Simulation of Transport and Diffusion on the Voronoi Network

V.A. Luchnikov[1], N.N. Medvedev[1], V.P. Voloshin[1], and A. Geiger[2]

[1] Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
[2] Physical Chemistry, University of Dortmund, Germany

Abstract. The idea that the Voronoi network of a granular system lies "in the depth" of the empty space is used intuitively in different fields of science to study the transport of fluids, diffusion and other percolation and path problems. We discuss the concept of a "navigation map" for the interparticle empty space. It helps to study the spatial distribution and hierarchy of pores in noncrystalline packings generated in computer simulations. The approach is applied for a porosimetry analysis of packings of monodisperse spheres of different density. A generalization of the technique to systems of polydisperse spheres and nonspherical particles is also taken up.

1 Introduction.

The structure and distribution of pores is a factor, which governs many important physical phenomena in physical chemistry, catalysis and materials science. It determines the permeability of porous media, stability of powder materials, diffusion and thermodynamic properties of simple and complex liquids and glasses.

A promising way to study the structure of pores is the application of computer simulations. A model obtained by molecular dynamics or Monte Carlo methods comprises the coordinates of all atoms (particles). However the voids are not simply related to these coordinates. It needs additional efforts and algorithms to extract "physical" informations about the unoccupied volume and to make a quantitative analysis. This question had been understood and was raised long ago [1]. However, advances have been obtained in the last decade only. A reason for this is the use of a rigorous mathematical basis, which gives a geometrical technique to partition the space between the atoms [2,3]. This Voronoi-Delaunay approach is well-known in the study of atomic arrangements in liquids and amorphous structures [4]. Next, it had been applied to study interatomic voids [5,6]. The permeability and flow through packings of monodisperse spheres was simulated in [7,8]; paths for the diffusion of particles with different size in liquid and glassy polymers was studied in [9]; the thermodynamic aspects of voids in simple liquids was discussed in [10,11]; a porosimetry analysis for sphere packings was made in [12].

The main idea for a quantitative analysis of the voids inside an arbitrary ensemble of atoms (particles) is based on the analysis of "the navigation

map" of this ensemble. This map keeps track of the location of the "deepest" points (most distant from the surfaces of the particles) inside an ensemble and defines channels (fairways) connecting these points [13]. There are no principal problems to get this map because its mathematical construction is well-known. It is the Voronoi network [2,3] which exists for any system [14]. A practical question, however, is to have an efficient algorithm to calculate it for a given system. Of course, before the calculation of the Voronoi network, one has to construct the system to be studied. The next stage is then the analysis: the computation of the Voronoi network, of the holes of a given size, their spatial distribution, channels acceptable to a given probe, percolation characteristics of the porous space. This needs also mathematical and programming work.

Note, the conception of the navigation map is close to the idea of "the medial axes", which is used to describe the structure of a cavity inside a continuous medium, or, in the opposite, the structure of an individual domain with a given shape [15,16]. As it was remarked in [16], the medial axis is a "continuous version" of the Voronoi network.

2 Geometrical analysis

. The Voronoi-Delaunay approach is originally known for systems of discrete points. The mosaic of the Voronoi polyhedra (the Voronoi tessellation) covers the entire space without overlaps and gaps. The set of all edges and vertices of the Voronoi polyhedra defines the Voronoi network. Therefore it is a simply-connected and four-bonded network for any nondegenerate ensemble of points. The bonds of this network are segments of straight lines.

However for physical-chemical applications we deal with systems of *finite size* particles, the most simple one being a system of equal spheres. Fortunately, the properties of the Voronoi network for point systems are also true for this case.

The idea to use the Voronoi-Delaunay approach for a broader class of particles is very tempting. However, as it was remarked many times, the classical Voronoi-Delaunay construction cannot be used in general, see for example [17]. The original Voronoi-Delaunay tessellation does not take into account the size and the shape of particles.

The problem had been solved for systems of spheres of different radii [13,11,14]. Such systems are used as models of polydisperse powders, polyatomic materials and alloys. To take into account the surface of the particles, one should introduce a new geometrical construction: instead of the classical Voronoi polyhedron defined by the centers of spheres, one should define another volume, 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 a Voronoi S-region [13]. It is analogous to the usual Voronoi polyhedron, but its faces and edges are curved. The Voronoi S-regions generate a Voronoi

S-tessellation. The set of vertices and edges defines the Voro... S-network of the system of polydisperse spheres. A special algorithm was created to calculate the S-constructions. An application of this technique to study 3D Apollonian packings was made in [18].

Studying the porous space, we are working with the Voronoi S-construction only. Here we will omit the letter S in the names, for simplicity.

