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Joint scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences and the United Physical Society of the Russian Federation (26 September 2001)

A joint scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences (RAS) and the United Physical Society of the Russian Federation took place on 26 September 2001 at the P N Lebedev Physics Institute, RAS. The following reports were presented at the session:

(1) **Galiulin R V** (Institute of Crystallography, RAS, Moscow) "Crystallographic picture of the world";

(2) **Lozovik Yu E** (Institute of Spectroscopy, RAS, Troitsk) "Structure and melting of classical and quantum crystals";

(3) **Vekilov Yu Kh** (Moscow State Institute of Steel and Alloys, Moscow) "Electron conductivity of icosahedral quasi-crystals".

An abridge version of presentations 1 and 3 is given below.

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Crystallographic picture of the world

R V Galiulin

1. Introduction

F Dyson begins his paper on the stability of elementary substances [1] with apologies for his proof being extremely long, complicated and unattractive. It is necessary therefore that someone else should treat the entire problem from a different fresh viewpoint. The present paper is based on the assumption that a substance achieves the minimum of its energy by crystallization. This concept follows from reasoning of R Feynman [2]: if somewhere the atoms settled themselves in such a way that their arrangement corresponded to the lowest energy, then in another place the atoms will assume a similar pattern. Recent advances in geometry and crystallography [3, 4] permit one to make this syllogism geometrically rigorous and extend it to any discrete states of matter (quarks, neutrons, atoms, molecules, and supergalaxies).

2. Delaunay gas

In 1924, the prominent Russian geometrician B Delaunay (Delone) proposed an original technique for studying discrete sets [5], later to become known as the Delaunay empty sphere method. Consider a system of points (the Delaunay system [6, 7]) that satisfies two requirements:

(1) r-discreteness — there exists a shortest distance between the points of the Delaunay system;

(2) R-homogeneity — the space is covered with spheres of radius R, described around all points of the Delaunay system.

In the general case, Delaunay systems may be regarded as a model of ideal gas (Delaunay gas). If $r = \text{const}$ for all points of the system (i.e. the shortest distance between all points is the same), then such Delaunay systems represent all arrangements of centers of hard spheres in the packings of spheres. Notwithstanding the generality of requirements, Delaunay systems are very informative from the standpoint of mathematics, and quite natural from the standpoint of physics. Let us enumerate some general features of Delaunay systems.

Lemma 1. $r \leqslant 2R$.

Observe that the centers of atoms in most real atomic structures form the Delaunay systems for which $r \geqslant R$.

Lemma 2. For the construction of a Dirichlet – Voronoĭ polyhedron of any point of the Delaunay system, sufficient are the points of this system that fall within a sphere of radius $2R$, described around this point, and the diameter of the polyhedron does not exceed R.

Lemma 3. The Delaunay system is $2R$-connected — that is, any two points of the system can be connected with a broken line whose vertices are the points of the system, and each segment is not longer than $2R$.

3. Delaunay condensate

Consider now a sphere that does not contain points of the Delaunay system. We keep blowing this sphere up until it touches some point of the Delaunay system. Increasing the radius of the empty sphere in such a way that the points it has touched remain on its surface, we finally get a 3D complex of points of this system. A convex envelope spanned on such points is known as a Delaunay polyhedron. All such polyhedrons form a partition called the Delaunay triangulation. The Delaunay triangulation is currently becoming one of the main methods of computational geometry and computational physics [8].

Lemma 4. For any Delaunay system located on a sphere, the Delaunay triangulation is the edge net of the polyhedron inscribed in the sphere.

Lemma 5. If the Delaunay triangulation for a finite system of points on a 2D sphere is combinatorially regular (i.e. for any two points there exists a combinatorially topological transformation that converts these points one into the other and the entire system into itself), then it is combinatorially equivalent to one of the Platonic solids, Archimedean solids, and two infinite sequences of prisms and antiprisms (Fig. 1).

