Particles interacting via pair potentials with repulsive cores, which are either bounded or only slowly diverging—like those found naturally in soft matter systems [1]—can be made to overlap under pressure to form clusters [2], which then self-assemble to form crystalline phases [3]. The existence of such cluster crystals was recently confirmed in amphiphilic dendritic macromolecules using monomer-resolved simulations [4], and in certain bosonic systems [5]. They occur even when the particles are purely repulsive, and typically exhibit periodic fcc or bcc structures. Here we employ molecular dynamics (MD) simulations in two dimensions, guided by analytical insight, to show how isotropic pair potentials can be designed to control the self-assembly of the clusters, suggesting a practical approach for their controlled self-assembly in laboratory realizations using synthesized soft-matter particles.

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Soft particles are known to overlap and form stable clusters that self-assemble into periodic crystalline phases with density-independent lattice constants. We use molecular dynamics simulations in two dimensions to demonstrate that, through a judicious design of an isotropic pair potential, one can control the ordering of the clusters and generate a variety of phases, including decagonal and dodecagonal quasicrystals. Our results confirm analytical predictions based on a mean-field approximation, providing insight into the stabilization of quasicrystals in soft macromolecular systems, and suggesting a practical approach for their controlled self-assembly in laboratory realizations using synthesized soft-matter particles.

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 controlled self-assembly of periodic and aperiodic cluster crystals

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the effective potential used by LP. We then multiply this explicitly be positioned at 1 and wave number \( k \), such that two equal-depth minima can simply be positioned at 1 and \( q = k_n \), similar in form to the effective potential used by LP. We then multiply this polynomial by a Gaussian to limit the extent of the potential. These LP-Gaussian potentials are given in Fourier space by

\[
\tilde{U}(k) = e^{-k^2/2\sigma^2}(D_0 + D_2k^2 + D_4k^4 + D_6k^6 + D_8k^8),
\]

and are self-dual in the sense that they have the same functional form in real space. Using a two-dimensional Fourier transform we obtain

\[
U(r) = \frac{1}{2\pi} \int_0^\infty \tilde{U}(k)J_0(kr)kdk = e^{-r^2/8\sigma^2}(C_0 + C_2r^2 + C_4r^4 + C_6r^6 + C_8r^8),
\]

where \( J_0 \) is the zeroth-order Bessel function, and the polynomial coefficients \( C_0, \ldots, C_8 \) are linear functions of the Fourier-space coefficients \( D_0, \ldots, D_8 \). We set the latter five independent coefficients such that \( U(0) = C_0 = 1 \) and there are two equal-depth minima at positions 1 and \( k_n \) in reciprocal space with \( \tilde{U}(1) = \tilde{U}(k_n) = -0.08 \). This sets both the energy scale and the length scale in our description of the problem. The standard deviation \( \sigma \) of the Gaussian in reciprocal space is chosen such that the potentials are purely repulsive in real space, although this is not required. Note that while it is difficult to tell the potentials apart in real space [Fig. 1(a)] and therefore not obvious to anticipate which cluster crystal they will obvious to anticipate which cluster crystal they will stabilze, the potentials are clearly distinguishable in reciprocal space [Fig. 1(b)], where the wave-number ratio \( q \) is visible. Similarly, one would need to tune the real-space parameters of any realistic potential to possess the required minima in Fourier space. The LP-Gaussian potentials benefit from being simple, bounded, and rapidly decaying and therefore amenable to MD simulations.

We initialize GPU-accelerated MD simulations [29] in the liquid phase above the melting temperature. The system is slowly cooled down in the \( NVT \) ensemble to induce self-assembly. At \( T = 0 \), the protocol is reversed until melting occurs. Typically, the first signs of ordering are

copolymers [15], in systems of nanoparticles [16], with anisotropic particles [17] and pentameric molecules [18], and in mesoporous silica [19]. These systems provide exciting platforms for the fundamental study of the physics of quasicrystals [20] and promise new applications of self-assembled nanomaterials [21].

