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Hierarchical structure of defects in non-crystalline sphere packings

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Résumé. — Nous décrivons les défauts dans un empilement tétraédrique compact. Les défauts apparaissent comme des réseaux enchevêtrés de disinclinaisons qui sont le lieu des sites ayant un ordre local non icosaédrique. Cette structure est produite par un processus itératif qui abaisse progressivement la courbure d'un polytope utilisé comme modèle idéal.

Abstract. — We describe the defect structure of a tetrahedral close packed model. Defects appear as a hierarchy of interlaced disclination networks which form the locus of sites where the local order deviates from a perfect icosahedral environment. This defect structure is generated by an iterative process which gradually decreases the curvature of an ideal polytope model.

Amorphous systems are structurally characterized by the lack of long-range periodicity and the presence of a rather well defined short-range order (SRO). The local configurations are generally such that they cannot tile perfectly the 3D Euclidean space (R^3). As an example let us consider amorphous metallic systems. It is well known that a satisfactory approximation of the structure is given by close packing tetrahedra. A regular tetrahedron is the densest configuration for the packing of four equal spheres. The dense random packing of hard spheres problem can thus be mapped on the tetrahedral packing problem. The dihedral angle of a tetrahedron is not a submultiple of 2 π, consequently a perfect tiling of the Euclidean space with regular tetrahedra is impossible. One of us (J.F.S.) has proposed to define an ideal amorphous structure by allowing for curvature in the space in order for the local configuration to propagate throughout the whole space without defects [1]. The analogue in 2D is the perfect tiling with regular pentagons, impossible on the plane and realized on the surface of a sphere (S2) by the pentagonal dodecahedron. In 3D space it is possible to pave the (hyper) surface of a hypersphere (S3) by regular tetrahedra arranged by five around a common edge. This (finite) structure is called the polytope { 3, 3, 5 } using standard notation [2]. Note that the underlying space is 3 Dimensional although not Euclidean even if one often thinks of S3 as being imbedded in R^4. This « constant curvature »

idealization has been extended to several other kinds of disordered materials such as tetra-coordinated covalent systems [3]. A simple example is given by the packing of pentagonal dodecahedra which is forbidden in R^3 because of the polyhedron's dihedral angle value. Packing these dodecahedra on S3 leads to the regular polytope { 5, 3, 3 } which is dual of the above mentioned { 3, 3, 5 } and thus possesses the same symmetry group. However the curvatures associated with these two polytopes are not identical (when scaled to the edge length) and this reflects the unequal difficulty in tiling R^3 with tetrahedra or dodecahedra due to their different deficit dihedral angles. A given cell may also give rise to various ideal packings specified by the number of such cells sharing a common edge. We expect that a suitable map of this ideal model onto R^3 (minimizing the energy) will provide a realistic amorphous structure. It is then clear that, for physical reasons, the best ideal model associated to a given local configuration will correspond to a minimum absolute value of the curvature (either in spherical or hyperbolic space). The mapping introduces distortions and topological defects, among which disclination lines play an important rôle. In the present paper we show how it is possible to annul the curvature using an iterative procedure which introduces step by step disclination networks. It could seem to be simpler to introduce disclinations one by one. But up to now one is then faced to unsolved problems, which we briefly discuss now. The defect lines can be classified using the homotopy theory of defects [4] and belong to conjugacy classes of the fundamental group $R = \pi_1(SO(4)/G)$ where G is the polytope symmetry group. Recently D. Nelson [5] has labelled line defects in a « Euclidean icosahedral medium » using $\pi_1(SO(3)/Y) = Y'$ where Y is the icosahedral group and Y' its lift in SU(2). Note that Y' is a subgroup of G^6 and the only structure free of defects in this context is precisely the polytope { 3, 3, 5 }. Nelson argues that it is possible to describe the linear defects in the { 3, 3, 5 } by the conjugacy classes of Y'. To show this he splits SO(4) into a rotational part SO(3) and a translational one SO(4)/SO(3) and suggests that it is enough to consider defects in the orientational part, these fundamental defects being then used to build the more composite translational ones. Sethna [7] has objected to this simplification but the question still remains open [13]. In fact, elements of Y' are not true rotations on S3 but act as screws, with no points left invariant and with geodesic great circles as orbits. The introduction of a single disclination line along a five-fold symmetry axis (being then the locus of Z14 vertices following standard notations [8]), which is purely rotational, corresponds to combined left and right screws, an element of $G = Y' \times Y'/C_2$ (where C_2 is the two-elements group). Note that $R = \pi_1(SO(4)/G) = Y' \times Y'$. We have already shown that it is possible to interlace two such disclination lines into the 120 vertices polytope { 3, 3, 5 } and get a polytope containing 144 Z12 vertices and 24 Z14 vertices [9] with less intrinsic curvature. One might hope to iterate this and achieve the complete flattening of the structure. The final model will consist of regions of positive curvature, where the polytope SRO is maintained, and of negative curvature associated with the line defects, arranged in such a way that the mean curvature is zero. In this corrugated space approach [10], or variable curvature idealization, the local order is still perfect within coherence regions.

