Programmable 2D materials through shape-controlled capillary forces

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Author Contributions: JLE and SOM performed the minimum energy calculations and data analysis, JLE performed the Monte Carlo simulations, DMAB wrote the manuscript with the help of JLE and SOM, all the authors commented on the manuscript, DMAB conceptualized and supervised the study.

Competing Interest Statement: no competing interests.

Classification: Physical Sciences/Physics

Keywords: Colloids, interfaces, self-assembly, particle simulations

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Abstract

In recent years, self-assembly has emerged as a powerful tool for fabricating functional materials. Since self-assembly is fundamentally determined by the particle interactions in the system, if we can gain full control over these interactions, it would open the door for creating functional materials by design. In this paper, we exploit capillary interactions between colloidal particles at liquid interfaces to create two-dimensional (2D) materials where particle interactions and self-assembly can be fully programmed using particle shape alone. Specifically, we consider colloidal particles which are polygonal plates with homogeneous surface chemistry and undulating edges as this novel particle geometry gives us precise and independent control over both short-range hard-core repulsions and longer-range capillary interactions. To illustrate the immense potential provided by our system for programming self-assembly, we use minimum energy calculations and Monte Carlo simulations to show that polygonal plates with different in-plane shapes (hexagons, truncated triangles, triangles, squares) and edge undulations of different multipolar order (hexapolar, octapolar, dodecapolar) can be used to create a rich variety of 2D structures, including hexagonal close packed, honeycomb, Kagome and quasicrystal lattices. Since the required particle shapes can be readily fabricated experimentally, we can use our colloidal system to control the entire process chain for materials design, from initial design and fabrication of the building blocks, to final assembly of the emergent 2D material.

Significance Statement

The tremendous power of capillary forces for organizing anisotropic particles at liquid interfaces into complex 2D structures has been known for over two decades, but a major roadblock in creating fully programmable 2D materials is the fact that the capillary interactions in current systems are determined indirectly by particle anisotropy. In this study, we consider a novel particle geometry where particle interactions and self-assembly at the liquid interface can be directly controlled and hence fully programmed using particle shape alone. Since the required particle shapes can be readily fabricated experimentally, our novel colloidal system could revolutionise colloidal self-assembly in two dimensions, in the same way that DNA linker technology has revolutionised colloidal self-assembly in three dimensions.

Introduction

Self-assembly is the remarkable process where small building blocks spontaneously organize themselves into larger complex structures due to the combined action of Brownian motion (which allows the system to explore phase space) and particle interactions (which drive ordering). It is central to understanding fundamental processes in condensed matter physics such as crystallization (1-3) and it is also emerging as a powerful tool for fabricating functional materials such as plasmonic nanostructures (4), nanoscale electronic devices (5) and photonic bandgap materials (6). Since self-assembly is fundamentally determined by the interaction between the building blocks, if we can gain full control over these interactions, it would open the door for creating functional materials by design. In this context, colloids have long been used as model systems for studying and harnessing self-assembly because, unlike atoms and molecules where interactions are predefined and cannot be easily modified, colloids possess a rich variety of interactions that are highly tuneable, providing powerful handles with which to program self-assembly (7-9). In the case of colloidal particles adsorbed at a liquid interface, the variety of interactions that are present is even richer than in the bulk (10): not only are electrostatic, van der Waals and steric forces qualitatively different at an interface compared to in the bulk (10-13), but the fluid interface also gives rise to interactions which have no analogue in the bulk, for example capillary interactions (14,15). Furthermore, by coupling these interactions to dynamic external fields, we open up the exciting prospect of creating reconfigurable devices which can transition between different self-assembled structures on demand, or which can change their own configuration as they explore their environment (16,17).

The aim of this paper is to use capillary interactions to create fully programmable two-dimensional (2D) materials. Capillary interactions arise when the fluid interface is deformed by the presence of the particle because of gravity or particle anisotropy (either in shape or surface chemistry) (14,15). When distortions from neighboring particles overlap, depending on whether the distortions have the same or opposite sign (relative to the unperturbed interface), the capillary interaction between particles will be attractive or repulsive respectively. A familiar example of how capillary forces can drive self-assembly is the 'Cheerios effect', the phenomenon where breakfast cereals floating in a bowl of milk aggregate together due to capillary forces induced by gravity (18). However, a more powerful method for creating ordered, 2D structures is to use capillary forces induced by particle anisotropy instead. This was first demonstrated by Whitesides and co-workers using millimetre-scale flat polygonal plates at an air-water interface, with the particles density-matched with the water subphase to minimize the effect of gravity (19,20). By patterning the edge of the polygonal plates with hydrophilic or hydrophobic surface chemistries, they created positive or negative deformations of the liquid interface around the particle, and by using different combinations of hydrophilic and hydrophobic edges, they could assemble the polygonal plates into complex clusters, linear and non-linear chains, hexagonal close-packed and honeycomb lattices. Later studies extended the seminal work of Whitesides *et al*. to colloids with homogeneous surface chemistry but anisotropic shapes, e.g., ellipsoids (21,22), cylinders (23) and cubes (24-26). When adsorbed at a fluid interface, the constant contact angle condition at the three-phase contact line around such particles can only be satisfied when the interface is deformed, leading to quadrupolar or higher order multipole contact line undulations, depending on the shape and orientation of the adsorbed particles (14,27,28). The resultant anisotropic capillary interactions between particles drives the self-assembly of the particles into a rich variety of chain-like and extended lattice structures (14,21-26).

While the studies above demonstrate the tremendous possibilities for controlling capillary assembly by tuning particle anisotropy, an important limitation in these systems is the fact that the position of the three-phase contact line is not fixed *a priori* but is determined indirectly by the constant contact angle condition. The indirect link between particle anisotropy and contact line position makes it difficult to gain full control over the capillary interactions in these systems. Furthermore, the complex patchy particle morphology used by Whitesides and co-workers is very challenging to scale down below the millimeter scale, limiting the system sizes that can be produced (29).

In order to overcome these important challenges, in this paper, we consider a novel particle geometry where our colloidal building blocks are polygonal plates with homogeneous surface chemistry and undulating edges. In terms of the aims of our study, this particle geometry possesses a number of game-changing advantages. Firstly, as we show later, provided the plates are thin enough and the amplitude of the undulations is small enough, the three-phase contact line is effectively pinned to the particle edge, giving us direct control over the position of contact line undulations and hence capillary interactions in the system. This control allows us to introduce selective interactions between polygon sides, favouring specific polymorphs over others and thus create 2D structures with much longer-ranged order than was possible with previous systems.

