

De Nive Quinquangula: On the pentagonal snowflake

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Johannes Kepler was mistaken in his book "Mysterium Cosmographicum" (1596) when he suggested that the five regular polyhedra were the 'spherical harmonics' which were the key to the structure of the Solar System. Unfortunately, he never knew that they were, in fact, the eigenfunctions of Schrödinger's equation and the solution to the mystery of the microcosmos at the atomic level. He just knew that they must be the answer to something. Kepler was, however, one of the first to explain the visible forms of matter in terms of the spatial arrangement of component atoms. In particular, in "De Nive Sexangula" (1611),¹ in a New Year's gift for his patron (the equivalent of the modern research council supporting his work) he attributed the hexagonal symmetry of the snowflake to the close packing of spherical atoms.

Since then, through the development of the 32 crystallographic point groups and the 230 space groups, classi-

cal crystallography has been dominated by the concept of the infinite repetition of identical atoms. Now, however, the rigid classical crystallography is giving way to modern crystallography. Here we will be confined to a partial discussion of one of the most striking absences from classical crystallography, namely that of pentagonal symmetry, but a list is included (Table I) of some others of the nonclassical characteristics which are now appearing.

We may refer to two examples of nonclassical structures to illustrate relevant points, especially the occurrence of five-fold symmetry.

The first is the structure of very small clusters of, for example, gold atoms. It has been shown, both experimentally and theoretically, that icosahedral shells of 13, 55, 147, 309 and 561 atoms are stable with respect to the face-centered-cubic arrangement.² This preference is shown usually when the importance of short-range interactions exceeds that for longer-range interactions.

It should be noted that such a particle is not a defective crystal, its only defect might be its surface, and it should not be considered as a multiply twinned particle since it is not a faulted fcc arrangement but is in a lower energy minimum than the corresponding fcc stacking. We might name such clusters as "crystalloids," considering that they merit a special name as a kind of molecule.³ The atoms in a "crystalloid" are only quasiequivalent,

TABLE I. The Transition from Classical Crystallography to the Modern Science of Structure at the Atomic Level

Classical Concepts	Modern Concepts
Absolute identity of components	Substitution and nonstoichiometry
Absolute identity of the environment of each unit	Quasi-identity and quasi-equivalence
Operations of infinite range ω	Local elements of symmetry of finite range
"Euclidean" space elements (plane sheets, straight lines)	Curved space elements. Membranes, micelles, helices. Higher structures by curvature of lower structures
Unique dominant minimum in free energy configuration space	One of many quasi-equivalent states: metastability recording arbitrary information (pathway); progressive segregation and specialization of information structure
Infinite number of units. Crystals	Finite numbers of units. Clusters: "crystalloids"
Assembly by incremental growth (one unit at a time)	Assembly by intervention of other components ("crystalase" enzyme). Information-controlled assembly. Hierarchic assembly
Single level of organization (with large span of level)	Hierarchy of levels of organization. Small span of each level
Repetition according to symmetry operations	Repetition according to program. Cellular automata
Crystallographic symmetry operations	General symmetry operations (equal "program statements")
Assembly by a single pathway in configuration space	Assembly by branched lines in configuration space. Bifurcations guided by "information" i.e., low energy events of the hierarchy below

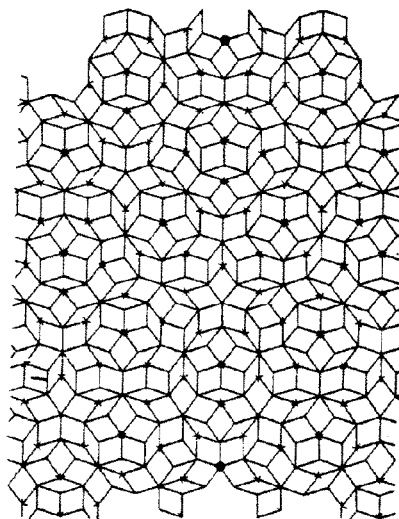


FIG. 1. A portion of the nonperiodic Penrose pattern. The exact 5-fold axes to left and right are marked with larger dots. The pattern may be repeated by five-fold rotation about either.

