

Application of Voronoi diagrams
for calculation of the radial correlation of the intermolecular voids.

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Abstract. In this paper we discuss applications of the Voronoi diagram and Delaunay tessellation (and their additively-weighted analogies) for studying pair correlation of voids in packings of spheres and molecular systems. Advance analysis of voids (calculation of size, spatial distribution morphology, connectivity of the voids, percolation properties of free volume) was discussed in our recent works (*A.V. Anikeenko, et.al., ICCSA 2004, A. Laganà et al. (Eds.): LNCS 3045, pp. 217-226, 2004, M.G. Alinchenko, et.al., J. Phys. Chem. B, 2004, 108, 19056*). In this paper we devote attention to another type of analysis: calculation of the radial correlation of voids. This way is analogous to traditional calculation of the atom-to-atom correlations widely used in physics of liquids. Additionally, we discuss weighted radial distribution functions, where pair distances are taken into account with a weight depending of the empty volumes of the voids. Partial correlation of "broad" voids is calculated to describe structure difference of local order in pentane isomer liquids. Hydrated shell of ions in water solution is investigated with help of ion-void radial distribution function.

1. Introduction.

Investigation of voids (cavities, channels) between molecules is an important problem in many fields of science. In liquids, the voids govern atomic diffusion and self-diffusion, in solids they are related with the strength of materials and diffusion of impurities. Size, spatial distribution and connectivity of voids are very important to explain permeability of granular materials and polymer films, passive diffusion of small non-charged molecules in membrane, accessibility of functional groups in folded proteins. Besides of that investigation of voids helps for better understanding of the structure of atomic and molecular systems. Voids reflect a complementary aspect of the structure, which is latent in the set of atomic co-ordinates. It is because a void is not connected with a single atom, but defined by a group of atoms (by four in the simplest case). Such approach is known in crystallography for a long time, but for liquids and other disordered systems the problem is relatively new [19,8]. The complication is how to define voids and their locations quantitatively, which are very diverse in general case. However, the problem can be solved easily utilizing the Voronoi-Delaunay method [5, 15, 18].

The basic geometrical concepts of Voronoi and Delaunay diagrams are well-known to reader. Definitions and properties both of classical and additively-weighted Voronoi diagrams are discussed in details in many articles and books [1, 2, 10, 13]. Here we only remind about the main points of the approach looking on the problem from the point of view of physicists. It differs slightly from what is used in mathematical literature, where the object for the Voronoi-Delaunay analysis is a set of discrete point and different distance measures are used [6, 13, 17]. Physicists work usually with 3D bodies. In our case it is spherical atoms, which are characterized by radius and co-ordinates of the center. The distance between a point in space and an atom is implied always as the Euclidean measure to surface of the atom [4, 13]. Therefore, it is naturally to call about a *Voronoi S-region*, which is a region of space all points closer to the *surface* of a given atom than to the *surfaces* of the other atoms of the system. For atoms of the same size these regions coincides with the classical Voronoi polyhedra defined for the atomic centers. In general, the Voronoi S-region is not a polyhedron: its faces are pieces of hyperboloids, and edges are pieces of hyperbolas or ellipses. The union of the Voronoi S-regions generates the *Voronoi S-tessellation* of the system. It divides the atoms into quadruplets of atoms (*Delaunay S-simplexes*). They represent elementary cavities between the atoms. The edges and vertices of the Voronoi S-tessellation form the *Voronoi S-network*. This network "lies in the deeps" between atoms and plays a role of a navigation map for interatomic voids [4, 11].

A network is defined by the co-ordinates and connectivity of its sites. To characterize voids one needs to know also radii of the interstitial spheres, empty volumes for the Delaunay S-simplexes, and radii of bottle-necks in the system. We propose to present this information as the next. Array D contains the coordinates of the network sites. An order in which the sites are recorded in this array defines the numbering of the sites. Array R_i contains the radii of interstitial spheres. Each sphere corresponds to one of the sites of the network. Array DD establishes the connectivity of network sites. It determines the bonds of the network. Each bond defines the bottleneck between a pair of sites. Array R_b contains the radii of bottlenecks for all bonds of the network. The Delaunay S-simplexes are kept in array DA representing the incidence of the network sites and the numbers of atoms relating to the corresponding Delaunay S-simplex. All this information can be immediately obtained at the calculation of the Voronoi S-network. The empty volume of the S-simplexes can be calculated separately and recorded in an array V_e . Coordinates of the atomic centers of a model A and atomic radii R_a are used both for the Voronoi diagram calculation and its analysis.

