Supporting Information for "Predicting Self-Assembled Patterns on Spheres With Multicomponent Coatings"

Erik Edlund, Oskar Lindgren, and Martin Nilsson Jacobi*

Complex Systems Group, Department of Energy and Environment, Chalmers University of Technology, SE-41296 Göteborg, Sweden

E-mail: mjacobi@chalmers.se

Comparing the alkanethiol model to DPD simulations

The formulation of the minimalistic alkanethiol model described in the main text is based on the dissipative particle dynamics (DPD) simulations of the chains-of-beads model by Pons-Sieperman and Glotzer.[1] We will here compare the systems.

In our alkanethiol model we have a single global parameter ε and the species-specific parameters L_α. In the DPD simulations in [1], relevant parameters are the surfactant lengths, the interbead repulsion between unlike surfactants, and the nanoparticle radius. The ε parameter corresponds approximately to the inverse of the interbead repulsion. The parameters L_α are explicitly modeled on the surfactant lengths, but due to the simplicity of the model they also include any effect of the nanoparticle radius on the curvature of the surface. Another simplification is due to the purely relative dependence of the potentials on the lengths (only $\left| L_\alpha - L_\beta \right|$ enters the expressions): for K

*To whom correspondence should be addressed

particle types, we have only $K - 1$ independent length parameters, as compared to the K surfactant lengths in the DPD simulations. As we will see, increasing all surfactant lengths in the DPD simulations gives similar result as reducing ε in our model.
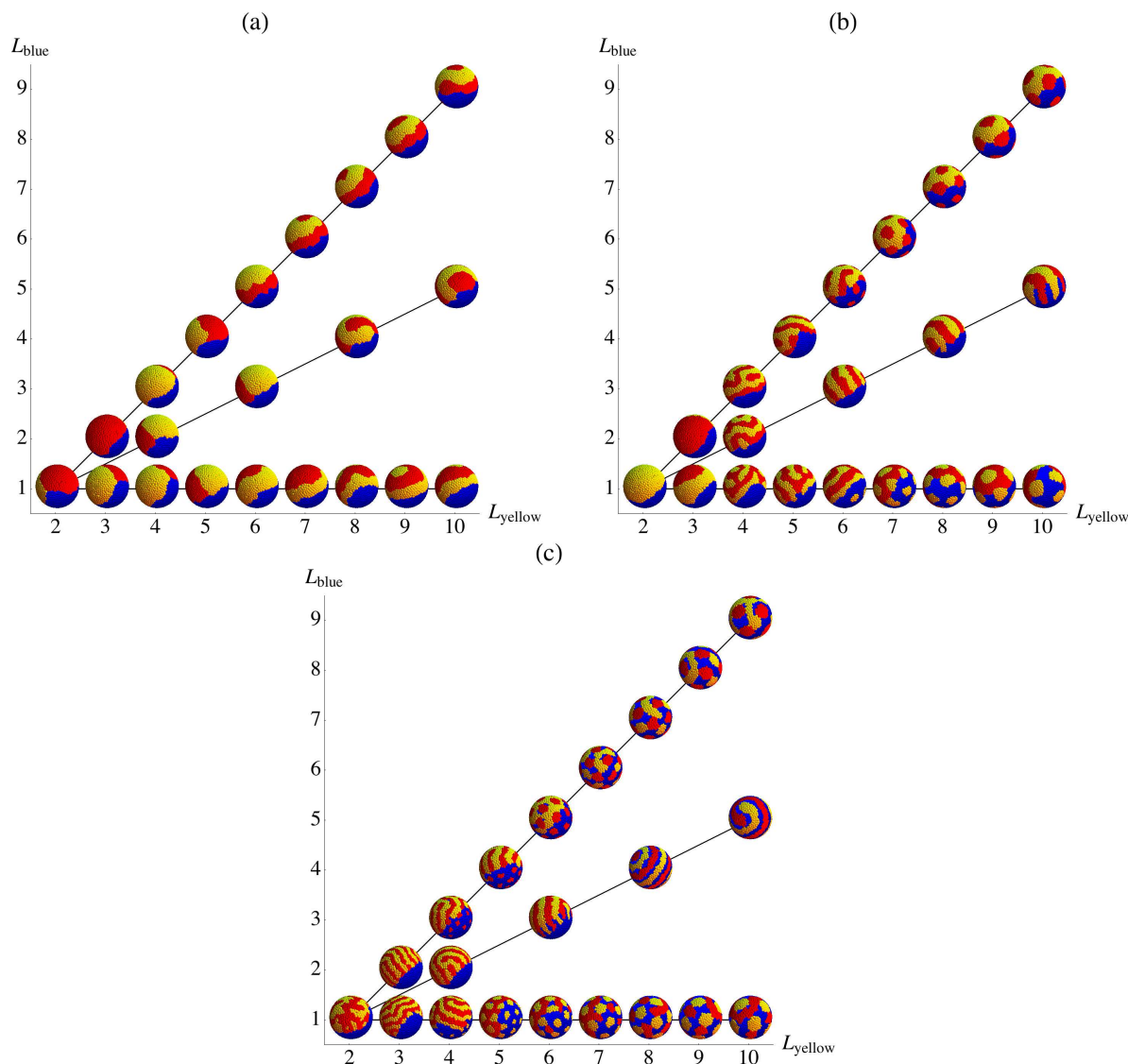

