VORONOI POLYHEDRA AS A TOOL FOR DEALING WITH SPATIAL STRUCTURES OF AMORPHOUS SOLIDS, LIQUIDS AND DENSE GASES

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ABSTRACT

Methods of dealing with crystal structures are described in detail in every textbook of Materials Science and Engineering. Structures of non-crystalline materials (amorphous solids, liquids, dense gases) are no less important, but usually treated in textbooks briefly - if at all. Voronoi polyhedra have been employed for describing non-crystalline structures in a way at least complementary with other descriptions, and often more meaningful. The structure is divided into a set of polyhedra in a unique way, with a polyhedron assigned to each center (atom, ion, polymer chain segment). The Voronoi diagram (the set of polyhedra for a given set of centers) constitutes the basis of an informational theory of amorphous solids and liquids; the theory includes also the structure representation in terms of the radial distribution function. The Voronoi diagram and its mathematical dual, the Delaunay diagram, also make possible the distinction between a solid and a liquid, thus capturing the essence of the difference between these two states of matter. Pattern recognition can be performed by analyzing shapes of the Voronoi polyhedra. A procedure for contraction of short edges and small faces of the polyhedra is available; it provides slightly simplified structures, but with a large gain in the perspicuity. The pattern recognition method is also applicable to crystals, thus making possible comparisons of crystalline and non-crystalline structures in a simple way. The relation of the Voronoi polyhedra to the radial distribution function, a well-known tool used in diffractive imaging of materials to elucidate their spatial structure, is analyzed as well. Finally, alternative methods for characterizing the structures of materials are discussed.

Keywords: *Voronoi polyhedra; Wigner-Seitz cells; radial distribution function; amorphous solids structures; liquid structures; dense gas structures; diffractometry; coordination numbers; thermodynamic functions*

INTRODUCTION

The problem of unequivocally characterizing spatial structures of non-crystalline materials, which necessarily include amorphous solids, liquids and dense gases, is an open question in modern science. From the technological point of view this is also important, since amorphous solids include a number of valuable materials, such as polymeric ones and polymer-based composites. Even a cursory observation of the contemporary technology shows how gradually

but steadily metal parts in airplanes, cars, and also in electronic and other industries are being replaced by polymers. Since thus the relative role of crystallography is decreasing, the instruction in materials science and engineering (MSE) has to cover structures of non-crystalline materials in a meaningful way, at both undergraduate and graduate levels.

Voronoi polyhedra, described in what follows, represent along with other mathematical concepts – including the so-called radial distribution function $g(R)$ – another important tool for describing the structures of non-crystalline materials, including complex ones.

The polyhedra owe their name to the Ukrainian mathematician Heorhiy (Georgiy) Voronoi. Born in the village of Zhuravka near Kyiv in 1868, he created his seminal papers in the first decade of the 20th century while working in Warsaw. He did not have to cross state borders; at that time a large part of Ukraine including Kyiv and a part of Poland including Warsaw were both under Russian occupation. Voronoi wrote his papers in French (writing his first name in French as Georges) and published them in a German journal [1,2]. Science was apparently truly international already then – or at least Mathematics was.

Non-crystalline materials, apart from amorphous solids, liquids, and dense gases include dilute gases as well. However in this last category, low material densities prevents us from obtaining reliable experimental data with which the concepts could be confronted. The theory is available; we have to wait until the experiments will be more accurate.

DEFINITIONS

We shall start with the formal definition of the Voronoi polyhedron[1,2]. Consider a set of centers P_1, P_2, ..., P_n in the L-dimensional Euclidean space E. The Voronoi polyhedron V_i around a given center P_i is the set of points in E closer to P_i than to any P_j. One can write (NOTE: The following symbols will be used in

our discussion of the Voronoi concepts $\in$ signifies "belongs to"; $\cap$ is the "intersection of"; $\subset$ is the "proper subset of"; $\varnothing$ is "an empty set").

$$V_i = \{x \in E \ : \ d(x, P_i) \le d(x, P_j),$$
$$j = 1, 2, ..., i\text{-}1, i\text{+}1, ..., n\} \qquad (1)$$

where d represents distance. The polyhedra are, therefore, intersections of half-spaces; they are convex but not necessarily bounded. The space E is partitioned by the polyhedra in an unique way. We can define the Voronoi diagram as the set of Voronoi polyhedra corresponding to a given configuration of centers.

