

## QUASICRYSTALS: A DISTANCED OVERVIEW\*

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## ABSTRACT

A short overview of the current state in the field of quasicrystals is presented with an emphasis on the fundamental questions brought into focus by the advent of the field. Placing the research on quasicrystals in a broader context, it becomes apparent that the main questions which remain open are about the connections between the ground state structure and the interparticle interactions and between the nonequilibrium growth conditions and metastable states. From the point of view of experimental results, the main question about the structure of real quasicrystals remains unresolved.

Like in so many other cases in physics, the discovery of "real" icosahedral quasicrystals [1] was anticipated, although not predicted, several years earlier [2]. In fact, long before the discovery of quasicrystals, the group theory community had an opportunity to witness a development of the theoretical ground-work for studying quasicrystals as a special case of incommensurate crystals. For example, Janner and his co-workers [3] have insisted on several previous conferences on a beautiful and now indispensable view of incommensurate crystals as cuts through higher-dimensional crystals [4-6]; Reciprocal space description of translational order, now essential in the classification of Bravais classes of incommensurate and

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quasicrystals [7,8], was employed by Jarić [9] in the context of structural phase transitions; Kramer and his collaborators [10] initiated the use of group theoretical analysis to construct regular structures with non-crystallographic symmetry from higher-dimensional, reducible, but crystallographic, representations of the same symmetry [11]; Mackay [12] presented optical transform of the Penrose quasilattice and suggested, what is now a common knowledge, it consisted of Bragg spots, manifesting a perfect, albeit aperiodic translational order.

In this lecture, I would like to present a short overview of the state of the art in the field which has experienced an exponential growth over the last three years. Rather than going into reviewing numerous detailed and specialized contributions, often with a narrow and technical point of view, I would like to take a step back and try to place this field in a broader context so that unresolved fundamental and general questions, whose answers have ramifications beyond the current quasicrystal research, are brought into focus. More detailed introductory reviews of the field can be found in several new books [13].

What is, then, the reason many researchers are still skeptical about the existence of icosahedral quasicrystals? Are they right or has the existence been at least experimentally verified? Before answering these questions, we will first have to specify what is an acceptable mathematical ideal of a quasicrystal, what are the physical requirements for this ideal to be realized, and to which extent the real, experimentally observed quasicrystals exhibit the properties of this ideal.

A mathematically ideal translationally ordered structure should be represented by:

- (a) Discrete set of point-like atoms (delta functions);
- (b) Non-zero lower bound on the separation between the atoms;
- (c) Diffraction pattern consisting of Bragg peaks (purely discrete Fourier transform) at integral linear combinations of a finite set of scattering vectors.

The first two conditions are appropriate for a classical zero-temperature structure. At finite temperatures it might be more useful to view the structure in terms of a more general occupation probability (density), in which case (a) and (b) should be replaced by a more subtle condition. Note that the last condition also implies that a structure which satisfies (a) and (b) fills the whole space uniformly.

If the minimal number of scattering vectors which generate the diffraction pattern is  $D$ , and the maximal number of linearly independent vectors among them is  $r$ , then the structure is periodic if and only if  $D = r$ . Therefore, incommensurate crystals are further specified by:

(d)  $D > r$ .

Since  $r$  is at most equal to  $d$ , the dimensionality of the physical space, a structure is incommensurate whenever  $D > d$ . However, it is possible to encounter a situation when  $d > D > r$  in which case the structure would be an incommensurate liquid crystal, uniform in the  $(d-r)$ -dimensional space perpendicular to the  $r$ -dimensional space in which the density is quasiperiodic.

Since all integral linear combinations of the  $D$  fundamental scattering vectors form by definition a  $D$ -dimensional lattice, they can be embedded in a  $D$ -dimensional real space and chosen, for example, to generate a  $D$ -dimensional hypercubic reciprocal lattice. The physical "reciprocal" space with nonvanishing scattering intensity corresponds to an  $r$ -dimensional hyperplane. In fact, it can be shown that whatever density produced the diffraction pattern, it can be always represented by a  $d$ -dimensional planar cut through a  $(D+d-r)$ -dimensional density, hypercubic in the  $D$ -dimensional subspace and uniform in the remaining  $(d-r)$  dimensions. In particular, ideal atomic positions of an incommensurate (liquid) crystal, must be represented by the  $d$ -dimensional cut through the  $(D+d-r)$ -dimensional (liquid) crystal of  $(D-d)$ -dimensional atomic hypersurfaces.

It is conceptually important to make a distinction between the usual incommensurate crystals and quasicrystals characterized by the condition which implies and, consequently, replaces condition (d):

(e) Diffraction pattern has a non-crystallographic symmetry.

