Voronoi-Delaunay analysis of voids in systems of nonspherical particles

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The Voronoi network is known to be a useful tool for the structural description of voids in the packings of spheres produced by computer simulations. In this article we extend the Voronoi-Delaunay analysis to packings of nonspherical convex objects. Main properties of the Voronoi network, which are known for systems of spheres, are valid for systems of any convex objects. A general numerical algorithm for calculation of the Voronoi network in three dimensions is proposed. It is based on the calculation of the trajectory of the imaginary empty sphere of variable size, moving inside a system (the Delaunay empty sphere method). Analysis of voids is presented for an ensemble of random straight lines and for a molecular dynamics model of liquid crystal. The spatial distribution of voids and a simple percolation analysis are obtained. The distributions of the bottleneck radii and the radii of spheres inscribed in the voids are calculated. [S1063-651X(99)05606-8]

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I. INTRODUCTION

The structure of voids is an important factor in many problems of physical chemistry, catalysis, and material science. It governs the permeability, fluid flow, and diffusion of admixtures in porous and granular media [1,2]. The voids in atomic systems (liquids and glasses) are related directly to solubility and other thermodynamic properties [3]. Computer simulation is a productive way to investigate these physical phenomena. However, it needs an adequate description of the empty space inside a model.

The known Voronoi-Delaunay approach [4] used successfully to study the structure of noncrystalline systems [5–10] is proved to be very helpful also to study the structure of voids. In this way main results have been obtained for packings of monosize spheres, which are the simplest models for granular materials, as well as for monoatomic liquids and glasses.

The basic construction to study unoccupied volume inside a packing of monosize atoms is the network of edges and vertices of the mosaic of the Voronoi polyhedra [Fig. 1(a)]. The Voronoi network lies in ''the depth'' between the atoms [11] and plays the role of ''a navigation map'' [12] of the system. This property of the Voronoi network has been applied to different problems. The permeability and fluid flow through packings of equal spheres are studied by Bryant and co-workers [13,14] and Thompson and Fogler [15]. An approach for modeling of the mercury porosimetry phenomena was proposed by Voloshin *et al.* [16]. Diffusion of a small ball under gravity was simulated as a Monte Carlo walk on the Voronoi network by Richard *et al.* [17]. An unexpected application of the Voronoi-Delaunay technique was made by Bieshaar *et al.* [18] for acceleration of the particle insertion

method for chemical potential calculation for dense liquids. The Voronoi network as a tool for ''a computational porosimetry'' was discussed recently by Medvedev [19].

An application of the Voronoi-Delaunay approach for a broader class of particles seems to be interesting. However, as was remarked many times, the classical Voronoi-Delaunay constructions cannot be used in the general case [11,13,20,21]. Originally the Voronoi-Delaunay tessellation is defined for a system of points (centers of objects) and it does not take into account the size and the shape of objects. This is the reason the known ideology and algorithms were not applied for more complex particles. They can be used for systems of monosize spheres only.

Recently the problem has been solved for spheres of different radii [12,19,22]. Such systems are used as models of polydisperse powders, polyatomic materials, and alloys [23,24]. To take into account the surface of the particles, one should introduce actually a new geometrical construction: instead of the classical Voronoi polyhedron, defined for a center of sphere, one should define another volume of space, all points of which are closer to the *surface* of a given sphere than to the *surfaces* of the other spheres of the systems. This region was called the *Voronoi S region* [12]. It is analogous to the usual Voronoi polyhedra, but their faces and edges are curved [Fig. 1(b)]. The Voronoi *S* regions generate *the Voronoi S tessellation*. The set of vertices and edges defines *the Voronoi S network* of the system of polydisperse spheres. A special algorithm had been created to calculate the *S* constructions [25]. An application of this technique to study three-dimensional (3D) Apollonian packings was made in [26]. An analysis of different polydisperse sphere packings was given in [12,27].

Note that there are a lot of generalizations of the Voronoi tessellation in mathematical sciences (mainly in 2D) [28]. Here for physical applications we use a ''physical'' one. In the terminology of the book [28] the ''assignment rule'' for a definition of the *S* tessellation is a condition on the closest distance from a point of space to the surface of the objects. A two-dimensional illustration of such a tessellation for non-

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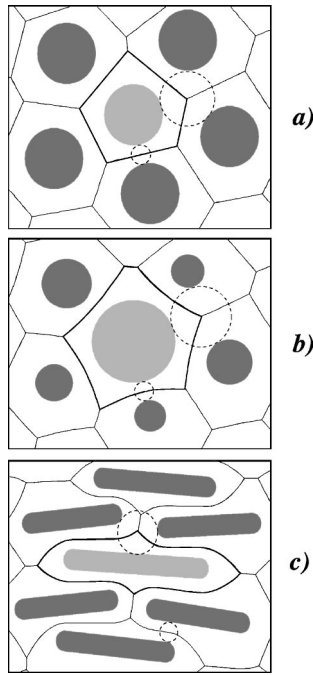§Electronic address: troadec@univ-rennes1.fr