Secondly, since we control capillary interactions through particle shape rather than surface chemistry, this considerably simplifies the fabrication of the colloidal building blocks, allowing us to increase throughput and reduce particle size. For example, relatively low throughput production of the required particle shapes (e.g., ~10s of particles) can be achieved using 3D printing (16,17), with sub-micron resolution achievable using two-photon polymerization techniques (30,31). Much higher throughput production (>100 particles) can be achieved by stamping defined surface textures onto a flat sheet and morphing the resultant flat objects into the required 3D shapes, for example through asynchronous swelling (32).

Thirdly, our novel particle geometry above gives us independent control over both short-ranged and long-ranged interactions using particle shape alone. Specifically, short-ranged hard-core repulsions can be controlled by changing the shape of the polygonal plates in the interfacial plane, while longer-ranged capillary interactions can be controlled by changing edge undulations normal to the interface. For colloidal polyhedra interacting only through hard-core repulsions, Glotzer and co-workers found that changing particle shape allowed them to access an incredibly rich variety of self-assembled structures, including crystals, liquid crystals, plastic crystals and quasicrystals (33). For our system, where we can use shape to fully control the interplay between short-ranged hard-core repulsions (which determine local packing) and longer-ranged capillary interactions (which determine directional aggregation), the possibilities for self-assembly are even richer.

To illustrate the immense potential provided by our system for programing self-assembly, in this paper we use both minimum energy calculations and Monte Carlo simulations to show how we can engineer the shape of the colloidal building blocks to create a variety of 2D structures, including hexagonal, honeycomb, open Kagome and quasi-crystalline lattices. Note that the complex structures we create arise from higher order multipole capillary interactions. These multipolar interactions would be overwhelmed if gravity-induced capillary interactions are present, as the latter are monopolar in nature and therefore have a much longer range (14,15). In our calculations, we assume that gravitational forces are negligible. Our calculations therefore apply to polygonal plates on the micron-scale, which are small enough for gravity to be negligible (34) and Brownian motion to be significant, but large enough for the energy scale for capillary interactions to much greater than thermal energy k_BT, so that we are in the low temperature regime where minimum energy calculations are valid (24,25). However, our calculations are also applicable to larger particles (say on the millimeter-scale) if we 'switch-off' gravity by density-matching the adsorbed particles with the liquid subphase and introduce random motion by using external mechanical vibration (19,20).

Results & Discussions

Theoretical Model

We consider a system of polygonal plate-like particles adsorbed at a flat fluid-fluid interface. We define the lab frame coordinates (x, y, z) such that the z axis is perpendicular to the fluid interface when no particles are adsorbed and the fluid interface is in the $z = 0$ plane. It is also convenient to define particle frame coordinates (x', y', z'), where the z' axis is perpendicular to the average plane of the polygonal plate and, depending on the orientation of the particle, they are related to the lab frame coordinates (x, y, z) via appropriate rotational coordinate transformations (35), see Figure S1 and accompanying text in Supplementary Information.

To describe the geometry of the polygonal plate particles with undulating edges, we use the generalized super-ellipsoid equation

$$\left(\frac{x'\cos\psi_1 + y'\sin\psi_1 - \Delta}{a}\right)^{\zeta_1} + \left(\frac{x'\cos\psi_2 + y'\sin\psi_2 - \Delta}{a}\right)^{\zeta_1} + \left(\frac{x'\cos\psi_3 + y'\sin\psi_3 - \Delta}{a}\right)^{\zeta_1} + \left(\frac{z' - z_0(r,\theta)}{b}\right)^{\zeta_2} = 1 \qquad (1)$$

where the undulation of the plate edge is given by the function

$$z_0(r,\theta) = Ar\cos[m(\theta - \theta_0)]. \qquad (2)$$

Equation (1) essentially controls the in-plane shape of the polygonal plate and allows us to describe a wide range of polygon shapes (see Figure S2 and accompanying discussion). Specifically, the angles ψ_1, ψ_2, ψ_3 control the orientation of pairs of parallel sides making up the polygon in the (x', y') plane. Note that Equation (1) as written assumes a polygon made of three pairs of parallel sides, i.e., a six-sided polygon, but the number of sides can be varied by adding or removing terms on the left-hand-side of the equation as necessary. The parameters ζ_1, ζ_2 are even integers that determine the sharpness of the corners for the polygon and plate cross section respectively, with higher values leading to sharper corners. In our study, we use $\zeta_1 = 20$ and $\zeta_2 = 2$, i.e., relatively sharp polygon corners and rounded plate cross sections (see Figure 1). The parameters a, b are the average radius and half thickness of the plate respectively while Δ allows us to control the distortion of the polygon away from a regular polygon. In our study, we consider thin plates where $a/b \gg 1$. On the other hand, Equation (2) essentially controls the out-of-plane shape of the polygonal plate. Specifically, (r, θ) are circular polar coordinates in the (x', y') plane, A is a parameter that determines the amplitude of the edge undulations, m is the multipole order of the edge undulations (with $m = 2, 3, \ldots$, corresponding to quadrupolar, hexapolar etc.) and θ_0 controls the phase shift between the edge undulations and polygon shape. A full explanation of Equations (1), (2) and their control parameters can be found in Supplementary Information.

As discussed in the Introduction, the focus of our study is on adsorbed particle systems where gravity is negligible, e.g., micron-scale particles or larger particles which are density-matched with the fluid subphase. In this case, the energy of the system is primarily due to interfacial energy and is given by (24,25)

$$E = \gamma(S - S_0 + W \cos\theta_w) \qquad (3)$$

where S, S_0 are the total area of the fluid-fluid interface with and without adsorbed particles respectively (so that $S - S_0$ is essentially the area of the fluid-fluid interface excluded by the presence of the adsorbed particles), W is the area of the particle in contact with the fluid above the interface, θ_w is the contact angle and γ is the interfacial tension of the fluid-fluid interface. To highlight the role played by particle shape in controlling self-assembly, in our paper, we assume $\theta_w = 90°$, i.e., the adsorbed particles are neutrally wetting. In fact, the specific value of θ_w is not crucial since the fluid interface is pinned to the particle edge for the thin plate geometry we consider in this paper (see later). For a given configuration of adsorbed particles, the energy of the system, given by Equation (3), is calculated using the finite element software Surface Evolver (36), see Methods for further details.