On dealing with real materials structures, we focus on the three dimensional case, $L = 3$. Given a point P_i and its neighbor P_j, the line $P_i P_j$ is cut perpendicularly at its midpoint y_{ij} by the plane h_{ij} . We call H_{ij} the half-space generated by h_{ij} that consists of the subset of E on the same side of h_{ij} as P_i . Therefore

$$V_i = \cap_j H_{ij} \qquad (2)$$

A Voronoi polyhedron V_i is bounded by faces so that each face f_{ij} belongs to a distinct plane h_{ij}. We can characterize each face by listing its vertices and edges in cyclic order. For example, by using a scheme of proceeding in a clockwise fashion when the face is viewed from the internal point central to the polyhedron.

If MSE students, particularly undergraduates, find the above formal definitions "too dry", then there is an alternative definition with high perspicuity. The points from which the Voronoi diagram is constructed are for us entities such as atoms, ions, or polymer chain segments. To get away from pure mathematics, let us call our entities particles. As already noted, partitioning of the space (including the 3-dimensional space) by the polyhedra is unique. In other words, each particle becomes an "owner" of a fraction of the material surrounding it. The mathematics defined above

provides the rules so that the "owners" would not "dispute" what fraction of space belongs to whom. This situation becomes even more clear when looking at an example of a fraction of a Voronoi diagram; see Figure 1. That figure
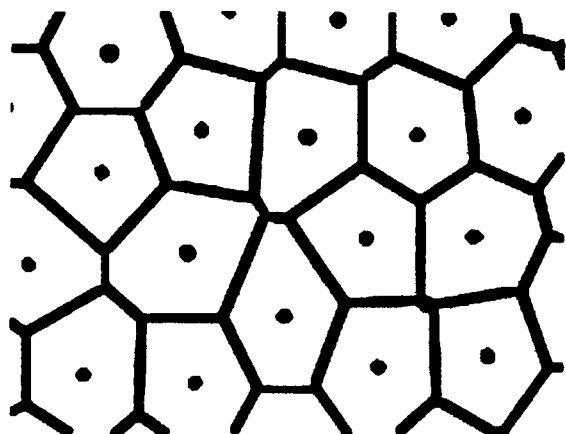

Figure 1. A fragment of a 2-dimensional Voronoi diagram.

corresponds to a 2-dimensional material with the dots being the locus of the points, Pi, Pj, etc., and the lines being the projection of the bounding planes, h_{ij} between adjacent points. One can easily imagine how in 3 dimensions the points become lines, e.g., for a polymer chain, the lines become faces and the polygons become polyhedra.

Incidentally, other names for the Voronoi polyhedra are also in use in the literature; for instance, the term *Wigner-Seitz cells* is used on occasions for crystalline solids.

The above ideas are contained in the work of Voronoi. While we are concerned mostly with non-crystalline materials, it would be good to have a general approach usable for all materials. However, when one applies the Voronoi tessalation (partition) to a crystal, one obtains certain faces which consist of lines only. Therefore, dealing with the Voronoi diagrams for MSE purposes, one of us has

found that new definitions are necessary [3] to distinguish between various possible types of neighbors of P_i. Thus, the following definitions have been introduced [3] :

a) *direct neighbor*: if y_{ij} (the midpoint of the line connecting P_i P_j) belongs to V_i , then P_j is a direct neighbor of P_j. Meijering [4] has recognized such neighbors in 1953 and called them *full neighbors*;

b) *indirect neighbors*: if a subset of h_{ij} is a face of V_i but y_{ij} does not belong to V_i , then P_j is an indirect neighbor; or P_j is an indirect neighbor if $f_{ij} \cap y_{ij} = \varnothing$;

c) *degenerate neighbors*: if the intersection of h_{ij} and V_i is just a vertex or an edge, then P_j is a degenerate neighbor;

d) *quasi-direct neighbors*: if P_j is a direct neighbor or if P_j would be a direct neighbor in the absence of all indirect neighbors, then P_j is a quasi-direct neighbor of P_i .