2. Remarks about revealing and analysis of the individual voids.

Ri-coloring. A set of interstitial spheres (array R_i) is a simple but very important characteristic of the empty interatomic space. Such sphere represents a real hole between atoms. Therefore, the radii of the interstitial spheres indicate a scale of the holes presented in the system. Having arrays D and R_i one can easily find location of the holes of a given radius inside the model. For example, the largest holes can be simply distinguished by marking (coloring) the network sites, which interstitial sphere radii are larger than a limiting value R_{limit} . This procedure for distinguishing of such sites on the Voronoi S-network was called *Ri-coloring* of the Voronoi network [1, 10, 12].

Rb-coloring. A physically meaningful definition of an interatomic void is that region of space between molecules that is accessible for a probe of a radius R_{probe} is regarded as a void. Obviously, when using this definition the voids that are present in a given system depend on the R_{probe} value used, which should therefore be always indicated. These voids can be unambiguously determined through the Voronoi – Delaunay technique using DD and R_b . Indeed, since the R_i radius of any of the two sites connected by the edge is always greater or equal to the bottle-neck radius of this edge, a spherical probe of the radius R_{probe} can move along the edges from one of its site to the other one if the relation $R_b > R_{probe}$ holds. Therefore, the probe can move along any clusters on the Voronoi S-network bonds the bottle-neck radii of which exceed the value of R_{probe} . Such S-network bond clusters represent the “skeletons” of the interatomic voids (The procedure for such distinguishing of voids on the Voronoi S-network was called *Rb-coloring* of the Voronoi network [1, 10, 16]).

Having a skeleton, the void can be determined as the union of the empty parts of the Delaunay S-simplexes corresponding to the cluster.

Having a void as a cluster of the Delaunay S-simplexes, we know (through the array DA) all atoms surrounding the void. It means the obtained voids can be analyzed using any methods and techniques known in computer geometry, biology, and other fields of science. In particular, it is possible to calculate surfaces of voids [9, 14], or represent them as a bodies of simple shape like spherocylinder [1] or ellipse [7]. However, this problem is another area of applications of the method and discussed elsewhere.

Below, we discuss more simple analysis of data structure generated by the Voronoi-Delaunay technique. It is based on the calculation of the radial correlation of voids which locations and characteristics may be defined by the sites of the Voronoi S-network and characteristics of the corresponding Delaunay S-simplexes.

3. Investigation of local and intermediate range order.

3.1. Radial distribution function and the structure factor of system D .

Radial distribution function (RDF), or pair correlation function $g(r)$ in a special case, is one of the most important structure characteristics in the condensed matter physics. It gives a probability to find atom at the distance r from a given one. For liquids and amorphous solids this function demonstrates a pronounced first peak located at the value r close to the value of the atomic diameter and demonstrates damped maxima and minima at the larger r , Fig.1a. The first peak of RDF presents the "first coordination shell" of atoms and characterizes "a local order" in the system. The next oscillations, which can be recognized sometime up to ten atomic diameters, illustrate "an intermediate range order", which can be rather non-trivial in some liquids and solids. RDF has a special physical significance because it can be obtained experimentally as a Fourier-transform of the structure factor measured from X-ray or neutron scattering.