Hexagonal Plates

The first particle shape we consider is that of a thin hexagonal plate with hexapolar edge undulations. The shape parameters we use in Equations (1) and (2) for this shape are $\psi_1 = \pi/2$, $\psi_2 = 7\pi/6$, $\psi_3 = 11\pi/6$, $\Delta = 0$, $a/b = 10$, $m = 3$ and we work with length units where the side length of the hexagon $L = 1$ so that $a = \sqrt{3}/2$, see Supplementary Information. We consider two types of hexagonal plates, H0 where the maximum displacement of the undulations coincides with the corners of the hexagon (i.e., $\theta_0 = 0$ in Equation (2), see Figure 1a,c), and H30 where the maximum displacement coincides with the middle of the hexagonal side (i.e., $\theta_0 = \pi/6$ in Equation (2), see Figure 1b,d). As we shall see later, the subtle change in the phase angle between edge undulations and the hexagonal shape for these two types of particles leads to dramatic changes in their self-assembly behavior.

We first consider the properties of isolated adsorbed particles. In general, we require six variables to fully specify the position and orientation of a non-axisymmetric plate (24,25), namely the centre of mass coordinates x_p, y_p, z_p of the plate in the lab frame, the azimuthal angle φ of the plate about the interface normal (i.e., z axis), the polar angle α between the plate normal and the interface normal and the rotation angle β of the plate about its normal (i.e., z' axis), see Figure S1 in

Supplementary Information. However, for an isolated adsorbed particle, the energy depends only on z_p, α and β. In Figure S3 in Supplementary Information, we plot the energy of a H0 particle as a function of α and β, with the energy minimized with respect to z_p for each particle orientation. We see that the equilibrium orientation of the hexagonal plate is $\alpha = 0°$ (where β becomes irrelevant). This result is in good agreement with our previous results for adsorbed cylindrical particles, where in the limit of thin cylindrical plates, the plate normal is perpendicular to the interface (37). The result is also in good agreement with the results of Whitesides and coworkers for patchy hexagonal plates (20), where plates with centrosymmetric arrangements for their patchy edges have plate normals that are perpendicular to the liquid interface. Since all the polygonal particles we consider in this study are thin and have centrosymmetric edge undulations, in what follows we set $\alpha = \beta = 0°$ in our calculations.

Next, we consider the degree to which the edge undulations of the particles control the deformation of the liquid meniscus around the particle. In Fig 1a,b we plot the top view of the particle and the height of the liquid meniscus around H0 and H30 respectively for edge undulations with amplitude parameter $A = 0.1L$ in Equation (2); we use positive and negative signs to denote the positive and negative antinodes of the undulations in each case. We see that the liquid meniscus follows closely the deformation of the particle edge. Indeed, in Supplementary Information, we demonstrate quantitatively that for the small values of A considered in this paper, the three-phase contact line is effectively pinned to the plate edge (see Figure S4 and accompanying discussion). In the rest of the paper, we therefore simplify our Surface Evolver calculations by eliminating the particle surface and set the z' coordinate of the contact line to satisfy Equation (2), and the (x', y') coordinates of the contact line to satisfy Equation (1) but without the term containing z' on the left-hand side.

(Figure 1)

Figure 1: (a,b) Top view of particle geometry and contour plot of the liquid interface height (normalized to the hexagon side length L) around (a) H0 and (b) H30 hexagonal plates adsorbed at a liquid interface. The positive and negative signs denote the position of the positive and negative antinodes of the particle edge undulations respectively. (c,d) Side view of the system for (c) H0 and (d) H30 hexagonal plates.

Having established the equilibrium properties for isolated particles, we now study the pair interaction and self-assembly of many particles. Note that when calculating the energy of two- or many-particle systems, we fix z_p, α and β for each particle to their isolated-particle values since previous studies have shown that the height and polar orientation of adsorbed particles is essentially unaffected by the proximity of other particles (24,25,38). In this case, the configuration of a system consisting of N polygonal plates is specified by the set of variables $\{x_{pi}, y_{pi}, \varphi_i\}$ with $i = 1, \dots, N$, where x_{pi}, y_{pi} are the x, y centre of mass coordinates of the i-th plate and φ_i is the azimuthal angle of the i-th plate (see Figure S1).

We first consider the capillary pair interaction potential between two hexagonal plates as a function of their centre-to-centre separation d and the orientation of the two particles which is defined as

$$V_2(d, \phi_1, \phi_2) = E_2(d, \phi_1, \phi_2) - E_2(\infty), \qquad (4)$$

where ϕ_1, ϕ_2 are the azimuthal angles of the capillary multipoles for particle 1 and 2 respectively relative to the centre-to-centre line between the particles (see Figure S5 in Supplementary Information) and $E_2(d, \phi_1, \phi_2)$, $E_2(\infty)$ are the energies of the two-particle system at separation d and orientation ϕ_1, ϕ_2 and at infinite separation respectively, calculated from Equation (3).

(Figure 2)

Figure 2: (a,b) Attractive (top) and repulsive (bottom) capillary pair interactions as a function of centre-to-centre separation for different relative orientations of interacting particles for (a) H0 and

(b) H30 particles. The solid and dotted vertical lines denote the separation for side-to-side and corner-to-corner contact of the hexagons respectively. (c,d) The crystal structures we consider for (c) H0 and (d) H30. For each crystal structure, we show the lattice vectors $\boldsymbol{a}$, $\boldsymbol{b}$, *the nearest neighbour separation* d, *and the unit cell used in the Surface Evolver calculations, where sides of the unit cell with the same colour have the same interface height. The yellow and purple spots in (a-d) denote positive and negative capillary poles respectively. (e,f) Plot of* ηv_{∞} *vs.* η *for the different crystals structures shown in (c) and (d), where* η *is the area fraction and* v_{∞} *is the many-body capillary interaction per particle given by Equation (5). The data points are numerical results calculated from Surface Evolver and the solid lines are the fits to the numerical data using the form* $B\eta^{C}$, *where the fitting parameters* B, C *for each crystal phase are given in Table S2 in Supplementary Information. The vertical dashed lines are the highest area fraction for each crystal phase and the black solid and dashed lines are the equilibrium common tangent lines.*

In Figure 2a,b, we show the capillary interaction for H0 and H30 respectively for different relative azimuthal orientations of the interacting particles. Note that the yellow and purple spots in Figure 2 indicate positive and negative interfacial deformations (or capillary poles) respectively. We see that particles attract each other when capillary poles of the same sign overlap (Figure 2a,b top), and they repel each other when capillary poles of opposite sign overlap (Figure 2a,b bottom). Specifically, following the terminology used by Soligno *et al.* (24,25), there are two types of particle orientations that are attractive: (i) dipole-dipole attraction, where one set of two capillary poles from one plate (one positive, one negative) overlap with the same set of two capillary poles from the other plate (red curves); (ii) tripole-tripole attraction, where one set of three capillary poles from one plate (positive-negative-positive or negative-positive-negative) overlap with the same set of three capillary poles from the other plate (blue curves). From Figure 2a,b, we see that for both H0 and H30, the interaction energy at the same particle separation is essentially the same for dipole-dipole and tripole-tripole attractions. For a given particle type, the minimum interaction energy is therefore given by the relative orientation that allows the two particles to come closest to each other, i.e., where the hexagons are in side-to-side contact. Since the orientation of the capillary hexapole relative to the hexagonal shape is different for H0 and H30, the lowest energy (i.e., strongest) capillary bond is the dipole-dipole bond for H0 (red curve in Figure 2a top) but the tripole-tripole bond for H30 (blue curve in Figure 2b top).

