period. Mathematically this may be explained by the fact that systems of points *A* and *D* are unambiguously interrelated: Voronoi–Delaunay partitioning is unambiguously defined by the initial atomic system. Nevertheless, this moment is not trivial, the spatial arrangements of points *A* and *D* being absolutely different. At small r the curves differ. The atomic RDF is strictly zero for distances r smaller than the atomic diameter; for voids, the radial function is maximum at zero. This is associated with the fact that, in contrast to the centers of atoms, the centers of the elementary voids can be arbitrarily close to each other. Also note that known splitting of the second maximum on the RDF of an amorphous phase, clearly seen in Fig. 1*a*, is absent in correlations of voids (Fig. 1*b*).

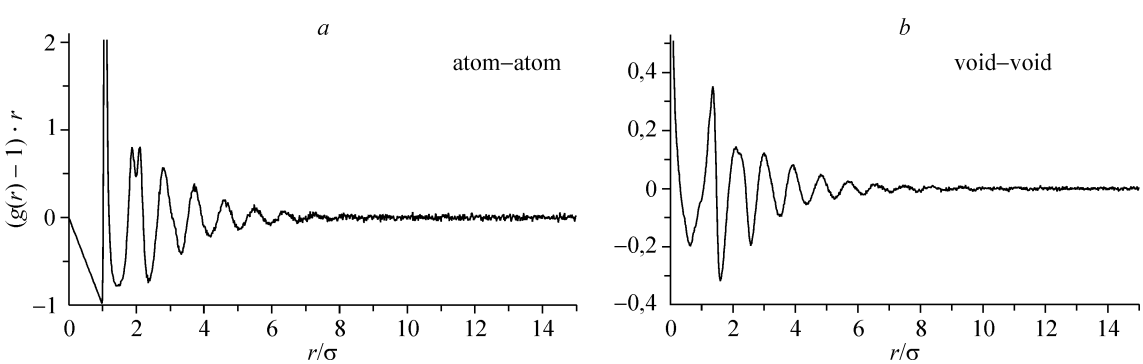

Fig. 1. Radial distribution function for atoms (*a*) and voids (*b*) in a disordered close packing of spherical particles (27,000 atoms in a cube with periodic boundary conditions); the drawing taken from [6].

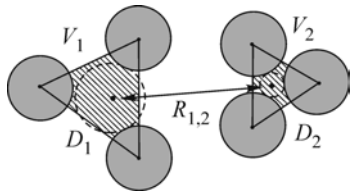

Fig. 2. The distance between two simplicial voids $R_{1,2}$ may be included with a weight equal to the product of void volumes $V_1 \cdot V_2$.

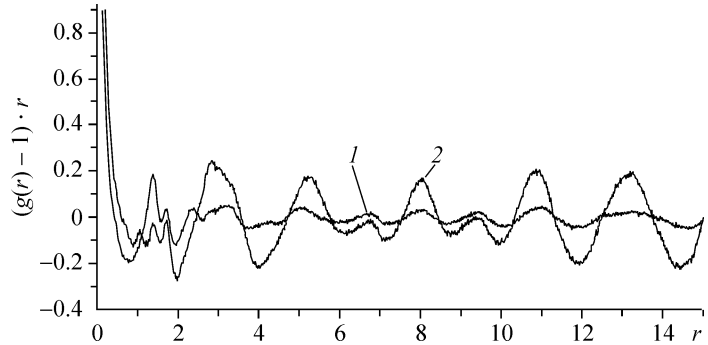

Fig. 3. RDF of voids for the model of the disordered packing of spheres with correlated voids: *1* — standard function, *2* — multiplicatively weighted function.

