Quasicrystalline tilings with nematic colloidal platelets

Jayarsi Dontabhaktuni,a,b Miha Ravnik,a and Slobodan Žumera,c

aFaculty of Mathematics and Physics, University of Ljubljana, SI-1000 Ljubljana, Slovenia; bCentre for Modelling Simulation and Design, University of Hyderabad, Hyderabad 500 046, India; and cJožef Stefan Institute, SI-1000 Ljubljana, Slovenia

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Complex nematic fluids have the remarkable capability for self-assembling regular colloidal structures of various symmetries and dimensionality according to their micromolecular orientational order. Colloidal chains, clusters, and crystals were demonstrated recently, exhibiting soft-matter functionalities of robust binding, spontaneous chiral symmetry breaking, entanglement, shape-driven and topological driven assembly, and even memory imprinting. However, no quasicrystalline structures were found. Here, we show with numerical modeling that quasicrystalline colloidal lattices can be achieved in the form of original Penrose P1 tiling by using pentagonal colloidal platelets in layers of nematic liquid crystals. The tilings are energetically stabilized with binding energies up to 2500 k_BT for micrometer-sized platelets and further allow for hierarchical substitution tiling, i.e., hierarchical pentagulation. Quasicrystalline structures are constructed bottom-up by assembling the boat, rhombus, and star maximum density clusters, thus avoiding other (nonquasicrystalline) stable or metastable configurations of platelets. Central to our design of the quasicrystalline tilings is the symmetry breaking imposed by the platelet shape and the surface anchoring conditions at the colloidal platelets, which are misaligning and asymmetric over two perpendicular mirror planes. Finally, the design of the quasicrystalline tilings as platelets in nematic liquid crystals is inherently capable of a continuous variety of length scales of the tiling, ranging over three orders of magnitude in the typical length (from ~10 nm to ~10 μm), which could allow for the design of quasicrystalline photonics at multiple frequency ranges.

colloids | quasicrystals | Penrose tiling | hierarchy

Quasicrystals are aperiodic crystalline materials, distinguished by noncrystallographic rotational symmetry of fivefold, sevenfold, eightfold, and higher rotational symmetry axes (1–3). These symmetries are typically found in atomic lattices of distinct metallic alloys (1, 4). However, more recently, a unique class of soft-matter quasicrystals is emerging (5–8), where the basic building blocks are not single atoms but rather macromolecules (9, 10), copolymers (11), molecular liquid crystalline fields (12, 13), or colloidal particles (14, 15). Two-dimensional realizations of materials with quasicrystalline symmetries are quasicrystalline tilings (2, 16, 17). In tilings, the structures of polygons or platelets—tiles—cover an area in complex patterns, typically following geometric rules. Tilings of fivefold (18, 19), sevenfold (20), eightfold (21), ninefold (22), tenfold (23), twelfold (24), and other (25) quasicrystalline symmetries were realized, demonstrating analogous ordering mechanisms as in quasicrystals (26, 27). These ordering mechanisms and the formation dynamics were particularly explored in quasicrystalline colloidal monolayers stabilized by interfering laser beams (28, 29).

Nematic liquid crystals are fluids with molecular orientational order, called the director field, and it is by designing the profiles of this field that colloidal structures of various functionalities can be self-assembled. The self-assembly is based on effective structural forces emerging between the particles (typically ~1–10 pN for micrometer-sized particles), caused by the inhomogeneous and anisotropic director profiles imposed by the particle surfaces or general shapes (30). Already simple spherical colloidal particles were shown to self-assemble into chains (31), clusters (32), 2D (33), and 3D colloidal crystals (34, 35). A specifically strong way to affect the self-assembly is by shape-controlled colloidal interactions (36–38) and faceted colloidal particles (39), where the shape of the particles determines the interparticle potentials and the symmetry of the structures (40) as well as their rotational dynamics (41). However, despite using particles with geometrically quasicrystalline symmetry, e.g., pentagonal or heptagonal platelets, generically, structures with strictly crystalline symmetry are found (36, 40, 42). It was shown that such platelets effectively lose their faceted nature and behave as dipoles and quadrupoles in the distortion field of the fluid (36), exactly as already known for spherical particles. More generally, therefore, finding relations between the inherent symmetry of the building blocks and the actual symmetry of the structures made from these building blocks presents a far-reaching challenge in the design of advanced quasicrystalline and crystalline materials.