The apparently subtle difference between H0 and H30 in the nature of their ground state capillary bonds has profound consequences for their self-assembly as we shall now discuss. When H0 or H30 are bonded to six nearest-neighbours via dipole-dipole bonds, they form a hexagonal lattice (Hex), specifically a hexagonal close-packed lattice for H0 (Figure 2c top left) and a Kagome lattice (Kag) for H30 (Figure 2d top left). On the other hand, when these particles are bonded to two opposite nearest-neighbours via dipole-dipole bonds and two other nearest-neighbours via tripole-tripole bonds, they form a rectangular lattice (Rec, Figure 2c,d top right). Finally, when these particles are bonded to three nearest-neighbours via tripole-tripole bonds, they form a honeycomb lattice (Hon, Figure 2c,d bottom). Note that there are two versions of the honeycomb phase, namely where the primary overlapping capillary pole is positive (Hon+, Figure 2c,d bottom left) or negative (Hon-, Figure 2c,d bottom right). For the neutrally wetting particles we are considering in this paper ($\theta_w = 90°$), Hon+ and Hon- are degenerate in energy. Note also the honeycomb phase is not an incomplete hexagonal phase because the holes in the honeycomb lattice are surrounded by capillary poles of the same sign (either negative for Hon+ or positive for Hon-), so that it is energetically unfavourable to insert hexapolar particles to fill these holes (24,25).

Since the ground state capillary bond is the dipole-dipole bond for H0 and the tripole-tripole bond for H30, we anticipate that in the low temperature regime that we are considering in this paper, the equilibrium phase is the hexagonal close-packed structure for H0 but the honeycomb structure for H30. In order to check this prediction, we calculate the equilibrium state of the two particle shapes by plotting ηv_{∞} vs. η for the different phases discussed above for H0 (Figure 2e) and H30 (Figure

2f), where η is the area fraction of the hexagonal plates and v_∞ is the many-body capillary interaction per particle for a given phase which is defined by

$$v_\infty(d) = \varepsilon_\infty(d) - \varepsilon_\infty(\infty). \qquad (5)$$

Here d is the separation between nearest neighbours (shown in Figure 2c,d for the different phases) and $\varepsilon_\infty(d)$, $\varepsilon_\infty(\infty)$ is the energy per particle in a given phase at separation d and at infinite separation respectively. These energies are obtained by using Surface Evolver to calculate the energy of a unit cell (shown in Figure 2c,d for the different phases) and applying periodic boundary conditions to the sides of the unit cell as indicated in Figure 2c,d. Note that the Hex phase contains one particle per unit cell, while the Rec and Hon phases contain two particles per unit cell, with one of the particles rotated azimuthally by $180°$ relative to the other. Note also that since Hon+ and Hon- are degenerate, we only plot a single curve for the honeycomb phase in Figure 2,e,f. In addition, the maximum area fraction for each phase η_c (i.e., when nearest neighbours are in contact $d = d_c$) is represented by vertical dashed lines in Figure 2e,f. The parameters for all the crystal structures considered in this paper are given in Table S1 in Supplementary Information.

Since Figure 2e,f are essentially plots of energy per unit area versus density, we can determine the equilibrium state for each particle shape graphically by using a common tangent analysis (24,25). Specifically, the common tangent line for each crystal structure is the straight line joining the points on the plot corresponding to the empty phase $\eta = 0$ and the highest density state of that crystal $\eta = \eta_c$; the equilibrium state of the system for any given value of η is then given by the lowest common tangent line at that value of η, and these lines are denoted by black solid or dashed lines in Figure 2e,f. From the common tangent analysis of Figure 2e, we see that (for small enough η) the equilibrium state for H0 is where the empty phase coexists with the hexagonal close-packed structure, while from Figure 2f, the equilibrium state for H30 is where the empty phase coexists with the honeycomb structure. These results confirm our earlier prediction that the ground state crystal structure for H0 and H30 are the hexagonal close-packed structure and the honeycomb structure respectively. Thus, by a subtle change in the orientation of the capillary hexapole relative to the hexagonal shape, we have changed the equilibrium crystal structure of the hexagonal plates dramatically.

To check whether the ground state crystal structures for H0 and H30 are accessible kinetically, we performed finite temperature Monte Carlo (MC) simulations for these particle shapes, including both hard-core and capillary interactions between the particles in our simulations. The MC simulations were performed at an area fraction of $\eta = 0.3$. This area fraction was chosen since it is low enough for the system to be in the dilute regime (i.e., polygons on a hexagonal lattice can freely rotate about their centres without interfering with each other) but high enough for extended structures to be formed in reasonable simulation time. In Supplementary Information, we show that for particles on the micron-scale or larger, the system is in the low temperature regime $T^* = k_BT/U_0 \ll 1$, where k_BT is the thermal energy and U_0 is the energy of the ground state capillary bond; values for U_0 for the different particle shape pairs are given in Table S3. For larger than micron-scale particles whose random motion is induced by external mechanical vibrations rather than thermal energy, motivated by the equipartition theorem, we can define an effective temperature for the system T_{eff} from the relation $k_BT_{\text{eff}} \approx \gamma\langle u^2\rangle$, where γ is the interfacial tension and $\langle u^2\rangle$ is the mean-squared vertical displacement of the fluid-fluid interface relative to its equilibrium height (39). The low temperature regime in this case therefore corresponds to the condition $T^* = \gamma\langle u^2\rangle/U_0 \ll 1$. To ensure efficient equilibration of the system in our MC simulation, the system is slowly cooled from a high initial temperature to a final normalised temperature of $T^* = 0.05$ (see Methods). The choice of the final temperature represents a good compromise between being low enough for the system to be in the low temperature regime while still being high enough for the MC simulation to equilibrate the system efficiently.

In our simulations, we assume that the capillary interactions are pair-wise additive and quasistatic. We therefore model capillary interactions by calculating V_2 given by Equation (4) for d, ϕ_1, ϕ_2 values on a grid and use this data to generate a look-up table. Note that the quasistatic approximation is accurate for $T^* \ll 1$, as evidenced by the fact that it is possible to accurately model the trajectory of micron-sized particles moving under the action of capillary forces by using this approximation (23,40). Note also that V_2 represents the capillary interaction at zero temperature. At finite temperature, thermal fluctuations of the liquid interface induce additional interactions due to the Casimir effect (41-43). However, since such thermal Casimir interactions are proportional to $k_B T$ (41,42), we can safely neglect them in the low temperature regime $k_B T \ll U_0$ that are we considering here. Further details of our MC simulations, including how we model particle interactions, can be found in Methods and Supplementary Information.

