Entropic formation of a thermodynamically stable colloidal quasicrystal with negligible phason strain

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Quasicrystals have been discovered in a variety of materials ranging from metals to polymers. Yet, why and how they form is incompletely understood. In situ transmission electron microscopy of alloy quasicrystal formation in metals suggests an error-and-repair mechanism, whereby quasiperiodic crystals grow imperfectly with phason strain present, and only perfect themselves later into a high-quality quasicrystal with negligible phason strain. The growth mechanism has not been investigated for other types of quasicrystals, such as dendrimers, polymeric, or colloidal quasicrystals. Soft-matter quasicrystals typically result from entropic, rather than energetic, interactions, and are not usually grown (either in laboratories or in silico) into large-volume quasicrystals. Consequently, it is unknown whether soft-matter quasicrystals form with the high degree of structural quality found in metal alloy quasicrystals. Here, we investigate the entropically driven growth of colloidal dodecagonal quasicrystals (DQCs) via computer simulation of systems of hard tetrahedra, which are simple models for anisotropic colloidal particles that form a quasicrystal. Using a pattern recognition algorithm applied to particle trajectories during DQC growth, we analyze 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.

Quasicrystals are crystals that possess long-range quasiperiodic order without translational periodicity. Since the first report of an icosahedral quasicrystal in an Al–Mn alloy melt (1), quasicrystals with 8-, 10-, 12-, and 18-fold symmetry as well as icosahedral symmetry have been discovered in many alloys (2), carbon allotropes (3, 4), metal oxides (5), and various soft-matter systems including dendrimers (6), block copolymers (7, 8), and colloids (9–12). The apparent structural universality of quasicrystals across these very disparate systems begs the question: Is quasicrystal growth the same across all systems, regardless of length scale?

How quasicrystalline growth is a matter of some debate (13, 14). Two growth models have been proposed: the matching rule model and the error-and-repair model. The matching rule model (15) asserts that quasicrystals form as tiles—i.e., subunits of the quasicrystal pattern comprising clusters of particles in specific arrangements—attach at the growth front to match the existing pattern. Matching rules dictate which attachments are allowed and which are not, and the model imagines that the tiles act as puzzle pieces with precise local fit. Via matching rules, quasicrystals grow “perfectly,” maintaining strict quasiperiodicity at all times, thereby resulting in an ideal (or perfect) tiling. In contrast, the error-and-repair model (16, 17) describes quasicrystal formation as a two-step process. In the first step, tiles or particle clusters quickly attach to the growing quasicrystal in a way that is at least to some degree random. These imperfect attachments eventually produce phason strain, a measure of quasiperiodic disorder over long distances (18, 19). In the second—much slower—step, phason strain is relaxed through local particle rearrangements called phason flips. Ultimately, a quasicrystal with negligible phason strain is possible, so that the end result for both models can be very similar.

Recent in situ observations of decagonal (10-fold) quasicrystal growth from Al–Ni–Co melts using transmission electron microscopy (17) and of a self-assembling icosahedral quasicrystal using molecular dynamics simulations from a single-particle species interacting via an isotropic pair potential (20) support the error-and-repair mechanism. While these two systems, one experimental and one computational, are clearly different, in both cases potential energy, rather than entropy, drives quasicrystal growth. Which growth model holds for entropically driven quasicrystal formation (21–23)? There is recent evidence that kinetic crystallization pathways in energy-dominated and entropy-dominated systems are similar (24). Does it follow that soft-matter quasicrystals form via error-and-repair, and thus that high-quality quasicrystals are realizable in entropy-driven soft-matter systems?

In this work, we answer this question for the case of the dodecagonal quasicrystal (DQC) in the hard tetrahedron system (25). Because the tetrahedron particles are hard, i.e., interact only via excluded volume, the system we study is governed solely by entropy. Using a pattern recognition algorithm applied to particle trajectories during DQC growth, we analyze 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.