MULTIPLICATIVELY WEIGHTED RDF FOR VOIDS

Each point from set *D* is explicitly related to its Delaunay simplex. This means that any characteristic of the simplex may be assigned to the corresponding point from *D*. Therefore instead of the standard RDF one can calculate "weighted" functions, where each pair distance is taken with a certain weight that depends on the characteristics of the corresponding simplices. Recall that for conventional pair correlation functions, each distance is taken with the same weight equal to unity; in the general case, however, if a numerical characteristic is specified for each point of a system, correlations may be calculated with allowance for these data, which is sometimes employed in mathematical statistics [16]. Using weighted RDF makes it possible to emphasize the peculiarities of the spatial distribution of the given subfamily of points. This is an effective approach for analyzing nonuniform packings of spheres having relatively large voids.

Here we calculate a multiplicatively weighted RDF, where the weight of the pair distance r_{ij} between two simplicial voids is given by the product of their free volumes: $V_{e_i} \cdot V_{e_j}$ (Fig. 2). Calculation of a multiplicatively weighted RDF permits us to "reveal" distances between large simplices. Thus correlations between the largest pores (if any) become more pronounced. For the weight of a pair distance one can use other expressions depending on the problem being solved; in particular, one can use the square of the difference of the given characteristics of points.

Figure 3 shows the conventional and multiplicatively weighted RDF of voids for the model of nonuniform packing of spherical atoms. Inhomogeneities (extra large voids) appeared in this model after 15% of atoms had been removed from the starting uniform system. The removal was performed according to a pattern of an fcc structure with a lattice parameter equal to three atomic diameters. The atoms to be removed were those that were the nearest neighbors of the nodes of the pattern. The resulting extra voids are variegated. As shown in [6, 15], atom-atom RDF is absolutely insensitive to the structural peculiarities of these systems. However, they are well visualized on the multiplicatively weighted RDF (Fig. 3, curve *2*), where one can clearly see sustained long-wave oscillations, reflecting the motif of the arrangement of extra voids in space. If the system is uniform and all simplices are nearly equal in volume (this takes place, e.g., in close packings of spherical atoms), then the multiplicatively weighted RDF differs but slightly from the conventional RDF since the weight of the pair distances is approximately the same and is reduced after normalization.

PARTIAL RADIAL DISTRIBUTION FUNCTION OF VOIDS

The notion of a partial RDF is well known for atomic systems. If a system under study consists of different sorts of atoms, e.g., atoms *A* and *B*, we can calculate different RDFs for each of the stated types of atom separately: for *A–A*, *B–B*, or