In Figures 3a and 3b, we show the final snapshots from our MC simulations for H0 and H30 respectively. We see that H0 forms hexagonal close packed structures, in good agreement with the thermodynamic analysis in Figure 2e. However, rather surprisingly, H30 forms a mixture of different structures, with only small domains of honeycomb order, even though the latter is predicted by Figure 2f to be the ground state structure. One reason for this surprising result is the fact that from Figure 2f, H30 has a number of competing metastable structures which are very close in energy to the honeycomb structure, i.e., the common tangent lines for the rectangular (Rec) and Kagome (Kag) structures in Figure 2f are very close to the ground state common tangent line. Indeed, as highlighted in Figure 3b, we do see small domains of Rec and Kag structures in the final snapshot.

(Figure 3)

Figure 3: (a-c) Final snapshots for Monte Carlo simulations of (a) H0, (b) H30 and (c) H30+ particles. In (b), we highlight small domains of Kagome (red) and Rectangular (black) structures and in the inset we show the linear structures that poison the formation of extended honeycombs. In the inset of (c), we confirm that the honeycomb structures are Hon+. (d) Two options for adding a third H30 particle to an existing dimer of H30 particles. (e) Superposition of hexapole and dodecapole edge undulations to create H30+. (f) Top view of the particle geometry and contour plot of the liquid interface height (normalized to the hexagon side length L) around H30+. (g,h) The negative and positive tripole-tripole interaction potentials as a function of particle separation for (g) H30 and (h) H30+. The solid vertical lines denote the separation for side-to-side contact of the hexagons. The yellow and purple spots in (g,h) denote positive and negative capillary poles respectively.

However, the absence of extended honeycomb structures in Figure 3b also arises from a deeper kinetic problem where the formation of the two degenerate honeycomb phases Hon+ and Hon- are antagonistic to each other. This point is illustrated in Figure 3d (Figure 3c will be discussed later in this section). Consider a dimer consisting of two H30 particles which are attached to each other via a positive tripole-tripole bond. When a third H30 particle is introduced, this particle can either attach itself to the dimer via a tripole-tripole bond of the same sign to form a bent trimer which is compatible with the subsequent formation of a honeycomb structure (in this case Hon+), or it can attach itself to the dimer via a tripole-tripole bond of the opposite sign to form a linear trimer which blocks the further formation of the honeycomb structure. However, since positive and negative tripole-tripole bonds are degenerate in energy, both pathways are equally likely. This means that as successive H30 particles are added to a growing cluster, the probability that all particles in the cluster are bonded to each other via tripole-tripole bonds of the same sign becomes vanishingly small. Thus, although Hon+ and Hon- are the thermodynamic ground states for H30, neither structure is accessible kinetically. The prevalence of the linear structures discussed above in Figure 3b (see for example the inset), confirms that the self-assembly process is indeed ‘poisoned’ by the bottom pathway in Figure 3d, preventing H30 from forming extended honeycomb structures.

To overcome this problem, we can make one set of alternate sides in H30 more ‘sticky’ than the other by adding a $m = 6$ multipole (dodecapole) to the contact line undulations of the hexapolar particle. This is illustrated in Figure 3e, where the dodecapole is oriented such that it reinforces the positive poles and suppresses the negative poles of the hexapole. Specifically, we modify the edge undulation given by including both $m = 3$ and $m = 6$ multipoles in Equation (2), with $A_3, A_6 = 0.05L$ and $\theta_{03}, \theta_{06} = \pi/6$, where A_m, θ_{0m} are the amplitude and phase angle of the mth multipole, and we call this particle shape H30+. In Figure 3f, we plot the height of the liquid meniscus around an isolated H30+ particle and we see that the addition of the $m = 6$ multipole amplifies the magnitude and range of the positive deformations of the liquid interface and suppresses the same for the negative deformations. In Figures 3g and 3h, we plot the positive and negative tripole-tripole interaction potential as a function of particle separation for H30 and H30+ respectively. We see that adding the $m = 6$ multipole indeed makes the positive tripole-tripole bonds much stronger than the negative tripole-tripole bonds for H30+. These results suggest that adding the $m = 6$ multipole breaks the degeneracy between Hon+ and Hon-, causing Hon+ to be the thermodynamic ground state for H30+.

The fact that the Hon+ structure is the kinetically accessible ground state structure for H30+ is confirmed in Figure 3c where we show the final snapshots from MC simulations for H30+. We see that, in contrast to H30, the H30+ particles are able to self-assemble into extended honeycomb structures, and the inset confirms that the honeycomb structures are Hon+ rather than Hon-. The good agreement in the ground state crystal structure between the Surface Evolver calculations in Figure 2 (which include all many-body interactions through the periodic boundary conditions) and the Monte Carlo simulations in Figure 3 (which include two-body interactions only) suggests that many-body interactions are negligible in this system. This fact is not surprising since the capillary interactions between high order multipoles are very short-ranged and we therefore expect two-body interactions to be dominant over many-body interactions in this case.

Truncated Triangles

In the previous section, we saw that the Kagome lattice in Figure 2d (top left) is a metastable crystal structure for H30. However, we can also form a Kagome lattice using equilateral triangular plates instead of hexagonal plates by interchanging the role of particle and free space in the figure. Since the polygonal plates in all the lattice structures considered in this paper are bonded to each other by soft, flexible capillary bonds, the resultant open Kagome lattice is isostatic, i.e., it has marginal mechanical stability, and there has been growing interest in such lattices in recent years because of the unique mechanical properties they possess (44,45).

To create the open Kagome lattice, in principle we could use equilateral triangular plates with appropriate edge undulations to promote capillary bonding between the corners of the triangles. However, the relatively large separation between triangular plates when they are in corner-to-corner contact reduces the capillary bond strength significantly, making it challenging to stabilize the open lattice structure against collapse into compact lattice structures where the plates are in side-to-side contact. In order to address this problem, we reduce the particle separation for corner-to-corner contact by considering triangles with slightly truncated corners (see Figure 4a). Denoting the long and short side lengths of the truncated triangle as L and S respectively, the shape parameters in Equation (1) for this particle shape are $\psi_1 = \pi/2\,, \psi_2 = 7\pi/6\,, \psi_3 = 11\pi/6\,, \Delta = (L - S)/\big(4\sqrt{3}\big)\,, a = \sqrt{3}(L + S)/4$ and we work with length units where $L = 1$, see Supplementary Information. In order to encourage the truncated triangles to associate with each other along their short sides rather than their long sides, we use the same strategy that was used to create honeycombs in the previous section, namely we include both hexapoles ($m = 3$) and dodecapoles ($m = 6$) in the edge undulations, orienting the hexapole so that it’s poles coincide with the middle of the short or long sides, and orienting the dodecapole so that it reinforces the poles on short sides and suppresses the poles on the long sides, see Figure 4a. Specifically, we include both $m = 3$

and $m = 6$ multipoles in Equation (2), with $A_3, A_6 = 0.05L$ and $\theta_{03}, \theta_{06} = \pi/2$, where A_m, θ_{0m} are the amplitude and phase angle of the mth multipole.