In this paper, we combine the energy-based concept of structural forces in complex nematic fluids and geometry of building blocks to self-assemble quasicrystalline Penrose P1 tiling of pentagonal colloidal platelets. More specifically, we consider submicrometer-sized platelets whose top and bottom surfaces are treated to impose different alignment directions on the director field (Fig. 1), which generates interparticle potentials compatible with the quasicrystalline fivefold symmetry. The platelets are pre-positioned according to the symmetry of the Penrose lattice in thin nematic cells, typically ~5 times platelet thickness, whose surfaces are taken to yield strong uniform planar anchoring along a common direction (denoted as the rubbing direction), and then relaxed to equilibrium. Such an approach creates strongly bound equilibrium platelet structures, which, however, do not necessarily correspond to the global

Significance

Complex nematic fluids have the remarkable capability to organize microparticles and nanoparticles into regular structures of various symmetries and dimensionality, according to their micromolecular orientational order. Structures of particles such as chains, clusters, and crystals are found, but no quasicrystals. In this paper, we demonstrate that quasicrystalline structures can be achieved in the form of Penrose tiling by assembling microplatelets in the shape of pentagons within a thin layer of nematic fluid. The tiling is energetically stabilized with binding energies of typically several orders of magnitude higher than thermal energy and further allows for hierarchical substitution of individual pentagonal tiles with smaller tiles, which is interesting for the design of photonics at multiple frequency ranges.

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1To whom correspondence should be addressed. E-mail: slobodan.zumer@fmf.uni-lj.si.

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ground states of the system. The quasicrystalline assembly is robust over multiple length scales of the tiling pattern, and allows a hierarchy of scales, i.e., quasicrystalline tilings at one scale, with smaller-scale (quasicrystalline) substitutions. Our main methodological approach is phenomenological numerical modeling based on the minimization of the Landau-de Gennes free energy (see SI Text and Theory and Method), which proves particularly efficient exactly in strongly confined systems with multiple particles, like tilings, and which can give full quantitative or qualitative agreement with experiments (36, 40). Finally, experimental strategies for the self-assembly of Penrose nematic colloidal tilings are proposed, suggesting optical fields or quasicrystalline seed colloidal particles as possible approaches.

Prototiles: Pentagonal Colloidal Platelets

The assembly of quasicrystalline tilings depends centrally on the symmetry properties of the elementary building blocks—the prototiles—which determine the prototile-to-prototile interaction potential. Our prototiles are regular pentagonal platelets of uniform size (edge length $d = 300$ nm), with designed surfaces. The top and bottom large faces of the platelets are taken to impose in-plane uniform alignment of the nematic molecules—strong uniform planar anchoring—in mutually perpendicular directions (Fig. 1A–C). All other (side) surfaces induce degenerate planar anchoring. Experimentally realizing such surface anchoring on all platelet surfaces could possibly be achieved by using photoimprinting of the surface anchoring profile. Such a choice of anchoring surface preparation aligns the platelets at an angle of 0° or 72° relative to the far-field director—see potential minima at 0° and 72° in Fig. 1D—and, more importantly, breaks the top–bottom symmetry about the midplane passing through the platelet, which effectively removes the repulsive directions in the interaction potential of platelets, common for elastic dipoles or quadrupoles (30, 36). This additional symmetry breaking in turn gives rise to complex interactions between the platelets, leading to various possibilities of assembling them into quasiperiodic arrangements.

The frustration of preferred molecular orientations at the edges and corners of the platelets gives rise to topological defects along the edges of the platelets, as shown in Fig. 1C. The disclination lines surrounding individual platelets are surface defects, i.e., effective generalizations of surface boojum defects, that wind around the edges of the platelets, alternating between the top and bottom surfaces (for more, see SI Text and Fig. S1).

