A Design Path for Hierarchical Self-Assembly of Patchy Colloids

E. Edlund, O. Lindgren, M. Nilsson Jacobi
Chalmers University of Technology, Gothenburg
mjacobi@chalmers.se

Abstract

Patchy colloids are promising candidates for building blocks in directed self-assembly. To be successful the surface patterns need to both be simple enough to be synthesized, while feature-rich enough to cause the colloids to self-assemble into desired structures. Achieving this is a challenge for traditional synthesis methods. Recently it has been suggested that the surface pattern themselves can be made to self-assemble. In this paper we show that a wide range of functional structures can be made to self-assemble using this approach. More generally we present a design path for hierarchical targeted self-assembly of patchy colloids. At the level of the surface structure, we use a predictive method utilizing universality of patterns of stripes and spots, coupled with stoichiometric constraints, to cause highly specific and functional patterns to self-assemble on spherical surfaces. We use a minimalistic model of an alkanethiol on gold as a model system and demonstrate that, even with limited control over the interaction between surface constituents, we can obtain patterns that causes the colloids themselves to self-assemble into various complex geometric structures. We demonstrate how variations of the same design path cause in-silico self-assembly of strings, membranes, cubic and spherical aggregates, as well as various crystalline patterns.

During the last decade, patchy colloids have emerged as candidate building blocks for colloidal self-assembly. By altering the position of attractive patches, patchy colloids can for example be used to mimic the anisotropic interactions between folded proteins, drawing inspiration from how certain proteins self-assemble into capsid shells enclosing the viral genome [1]. With an ambition towards self-assembling meta materials and nano sized functional structures, the number of colloidal structures self-assembled in-silico or in-vivo have since then grown to encompass structures ranging from kagome lattice systems to colloidal strings [2,3] using equally varied techniques. In this paper, we demonstrate in-silico hierarchical self-assembly of a range of geometrical structures: different crystals, membranes, strings, vesicles of different size and cubic aggregates, all in the context of a single model system. By modifying parameters of the colloids’ coating, we are able to select which of the geometries that self-assembles. The parameter choices are based on a combination of more general design principles, also presented in this paper, and analytical predictions of the self-assembly processes [4].

Synthesization of large quantities of colloids with attractive patches in specific directions and high specificity is difficult. The methods developed for this in the last decade [5] range from various coating techniques on thin films of colloids on a substrate like dip-coating and glancing angle deposition [6], to techniques where colloids are aligned using an external electric field combined with an evaporator [7], to multiphase colloidal particles where constituents are added or subtracted sequentially to produce highly anisotropic colloidal shapes [8]. A rather different method, suggested recently, is to let the surface coating itself self-assemble into desired patterns as a part of a hierarchical self-assembly process. Experimental findings indicate that certain mixtures of alkanethiols adsorbed on gold nanoparticles phase separate into various morphologies depending on the properties of ligands and nanoparticles [9]. The results in this
article support the idea of self-assembled coatings on patchy colloids by showing that limited control over how the ligands interact is sufficient to template for targeted self-assembly of a wide range of surface patterns, and in extension, colloidal structures. Letting the surface patterns self-organize naturally leads to patches and stripes which are well suited for directing self-assembly on the colloidal scale. An important advantage of using self-assembly to form the patterns is that there is no intrinsic difficulty in making patterns with many patches and high specificity. The method can therefore give access to many patterns that seem hard to come by using other techniques.

I. A MODEL SYSTEM — ALKANETHIOL-ON-GOLD

A proposed candidate for self-assembling patchy morphologies on spheres is the alkanethiol-on-gold system [9]. It consists of spherical gold nanoparticles (colloids) coated with different species of alkanethiols. These alkanethiols organize into patterns due to a competition between their immiscibility and a mixing effect of entropic origin [10]. Depending on the number of alkanethiol types, many different patterns can appear [11, 12].