FIG. 1. Two-dimensional illustration of the Voronoi tessellation for systems of monosize spheres (a), polydisperse spheres (b), and spherocylinders (c). The Voronoi region of the central object is selected by thick lines. For the system of monosize spheres, the Voronoi region is a polygon with straight edges. For the polydisperse spheres and for the spherocylinders, the edges are curved. The edges of all the Voronoi regions define the Voronoi network of the system. The Voronoi network lies ''in the depth'' between objects and plays the role of the navigation map of void space. Every site of the network is characterized by the value of the radius r_i of the inscribed (interstitial) sphere, see large open circles. Every bond of the Voronoi network is characterized by the value of its bottleneck radius r_b, see small open circles.

spherical objects can be seen in Fig. 1(c). S tessellations in 3D have some interesting geometrical properties. The mathematical aspect of the S tessellations should be studied in more detail, however, it is outside the scope of this paper. The concept of a navigation map is close to the idea of ''medial axes,'' which is used to describe the structure of a cavity inside a continuous medium, or, the structure of an individual domain with a given shape [29,30]. As was remarked by Choi *et al.* [30], the medial axis is a ''continuous version'' of the Voronoi network.

In this paper we apply the Voronoi-Delaunay idea to systems of particles (objects) of nonspherical convex shapes. It opens a way to use a rigorous geometrical technique for studying the structure of systems of a wide class of nonspherical particles. Here we restrict ourselves to systems of straight lines and spherocylinders, which can be used as models of fibrous filters [31] and liquid crystals [32].

In this paper we work with the Voronoi S constructions only. For simplicity we will omit the letter S in the names, keeping in mind that we measure the distance to the surface of an object.

II. GENERAL GEOMETRICAL REMARKS

The systems of convex objects. We work with convex objects because they possess an important property: the closest

distance from any point of space to the surface of a convex object is single valued. This condition is sufficient to be sure that the Voronoi tessellation exists for any system of convex objects. Indeed, if the closest distance from a point to an object is single valued, following Delaunay [33] one can say that any point of unoccupied space can be (i) closer to one object (in this case it is inside the Voronoi region of the object), (ii) at the same distance from several objects (in this case the point lies on the common border of the Voronoi regions of these objects). This statement means that the Voronoi regions cover all the space without gaps. This covering is also without overlapping of the Voronoi regions because any point of space cannot be ''closer to several objects'' in the same time. Actually this simple reasoning proves the existence of the Voronoi tessellation for any convex objects.

Some definitions and notations. It is convenient to use an imaginary empty sphere of variable size (*the Delaunay empty sphere* or simply *the Delaunay sphere*), which had been proposed by Delaunay in [34]. This sphere can move and change its radius while touching the surfaces of the neighboring objects. However, it is always empty, i.e., points of the objects cannot be inside the Delaunay sphere.

Let us consider two objects, i and j. The geometric locus of points which are at the same distance from the two objects is a two-dimensional surface $F_{ij}(\mathbf{r})$, called *the Voronoi surface*. The center of the Delaunay sphere touching the two objects lies on this surface. $F_{ij}(\mathbf{r})$ is a plane if our objects are monosize spheres. For spheres of different radii it is a hyperboloid (*the Voronoi hyperboloid* [12,19]). For straight lines one can show that it is a hyperbolic paraboloid.

The geometric locus of points which are at the same distance from three objects is a one-dimensional line $C_{ijk}(\mathbf{r})$ called *the Voronoi channel*. This channel is a straight line for equal spheres. In the general case the Voronoi channel is a curved line. The Voronoi channel is the intersection of the Voronoi surfaces: $F_{ij}(\mathbf{r})$, $F_{ik}(\mathbf{r})$, and $F_{jk}(\mathbf{r})$ [25]. The center of the Delaunay sphere moves along the Voronoi channel when the sphere keeps contacts with the three objects.

If the Delaunay sphere touches four objects i,j,k,l, it cannot be moved any more. This is a result of elementary geometry and the convexity of the objects: four points on a sphere define the sphere uniquely, but every convex object defines one and only one point on the Delaunay sphere. The center D_{ijkl} of this Delaunay sphere is equidistant from the four objects. We call it *a Voronoi site*. For monosize spheres it is known as the circumcenter of *the Delaunay simplex*. This point ends the moving of the Delaunay sphere along the Voronoi channel $C_{ijk}(\mathbf{r})$ and opens three new channels $C_{ijl}(\mathbf{r})$, $C_{ikl}(\mathbf{r})$, and $C_{jkl}(\mathbf{r})$.