The pair interaction potential between two pentagonal prototiles in a selected region of separations—calculated as changes in the free energy upon shifting the platelets (see SI Text)—is shown in Fig. 1E. Interestingly, the potential exhibits multiple minima, corresponding to different alignments of bound colloidal pairs with respect to the undistorted nematic direction (Fig. 1F–H). At short separations, as the platelets get laterally close to one another with only a thin layer of nematic ($\sim 10$ nm) between them, the surface anchoring on the side walls of the platelets dictates the assembly. Because the surface anchoring on the side walls of two platelets is compatible, the platelets attract. In all equilibrium pair configurations, the attraction is almost exactly side surface to side surface, which proves central to stabilize the quasicrystalline tilings, but could also stabilize other,
e.g., crystalline, structures. Notably, this side surface to side surface pair attraction is very different from the strictly steric repulsion in the typical geometric tilings, where the tiles can easily slide with respect to each other. Also important is that we consider the platelet assembly in a rather thin layer of nematic planar cell with a thickness comparable to the platelet thickness (ratio of $\sim 5$).

Working in this regime prevents: (i) possible top–bottom flipping of the platelets and (ii) out-of-plane stacking of the platelets (Fig. S2). Having all platelets with equal top and bottom surfaces, i.e., nonflipped, prevents possible structural defects in the tiling, as flips notably change the pair interaction potential (Fig. S3). Alternatively, the assembly in the regime of large cell thickness to platelet thickness ratio could be importantly affected by the stacking of platelets, likely into columns, building 3D structures of diverse complexity. Finally, the proposed design of platelet assembly in thin nematic layers gives equilibrium directions of the platelet pairs with respect to the undistorted nematic direction that correspond well to the nearest neighbor directions, characteristic for the Penrose tilings.

**Elementary Quasi-Building Units: Star, Rhombus, Boat, and Decagonal Colloidal Clusters**

Quasicrystalline tilings require a distinct approach to assembly, as by definition they cannot be constructed by simply repeating a unit cell according to the Bravais lattice vectors. Two approaches are known to construct the quasicrystalline tilings (16, 17, 43–45), and we show that actually both can be—within some limitations—used with our nematic platelets to assemble the Penrose lattice.

The first approach for the Penrose $P1$ lattice is based on three basic quasi-building units (clusters), called the star, rhombus, and boat structures (named after the shapes of voids formed between the pentagonal platelets in these structures), and uses them as elements of the tiling. When assembled into the tiling, the neighboring clusters partially overlap, i.e., share some tiles, effectively covering the whole tiling according to distinct overlap rules. Fig. 2 $A–C$ shows that star, rhombus, and boat quasi-building units form from pentagonal nematic platelets, and it is the pair potential originating from the designed nematic distortion field between the platelets that stabilizes the quasi-building blocks (for more, see SI Text and Fig. S4). Topological defect line segments connecting the edges of all of the platelets in all of the quasi-building units, acting energetically as effective “sticky” edges connecting the adjacent platelets. Short defect line segments of winding number $1/2$ are observed also in the voids between the platelets (see inset in Fig. 2C), and typically emerge at distinct orientation angles of the building units. In equilibrium, the quasi-building units are oriented at stable configuration angles of $0^\circ$ (rhombus), $90^\circ$ (boat), and $72^\circ$ (star) with respect to the far-field nematic director, as seen in Figs. 2 $D–F$; the boat and the star clusters have the total free energy for $470 \ k_B T$ and $780 \ k_B T$ higher, respectively, than the rhombus cluster ($k_B T$ is thermal energy at room temperature $T$ and $k_B$ is Boltzmann constant).

Note, however, that the quasi-building-unit clusters also remain bound if oriented at other (nonequilibrium) angles, which is important for achieving the stability of the full-plane tiling.