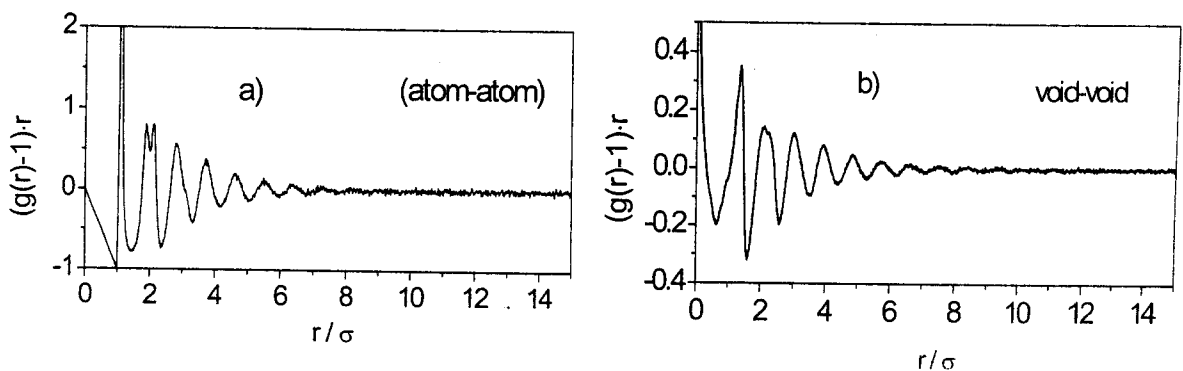


Fig.1. Atom-atom (a) and void-void (b) radial distribution function for amorphous packing of 27000 atoms. (From paper [15]).

To calculate atom-atom RDF one uses co-ordinates of atoms A of the studied system. Co-ordinates of points D can be also directly used for such calculation. A physical significance of these points is clear. Every one of them can be considered as the centre of a simplest void, because they are centres of the interstitial spheres. Corresponding void-void RDF is shown in Fig.1b. Both curves in Fig.1 look similar. They demonstrate resembling oscillations with the same period and damping. Mathematically it is maybe not very surprising because the sets A and D are connected one to one. However it was not being understood a priori because positions of points in D are much more irregular than positions of atoms.

Fig.2 shows the structure factors calculated for the model used in Fig.1. It is calculated as the Fourier transform of RDF and emphasizes features on the structure which difficult to see directly in the RDF. Homogeneous disordered systems (simple liquids and glasses) demonstrate a uniform main peak of the structure factor which position reflects "a scale of length" in the model: ($r_1 \sim 2\pi/q_1$).

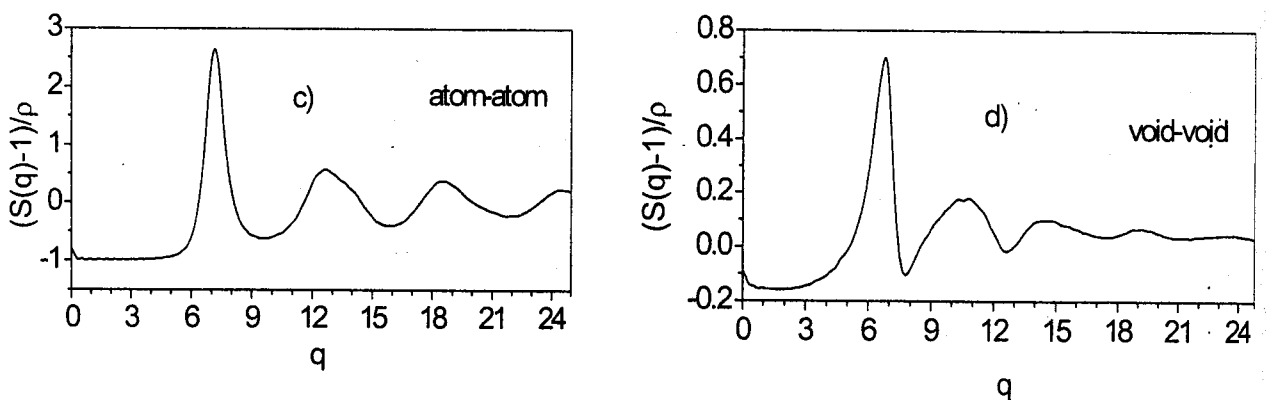


Fig.2. Atom-atom (a) and void-void (b) structure factor for a homogeneous amorphous packing of 27000 atoms. It is obtained as the Fourier-transform of functions in Fig.1 (from paper [5]).

