

Entropy-Mediated Patterning of Surfactant-Coated Nanoparticles and Surfaces

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We perform atomistic and mesoscale simulations to explain the origin of experimentally observed stripelike patterns formed by immiscible ligands coadsorbed on the surfaces of gold and silver nanoparticles. We show that when the conformational entropy gained via this morphology is sufficient, microphase-separated stripelike patterns form. When the entropic gain is not sufficient, we instead predict bulk phase-separated Janus particles. We also show corroborating experimental results that confirm our simulational predictions that stripes form on flat surfaces as well as on curved nanoparticle surfaces.

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Understanding and controlling the properties of molecular coatings on surfaces is an important challenge for many applications, and is a key factor in the fabrication of, e.g., protein repellent [1], wear resistant [2], and cell-adherent [3,4] surfaces. Self-assembled monolayers (SAMs) are monolayers of ligand molecules that chemisorb on flat substrates [5,6] or the surfaces of nanoparticles (NPs) [7], and control and regulate the surface interactions. In the case of NPs, patterns—even unintentional ones—formed within these monolayers can affect particle interactions and their subsequent self-assembly [8–10]. Recently, Jackson *et al.* [1,11] demonstrated that SAMs assembled onto gold and silver NPs could be patterned in an unusual way using two species of ligands with identical binding groups (thiols) and chemically distinct tails. Rather than undergoing bulk phase separation upon adsorption due to the immiscibility between tails, the surfactants on the NP surface microphase separated unexpectedly into stripes (ripples) less than 1 nm in width. Subsequently, DeVries *et al.* [12] exploited the patterned surface to attach diametrically opposing tethers to the surface of gold NPs, enabling self-assembly of these NPs into chains and rings as predicted by earlier simulations of tethered NPs [13]. Microphase separation on these particles was recently confirmed via vibrational spectroscopy studies [14]. But, the origin of microphase separation and patterning of the ligands on the NP surface remained unknown.

In this Letter, we reproduce the experimentally observed stripe formation [1,11] using atomistic and mesoscale simulations of surfactant mixtures on NP surfaces, and show that for equimolar mixtures of surfactants with immiscible tails, stripes result from entropic considerations that arise due to a mismatch in tail length or bulkiness. Specifically, the tendency toward bulk phase separation driven by free energy minimization—occurring through a reduction in energy at the expense of configurational entropy—is modified by a significant increase in tail conformational entropy that arises when long or bulky surfactants are surrounded by shorter or less bulky ones. This

competition results in microphase separation (Fig. 1). Our simulations further predict similar phenomena on flat surfaces, provided the length mismatch or difference in bulkiness is sufficient. We confirm this prediction experimentally, and demonstrate via simulation the role of curvature in stripe formation.