(Figure 4)

Figure 4: (a) Superposition of hexapole and dodecapole edge undulations in the truncated triangle (TT) particles. (b) Top view of the particle geometry and contour plot of the liquid interface height (normalized to the long side length L) around the TT particles. (c) Capillary bond energy at contact V_c as a function of L/S for short side-short side and long side-long side contact of the TT particles. (d) The crystal structures we consider for the TT particles. For each crystal structure, we show the lattice vectors $\boldsymbol{a}$, $\boldsymbol{b}$, the nearest neighbour separation d, and the unit cell used in the Surface Evolver calculations, where sides of the unit cell with the same colour have the same interface height. The yellow spots in (c,d) denote positive capillary poles. (e) Plot of ηv_∞ vs. η for the different crystals structures shown in (d), where η is the area fraction and v_∞ is the many-body capillary interaction per particle given by Equation (5). The data points are numerical results calculated from Surface Evolver and the solid lines are the fits to the numerical data using the form $B\eta^C$, where the fitting parameters B, C for each crystal phase are given in Table S2 in Supplementary Information. The vertical dashed lines are the highest area fraction for each crystal phase and the black solid and dashed lines are the equilibrium common tangent lines. (f) Final snapshots for Monte Carlo simulations of the TT particles.

In Figure 4b, we plot the height of the liquid meniscus around an isolated truncated triangle (TT) with $L/S = 2$ and we see that the addition of the $m = 6$ multipole indeed amplifies the magnitude and range of interfacial deformations near the short sides and suppresses interfacial deformations near the long sides. In Figure 4c, we plot the capillary bond energy at contact V_c as a function of L/S for short side-short side (SS) contact (V_C^{SS}, red curve) and long side-long side (LL) contact (V_C^{LL}, blue curve). These results show that we can change the ground state capillary bond of the system by tuning the ratio L/S. Specifically, the ground state capillary bond is SS for L/S values below the crossover point $L/S = 2.23$, and it is LL for L/S values above the crossover point.

Figure 4c suggests that the ground state crystal structure for TT particles with $L/S < 2.23$ is the open Kagome lattice (Kag-O, Figure 4d, bottom left) while for $L/S > 2.23$, it is the compact Kagome lattice (Kag-C, Figure 4d, bottom right). In order to check this prediction, in Figure 4e, we perform a common tangent analysis for TT particles with $L/S = 2$ by plotting ηv_∞ against η for all the crystal structures shown in Figure 4d. Note that in Figure 4d, we show the nearest neighbor separation d and the unit cell for each crystal structure, while in Figure 4e, the vertical dashed lines represent the maximum area fraction η_c for each crystal phase and the black solid and dashed lines are the equilibrium common tangent lines of the system. The results in Figure 4e confirm that Kag-O is indeed the ground state crystal structure for $L/S = 2$. In Figure 4f, we show the final snapshot from MC simulations of TT particles with $L/S = 2$ with area fraction $\eta = 0.3$, where the system is slowly cooled from a high initial temperature to a final temperature of $T^* = 0.05$. We see that the TT particles indeed self-assemble into open Kagome lattice structures, confirming that this structure is kinetically accessible to the system.

To study how the self-assembly of TT particles depends on the value of L/S in more detail, in Figure S8 in Supplementary Information, we show the final snapshot from MC simulations of TT particles with area fraction $\eta = 0.3$ and a range of different L/S values around the crossover point, where the system is slowly cooled from a high initial temperature to a final temperature of $T^* = 0.05$. We also plot the difference in the capillary bond energy per particle between Kag-O and Kag-C, i.e., $\Delta v_C = 3(V_C^{SS} - V_C^{LL})/2$, as a function of L/S, where the factor $3/2$ comes from the fact that there are $3/2$ capillary bonds per particle in the Kagome structures. As expected, the system forms Kag-O for $L/S = 2$ where $\Delta v_C \approx -3k_BT$, while it forms Kag-C for $L/S = 2.5$ where $\Delta v_C \approx +3k_BT$. Interestingly, for L/S values very close to the crossover point, i.e., where $|\Delta v_C| \lesssim k_BT$, the system forms a mixture of Kag-O, Kag-C, Rec (Figure 4d top right) and intricate hybrid structures involving both SS and LL bonds, with a bias towards Kag-O below the crossover point, and towards Kag-C above the crossover point. The results in Figure S8 demonstrate that the ground state structure is the one with the lowest capillary interaction energy per particle, and that we can exclusively select one polymorph over another by ensuring that the difference in this energy for the different polymorphs is significantly greater than $k_B T$. This result provides a simple but powerful design principle for programming self-assembly in our system.

Mixtures of Squares and Equilateral Triangles

So far, we have studied the self-assembly of one-component systems consisting of a single particle shape. However, we can access an even richer range of self-assembled structures if we consider mixtures of different particle shapes. In this section, we illustrate this point by using a binary mixture of squares and equilateral triangles to form randomly tiled 12-fold quasicrystals (46,47). Specifically, we consider squares and equilateral triangle plates with side length L where the shape parameters in Equation (1) are $\psi_1 = \pi/2, \psi_2 = 7\pi/6, \psi_3 = 11\pi/6, \Delta = L/(4\sqrt{3}), a = \sqrt{3}L/4$ for the triangles and $\psi_1 = 0$, $\psi_2 = \pi/2$, $\Delta = 0$, $a = L/2$ for the squares (we only need two sets of parallel sides to form squares) and we work in units of length where $L = 1$, see Supplementary Information.