Significance

Quasicrystals—ordered crystals lacking translational periodicity—occur in systems comprising building blocks ranging from atoms to nanoparticles. These quasicrystals can have the same structure despite the obvious differences in building-block type or size. Do they all form in the same way? Or do colloidal quasicrystals grow differently than atomic quasicrystals? We study the formation of a colloidal quasicrystal in a hard tetrahedron system, where structural ordering is solely governed by entropy. We observe that the colloidal quasicrystal forms with high structural quality when simulations begin in the melt. We also find that structural imperfections in approximant crystals can be repaired by the relaxation process observed during quasicrystal formation. This demonstrates that our quasicrystal is thermodynamically stable.
by entropy—that is, the DQC forms from entropy maximization—and thus is a good representation of a soft-matter quasicrystal. We discover from Monte Carlo (MC) simulation runs that phason strain remains small during DQC growth and only weakly relaxes further, resulting in a high-quality DQC with negligible phason strain directly from the melt. We also observe that an approximant structure, a periodic crystal closely resembling the DQC and with inherent linear phason strain (25, 26), can relax to the DQC via continuous phason strain relaxation; that is, the solid–solid transition (27, 28) occurs via a process analogous to the repair step of the error-and-repair model (16, 17).

**Results**

**Tiling Hierarchy.** Phason strain analysis is best performed by considering the tiling patterns for the quasicrystal under study. Fig. 1A introduces a hierarchical series of four tilings. All tilings are generated by inflation or deflation (2) with inflation factor $f = 2 \cos(\pi/15) \approx 1.956$ to rescale the tile edge length. At each hierarchy level, the centers of vertex motifs (Fig. 1B) form vertices of square, triangle, and rhombus tiles. The tiling employed in previous work (25) corresponds to the third hierarchy level (red color in Fig. 1B), in which clusters of 22 tetrahedra are arranged in a noninterdigitating fashion; that is, the clusters do not share tetrahedra. A single 22-tetrahedron cluster (22-T) consists of a ring of 12 tetrahedra and 2 pentagonal dipyramids (SI Appendix, Fig. S1) (25).

Phason strain in quasicrystals is quantified by numerically evaluating the geometry of the tiling. This analysis is independent of the tiling chosen within the series up to linear scaling. This means the DQC structure can in principle be analyzed using any of the four tilings in Fig. 1. The second hierarchy level (green color in Fig. 1B) is used in the present work. Details on tile decorations are shown in SI Appendix, Fig. S2.

**Growth of the Quasicrystalline Tiling.** As an initial step, we investigate the appearance of densely packed local motifs that are involved in the formation of various quasicrystals including DQCs (29–32). In dense fluid of hard tetrahedra, three local motifs have been identified: the pentagonal dipyramid (PD), icosahedron, and 22-T (SI Appendix, Figs. S3 and S4). We investigate the evolution of these motifs along the DQC assembly pathway obtained from an MC simulation initialized in a dense fluid phase at constant packing fraction $\phi = 0.49$ (Fig. 2A). At this packing fraction, previous work has shown that fluid-DQC coexistence is thermodynamically preferred (25). After $8 \times 10^6$ MC sweeps, the fraction of tetrahedra belonging to a 22-T motif significantly increases, while the fraction of tetrahedra belonging to the icosahedron and/or PD motifs only decreases. In the late stages of the simulation, 22-T becomes the dominant motif. In parallel with this, the local density distribution gradually evolves from unimodal to bimodal by growing a second, high-density peak (Fig. 2B).

Both observations indicate that quasicrystal nucleation occurs at $8 \times 10^6$ MC sweeps and that the motif involved in nucleation and growth in the hard tetrahedron system is the 22-T (Movie S1).

We can obtain an intuitive picture of the contribution of 22-Ts to DQC formation by considering their spatial arrangements in the dense fluid. For this, we identify clusters of particle-sharing 22-Ts. Specifically, we track the clusters that comprise 22-Ts with six or more neighboring 22-Ts (SI Appendix, Fig. S5). As shown in SI Appendix, Fig. S6A, relatively small clusters emerge and disappear in the fluid in the early stages of the simulation trajectory (before nucleation). After $8 \times 10^6$ MC sweeps (postnucleation), a single large cluster emerges (SI Appendix, Fig. S6B and Movie S2). The diffraction pattern of the growing cluster exhibits 12-fold symmetry (Fig. 2C), indicating that the cluster is growing as a DQC. More discussion on the self-assembly of the DQC is provided in SI Appendix, Figs. S7 and S8.