Thus, all direct neighbors are also quasi-direct. Examples of all classes of neighbors defined in [3] and above are shown in Figure 2, again for the case of two dimensions. Extension to three dimensions is obvious here also. We can define a direct polyhedron D generated by the quasi-direct neighbors in the same way that direct and indirect neighbors generate V. It is clear that for each i we have

$$V_i \subset D_i \qquad (3)$$

We define the *geometric coordination number* f_i as the number of nondegenerate direct or indirect neighbors of P_i. The average value of f for random 3-D structures is ≈ 15 [5], for random 2-D structures it is close to 6. Voronoi polyhedra with $f = 20$ have been constructed [6], and in principle arbitrarily high values of f are possible. As noted in [7] and [3], f_i have to be distinguished from the *structural coordination numbers* z. The latter are well know from MSE textbooks and also will be discussed in the next Section.
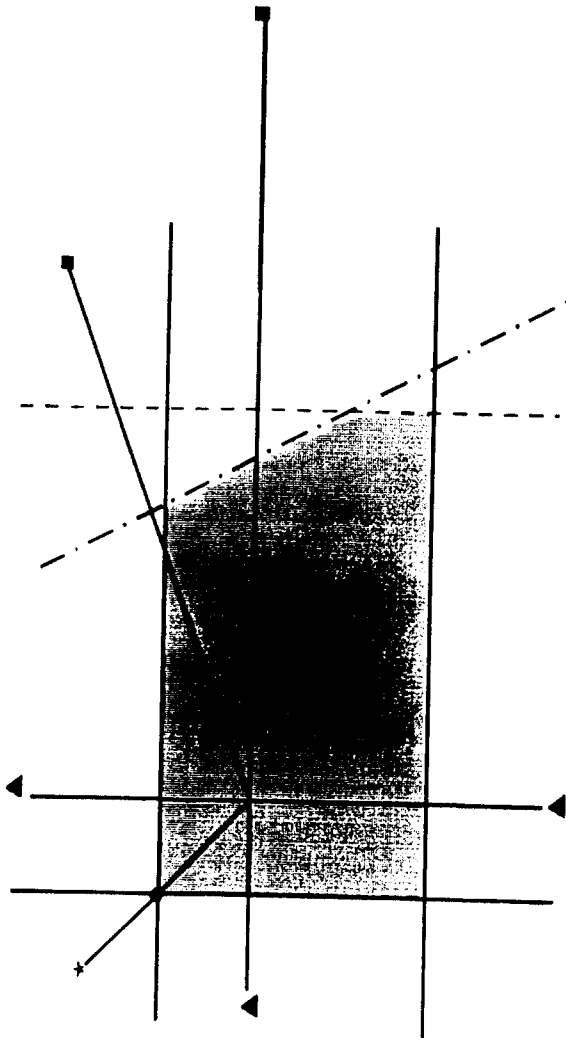
structural coordination number of that lattice known from crystallography is $z = 4$. These numbers are analyzed in detail in every MSE textbook, usually without mentioning that the geometric coordination numbers exist also, although exceptions to that rule can be found[8]. In our square lattice, each center has also neighbors along diagonals to the lattice that do not contribute to the structural coordination number - in spite of the fact that there is nothing between a given center and these second range neighbors. To imagine this one can look at the bottom-left center in Figure 2. That center is a degenerate neighbor of the center of the Voronoi polygon shown. In a square lattice there will 4 such degenerate neighbors (along the four diagonals) of any given center - in addition to the 4 direct neighbors. A study of non-crystalline structures often involves *comparison to crystals*. Clearly our definitions help to characterize not only regular structures but even better irregular - that is non-crystalline - structures.

