Electronic Supplementary Information for "Assembly of Multi-flavored Two-Dimensional Colloidal Crystals"

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Global Structure Optimization of Clusters



Figure S1: Minimum energy structures for various interactions as determined by basinhopping. Lines approximately separating different domains are drawn as a guide to the eye. Representative structures are outlined with the color corresponding to the points in the region of phase space they were found in, indicated by the legend. For clarity colloids are shown simply as points colored according to their type, however, in all cases they lie tangent to the surface of their nearest neighbors.

We used stochastic global optimization to predict the lowest energy structure of a small subset of colloids used in larger scale Monte Carlo simulations. This reflects the most thermodynamically stable structure in the limit of $T^* \to 0$. Specifically, we used basin-hopping^{1,2} as implemented in the SciPy library³ for Python.⁴ Details are provided in the main text. Figure S1 depicts the results for a size-symmetric system ($\sigma_{A,A} = \sigma_{B,B} = 1.00$) of six blue "A" colloids and six red "B" colloids. As twelve total colloids were deemed too few to reliably determine large scale morphologies, we classified structures which formed an underlying hexagonal lattice, regardless of its compositional order, simply as being six-fold rotationally

symmetric unless the resulting structure phase separated into two different domains (phaseseparated hexagonal). Representative configurations of the structures corresponding to the global minimum in energy found are shown in the figure. We considered various cases where $\lambda_{i,j} \in [1.0, 0.5, 0.1, 0.0, -0.1, -0.5, -1.0]$. We plot the data here in terms of the average cohesive energy, $(\lambda_{A,A} + \lambda_{B,B})/2$, versus the adhesive energy, $\lambda_{A,B}$. Linear discriminant analysis $(LDA)^{5,6}$ was used to identify this lower dimensional subspace where the morphologies collapse into separate contiguous domains. Moving counterclockwise about the origin of Fig. S1, these domains reflect a transformation of the system from a disordered state, to a string-like aggregate (two-fold rotational symmetry), to a square lattice (four-fold rotational symmetry), to hexagonal crystals (six-fold rotational symmetry). This transformation is further discussed in the main text, however, we emphasize that this two-dimensional phase space is effective at representing this data only when all non-phase-separated six-fold lattices, such as honeycomb and mixed hexagonal, are considered as part of the same class. To distinguish these structures from one another, an additional degree of freedom is required, necessitating the three-dimensional phase space, $\langle \lambda_{A,A}, \lambda_{A,B}, \lambda_{B,B} \rangle$, used in the main text. When the system is size-asymmetric, classifying resulting structures is less trivial, which is consistent with the complex domain shapes and locations corresponding to different morphologies, also depicted in the main text. Hence, simple linear data transformation techniques, such as LDA or principle component analysis, did not provide any meaningful collapse of the optimized structure data into a lower dimensional subspace.

Mean-Field Model

In our mean-field model we considered ten possible candidate morphologies which are given in the main text along with the relevant parameters for computing their potential energy. With this, we predicted the most thermodynamically stable morphology in the limit of $T^* \to 0$ for size-symmetric systems ($\sigma_{A,A} = \sigma_{B,B} = 1.00$). Examples of most of the structures considered may be found in the main text with the exception of the alternating hexagonal layer morphology, which is depicted in Fig. S2 for reference. In the main text, we presented the mean-field model's predictions of the most stable structure when this morphology was neglected from our analysis. The reason was that this structure was not broadly observed in simulations at a finite temperature. Instead, the mixed hexagonal lattice was generally found. Figure S2 illustrates the mean-field model's predictions when this morphology was included. Comparatively, this alternating hexagonal layer morphology (gray region) generally tends to simply replace the mixed hexagonal lattice domain (green region in main text) in $\langle \lambda_{A,A}, \lambda_{A,B}, \lambda_{B,B} \rangle$ phase space without significantly affecting the other domains. Thus, it is clear that the mixed hexagonal lattice tends to have the second lowest energy, next to the alternating hexagonal layer morphology, in that region of phase space. However, while the latter is expected to be the most stable structure in the limit of $T^* \to 0$, at finite temperature entropy will contribute to the free energy of each structure. The mixed hexagonal lattice, which is much more substitutionally disordered, is expected to have a higher entropy than the alternating hexagonal layer structure; this is apparently enough to cause the mixed hexagonal lattice morphology to dominate this region of phase space at the conditions reported in the main text $(T^* = 0.10)$.



