How do Quasicrystals Grow?

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We investigate the physical mechanism underlying the formation of the quasicrystal phase from a supercooled liquid. Using molecular simulations, we show that quasicrystal growth is controlled by a tendency for atoms to retain their local liquid configuration when attaching to the growing solid nucleus. In the system under investigation, which forms a dodecagonal quasicrystal, we show that this process occurs through the assimilation of stable icosahedral clusters in the supercooled liquid by the growing quasicrystal, which hinders periodic crystal formation in favor of aperiodic crystal formation.

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Quasicrystals\textsuperscript{1} are a unique class of ordered solids that display long-range aperiodicity, which distinguishes them from ordinary crystals. It is not known what “special” qualities systems must possess in order to form quasicrystals versus crystals. In a basic sense quasicrystals, like crystals, form via nucleation and growth\textsuperscript{1}, whereby a microscopic ‘nucleus’ of the solid phase spontaneously arises in the supercooled liquid and spreads outward, converting the system from liquid to solid\textsuperscript{2}. One of the fundamental problems in quasicrystal physics is to reconcile the typical picture of nucleation and growth with the formation of an aperiodic solid. Quasicrystals cannot grow like crystals, where the nucleus surface acts as a template for copying a unit cell via local interactions. Rather, quasicrystals, require specialized “growth rules” that dictate their formation\textsuperscript{3}.

Quasicrystal growth rules fall into two categories: energy-driven quasiperiodic tiling models\textsuperscript{4, 5} and entropy-driven random tiling models\textsuperscript{6, 7}. While energy-driven models rely on ”matching rules” to dictate how atomic clusters or tiles attach to the nucleus, entropic models allow tiles to attach randomly to the nucleus with some probability. Although these models provide important insight into the rules that systems must follow to grow quasicrystals, they do not provide a detailed physical grounds to justify why such rules exist. The physical driving force underlying quasicrystal growth, and whether it is based on local interactions or long-range correlations, is not well understood.

In this Letter, we elucidate the atomistic mechanism of quasicrystal growth by studying the formation of a metastable dodecagonal quasicrystal from a model supercooled liquid. We show that quasicrystal growth is facilitated by structurally persistent atoms that become kinetically trapped in the supercooled liquid. As the solid nucleus grows, it incorporates these atoms in a way that minimizes expensive rearrangements and eases propagation allowing the quasicrystal to form instead of the stable crystalline phase. In the system under investigation, we find that structurally persistent atoms are highly icosahedral, indicating that they were in icosahedral clusters prior to nucleation. Our results provide a significant step forward in understanding quasicrystal formation and are consistent with the class of systems that are known to form quasicrystals experimentally.

To obtain these results, we utilize both conventional Monte-Carlo (MC) simulations and umbrella sampling\textsuperscript{8}. First, we use isothermal (NVT) MC to observe the growth of the quasicrystal from a static seed nucleus. We then use isothermal-isobaric (NPT) MC to observe the growth of large quasicrystal nuclei, generated via umbrella sampling. Finally, we use umbrella sampling to generate many configurations containing nuclei to study the relationship between quasicrystal nuclei and icosahedral clusters. All simulations consist of 3375 atoms with pair interactions modeled via the Dzugutov potential\textsuperscript{9}. Upon shifting the energy scale the Dzugutov potential tracks the 12-6 Lennard-Jones potential up to a distance at which an additional repulsive term dominates, suppressing the formation of BCC, FCC, and HCP.

![FIG. 1: Dodecagonal quasicrystal and approximants. (a) The inherent structure of a 17,576 atom dodecagonal quasicrystal formed by the Dzugutov system using molecular dynamics at $T^*=0.42$ and $\rho^*=0.85$. The image on the right shows the aperiodic tiles formed by connecting the centers of the dodecagonal rings of atoms. (b) Unit cells of various quasicrystal approximants.](image-url)
crystals and favoring polytetrahedral local ordering. This causes the system to form a dodecagonal quasicrystal from the melt at certain state points\[10, 11\] (see Fig. 1a). Although the quasicrystal is physically stable over the timescale of a typical simulation, it is thermodynamically metastable with respect to the $\sigma$-phase periodic approximant\[11\] (see Fig. 1b). Here, we run simulations at temperature $T^*=0.55$, pressure $P^*=3.5$ and density $\rho^*=0.85$, which is slightly below the degree of undercooling at which the system spontaneously forms a quasicrystal. At this state point it is improbable to form multiple nuclei simultaneously.