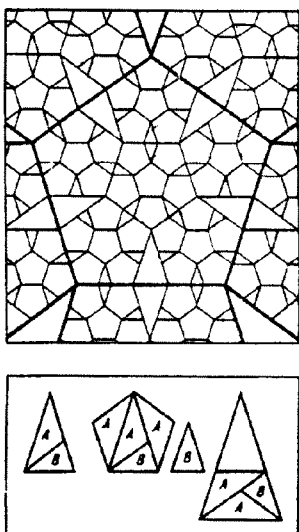


FIG. 2. The hierarchic packing of pentagons and the two units A and B into which it can be dissected.

like the carbon atoms regularly arranged in coronene and such higher polycyclic aromatics. A very small crystal has properties which may be very different from those of a large crystal, since in a crystallite of only $10 \times 10 \times 10$ cells half of these 1000 unit cells will be on the outside and thus markedly different from the others. We can only keep the unit cell concept for such crystallites by saying that the unit cells are only quasiequivalent to each other.

Quasiequivalence arises in the domain where, for example, protein molecules may be strictly equivalent for assemblies of 60 in the point group 532 or 24 in the point groups 432 or 12 in the point group 23 or 622, and strictly equivalent in the large arrays of big crystals which provide translation equivalence, but in between can be equivalent neither by translation nor by rotation.

The second example, which represents the next stage of complexity, is that of the adenovirus particle,³ which consists of a hierarchic assembly of 252 quasiequivalent morphological units to give the $T = 25$ tessellation of the icosahedron. It shows some of the features of Table I in which biological structures begin to differ from purely chemical ones. The component particles are only quasiequivalent and some may indeed also be chemically somewhat different from others. The structure assembles itself in stages.

Such finite particles of many quasiequivalent units are now well known, but we wish here to draw attention to a class of geometrical structures with lattice-like properties, the consideration of which may extend classical crystallography in one of the directions necessary for the development of a new biological crystallography.

VORONOI POLYHEDRA VERSUS UNIT CELLS

Geometrical crystallography provides two ways of looking at natural spatial structures made of large numbers of identical units. The system customarily used analyzes a crystal as being composed of unit cells, identi-

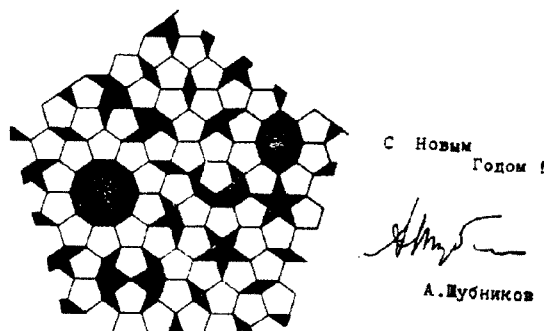


FIG. 3. New Year card from A. V. Shubnikov showing possible tiles in a pentagonal tessellation.

cal parallelepipeds in identical orientation, which repeat by lattice translations. Here "identical" means surroundings identical also in absolute orientation with respect to some external frame or to some internal "compass."

The alternative system also breaks the crystal into identical space-filling polyhedra, but these need now not be translation-equivalent parallelepipeds. A space-filling polyhedron corresponding to a point is that region within which every point is nearer to the given lattice point than to any other. This region is called a Voronoi polyhedron or Dirichlet domain or a "Wirkungsbereich." Such regions can be defined for n -dimensions.

The dissection into Voronoi polyhedra can be performed for several levels:

(a) With respect to Bravais lattice points. B. N. Delaunay has enumerated the 24 types of polyhedron (differing in the topology of their faces) which correspond to the 14 Bravais lattices.

(b) With respect to a point representing the asymmetric unit in a crystal structure. Each polyhedron is identical with every other but they occur in a number of orientations. It seems that all but on one of the space groups can be uniquely generated by the packing of appropriate convex polyhedra.^{5,6} The different proportions possible produce a great variety of topologically different polyhedra and it appears that the maximum number of faces is probably 38.⁷

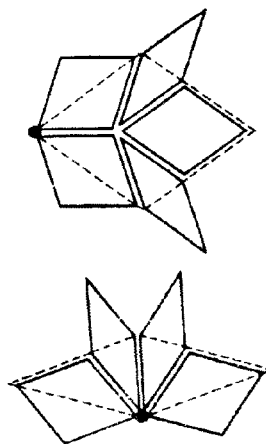


FIG. 4. The recursive rule for the subdivision of the two rhombic quasi-unit cells in two dimensions.