Note that one can construct a configuration where the Delaunay sphere touches more than four objects at the same time. For example, the sphere inside the perfect octahedral configuration of equal balls touches six balls. Such configurations are called degenerated. However, a small perturbation of the objects removes the degeneracy. The probability of finding a degenerated configuration in noncrystalline packings is negligible. We assume in this paper that our systems are *nondegenerated*.

The Voronoi region of a given object is the volume of space closest to the object. The faces of the Voronoi region
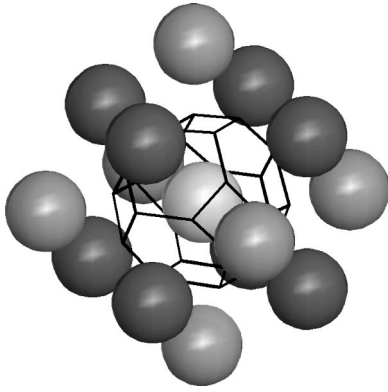
FIG. 2. Three-dimensional illustration of the Voronoi region (Voronoi S region, see text) in a system of equal spheres. The spheres are arranged in the bcc-crystalline structure. The Voronoi region is a polyhedron with 14 faces (eight faces with six edges and six faces with four edges). The central sphere for which the polyhedron is constructed is light. The closest eight neighbors, which are located on the corners of the cube, are colored in dark. The next six neighbors (at the cubic faces) are colored in gray.

are pieces of the Voronoi surfaces; the edges are segments of the Voronoi channels; the vertices are the Voronoi sites. Every Voronoi region is a tile of the Voronoi tessellation. Figures 2–4 illustrate Voronoi regions for 3D systems of monosize and polydisperse spheres and for a system of spherocylinders.

The Voronoi network. The Voronoi network is the set of edges (bonds) and vertices (sites) of *the Voronoi regions* in the Voronoi tessellation. The fact that the Voronoi network lies ''in the depth'' of unoccupied space is valid for systems of monosize spheres as well as for systems of any convex objects. It follows directly from the definition of the Voronoi region: if we leave a common edge of the Voronoi regions (a bond of the Voronoi network), we will be closer to the surface of one of the objects. In this respect a bond is a ''fairway'' between two sites: if a probe leaves this line it can ''run around'' on an object. The sites are locally ''the deepest'' points between objects. The Voronoi network plays the
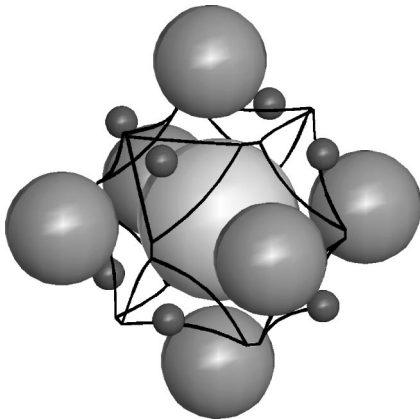

FIG. 3. Three-dimensional illustration of the Voronoi region (Voronoi S region, see text) in a system of spheres of different radii. The centers of spheres are arranged as in the bcc-crystalline structure. The ''color'' of the spheres is the same as in Fig. 2. The Voronoi region is a 14-faced body with eight three-edged faces and six eight-edged faces. The faces and edges are curved.
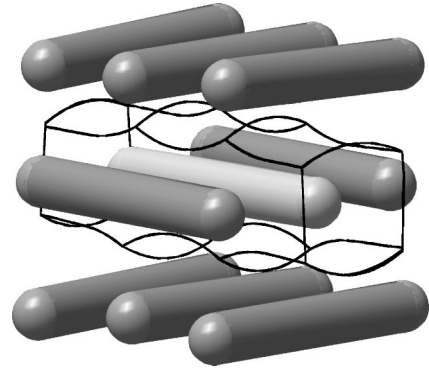

FIG. 4. Three-dimensional illustration of the Voronoi region in a system of spherocylinders. The central spherocylinder is light. The faces of the region are pieces of hyperbolic paraboloids (for the perpendicular neighbors) and planes (for the parallel neighbors). The butt ends of the Voronoi regions are open because of the small size of the system.

role of the navigation map of unoccupied space inside a system in the general case.

In 3D the Voronoi network is four valenced, i.e., every site is the origin of four bonds. This is easy to understand. Indeed, any site of the Voronoi network is defined by four objects, but four objects define four different triplets of these objects. These four triplets open four and only four Voronoi channels (bonds) at this site. This result is general for any nondegenerated (see above) system of convex objects.

There is also a serious difference between general and classical Voronoi networks. It is the problem of the simple connectedness of the network in 3D. The Voronoi network is one connected for systems of monosize spheres. However, even for polydisperse spheres this is not true in general. For example, a few small spheres have their own part of the Voronoi network if they are located inside a very narrow gap between two big spheres of the system [25,19]. Fortunately, such specific configurations are not typical for physical models. Usually we can ignore this theoretical possibility of the disconnection of the Voronoi network. We did not meet it in our models of Apollonian balls in [26]. For systems of nonspherical objects the problem has not been studied yet. However, we have found that the Voronoi network is one connected for rather homogeneous systems of straight lines or cylinders.