Not only that the difference between quasicrystals and the usual incommensurate crystals is manifested in some physical properties, such as the absence of hydrodynamic phase degrees of freedom, but it also played an important role in the initial skepticism about quasicrystals. Namely, by a small incommensurate modulation of a crystal structure, it is easy to construct incommensurate structures which satisfy conditions (a)-(d). Since the modulation is by assumption small, such an incommensurate structure has symmetry which is a subgroup of

the original crystal symmetry. Therefore, it is crystallographic. On the other hand, incommensurate structures with noncrystallographic symmetry can not be constructed in such a simple way; necessary symmetry increase requires a modulation amplitude on the order of the original interatomic spacing [14], so that it is nontrivial to guarantee the fulfillment of the condition (b). Only after the experimental discoveries of icosahedral and decagonal quasicrystals, it was realized that the decagonal Penrose quasilattice [15], and its icosahedral three-dimensional extension, the Ammann quasilattice [16], satisfy all the conditions (a)-(e).

In terms of the atomic hypersurfaces, the difference between crystallographic and noncrystallographic symmetry is manifested in the fact that noncrystallographic symmetry forces discontinuity of these hypersurfaces. Whether the hypersurfaces are continuous or not has important consequences on the excitation dynamics and elasticity at low temperatures [17]. Discontinuity of the hypersurfaces leads to the presence of  $(d - r - 1)$ -dimensional structural defects whose energy is only  $(d - r - 2)$ -dimensional. One of the possible consequences is the "hierarchical" melting of quasicrystals on successively shorter scales, accompanied with a broadening of diffraction peaks [17].

The most important requirement which a mathematically ideal quasicrystalline structure must satisfy in order to represent a physical idealization, is that it minimizes a physically reasonable interaction energy or, at finite temperature, a thermodynamic potential. Of course, what should be accepted as a "physically reasonable" interaction, is not at all obvious. Certainly, the interaction should be finite-range, decaying, for example, exponentially at large distances, sufficiently repulsive below certain distance (to prevent a local collapse), and attractive above certain distance (to ensure a solid-like ground state at zero external pressure). Furthermore, the interaction should not be too specific. In a certain sense, it should be generic. Namely, one would like to be able to construct a *family* of interactions, parametrized by some physically significant quantities such as interaction strength, range, anisotropy, etc. Then, this parameter space should have sufficiently large dimensionality and richness to allow various equilibrium structures, such as periodic and perhaps aperiodic ones, occupying in the parameter space regions of nonzero volume (i.e. of co-dimension zero).

Most of the current skepticism about quasicrystals is based on the following

conjecture:

The ground state of an infinite number of (classical) particles of finitely many types, interacting via “physically reasonable” interactions, contains only a finite number of different environments.

Clearly, a structure with a finite number of distinct infinite-range environments is indeed periodic. However, the above conjecture is based on the *fact* that for most interactions there is a finite number of minimum energy finite-range environments, and on the *hope* that for finite-range interactions, such (sufficiently large) finite-range environments could be assembled into a minimum energy infinite structure. In this way minimization of the interaction energy would become a tiling problem. Unfortunately, even in the tiling problem, given a finite number of tiles, with a finite-range matching rules, it can not be generally asserted that a space-filling tiling with a finite number of infinite-range environments would result. Indeed, even the space-filling property might not be satisfied.

For example, most of the central potentials for a single species system have thirteen-particle icosahedral clusters as a minimum energy finite-range environment, so that the minimization problem reduces to the tiling problem with regular dodecahedra. Clearly, dodecahedra do not tile the three-dimensional space. This is an expression of the “frustration” which is intrinsic to such potentials and which is thought responsible for the formation of amorphous structures. On the other hand, a class of quasilattices, including Penrose and Ammann quasilattices, which satisfy (a)-(e), can be constructed having a finite set of finite-range environments and, at the same time, an infinite number of infinite-range environments. Unfortunately, except for the obvious and clearly non-generic interaction expressed by the matching rules, no generic interaction has been invented for which such a quasilattice would be the ground state. Similarly, most of the model free energies which can give quasicrystal states, fail the requirement that they are generic. The only exceptions can be found in the approximate density functional theories [18] and [19], the latter of which gives only a metastable quasicrystalline state.

Therefore, the conjecture is neither proved, nor a counter example is known. Those who believe in periodicity of the ground state do not seem too eager to find a proof, and often look for an excuse in the statement that a proof of the conjecture must be too complicated, otherwise it would have been already found. On the other

hand, those who are looking for an analytical counter example to the conjecture have not been successful. In this situation it seems most promising to resort to computer simulations. Unfortunately, even computer simulations have so far failed to produce quasicrystalline equilibrium states. Current molecular dynamics simulations [20] of a system of Lennard-Jones clusters with an orientationally dependent modulation could change this situation dramatically.