In order to promote random tiling, the edge undulations along the square and triangle sides need be commensurate with each other so that the capillary bond energies for square-square, triangle-triangle and square-triangle side-to-side contact are equal to each other (48). Having the same contact energies between the different species is important for two reasons. Firstly, the contact energy for triangle-square contacts needs to be at least as large as that for triangle-triangle and square-square contacts in order to suppress phase separation between the two species (46,49). Secondly, the triangle-triangle and square-square contact energies need to be the same to prevent the two species from crystallizing at different points as we cool the system which would lead to kinetic de-mixing (see later). In order to obtain commensurate edge undulations for squares and triangles, we use hexapolar edge undulations for the triangles and octopolar edge undulations for squares, with the multipoles oriented so that the positive poles coincide with the middle of each side, i.e., $m = 3$, $\theta_0 = \pi/6$ for triangles and $m = 4$, $\theta_0 = 0$ for squares in Equation (2). In Figures 5a and 5b respectively, we plot the interfacial deformations around an isolated square with $A_s = 0.200L$ and around a triangle with $A_t/A_s = 1.48$, where A_s, A_t are the A values in Equation (2) for squares and triangles respectively, and we see that the interfacial deformations conform well to the edge undulations in both cases. Note that we use slightly larger A values for both squares and triangles compared to the other shapes we have studied in this paper to increase the signal-to-noise ratio in our Surface Evolver simulations as the centre-to-side distances (relative to L) are smaller for triangles and squares compared hexagons and truncated triangles.

(Figure 5)

Figure 5: (a,b) Top view of the particle geometry and contour plot of liquid interface height (normalized to the side length L) around (a) triangular and (b) square particles. (c) Contact energies for the different shape pairs V_c^{IJ} (normalized to the square-square contact energy) as a function of A_t/A_s, where A_s, A_t are the A values in Equation (2) for squares and triangles respectively. The vertical dotted and dashed lines correspond to the cases $A_t/A_s = 1.00$ and $A_t/A_s = 1.48$ respectively. (d) Final snapshots for Monte Carlo simulations of a mixture of squares and triangles for $A_t/A_s = 1.00$. The largest cluster is highlighted. (e) The m-fold bond orientational order parameter χ_m as a function of m for the largest cluster in (d). The inset shows the structure factor for the largest cluster. (f), (g) show the plots corresponding to (d), (e) for $A_t/A_s = 1.48$.

Note that since the centre-to-side distance is different for squares and triangles, we need to use different A_t and A_s values to match the amplitude of interfacial undulations for the two shapes and hence match the contact energy between the different species. This point is illustrated in Figure 5c where we plot the contact energies for the different shape pairs V_c^{IJ} (normalized to the square-square contact energy) as a function of A_t/A_s for $A_s = 0.200L$, where $I, J = s$ (square) or t (triangle). We see that for $A_t/A_s = 1.00$ (vertical dotted line), there is a large discrepancy in contact energies for the different shape pairs, while for $A_t/A_s = 1.48$ (vertical dashed line), the contact energies for the different shape pairs are essentially equal.

To illustrate the importance of tuning A_t/A_s in order to obtain 12-fold quasicrystals, we performed MC simulations of mixtures of squares and triangles with a total area fraction of $\eta = 0.3$, $A_s = 0.200L$ and different A_t/A_s values. Theoretically, the optimum number ratio of squares to triangles to form randomly tiled 12-fold quasicrystals is $\sqrt{3}/4$, i.e., a square number fraction of $\sqrt{3}/(4+\sqrt{3}) \approx 0.30$ (46,50). In fact, we found that the highest quality quasicrystals were obtained for a slightly higher square number fraction of 0.33, and we therefore report results for this composition in Figure 5d-g below. However, in Supplementary Information we show that quasicrystals (albeit of poorer quality) are also formed for the compositions 0.27, 0.30, 0.36 and 0.39, indicating that the formation of quasicrystals is relatively insensitive to composition for the composition range we have studied. Quasicrystals are very delicate structures that are easily destroyed by the presence of too many defects (46). We therefore cooled the mixture much more slowly compared to the other systems studied in this paper (see Methods), with a final temperature of $T^* = 0.05$, allowing us to minimize defects and grow large enough crystal domains to produce clear diffraction patterns.

In Figure 5d, we show the final snapshot from MC simulations of a mixture of squares and triangles with $A_t/A_s = 1.00$ (i.e., dotted vertical line in Figure 5c). We see that no 12-fold quasicrystals are formed in this case as there is a clear phase separation between squares and triangles within the clusters, with the square crystals forming the core and the triangle crystals forming the corona. The observed core-corona cluster morphology is a consequence of the square-square capillary bond energy being significantly higher than the square-triangle and triangle-triangle bond energies. This means that as the system is slowly cooled during the MC simulation, the squares crystallize out of solution first, and act as the nuclei for the subsequent crystallization of the triangles. The dominance of square crystalline order, and absence of 12-fold quasicrystalline order, is confirmed in Figure 5e where we plot the m-fold bond orientational order parameter χ_m for different values of m for the largest cluster (highlighted in Figure 5d). The order parameter $\chi_m \in [0,1]$ characterizes the degree of m-fold orientational order of the system (see Supplementary Information), and we see that there is significant orientational order for $m = 4, 8, 12$, consistent with the presence of 4-fold orientational order in the cluster. In the inset, we show the scattering structure factor for the largest cluster, which clearly shows strong square crystalline order in the sample.

In Figure 5f, we show the final snapshot from MC simulations of a mixture of squares and triangles with $A_t/A_s = 1.48$ (i.e., dashed vertical line in Figure 5c). In contrast to Figure 5d, there is now very good mixing between squares and triangles within the clusters. However, because the clusters consist of close-packed polygons, rearrangements are very restricted after structures are formed, making it very difficult to heal any defects in the interior or boundary of the cluster. The very slow structural relaxation limits the maximum crystalline domain size to just over 100 particles, even with the very slow cooling protocol we use. Notwithstanding this limitation, we can clearly see characteristic features of 12-fold quasicrystalline order in the largest cluster (highlighted in Figure 5f), for example the presence of complete or partially complete dodecagons consisting of 6 triangles in the core surrounded by 6 squares and 6 triangles (46,47).

The presence of 12-fold quasicrystalline order for the system with $A_t/A_s = 1.48$ is more strikingly demonstrated in Figure 5g, where we plot the bond orientational order parameter χ_m for different m for the largest cluster. We see that the cluster has significant 12-fold orientational order ($\chi_{12} \approx$

0.95), but negligible orientational order for all lower m, in particular for $m = 3, 4, 6$, the factors of 12. In the inset we show the scattering structure factor of the cluster, and we clearly see 12 scattering peaks around each of the circles that have been highlighted. Furthermore, the wavenumber ratio between successive circles is 1.93, consistent with the presence of 12-fold quasicrystalline order in the system (51).