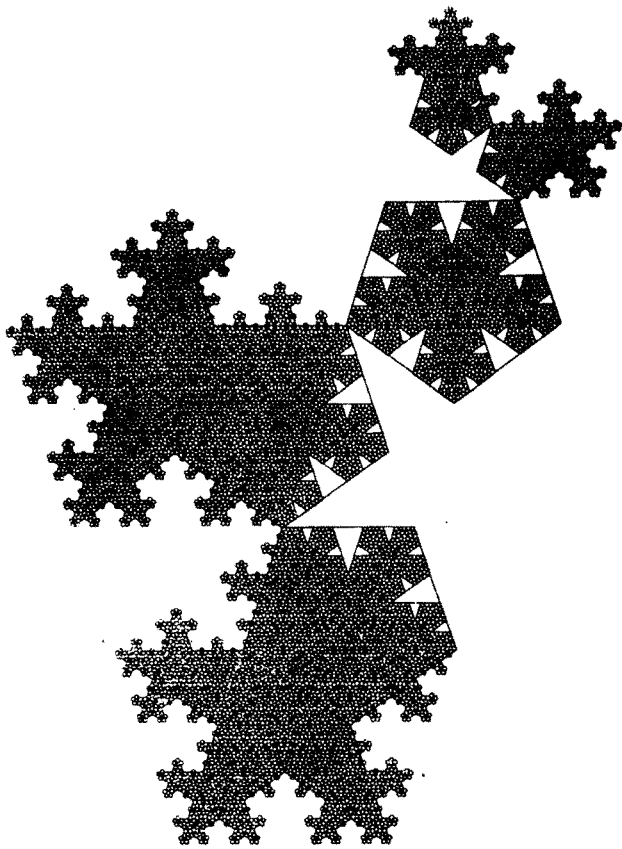


FIG. 5. The pentagonal snowflake. The hierarchic packing of pentagons. (Computer drawing by R. H. Mackay).

(c) With respect to single atoms. The polyhedron about each atom begins to have physical significance, since each face corresponds to a coordinating atom and gives a precise, quantitative definition of coordination in terms of solid angle. Using the radical plane instead of the bisecting plane, atomic radii can also be represented. These polyhedra can also be modified to represent, following J. C. Maxwell,⁸ the forces between atoms.

Although the dissection of a crystal into unit cells arises naturally from the experimental procedures of x-ray diffraction, where the real lattice is the transform of the reciprocal lattice, it induces the attitude that the crystal structure consists of molecular motifs hung in a framework of symmetry elements. In fact the opposite is the case and the space group arises from the local interactions of the components, although a consideration of the vibrational modes of the lattice makes the two descriptions more equivalent.

The Wirkungsereich approach emphasizes that the domains have some physical significance in real space, being closely allied to coordination polyhedra. Correspondingly, it also carries over directly to the discussion of noncrystalline structures (or clusters or individual molecules) where there are no unit cells and it permits a uniform treatment in all cases. J. L. Finney and others have shown how finite structures can be treated as terminated by allowing a sphere of appropriate radius to roll

all over the external surface and contribute to terminating faces for the polyhedra.

SEMIREGULAR QUASILATTICES

We wish to consider here types of structure in which there are two different shapes of "unit cells" arranged in what we might call a semiregular quasilattice. These patterns arise from purely mathematical considerations, but even if they do not correspond to physical structure, they may provide interesting suggestions as to some ways in which a biological crystallography may develop.

These structures arise through various attempts to extend the conventional compass of symmetry theory. We will consider, in particular, a solid structure composed of two kinds of rhombohedra. Their sides are equal and their vertex angles are 63.43° and 116.57° . Thus one rhombohedron is acute and the other obtuse. (We might recall that fcc iron has a unit rhombohedral cell with $\alpha = 60^\circ$ and bcc iron has a unit rhombohedral cell with $\alpha = 109.47^\circ$ although we cannot find any evidence for the actual appearance of our pentagonal structure). Because of the great difficulty in illustrating the complexities of the three-dimensional structure, the development of the pattern will be explained in terms of the corresponding pattern in two dimensions, which is obtained as a section broken (so as not to cut any of the cells) through the three-dimensional structure rather than as a strict section.