An additional difficulty in understanding the occurrence of quasi-crystalline structures stems from the impossibility of growing such ideal structures using only local growth rules [21]. For example, in the case of the Penrose quasilattice, in order to decide whether a portion of the lattice contains a defect or is in equilibrium, it is generally necessary to examine parts of the lattice arbitrarily far from this portion [22]. However it might be possible to always relax such defects by a soliton-like rearrangement of a number of sites of the order of the sample's surface, although the rearranged sites will generally not be confined to the surface. In case of the Penrose quasilattice, defective sites at the surface of a finite quasilattice, can be confined to the boundary of a Conway decagon, and thus eliminated by a successful soliton-like flipping of Conway worms. This mode of annealing and growth is not that much different from growth of ordinary crystals.

Without any conclusive theoretical results about the existence or nonexistence of quasicrystals one would like to turn to experiments for an answer. Unfortunately, the experimental results are not conclusive either: The diffraction patterns show distortions from perfect icosahedral symmetry; The peak widths indicate translational correlation lengths no longer than  $\approx 1000\text{\AA}$ ; The diffraction pattern of a single quasicrystallite can not be fitted using a single, perhaps twinned crystal structure; No "quasicrystalline" structure seems to be stable.

Three proposals, the twin model, the icosahedral glass model, and the quasicrystal model, are currently competing for an explanation of the experimental data. In twin models [23] appearance of icosahedral symmetry is interpreted as resulting from twinning a cubic or rhombohedral crystal in five or twenty icosahedrally related orientations. Current twin models are unable to explain a single complete set of diffraction data. They require crystals with unit cells containing in excess of  $\sim 1000$  atoms and, more seriously, different grains of the same quasicrystal seem to require different size unit cells.

The icosahedral glass models [23] attempt to explain the structure of "quasicrystals" as perfectly orientationally ordered but positionally glassy with a finite translational correlation length. Such an "icosahedritic" state emerges naturally as an intermediate state between a liquid and a perfect quasicrystal [18]. The icosahedral glass model has a difficulty explaining apparent regularity in transmission electron micrographs along the high symmetry axes. It is also difficult to obtain peak widths, shapes, and intensities in good agreement with experiments.

A satisfactory phenomenological ideal-quasicrystal model must first describe the ideal atomic structure of the quasicrystal, that is, it must provide a description of the three-dimensional atomic surfaces decorating the equivalent six-dimensional hypercrystal. Then, some kind of disorder must be introduced to account for deviations observed in experiments. Unfortunately, neither of these two steps has yet been completed. Several partial answers to the first step have been proposed in terms of tiling models [23]. In such models a quasicrystal structure is described by identifying certain structural units, atomic clusters, which are then packed using a tiling such as the Ammann tiling. An alternative approach, which seems quite successful [24], is to directly describe the three-dimensional atomic surfaces in six-dimensions.

A procedure which combines both of the above approaches, would be to consider a known large unit cell crystallographic structure related to the quasicrystal structure as a rational cut through the hypercrystal. In this way a finite set of points at the atomic surface would be determined, and the surface could be interpolated. By extending each point into a locally planar surface, one would be embedding the atomic clusters from the crystal into the quasicrystal in a systematic fashion. Whether a crystal structure is a good candidate for this procedure can be decided by directly using the diffraction data: one first constructs the six-dimensional Patterson function (density-density correlation function, Fourier transform of the diffraction pattern); the three-dimensional Patterson function of a good candidate crystal structure should be well approximated by the appropriate cut through the six-dimensional Patterson function of the hypercrystal.

As we mentioned above, it is not sufficient just to describe the atomic surfaces. In order to reproduce experimental results, it is necessary to be able to identify and describe disordering mechanisms responsible for peak shifts, broadening, asymme-

try, etc. Several groups have been able to qualitatively account for some features of the experimentally observed disorder assuming quenched phase dislocations [25] in addition to a growth induced uniform phase strain [26]. Another possible source of disorder is provided by the low energy structural defects, mentioned earlier in the text [17], which are characteristic of quasicrystals.

Nature of disorder in real quasicrystals can not be fully addressed without a reference to their metastability and nonequilibrium nature of their growth. It is quite possible, and suggested by experiments, that depending on the cooling rate, a transition could be observed between crystal, quasicrystal, orientationally ordered glass, and the usual glass structures. This brings into the focus another fundamental question: what is the nature of nonequilibrium structure formation and how the cooling rates affect the resulting structure. For example, even the equilibrium growth of large unit cell crystals is poorly understood.

In conclusion, the discovery of the icosahedral quasicrystals brought into focus two fundamental questions, about the nature of ground state structures and about the nature of nonequilibrium growth of stable and metastable structures. This in itself could turn out to be a sufficient outcome of the quasicrystal euphoria. Moreover, even if it turns out that real quasicrystals are orientationally ordered glasses, or even (twins of) large unit cell crystals, the ideal quasicrystal with a prescribed "disorder" will probably offer the most efficient and natural description of the system.

Quasicrystals are dead. Long live quasicrystals!

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