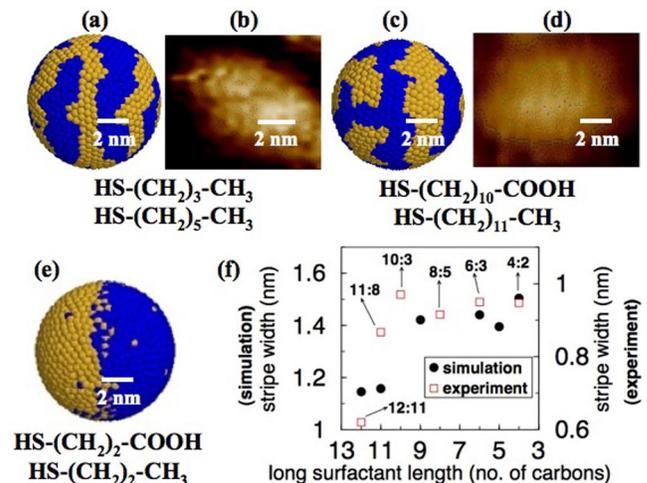


FIG. 1 (color online). (a),(b) C4:C6 surfactant mixture of SAMs from atomistic simulations and experiments (STM images), respectively. The tail end-groups are identical, but the lengths differ. (c),(d) Dodecanethiol/Mercaptoundecanoic acid (C11:C12) surfactant mixture of SAMs from atomistic simulations and experiment (STM images), respectively. Here the tail end-groups differ somewhat in size and the tail lengths are nearly identical. (e) Atomistic simulation of mixture of equal-length (C3:C3) surfactants, with different tail end-groups. For atomistic snapshots, dark (blue) and light (yellow) beads are head groups of surfactants that are short (or contain -COOH) and long (or contain -CH₃), respectively. In all cases, the head groups (-SH) are identical. (f) Variation of stripe width with the length of long surfactant in number of carbon atoms. The same trend is seen when stripe width is plotted against short surfactant length. The atomistic simulation data points are for equal-length surfactants.

Atomistic molecular dynamics simulations of several equimolar mixtures of surfactants coadsorbed on the surface of a NP 7.0 nm in diameter, corresponding to the experimental systems we study, are carried out using DLPOLY [15] with a fully flexible united atom model [16,17]. As indicated in Fig. 1, these surfactants have identical head groups (-SH) and immiscible tails. Nonbonded interactions between atoms or groups of atoms on the same type of surfactants are modeled via a 6-12 Lennard-Jones (LJ) potential with a cutoff of 0.1 nm. The LJ potential parameters for the surfactants used in this study are available in Refs. [16,17]. Nonbonded interactions between unlike atoms or groups of atoms are modeled via the Buckingham potential without the attractive component [$U(r) = 500e^{-r/0.4}$, where r is the distance between unlike atoms or groups] and a cutoff given by the collision diameter σ_s . The simulations are carried out in the *NVT* ensemble using a Nosé-Hoover thermostat at a temperature of 360 K [18]. We model the NP surface as a sphere and employ the SHAKE algorithm [19] to confine the surfactant head groups on the surface at a density of 0.07 chains/Å². The surfactants are initialized in a mixed state at high temperature, and the system is subsequently cooled to the desired temperature and allowed to evolve until no further change in structure is observed. A typical simulation requires ~1000 hours CPU time on a 2-GHz Apple G5 processor. Multiple processors reduce the wall clock time.

Mesoscale simulations of equimolar mixtures of immiscible surfactants coadsorbed on a surface are carried out using dissipative particle dynamics (DPD) [20], a method that samples the *NVT* ensemble [21]. The surfactants are modeled as bead-spring tails connected to single-bead head groups, wherein consecutive beads along each surfactant backbone are permanently bonded together via a harmonic spring. Lengths of the surfactants are expressed in total number of beads connected together in the molecule. Nonbonded interactions between species are modeled using a harmonic potential [20]. Dimensionless mass, length, and time scales are chosen such that mass and diameter, σ , of a bead and $k_B T$ are all unity (k_B is the Boltzmann factor and T is the temperature) [20]. For interactions between like species the repulsion parameter [20], a_{ii} , is chosen to be 18.75, and between unlike surfactant beads $a_{ij} = 33.75$. The surface density of surfactants is 4 beads/ σ^2 . We employ constrained dynamics [22] to confine the surfactant head groups to the surface. For flat substrates periodic boundaries are applied in the plane of the surface. Systems are initially prepared in a mixed state at high temperature and then cooled to the target temperature at which phase separation occurs. For several runs on surfaces of low curvature, after very long equilibration times with the traditional DPD algorithm, groups of like surfactants comprising a domain are moved together briefly to expedite equilibration. We have ascertained that the final structures are independent of the cooling rate and obtainable via alternate thermodynamic paths. A typical simula-

tion requires ~170 CPU hours on a 2-GHz Apple G5 processor.