The 22-T motifs in the growing cluster form square, triangle, and rhombus tiles as demonstrated by the networks of 22-T centers (green solid circles) in Fig. 2D (SI Appendix, Fig. S9 and Movie S3). Diffraction patterns and bond orientational order diagrams of the 22-T centers in the growing cluster also show 12-fold symmetry (Fig. 2D and SI Appendix, Fig. S9B) with sharpening peaks, confirming that the evolving arrangements of the tiles correspond to a growing DQC tiling.

**Analysis of Phason Strain.** We calculated the phason strain in the DQC tiling during quasicrystal growth by performing a phason displacement field analysis (11, 20, 33). For this purpose, we prepared a large DQC in a thin tetragonal box by seed-assisted growth with $N = 129,030$ hard tetrahedra. The 12-fold axis of the...
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dimensional (4D) configurational space by a lifting procedure two-dimensional (2D) tiling is assigned to a point in a four-

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patterns of the solid (Lower Right Inset) exhibit 12-fold symmetry indicating that the solid is a DQC. (D) Networks of 22-T centers in C, which define the quasicrystalline tiling of DQC (green hierarchy level in Fig. 1). Spots in bond orientational order diagrams (Upper Right Inset) and diffraction patterns (Lower Right Inset) of the tilings gradually sharpen as DQC growth proceeds.

Fig. 2. Evolution of the quasicrystalline tiling during DQC growth. (A) Fractions of tetrahedra that are part of an icosahedron, a 22-T, both an icosahedron and a 22-T, a PD but not an icosahedron or a 22-T, and none of these motifs (“None”) during DQC growth. All five labels add up to 100% (SI Appendix, Fig. S4). (B) Distribution of local density \( \phi \) sampled at four different MC checkpoints as marked by the four vertical lines in A. The distribution changes from unimodal to bimodal and back to mostly unimodal, indicating first the appearance and then the partial disappearance of solid-fluid coexistence. Because the simulation is conducted in the isochoric ensemble at \( \phi = 0.49 \), peaks shift toward lower densities as the solid grows. (C) The growing solid is identified by clustering 22-Ts that share tetrahedra as shown after 10 \( \times \) 10^6 and 15 \( \times \) 10^6 MC sweeps. Tetrahedra belonging to the fluid are translucent gray. Diffraction patterns of the solid (Lower Right Inset) exhibit 12-fold symmetry indicating that the solid is a DQC. (D) Networks of 22-T centers in C, which define the quasicrystalline tiling of DQC (green hierarchy level in Fig. 1). Spots in bond orientational order diagrams (Upper Right Inset) and diffraction patterns (Lower Right Inset) of the tilings gradually sharpen as DQC growth proceeds.

seed was aligned parallel to the short box axis such that growth of the 12-fold tiling proceeded laterally (see Materials and Methods for more details). We find that it is important to not restrict phason strain relaxation by periodic boundary conditions. For this reason, we performed the simulation at constant packing fraction \( \phi = 0.47 \), which corresponds to a density at which the DQC coexists with its fluid. In this way, the DQC does not grow into itself across periodic boundaries and is always surrounded by fluid. The contact with the fluid allows the quasicrystal to continuously relax its phason strain and reach thermodynamic equilibrium.

