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Methamorphosis of Voronoi polyhedra as a definite measure of the elastic-to-dissipative atomic displacement transition

Summary — The present method allows to describe the structure of non-crystalline and crystalline solids by constructing a Voronoi diagram. The method gives a detailed structural information about individual atoms and their surroundings. The deformation and methamorphosis of the Voronoi polyhedron is described for an interstitial atom in an *fcc* crystal; an associated criterion is given for the elastic-to-anelastic transition. An extension of the idea to include amorphous materials is indicated. Voronoi tessellation has been applied in the fields of materials science, physics and chemistry.

Key words: Voronoi polyhedra, Voronoi diagram, deformation and methamorphosis of Voronoi polyhedron for interstitial atom in *fcc* crystal.

MICROSTRUCTURE OF AMORPHOUS MATERIALS

The relaxation behavior of amorphous glassy systems is complex, rich in structure and pertinent to applications that are expected to remain an active area of research for years to come. In general, we need a more and more detailed knowledge of the molecular structures of these materials, as may be inferred, *e.g.*, from the monograph [1] published under the auspices of the International Union of Crystallography.

The need to define the microstructure of amorphous materials, analogous to the crystallographic method for the ordered solid state, has led to several conceptual advances based on both theoretical concepts and experimental methods. There are two basic methods of representation of non-crystalline structures. One is based on the use of the binary radial distribution function, $g(R)$, where R is the distance between particles [2—5]. In this work, by particles we understand atoms, ions or polymer chain segments. The other method is the construction of the Voronoi diagram. A Voronoi polyhedron is constructed for each particle according to a unique mathematical procedure [6—11] which we shall define exactly below. Each particle owns a certain amount of space in the material. The polyhedra formation is the Voronoi tessellation and the resulting set of the polyhedra constitutes the Voronoi diagram. The shape and volume of the diagram are identical to those of the real material.

APPLICATION OF VORONOI TESSELLATION TO AMORPHOUS STRUCTURES

The mathematics of the polyhedra in question begins with the work of Dirichlet [6]. Applications in materials science and engineering, physics and chemistry have been spurred on by the work of Gregoryi (pronounced Hrehoryi) Voronoi, a Ukrainian mathematician working in Warsaw at the beginning of the XX-th century [7, 8]. This is why the polyhedra are most often named after him. However, crystallographers sometimes use the name Wigner-Seitz cells, unaware that Wigner and Seitz [9] have applied to crystals the concepts already known before. We need to note that the basic tools of materials description used by crystallographers, including those of the unit cell, cannot be applied to non-crystalline materials. By contrast, the Voronoi diagram can represent materials in any state of atomic arrangement. At present, there is no experimental method capable of determination of individual Voronoi polyhedra. The "experimental" corroboration can only come from computer simulation and modelling.

We note that Voronoi polygons have applications in other branches of science, for instance, for surface visualization [12, 13 and numerous refs. cited therein]. Application of the Voronoi tessellation method (*i.e.* construction of the Voronoi diagram) to describe amorphous structures can be traced to the early work by Bernal and his co-workers on the structure of liquids. Thus, in 1970, Finney [14] constructed the Voronoi diagram for random close packed monoatomic structures. He also tried to connect the distribution of the polyhedra volumes to the radial distribution function, $g(R)$, of the same simple monoatomic structures [15].

The method of the Voronoi diagram construction

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developed by Finney was approximate and slow; the execution time was proportional to the fourth power of N, where N is the number of particles. One of us, Dussault and Fox have developed the first exact method of Voronoi tessellation [10]. Definitions of indirect, degenerate and *quasi*-direct neighbors of a given particle (point) have been introduced at the same time. The method developed in [10] consists in first constructing the so-called direct polyhedra, relatively simple, with a considerable saving of time. As for polymers, the Voronoi diagrams have been constructed and published first by Theodorou and Suter [16] and Rigby and Roe [17]. The tessellation computations were carried out for static, equilibrated structures, with the results describing mainly free volume distribution. One of us [18] used the concept of Voronoi polyhedron around a polymer chain to postulate a deformation mechanism in amorphous polymers. For inorganic glasses the Voronoi tessellation approach was used by Tsumuraya *et al.* [19]. Also Watanabe and Tsumuraya studied liquid sodium by molecular dynamics and applied the Voronoi approach to distinguish glass formation from crystallization [20]. Three more papers deserve mention. The Voronoi diagram has been used to define the fundamental difference between the amorphous solid and the liquid [21] in terms of percolations of two kinds of structures. The atomic level strain has been connected with the Voronoi diagram [22]. A method of construction of the Voronoi polyhedra which eliminates artefact small faces has been developed [23].