The synthesis of mixed ligand NPs and study of the morphology of the SAMs that comprise their ligand shell are performed according to procedures described elsewhere [1,11], and are not repeated here. For the experimental study of mixed SAMs on flat surfaces, all chemicals were purchased from Sigma-Aldrich and used as received. Flame annealed Au(111) on mica substrates were obtained from Molecular Imaging. SAMs are formed by immersing gold on mica substrates into a 1 mM ethanol solution [equimolar in SH-(CH₂)₃-CH₃ and SH-(CH₂)₅-CH₃], for 9 days at 50 °C. Substrates are removed from solution, rinsed with toluene, absolute ethanol, and acetonitrile, and then air-dried. Scanning tunneling microscopy (STM) images are recorded in air using a Digital Instruments Multimode Nanoscope IIIa using an *E* scanner with mechanically cut platinum-iridium tips. The tip bias used is between 900 and 1400 mV with set currents of 350 to 700 pA, and with tip speeds between 0.3 and 1 μm/s. The integral gain used to obtain images is in the range of 0.3 to 0.65 with the proportional gain from 0.3 to 1.4.

Figures 1(a)–1(d) show the results of atomistic simulations of two ligand mixtures on NPs and the corresponding experimental STM images. Our simulations demonstrate that stripelike patterns form in both cases as the surfactants phase separate on the surface due to immiscibility of the tails with each other. These stripes persist, are not simply frozen patterns of intermediate or late-stage spinodal decomposition [23], and are independent of the cooling rate. In Figs. 1(a) and 1(b), the surfactants differ only in length, and in Figs. 1(c) and 1(d) they differ only in tail end-group.

For very short surfactants, e.g., C3:C3, atomistic simulations predict bulk phase separation despite the difference in bulkiness of the tail end-group [Fig. 1(e)]. This demonstrates that for small enough molecular length the mixture behaves as a binary mixture of immiscible single-bead molecules, while for longer molecules bulk phase separation is modified to microphase separation. Both experiments and simulations show that the stripe thickness decreases with an increase in surfactant length [Fig. 1(f)].

We hypothesize that microphase separation of immiscible surfactants into stripelike patterns on NP surfaces is entropic in origin. For sufficiently long surfactants, the additional conformational entropy gained by creating interfaces at which bulky tail groups are adjacent to less bulky tail groups, providing the bulky tails with additional free volume, is sufficient to overcome the decrease in energy that would be gained from bulk separation and the energetic penalty for creating the extra interfaces. As a result, the system compromises by forming microphase-separated stripes. In fact, this motif should hold generally for immiscible mixtures whenever the creation of interfaces allows for a sufficient increase in conformational entropy. For example, we argue that such should be the case for a mixture of surfactants with immiscible tails of sufficiently unequal lengths, as shown schematically in

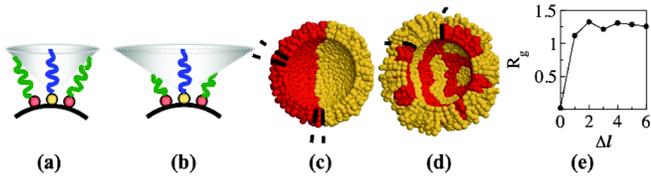


FIG. 2 (color online). (a),(b) Schematic two-dimensional representation of shared free volume (conical shaded area) available to surfactant tails when they are surrounded by other surfactants on curved surfaces, for equal-length and unequal-length surfactants, respectively. Extension of these diagrams to 3D and to flat surfaces is trivial. The free volume available to surfactant tails on flat surfaces in both cases (same length and different length) is less than that available on curved surfaces due to geometry. (c) Cross sectional view of DPD simulation of equal-length surfactants showing that a surfactant tail has the same available free volume (indicated by dashed lines) when it is placed next to a similar or different surfactant. This snapshot is for surfactants of length 4 each on a sphere of radius 5σ . (d) Cross sectional view of DPD simulation of unequal-length surfactants (lengths 4 and 8) on a sphere of radius 5σ showing how the longer tails (lighter/yellow) fill the extra available free volume by bending over shorter ones (darker/red). The wedgelike structures thus formed are shown by dashed lines. (e) Radius of gyration, R_g , vs length difference, Δl , with length of longer surfactant fixed at 9.