Here we use a simplified model of the alkanethiol-on-gold system, described in detail in [4]. It models the alkanethiols as spherical particles interacting with a set of effective interactions. Between alkanethiols of different type, the interaction consists of a hard core with diameter \( \sigma_0 \), a soft shoulder potential with range \( \sigma_1 \) (causing immiscibility), and a square-well potential of depth \( \epsilon \) (representing the mixing effect),

\[
V_{\alpha\beta}(r) = \begin{cases} 
\infty, & \text{if } r < \sigma_0 \\
1, & \text{if } \sigma_0 < r < \sigma_1 \\
-\epsilon, & \text{if } \sigma_1 < r < |L_{\alpha} - L_{\beta}| \\
0, & \text{otherwise}
\end{cases} \quad (1a)
\]

where the \( L_{\alpha} \) are abstracts parameters defined for each alkanethiol type, representing the different lengths or bulkiness of the tail groups.

The interaction between alkanethiols of the same type is taken to be a simple hard-core repulsion,

\[
V^{a\alpha}(r) = \begin{cases} 
\infty, & \text{if } r < \sigma_0 \\
0, & \text{otherwise}
\end{cases} \quad (1b)
\]

While minimalistic, it captures much of the behavior of the original system [4]. It is also a good model system for our design-path since the interactions are determined by only a few parameters, making the model more relevant as a proxy for an experimental system than a model with more complex interactions.

II. THEORY

In [4] we formulate the problem of predicting the morphology of a particle system in terms of a Potts-like spin model [13]. Assuming that we have a model of the effective interactions in the systems, here described as a set of potentials \( V^{a\beta}(r) \), we can construct a Hamiltonian for this spin model as

\[
H = \sum_{a\beta} \sum_{ij} \Pi_{ia} V^{a\beta}_{ij} \Pi_{j\beta} \quad (2)
\]

where \( N \) is the number of lattice sites, \( K \) the number of particle types, \( V^{a\beta}_{ij} = V^{a\beta}(|\vec{r}_i - \vec{r}_j|) \), and \( \Pi_{ia} \) is 1 if site \( i \) contains a particle of type \( a \) and 0 otherwise.

The task is then to find the low-energy states of this Hamiltonian. While we cannot hope to solve it exactly for general interaction matrices \( V \), if we relax the constraints and allow the state \( \Pi \) to take any real values while keeping its norm fixed we get a quadratic problem that is solvable. First the potentials \( V^{a\beta} \) are diagonalized independently by using the spherical harmonics analogue of the Fourier transform, then one small matrix for each orbital number is diagonalized. The result is an energy spectrum with \( K \) branches whose minimum will be the ground state for the relaxed model.

Each branch describes variation between two partitions of the particle types. To predict
the behavior of the original model we combine
the minima of enough branches to completely
specify a particle configuration, excluding un-
physical branches that does not describe sep-
arations between any types. An example is
shown in Fig. 1B, where the global minimum
describes the phase separation of the blue parti-
cles and the next branch is needed to determine
the behavior of the red and yellow particles,
here a striped state. For further details see [4].

III. A DESIGN PATH FOR TARGETED
HIERARCHICAL SELF-ASSEMBLY OF
PATCHY NANO-PARTICLES

Since the self-assembling morphologies are so
closely tied to their energy spectra, we can use
it as an intermediate between the parameters
describing the coating and the resulting ground
state. The theoretical model for what constit-
tutes a ground state helps us decide on reason-
able targets to aim for, patterns with stripes
and spots symmetrically distributed over the
surface, and which corresponding features are
required in the energy spectrum.

While different functional patterns require
different approaches, the overarching design
path can be summarized in a few steps;

- The locations of attractive patches in the
target surface pattern are determined by
the target nano-particle configuration.
- An achievable target pattern is one with
a hierarchy of spots and stripes symmet-
rically distributed over the surface.
- Decompose the target pattern into spher-
ical harmonics. The weights on the har-
monic modes identify the length scales
at which segregation occurs and which
segregations takes precedence.
- Iterate through different parameter set-
ings for the surface constituents, until
the effective interaction potentials trans-
forms into an energy spectrum with the
necessary features.
- Set the stoichiometry to match the target
pattern.
- Verify in-silico that the designed interac-
tions lead to the desired surface pattern.

If the stoichiometry is too skewed in the
attempt to create patches with high specificity,
the ground state can turn out to be a pattern of
fewer, clustered patches instead. The following
sections cover a straight forward example of
the design path followed by examples of what
is possible given different degree of control
over the energy spectrum and the interactions
between surface constituents.