III. ALGORITHM

The distance function. Let $d_i(\mathbf{r})$ be a distance function generated by the ith object of the system. This function is defined as *the minimal distance* from a given point $\mathbf{r}$ in the space to the surface of the object. The point $\mathbf{p(r)}$ on the surface, which corresponds to the minimal distance, is called a metric projection of $\mathbf{r}$ on the object. There is only one metric projection of a given point $\mathbf{r}$ on a convex object.

A remarkable property of the distance function of a convex object is its differentiability [35,36]. It means that we are able to calculate the first order derivatives of $d(\mathbf{r})$ with respect to the coordinates at any point of space outside the object. This seems obvious for smooth objects like spheres, but is true also for objects with sharp edges and vertices (like bricks or segments of straight lines). The Voronoi surfaces
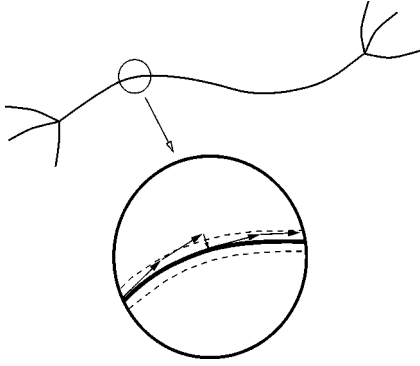
FIG. 5. Calculation of the Voronoi channel by the infinitesimal displacements **v** of the Delaunay sphere. The thick line indicates the exact position of the channel. Dashed lines indicate the desired exactness of the calculation. The small arrow perpendicular to the channel indicates the correction of the calculation by the gradient decay of the estimation function Φ.

and the Voronoi channels are also smooth (this follows from the differentiability of the distance function). This fact is very important for us because it permits us to calculate a Voronoi channel by the method of infinitesimal displacements along the channel.

Calculation of the Voronoi channel. Let us consider the equation of the Voronoi channel (trajectory of the Delaunay sphere center) for the triplet of objects $\{i,j,k\}$:

$$d_i(\mathbf{r})=d_j(\mathbf{r})=d_k(\mathbf{r}). \qquad (1)$$

Let **v** be a small shift along the channel so that the point $\mathbf{r}' = \mathbf{r}+\mathbf{v}$ should satisfy the equations

$$d_i(\mathbf{r}+\mathbf{v})=d_j(\mathbf{r}+\mathbf{v})=d_k(\mathbf{r}+\mathbf{v}). \qquad (2)$$

Linearization of this system with respect to Eq. (1) gives

$$(\boldsymbol{\nabla} d_i\cdot\mathbf{v})|_{\mathbf{r}}=(\boldsymbol{\nabla} d_j\cdot\mathbf{v})|_{\mathbf{r}}=(\boldsymbol{\nabla} d_k\cdot\mathbf{v})|_{\mathbf{r}}. \qquad (3)$$

This allows us to find the direction of the displacement **v**, which is actually the tangent to the Voronoi channel at the point **r**. So we make a small displacement along the vector to get a new point $\mathbf{r}'$. After that the procedure can be continued. However, because of computer-based accuracy we should control deviation of the trajectory from the Voronoi channel after every displacement. An estimation function $\Phi(\mathbf{r})$ is calculated for this purpose:

$$\Phi=(d_i-d_j)^2+(d_i-d_k)^2+(d_j-d_k)^2. \qquad (4)$$

It takes its minimal value $\Phi=0$ on the Voronoi channel. If $\Phi>\delta^2$, then the center of our Delaunay sphere is returned on the Voronoi channel by the gradient decay procedure. The value δ characterizes a desired exactness for calculation. Figure 5 illustrates our infinitesimal displacements along the Voronoi channel. The coordinates of the center of the Delaunay sphere moving between three objects are calculated step by step in this procedure.

Calculation of the Voronoi network. To know the Voronoi network we should have the following sets of data: a list $\{D\}$ to keep the coordinates of the Voronoi sites, a list $\{DA\}$ to record the numbers of the objects i,j,k,l, which define each

Voronoi site, and a table $\{DD\}$ for the connectivity of the sites. For metric analysis of voids we must additionally keep the radius of the Delaunay sphere at every site (a list $\{R_i\}$) and the minimal value of radius of the Delaunay sphere along every bond (a list $\{R_b\}$). These data give us full information to use the Voronoi network as a navigation map: the locations of all the "deepest" points, their connectivity, and the values of the bottleneck radii. Beside that, during the calculation we can store the step by step positions of the center of the Delaunay sphere. We do it to draw a picture of the Voronoi network.