In fact, the Voronoi-Delaunay ideas can be extended to systems of particles with arbitrary convex shapes. It opens a way to use a rigorous geometrical technique to study the structure of pores for a much broader class of particles then systems of spheres. Recently, the corresponding algorithm was developed and a system of straight lines and spherocylinders was analyzed [19]. Convex particles possess an important property: the closest distance from any point of space to the surface of a convex particle is single-valued. This condition is sufficient to be sure that the Voronoi tessellation exists for any system of convex particles.

In the general case the Voronoi network is the set of edges (bonds) and vertices (sites) of the Voronoi regions in the Voronoi tessellation of a given system of particles. The fact that the Voronoi network lies "in the depth" of the unoccupied space is valid in general. It follows directly from the definition of the Voronoi region. If we leave a bond of the Voronoi network (which is a common edge of the adjacent Voronoi regions), we will be inside of a Voronoi region and therefore closer to the surface of one of the particles. In this respect a bond is a fairway: if a probe leaves this line it can "run aground" on a surface of a particle. The Voronoi network is four-valenced: every site of the Voronoi network is the origin of four bonds. (It is assumed that the system is nondegenerate). This is easy to understand: any site of the Voronoi network is defined by four particles, but four particles open four and only four channels (bonds) from this site. This is true for any particle which has one and only one point of contact with a sphere [19].

There are also differences between the general and classical Voronoi network. A major one being the problem of simple connectedness of the network in 3D. Indeed, even for a system of polydisperse spheres an example can be constructed for a totally disconnected Voronoi network. Fortunately, we can ignore this theoretical possibility of the disconnectedness of the Voronoi network for relevant physical systems [14,19].

3 Algorithms for the navigation map

. To describe the Voronoi network, we should have the following sets of data: the list $\{D\}$ of the coordinates of the Voronoi sites and the table $\{DD\}$ for the connectivity of the sites. For thr metric analysis of the voids we should additionally keep the value of the radius of the inscribed sphere at every site (list $\{R_i\}$) and the minimum radius of the Delaunay spheres along every bond, the so called bottleneck radii (list $\{R_b\}$). These data give us the full

information to u... the Voronoi network as a navigation map: the location of all "deepest" points, their connectivity, and the corresponding values of the bottleneck radii.

To create the Voronoi network of a monodisperse system one can use any algorithm for a classical Voronoi polyhedra calculation. The main task of these algorithms is usually the calculation of the circumsphere for a given set of four centers (a site of the Voronoi network) by solving the system of equations

$$(x_i - x)^2 + (y_i - y)^2 + (z_i - z)^2 = R^2, \quad i = 1, 2, 3, 4. \tag{1}$$

x_i, y_i, z_i are the coordinates of the centre of the i-th particle of a given quartet. The four unknown variables x, y, z and R are the coordinates and the radius of the circumsphere. The main step of the algorithm is the determination of the vertex which is adjacent to a given one (to find the second endpoint on the Voronoi bond). This can easily be done, because the second site on a bond is the center of the inscribed sphere, which is closest to the known vertex on the given Voronoi channel, see e.g. [20].

To create an algorithm for the Voronoi network of polydisperse spheres one can use the same ideas, however to find a site of the Voronoi network we should be able to obtain an inscribed sphere between four spherical particles of arbitrary radii. The solution of the following system of equations gives an answer to the question:

$$(x_i - x)^2 + (y_i - y)^2 + (z_i - z)^2 = (R_i + R)^2, \quad i = 1, 2, 3, 4. \tag{2}$$

Where R_i is the radius of the i-th particle. Fortunately, this system can be solved and analytical formulas for x_i, y_i, z_i and R can be obtained. As a result, the algorithm for a polydisperse system has the same efficiency as for monodisperse one. For details see [14].

In the general case of convex particles we cannot calculate Voronoi sites analytically. However we can use the same idea to find the next site of the Voronoi network: the adjacent site is the closest one to the known site on a given Voronoi bond. In this case we have to go step by step along the Voronoi bond from a known site to define a new site numerically. A general algorithm for the Voronoi network of such systems is proposed in [19]. It can be used for particles of any shape. The peculiarities of the particles are hidden in the distance function $d_i(\mathbf{r})$, which defines the minimal distance from a given point $\mathbf{r}$ to the surface of the i-th particle.