The next question is: when we have a set of particles, how do we practically construct the Voronoi diagram ? An efficient and exact algorithm for the construction of the diagram exists [3]. It relies on embedding P_i in a cube C_i such that the face of C_i closest to P_i is relatively far away from the furthest quasi-direct neighbor of P_i. In spite of the size of C_i, its existence saves a large amount of computation for P_j centers which do not contribute to V_i. This computer code produces the exact V_i. Some later algorithms are either approximate or slower than that described [3].

Figure 2. A Voronoi polygon with various classes of neighbors; after [3].

____ an edge (polygon side) resulting from a direct neighbor; _ _ _ _ an edge resulting from a quasi-direct neighbor; __ . __ an edge resulting from an indirect neighbor; ▲a direct neighbor; ■ an indirect neighbor; ✳ a degenerate neighbor. The polygon corresponding to one of the centers is represented by the shaded area.

The significance of the definitions quoted above can be shown by considering a simple regular lattice as an example, such as the planar square lattice. Each Voronoi polygon here is a square, with all squares identical. The

REPRESENTATIONS OF STRUCTURES OF AMORPHOUS SOLIDS AND LIQUIDS

A representation of such structures alternative to the Voronoi diagram, commonly employed in many areas of MSE, particularly by X-ray diffractionists, consists in the use of the so-called radial distribution function $g(R)$. The probability of finding a second center at a distance R from the first center is defined as

$$\rho(R) = [N/V]^2 g(R) \qquad (4)$$

Where, $g(R)$ is the conditional probability of finding a second center P_j at a distance R from P_i, and, N/V is the number of centers, or particles, contained in a volume, V. When the distance R becomes very large, any correlation between the positions of the particles disappears. The particles become independent, and the probability of finding each of them in a small volume element is N/V; the probability of having them both simultaneously in the respective volume elements is $(N/V)^2$. This is fact the reason for Equation (4), which serves as the definition of $g(R)$. The function $g(R)$ represents the correlation between the particle positions and is so normalized that $\lim_{R\to\infty} g(R) = 1$. The structural coordination number can then be defined[7] as

$$z_{ik} = \rho \int_{R\,min\,(k)}^{R\,min\,(k+1)} 4\pi R^2 g(R)\, dR \qquad (5)$$

ρ is the number density equal to the number of centers per unit volume. The index i pertains to the center P_i; the index k represents the k-th coordination sphere around P_i; the respective peak of $g(R)$ is located between two minima of the function, namely R min (k) and R min (k + 1). Experimental values obtained by Fourier-transforming diffractometric data produce $g(R)$ curves for the material as a whole. As we know from MSE textbooks, for crystals the values of z_j are well established, such as $z_1 = 6$ for the simple cubic and $z_1 = 12$ for closed packed lattices. It is, however, for non-crystalline materials that we need the Voronoi polyhedra and/or the g(r) curves and z values resulting therefrom, since no direct information can be extracted from diffraction data of non-crystalline materials. Equation (5) can be integrated easily since an accurate analytical formula for $g(R)$ exists[9]. The formula has been tested for a variety of materials, for experimental as well as for computer-simulated $g(R)$ diagrams. In general, the average geometric coordination number f_k for a given material is *higher* than the structural coordination number z_k; this applies to any k value, that is to any shell.

We should mention here also the efforts of Alan Mackay in the development of what he called *flexi-crystallography* for materials other than crystals [10, 11], including currently fashionable fullerenes, first predicted by Buckminster Fuller, and nanotubes. Mackay noted the importance of the Voronoi polyhedra in this endeavor, but his considerations were largely qualitative. Alternative approaches will be described in Sections 4 and 6.