The first step. A first Voronoi site should be obtained to start the work. The function $\Psi(\mathbf{r})$ is constructed with this aim:

$$\Psi(\mathbf{r})=\sum_{i<j}[d_i(\mathbf{r})-d_j(\mathbf{r})]^2, \qquad (5)$$

where i,j belong to the quartet of indices of the four objects, which are the nearest ones to the point **r**.

The function $\Psi(\mathbf{r})$ is equal to zero on the Voronoi site. To find it, we put an initial point **r** inside a system, then we move it to look for a minimum of $\Psi(\mathbf{r})$ by the procedure of gradient decay [37] changing the quartet of the nearest objects when it is necessary. The procedure stops when $\Psi(\mathbf{r}) < \delta^2$. The coordinates of the first Voronoi site, the numbers of objects i,j,k,l, and the value of the first interstitial sphere radius open the lists $\{D\}$, $\{DA\}$, and $\{R_i\}$.

The main step. Now we can calculate new Voronoi sites and define Voronoi network bonds. Starting from a known Voronoi site we look for an adjacent site on a given Voronoi channel. Obviously, the adjacent site is the closest one to the known site on the Voronoi channel. This idea to choose a new site is not new and is used for monosize [38] as well as for polydisperse sphere systems [19]. However, in the case of spheres it was possible to calculate coordinates of Voronoi sites analytically. For nonspherical objects it is impossible. One can obtain them only numerically. We do it by moving the Delaunay sphere along the Voronoi channel.

Suppose that the Delaunay sphere is placed on a known Voronoi site $D_{i,j,k,l}$ with coordinates $\mathbf{r}_0$ defined by the quartet of objects i,j,k,l. Let us obtain an adjacent site on the Voronoi channel of the triplet $\{i,j,k\}$. Using Eq. (3) we determine a displacement **v** to calculate the Voronoi channel. At the first step the correct sign of the displacement must be chosen. In this case a new point $\mathbf{r}_1=\mathbf{r}_0+\mathbf{v}$ must have the same triplet of the closest objects $\{i,j,k\}$. The absolute value of **v** is rather arbitrary and should be optimal. Then we calculate new coefficients of the system (3) at the point $\mathbf{r}_1$ and make a new shift $\mathbf{v}'$ to go along the Voronoi channel as was discussed above.

The moving along the Voronoi channel is stopped when the Delaunay sphere encounters a fourth object m. It means that the center of the Delaunay sphere has reached the vicinity of a new Voronoi site $D_{i,j,k,m}$. The position of this site is precised by the gradient decay of the function $\Psi(\mathbf{r})$ for the quartet $\{i,j,k,m\}$. Then we should compare the new site with all sites which have already been added to the lists $\{D\}$ and $\{DA\}$. If the site is new, it is added to the lists. The connectivity between the old and the new sites is marked in the table $\{DD\}$. Two adjacent Voronoi sites define a segment on

the Voronoi channel, which is a bond of the Voronoi network. It means that the table $\{DD\}$ keeps the information about the connectivity of the bonds of the Voronoi network. The bottleneck radius of the bond is recorded in the list $\{R_b\}$. A new site defines three new Voronoi channels $C_{j,k,m}$, $C_{i,j,m}$, and $C_{i,k,m}$, which should be tested for new adjacent sites.

When all Voronoi channels of a starting site are traced out to define bonds, we go to the next site which still has untraced channels. This procedure continues to obtain all sites and bonds of the Voronoi network. The algorithm stops when the last site is recorded, and no one Voronoi channel is still open to obtain a bond.

These basic steps of the algorithm are general for systems of any convex objects. The peculiarities of the shape of objects are hidden in the distance function $d_i(\mathbf{r})$. It means that the main computer code is the same for all convex objects. Only the subroutine for calculation of the distance function and some parameters need to be changed for applying the algorithm to a system of new objects.

IV. A TEST OF THE ALGORITHM ON PACKINGS OF SPHERES

To test the algorithm we have calculated the Voronoi network of systems of monosize and polydisperse spheres. Two disordered packings of 2000 hard spheres in a model box with periodic boundary conditions were generated by the Monte Carlo relaxation. Packing fraction for both models was $\eta = 0.54$. The first packing consists of uniform spheres of a unit diameter. For the second packing, the values of the diameter have a Gaussian distribution with an average value equal to unit and a dispersion of 0.08. The distance function, generated by the sphere of a radius R_i, is

$$d(\mathbf{r}) = |\mathbf{r} - \mathbf{r}_i| - R_i, \tag{6}$$

where $\mathbf{r}_i$ is the position of the center of the sphere.

We have compared our algorithm with the classical algorithms for spheres in which the Voronoi sites are calculated directly without tracing the bonds. The algorithm for uniform spheres was applied intensively in our previous researches, see, e.g., [7,8]. The algorithm for polydisperse packing was developed and applied a few years ago to the Apollonian problem [26]. A Pentium-100 MHz computer was used to compare the algorithms. Our numerical algorithm takes about 67 minutes to calculate the Voronoi network for each packing of spheres. The classical algorithms take approximately 3.2 minutes for this work. The obtained Voronoi networks are the same for the same packings. For the monosize packing it contains 12 695 sites, for the polydisperse one 12 540 sites. The distributions of radii of the interstitial spheres r_i and the bottleneck radii r_b for our models are shown in Fig. 6.