4 Permeability and diffusion.

The navigation map is a rigorous geometric construction and represents a real channel system in a sample. Physical assumptions will be made at the step of application to a given physical problem. For example one should define

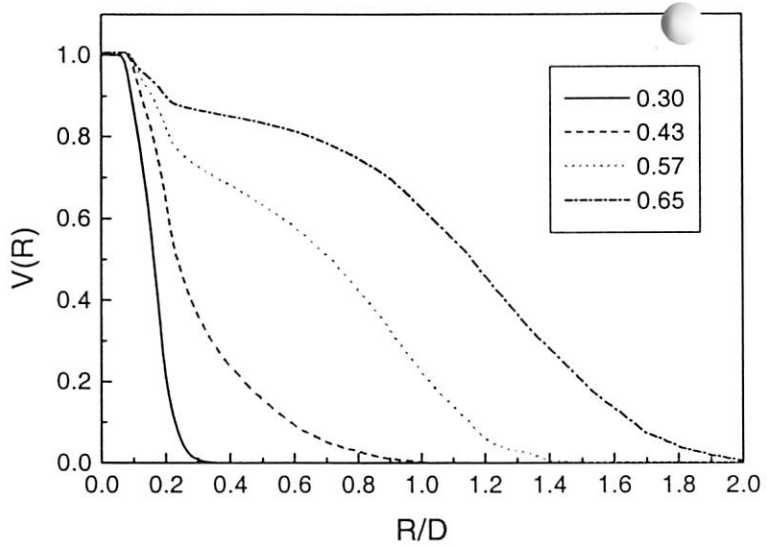

Fig. 1. Fraction of pore volume accessible to a probe of radius R_{probe} ("intrusion" curve) for packings of monodisperse spheres at different values of porosity ϵ (given in the insert). Diameter of spheres D is unity.

a "resistance" for fluids moving through a bottleneck, as it was made in [7,8] to study the permeability in a granular porous media. The results were successfully compared with experimental data measured on sand packs, bead packs, and a simple sandstone.

The problem of diffusion of hard particles in a porous media, can be simulated as a random walk on the navigation map. The probability to go along a given edge can be assumed to be proportional to the value of the Voronoi bond bottleneck for a given direction. Knowing the location of all vertices, their connectivity, and probabilities to go from one vertex to another, a Monte Carlo process for particle transport can easily be realized. In particular, forbidding the possibility to go up, we can simulate a rolling process of a ball inside a packing of spheres [21].

As an application of the Voronoi network analysis, we present the results of a study to characterize the hierarchy of pores in monodisperse packings of spherical particles at different densities. Recently such an analysis was proposed for the interpretation of mercury porosimetry experiments [12]. We have created a set of noncrystalline packings of 8000 Lennard Jones particles relaxed at zero temperature. The porosity of the different packings is in an interval from $\epsilon = 0.30$ to $\epsilon = 0.70$. The denser models represent the well-known Bernal-like noncrystalline packings of spheres. As the density decreases, we get more and more cavities inside the packing. The low density packings contain a percolative cluster of relatively large pores and, at the same time, a percolative cluster of closed packed particles.

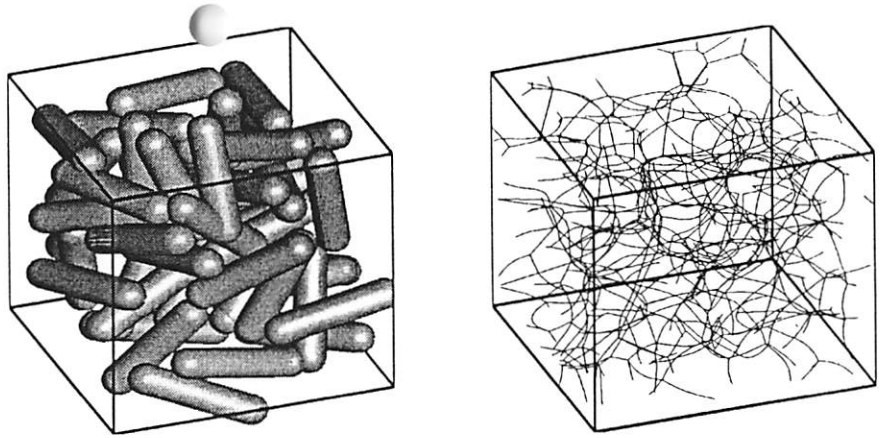

Fig. 2. Voronoi network of a system of nonspherical particles. a.) Representation of a molecular dynamic model of the isotropic phase of a liquid crystal by 50 spherocylinders. b.) The Voronoi network of this model (401 sites and 802 bonds). Periodic boundary conditions are used.

The "intrusion" curves for a set of our structural models are shown in Fig.1. They show the volume fraction of pores, where a probe of a given radius R_{probe} (radius of meniscus) can be placed, as a function of the value of R_{probe}. With decreasing probe size, the fraction of the volume increases to the total empty volume inside the model and becomes equal to unity with $R_{probe} = 0$. The curves characterize the nature of pores at different densities of packing.

In the terminology of percolation theory the study of pores is a bond percolation problem on the navigation map. Indeed, all bonds with a value of the bottleneck radius greater than the radius of a given probe, can be distinguished (coloured) on the network. Any cluster of coloured bonds defines a pore for a given probe: the probe can be moved inside the pore along the coloured bonds. Depending on the size of the probe particle, this can be a finite pore or a percolative one. It is not difficult to define all clusters of coloured bonds on the network and then to make their analysis, e.g., to calculate the volume of every pore.