IV. SINGLE LENGTH SCALE COUPLED
WITH STOICHIOMETRIC CONSTRAINTS

While the square well potentials of the model
(Eqs. 1a and b) are not realistic, striped pat-
terns have been observed both in first principle
simulations [11] and experiments [14]. There
are also fundamental theoretical reasons ex-
plaining why stripes are expected to appear
universally [15]. This supports the idea that at
least one (non $l = 0$) minimum in the energy
spectrum can be selected for, the minimum that
determines the length scale of the striped pat-
tern. This is sufficient for causing hierarchical
self-assembly of different crystal patterns when
combined with stoichiometric constraints.

Suppose that we want to cause patchy par-
ticles to self-assemble into a crystal pattern, for
example a diamond or a cubic lattice. A sim-
ple pattern that achieve this would be patches
in each direction where a neighboring colloid
should reside. For a diamond lattice, this
would mean four patches equally distanced
to each other on the surface of the nanoparti-
cle, for a cubic lattice, the number of patches
would be six. Expanding these patterns in
terms of spherical harmonic functions shows
that they are almost completely dominated by
$l = 0$ modes, determining the stoichiometry,
as well as $l = 3$ resp. $l = 4$ modes, determin-
ing the length scale of the spotted pattern. By
choosing parameters in the alkanethiol-on-gold
model (or indeed, in an experimental setup)
that causes the global minimum of the energy
spectrum, as well as the stoichiometry, to co-
incide with the target pattern’s will cause the
target pattern to self-assemble, see Fig. 2 A.
Systems of particles with attractive patches po-
The wavelength is determined by the minimum in the energy spectrum. Here $L_{\text{blue}} - L_{\text{red}} = 1.1$ radii (radius of the colloid), $\epsilon = 0.1$. b) With multiple particle types, the ground state is described by multiple minima in the energy spectrum, sufficiently many to account for the entire stoichiometry. The global minimum takes precedence and separates blue from red and yellow, the second minimum then determines the wavelength of the yellow-red striped part. $L_{\text{blue}} = 0.44$, $L_{\text{red}} = 0$, $L_{\text{yellow}} = 0.88$ radii, $\epsilon = 0.1$. c) Here the dominating segregation is between red and the surrounding colors, but stripes cannot form due to stoichiometric constraints (red, blue and yellow have equal proportions), causing the red state to be spotty instead. Here $L_{\text{blue}} = 1.1$, $L_{\text{red}} = 0$, $L_{\text{yellow}} = 1$ radii, $\epsilon = 0.1$.

V. SINGLE LENGTH SCALE COUPLED WITH STOICHIOMETRIC CONSTRAINTS AND SEGREGATING SUBTYPES

Using only two particle types, the patterns tend to be spherical symmetric and the previous approach of selecting a single length scale usually falls short when trying to obtain more complicated (asymmetric) patterns. This issue can be remedied by introducing more surface constituent types. For simplicity, lets consider the introduction of very similar subtypes of one particle type; type blue is replaced by type blue and yellow. These subtypes behaves identical at long range ($L_{\text{blue}} = L_{\text{yellow}}$), but they are immiscible and tend to segregate, all else being equal. The internal segregation between subtypes causes the system to strive towards achieve something similar to the previous striped or spotted pattern, while also minimizing the subtype blue to yellow interfaces. If we choose a stoichiometry where the subtypes can completely occupy different subsets of the previously blue spots/stripes, we can completely retain the ground state pattern, without any subtype interface. Such a pattern should be a ground state.

We now show how this can be used to design hierarchical self-assembly of strings and membranes. Patterns with two patches at opposing sides of every nanoparticle would cause the self-assembly of a string, while a single attractive band at the equatorial would cause the self-assembly of a membrane. One way to select for this pattern would be to choose parameters for a binary coating where segregation occurs at length scale corresponding to $l = 4$, causing a striped pattern as the ground state. By differentiating type blue into subtypes blue, yellow, and green, we can ensure that e.g. yellow and green occupy each polar patch respectively, and blue occupies the equatorial stripe. If yellow and green are attractive, the polar patches will be too, causing self-assembly of strings. If blue is attractive, the nanoparticles will instead form membranes. Fig. shows how this construction cause hierarchical self-assembly of string and membranes.
This suggests a third minimum that also separates the others. The small changes make the difference between a self-assembling diamond lattice b) or a cubic lattice c). Both surface patterns and the colloidal structures are obtained from Monte Carlo simulations using simulated annealing.