Alternatively, under the second approach (17, 43–45), the Penrose tiling is constructed by assembling only one basic quasi-building unit—the decagonal colloidal cluster—which also partially overlaps with neighboring clusters when assembled into the tiling. This decagonal cluster is also frequently called the quasi-unit cell of the Penrose tiling. Indeed, we show that the decagonal colloidal cluster can be assembled from nematic pentagons as presented in Fig. 2G. The decagon is stable at orientation angles of $70^\circ$ and $260^\circ$ (and metastable at $170^\circ$ and $350^\circ$) with respect to the rubbing direction, as depicted in Fig. 2H, but, similarly to the rhombus, star, and boat clusters of the first approach, also remains laterally bound at all other orientation angles. The total free energy of the decagonal cluster is for $1130 \ k_B T$ higher than for the rhombus cluster. More generally, finding the decagonal colloidal cluster stable indicates that in the tiling, there will be overlapping regions of attraction, effectively corresponding to the overlapping decagonal clusters, which are compatible with the quasicrystalline symmetry and will stabilize the tiling. Finally, it is important to comment that the concept of overlapping decagonal clusters as quasi-unit cells also requires that the decagons overlap cleanly only in two ways (17, 43–45), which is not observed in our nematic colloidal tiling, where we see more different overlaps, in particular caused by the locally different structure of the nematic orientational field.

**Penrose Tilings: Simple and Hierarchical**

Having confirmed the stability of the individual tiling quasi-building units, we design a quasicrystallite with $N=55$ particles (Fig. 3A) to form a robust and stable structure. Indeed, upon stretching under the “breathing mode” (i.e., equally increasing all platelet-to-platelet separations), the free energy of the structure increases by several thousand $k_B T$ (Fig. 3B).

Finally, we design and demonstrate colloidal Penrose tiling with as many as $N=176$ platelets, as shown in Fig. 3C. The calculations of the whole structure are performed directly, within a single simulation box, using large-scale parallelization and edge of computer resources. The presented structure is the Penrose $P1$ tiling with...
distinguished fivefold symmetry axes and rhombus, star, and boat voids. Importantly, this fivefold symmetry applies to the positional order of the platelets, and it breaks if also considering the symmetry of the surrounding nematic field, which is also evident from the anchoring direction imposed by the top (and bottom) surfaces of the platelets that is equal for all platelets in the tiling (blue double-headed arrow in Fig. 3A and C). The stability of the tiling is ensured by the complex director field surrounding the tilings as seen in Fig. 3D and E. More generally, the complex director is reflected in the highly anisotropic structural forces between the tiles, which are caused by a remarkable interplay of inherent symmetries in the material, i.e., quasicrystalline from the positioning of the tiles and the uniaxial of the nematic order parameter field.

The Penrose tilings assembled from pentagonal platelets in nematics have an interesting property: Tile interaction potentials allow for hierarchical substitution of individual prototiles, by a geometrically matching and energetically bound structure of physically smaller prototiles. Fig. 4A shows three platelet structures, assembled from various-size pentagons, but of the same thickness, that are stable and that effectively behave as one larger-scale prototile. Indeed, because of the nematic elastic origin, the interaction forces between the platelets of various sizes follow roughly the same profile of the interaction potential over a range of length scales from a few hundred nanometers to microscopic scales, as illustrated in Fig. 4B, which is usually more complex in other soft-matter quasicrystalline systems (9, 11, 28). Therefore, if the structures from smaller-size pentagons geometrically match the size of one larger platelet, hierarchical Penrose

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**Fig. 3.** Penrose P1 tiling structures. (A) Quasicrystallite assembled with 55 particles. (B) Stretching potential of the quasicrystallite upon the breathing mode. (C) Colloidal quasicrystalline Penrose tiling P1 assembled from 176 particles in nematic liquid crystal layer with the indicated fivefold symmetry axis. (D and E) Close-up view of the director field in the P1 tiling. Dark green regions surrounding the platelets correspond to surface and bulk topological defects, visualized as isosurfaces of the nematic degree of order $S = 0.52$. Rubbing direction of the undistorted nematic director is indicated by the white or black double-headed arrows; blue double-headed arrows indicate the imposed anchoring direction on top surface of the platelets, which is the same for all platelets in the tiling.

