

Activity-enhanced self-assembly of a colloidal kagome lattice

Stewart A. Mallory^{*,†} and Angelo Cacciuto^{*,‡}

[†]*Division of Chemistry and Chemical Engineering, California Institute of Technology,
Pasadena, CA 91125*

[‡]*Department of Chemistry, Columbia University, New York, New York 10027*

E-mail: smallory@caltech.edu; ac2822@columbia.edu

Supporting Information

Model Details

The two hydrophobic patches which gives the colloids its triblock nature are located at opposite poles of the colloid with each hydrophobic patch accounting for $\approx 28\%$ of the particle surface area. The polar equatorial region accounts for the remaining 44% of the surface area. The conservative interparticle forces and torques acting on the colloid are given by $\mathbf{F}(\{r_{ij}\})$ and $\mathbf{T}(\{r_{ij}\})$, respectively, and can be computed as

$$\mathbf{F}(\{r_{ij}\}) = \sum_j \mathbf{F}_{ij} = \sum_j -\frac{\partial U_{ij}}{\partial \mathbf{r}_{ij}} \quad (1)$$

and

$$\mathbf{T}(\{r_{ij}\}) = \sum_j \mathbf{T}_{ij} = \sum_j -\frac{\partial U_{ij}}{\partial \theta_j} \quad (2)$$

where U_{ij} is the interaction potential between colloids. The interaction potential, U_{ij} , between colloids has the form

$$U_{ij}(r_{ij}, \theta_i, \theta_j) = U_R(r_{ij}) + U_A(r_{ij})\phi(\theta_i)\phi(\theta_j) \quad (3)$$

where

$$U_R(r_{ij}) = \begin{cases} 4\varepsilon_{rep} \left(\frac{\sigma}{r_{ij}}\right)^{12} & r_{ij} \leq 1.5\sigma \\ 0 & r_{ij} > 1.5\sigma \end{cases} \quad (4)$$

accounts for the excluded volume interactions between the particles, and

$$U_A(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma/2}{r_s + \sigma/2 \times 2^{1/6}}\right)^{12} - \left(\frac{\sigma/2}{r_s + \sigma/2 \times 2^{1/6}}\right)^6 \right] \quad (5)$$

Here ε is the binding energy, $r_s = |r_{ij} - \sigma|$ is the distance between the particles surfaces, while r_{ij} is the distance between the centers of particles i and j . The interaction extends up to a distance $r_{ij} = 1.5\sigma$. The angular potential $\phi(\theta_i)$ setting the interaction between any two hydrophobic patches is given by

$$\phi(\theta_i) = \begin{cases} 1 & \theta_i \leq \theta_{max} \\ \cos^2\left(\frac{\pi(\theta_i - \theta_{max})}{2\theta_{tail}}\right) & \theta_{max} \leq \theta_i \leq \theta_{max} + \theta_{tail} \end{cases} \quad (6)$$

where θ_i is defined as the angle between a hydrophobic patch unit vector \mathbf{n}_i and the inter-particle vector $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$ (similarly θ_j is the angle between patch vector \mathbf{n}_j and inter-particle vector $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$). The angular potential ϕ is a smooth step function that modulates the angular dependence of the potential and is equal to 1 within the region $\theta_i < \theta_{max} = 25.2^\circ$ and decays to zero following the expression above. The particular value of $\theta_{tail} = 25^\circ$ has been selected to generate a sufficiently smooth potential at the Janus interfaces. This potential is appropriate to describe the behavior of patchy particles at high salt concentration where the charge on the polar side of the colloid is well screened and short ranged.

Structure Identification

For a particle to be considered as part of a kagome lattice, it must have the correct coordination number and the appropriate relative orientation with its neighbors, the latter is determined using a local bond order parameter given by

$$\psi_6(m) = \frac{1}{N_b} \sum_{n=1}^{N_b} e^{6i\theta_{mn}} \quad (7)$$

where, N_b is the number of nearest neighbors of the m^{th} particle, and θ_{mn} is the angle between some fixed axis and the bond joining the m^{th} and the n^{th} particle. Following Chen et al.,¹ we identify colloids as belonging to the kagome lattice if they have both $\psi_6(m) > 0.7$ and exactly four nearest-neighboring bonds. If the colloid has six neighbors and $\psi_6(m) > 0.7$, the colloid is recognized to belong to the hexagonal phase. All colloids that satisfy neither of these criteria are associated with the disorder fluid phase. We find it useful to characterize the different phases observed in this system by considering the percent yield of kagome, hexagonal, and more in general crystalline (kagome plus hexagonal) particles, as a function of temperature T and activity U . The percent yield is defined as the ratio between the number of particles of a given type divided by the total number of particle N times one hundred.

Supplementary Movies

MOVIE S1. Self-assembly of the equilibrium triblock system at state point: ($\phi = 0.4$, $U = 0$, $T = 1.0$). Here, the system is outside the optimal window in volume fraction and equilibrium self-assembly of the kagome lattice is not heavily favored. The web-like network or gel that forms is characteristic of the metastable states observed for the equilibrium triblock system. The color coding in the trajectory corresponds to the structural identity of the colloid: Kagome (Red), Hexagonal (Green), and the disordered fluid (Blue). The system was initialized from a uniform square lattice configuration and the length of the trajectory

shown is $10^3\tau$.

MOVIE S2. Self-assembly of the active triblock system at state point: ($\phi = 0.4$, $U = 4$, $T = 1.0$). For this state point, the triblock system is within the region of parameter space where there is a high yield of kagome self-assembly. The color coding in the trajectory corresponds to the structural identity of the colloid: Kagome (Red), Hexagonal (Green), and the disordered fluid (Blue). The system was initialized from a uniform square lattice configuration and the length of the trajectory shown is $10^3\tau$.

MOVIE S3. Self-assembly of the active triblock system at state point: ($\phi = 0.4$, $U = 8$, $T = 0.2$). At this state point, we observe coexistence between kagome and hexagonal structures. At this low temperature, we observe no orientational ordering of the propelling axes in either crystal structure. At low temperatures, unbalanced shear forces can easily develop within the orientationally disordered kagome lattice for large values of U . When the active forces dominate over the adhesive forces between the particles the kagome lattice is destabilized in favor of the hexagonal crystal. The color coding in the trajectory corresponds to the structural identity of the colloid: Kagome (Red), Hexagonal (Green), and the disordered fluid (Blue). The system was initialized from a uniform square lattice configuration and the length of the trajectory shown is $10^3\tau$.

MOVIE S4. Self-assembly of the active triblock system at state point: ($\phi = 0.4$, $U = 8$, $T = 1.2$). At this state point, we continue to observe coexistence between kagome and hexagonal structures. However, the hexagonal crystal structure is favored over the kagome at these higher temperatures. Note that in this high temperature and highly active regime, orientational alignment does not develop from within the core of an already assembled crystal structure, but rather develops early on in the assembly process. It is the merging of these highly oriented crystalline domains that gives rise to the stable hexagonal crystals that

result in the later stages of self-assembly. The color coding in the trajectory corresponds to the structural identity of the colloid: Kagome (Red), Hexagonal (Green), and the disordered fluid (Blue). The system was initialized from a uniform square lattice configuration and the length of the trajectory shown is $10^3\tau$.

References

- (1) Chen, Q.; Bae, S. C.; Granick, S. Directed self-assembly of a colloidal kagome lattice. *Nature* **2011**, *469*, 381–384.