A problem of existing of different scales of length in liquids was studied in works [5, 15, 18]. Calculation of the void-void RDF and the void-void structure factor had been applied for that. Models with different kinds of the intermediate range order were modeled in [15] by creation of extra voids in the large non-crystalline packing of Lennard-Jones atoms. It was shown that the system of D is sensitive to such structure peculiarities, while the atom-atom correlation are not always indicative. In simple systems there is only one scale of length determined by size (diameter) on atoms. An additional scale of length r_{add} is caused by a specific structure of the system.

Experimentally it results a sharp "prepeak" in the atom-atom structure factor at the value $q_{add} \sim 2\pi/r_{add}$.

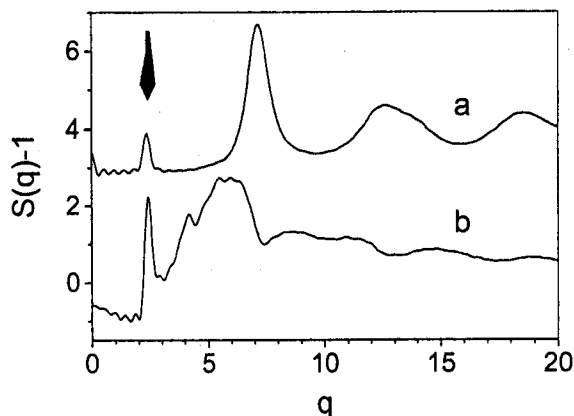


Fig.3. The atom-atom (a) and the void-void (b) structure factor calculated for a amorphous packing with a specific intermediate structure. This peculiarity is developed as a sharp peak at $q \sim 2.5$ in the atom-atom function (a). The main peak in the void-void structure factor (b) has the same position, shown by arrow.

In the paper [15] it was shown that an additional scale of length, which can exceed the value of the atomic diameter in a few times, is governed by voids. Fig.3 demonstrates it: the main peak in the void-void structure factor (b) is located at the same position as the prepeak in the atom-atom structure factor.

3.2. Multiplicatively weighted radial distribution function. (marked correlations)

The points in D is associated with the Delaunay simplexes. It means any characteristic of the simplex can be assigned to the corresponding point. In respect to study free volume correlation, the empty volume of the Delaunay simplex V_e is interesting. So, D and V_e allow us to calculate a *marked* radial distribution function.

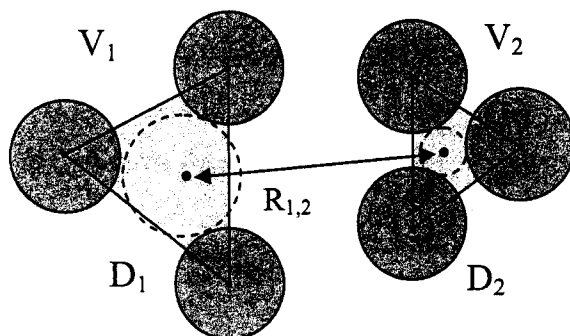


Fig.4. A distance between two Delaunay simplexes $R_{1,2}$ can be taken into account with a weight $\sim V_1 * V_2$

In particular, we calculated a *multiplicatively weighted* RDF, Fig.4. Here, we take every distance in to account with a weight, which is equal to a product of empty volumes of the corresponding Delaunay simplexes. Note, usually one takes distances with the same "weight" which is equal to unit. Fig. 5 demonstrates comparison of the normal void-void RDF and multiplicatively weighted void-void RDF for a model of heterogeneous disordered packing of spherical atoms. If system is homogeneous (like Lennard Jones liquid or glass), all Delaunay simplexes have approximately the same volume. In this case the normalized multiplicatively weighted radial distribution function looks like the normal one. However, if there are simplexes of different size, it becomes immediately visible on the multiplicatively weighted function.