For the phason displacement analysis, each vertex \( a_m \) of the two-dimensional (2D) tiling is assigned to a point in a four-dimensional (4D) configurational space by a lifting procedure (SI Appendix). The lifted 4D point is then projected onto the phonon-corrected position of the vertex \( a_m^\| \) in 2D parallel space and a coordinate in 2D perpendicular space \( a_m^\perp \) that encodes phason displacement (SI Appendix) (34). The relationship of the distance between two tile vertices in parallel space, \( r^\|_{mn} = |a^\|_m - a^\|_n| \), and the corresponding distance in perpendicular space, \( r^\perp_{mn} = |a^\perp_m - a^\perp_n| \), characterizes phason strain and is defined as the phason displacement (SI Appendix) (33). In particular, the slope \( \alpha \) of the linear fit, \( r^\perp = \alpha r^\| + \beta \), is known as the phason strain (SI Appendix) (35). We calculate \( \alpha \) after removing background noise (SI Appendix, Fig. S10) and scale \( \alpha \) by the value of phason strain in the first-order approximant (SI Appendix) (25, 26) \( \alpha_{\text{st}} \).

Fig. 3A shows a growing DQC (first row) and its corresponding quasicrystalline tiling (second row). DQC growth is complete after approximately \( 9 \times 10^6 \) MC sweeps, which is reflected in the convergence of the reduced pressure \( P^* = P/k_B T \) (magenta arrowhead in Fig. 3B) and that of the fraction of particles belonging to the solid (SI Appendix, Fig. S11). At \( 9 \times 10^6 \) MC sweeps, the phason strain is \( \alpha/\alpha_{\text{st}} = 0.013 \) (green arrow in Fig. 3B and C), which is comparable to the phason strain in the third-order approximant of the DQC (SI Appendix) (25), \( \alpha_{\text{3rd}}/\alpha_{\text{st}} = 0.010 \) (SI Appendix, Fig. S12). The phason strain then gradually decreases, becoming negligible (zero) at around \( 18 \times 10^6 \) MC sweeps (cyan arrow in Fig. 3B and C). These results demonstrate that only weak phason strain is introduced during
growth and subsequent relaxation eventually results in a high-quality DQC with negligible phason strain and weak equilibrium phason fluctuations (SI Appendix, Fig. S13A and B). We confirm formation of high-quality DQCs with negligible phason strain in three independent simulations (SI Appendix, Fig. S14). More discussion on the phason strain relaxation in our DQC is provided in SI Appendix. Next, we show that the observed phason relaxation can even occur in quasicrystalline approximants with inherent phason strain, which demonstrates thermodynamic stability of DQCs over the approximants.

Transformation of the First-Order Approximant. Quasicrystal approximants are characterized by linear phason strain (36). Lower free energy of the quasicrystal compared to its approximants is a prerequisite for thermodynamic stability of the quasicrystal and has thus been investigated in both experiment (37) and simulation (38). Specifically, the first-order DQC approximant was tested for relative stability with respect to DQC in the hard tetrahedron system (26). Equations of state demonstrated that the first-order approximant is more densely packed than both the DQC and higher-order approximants (26). These results suggested that the first-order approximant is the thermodynamically stable phase. But, no tests of its stability have been reported.

We revisited the stability of the DQC by initializing a simulation from the first-order approximant (SI Appendix, Fig. S20) (25, 26) in a tetragonal box at packing fraction $\phi = 0.47$. We now find that the approximant gradually transforms into the DQC. This is demonstrated by the evolution of the diffraction pattern from 4-fold symmetry to 12-fold symmetry (Fig. 4A and SI Appendix, Figs. S15 and S16 and Movie S4). The transformation is also observed at a lower packing fraction $\phi = 0.46$ (SI Appendix, Fig. S17). These results indicate that the DQC is thermodynamically more stable than approximants at these packing fractions. We confirmed that the geometry of the simulation box does not affect the transformation (SI Appendix, Fig. S18).

We calculated phason strain during the transformation using the phason displacement field analysis. The phason strain decays exponentially as $\alpha/\alpha_{1st} \propto \exp(-t/t_0)$ with $t_0 = 14 \times 10^6$ as a function of MC sweeps $t$. Phason strain is zero within fluctuations after $t = 80 \times 10^6$ (Fig. 4B). Both types of simulations, growth from the fluid and transformation of the approximant, converge to a high-quality DQC free of phason strain, demonstrating unambiguously the thermodynamic stability of the DQC. This is an observation of a transformation from an approximant to a quasicrystal in a three-dimensional (3D) simulation and the demonstration of thermodynamic stability of a simulated DQC in 3D. Our observation is in line with previous simulation reports of entropically stabilized dodecagonal or decagonal quasicrystals in 2D (38-40).

