Icosahedral quasicrystals formed by particles with directional bonds

Eva G. Noya[1#] and Jonathan P.K. Doye[2#]

[1]*Instituto de Química-Física Rocasolano, Consejo Superior de Investigaciones Científicas (CSIC), Calle Serrano 119, Madrid 28006, Spain*
[2]*Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK*

[#]e-mail: eva.noya@iqfr.csic.es, jonathan.doye@chem.ox.ac.uk

The first experimentally observed quasicrystal was obtained by rapid quench of an Al-Mn alloy and had icosahedral symmetry. Since then, many icosahedral quasicrystals (IQC) have been found in other metallic alloys, but, so far, never in non-metallic or one-component systems. By contrast, axial quasicrystals, which are aperiodic in two dimensions but periodic in the third, have been also observed in some soft matter systems, in some cases with only one component.

Using computer simulations, we have recently shown that IQCs can be formed from particles with directional bonds by designing model particles whose geometries mimic the local environments of target IQCs generated by the cut-and-project method. This strategy was first validated for IQCs of body-centered (BC) and primitive (P) types, with the simplest models consisting of two particle types [1]. Now we have used the same approach to design model patchy-particle systems with only one-particle type that robustly assemble into a face-centered (FC) IQC (Fig. 1). The FC IQC assembled in our simulations is approximately isoenergetic with periodic approximants and has close to zero phason strain. We also assess the potential for realizing experimental analogues of our model systems by exploiting the impressive recent advances in the design of DNA origamis [2] and proteins [3] that can form periodic crystals.

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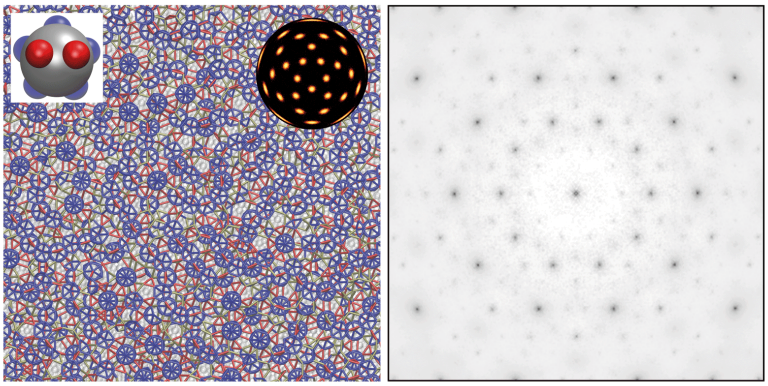

Fig.1: One-component FC IQC structure formed from patchy particles with seven interaction sites. Its diffraction pattern projected along a 5-fold symmetry axes is also shown.

3-dimensional patchy-particle axial quasicrystals

Jonathan P.K. Doye[1#], Daniel F. Tracey[1], Akie Kowaguchi[1,2], Savan Mehta[1] and Eva G. Noya[3]

[1]*Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK*
[2]*Department of Mechanical Engineering, Keio University, Yokohama 223-8522, Japan*
[3]*Instituto de Química Física Rocasolano, Consejo Superior de Investigaciones Científicas, CSIC, Calle Serrano 119, 28006 Madrid, Spain*
[#]e-mail: jonathan.doye@chem.ox.ac.uk; email: eva.noya@iqfr.csic.es

Here we describe our progress in designing and simulating particles with directional interactions that are able to assemble into 3-dimensional axial quasicrystals. We report examples with dodecagonal and octagonal symmetry. In the dodecagonal example, we generalize previous success in forming a 2D dodecagonal quasicrystal from 5-patch discs [1] and binary mixtures of 5- and 6-patch discs [2] by designing particles that forms stacks of such layers [3]. The nature of the interactions between such layers is simple with particles designed to sit directly above the particles in the previous layer. One of the interesting features of the obtained 3D dodecagonal quasicrystals is that they almost invariably grow with at least one screw dislocation (the Burgers vectors are along the periodic direction).