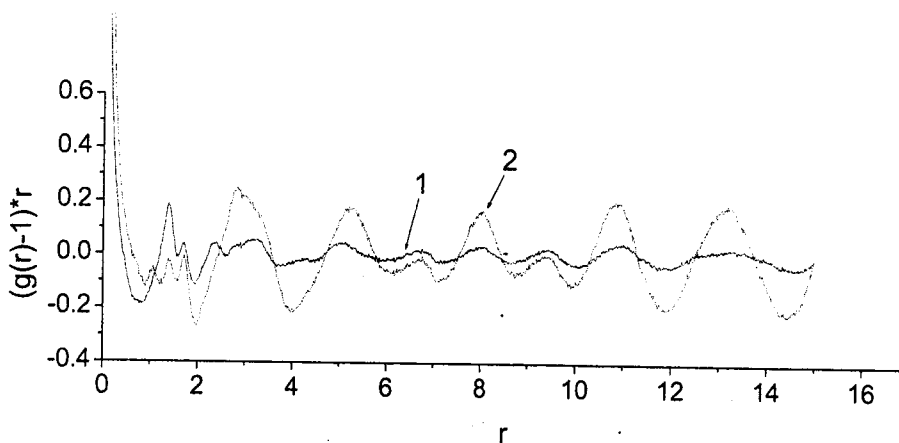


Fig.5. Comparison of a normal (1) and multiplicatively weighted radial distribution functions (2) for a model of disordered packing of sphere with correlated extra voids.

3.3. Partial radial distribution function.

Another numerical measure which can be assigned to the points of D is the mentioned above radius of the interstitial spheres, R_i . There is a remarkable difference in using measure R_i and V_e . The interstitial spheres can be strongly overlapped in opposite to empty volumes of the Delaunay simplexes which cover empty intermolecular space without overlapping and gaps. Because of it the using of measure R_i for calculation of a multiplicatively weighted RDF will result to non-physical overestimation of some configurations inside a model. However, R_i helps to obtain another interesting information about empty space distribution. As an example, a *partial* radial distribution functions can be calculated. In this case we select voids of a given size. On models of liquid pentanes we compared the normal void-void RDF (Fig.6a) and the partial void-void RDF, where the voids (points of D) only having R_i values greater then 1.5A were taken into account, Fig.6b.

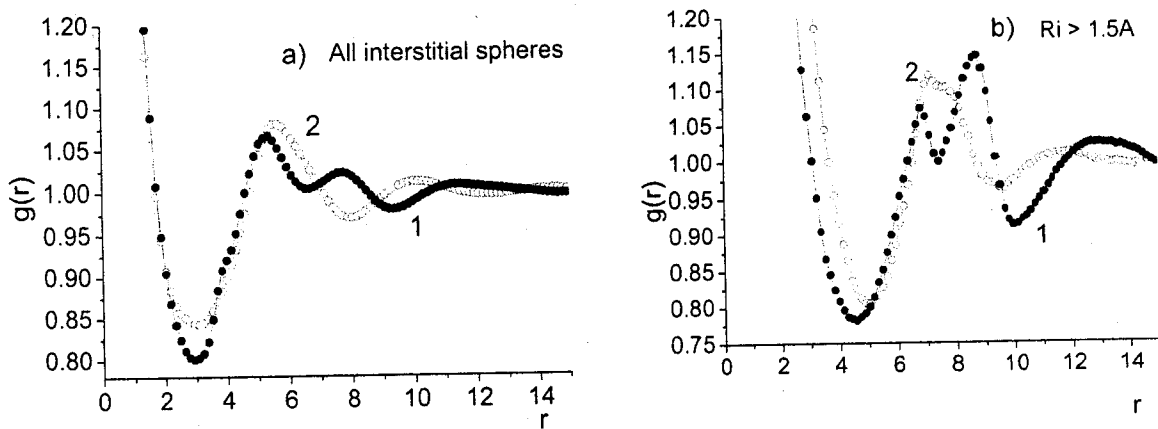


Fig.6. The total (a) and partial (b) void-void RDF for liquid pentanes: curves (1) for normal pentane, curves (2) for iso-pentane. For the total function all voids were taken into account, for the partial: only with $R_i > 1.5\text{\AA}$.