We begin by considering the growth of the solid phase from a small static seed nucleus in the form of a periodic approximant\[12\] that is inserted into the MC simulation cell (see Fig. 2). Periodic approximants are crystals with identical local ordering to the quasicrystals; therefore, for small nuclei, quasicrystals and approximants are identical and the difference in long-range ordering results from a different growth mechanism. Constraining the seed allows us to study the effect of seed structure on the quasicrystal growth. We randomize the atoms in our isothermal MC simulations at high temperature before quenching to $T^*=0.55$, at which point atoms begin to attach to the seed, causing rapid solidification. We observe that the system consistently forms a dodecagonal quasicrystal for all seed sizes, positions, and approximant structures, indicating that the system does not copy the seed, but rather incorporates atoms into the solid via a different paradigm.

Energy-driven quasicrystal growth models suggest that atomic attachment to the nucleus is deterministic, whereas entropy-driven models suggest that it is stochastic. We test the applicability of these models for our system by modifying the sequence of random numbers generated during the simulation, holding all else constant. As depicted in Fig. 2, for the same seed nucleus (blue), we consistently obtain distinguishable quasicrystal tiling arrangements, indicating that quasicrystal growth in this system is stochastic. We note that most of the tiling discrepancies (yellow) represent phasons\[13\], local tiling arrangements that can be converted into one another via so-called phason flips\[7, 13\]. Because the energetic difference between phasons is small, phasons represent equivalent pathways by which the quasicrystal can grow, thereby providing additional degrees of freedom for the growth of quasicrystals versus approximants.

Although the random tiling model appears to provide a suitable description of quasicrystal growth in our system, we note that discrepancies in the tiles appear to lag behind changes to the random number sequence. Thus, the process is not truly random, but dependent on some system variable that mimics randomness but reacts slowly to random number perturbations. The spatial arrangement of atoms in the liquid phase is a logical candidate for such a variable, since it displays both properties. We test this directly by detecting structural correlations between atoms in the liquid and the quasicrystal tiles that they subsequently form.

To detect such correlations, we introduce two new metrics: an order parameter to differentiate between liquid and solid atoms on a per-atom basis, and a configurational persistence function to measure how closely atoms retain their configurations as a function of time. Our order parameter is a modification of the $q_6(i) \cdot q_6(j)$ scheme of reference\[14\]. Here, $q_6(i) \cdot q_6(j)$ measures whether two atoms $i$ and $j$ have correlated first neighbor shells in terms of shape and orientation, with 1 (0) representing perfectly correlated (uncorrelated) configurations. Atoms form a solid-like connection if $q_6(i) \cdot q_6(j)$ exceeds a certain value, and atoms that form many solid-like connections with neighboring atoms are defined as being solid-like, reflecting the fact that in simple crystals all atoms have identical coordination shells. This scheme must be modified for quasicrystals and approximants, since neighboring atoms have different coordination shells corresponding to Frank-Kasper polyhedra\[15\]. For dodecagonal quasicrystals, we increase the range of the neighbor cutoff to $r_{cut} = 2.31 \sigma$, corresponding to the first $\sim 2.5$ neighbor shells. Also, we modify the harmonic frequency $l$ to from 6 to 12, to arrive at a new order parameter, $q_{12}(i) \cdot q_{12}(j)$. Pairs of atoms form a solid-like connection if $q_{12}(i) \cdot q_{12}(j) \geq 0.45$. atoms with 50% solid-like connections are solid-like, otherwise they are liquid-like. These cutoffs are chosen so as to maximize the distinction between liquid and quasicrystal. As quasicrystals and approximants have identical local ordering, $q_{12}(i) \cdot q_{12}(j)$ makes no distinction between them.

We use a similar approach to quantify the configurational persistence of atoms as a function of time. We de-
fine an autocorrelation function \( q_6(t) = q_6(i; t_0) \cdot q_6(i; t) \), where \( q_6(i; t_0) \cdot q_6(i; t) \) is equivalent to \( q_6(i) \cdot q_6(j) \), except that we apply the dot product to the same atom \( i \) at two different times instead of to different atoms at the same time. We define \( r_{cut} = 1.65 \) to include the first neighbor shell in our analysis. We use \( l = 6 \) since this yields the strongest signal, although we obtain qualitatively equivalent results for other choices of \( l \). We normalize \( q_6(t) \) on the interval \([0, 1]\), where \( q_6(t) = 1(0) \) for perfectly correlated (uncorrelated) configurations.