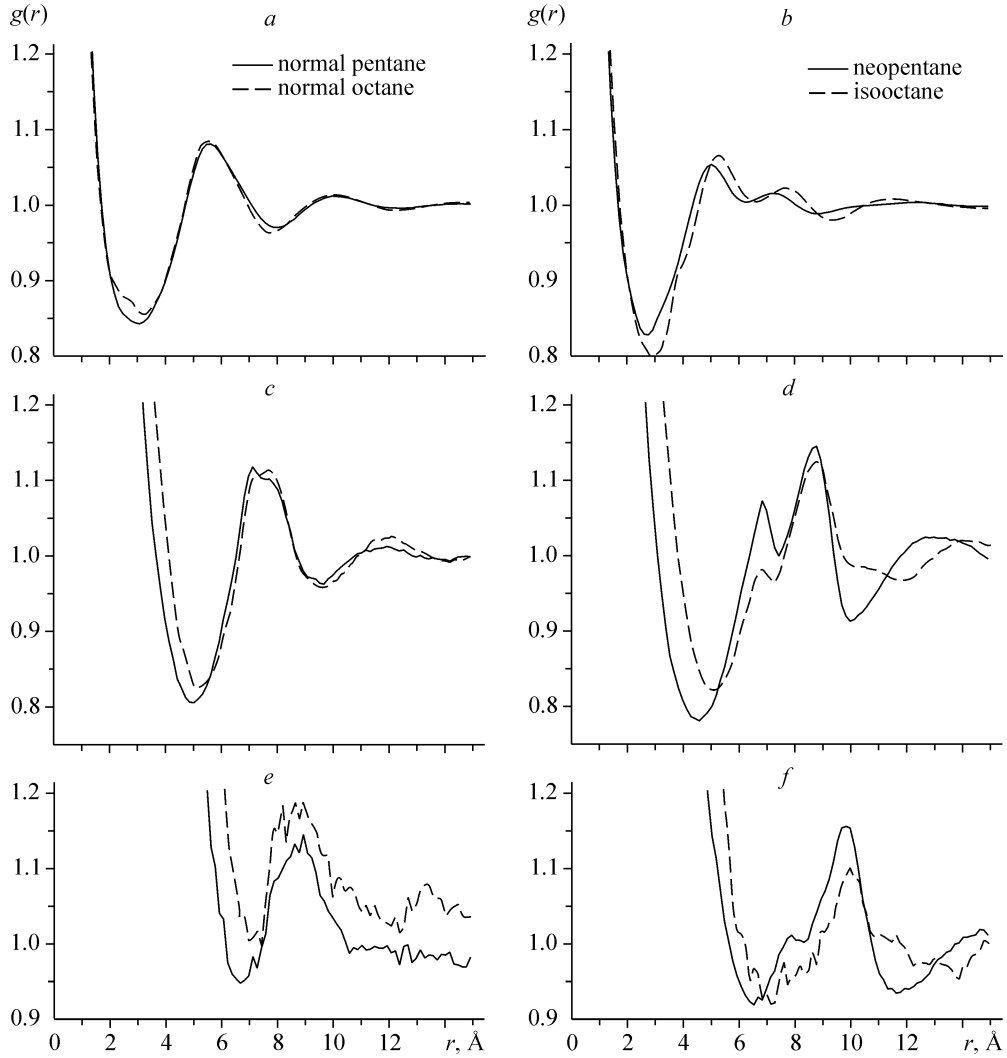

Fig. 4. Radial distribution functions of voids in liquid normal alkanes (left) and their isomers (right): *a*, *b* — total RDF including all simplicial voids; *c*, *d* — partial RDFs that take into account voids whose *Ri* is 1.5-2.0 Å; *e*, *f* — partial RDFs that allow for voids with *Ri* longer than 2.0 Å.

A–B. These are partial RDFs. Similarly, partial functions may be calculated for system *D*. In this case, however, we have no discrete sorts of simplex as when handling atoms. In liquids, simplices are always characterized by a continuous set of parameters: free volume, radius of an insphere, or measure of simplex shape. Nevertheless, the partial function approach is also useful. For a particular physical problem, simplices may be divided into classes related to a given problem. For example, one can consider correlations only between the most spacious or, vice versa, most cramped simplicial voids. For this it is reasonable to use the measure *Ri* of the simplex — the radius of an empty insphere that defines accessibility of the given simplicial configuration for the external probe.

This approach was used for investigating the structure of liquid alkane isomers: normal pentane (n5), neopentane (neo5), normal octane (n8), and isooctane (iso8). As is known from experiment, free electron mobility may differ widely between different isomers of the same liquid alkane. In particular, the mobility in normal octane is 1/175 of that in isooctane [17, 18]. Reasons for this discrepancy is an open question. Liquid alkanes are good dielectrics possessing similar physical characteristics, therefore this mobility problem needs explanation. It would be logical to attribute this effect to the structural peculiarities of liquids. Indeed, these may be specific cavities that serve as electron traps, which are present in some liquids,

but absent in others. In this case, electron trapping decreases the mean mobility. Other reasons include conceivable differences in the nature of spatial inhomogeneities in liquids, affecting electron scattering in different alkanes and thus mobility. However, quantitative structural studies have never been conducted to examine this problem. Analysis of computer models of liquids can shed light on this problem. We demonstrate the results of our analysis of molecular dynamic models of liquid alkanes. Each model consists of 1000 alkane molecules in a model box with periodic boundary conditions. Each CH_n (n = 1, 2, 3) group of the alkane molecule is represented as a single sphere with a corresponding van der Waals radius. Each alkane molecule is formed from its own CH_n groups that admit torsional rotations. The parameters of the interatomic interaction potentials are taken from [19, 20].