Figure S1: Typical morphologies obtained in Monte Carlo simulations of our alkanethiol model for $\varepsilon = 0.01$ (a), $\varepsilon = 0.1$ (b) and $\varepsilon = 1$ (c) for $L_{red} = 0$ and various L_{blue}, L_{yellow}.

Figure S1 show diagrams modeled on Fig. 2 in ref. [1] for three values of ε. We see that for a smaller value of ε (a), it corresponds closely to the states obtained for long surfactant lengths in Fig. 2d of ref. [1]. For larger ε (b-c), we instead move toward shorter surfactant lengths (Fig. 2b in [1]). In general, there is a close agreement between the states obtained from DPD simulations

of the chains-of-beads model and Monte Carlo simulations of our isotropic potential model. The same types of states appear in the same general regions of the diagrams once the effect of ε is taken into account. Therefore, let us focus on the differences.

The Cerberus particles in the lower left are the same. The striped Janus particles are obtained in both systems, but while in the DPD system the red stripes always are in the direction of the interface between the blue and yellow regions, the simplification of our alkanethiol model loses this property. For longer blue and yellow surfactants, the DPD system shows Janus particles with stripes on both sides. Our alkanethiol model shows a similar state except the stripes turn into spots due to an implicit overestimation of the surface tension of the red domains as compared to the DPD simulations. Finally, for well-separated surfactant lengths (e.g., 3, 6, and 9 in Fig. 2b of [1]), alternating stripes appear. These are also seen in our alkanethiol model ($L_{blue} = 5$ and $L_{yellow} = 10$ in Figure S1c) with the difference that the interfacing stripes are blue rather than red. It is unclear to us what causes this difference.

In summary, all morphologies of the DPD simulations from ref. [1] appear also in our alkanethiol model, with some differences in shapes of some features mainly due to interface effects. It is plausible that these differences could be accounted for by a more complex set of effective interactions, but in the present work we have chosen to prioritize simplicity. Such an extended model would still be possible to analyze with the spectral method of the main article.