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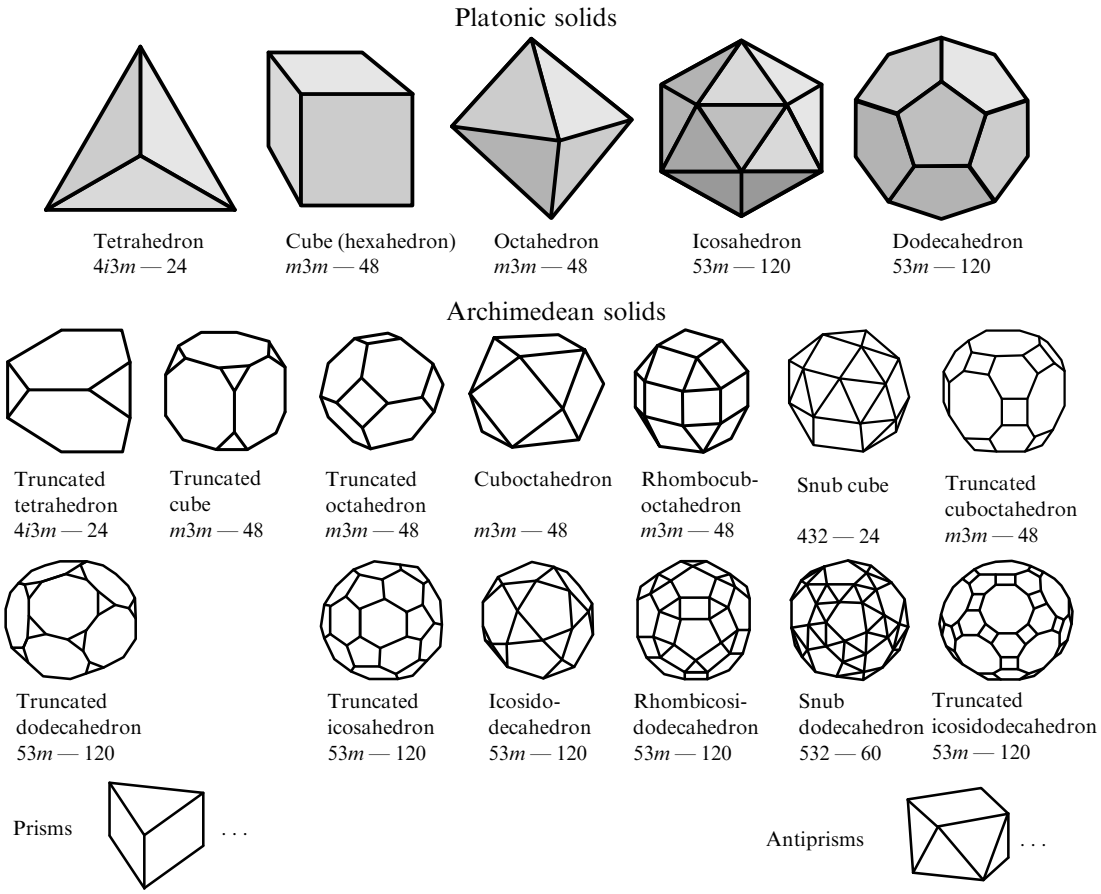

Figure 1. Regular and semiregular isogons.

Lemma 6. The Delaunay triangulation of any orbit of points on the Euclidean plane is combinatorially equivalent to one of the Kepler nets — that is, one of the isogonally regular nets composed from regular polygons.

The physical meaning of the Delaunay triangulation derives from the fact that it contains all the most important bonds in the atomic structures — amorphous and crystalline [9]. Observe also that the radius r for atomic structures (amorphous and crystalline) is calculated from experimental data, and is restricted from above by the criterion of Lemma 1. The Delaunay triangulation is unique, and its edges do not exceed $2R$ in length. When a new point is added to or removed from the Delaunay system, the triangulation edge net only changes in the small neighborhood of this point. This is the reason why triangulation becomes a powerful method for studying discrete matter. It unambiguously characterizes the topology of its links.