As we see, our numerical algorithm is approximately 20 times slower. This is due to the tracing of every Voronoi bond, which is time consuming work. There is no reason to apply this algorithm to systems of spheres. It should be used only for nonspherical objects, when the analytical calculation of the Voronoi sites is impossible.
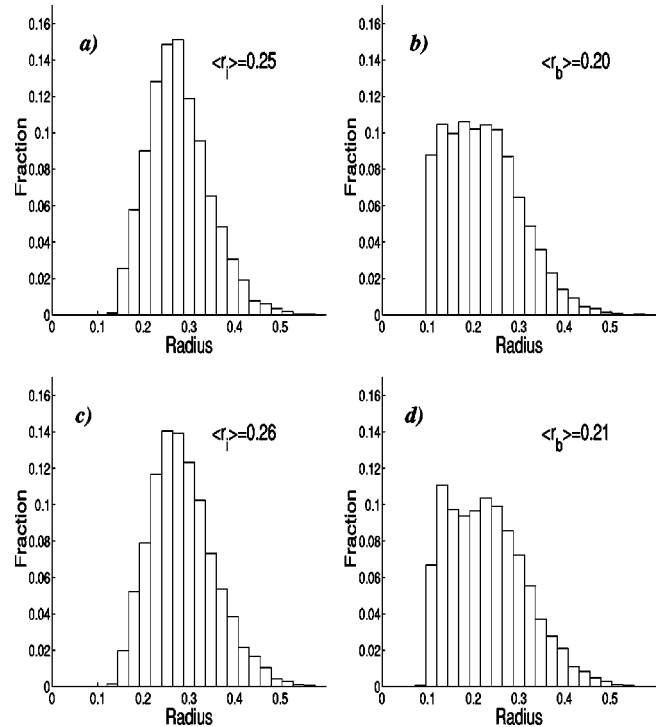

FIG. 6. Distribution of radii of the interstitial spheres (the radii of the Delaunay empty spheres at the Voronoi sites) r_i, and of radii of bottlenecks (the minimal values of the Delaunay sphere radius along the Voronoi bonds), r_b. Top array: distribution of r_i (a), and distribution of r_b (b), for the model of 2000 monosize hard spheres. Bottom array: distribution of r_i (c), and distribution of r_b (d), for the model of 2000 polydisperse hard spheres.

V. A SYSTEM OF RANDOM LINES

The infinite straight lines are the simplest nonspherical convex objects. We generated a system of 915 random lines crossing a box of unit volume, using uniform distribution for their location and orientation (Fig. 7).

A straight line can be represented parametrically as $\mathbf{L}(t) = \mathbf{a} + \mathbf{n}t$, where $\mathbf{a}$ and $\mathbf{n}$ are 3D vectors so that $|\mathbf{n}| = 1$, and $\mathbf{n} \perp \mathbf{a}$. The distance function generated by a line in this notation is
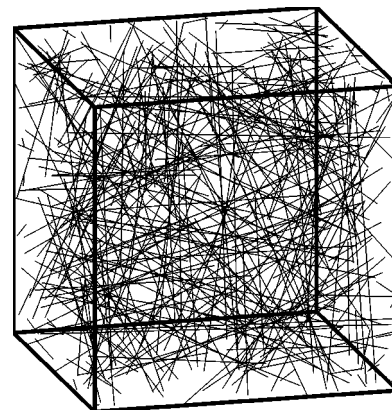

FIG. 7. Illustration of the 3D system of infinite random lines. A model of 915 lines crossing the box was created (see text). Only 300 lines of this model are drawn to keep visibility of individual lines. The edge length of the box is equal to 1.
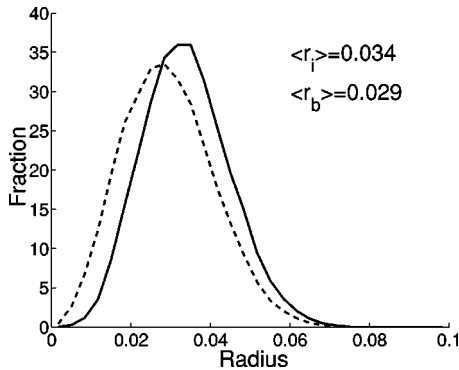
FIG. 8. Distribution of the radii of interstitial spheres r_i, solid line, and of radii of bottlenecks r_b, dashed line, for the system of 915 random lines in the unit cubic box. Critical radius $r_b^c = 0.033$.

$$d(\mathbf{r}) = \{\mathbf{r}^2 + \mathbf{a}^2 - 2(\mathbf{r} \cdot \mathbf{a}) - (\mathbf{r} \cdot \mathbf{n})^2\}^{1/2}. \quad (7)$$

Here we use free boundary conditions. The Voronoi bonds which cross a face of the box are ended by false sites at the face. (These false sites and the bonds ended by them are not considered in the analysis below.) To calculate the Voronoi network we take into account the lines inside the box as well as the lines in the vicinity of the box (which are not drawn in the figure).