Figs. 2(a) and 2(b). Moreover, the amount of entropy gained per unit length of interface created increases for longer tails [Fig. 1(f)], larger mismatch between tail lengths, and/or a higher degree of curvature of the surface (up to a point, as discussed later) since the free volume available to the longer surfactant tails at the interface increases with distance from a convex surface [5,24].

To test our hypothesis, we perform mesoscale simulations where all chemical details other than immiscibility and either bulkiness or length difference are ignored, and ascertain the role of a mismatch in length and/or bulkiness between surfactants and also the surfactant tail length relative to the curvature of the surface. Cross sections of simulation snapshots [Figs. 2(c) and 2(d)] confirm that long surfactants bend over the shorter ones when the length difference is significant [Fig. 2(d)], while no such bending is seen for equal-length surfactant mixtures [Fig. 2(c)]. An inspection of these cross sections also shows that complicated phenomena like the bending over of the chains upon themselves and looping do not occur since all chains are reasonably short. The simplified model of Figs. 2(a) and 2(b) is therefore supported by simulation. That the long chains are able to explore a larger free volume for shorter chains can also be confirmed by calculating the radius of gyration, R_g , of the long chains in the presence of short chains of varying lengths [Fig. 2(e)]. We see that R_g increases as the length of the shorter surfactant decreases for a fixed long surfactant length, up to a point beyond which it remains nearly constant. Since R_g is an indirect measure of conformational entropy available to a surfactant tail, this supports our contention that conformational entropy increases with increasing mismatch in tail lengths.

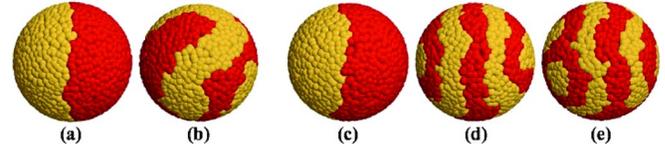


FIG. 3 (color online). Equilibrium structures obtained by mesoscale simulations of self-assembly of binary mixtures of surfactants with varying length difference or bulkiness difference on a sphere of radius 5σ . Dark (red) beads and light (yellow) beads represent head groups of the two species of surfactants (tails not shown). (a) Length ratio 4:4, equal bulkiness. (b) Length ratio 6:6 with one surfactant (yellow heads) having a bulkier tail group. (c)–(e) Length ratios 4:6, 4:7 and 4:13, respectively, with equal bulkiness.

For a system of immiscible surfactants of equal length and bulkiness, we find that bulk phase separation occurs regardless of the radius of curvature of the surface or tail length [Fig. 3(a) shows our result for a system of tail length ratio 4:4]. Thus, surfactants with immiscible tails of equal length and otherwise identical architecture behave as immiscible single-bead molecules undergoing bulk phase separation. We next simulate a system of immiscible surfactants of equal length but with differently sized tail end-groups and observe stripe formation [Fig. 3(b)]. We find that stripes do not form for very short chains or small difference in bulkiness (not shown), demonstrating that a sufficient gain in conformational entropy is needed to stabilize stripes. Figures 3(c)–3(e) show our results for systems of immiscible surfactants with tails of identical architecture but unequal tail lengths, with length ratios 4:6, 4:7, and 4:13 on a sphere of radius 5σ . We find that for this size sphere, stripes form only for a length difference equal to or greater than 3, again demonstrating the role of conformational entropy, which increases with increasing length difference, in stabilizing stripes.