**Fig. 4.** Hierarchical tiling. (A) A single pentagonal prototile of edge length 400 nm can be replaced with six smaller-sized (160 nm) pentagonal tiles and further dissociated into 36 pentagonal tiles of edge length 60 nm. (B) Interaction forces of a pair of particles as a function of their separation for edge lengths 60 nm, 250 nm, and 1 mm. (C) Scheme of Penrose P1 tiling with hierarchically organized tiles of three length scales. (D) Numerically calculated hierarchical Penrose P1 tiling, with one pentagonal tile replaced with smaller-scale pentagonal tiles. Gray streamlines show the projection of director field on the visualized plane.
tiling can be achieved, as presented in Fig. 4 C and D. Effectively, this tiling still carries the general properties of the Penrose lattice, yet with refined smaller-scale additions. More quantitatively, we compared the free energies of one pentagonal prototile and one effective prototile assembled from smaller-size pentagons. We observed that the free energies are comparable to each other except for the interaction energy of the smaller-size pentagons in the voids. In the hierarchical Penrose tilings, the nematic-embedded pentagons are energetically bound at all scales, whereas in a strictly geometric hierarchical tiling of pentagons (e.g., with only hard-core repulsions), the smaller-scale tiles in particular can become loose and break the tiling symmetry. Finally, knowing that quasicrystalline materials can have distinct photonic properties such as complete band gaps (46–48), the Penrose tiling from hierarchically organized nematic platelets presented here may offer unique photonic responses, for example as multiple-frequency photonic crystals.

Discussion

Experimentally realizing the proposed nematic Penrose tilings will critically depend on being able to minimize the possibility of forming conformations in the tiling patterns that break the quasicrystalline symmetry. The platelet-platelet interaction potentials presented here are typically in the range of 100–1000 $k_BT$, which suggests that thermal fluctuations will be unable to make any changes to the structure once bound. We list two possible experimental approaches that could avoid, or at least reduce, the structural imperfections: (i) the optical tweezers-assisted assembly and (ii) the step-wise assembly by a pre-assembly of colloidal clusters as seeds. Optical tweezers and tweezers with complex beams have proven to be robust tools for precise assembly of liquid crystal colloids, including dynamic manipulation and rotation (41), and could be used to assemble the tiling. Alternatively, colloidal protocrystals or particles of complex shapes (e.g., rhombi, stars, or boats) could be used as quasicrystalline seeds in the dispersion of pentagons, in particular if combined with a slow and gradual assembly of the tiling (order of magnitude of one platelet at a time). Indeed, the concept of creating sticky edges by designing surface anchoring could be generalized also to particles of other—more complex—shapes, possibly allowing for their use as quasicrystalline seeds in the assembly.

The demonstrated tiling reveals an interesting combination of the fivefold quasicrystalline symmetry of the platelets and the inherent uniaxial symmetry of the anisotropic nematic host, which originates from the soft nematic response via the formation of topological defects and the effective elastic deformations of the director. The topological defects surrounding the platelets (e.g., Fig.1 and Fig. S1) allow the uniaxial nematic director to compensate the fivefold geometrical symmetry of the platelets by using the defect lines with core singularities, where the nematic order is lost. Further insight into the interplay of symmetries can be obtained by roughly generalizing the nematic field into two characteristic regions: (i) the voids between the platelets and (ii) the layers above and below the platelets. In the voids, the nematic field is primarily determined by the boundary conditions imposed by the tiles as opposed to nematic elasticity. In the nematic layers below and above, however, the director is determined primarily by the competition between the uniform planar alignment at the cell walls and the in-plane alignment at the top and bottom surfaces of the platelets. In all structures of platelets, the imposed direction by the top or bottom surface of the platelets forms an angle in respect to the rubbing direction imposed by the cell walls, which results in a twist deformation of the nematic director above and below the platelets. And it is this twist that effectively couples the detailed structure and geometrical symmetry of the platelets with the uniform uniaxial symmetry of the undistorted nematic imposed by the nematic planar cell. Finally, it is the softness of the nematic deformation that combines these elementary diverse—quasicrystalline and uniaxial—symmetries in the same system.