To put all this in a concrete form, one has to incorporate step by step disclination lines into the polytope. The non-commutative character of the required operations (R is non Abelian) introduces new difficulties which have not been cleared up at the moment. On the other hand this non-Abelian character is the key to understanding how it could be possible to generate very complex disordered structures starting from a regular polytope and using only a finite collection of defect operations. An « alphabet » can be defined whose elements, the « letters », denote each kind of defect (the conjugacy classes of R). The structure is then represented by a « word », an ordered set of letters, and its complexity is encoded in the information content of the word.

We show how it is possible to bypass the above mentioned difficulties and achieve the complete flattening of the polytope in a simple and tractable manner. The key idea is to introduce, at each step, a disclination network (instead of a single disclination line) whose symmetry group is

contained in G. The first and second-neighbour shells of a { 3, 3, 5 } vertex are an icosahedron and a dodecahedron [1] respectively. Such a configuration has an intrinsic length associated to it, the { 3, 3, 5 } radius of curvature R_1. Ignoring the central vertex and its icosahedral shell one can build a perfect tiling of the dodecahedral shells on S3, the polytope { 5, 3, 3 }, which is characterized by another radius of curvature $R_2 (> R_1)$. Filling in the dodecahedral cells by the centred icosahedra, one obtains a new polytope, called P_1, containing 1560 12-coordinated vertices (Z12 sites) and 600 16-coordinated vertices (Z16 sites). The disclination network, which we call D_1, of this new polytope consists of the edges of the large { 5, 3, 3 } inscribed in it and connecting the Z16 sites. A 2D image of such structure would be a big sphere of radius R_2 covered by small domes of radius R_1 smaller than R_2 (think of a strawberry surface). Note that by centring the 12 000 tetrahedral cells of polytope P_1, one gets the dual polytope Q_1 which is tetracoordinated and consists in a tiling of dodecahedra and 16-sided cells which are the Voronoï cells of the Z16 sites. Because both the polytope and the defect structure have the same symmetry group, it is very easy to iterate this transformation and get a new polytope P_2. The precise way to do this will be published later. It involves the definition of a primitive cell, called the orthoscheme tetrahedron [14], from which the polytope vertices are generated under the action of the symmetry group operations. This primitive cell contains 1 site in the case the { 3, 3, 5 } (which can be called P_0), 3 sites in the P_1 case, 14 sites in the P_2 case... If one orients the { 3, 3, 5 } polytope in such a way that one vertex is on the « north pole » (with coordinates 0, 0, 0, $x_4 = 1$) of the unit radius hypersphere S_3, its icosahedral first coordination shell lies on the hyperplane $x_4 = 0.809$ and the dodecahedral second coordination shell lies on the hyperplane $x_4 = 0.5$. The dual polytope { 5, 3, 3 } has a dodecahedral cell which surrounds the north pole at $x_4 = 0.926$. The first iteration consists in « pushing » the { 3, 3, 5 } sites toward the north pole in order to make the { 3, 3, 5 } dodecahedral cell (at $x_4 = 0.5$) coincide with the { 5, 3, 3 } dodecahedral cell (at $x_4 = 0.926$). Sites lying inside the orthoscheme tetrahedron are then used to generate the P_1 polytope by application of the G group symmetry operation. This process is easily iterated in order to build the next P_n.

The polytope P_2 obtained at the second iteration contains two interlaced disclination networks, whose union is denoted D_2, which have different characteristic length scales related to their nearest node separation. The first one, D'_2, has the polytope { 5, 3, 3 } structure with a large edge length value. Its edges thread the 6-fold rings of the second disclination network D''_2 which has the structure of the Q_1 polytope. The polytope P_2 contains Z12, Z16 and Z14 sites. These new Z14 sites are edge vertices of the D'_2 disclination network. The coordination shell of the Z12, Z14 and Z16 sites are shown in figure 1. The local arrangement of D'_2 and D''_2 is represented in figure 2. When the transformation is iterated again, larger polytopes P_n are obtained with increasing mean radius of curvature. Their defect structure D_n is given by the union of n disclination networks, which have no point in common and have the same geometrical structure as the n polytopes

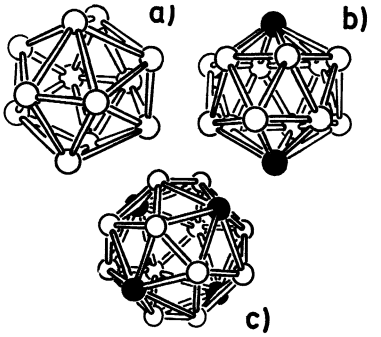

Fig. 1. — Coordination shells of Z12(a), Z14(b) and Z16(c) sites. Sites lying on disclinations are darkened.

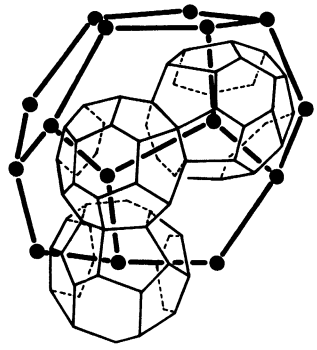

Fig. 2. — Local view of the disclination network. Heavy line : D'_2 disclinations (which have the same topological structure as D_1). Light line : D''_2 disclinations interlaced with the previous network.