On the basis of our work on deformation of polymeric materials [18, 23, 24] and its connection to performance [25—28], the present paper sets out to apply the Voronoi construct to characterize deformation. We develop a criterion for distinguishing between the conservative (elastic) and the dissipative (anelastic) atomic displacements by using a metamorphosis of the Voronoi polyhedra. It is postulated that Voronoi diagrams can be used to define elastic and non-elastic deformation in materials.

At this point, we need to provide the definition of the Voronoi polyhedron. Precise definitions have been described elsewhere, *e.g.* [10]. For the present purposes we give an operational definition and, for perspicuity, we limit it to two dimensions. Consider a set of points, each representing a particle as defined in the preceding Section. First, we draw links between neighboring points. Then, we take each link and produce a line perpendicular to it and passing through the point equidistant from terminal points. Such bisectors produce polygons around the particles. For each particle, the smallest polygon so constructed is the Voronoi polygon. It delineates the surface that belongs to that particle. Extension to three dimensions is straightforward.

METAMORPHOSIS OF VORONOI POLYHEDRON AND ATOMIC STRAIN

The dynamics of atomic and point defect migration is a well researched area [29]. The displacement of the interstitial atom is adequately described by the classical elasticity theory. However, in discrete bonded systems, such as we create in computer simulations of atomic and molecular structures, atomic-level stresses and strains have to be re-defined because the value of strain in the intervening spaces is meaningless; only the change in the relative position of two atoms can be defined unambiguously by the relative displacement vector. The frequently used affine description of strain is impossible in the atomic system because it entails distortions of bond lengths and angles inconsistent with the configurations obtained by minimization of the Gibbs function. Following Theodorou and Suter, it is possible to define an inhomogeneous strain vector [16]. Furthermore, the atomic strain produced by such a motion can be described by a generalization of the strain concept as developed by Mott *et al.* [22], who have decided to identify the positions of atoms by their surrounding volumes. This has led them to the Voronoi tessellation described above. Mott *et al.* [22] define the Lagrangian atomic level displacement gradient as:

$$F_i = \sum_{i}^{DT} v_{ij} F_j \qquad (1)$$

where the summation is over all the Delauney tetrahedra (*DTs*). We recall that, in the first stage of creation of the Voronoi diagram, we connect the neighboring atoms by lines. This creates the Delauney diagram [30] which consists of *DTs* and is the dual of the Voronoi diagram. Then v_{ij} in equation (1) represents the fraction of the Voronoi polyhedron that falls within the j-th *DT*.

Equation (1) is a smooth, continuous and periodic function of the displacement, with a set of maxima and minima. In principle, some points on this function can be identified with the transition stage from the elastic displacement to the dissipative anelastic displacement of the interstitial atom. However, there is no clear practical criterion as to how these points should be defined.

Instead, we propose another method based on the discontinuous changes of the Voronoi polyhedron during deformation. In order to illustrate this method, we use as example the simple case of the motion of an interstitial atom in a crystalline lattice. The motion is periodic and symmetric, whereby the representation of displacement and strain becomes simplified. The atoms are assumed to be in their equilibrium positions, and thermal vibrations are averaged. Construction of the Voronoi polyhedron around the interstitial atom in the octahedral site results in a cube (6 nearest neighbors) as