Figure 4 shows the pair correlation functions of the voids of alkanes averaged over 100 independent configurations for each model. The top line (Fig. 4*a*, *b*) shows the functions calculated using all points from system *D* (as done previously; see, e.g., Fig. 1*b*); the lower lines contain the partial RDFs that take into account only those simplicial voids that have relatively large values of *Ri*.

It is interesting to note that for the partial function, the peaks are shifted toward large *r* for all models. The shift is explained by the fact that simplices with large radii *Ri* are generally part of relatively large pores, while the characteristic distance between the pores naturally exceeds the characteristic distance between adjacent interatomic voids. On the other hand, even for the largest voids (Fig. 4*e*, *f*), there is a clear-cut peak on the $g(r)$, which points to correlations between such pores. We emphasize that correlations between pores are the consequence of large-scale correlations between molecules, which are, though, difficult to establish by considering the atom-atom RDF. Calculating the partial functions makes it possible to observe these structural features of liquids. Note that all RDFs of normal and isomeric alkanes (left and right columns in Fig. 4) differ considerably, which points to differences in the structure of normal and isomeric liquid alkanes at distances of 6-10 Å.

Thus considering the partial radial distribution functions of voids, we can see systematic structural differences between normal and isomeric liquid alkanes. This gives us grounds to say that the spatial correlations of voids may be related to free electron mobility in these liquids. This problem, however, calls for further studies.

RADIAL DISTRIBUTION OF VOIDS AROUND THE ION IN WATER

Previous sections dealt with "symmetric" RDFs for which we considered distances between related physical objects, namely, atom–atom or void–void distances. Now one can also calculate atom–void distances. Thus to study the structure of a solvation shell, one can calculate the radial distribution function of voids (between solvent molecules) with respect to atoms (ions) of the solute. Using molecular dynamic models of aqueous alkali metal (Li, Na, K, Rb, and Cs) halides, we investigated the hydration shells of ions to elucidate the mechanism of motion of water molecules around different ions. Each model contains 500 water molecules, 16 anions, and 16 cations in a box with periodic boundary conditions [21, 22]. The curves given below were derived by averaging over 100 independent configurations of the model.

Figure 5 (top) shows the radial distribution functions of water molecules (oxygen atoms) around different ions. At the bottom of this figure one can see the corresponding functions of the voids of the same models.

The cations used have different radii, as can be clearly seen from the position of the first maximum on the ion–atom RDF. Similarly, the first maxima of RDF for voids lie at different values of *r*. The corresponding simplicial voids generally involve ions, the centers of these voids lying near the ion surface.

From physical viewpoint, free volume distribution is of interest in hydration shells. To obtain a correct estimate of free volume, we calculated weighted radial distributions; i.e., each ion–void distance was included with a weight proportional to the free volume of the corresponding simplicial void (Fig. 6). We can see that free volume in the hydration shells of small ions (Li, Na) is not so important as in the hydration shells of K, Rb, and Cs ions. This result reveals the structural sense of the difference between positive and negative hydration. As is well known from experiment, mobility of water molecules in the