INFORMATION THEORY OF NON-CRYSTALLINE STRUCTURES

The Voronoi diagram serves also as a basis for the development of a theory of non-crystalline structures using the tools provided by the theory of information [8, 12 – 14]. According to this theory, one considers coding the information about a structure for transmission via a communications channel. Thus one needs here the minimum amount of information necessary to assure the task. In other words, the coding has to be performed in such a way that redundant information is not transmitted. Such a coding procedure has been devised by Collins [12] in terms of distances between neighboring centers. The links form impenetrable barriers to other centers (again molecules, atoms, polymer segments, etc.) so that a Delaunay diagram is constructed. That diagram constitutes an assembly of irregular Delaunay polyhedra (simplices), with centers as vertices of each polyhedron [15,16]. Thus, the Delaunay diagram is a mathematical dual of the Voronoi diagram; see Figure 3.

The non-redundant information can be transmitted over a channel in terms of interparticle distances (links, or edges in the Delaunay diagram), angles between the links, or in a combined way involving both, distances and angles. One can define a distribution of probabilities of link lengths, and obtain there from a formula for the entropy S of the
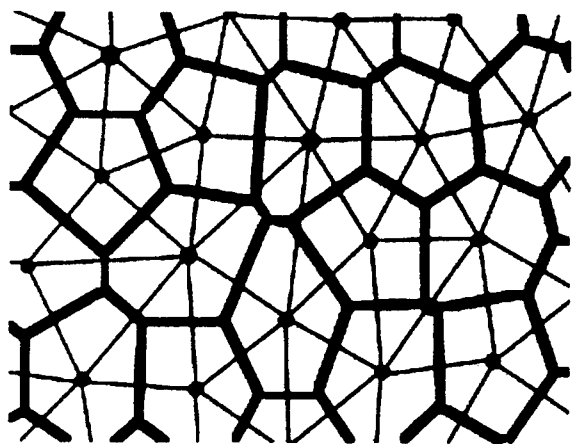
Figure 3. An example of simultaneous Voronoi and Delaunay tesselations for a system of centers. Thick lines show the Voronoi polygons, thin lines delineate the Delaunay polygons.

material. S contains three types of contributions: kinetic resulting from momentum, configurational and topological. Consistently with coding in terms of center pairs, the configurational (also called potential) energy U^C is obtained as a sum of pair interactions. That is, given the pair interaction potential u(R) and g(R) from diffractometry, we can calculate $U^{C\ 8}$. The knowledge of du(R)/dR and again of g(R) makes possible also calculation of the volume V of the system [8]. With the Helmholtz function A = U − TS, given pressure P, we can also compute the Gibbs function G = A + PV and other thermodynamic potentials. We shall discuss the connections between g(R) and thermodynamic functions more in a later article.

It is also possible to limit the consideration of g(R) to the region inside of the first coordination shell (in other words, to the Delaunay figures which involve a given center). Thus, *a connection between the Voronoi and the g(R) approaches has been derived*[13].

THE DIFFERENCE BETWEEN AMORPHOUS SOLIDS AND LIQUIDS

In the previous Section we have mentioned the Delaunay simplices as the duals of the Voronoi polyhedra. There is one Delaunay figure of particular interest in the field under discussion, namely the regular tetrahedron. Medvedev and Naberukhin, two contemporary Russian physicists, have defined a measure they called T for tetrahedricity [17 – 19]; so as to avoid confusion with the thermodynamic temperature, we are going to use the symbol F for that measure:

$$F = \sum_{i > j} (l_i - l_j)^2 / 15 <l>^2 \qquad (6)$$

where l_i is the length of the i-th simplex edge and $<l>$ is the average edge length value for the simplex. Since for the regular tetrahedron F = 0, low F values correspond to small distortions from the regular shape.

We have investigated the mutual arrangement of the Delaunay 4-center simplices [20] for the models of liquid and quenched solid rubidium created by the method of molecular dynamics (MD) by Tanaka [21]. The MD computer simulation procedure is described in [8, 22] and [23]. With rubidium atoms as the Voronoi centers and the Delaunay vertices, the distribution of the circumradii of the Delaunay simplices, and also the tetrahedricities F of the simplices were established. Clearly this can be done for other materials as well.