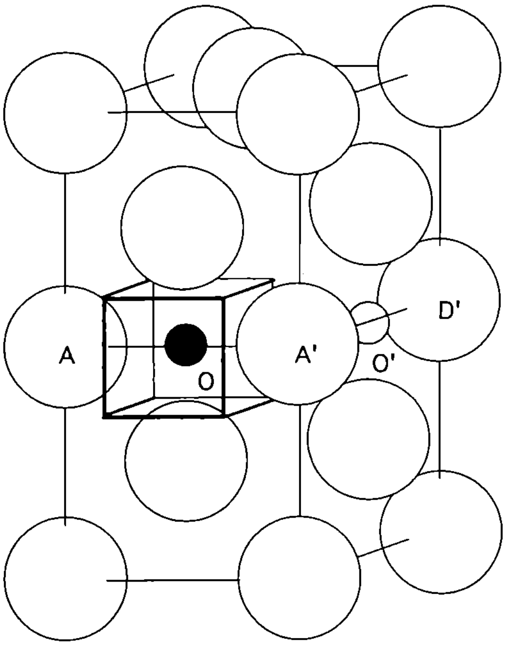

Fig. 1. Two unit cells of an fcc crystal with an interstitial atom in octahedral site at O (between A and A'). Consider the jump in a straigth line from O to O' (between A' and D')

shown in Fig. 1. During motion, the Voronoi polyhedron associated with the atom changes its shape, achieving a special status at the half way point between the octahedral sites. If the crystal is subjected to mechanical loading, the interstitial motion may result in an anelastic relaxation.

In Fig. 1, the interstitial atom (marked as a small black circle) moves from the initial octahedral position at O, towards the neighboring octahedral position at O'. Figure 2 shows — in a different projection — three incremental stages of the move: (i) first at the original position, (ii) next at a distance a quarter of the way, and (iii) at the mid-way point; the rest of the displacement is a mirror image of the three stages shown. The unit cells on the left side show the [001] view; in the right upper corner we see the [110] projections of the *fcc* cells, with the interstitial atom appearing on the basal plane.

The original position

When the interstitial atom is precisely at the center of the octahedral site, the corresponding Voronoi polyhedron surrounding it is a cube equal in size to one half of the lattice cell size. Its [001] projection is a square, and its [110] projection is a rectangle as shown. Our Voronoi polyhedron has 6 faces (*F*, not to be confused with *F* subscripted in Eq. (1)), 8 vertices (*V*) and 12 edges (*E*), satisfying the Euler relationship: $V - E + F = 2$. The number of Delauney tetrahedra based on the line segment, Oa, is 24 as can be easily verified.

One quarter of the way

As soon as the interstitial atom moves away from its octahedral site location, the Voronoi cube begins to distort. When in the indicated position, the Voronoi polyhedron takes the shape shown by the second outline (with both [001] and [100] views). Geometrical analysis of this object yields 8 faces, 12 vertices and 18 edges, and 24 associated Delauney tetrahedra.

The mid-way point

When the interstitial atom reaches the position precisely half way between the octahedral sites and the two "gating" atoms C" and A"', the corresponding Voronoi polyhedron becomes symmetrical as shown. It comprises 10 faces, 16 vertices and 24 edges, and is characterized by 36 associated Delauney tetrahedra. The calculations of the geometrical Delauney elements are indicated in Fig 2 for each case. We note that each lattice point is associated with 8 neighboring unit cells.

PROPERTIES OF THE VORONOI METHOD

We define an integer function, N_{DT}, which maps the number of Delauney tetrahedra associated with a given Voronoi polyhedron onto the interval representing the displacement of the interstitial atom between the two octahedral sites:

$$f_I(x_i) = N_{DT}(x_i) \tag{2}$$

where: $x_i = x_i(X_1, X_2, X_3, t)$; *which gives the present location of the particle that occupied the point* (X_1, X_2, X_3) *at moment* $t = 0$.