4. Ideal crystal

The physically acceptable rigorous definition of ideal crystal is only possible today on the basis of Delaunay systems.

Take a point in an arbitrary Delaunay system and connect it with all other points in this system. Such a construction is known as the global star of the given point in the given Delaunay system. Generally, the global stars for different points in the same Delaunay system are different. The Delaunay system is referred to as regular (an ideal crystal) if the global Delaunay stars of all its points are congruent. In other words, each point of the system is surrounded by all other points of the system in the same way. From the condition of an equal surrounding of all the points it follows that for any two points there exists a transformation that converts the first point into the second, and the entire system into itself. The total set of such transformations constitutes a group known as the Fedorov (spatial) crystallographic group. Geometrically, the Fedorov group is defined as the discrete group with a finite fundamental domain [10]. (The fundamental domain of a group denotes that portion of space that does not contain points equivalent with respect to the group transformations, but any point of the space is equivalent to the point from this population.) There are 219 such abstractly different groups [11] or 230 Fedorov groups counting the enantiomorphic pairs. The principal unitary representations of Fedorov groups can be found in Ref. [12].

In this way, the ideal crystal is said to be any arrangement of atoms or finite groups of atoms that are equivalent with respect to a Fedorov group. The crystal is defined in terms of the Fedorov group. Notice that the Fedorov groups are n-dimensional and exist in all constant curvature spaces [13].

From the standpoint of conservation laws [14], crystallographic symmetry corresponds to atomic indistinguishability. It is in crystal and only in crystal that atoms can be absolutely indistinguishable.

5. Local theory of crystal growth

The above definition of ideal crystal, however, does not explain the reasons for its nucleation and growth, because there are no natural causes by which every atom could control the atoms that surround it all the way to infinity. Because of this, the local definition of regularity was formulated in the spirit of Feynman's reasoning [3, 15].

Stogrin's theorem. If each point of the Delaunay system on the Euclidean plane is equally surrounded by other points of the system in the circle of radius $4R$, then such a Delaunay system is regular, i.e. it constitutes an ideal two-dimensional Euclidean crystal.

This local theorem was reproved by L Danzer in a different formulation, which is better suited for studying the processes of condensation of matter [16].

Danzer's theorem. If the Delaunay system can be uniquely reconstructed from a finite number of points and a finite number of conditions imposed on their extensions, then such a system is an ideal crystal.

From the Danzer theorem it follows that the statement that quasi-crystals such as Penrose tilings are not an artefact but experimental reality is equivalent to the statement that it is possible to measure exactly the diagonal of a square. However, quasi-crystals may also be regarded as ideal crystals in the Lobachevsky space [17].

6. How large is the gap between chaos and order?

In the world there are only two practically unattainable states of matter: chaos (Delaunay gas) and ideal crystal (a regular Delaunay system). All other states of discrete and homogeneous matter can be regarded as intermediate between these two. If the substance acquires such an amount of energy that is capable of destroying it, then it moves towards chaos, otherwise it will spend its energy on ordering. Ideal (or long-range) order, however, can only be attained in crystals. "Crystals are death", — declared E S Fedorov, the founder of contemporary crystallography [18], and this idea agrees with Feynman's reasoning [2].

Now let us see how large is the gap between ideal crystal and chaos in the case of the Euclidean plane. From the arguments developed above it follows that if every particle of discrete homogeneous matter is equally surrounded in a circle of radius $4R$, then we get an ideal crystal. As the radius of this surrounding decreases, we start getting twins — that is, Delaunay systems whose extension from the selected finite point set is not unique. When the radius of equal surrounding becomes smaller than $2R$, we get the Delaunay systems where the islands of similar environment reduce to one dimension, which leads to chaos. In this way, by the criterion of similar environment (note, however, that other criteria are also possible), the gap between chaos and ideal crystal is not greater than $2R$.