Analysis of the results reported in [20] shows that low density (high tetrahedricity) atomic configurations in the liquid phase form a percolative cluster. Such a cluster does *not* exist in the solid phase. By contrast, there is a percolative cluster in solid rubidium, but it is created by high density configurations with *low tetrahedricity* values. Thus, although the structural difference between the amorphous

solid and liquid materials had been elusive for quite a long time, that difference has now been captured [20] on the basis of concepts derived from the work of Voronoi.

QUASI-CRYSTALLOGRAPHY AND PATTERN RECOGNITION

The efforts of Mackay in the development of what he called flexi-crystallography or quasi-crystallography have been noted at the end of Section 3. He has developed methods for representing and handling structures other than crystalline - in such a way that comparisons with crystalline structures should be possible[10, 11].

One can apply the Voronoi and Delaunay tessellations to *pattern recognition* of atomic environments and to investigation of the non-local order in materials, including those simulated by molecular dynamics. The pattern recognition is based on an analysis of the *shapes* of the Voronoi polyhedra. For that reason the procedure is applicable outside of MSE as well, for instance in astronomy to study the fragmentation of celestial bodies such as meteorites on collision. A procedure for contraction of short edges and small faces of the polyhedra has been developed [24]. This provides slightly simplified structures, but implies a large gain in the perspicuity. *Removal of effects of fluctuations* is thus achieved.

To see this better, consider an example of a hexagonal closed packed ($z_1 = 12$) lattice which we have subjected to a small distortion. As a consequence of that distortion, small faces have appeared, such that their surface areas are smaller than 0.2 of the average surface area. One can eliminate such faces[24]. Figure 4 shows the distribution of the edge lengths afterwards. We see that all the edges are divided into two subsets. The subset of the short edges is originates from perturbations results from the distortions introduced deliberately.
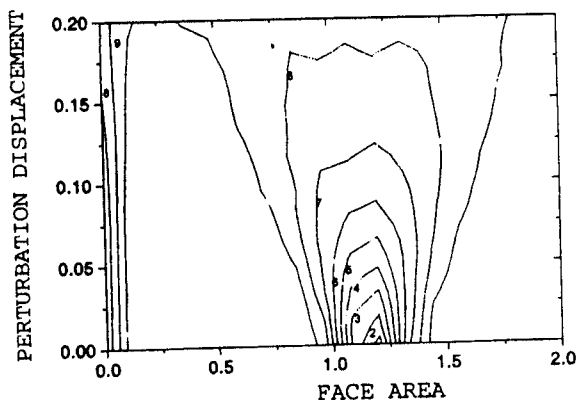

Figure 4. A distribution of face areas, averaged for all Voronoi polyhedra, plotted for a distortion perturbed hexagonal closed packed lattice after the elimination of small faces (see text). The points in the structure have been shifted by the perturbation displacement in a random direction. The displacements are scaled to the nearest-neighbor distance and face areas are expressed in units of the average face area; after 24. The numbers from 1 to 10 increase along with the decreasing probability of occurrence of a given face area.

Non-local order analysis involves geometric relations between Delaunay simplices. The contraction method has been applied to the analysis of the structures of MD-simulated lead and germanium in solid phases[24]. Given the large differences between the structures of these metal and the amorphous materials, and considering the successful handling of both elements by the contraction procedure, the method appears fairly general.

CONCLUDING REMARKS

Given the limited length of this article, we could only point out some of the results obtained in the study of materials structures with the use of the Voronoi concepts. Further details can be found in the literature, including for instance representing heterogeneous

polymers by the Voronoi polyhedra [25]. However, even this brief survey should provide an idea of how important are the concepts that Voronoi pursued a century ago are for contemporary Materials Science and Engineering.

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