Also, we define another integer function N_{VF} which maps the sum of the number of vertices and faces of a given Voronoi polyhedron onto the interval representing the displacement of the interstitial atom between the two octahedral sites:

$$f_{II}(x_i) = N_{VF}(x_i) \tag{3}$$

We postulate, without proof at this stage, that the N_{DT} function reaches a maximum value when the interstitial atom arrives at the mid-point position (the saddle-point) signifying the onset of the transition. Furthermore, we postulate that the N_{VF} function always has a minimum value when the interstitial atom occupies one of the stable sites (octahedral positions). We observe in Fig. 2 that N_{DT} reaches the maximum value of 36 at the transition position, whereas $N_{VF} = 14$ (smallest value) for the particle in the octahedral positions. This example shows how a Voronoi polyhedron reflects in its complexity — or otherwise — movements of atoms under the effect of an external mechanical force. We have thus

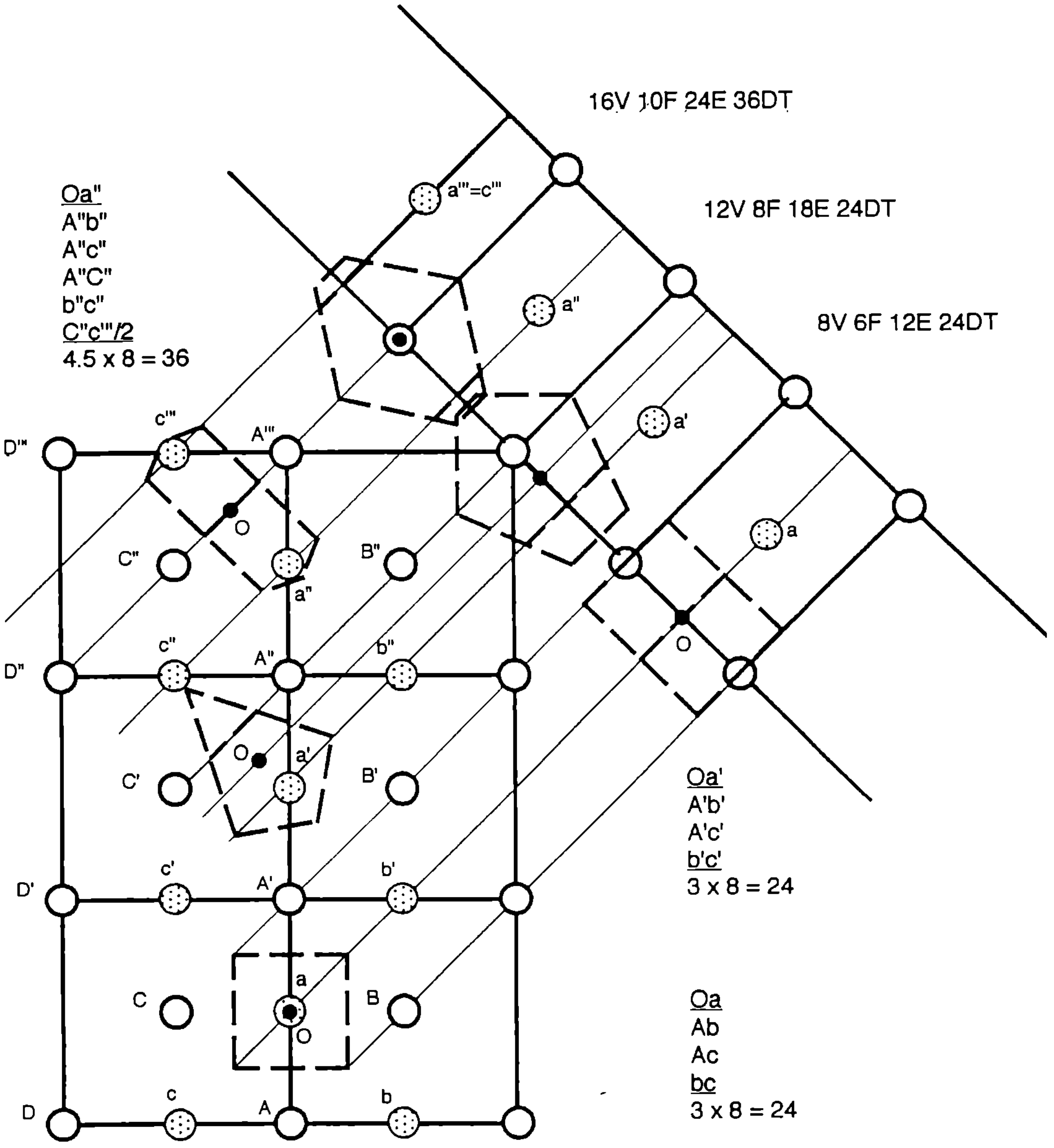

Fig. 2. Metamorphosis of Voronoi polyhedron (broken lines) of the interstitial atom in fcc lattice (continuous lines). The atom moves from its initial site O towards site O′ below atom c′. The diagram shows three positions: original, 1/4 of the way, and half-way. One the left view from [001] direction, top-right shows projections [110]

acquired a useful tool for the characterization of deformation.