A zonohedron is a polyhedron, all faces of which are centrosymmetrical and bounded by pairs of equal and parallel faces. However, we will take the restricted definition which requires that each face should be a rhombus. There are two main families of such zonohedra, one with cubic symmetry and the other one with icosahedral. The plane pattern we are considering might be regarded as a member of the latter family but of infinite radius. The rhombic dodecahedron [with $\alpha = \arccos(1/3) = 70.53^\circ$] is the space-filling Voronoi polyhedron for the bcc lattice and represents the first of the cubic-symmetry series. The rhombic triacontahedron [with 30 rhombus faces with $\alpha = \arctan(2) = 63.43^\circ$], a member of the icosahedral series, will prove to be the key figure for the three-dimensional Penrose pattern. Further tessellations with icosahedral symmetry give figures with more than one kind of face. The first case, $T = 3$, gives a polyhedron with 90 rhombic faces of two kinds 60 with $\alpha = 70.53^\circ$ [$\arccos(1/3)$] and 30 with $\alpha = 41.81^\circ$ [$\arcsin(2/3)$].

The fundamental plane pattern from which the theory will be developed is shown in Fig. 1. It consists of a plane tessellation of two kinds of rhombus; one with $\alpha = 72^\circ$ and the other with $\alpha = 36^\circ$ or 144° .

This figure was developed independently by several authors but is best called the Penrose pattern to mark its principal contributor, R. Penrose,⁹ with the aim of developing sets of tiles which would cover the plane only nonperiodically, produced first a set of six tiles and then a pair of tiles with this property.¹⁰ Looking back from this, K. Husimi¹¹ had published a diagram showing how spaces in a hierarchic tiling of regular pentagons could contain smaller pentagons, but he did not fill the interstices fully. Later, A. L. Mackay¹² attempting to

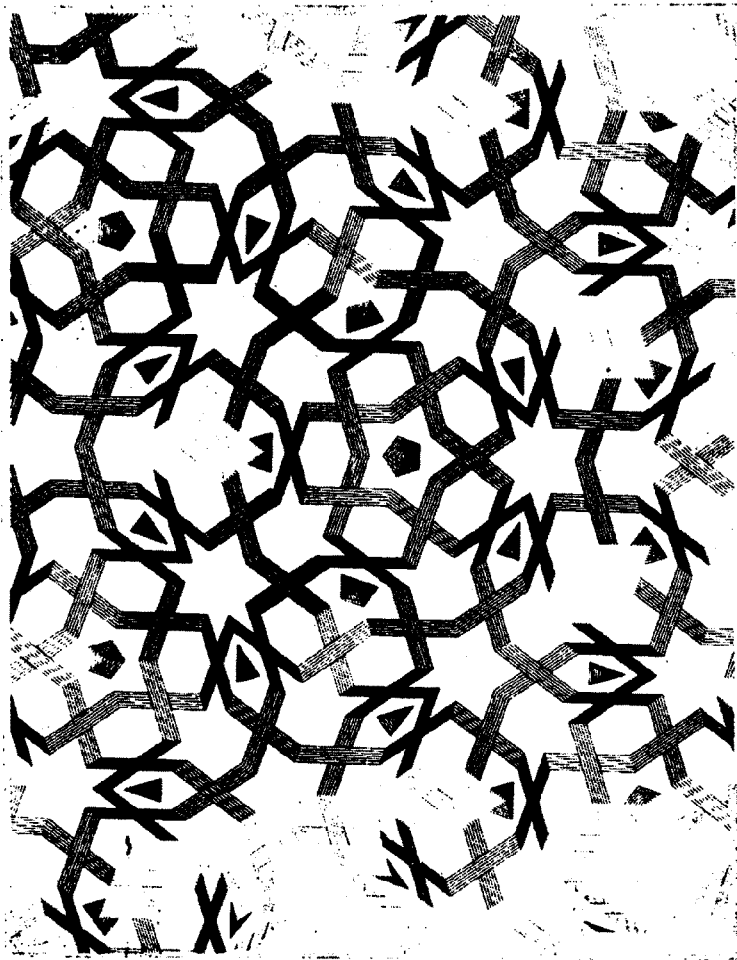


FIG. 6. The use of an Islamic motif to give asymmetric units which repeat in an infinite non-periodic pattern.

incorporate local five-fold axes into sphere packings by the hierarchic packing of pentagons in the plane and icosahedra in space, came upon essentially the same pattern. He found two units A and B (Fig. 2) each of which is the gnomon of the other. (A gnomon is a figure which, being added to another figure, leaves the resultant figure similar to the original). However, very many people from Albrecht Durer to A. V. Shubnikov, have examined the intriguing properties of packings of pentagons (Fig. 3). The triangles A and B of Fig. 2 are, in fact, each half of the rhombs of Fig. 1. In Penrose's version his units of "kites and darts" are the same units A and B combined differently.