The total Voronoi network contains 31 857 sites (from which 4551 are false). The distributions of r_b and r_i values for our ensemble of random lines are shown in Fig. 8. The value of r_i characterizes a size of voids in the system. It is a measure of a spherical probe which can be placed between objects. The value of r_b corresponds to a bottleneck radius on the way between two neighboring Voronoi sites.

Having the Voronoi network and the bottleneck radii, one can make a percolation analysis of empty space in a system as it was made for systems of spheres, see, e.g., [11,19]. By coloring the Voronoi bonds with $r_b \geq R$ one can visualize the pores which are passable for a probe of the radius R. The passable pores for a large value of R appear as isolated clusters. Figure 9 shows such clusters for $R = 0.05$ (in units of model box length). As we take a smaller value of R, the clusters of the accessible pores become larger and connect
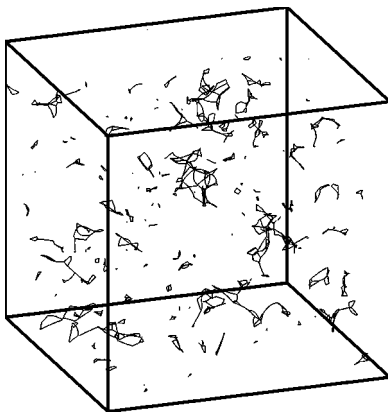

FIG. 9. Voronoi bonds with bottleneck radii $r_b \geq 0.05$ of the system of 915 random lines in the unit cubic box. Only the skeletons of the clusters are shown. Only these clusters are accessible to a probe of radius 0.05.
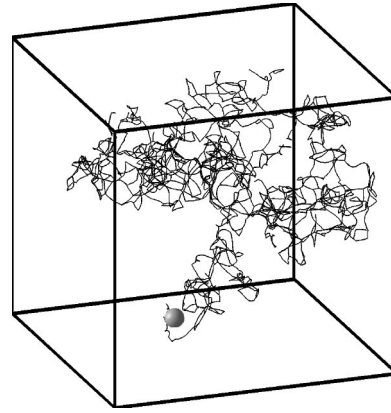

FIG. 10. Percolative cluster of pores in the system of 915 random lines in the unit cubic box. A skeleton of the percolative cluster of Voronoi bonds passable by a critical probe of radius 0.033 is shown. The ball inside the model box illustrates a probe of the critical size. It can be moved along the bonds of the cluster.

each other. There is a critical value $R = r_b^c$, when the passable pores join in a percolative cluster. For our system of lines we have found the critical radius is 0.033. It is the value of the maximal size of a probe which can penetrate through the system. Figure 10 shows this percolative cluster on the Voronoi network. The figure gives an impression about a scale of the passable pores.

VI. MOLECULAR DYNAMICS MODEL OF LIQUID CRYSTAL

As an example of a physical system of nonspherical particles we use a molecular dynamics model of a liquid crystal $C_{18}H_{25}N$ in the isotropic phase. The model box with 50 molecules at $T = 330$ K is shown in Fig. 11 [39]. We have represented the molecules of the liquid crystal by spherocylinders (cylinders with hemispheres at the ends). The length of every spherocylinder is $L = 1.3$ nm and the radius $\rho = 0.2$ nm. The spherocylinders may slightly overlap each other, because they do not take into account a flexibility of the molecules. However, it is not essential here for our algorithm.
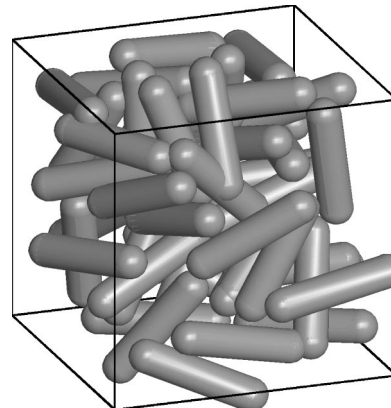

FIG. 11. Model of the isotropic phase of a liquid crystal at $T = 330$ K obtained by molecular dynamics method (50 molecules of $C_{18}H_{25}N$). The molecules are represented by spherocylinders.
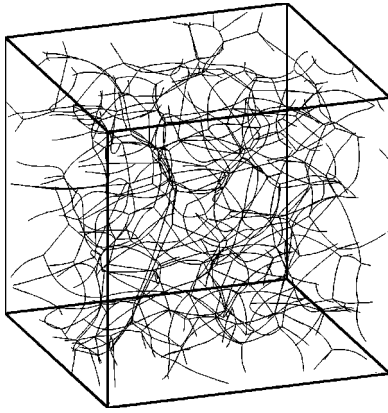
FIG. 12. The total Voronoi network of the model of a liquid crystal (Fig. 11). The network contains 401 sites and 802 bonds. Periodic boundary conditions are used.