The results in Figure 5 once again highlight the advantage of using polygonal plates with undulating edges to control self-assembly. Specifically, this geometry gives us very precise control over capillary interactions, allowing us to access delicate structures such as quasicrystals which only exist over a very narrow range of relative contact energies (Figure 5c). For future work, we plan to use edge undulations to impose matching rules, i.e., rules that dictate which polygon sides may or may not be next to each other (48), allowing us to assemble deterministic quasicrystal which should form much larger clusters (50). The application of such matching rules may also allow us to use self-assembly to create the recently discovered quasicrystals made from a single tile shape (52). Without such matching rules, the concave shape of these tiles would greatly restrict structural rearrangements during self-assembly, potentially causing the system to be kinetically trapped in metastable states with many defects and preventing the system from reaching its ground state.

Conclusions

We have used minimum energy calculations and Monte Carlo simulations to study the capillary assembly of a novel class of colloidal particles at a liquid interface, namely polygonal plates with homogeneous surface chemistry and undulating edges. This particle geometry gives us precise and independent control over both short-ranged hard-core repulsions (through the polygonal shape) and longer-range capillary interactions (through the edge undulations), allowing us to select specific polymorphs over others and providing essentially limitless possibilities for programming self-assembly in 2D. In addition, the fact that particle interactions are controlled by particle shape rather than surface chemistry considerably simplifies the task of fabricating the colloidal building blocks, allowing us to synthesise the required particle shapes down to the micron scale using currently available fabrication technologies (30-32).

To illustrate the immense potential provided by our system for programming self-assembly, we used polygonal plates with different in-plane shapes and edge undulations to create a rich variety of complex 2D structures. Specifically, for hexagonal plates, we showed that a subtle change in the phase angle between the hexapolar edge undulations and the hexagon shape led to a dramatic change in the thermodynamic ground state from a hexagonal close packed structure to an open honeycomb structure. We also showed that by using a suitable superposition of hexapolar and dodecapolar edge undulations, we could selectively make some edges of a hexagon or truncated triangle more ‘sticky’ than others, allowing us to effectively create 2D patchy particles using shape alone. Using such particles allowed us to control both the thermodynamics and kinetics of self-assembly to create open structures such as honeycomb and Kagome lattices. Finally, by carefully tuning the multipole order and amplitude of edge undulations in triangles and squares, we were able to accurately tune the contact energies between the two shapes and create 12-fold quasicrystals.

Since the particle shapes above can be readily fabricated experimentally, we can use our novel colloidal system to control the entire process chain for materials design, from initial design and fabrication of the building blocks to final self-assembled structure and emergent properties of the material. As such, our novel colloidal system could revolutionise colloidal self-assembly in two dimensions, in the same way that DNA linker technology has revolutionised colloidal self-assembly in three dimensions (9).

Materials & Methods

Surface Evolver: The interfacial energy given by Equation (3) is calculated using Surface Evolver, a finite element program that represents each interface as a mesh of triangles (36). The resultant vertices are displaced to minimise the interfacial energy, subject to the constraints of the boundary conditions at the edge of the simulation box and the particle contact line. We work with length and energy units where the particle side length $L = 1$ and the fluid-fluid interfacial tension $\gamma = 1$ and use a variable triangular mesh with edge length between $0.02L$ to $0.1L$ with quadratic edges to capture the shape of the fluid-fluid interface more accurately. When calculating pair capillary interactions using Equation (4), we use reflecting boundary conditions at the simulation box edge. Since we are considering higher order capillary multipoles whose interactions fall off rapidly with separation, finite size effects are less severe and we can use relatively small simulation box sizes. Specifically, we use a simulation box with boundaries at $x = \pm 8r_0$, $y = \pm 4r_0$, the interacting particles are at $(\pm 2r_0, 0)$ at maximum separation, and at $(\pm 4r_0, 0)$ at 'infinite' separation, where r_0 is the radius of the circle circumscribing the polygonal plates; in the case of squares and equilateral triangles, we use r_0 for the square, i.e., the larger circumscribing circle. When calculating many-body capillary interactions using Equation (5), we use periodic boundary conditions at the edge of the simulation box as described in Figure 2c,d, with a nearest neighbor separation of $d = 10L$ at 'infinite' separation. When calculating capillary interactions, the smallest surface-to-surface separation we consider is $0.1L$ for many-body interactions, $0.03L$ for pair interactions for binary mixtures of squares and triangles, and $0.03r_0$ for all other pair interactions, where r_0 is the radius of the circle circumscribing the polygon. These separations are small enough to give a good approximation to the true contact energy (either directly in Figures 4c and 5c, or through extrapolation in the MC simulation look-up tables), but large enough to avoid numerical problems in our finite element simulations. The Surface Evolver scripts that we use in this paper are available in the persistent repository detailed at the end of this article.

Monte Carlo (MC) simulations: NVT Metropolis simulations were performed on 400 polygonal plates interacting via both hard-core and capillary interactions with periodic boundary conditions. Details of how hard-core and capillary interactions are implemented in our simulation can be found in Supplementary Information. We used a rectangular simulation box with aspect ratio of $2{:}\sqrt{3}$ starting with particles in a hexagonal lattice with an area fraction of $\eta = 0.3$. In a MC move, particles were either translated or rotated (with equal probability) with adjustable step lengths or rotation angles to achieve an acceptance probability of 30% for each type of move. To ensure efficient equilibration, for hexagons and truncated triangles, the particles were first disordered at a temperature of $T^* = 100$ for 10^3 attempted moves per particle, then brought to the final temperature $T^* = 0.05$ through a slow cool process by successively quenching to $T^* = 0.15, 0.12, 0.1, 0.09, 0.08, 0.07, 0.05$, with 5×10^5 attempted moves per particle at each temperature. For the mixture of squares and equilateral triangles, we used a much slower cooling protocol to minimize the number of defects. Specifically, the system was first disordered at a temperature of $T^* = 100$ for 10^3 attempted moves per particle then quenched to $T^* = 0.25$. The temperature was then reduced by a factor of 0.95 every 3×10^5 attempted moves per particle until we reached $T^* = 0.1$. Finally, the temperature was reduced by a factor of 0.95 every 10^5 attempted moves per particle until we reached a final temperature of $T^* = 0.05$. For each composition of the squares and triangles, 10 simulation runs were carried out to increase the effective sample size from which to identify quasicrystalline structures.

Acknowledgments

JLE, TSH and DMAB acknowledge funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 861950, project POSEIDON, SOM acknowledges funding from a University of Hull PhD scholarship, and we acknowledge the Viper High Performance Computing facility of the University of Hull. We also acknowledge helpful discussions with Craig Brisband, Alberto Scacchi and Niki Vogel.

Data Availability Statement
Original data created for the study will be available in a persistent repository upon publication; Data Type: Computer code; Repository Name: University of Hull Research Repository; DOI/accession number(s): https://hull-repository.worktribe.com/output/4519219

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