The key idea of BDL was borrowed from Lifshitz and Petrich (LP) [22], who extended the Swift-Hohenberg equation [23] to study parametrically excited surface waves (Faraday waves), also exhibiting dodecagonal quasiperiodic order [24]. The Swift-Hohenberg equation is a generic model for pattern-forming systems [25] that describes the instability of a uniform state against the formation of Fourier modes with a fixed and finite wave number. In the LP modification the instability occurs simultaneously at two wave numbers, whose ratio \( q \) is tunable. It is then the role of resonant three-mode interactions to stabilize structures containing triplets of Fourier modes with wave vectors that add up to zero. By setting the value of the wave-number ratio \( q \) to \( k_n = 2\cos(\pi/n) \), one can form triplets containing two unit wave vectors separated by \( 2\pi/n \), and a third wave vector of length \( k_n \). Indeed, stable patterns with \( n \)-fold symmetry were shown to exist in the LP model for \( n = 4, 6, \) and 12, with wave-number ratios \( k_4 = \sqrt{2} \), \( k_6 = \sqrt{3} \), and \( k_12 = \sqrt{2 + \sqrt{3}} \), respectively, as well as stripes for \( k_\infty = 2 \) [22]. Patterns with eightfold symmetry are unstable within the LP model, but there is a narrow window of stability for tenfold patterns with a ratio of \( k_5 = (1 + \sqrt{5})/2 \), although not with \( k_{10} = \sqrt{(5 + \sqrt{5})/2} \) [26].

Based on these design principles, and to remain as pedagogical as possible, we work directly in Fourier space to construct the family of smooth pair potentials shown in Fig. 1. Yet, we emphasize that our approach can be applied to any realistic potential with sufficiently many tunable parameters. We use a polynomial in even powers of the wave number \( k \), such that two equal-depth minima can explicitly be positioned at 1 and \( q = k_n \), similar in form to the effective potential used by LP. We then multiply this polynomial by a Gaussian to limit the extent of the potential. These LP-Gaussian potentials are given in Fourier space by

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strong density fluctuations in the liquid, which then condense into clusters and spread to develop global order. Individual particles can migrate between neighboring clusters at elevated temperatures, even after cluster crystallization has set in, to average out density fluctuations and heal defects. We observe self-assembly at all densities in the studied range $0.1 \leq \bar{c} \leq 2.0$. While at low densities, below $\bar{c} \approx 0.5$, the particles behave more individually and the hexagonal crystal prevails, at higher densities the MD results exactly match the equilibrium structures predicted by mean-field theory, as demonstrated in the top row of Fig. 2. As expected, we find striped (lamellar), tetragonal, hexagonal, decagonal, and dodecagonal cluster crystals. In all cases, the strongest peaks in the diffraction diagrams are located at $1$ and $\kappa_n$, the two minima of $\tilde{U}(k)$, followed by a ring with little scattering where $\tilde{U}(k)$ has its maximum. The superstructures formed by thinner stripes within the striped phase and smaller clusters within the hexagonal phase, predicted by the mean-field densities in Figs. 2(a) and 2(c), are observed in the MD simulations at higher densities [27]. The hexagonal superstructure is analogous to the superlattice structures observed in Faraday waves [30].