Additional simulations on different size spheres demonstrate the dependence of stripe formation on substrate curvature, i.e., on the size of the NP relative to the size of the surfactant. In particular, we predict that even on flat surfaces stripes form if the length difference, and thus the free volume (and conformational entropy), gained is sufficient. Figure 4 shows the results of mesoscale simulations of fixed length ratio (4:7) on surfaces of varying degrees of curvature. For a very high degree of curvature (small NPs), we observe bulk phase separation [Fig. 4(a)]. Bulk separation on small enough particles is also predicted by our atomistic simulations (not shown). Because the sphere is sufficiently small relative to the surfactant length, the tails already have sufficient conformational entropy moving radially outward from the sphere, and the gain in entropy by creating additional interfaces (and thus stripes) is not significant. This prediction that Janus particles [25] may form for sufficiently small NPs awaits direct confirmation by experiment, although indirect evidence now exists [26].

For larger spheres [Figs. 4(b) and 4(c)], however, the surfactants assemble into stripelike domains as in the ex-

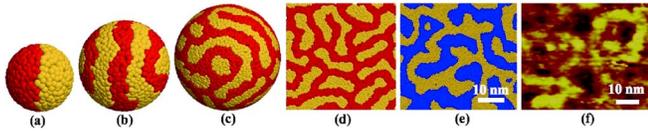


FIG. 4 (color online). (a)–(d) Equilibrium structures obtained by mesoscale simulations of self-assembly of a binary mixture of surfactants of length ratio 4:7 on surfaces with varying degrees of curvature. Dark (red) beads and light (yellow) beads represent head groups of shorter and longer surfactants, respectively (tails not shown). Sphere radius: (a) 3σ , (b) 5σ , (c) 10σ , (d) infinite. Sphere radii not drawn to scale. (e) Atomistic simulation of C4:C6 (both having $-\text{CH}_3$ tail end-group) mixed monolayer showing stripelike domains. Dark (blue) and light (yellow) beads are the head groups of the short and long surfactant, respectively. (f) STM height images of C4:C6 mixed monolayer showing stripelike morphology with a domain width of 5 nm.

periments and atomistic simulations. Even for infinite radii of curvature (flat surfaces), we predict wormlike stripes [Fig. 4(d)] for this tail length ratio. We have verified the formation of stripelike domains on flat substrates via atomistic simulations [Fig. 4(e)] and experiment [Fig. 4(f)]. Stripe formation is seen to be a function of substrate curvature in that the stripes formed on large spheres [Fig. 4(c)] and flat substrates [Fig. 4(d)] are not aligned and patchy domains are also seen, while aligned stripes form on medium-sized spheres [Fig. 4(b)]. This alignment regime predicted by our simulations is confirmed experimentally [26]. Both patches [27,28] and stripes [29] have previously been reported in the literature for SAMs. We will address the issue of patch vs stripe formation on flat surfaces in a forthcoming publication.

Since stripe formation depends on relative tail lengths and the radius of curvature of the substrate, it is physically intuitive to expect a geometric scaling relation for stripe spacing as a function of these parameters. We find that, although it is straightforward to establish general trends (e.g., stripe thickness decreases with an increase in surfactant length), it is not trivial to predict the stripe width for an arbitrary system. Our simulations appear to be in a cross-over regime between weak and strong segregation, where a purely geometric scaling relation is not possible.

In summary, we have explained the origin of the previously reported and unexpected stripelike patterns formed by immiscible surfactants coadsorbed onto NP surfaces. We hypothesized that the formation of stripes, which creates additional interfaces relative to a bulk-separated system, is entropic in origin. Specifically, interfaces at which long or bulky surfactant tails are adjacent to shorter or less bulky tails provide additional conformational entropy. If the entropy gain is sufficient, which depends on, e.g., the overall tail lengths and length mismatch relative to the surface degree of curvature, then microphase-separated stripes, rather than bulk phase separation, should occur as the equilibrium morphology. We also predicted the formation of bulk phase-separated Janus particles for mixtures of short surfactants, or surfactants with small length or bulki-

ness difference and for very small NPs. Other examples of stripes stabilized by competing thermodynamic driving forces during phase separation have been reported in the literature [30–34]. The motif described here, which exploits conformational entropy through judicious choice of surfactants, provides a new and powerful approach to patterning surfaces at the nanoscale.

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