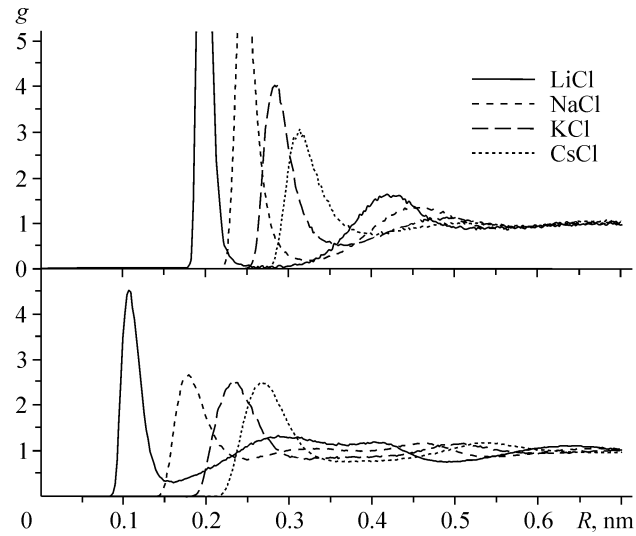

Fig. 5. RDFs of water molecules (oxygen atoms) around various salt cations (*top*). RDFs of simplicial voids around the same ions (*bottom*).

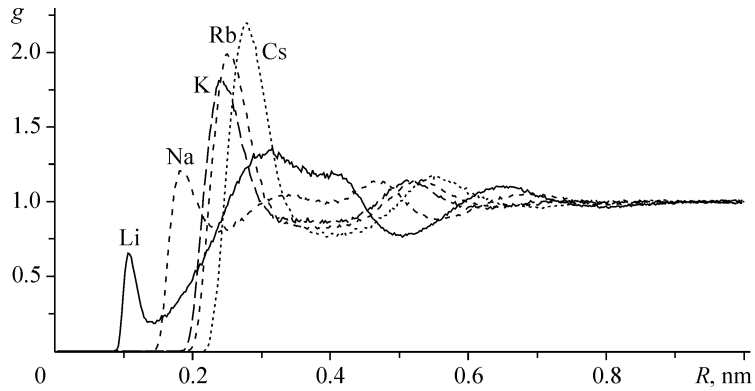

Fig. 6. Weighted radial distribution function of voids around cations in aqueous salts.

hydration shell of Li and Na cations is lower than in bulk water (positive hydration), while in the hydration shell of K, Rb, and Cs ions, this mobility is higher (negative hydration) [23]. Figure 6 shows that negative hydration is due to the extra free volume (including large voids) that appeared in the hydration shell of the ion. Detailed analysis of models indicates that around the Li cation, water molecules form a dense shell having no voids to accommodate a water molecule. Voids of this kind sometimes appear in the hydration shell of the Na cation and are always present around large K, Rb, and Cs cations. Thus the negative hydration phenomenon is due to the large extra voids that appear in the hydration shell and distort the structure of bulk water toward greater mobility of water molecules.

CONCLUSIONS

The Voronoi–Delaunay method is used here to study the spatial correlations of voids in various atomic and molecular systems. For calculations we employ a system of points D — a set of the centers of empty inspheres (centers of simplicial voids). The radial distribution function of these centers defines correlations in the distribution of the empty interatomic space. In addition to the traditional function $g(r)$ we have calculated its variations to emphasize the required aspects of the problem in question. A multiplicatively weighted RDF of voids has been suggested, where each distance

between simplicial voids is included with a weight that is proportional to the product of the free volumes of the corresponding voids. This function is employed for structural analysis of a nonuniform atomic packing. Using this function, one can reveal the available inhomogeneities not generally showing themselves on the standard RDF. Partial RDFs have been calculated for which one does not use all voids, but only those that satisfy the given condition. Here we have investigated the structure of liquid alkanes, considering those simplicial voids that have a relatively large radius of the insphere (these voids are accessible for large probes). It has been shown that the RDFs of normal liquid pentane and octane are similar, but differ widely from the RDFs of their isomers (neopentane and isooctane). This suggests that the large difference in free electron mobility between normal and isomeric alkanes may be explained by the structural features of the empty interatomic space of these liquids. The radial distributions of voids around alkali metal ions in water are used to examine the peculiarities of hydration shells of different ions. Small (lithium and sodium) ions typically have a lower fraction of empty space in hydration shells than do large ions (K, Rb, Cs). This result indicates that a transition from negative to positive hydration is due to the increased free volume in hydration shells.

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