The transition from the liquid to a cluster crystal is a first order phase transition and therefore accompanied by hysteresis. We use "error" bars in Fig. 3 to show the temperature range of coexistence, obtained from simulation, as a function of $\bar{c}$. The bars span the temperature range from where crystallization is observed upon cooling to where melting occurs upon heating. The lower ends are bounded from below by the mean-field predicted $T_{sp}$, shown in Fig. 3.
At lower temperatures, mean-field theory predicts that the quasicrystals should become unstable toward a secondary transformation into a periodic phase of lower rotational symmetry, such as a hexagonal cluster crystal [8]. We do not observe a transformation for the decagonal quasicrystal. We do observe a secondary transformation for the dodecagonal quasicrystal into either the so-called $\sigma$ phase [27], which is a known periodic approximant for dodecagonal quasicrystals that is commonly observed in soft-matter systems [13–16], or a compressed hexagonal phase [Fig. 5(a)], similar to the one considered by LP in their Fig. 2(b). In all cases we find that the transformation is reversible and the quasicrystal reforms in simulation upon heating, confirming the mean-field prediction regarding the role of entropy in its stabilization. We frequently observe significant density fluctuations already prior to ordering, as shown in Fig. 5(b), indicating the possibility that first a cluster liquid is formed, and then the clusters order. This opens up interesting questions about the formation mechanism of the cluster crystals. The observation that cluster crystals sometimes “lock-in” their orientation to the simulation box [33] suggests that fluctuations are important and classical nucleation theory might not be applicable.

To conclude, we have shown how to control the self-assembly of a variety of cluster crystals by using isotropic pair potentials with two length scales, and designing their ratio in Fourier space—a general procedure that can be applied to other kinds of potentials and in the lab, and which expands upon earlier potential design schemes [34]. This work can be continued in several directions. Longer and larger simulations, accompanied by numerical free-energy calculations [35], are necessary to obtain more precise phase diagrams and to accurately identify the stability regions and their dependence on cooling rates and finite size effects. The dynamics leading to crystallization and the study of collective phonon and phason degrees of freedom in the ordered state are open problems. Finally, an extension to three dimensions is a next step toward making a firmer contact with experimental observations of quasicrystals in soft matter systems.

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FIG. 4 (color online). Histograms of the cluster sizes in Fig. 2. (a),(b) Periodic crystals show sharp distributions. (c),(d) Quasicrystals exhibit broad distributions. We use the cluster size cutoff parameter $\text{MinPts} = 8$ for the DBSCAN algorithm [31].

as a straight line. Except for low densities, where the mean-field approximation fails, we observe a shift of about 0.01–0.03 between the simulated freezing points and the mean-field spinodal line. This shift is due to thermal fluctuations causing the cooled liquid to become unstable and freeze earlier.

We further characterize the ordered phases by identifying individual clusters using the DBSCAN algorithm [31]. Figure 4 demonstrates that while the cluster size distribution is narrowly peaked for periodic cluster crystals indicating a single characteristic cluster size, the cluster size distribution has a broad peak for the decagonal cluster crystal and is flat and almost featureless for the dodecagonal cluster crystal. This observation is in agreement with experimentally observed distributions of high-symmetry stars in quasiperiodic light fields [32] and with the mean-field density profiles shown alongside the MD simulation results in Fig. 2.

FIG. 5 (color online). (a) At low temperature and high density the dodecagonal quasicrystal can reversibly transform into a compressed hexagonal phase [27]. (b) Snapshot of the liquid phase at a temperature just above the onset of ordering, possibly showing a liquid of clusters. Clusters are colored according to their size from small (light blue, size $\leq 10$) to large (dark red, size $\geq 30$).
We confirmed the occurrence of the lock-in phenomena, which is very robust with its 24 Fourier modes and 32 stabilizing triplets. The $k_{12}$ quasicrystal has 16 modes with only 8 triplets, and the $k_{10}$ quasicrystal has 20 modes with 10 triplets, making them both always unstable with respect to the simple hexagonal phase with its 6 modes and 2 triplets. The $k_5$ quasicrystal has 20 modes with 20 triplets, making it just barely stable if parameters are exactly tuned, but it is not as robust as the dodecagonal phase against slight deviations from the exact requirements. We believe that for this reason decagonal quasicrystals have not yet been observed in real systems of soft isotropic particles.


We confirmed the occurrence of the lock-in phenomena, where a main crystallographic axis is oriented parallel to $N$ with $N$ in the simulation box, in about 10%–20% of the simulations with $N = 16384$ using two independent MD codes.

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