We observe the following properties of the Voronoi polyhedra:

— For pure and ideal crystalline substances, all Voronoi polyhedra are precisely of the same size and shape.

— For amorphous structures, the Voronoi polyhedra vary in size and shape. The distribution of volume follows a characteristic function, closely described by a Γ-function.

— The minimum Voronoi polyhedron is a tetrahedron.

— An atom enclosed by a Voronoi polyhedron in an amorphous solid is not, as a rule, at the center of the polyhedron, unless its surrounding neighbors are in the centro-symmetrical arrangement.

— Under homogeneous elastic deformation of crystalline substances, the deformation of the corresponding Voronoi polyhedra will obey the elastic field equations. There will be no change in the number of faces, edges and vertices.

— For amorphous solids, the deformation of Voronoi polyhedra will differ from atom to atom and from monomer to monomer. However, there will be no change in the number of faces, edges and vertices as long as the deformation is elastic.

— For anelastic and plastic flow deformation, in both crystalline and amorphous materials, Voronoi polyhedra will undergo transformations resulting in a change of shape, size and, most importantly, a change in the number of faces, edges and vertices.

THE NOWICK-HELLER THEORY AND THE VORONOI METHOD

The Nowick-Heller (NH) theory offers a criterion for anelastic effects in crystalline solids [31]. It assumes homogeneous external fields and low defect concentrations — so that any defect transition has a negligible effect on the Gibbs function of the crystal. The crystal has a point symmetry group, G_x, and a corresponding number of symmetry operations, h_x. The defects will produce anelastic strain given by

$$\varepsilon_{ij}^{an} = \sum_p \lambda_{ij}^p C_p \tag{4}$$

where: $C_p = N_p \cdot v_p$ *is the concentration of defects in terms of mole fractions and* λ_{ij} *is a second order symmetric tensor described by an ellipsoid dipole.*

When expressed in terms of the principal components, the symmetry of λ must reflect the symmetry of the defect. If h_t is the order of the tensor group of the applied field, then a defect will undergo a transition only if

$$n_t > 1, \quad \text{where} \quad n_t = \frac{h_x}{h_t} \tag{5}$$

In crystalline solids, the Voronoi tessellation is identical with the Wigner—Seitz cells, hence the symmetry elements of the Voronoi polyhedra reflect the symmetry elements of the crystal, and it will be a simple matter to show that condition (5) is satisfied for strains applied in certain crystallographic directions [29]. Consequently, the NH theory can be expressed in terms of the properties of the Voronoi polyhedra.

Our example presented above concerns a crystal. We have chosen such an example for the reason of perspicuity of our presentation. Since symmetry operations loose meaning in an amorphous structure, the NH theory cannot be applied to amorphous materials. In general, there is an obvious lack of a precise criterion for elastic (reversible) to non-elastic (dissipative) motion in such solids. We propose that the functional criterion expressed in the preceding Section is a sufficient and necessary condition to identify the transition for each particle (atom, atomic group, monomer, chain segment, *etc.*) in an amorphous polymer. In molecular dynamics terms, the potential energy surface around each monomer with its side-groups, from which an activation energy barrier is obtained, must be examined. In particular, for monomers of poly(methyl methacrylate) there will be two major minima in positions at right angle to the molecular chain axis. These are the positions in which the ester groups are found in equilibrium. However, the presence of surrounding monomers or atoms from other segments of chain(s) must modify this simple hyperbolic surface, especially in monomers with small Voronoi volumes [32]. Small additional potential energy minima may appear at other positions, allowing for more complex events, which can be analyzed and described by the method presented here.

ACKNOWLEDGMENT

One of us (W. B.) thanks the Robert A. Welch Foundation, Houston, for financial support under the Grant # B-1203.

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