GENERATION

The pattern is generated by the recursive subdivision of the two rhomboidal or rhombohedral units. In the plane Fig. 4 shows the system. The 72° unit (θ_1) is divided into two smaller 72° units (θ_2) and one 144° unit (θ_1) is divided into one θ_2 unit and one θ_2 unit. One vertex of each unit is marked as a pole and the three vertices which were not poles become poles in the next subdivision. The ratio of the numbers of the two kinds of tiles converges to $\tau = (1 + 5^{1/2})/2$ following the Fibonacci series: 2/1, 5/3, 13/8, 34/21 This ratio is irrational and demonstrates the

nonperiodicity of the infinite structure. In successive orders the linear dimensions of the tiles are reduced in the ratio τ .

The pattern has very many properties, only a few of which can be mentioned here. Reference may be made to a forthcoming monograph by B. Grünbaum and G. C. Shephard, "Tilings and Patterns," (Freeman, San Francisco).

THE HIERARCHIC PACKING OF PENTAGONS

Packing five pentagons around another of the same size to make a larger pentagon of the next order and filling in the interstices with the parts A and B mentioned, gives a pattern of the same geometry as that of Fig. 1. Figure 5 shows how the pattern builds up like a pentagonal snowflake. In this figure the outlines of the pentagons as well as of the pieces A and B are shown. If the two rhombuses are made fully asymmetric, by giving them interlocking perimeters or by applying a design motif continuous from one to the other, aggregable patterns can be produced (Fig. 6). Penrose has produced pairs of jigsaw puzzle pieces which force the nonperiodic pattern when they are assembled.

INDICES

The poles of the pattern from an array, which might

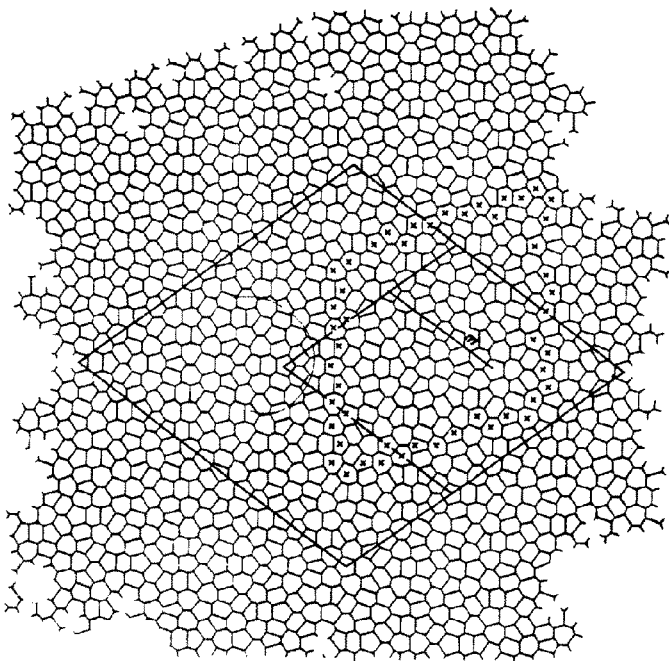


FIG. 7. The Penrose pattern drawn with a Voronoi polygon dissection. A local mirror plane and its domain of operation is marked by heavy lines.

be called a quasilattice, and their positions can be specified by indices which represent integral steps along the five vectors which make up the redundant set of axes in two dimensions. The five unit cell edges, a_1, a_2, a_3, a_4, a_5 , are 72° apart. A vector in direct space can be specified as $\mathbf{V} = U_1\mathbf{a}_1 + U_2\mathbf{a}_2 + U_3\mathbf{a}_3 + U_4\mathbf{a}_4 + U_5\mathbf{a}_5$ where $U_1 \dots$ are integers. When n redundant axes are used as in the hexagonal system of the four index Miller-Bravais indices, there are relations between the indices. It has been shown too that the redundant reciprocal axes can be defined using the generalized inverse of the metric matrix and that all normal calculations can thus be carried out. W. F. Lunnon (private communication), on the author's suggestion, has carried out the Fourier transformation of the Penrose pattern, both optically and algebraically, with the most elegant results.