We see a remarkable difference between total and partial functions for iso-pentane (curves 1). At the same time for the normal pentane both functions look similar (curves 2). It demonstrates a difference of local structure in liquid normal- and iso-pentanes in spite of they have the same chemical properties. This structure peculiarity could be important for explanation of different behaviors of free electron in lineal and branched alkanes.

3.4. Radial distribution of voids around ions in water.

Recently, we calculated radial distribution function of voids around ions in models of solutions of halogenides of Li, Na, K, Rb, and Cs in water [3]. In this work we characterized a solvate shell of ions to explain mobility of water molecules around different ions. Appreciable distinction of ion-void RDFs was obtained. For small ions (Li, Na) we see lower fraction of the empty volume in solvate shell in compare with K, Rb, and Cs. It correlates with experimentally observed slower mobility of water molecules in solvate shell of Li and Na and higher mobility for the others (positive and negative hydration). We can say the phenomenon of the positive and negative hydration is connected mainly with the size effect. Small ions provide for rather dense and regular water arrangement in its surroundings (low fraction of voids). The larger ions do not give any advantage to water molecules to make an optimal shell. Fig.7 demonstrates the "weighted" radial distribution functions of voids around the ions. We measure distances from ion to void, therefore only one of the Delaunay simplexes with its empty volume is taken into account for weighting a pair distance unlike to the multiplicatively weighted RDF discussed above.

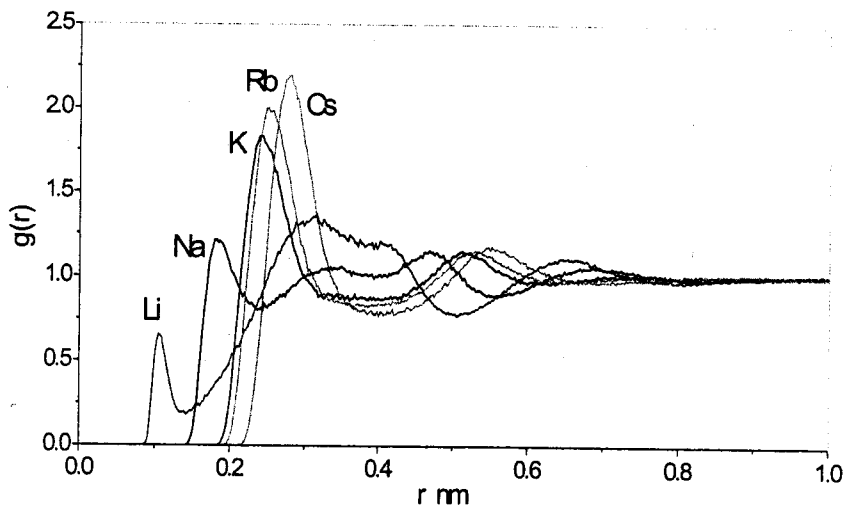


Fig.7. Weighted ion-void RDF for salt solutions of halogenides of Li, Na, K, Rb, Cs in water solution.

4. Conclusion.

We demonstrated a simple technique of application of the Voronoi-Delaunay method for studying radial correlation of voids in different atomic and molecular systems. The main data structure for such analysis is based on the co-ordinates of the Voronoi vertexes and Delaunay simplex characteristics of the studied system. Every Voronoi vertex is a centre of empty interstitial sphere and plays a role of the centre of a simplitial void. Radial distribution function of these centers presents a spatial correlation of the interatomic space. The result of calculations demonstrates a physical worth and concernment of this approach. It gives us the structure information which is complementary to data obtained from atom-atom correlation functions. Beside the traditional radial distribution function, the weighted and partial radial distributions of voids can be calculated. It is naturally in this case because every simplitial void is characterized by its own volume (empty volume of its Delaunay simplex) and by the radius of the corresponding empty interstitial sphere. In particular, a multiplicatively weighted radial distribution function was calculated for different kinds of atomic packings. Partial correlation of "broad" voids was proposed to demonstrate structure difference of local order in liquid pentane isomers. Hydrated shell of some ions in water solution is investigated with help of the weighted ion-void radial distribution function.

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