$Q_p (p = 0, ..., n - 1)$ dual to P_p. Here Q_0 denotes the polytope { 5, 3, 3 }. Table I displays information about the P_n up to $n = 5$. These quantities can be obtained for small n by the direct « inflation » method which uses the symmetry group operations in order to build structures of increasing size. But the table I data can be derived more simply without explicitly building the polytopes. The main effect of the iterative transformation can be put in the matrix form $\mathcal{N}^{(i)} = M\mathcal{N}^{(i-1)}$ where $\mathcal{N}^{(p)}$ is a 3D vector whose components $(N_{12}^{(p)}, N_{14}^{(p)}, N_{16}^{(p)})$ are the total number of Z12, Z14 and Z16 sites in the polytope P_p. At a given iteration the Voronoï cell of a Z12 vertex is filled by 13 new Z12 vertices and 20 new Z16 vertices. A Z16 vertex is common to 4 Voronoï cells, and thus a correct count of the new vertices requires that only 5 Z16 new vertices are associated to 1 « old » Z12 vertex. This can be written Z12 → 13.Z12 + 5.Z14.

A Z14 Voronoï cell is filled by 12 Z12 vertices, 3 Z14 vertices, and 24 Z16 vertices. Finally a Z16 Voronoï cell is filled by 12 Z12 vertices, 4 Z14 vertices, and (1 + 28) Z16 vertices (1 Z16 vertex in the centre and 28 Z16 vertex on the Voronoï cell vertices). In this case the matrix M is given by :

$$M = \begin{pmatrix} 13 & 12 & 12 \\ 0 & 3 & 4 \\ 5 & 5 & 8 \end{pmatrix}.$$

Table I. — *Data corresponding to the P_n polytopes. N_p is the number of sites with coordination number p and N the total number of sites. T is the number of tetrahedral cells. $\overline{Z}$ is the mean coordination number.*

	N_{12}	N_{14}	N_{16}	N	T	$\overline{Z}$
P_0	120	0	0	120	600	12.
P_1	1560	0	600	2160	12000	13.111
P_2	27480	2400	12600	42480	240000	13.2999
P_3	537240	57600	252600	847440	4800000	13.328
P_4	10706520	1183200	5052600	16942320	96000000	13.3325
P_5	214014360	23760000	101052600	338826960	1920000000	13.3332

Since iteration begins with P_0, the { 3, 3, 5 } polytope, one has $\mathcal{N}^{(0)} = (120, 0, 0)$. To the largest eigenvalue of M (the Perron root) corresponds an eigenvector which gives some information about the asymptotic P_∞ polytope. In particular the mean coordination number (MCN) can be easily derived and one sees in table I that the asymptotic value 40/3 is closely approached after only very few iterations. By mapping a small part of the P_p (with large p) onto a tangent 3D Euclidean space, it is possible to obtain a huge non-periodic model with an intricate defect structure. Such a model is not as disordered as the usual computer generated hard-sphere models and it is in many senses similar to the family of recurrent sets and Penrose-like tilings [11]. It is possible to get a more disordered model by using more than one type of iterative transformation. We have already described a second such transformation [12] which also obeys the group G symmetry operations and generates Z12, Z14 and Z18 vertices. By choosing randomly at each iteration one of these two processes, one gets disordered models which still possess interlaced but more complex defect structures. These models can again be labelled by words whose letters belong to the two-letter alphabet associated with the two different types of transformation. Since the asymptotic MCN value is 13.2 for this second process, it is then possible to obtain models with a MCN intermediate between 13.2 and 13.333. Let us point out that even this more disordered structure, although non-periodic, is probably still more regular than a real amorphous structure. This iterative procedure is, however, a new and powerful method which allows one to discuss the relation between short and intermediate-range order, and provides huge structural models with hierarchical defect geometries. The geometrical proof that the asymptotic structure is non-periodic is rather long and will not be given here. Let us restrict ourselves to a shorter illustration. Suppose that, after p iterations, a crystal P_p is obtained. Its unit cell necessarily contains parts of the disclination network D_p (whose periodicity is also required). Since the next iteration will add a new disclination network (interlaced with those contained in D_p), the size of the P_{p+1} unit cell is larger when scaled on the first neighbour distance. The P_∞ unit cell is thus infinite, which proves its non-periodic character. Note that some trivial iterative procedures can produce « crystalline » structures, such as, for instance, the derivation of B. Fuller geodesic domes which are triangular lattices embedded on S2 *via* the introduction of 12 5-fold defects. In this case the number of defects is finite while it is infinite in the non-crystalline P_∞ polytope described above. Even more in the Fuller geodesic dome case the separation between defects increases at each iteration, when scaled to the first neighbour distance.

Added Note. — The matrix formulation given here bears an interesting resemblance to the transfer matrix approach of fractals [15].

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