Let us denote $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ the centers of the hemispheres. The distance function generated by a spherocylinder is

$$d(\mathbf{r}) = \begin{cases} |\mathbf{r} - \mathbf{r}_\alpha| - \rho, & \text{if } t < 0 \\ |\mathbf{r} - \mathbf{r}_\alpha - \mathbf{n}t| - \rho, & \text{if } 0 \leq t \leq t_1 \\ |\mathbf{r} - \mathbf{r}_\beta| - \rho, & \text{if } t > t_1, \end{cases} \quad (8)$$

where $\mathbf{n} = (\mathbf{r}_\beta - \mathbf{r}_\alpha)/|\mathbf{r}_\beta - \mathbf{r}_\alpha|$, $t = (\mathbf{r} \cdot \mathbf{n}) - (\mathbf{r}_\alpha \cdot \mathbf{n})$, and $t_1 = |\mathbf{r}_\beta - \mathbf{r}_\alpha|$. The Voronoi surfaces $F(\mathbf{r})$ of a pair of spherocylinders with a general orientation consist of pieces of different second order surfaces: (i) hyperbolic paraboloids (between two cylindric parts of the spherocylinders, (ii) hyperbolic cylinders (between cylinder and hemisphere), (iii) planes (between two hemispheres). So the Voronoi bonds may consist of different types of spatial curves because of intersection of different types of the Voronoi surfaces. However, as was discussed above, the Voronoi channels are smooth. Different curves turn into each other without any break. This nature of the Voronoi bonds was discussed by Lee and Drysdale [40] for a system of straight segments in 2D.

The total Voronoi network of the system is shown in Fig. 12. Periodic boundary conditions are used for this model. Voronoi bonds, which are going out from one side of the model box, are connected with the sites at the opposite side of the box. Distributions of r_i and r_b radii of the model are shown in Fig. 13. However, we used only one configuration of the liquid crystal, and then the data presented are rather preliminary.

VII. CONCLUSION

We suggest a generalization of the Voronoi-Delaunay method for the analysis of unoccupied space in systems of nonspherical particles. The analysis is based on using the Voronoi network of a system. This network lies in the depth of the unoccupied space between the particles and plays the
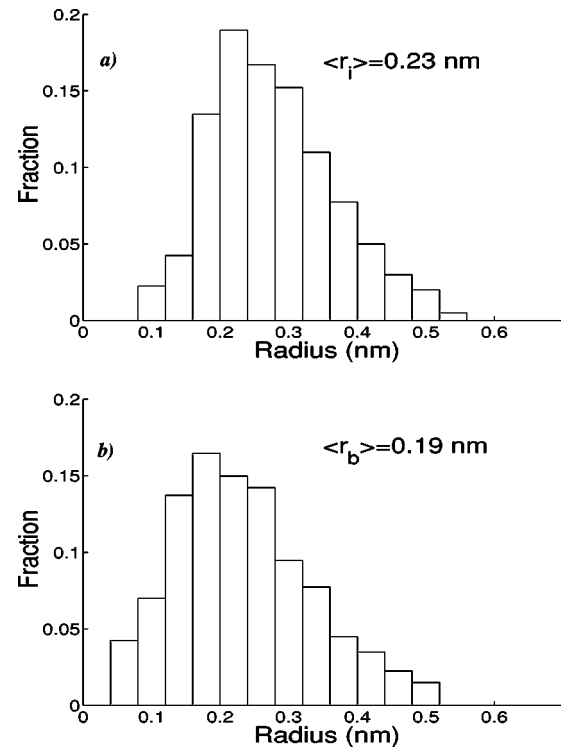

FIG. 13. Distribution of the radii of interstitial spheres r_i (a), and of the bottlenecks r_b (b), for the model of a liquid crystal of Fig. 11.

role of ''a navigation map'' of the system. It allows us to study the void distribution in the system. The algorithm for the calculation of the Voronoi network for packings of particles of arbitrary convex shapes is developed and applied to the analysis of 3D systems of random straight lines and of a molecular dynamics model of liquid crystal. Distributions of bottleneck radii and interstitial sphere radii are calculated. This work expands the traditional Voronoi-Delaunay analysis known for simple liquids and glasses to complex systems like fibrous filters and liquid crystals.

Although we have developed our algorithm for systems of convex objects, it can be adapted in some cases to systems of nonconvex particles. If nonconvex particles can be formally divided in convex parts, then these parts can be considered as independent convex objects.

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