For the octagonal quasicrystal our starting point is the 2-dimensional octagonal Ammann-Beenker tiling of squares and thin rhombs. We generalize this to 3 dimensions and analyse the environments within this ideal quasicrystal as a basis for designing patchy particles. These environments have from 3 to 8 neighbours. We first investigated a binary system of 5-patch and 8-patch particles and found that it forms an octagonal quasicrystal. Although the average coordination number is roughly the same as the ideal quasicrystal, the 8-patch particles very rarely use anywhere near all their patches. Indeed, we also found that a one-component system of 5-patch particles forms an octagonal quasicrystal. In both these systems, edge dislocations are common. In addition, we found that a one-component system of the 8-patch particles assembled into an aggregate with mulitiple twinned crystalline domains whose diffraction pattern also exhibits 8-fold symmetry.

Acknowledgements: E.G.N. acknowledges financial support from Agencia Estatal de Investigación, Grant No PID2020-115722GB-C21.

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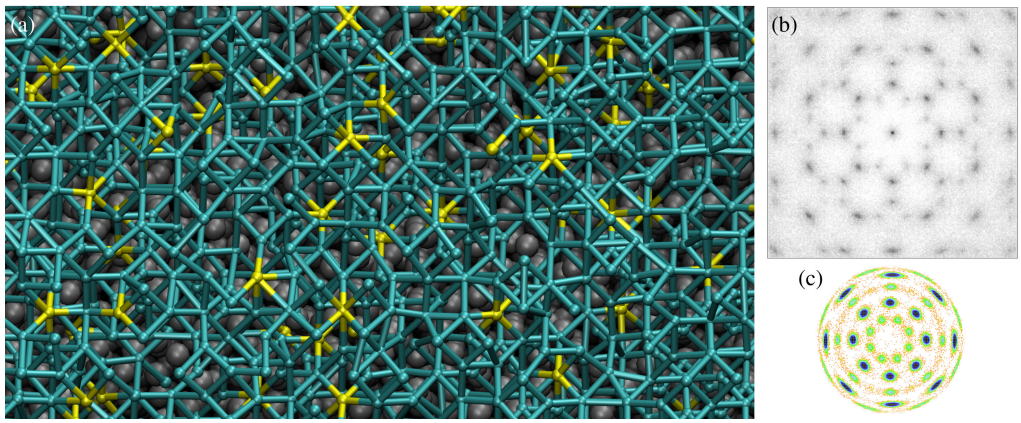

Fig.1: (a) a binary octagonal quasicrystal, (b) its diffraction pattern and (c) bond-orientational order diagram.

A Density Functional for Hard-Core Patchy Colloids

R. F. B. Weigel[#] and M. Schmiedeberg

Institut für Theoretische Physik I, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058 Erlangen, Germany

[#]e-mail: robert.rw.weigel@fau.de

Patchy colloids are particles with a decoration on their surface, making their interaction anisotropic. Recently we reported on a phase field crystal model of patchy colloids, where the density and orientation are treated as continuous fields [1]. The observed stable phases include multiple periodic crystals and even a quasicrystal, i.e., a pattern with long-ranged order, but no translational symmetry, see Fig. 1. For all structures the orientation vanishes on the density peaks. This feature, known for (ultra)soft particles forming rotator crystals and cluster crystals [2], is hard to reconcile with the notion of patchy colloids and the complex periodic and aperiodic structures observed in simulations of them [3], see Fig. 2.

To account for the essentially hard core of patchy colloids we now treat the density field with fundamental measure theory [4], still coupling it to an orientational field similar to [1]. We are especially interested in the differences between the structures emerging from patchy soft interactions, patchy hard-core interactions and isotropic hard-core interactions, which can already lead to complex aperiodic structures [5].

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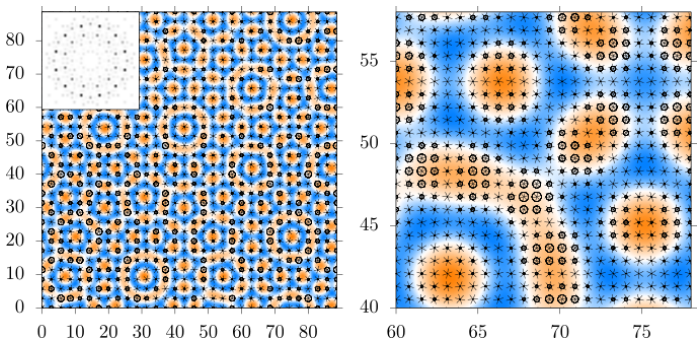

Fig.1: Density field (blue-orange) and orientation field (black markers) of a 12-fold quasicrystal from [1].