Since it is not possible to give a rigorous description of chaos, crystals are used as a kind of reference for describing other states of matter. In particular, there is hope to describe the structure of liquids as Delaunay systems in which small displacements of particles alter the topology of Delaunay triangulation.

In 1988, M I Stogrin [19] proved that there exist regular partitions of an Euclidean plane with planigons in which the centers of action of these planigons form chaotic systems. Shtogrin's result has not yet been interpreted either by mathematicians or by physicists.

7. Topological regularity

In 1916, A V Shubnikov formulated the following problem [20]. Let similar atoms on the plane have equal finite number of bonds with one another. What is the number of possible different two-dimensional crystal structures? It turned out that there are just 11 combinatorially different types, and each of these types can be represented by Kepler's net [21]. Thus, the emergence of two-dimensional crystal does not depend on the length of bonds between the atoms and the angles between these bonds — it is only necessary that the same number of bonds should join at each node of the net. After that these bonds and angles, without breaking, will rearrange in such a way that the nodes of the net form a regular Delaunay system. Consequently, it follows that the values of metric parameters do not play any significant role in the formation of 2D crystals. In the case of three-dimensional space, this question remains open.

8. Orbifolds

The exact representation of the independent domain of the Fedorov group consists in that the equivalent points of boundaries 'are glued' together. In this way in the topology we get compact locally Euclidean manifolds (orbifolds) [22, 23]. Such 'gluing' may also have physical meaning: the independent domain can be glued together along the boundary points in such a way that all available chemical bonds are compensated. Such an orbifold may be taken for the model of nanocrystal. Free atoms may also be regarded as compact manifolds.

The relaxation of enormous stresses may take place through the disintegration of the crystal structure into nanocrystals [24]. Such a crystal decay into nanocrystals may be triggered by decreasing temperature or by increasing pressure. The structure may disintegrate into separate nanocrystals (zero-dimensional decay), into separate linear chains of nanocrystals (one-dimensional decay), or into separate layers (two-dimensional decay). The decomposition of crystal into the hierarchy of blocks (whereby each block further disintegrates into smaller blocks, so that all blocks together make a fractal) is also the conversion of its structure into the nanocrystalline state. As the crystal grows, the nanocrystal (an individual neutral atom or group of atoms forming the independent structural domain) breaks the self-closed bonds and the corresponding bonds on the surface of the seed, and smoothly integrates into the crystal structure.

The charge of the orbifold is neutral, which, together with its very small size (one or several independent domains), facilitates the 'omnipresence' (in Vernadsky's sense) of such formations. Fine dispersion minerals apparently exist in the form of orbifolds. As the size of the orbifold reaches a certain threshold, however, the orbifold can no longer close on itself, and starts to form aggregates (not necessarily crystals).

9. Non-Euclidean structures

The fact that crystals favor the Lobachevskian geometry is vividly demonstrated by saddle-shaped dolomite crystals (Fig. 2). Their surface may be regarded as a portion of the Lobachevsky plane. All this plane, however, cannot be fitted into the Euclidean space without stress [25] which transforms this construction into dolomite dust, namely, a very natural phase state of the dolomite mineral.

The first purely spherical crystal is fullerene C_{60}, a *two-dimensional spherical diamond* (graphite is a *two-dimensional Euclidean diamond*) [26]. Since the constant curvature spaces, which alone can host the crystal growth, are locally Euclidean, the crystal can grow to a certain size (different for various species) according to its internal geometry. As the crystal grows further, internal stresses develop in it because of the nonuniformity of the real space (as follows from general relativity) or because its internal geometry is non-Euclidean.