Figure S2: Mean-field predictions for a 1:1 stoichiometry. (Left) Depiction of the alternating hexagonal layer morphology. (Right) Domains of predicted stability when all morphologies discussed in the main text are considered. Red corresponds to the phase-separated hexagonal structure, yellow to an alternating square lattice, blue to a honeycomb lattice, and the cyan dots to a disordered "gas" phase located precisely along the $\lambda_{A,B} = 0$ plane when $\lambda_{A,A}, \lambda_{B,B} \leq 0$.

The Kagome Lattices as Defects

We also considered two polymorphs of the trihexagonal tiling known as the kagome lattice in our mean-field approach: the more conventional one, which we simply refer to as "kagome," and the "square-kagome" lattice. Both are depicted in Fig. S3. We did not observe these structures forming globally in our Monte Carlo simulations at a 1:1 stoichiometric ratio, which is consistent with the fact that this structure never manifests as the lowest energy structure out of all the candidate morphologies in our mean-field model. However, we did find that toward the low $\lambda_{A,B}$ edge of the honeycomb (blue) regions, the lattice tended to display defects. The propensity of these defects increased as we reduced the temperature of the Monte Carlo simulations from $T^* = 0.10 \rightarrow 0.05$, but the overall morphology we continued to observe was still honeycomb. We attribute these defects to difficulty in sampling at lower temperature. These defects generally resulted in local kagome structures within the honeycomb lattice which formed. As shown in Fig. S4(a), a point defect in a honeycomb lattice results in a kagome structure around that defect. Furthermore, when a twinning plane develops from, for instance, layers sliding past one another, the structure across the plane is locally a square kagome lattice. Such a plane is shown in Fig. S4(b). The similarity of the kagome lattices with the honeycomb is clearly reflected in their nearly identical coordination numbers (cf. main text). Thus, although the kagome lattices were never found to be the most stable structure for a 1:1 stoichiometric ratio, it is possible that these structures may be observed in a similar region of phase space due to kinetic limitations.



Figure S3: (Left) Kagome lattice composed of two species, "A" (blue) and "B" (red). (Right) Square kagome polymorph with the same constituents. The white lines depict the local coordination numbers and how these polymorphs are made of smaller subunits which tile two dimensional space differently.



Figure S4: Honeycomb lattice with (a) a point defect showing a locally kagome structure and (b) a twinning plane across which the crystal manifests as a locally square kagome lattice.

Size Asymmetry for 1:1 Stoichiometry



Figure S5: Regions of phase space where each morphology appears in Monte Carlo simulations of size-asymmetric colloids when $\sigma_{A,A} = 1.00, \sigma_{B,B} = 0.40$, with corresponding representative snapshots from each. The disordered "gas" and phase-separated hexagonal regions have been neglected as their morphologies are qualitatively identical to the size-symmetric case ($\sigma_{A,A} = \sigma_{B,B} = 1.00$). A fully reconstructed three-dimensional phase space is presented in the main text.



Figure S6: Regions of phase space where each morphology appears in Monte Carlo simulations of size-asymmetric colloids when $\sigma_{A,A} = 1.00, \sigma_{B,B} = 0.14$, with corresponding representative snapshots from each. The disordered "gas" and phase-separated hexagonal regions have been neglected as their morphologies are qualitatively identical to the size-symmetric case ($\sigma_{A,A} = \sigma_{B,B} = 1.00$). A fully reconstructed three-dimensional phase space is presented in the main text.

Molecular Dynamics Simulations



Figure S7: Representative results from molecular dynamics simulations for a size-symmetric system at 1:1 stoichiometry showing each morphology found. (a) $\lambda_{A,A} = -0.5$, $\lambda_{B,B} = 0.5$, $\lambda_{A,B} = 0.5$ (Honeycomb lattice), (b) $\lambda_{A,A} = -0.5$, $\lambda_{B,B} = -0.5$, $\lambda_{A,B} = 0.75$ (Alternating square lattice), (c) $\lambda_{A,A} = 0.5$, $\lambda_{B,B} = 0.5$, $\lambda_{A,B} = 0.25$ (Phase-separated hexagonal lattice), (d) $\lambda_{A,A} = 0$, $\lambda_{B,B} = 0$, $\lambda_{A,B} = 0.75$ (Mixed hexagonal lattice), (e) $\lambda_{A,A} = -0.5$, $\lambda_{B,B} = -0.5$, $\lambda_{B,B} = -0.5$, $\lambda_{B,B} = 0.25$ (Disordered "gas"), (f) $\lambda_{A,A} = -1$, $\lambda_{B,B} = -1$, $\lambda_{A,B} = 0.5$ (Alternating string-like aggregate).

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