VI. VARIOUS DEGREE OF IMMISCIBILITY COUPLED WITH STOICHIOMETRIC CONSTRAINTS

By controlling the strength of the energetic drive towards segregation, we can also cause hierarchical self-assembly of vesicles. A thin, circular, attractive band causes colloids to self-assemble into vesicles, where the distance from the equatorial to the stripe determines the curvature of the vesicles. If the energy associated to the interface between a type red and a type yellow, the yellow constituent will form a stripe separating the others. The features are represented in the energy spectrum as a large minimum at a low \( l \) value, forcing two types to segregate to opposite sides and a much smaller minimum at the length scale corresponding to the width of the band that separates the two sides, see Fig. 3. Since the low \( l \) minimum is an order of magnitude larger than the second minimum, the ground state configuration will be one where type \( \text{blue} \) and \( \text{red} \) are separated as much as possible. This differentiates the target pattern from e.g. one where \( \text{blue} \) and \( \text{red} \) forms...
a Janus sphere with yellow as an overlapping spotty pattern as can be seen in Fig. 2C. The position of the attractive yellow stripe is only dependent on the stoichiometry and by adjusting the ratio between the surface constituents we can choose between vesicles with different curvatures, see Fig. 3.

VII. MULTIPLE MINIMA IN THE ENERGY SPECTRUM

We identify parameters in the alkanethiol-on-gold model that cause self-assembly into colloidal particles with three attractive patches separated by 90°, which will cause the colloids to self-assemble into cubes. It turns out that this target requires a more complicated construction than the previous. The patches of the desired pattern are primarily described by \( l = 4 \) modes. With two polymer types, \( L_{\text{red}} - L_{\text{blue}} = 1 \) radii, the surface pattern will form 6 patches separated by 90° for stoichiometry 7:1 to 2:1. To only obtain 3 patches, a third type is introduced with the intention of creating a Janus sphere with the patches on one of the two sides. The third polymer length is chosen so that the energy spectrum exhibits a minimum at \( l = 0 \) that separates the third type from the previous two. An important property of the pattern is the specificity of the attractive patches. If the three red patches are small to increase the specificity on the interactions, this prevents other geometric structures with bonds in similar directions to assemble. This suggests a third minimum that also separates blue and red from yellow at approximately double frequency \( l = 2 \times 4 \). The yellow regions that separate blue and red makes those patches thinner/smaller. If we try to reduce the patch sizes by stoichiometry alone, i.e. small red patches separated by a large yellow region, other patterns described by fewer components of the basis tend to form instead.

All three features are present for the alkanethiol-on-gold model if we choose \( \epsilon = 0.08, L_{\text{blue}} = 1.1, L_{\text{yellow}} = 0 \) and \( L_{\text{red}} = 0.66 \) radii. Choosing a stoichiometry of 21% blue particles, 8% red particles and 71% yellow particles yields patches sufficiently small and with correct spacing, see the energy spectrum in the inset in Fig. 5. The spacing and patch size can be adjusted to some degree by slight changes in the stoichiometry. We verify the design by a Monte Carlo simulation of a colloidal suspension. In Fig. 5, we see a low energy configuration where several cubes have self-assembled.

![Figure 5](image)

**Figure 5:** With greater control over the energy spectrum, more complex functional patterns can be made to self-assemble. Here three minima in the energy spectrum together encode for a pattern where three red patches with high specificity are separated by 90°. The first minimum concentrates red and blue to one side. The second minimum causes red patches to be separated by blue regions with a desired distance. The last minimum causes red and blue regions to be separated by yellow, allowing for a higher specificity. Surface patterns and cubic aggregates obtained from Monte Carlo simulations with simulated annealing.

VIII. CONCLUSIONS

We introduce a design path for self-assembly of target patterns on the surface of spherical colloids. We utilize that self-assembling systems have a strong tendency to form patterns with stripes and/or spots [15], which are used
as functional patches on the next level when the colloids self-assemble into target geometries. The central idea behind the first step in the design path is to match the essential features (the minima) of the energy spectrum of the interactions, to the maxima in the Fourier spectrum of the target surface pattern. By doing this the interactions are tuned to cause self-assembly of the target surface morphology. What structures can be made to self-assemble depend on the degree of influence we have over the interactions between surface constituents and the stoichiometry of the surface coating. A simple model for alkanethiol molecules on gold nanoparticles shows that only a few parameters is sufficient for hierarchical self-assembly of a wide range of geometries, for example diamond lattices, vesicles, and cubic aggregates.