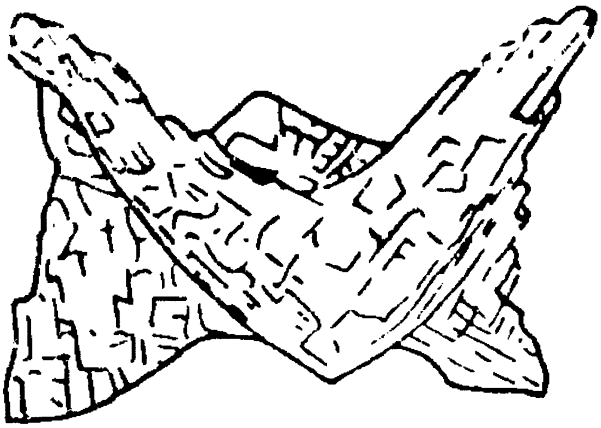

Figure 2. Crystal of dolomite.

The crystal relieves these stresses by producing imperfections through twinning, slipping, inclusion of foreign atoms, helical dislocations, edge dislocations, disintegration into blocks, and even bending the space [27]. Perfect diamond crystals are always highly stressed. For the same reason, their structure always contains atoms of nitrogen.

Observe also that the growth zones in crystal are regarded as its defects. However, a theory of finite zonal crystal was constructed on the basis of Riemann geometry [28].

10. Fractals

Some believe that only crystals with defects may exhibit fractal properties [29]. However, since the choice of boundaries of the fundamental domain of Fedorov groups (with the exception of Coxter groups) is not unique, fractal-type boundaries are also possible. In other words, ideal crystal can be built from the particles with fractal boundaries. In the quest for new approaches to high-temperature superconductivity, the motion of an electron in crystal was described by the simplest nonlinear equation with the periodicity feature [30, 31]. *Attractors* (points of attraction) in this motion are the points of a one-dimensional lattice (Fig. 3). On the complex plane, the nodes of this lattice are the integer points of the real axis. To visualize this motion, all the points that pertain to the same Dirichlet region of the node of one-dimensional lattice are painted with the same color that does not change as the point moves along. This gives us a dumbbell-shaped fractal pattern. This pattern will be reproduced when appropriate magnification is applied to any point on the boundary between the colors. This property of fractals is known as scale invariance. In the middle of each dumbbell we have the region of chaos — domains, where no information in principle can be gained with any experimental methods.

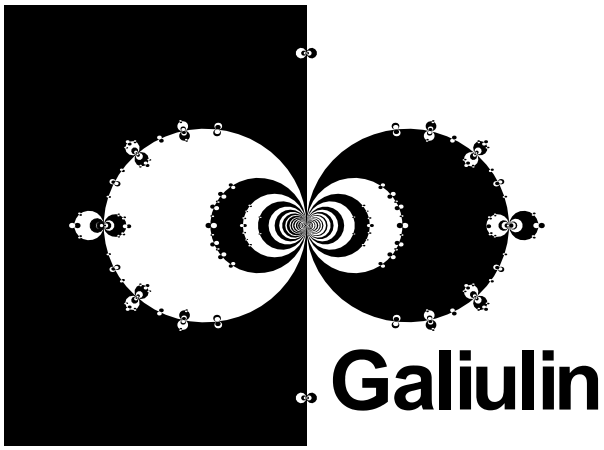

Figure 3. Fractal.

11. Crystal-like model of the Universe

Astronomers have noted that spiral galaxies, down to minor details, exhibit twofold rotation axes [32]. Had our world been two-dimensional, this would imply that the centers of galaxies in the Universe make up a regular system of points. In the case of three-dimensional Euclidean space, all admissible arrangements of twofold rotation axes are known. However, if the twofold rotation axes of galaxies correspond to one of the Fedorov groups in the Lobachevsky space, such regularity would be very hard to notice. This regularity will seem to be simply a chaos. It is quite possible therefore that the observable part of the Universe is a fragment of crystal structure in the Lobachevsky space [33]. Today there are already many publications devoted to the crystal-like model of the Universe (see, for example, Ref. [34]).