Relaxation of phason strain requires coherent phason flips within the tilings. We analyzed the enhancement of structural quality of the tiling by following the evolution of the spatial distribution of
tile vertices projected to perpendicular space. This distribution is known as the occupation domain. It is a polygonal domain with sharp boundaries for an ideal dodecagonal tiling with shield tiles, a spherical domain blurred out near the boundary in the case of a random tiling, and a noncompact domain in the case of an approximant (33). During transformation from the approximant to the DQC, the radial density of projected points in perpendicular space gradually sharpens (Fig. 4C and D), showing improvement in the structural quality of the tiling. The occupation domain remains blurred near the boundary, indicating that the DQC permits weak random phason fluctuations in equilibrium (SI Appendix, Fig. S13 C and D).

Discussion

Since 2004 a growing number of colloidal quasicrystals have been reported (6–12), including a quasicrystal comprising tetrahedron-shaped nanoparticles (41). But, the quasicrystals in these systems are characterized by relatively low structural quality when compared to that of classic examples of quasicrystals of atomic alloys (2, 42). This leads to the question of whether soft-matter quasicrystals are necessarily of inferior structural quality. The purely entropic hard tetrahedron system studied in this paper can be considered a soft-matter system because the particles interact weakly (i.e., not at all) compared to atoms. Our observation of the formation of high-quality DQCs with negligible phason strain demonstrates that soft-matter quasicrystals can indeed exhibit a high degree of quasiperiodic order comparable to their alloy counterparts. Our work also reveals a potential limiting factor toward quasicrystals with high structural quality: the need to anneal the quasicrystal long enough to heal out phason strain and other defects created initially during rapid growth. Atoms in alloys move orders of magnitude faster than the much more massive colloids, which explains why annealing is less of an issue in traditional QCs. Future work should search for formation modes that lead to soft-matter quasicrystals with few defects (43) or defects that heal quickly. Those soft-matter quasicrystals will be the best candidates for functional materials, e.g., complete photonic bandgap materials for next-generation optical devices (44, 45) made via self-assembly.

Materials and Methods

Particle Geometry. A tetrahedron is the convex hull of the four vertices $v_1 = (1,1,1), v_2 = (1, -1, -1), v_3 = (-1, 1, -1), v_4 = (-1, -1, 1)$. Edge length and volume of the tetrahedra are $a = 2\sqrt{2}$ and $V = 8/3$, respectively.

Simulation Code. Simulations were performed with the hard-particle MC (HPMC) (46) simulation code implemented in the HOOMD-blue software package, version 2.4.2 (47). We used HPMC on multiple central processing units for this work.
units (CPUs) with message passing interface domain decomposition or on a single graphics processing unit at XSEDE (48). All simulations were performed in the PhD Rev ensemble with periodic boundary conditions. The open-source analysis package freud (49) was used to detect motifs via pattern recognition and to quantify the local density distribution of tetrahedra.

Self-Assembly Simulation. Simulations were started from a fluid of 16,384 hard tetrahedra at low density, comprised to either packing fraction \( \phi = 0.49 \) or \( \phi = 0.52 \), and run for 20 \( \times \) 10^6 MC sweeps.

Analysis of Local Motifs. Positions and orientations of tetrahedra were averaged over short trajectories to reduce noise. Icosahedron and 22-T motifs were detected by grouping and vector displacement analysis. In the grouping analysis, tetrahedron vertices within distance cutoff 0.3\( \sigma \) were detected by grouping and vector displacement analysis. In the grouping analysis, tetrahedron vertices with distance cutoff 0.3\( \sigma \) were detected by grouping and vector displacement analysis. The vectors connecting the tetrahedron containing the segmented tetrahedron with local densities of polytetrahedral, and simple crystalline phases in Ti-Zr-Ni alloys: Verification of Frank’s hypothesis. Phys. Rev. B Condens. Matter Mater. Phys. 72, 174107 (2005).


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