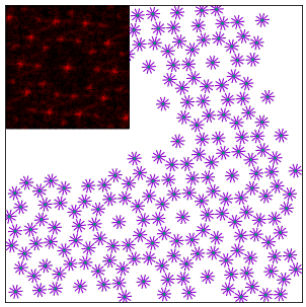

Fig.2: Configuration from a particle-based simulation of patchy colloids from [3].

On quasiperiodic functions, related quasicrystal tilings, and defects in binary tilings

Moritz Hirschmann, Johannes Schmitt, Ronja Westphal, Johannes Roth[#]

Institute for Functional Matter and Quantum Technologies, University of Stuttgart, Germany

[#]e-mail: johannes.roth@fmq.uni-stuttgart.de

Two-dimensional quasiperiodic functions generated by overlapping laser beams can be used as templates for colloidal quasicrystals. The laser fields are described by interfering plane waves with phase shifts measured with respect to an arbitrary origin. The minima of the quasiperiodic functions trap the colloids and may thus form the vertices of a quasicrystal tiling. In the case of five-fold symmetry the tiling can be nicely described as a binary rhombus or triangle tiling with the well-known rules for even and odd vertices (vertices with odd multiples of $2\pi/n$ are decorated with small atoms, vertices with even multiples of $2\pi/n$ with large atoms).

We study the possibility to decorate quasiperiodic functions with seven- and nine-fold symmetry with different kinds of rhombus binary tilings. We find that the range of decoration is rather limited for quasiperiodic functions without phase shift and does not work at all for quasiperiodic functions with arbitrary phase shifts (which is the same as decorating a non-shifted function far away from the origin).

We evaluate the possibility of generating arbitrary binary triangle tilings with n-fold symmetry using the seven-fold case as a prototype and describe the limitations of fitting tiles together which leads to unavoidable defects in many cases.

In the end we draw conclusions on the difference between quasicrystals with physical and perpendicular space of the same (as for five-fold symmetry) and different dimensionality (as for seven- and nine-fold symmetry).

Thermodynamically stable quasicrystal from tetrahedral colloids

M. Engel

Institute for Multiscale Simulation, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

e-mail: michael.engel@fau.de

The tetrahedral geometry is ubiquitous in natural and synthetic systems. Regular tetrahedra do not tile space, which makes understanding their self-assembly behavior a formidable challenge. Simulations of hard tetrahedra – that is particles with the shape of a regular tetrahedron interacting only by excluded volume interactions – discovered a dodecagonal quasicrystal (DQC) stabilized by entropy alone [1]. But while this quasicrystal forms robustly and reproducibly in simulation, it competes with periodic approximants and cannot be the thermodynamic ground state in the limit of infinite pressure. In this limit, the densest packing will eventually prevail, which is a simple (in comparison) dimer crystal [2]. Here, we advance research on tetrahedral particles in two directions. First, we demonstrate that the DQC is thermodynamically stable at intermediate density [3]. Using a pattern recognition algorithm applied to particle trajectories during DQC growth, we analyse phason strain to follow the evolution of quasiperiodic order. As in alloys, we observe high structural quality; DQCs with low phason strain crystallize directly from the melt and only require minimal further reduction of phason strain. We also observe transformation from a denser approximant to the DQC via continuous phason strain relaxation. Our results demonstrate that soft-matter quasicrystals dominated by entropy can be thermodynamically stable and grown with high structural quality—just like their alloy quasicrystal counterparts. Second, we discuss experimental realizations of phases of tetrahedral colloids where vertex sharpness, surface ligands, and the self-assembly environment play key roles in the formation of the quasicrystal, its approximants, and the dimer crystal.

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