Observe now that neutrons in a neutron star also form crystals. Carrying this analogy further, one may expect that when a neutron star collapses (i.e. the neutrons are crushed down) we get a crystal made up of quarks — a black hole. The gravitational collapse of a black hole (as a crystal) apparently leads to the Big Bang. This hypothesis may be related to the anisotropy of the relict radiation, which may help us to define the symmetry of the exploded crystal [35].

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Electronic conductivity of icosahedral quasi-crystals

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Quasi-crystals are characterized by aperiodical atomic long-range order and the rotation symmetry that is forbidden for periodical structures (the existence of the 5-, 8-, 10-, and 12-fold axes of rotation). The former feature distinguishes quasi-crystals from amorphous objects (glasses), while the latter distinguishes them from crystals and incommensurate structures. Quasi-crystals are usually alloys of metallic elements, but their properties are different from those of crystalline and amorphous metallic phases. Like metals, quasi-crystals bear a finite electron contribution to their heat capacity, but this contribution is approximately one order of magnitude smaller than that defined in the nearly free electron approximation (pseudogap and, accordingly, low density of states $N(E_F)$ at the Fermi level).

However, the low density of states at the Fermi level does not explain the abnormally small low-temperature electric conductivity of quasi-crystals. The electrical resistivity of quasi-crystals decreases with increasing temperature, and it increases with increasing structural order and annealing of defects. The resistivity ratio $\mathcal{R} = \rho(4.2\ \mathrm{K})/\rho(300\ \mathrm{K})$ for the majority of stable quasi-crystals is several units, but for the icosahedral alloy i-Al–Pd–Re, whose perfect samples have $\rho(4.2\ \mathrm{K}) \geqslant 1\ \Omega\ \mathrm{cm}$, the ratio $\mathcal{R}$ may be as high as 200 and even higher, depending on the perfectness of the specimen.

The conductivity of quasi-crystals is represented as $\sigma = \sigma(0) + \Delta\sigma(T)$, where $\sigma(0)$ is the conductivity at zero temperature, which depends on structural disorder, and $\Delta\sigma(T)$ is the temperature-dependent component which may also depend on structural disorder. Almost all quasi-crystals exhibit a power-law temperature dependence $\Delta\sigma(T) \sim T^{\beta}$, where the exponent β usually varies within the interval $1/\sqrt{3} \leqslant \beta \leqslant 1.5$ in the range from ultralow temperatures to 700–1000 K. Linear dependence is usually observed at high temperatures. A reasonable explanation of the power-law temperature dependence of conductivity and its value at $T = 0$ K was proposed by Burkov et al. [1], who used the model of a Fermi surface with a large number of electron and hole pockets.

Recent experiments with perfect quasi-crystals of i-Al–Pd–Re have shown that at $T \leqslant 10$ K the conductivity can obey the Mott law

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right],$$

which describes hopping conduction with variable jump length. This implies that the sample occurs in the insulator state (Fermi glass), when the density of states at the Fermi level is finite, but the electron states are localized. Electron localization plays an important role in the low-temperature electron transport in amorphous alloys, granulated metallic films, and doped semiconductors. For these systems, electron localization is the consequence of disorder in the system (the Anderson localization).

Localization of electrons in a quasi-crystal differs in its nature from appropriate localization in standard disordered systems. The alloy i-Al–Pd–Re is a well-ordered quasi-crystal, and the improvement of structural order leads to an increase in its resistivity. Localization in quasi-crystal is a consequence of interference (phase coherence) of the electron states, and thus is associated with the symmetry and structure of the object: the more perfect the material, the more localized its electrons. While in the case of conventional Anderson localization the electron states are localized because the phase coherence of extended wave functions is destroyed by disorder, the main cause of localization in quasi-crystals is the phase coherence of wave functions.

This can be proved by treating the quasi-crystal as the structural limit of the sequential of rational periodical approximants (crystal analogs) with increasing lattice period. The volume of the Brillouin zone decreases with increasing order of the approximant, because the lattice