For reference, we consider the ensemble average \( \langle q_6(t) \rangle \) versus \( t \) for atoms in the bulk liquid and the bulk quasicrystal, shown by the bottommost and topmost curves in Fig. 3a, respectively. Both systems sample the isothermal-isobaric ensemble at \( T^* = 0.55 \) and pressure \( P^* = 3.50 \) corresponding to \( \rho^* = 0.85 \). We see that atomic configurations in the liquid become completely decorrelated from their initial state after \( \sim 35,000 \) MC cycles when \( \langle q_6(t) \rangle \to 0 \), whereas configurations in the quasicrystal are persistent over long timescales. The initial drop in \( \langle q_6(t) \rangle \) from 1.0 to 0.7 is due to thermal vibrations.

We detect structural correlations between liquid atoms and quasicrystal tiles in many independent nucleation events whereby the system grows a quasicrystal. Previously, we used a seed to initiate nucleation; however, here we use umbrella sampling to generate many configurations with growing nuclei. This allows us to observe nucleation at the same moderate degree of undercooling, but also ensures that the configurations that we generate are physical. Our sampling scheme is similar to references [14, 16], where our NPT MC runs are biased according to

\[
\langle q_6(t) \rangle \to \langle q_6(t) \rangle.
\]

We run MC simulations of growing nuclei for 75,000 MC cycles, the time it takes for nuclei to grow from \( \sim 100 \) atoms to \( \sim 500 \) atoms. At this point, boundary effects due to the finite size of the simulation cell begin to appear. The middle curve in Fig. 3a shows \( \langle q_6(t) \rangle \) vs. \( t \) for atoms that attach to the growing quasicrystal nucleus at \( t_0 = 0 \), such that for \( t < 0 \), the atoms are in the liquid, and for \( t \geq 0 \), the atoms are in the solid nucleus. We observe that \( \langle q_6(t) \rangle \) exhibits relatively high values for all \( t < 0 \), indicating that atoms in the quasicrystal are correlated with their former liquid configurations over long timescales.

This interesting behavior may result from structural correlations between the quasicrystal and the liquid, or

simply slow relaxation of liquid atoms in the vicinity of the nucleus, or both. To ascertain whether quasicrystal-liquid correlations play a significant role, we consider the probability distribution \( P(q_6(t)) \) (see Fig. 3b) for both nucleating atoms (dashed line) and atoms for a reference state at which the probability distribution exhibits typical behavior (solid line, taken here to be the liquid at \( T^* = 1.0 \), \( \rho^* = 0.85 \)). The distributions are shown at time delays for which they are identical for low \( q_6(t) \). We observe that atoms attaching to the nucleus at \( t = 0 \) exhibit a noticeably higher proportion of strongly correlated atoms than the reference state, indicating that the quasicrystal tends to retain the liquid configurations of a particular subset of atoms. Thus, we conclude that quasicrystal-liquid structural correlations play a significant role in producing the behavior observed in Fig. 3a.

However, we note that slow relaxation around the nucleus is also a factor, since upon truncating the correlated tails of the distributions, we still obtain higher \( \langle q_6(t) \rangle \) than for the liquid at all \( t \).

It is probably no coincidence that the quasicrystal tends to grow in a way that allows certain particles to retain their liquid configuration. As quasicrystals typically form in rapidly quenched metallic alloys with strong icosahedral ordering [8] (similar to metallic glasses), atoms in quasicrystal-forming liquids tend to fall into local energy minima that resist rearrangement [19]. Such systems should favor quasicrystal formation since quasicrystals are seemingly able to reach a “structural compromise” with the liquid in order to grow more
freely. In the Dzugutov liquid, atoms organize into local energy-minimizing structures known as “icosahedral clusters [20, 21],” which exhibit lower mobility than the bulk [22]. Structural analysis [15] of the most persistent atoms in Fig. 3b (the correlated tails of the distributions) shows that they consist of 32% icosahedra, 25% Z13, 31% Z14, and 10% Z15 configurations, consistent with the structure of icosahedral clusters. The most persistent atoms exhibit stronger icosahedral character than either the liquid (6% icosahedra), or the dodecagonal quasicrystal (27% icosahedra). We note that although the icosahedral glass formed by the Dzugutov system has vibrational modes similar to the \( \sigma \)-phase [23] (25% icosahedra and 75% Z14), the most persistent atoms do not exhibit \( \sigma \)-like character.

It is curious that our results implicate icosahedral clusters as the driving force underlying quasicrystal growth, since icosahedral clusters are relatively scarce at the state point under investigation [20]. We can obtain a more intuitive picture of the role of icosahedral clusters by considering their spatial arrangement in relation to the growing quasicrystal nucleus. We generate a large number of nuclei using the umbrella sampling scheme outlined above. However, here, following reference [10], we allow configuration swapping between simulations via parallel tempering. In all, we run 10 simultaneous MC simulations for 3.5 million timesteps, where each simulation has a unique biasing potential minimum \( N_0 = 10, 20, \ldots, 100 \). for a given simulation. We save configurations every 100 MC steps, giving us 35,000 total microstates containing nuclei of sizes \( N=10-110 \) for analysis. We identify icosahedral clusters in our microstates using the method of reference [24], an extension of the method of reference [24].