Transition to yellow spots

Figure S2 shows a transition analogous to that of Figure 4 in the main text. Instead of increasing both long alkanethiols in tandem, we here keep L_{blue} constant and increase L_{yellow}. This gives first a transition to a striped Janus, as before, but then to a particle with yellow spots on a blue-red background instead of red spots on a blue-yellow background. This difference shows itself in the spectrum as a dominance of the yellow mode at $l = 5$ rather than the red mode.
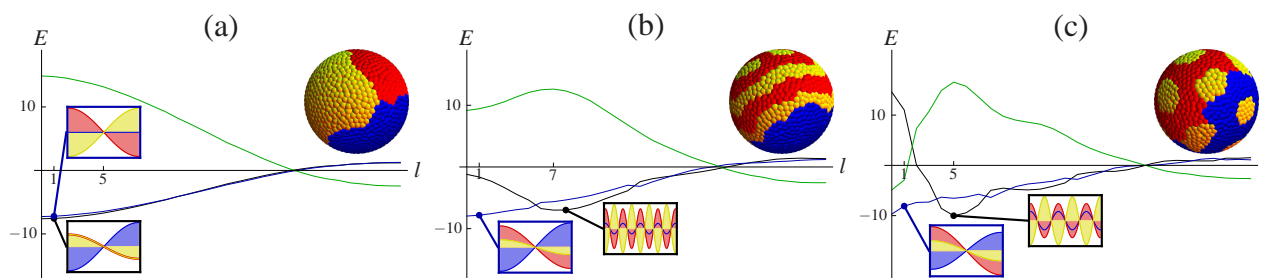
Figure S2: Energy spectra of the alkanethiol model with $\sigma_1 = \sqrt{3}\sigma_0$, $L_{red} = 0$ and $L_{blue} = 1$ and $L_{yellow} \in \{2,5,8\}$ for $\varepsilon = 0.1$, to be compared with Figure 4 of the main text. As before, we have a transition from a Cerberus (a) to a striped Janus particle (b), but in the following transition the yellow rather than the red mode dominates, giving a yellow-spotted Janus particle (c).
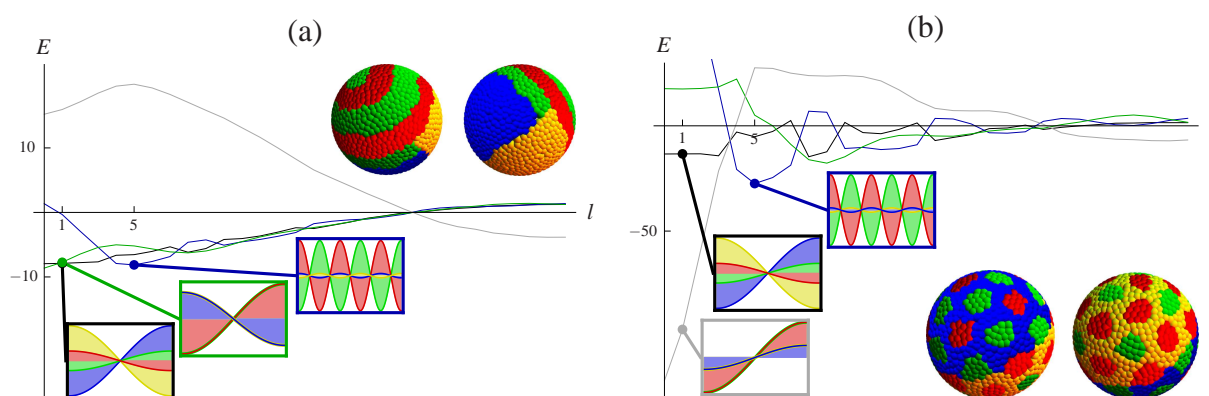
Notes on more particle types

Figure S3: Energy spectra of the alkanethiol model with $\sigma_1 = \sqrt{3}\sigma_0$, $L_{red} = 0$, $L_{blue} = 3$, $L_{yellow} = 5$, and $L_{green} = 8$ for $\varepsilon = 0.05$ (a) and $\varepsilon = 0.7$ (b). The green branch in (a) prescribes a state divided into one half with blue and yellow particles and one with red and green ones. The black branch shows that the blue-yellow half is phase separated into two domains, while the blue branch prescribes stripes in the red-green half, in summary giving a Cerberus particle decorated with green stripes on the red face. In (b) a sign change of the blue and yellow modes turns the global minimum into an unphysical one, causing a transition to a red-and-green spotted Janus particle.

All spectra analyzed in the main article where from systems with three particle types. The process is the same for more types, but the case with three types allows for simplifications that hides some of the complexity. We will here highlight some, with Figure S3 as example.

With four particle types it becomes clear that the minima of the spectrum's branches describe variation between *groups* of types, not necessarily one type versus all the others. For the case of three types, these are the same, but for more types this is not the case. For example, in Figure

S3a we see that the minima at $l = 1$ describe variation of the red and yellow versus the blue and green particles (black border), and between red and green versus blue and yellow (green border), respectively.

For K particle types, we in general need to consider $K - 1$ different minima of branches of the spectrum, as each minimum describes variation between two groups of types. In some cases, less minima may be required. In Figure S3b where the global physical minimum prescribes red and green spots and the next minimum a blue and a yellow domain. These two are sufficient to specify the whole state.

Interestingly, Figure S3a looks similar, with the two minima at $l = 1$ giving an in principle full specification of the state. Here however, we have to take the effect of the mapping to discrete variables into account, recognizing that the red and green modes of the black branch (leftmost inset) have a very small amplitude and thus does not describe a strong enough separation. Instead we must take the third minimum into account, which specifies a striped state in the red-green domain. Thus, in summary, in Figure S3a the minima specify variation of blue versus yellow (black branch), blue-yellow versus red-green (green branch), and red versus green particles (blue branch), respectively.

References

1. Pons-Siepermann, I. C.; Glotzer, S. C. Design of Patchy Particles using Ternary Self-Assembled Monolayers. *Soft Matter* **2012**, *8*, 6226–6231.