References

[1] Gi-Ra Yi, David J Pine, and Stefano Sacanna. Recent progress on patchy colloids and their self-assembly. Journal of Physics: Condensed Matter, 25(19):193101, 2013.

[2] Qian Chen, Sung Chul Bae, and Steve Granick. Directed self-assembly of a colloidal kagome lattice. Nature, 469(7330):381–384, 2011.

[3] Frank Smallenburg, Hanumantha Rao Vutukuri, Arnout Imhof, Alfons van Blaaderen, and Marjolein Dijkstra. Self-assembly of colloidal particles into strings in a homogeneous external electric or magnetic field. Journal of Physics: Condensed Matter, 24(46):464113, 2012.

[4] Erik Edlund, Oskar Lindgren, and Martin Nilsson Jacobi. Predicting self-assembled patterns on spheres with multicomponent coatings. Soft Matter, 10:2955–2960, 2014.

[5] Amar B. Pawar and Ilona Kretzschmar. Fabrication, assembly, and application of patchy particles. Macromolecular Rapid Communications, 31(2):150–168, 2010.

[6] Amar B. Pawar and Ilona Kretzschmar. Multifunctional patchy particles by glancing angle deposition. Langmuir, 25(16):9057–9063, 2009.

[7] Arnaud Demortière, Alexey Snezhko, Maksim V. Sapozhnikov, Nicholas Becker, Thomas Proslier, and Igor S. Aranson. Self-assembled tunable networks of sticky col-

Figure 4: a) The dominating global minimum separates red and blue to opposing sides of the colloid. The second minimum at \( l = 7 \) encourages an even yellow stripe of a thickness determined by the stoichiometry. By adjusting the stoichiometry, the distance to the yellow stripe and the equatorial can be tuned. b) A large distance from stripe to the equatorial will cause an attractive yellow stripe to force self-assembly of small vesicles. c) A smaller distance will cause the vesicle surface curvature to be lower and the vesicle(s) to be larger. All cross color particle interactions are shoulder potentials, but interactions with yellow particles are weaker (by a factor of 0.4).
loidal particles. *Nature Communications*, 5, 2014.

[8] Stefano Sacanna, Mark Korpics, Kelvin Rodriguez, Laura Colón-Meléndez, Seung-Hyun Kim, David J. Pine, and Gi-Ra Yi. Shaping colloids for self-assembly. *Nature Communications*, 4:1688, 2013.

[9] Alicia M. Jackson, Jacob W. Myerson, and Francesco Stellacci. Spontaneous assembly of subnanometre-ordered domains in the ligand shell of monolayer-protected nanoparticles. *Nature Materials*, 3(5):330–336, 2004.

[10] Chetana Singh, Pradip K. Ghorai, Mark A. Horsch, Alicia M. Jackson, Ronald G. Larson, Francesco Stellacci, and Sharon C. Glotzer. Entropy-mediated patterning of surfactant-coated nanoparticles and surfaces. *Physical Review Letters*, 99(22):226106, 2007.

[11] Ines C. Pons-Siepermann and Sharon C. Glotzer. Design of patchy particles using ternary self-assembled monolayers. *Soft Matter*, 8(23):6226–6231, 2012.

[12] Ines C. Pons-Siepermann and Sharon C. Glotzer. Design of patchy particles using quaternary self-assembled monolayers. *ACS Nano*, 6(5):3919–3924, 2012.

[13] R. J Baxter. *Exactly Solved Models in Statistical Mechanics*. Academic Press, London, 1982.

[14] Michel Godin, P. J. Williams, Vincent Tabard-Cossa, Olivier Laroche, L. Y. Beaulieu, R. B. Lennox, and Peter Grütter. Surface stress, kinetics, and structure of alkanethiol self-assembled monolayers. *Langmuir*, 20(17):7090–7096, 2004.

[15] E. Edlund and M. Nilsson Jacobi. Universality of striped morphologies. *Physical Review Letters*, 105:137203, 2010.