The Voronoi network of a system of nonspherical particles is illustrated in Fig.2. As an example of a physical sample we use a simplified model of a liquid crystal. At first an atomically resolved molecular dynamic model of 50 molecules of 4-(trans- 4' -pentyl-cyclohexyl)-benzonitrile (PCH5) in the isotropic phase at $T = 330\ K$ had been created [22]. Then we have represented every molecule of the liquid crystal by a spherocylinder (cylinder with hemispheres at the ends). The model box of this system is shown on Fig. 2a. The length of every spherocylinder is $L = 1.3\ nm$ and the radius $r = 0.2\ nm$. The Voronoi network of this model is demonstrated in Fig.2b.

Actually, this Voronoi network with the bottleneck radii can be used for a pore analysis similar to that of the packings of spheres.

5 Conclusions.

We discussed a method to study the structure of the pore space in granular and atomic systems. It is based on the analysis of the Voronoi network. This network lies in the depth of the unoccupied space between particles and plays the pole of a "navigation map" of the system. It gives quantitative informations about the spatial distribution of pores in a model, which help to study flow and diffusion phenomena. The main idea of an algorithm to calculate the navigation map in 3D for systems of spheres and nonspherical particles is discussed. The approach is applied for a porosimetry analysis of packings of monodisperse spheres of different density. An application of the method to a system of spherocylinders (as a model of liquid crystals) is demonstrated.

References

1. F.A.L. Dullien, *Porous media: Fluid transport and pore structure*, Academic Press, 1979.
2. G.F. Voronoi, Z. Reine Angew. Math. **136**, 67–181 (1909).
3. A. Okabe, B. Boots, K. Sugihara, *Spatial Tessellations - Concepts and Applications of Voronoi Diagrams*, John Wiley and Sons, 1992.
4. J.L. Finney, Proc. Roy. Soc. London **319**, 479–494 and 495–507 (1970).
5. N.N. Medvedev, Yu.I. Naberukhin, V.P. Voloshin, "Geometry of empty space inside of granular system", Proceeding of VI-th IFP conference: Physical chemistry of colloids and interfaces in oil production, ed. H. Toulhoat and J. Lecourtier, Paris, 1992.
6. Yu.I. Naberukhin, V.P. Voloshin, N.N. Medvedev, Zh. Fiz. Khimii. **66**, 155–162 (1992).
7. S. Bryant, M. Blunt, Phys. Rev. A **46**, 2004–2011, (1992).
8. K.E. Thompson, H.S. Fogler, AIChE Journal **43**, 1377–1389 (1997).
9. M.L. Greenfield, D.N. Theodorou, Macromolecules **26**, 5461–5472 (1993).
10. R. Bieshaar, A. Geiger, N.N. Medvedev, Mol. Simulation **15**, 189–196 (1995).
11. S. Sastry, D.S. Corti, P.G. Debenedetti, F.H. Stillinger, Phys. Rev. E **56** 5524–5532 (1997).
12. V.P. Voloshin, N.N. Medvedev, V.B. Fenelonov, V.N. Parmon, "Simulation of the mercury porosimetry on the Voronoi network", Abstracts of the XXth International IUPAP conference in Stat. Phys., Paris, July 20–24, 1998, P009/62.
13. N.N. Medvedev, Dokl. Akad. Nauk. **337**, 767-773 (1994) (in Russian); Engl. transl.: Doklady. Phys. Chem. **337**, 157–163 (1994).
14. N.N. Medvedev, Computational porosimetry. In *Voronoi's impact on modern science*, Edited by P. Engel and H. Syta, Institute of Math., Kiev. 1998, Vol. 2, p. 164–175.

15. W.B. Lindquist, S.-M. Lee, D.A. Coker, K.W. Jones, P. Spanne, J. Geophys. Research **101**, 8297–8310 (1996).
16. H.I. Choi, S.W. Choi, H.P. Moon, Pacific J. Math. **181**, 57–88 (1997).
17. A.R. Kerstein, J. Phys. A: Math. Gen. **16**, 3071 (1983).
18. S.V. Anishchik, N.N. Medvedev, Phys. Rev. Lett. **75**, 4314–4317 (1995).
19. V.A. Luchnikov, N.N. Medvedev, L. Oger, J.-P. Troadec, "The Voronoi–Delaunay analysis of voids in systems of nonspherical particles", Phys. Rev. E, in press.
20. M. Tanemura, T. Ogawa, N. Ogita, J. Comp. Phys. **51**, 191–207 (1983).
21. P. Richard, L. Oger, J. Lemaitre, L. Samson, N.N. Medvedev, Phys. Rev. E, to be published.
22. S.Ye. Yakovenko, A.A. Minko, G. Krömer, A. Geiger, Liquid Crystals **17**, 127–145 (1994).