SYMMETRY

The symmetry of the overall basic pattern (if asymmetric units are used) is five and there is one exact center at which the five-fold axis lies. If the units had their own symmetry, such as a mirror plane, then the overall symmetry would be $5mm$. However, the interesting feature is local symmetry of limited range. Figure 7 shows the domain of a local plane of symmetry in the version of the pattern in which Voronoi cells, rather than rhomboids, are drawn. There are also five-fold axes of limited range. A great variety of motifs can be put into the "quasi-unit-cells" given the basic succession rules. Circles, for example, give either coverings or packings which form useful models of atomic packings which may be used as starting points for energy minimization searches.

THE THREE-DIMENSIONAL PATTERN

The same type of construction can be made in three dimensions. Here the two basic quasi-unit-cell are acute

and obtuse rhombohedra with identical faces and interaxial angles of $\alpha = 63.43^\circ$ ($\arctan 2$) and its supplement. These combine into rhombic triacontrahedra (Fig. 8) which have 30 faces, 32 vertices and 60 edges and which are each composed of 10 acute and 10 obtuse rhombohedra. This packing is due to Robert Ammann, who first pointed out the key role which the rhombic triacontrahedron plays in three dimensions, the same role as the regular decagon plays in two dimensions. Large acute rhombohedra are divided recursively each into three acute and two obtuse rhombohedra of the next order. Each obtuse rhombohedron is divided into one acute and two obtuse rhombohedra. Again the ratio of the relative numbers converges to τ and the linear dimensions are also in that ratio.

In three dimensions there are six equivalent redundant axes parallel to the five-fold axes of an icosahedron and all quasi-unit-cell edges are parallel to these. Again, all vertices can be described by six integer coordinates with respect to these axes. It is on this account that we justify the name of "quasi-lattice." The vertices of each quasi-

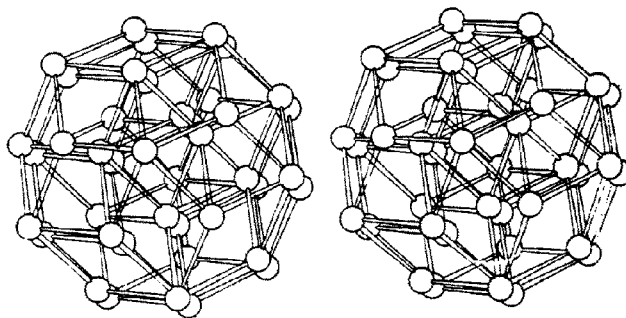


FIG. 8. Stereo-pair of the dissection of a rhombic triacontrahedron into acute and obtuse rhombohedra following the three-dimensional Penrose pattern.

unit-cell has three of the six indices in common and all indices are reckoned mod {111111}.

The three-dimensional structure reduces to the two-dimensional pattern by breaking across perpendicular to any of the six cell-edge directions. Representation of even a small volume of the three-dimensional pattern becomes complex and difficult for the observer to grasp and models are difficult to build to an adequate accuracy with a sufficient number of units. Figure 8 shows how a rhombic triacontahedron is built up.

SIGNIFICANCE

We consider that the significance of the pattern for crystallography is that:

(a) It offers an example of an infinite structure produced by a simple rule, albeit one a little more complicated than those relating units in one of the orthodox space groups;

(b) it shows some of the properties of local symmetry and quasiequivalence;

(c) it shows, perhaps, one step from classical crystallographic structures towards the biological;

(d) it gives an example of a pattern of the type which

might well be encountered but which might go unrecognized if unexpected; finally,

(e) it provides rather beautiful patterns, like the snowflakes of Kepler, which are appropriate for accompanying birthday congratulations to Boris Konstantinovich Vainshtein, from the Department of Crystallography at Birkbeck College, London and from the author personally.

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