In summary, we have demonstrated that quasicrystalline Penrose P1 tiling can be assembled from pentagonal colloidal platelets using fluid-mediated interactions in nematic liquid crystals. The assembly is approached by constructing elementary Penrose tiling quasi-building units of the star, boat, rhombus, and decagonal colloidal clusters. They are stable and bound at arbitrary orientation angles, which proves central for the stability of the tiling as a whole. The mechanism of hierarchical pentagulation at three hierarchical scales is shown, where targeted tiles are replaced with energetically bound clusters of smaller-size but same-thickness tiles, which is an approach toward the assembly of fractal tilings. The demonstrated Penrose tiling is achieved only from one type of prototile, i.e., pentagonal platelets, which is uncommon for colloidal quasicrystals, which typically need two or more species of particles to exhibit quasicrystalline structuring. Here, it is the structure of the nematic fluid that supports the quasicrystalline assembly. A notable difference between these nematic-embedded tilings and purely geometric ones is also that nematic mediated interplatelet interactions favor side surface to side surface alignment with, importantly, no sliding, which causes inherent energetically favorable positioning of the platelets along symmetry directions. From a broader perspective, our results demonstrate unique materials with quasicrystalline symmetry, hierarchical substitutions, and robust assembly, which are all among cutting-edge characteristics for advanced optical and photonic materials. Finally, the demonstrated nematic Penrose tilings have revealed a unique compatibility of the general material symmetries, combining the locally uniaxial symmetry of the nematic complex fluids and the quasicrystalline fivefold symmetry of the individual platelets, which could lead to a previously unknown insight into the fundamentals of quasicrystal formation.

Theory and Method

Phenomenological modeling based on Landau-de Gennes free energy was used as the central methodological approach for modeling and predicting the nematic Penrose tilings (see also SI Text). This has proven to be a particularly strong approach for modeling nematic colloids, as it can give qualitative and quantitative agreement with experiments (49, 50). The modeling is based on total free energy $F$ written in terms of tensorial order parameter $Q_{ij}$, and constitutes contributions from elasticity of the nematic medium, temperature-dependent bulk order, and the surface anchoring:

$$F = \int_{\mathcal{L}} \left( \frac{1}{2} \partial_{ij} Q_{ij} \partial_{ij} \phi_{\text{surf}} \right)^2 + \frac{1}{2} Q_{ij} \partial_{ij} \phi_{\text{surf}} + \frac{1}{2} \partial_{ij} Q_{ij} \phi_{\text{surf}} + \frac{1}{2} \partial_{ij} Q_{ij} \phi_{\text{surf}} \right) \partial V + \int f \phi_{\text{surf}} dS,$$

where $L$ is the single elastic constant, $A, B,$ and $C$ are nematic material parameters, $f$ is surface free energy density, $\mathcal{L}$ indicates integration over the whole nematic volume, and $\phi_{\text{surf}}$ indicates integration over the surface of the tiles. Surface free energy for degenerate planar anchoring on the side surfaces of the tiles is taken as $f_{\text{s}} = W_{Q_{ij} = Q_{ij}}$, for more details, see ref. (51), whereas surface free energy for uniform planar anchoring on the top and bottom surfaces of the tiles is taken as $f_{\text{b}} = W_{Q_{ij} = Q_{ij}} |Q_{ij} = Q_{ij}|$, where $W$ and $W_{Q_{ij}}$ are the anchoring strengths and $Q_{ij}$ is the surface preferred order parameter. Free energy is minimized using explicit finite difference relaxation method on a cubic mesh (51). Surface mesh point allocation is adapted for strongly confined regions of a few mesh points size. The top and bottom substrates of the cell induce strong uniform planar anchoring, and periodic boundary conditions are assumed along lateral XY directions. The material parameters are those of a standard nematic liquid crystal; if not stated differently, we take: pentagonal edge lengths $d = 300 \text{ nm}$, $L = 40 \text{ pN}$, $A = 0.172 \text{ MJ/m}^2$, $B = 2.12 \text{ MJ/m}^2$, $C = 1.73 \text{ MJ/m}^2$, $W = W_{Q_{ij}} = 10^2 \text{ J/m}^2$, and surface anchoring alignment angle of $36^\circ$ (126°) at the bottom (top) surface.

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