As depicted in Fig. 4a, we observe a high percentage of icosahedral clusters (yellow, white) in the region surrounding the nucleus (red). We quantify this by calculating the average probability of observing an atom at the center of an icosahedron a distance \( r \) away from the nucleus surface (see Fig. 4b). For nuclei of all sizes, we observe that \( P_{\text{ico}}(r) \) starts with a high value of 0.15 near the nucleus surface and decreases to the liquid value over a range of about three particle diameters. This result can be interpreted in one of two ways: either the presence of the nucleus encourages the formation of icosahedral clusters in the surrounding liquid, or vice versa. In either case, the growing nucleus must attach atoms from low-energy icosahedral clusters to its surface, which facilitates quasicrystal growth.

Our collective results imply that the driving force for quasicrystal formation vs. crystal formation is the ability for the solid phase to propagate more freely by growing aperiodically vs. periodically. In the system under investigation, this process is driven by the tendency for atoms to become kinetically trapped in icosahedral clusters in the supercooled liquid. However, we note that this cannot be the case in general since many quasicrystals do not contain icosahedral clusters. Despite this, we speculate that the basic mechanism at hand — the tendency for low-energy atoms in the liquid to retain their configuration when incorporated into the growing solid nucleus — may be widely applicable to quasicrystal-forming systems.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. 53, 1951 (1984).
[2] K. F. Kelton, Solid State Physics-Advances in Research and Applications 45, 75 (1991).
[3] U. Grimm and D. Joseph, Quasicrystals: An Introduction to Structure, Physical Properties, and Applications (Springer, 2002), chap. Modelling Quasicrystal Growth, pp. 49–66.
[4] D. Levine and P. J. Steinhardt, Phys. Rev. Lett. 53, 2477 (1984).
[5] H. C. Jeong and P. J. Steinhardt, Phys. Rev. B 55, 3520 (1997).
[6] V. Elser, Phys. Rev. Lett. 54, 1730 (1985).
[7] M. Oxborrow and C. L. Henley, Phys. Rev. B 48, 6966 (1993).
[8] G. M. Torrie and J. P. Valleau, J. Compute. Phys. 23, 187 (1977).
[9] M. Dzugutov, Phys. Rev. A 46, R2984 (1992).
[10] J. Roth and A. R. Denton, Phys. Rev. E 61, 6845 (2000).
[11] M. Dzugutov, Phys. Rev. Lett. 70, 2924 (1993).
[12] A. I. Goldman and R. F. Kelton, Rev. Mod. Phys. 65, 213 (1993).
[13] J. E. S. Socolar, T. C. Lubensky, and P. J. Steinhardt, Phys. Rev. B 34, 3345 (1986).
[14] P. R. ten Wolde, M. J. RuizMontoro, and D. Frenkel, J. Chem. Phys. 104, 9932 (1996), ISSN 0021-9606.
[15] F. C. Frank and J. S. Kasper, Acta Crystallographica 11,
184 (1958).

[16] S. Auer and D. Frenkel, J. Chem. Phys. 120, 3015 (2004).
[17] D. Moroni, P. R. ten Wolde, and P. G. Bolhuis, Phys. Rev. Lett. 94, 235703 (2005).
[18] C. Janot, Quasicrystals: a Primer (Clarendon Press, 1994).
[19] F. C. Frank, Proc. R. Soc. London A 215, 43 (1952).
[20] F. H. M. Zetterling, M. Dzugutov, and S. I. Simdyankin, J. Non-Cryst. Solids 293, 39 (2001).
[21] J. P. K. Doye, D. J. Wales, F. H. M. Zetterling, and M. Dzugutov, J. Chem. Phys. 118, 2792 (2003).
[22] M. Dzugutov, S. I. Simdyankin, and F. H. M. Zetterling, Phys. Rev. Lett. 89, 195701 (2002).
[23] S. I. Simdyankin, S. N. Taraskin, M. Dzugutov, and S. R. Elliott, Phys. Rev. B 62, 3223 (2000).
[24] C. Iacovella, A. Keys, M. Horsch, and S. Glotzer, Phys. Rev. E 75, 040801(R) (2007).
[25] P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B 28, 784 (1983).