Stripes, Clusters, and Nonequilibrium Ordering for Bidisperse Colloids with Repulsive Interactions

C. Reichardt and C.J. Olson Reichhardt
Theoretical Division and Center for Nonlinear Studies, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
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We show that two-dimensional bidisperse assemblies of colloids with strictly repulsive interactions exhibit stripe, cluster, and partially crystallized states when driven over a quenched random substrate. The nonequilibrium states on a substrate are significantly more ordered than equilibrium states both with and without substrates. A minimum substrate strength is necessary to induce the nonequilibrium pattern formation. Our results suggest that a combination of driving and quenched disorder offers a new approach to controlling pattern formation in colloid mixtures.

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Understanding how assemblies of particles organize is an outstanding problem in both equilibrium and nonequilibrium systems. The ability to control pattern formation would have a profound impact on applications that use large-scale self-assembly to create specific pattern morphologies. In equilibrium, it is known that particles with competing repulsive and attractive interactions can organize into clusters, stripes, and spongelike textures. Similar patterns can also arise for particles with strictly repulsive potentials that have a two step form. Recently, it was shown in both simulations and experiments that a two-dimensional (2D) bidisperse assembly of colloids interacting via repulsive magnetic dipoles of two different strengths can cluster into spongelike patterns. This suggests that other types of ordering are possible for bidisperse repulsively interacting particles.

Here, we demonstrate that a variety of distinct partially ordered states can occur for a bidisperse system of strictly repulsively interacting colloids driven over a random substrate that is sufficiently strong. There has been extensive work on the ordering of monodisperse charged particles moving over random quenched disorder for systems such as vortices in type-II superconductors, moving Wigner crystals, and colloids. In the absence of quenched disorder, a monodisperse system forms a triangular lattice, while strong quenched disorder distorts the lattice and generates numerous topological defects. These defects can be partially annihilated and the order partially regained by driving the system into a nonequilibrium moving smectic state. It is not known what type of nonequilibrium configurations would occur for two species of particles driven with identical force over quenched disorder. In contrast to the monodisperse case, for a bidisperse system even the equilibrium states in the absence of a random substrate are intrinsically disordered, so one might expect the addition of quenched disorder to further disorder the system. Instead, we find that for certain regimes, nonequilibrium bidisperse colloid assemblies moving over quenched disorder have more topological order than the corresponding equilibrium states, even those without quenched disorder. The quenched disorder must be sufficiently strong for the topological ordering to occur. We argue that for strong quenched disorder, significant plastic deformations of the driven colloid configuration occur due to the fact that the different species move at different average velocities close to the depinning threshold. We show that the system can organize into stripes with triangular ordering within each stripe. When the difference between the two species is small, a moving smectic state forms, whereas when the disparity is very large moving cluster states form. Our results are robust for a wide range of colloid densities, quenched disorder strengths, and system sizes.

We employ Brownian dynamics to simulate a 2D system of size $L \times L$ containing $N$ colloids and $N_p$ potential traps with periodic boundary conditions in the $x$ and $y$ directions. The overall density of the system is $n = N/L^2$. The colloids interact via a screened Coulomb potential $V(R_{ij}) = (E_0/R_{ij}) \exp(-\kappa R_{ij})$, where $R_{ij}$ is the position of colloid $i$ and $j$, $R_{ij} = |R_i - R_j|$, $E_0 = Z^2/(4\pi\epsilon\epsilon_0 a_0)$, $Z$ is the unit of charge, $\epsilon$ is the solvent dielectric constant, and $1/\kappa$ is the screening length. The unit of distance in the simulation is $a_0$, and unless otherwise noted, $L = 48a_0$. In this work we fix $\kappa = 4a_0$, which is reasonable for experiments on colloids in nonpolar fluids. Forces are measured in units of $F_0 = E_0/a_0$. The dynamics of colloid $i$ are given by the equation of motion

$$\eta \frac{dR_i}{dt} = -q_i \sum_{j=1}^{N} q_j \nabla V(R_{ij}) - \sum_{k=1}^{N_p} \nabla V_p(R_{ik}) + F_D + F_t^T$$

(1)

where $\eta$ is the damping term, $q_{i(j)}$ is the dimensionless charge of colloid $i$ and $j$, $R_{ik} = |R_i - R_k|$, and $R_k$ is the position of trap $k$. In this model, hydrodynamic effects are neglected; such effects can be strongly screened in a system confined within 2D walls. To introduce bidispersity to the system, half of the colloids have charge $q_i = q_A$ and the other half have $q_i = q_B$, where we fix $q_B = 1$. The quenched random substrate is modeled by randomly distributed parabolic traps of density $n_p$ and radius $r_p = 0.1a_0$ with $V_p(R_{ik}) = -(F_p/2r_p)(R_{ik} - r_p)^2$ for $R_{ik} \leq r_p$ and zero interaction for $R_{ik} > r_p$. Here $F_p$ is the maximum pinning force. This model for quenched
random disorder has given results comparable with other models in monodisperse particle systems. The externally applied driving force is identical for all particles and is given by $F_D = F_D \hat{x}$. A uniform drive of this type could be created electrophoretically \[\text{[16]}\]. Thermal effects are modeled by random Langevin kicks with $\langle F_i^2 \rangle = 0$ and $\langle F_i(t) F_i(t') \rangle = 2k_B T \delta(t - t')$. The initial colloid configurations are obtained using simulated annealing. We then set $F_D^2 = 0$ and gradually increase $F_D$ in increments of $\delta F_D = 0.001$ every $\tau = 5000$ simulation time steps. After each drive increment, once the system has reached a stationary state we measure the average velocity $\langle V_x \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} v_i \cdot \hat{x} \right\rangle$, where $v_i$ is the velocity of colloid $i$. The depinning threshold $F_C$ corresponds to the value of $F_D$ at which $\langle V_x \rangle = 0.04 F_0$. As an example, for $a_0 = 0.6 \mu m$, $\epsilon = 2$, and $Z^* = 300e$, $F_0 = 27.8$ pN.

We first consider a system where the ratio between the charges of the two colloid species is $q_A/q_B = 3$. In the absence of quenched disorder, the colloids form a disordered mixed assembly after annealing, illustrated in Fig. 1(a). To characterize the configuration, we determine the structure factor, $S(k) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \exp(-i \mathbf{k} \cdot \mathbf{R}_i) \right\rangle^2$. In Fig. 1(b), $S(k)$ for the equilibrium case with $N = 864$ colloids at density $n = 0.385/a_0^2$ shows a ring structure which is characteristic of disordered systems. We also analyze the fraction of six-fold coordinated colloids $P_6$ obtained from a Voronoi construction, $P_6 = (1/N) \sum_{i=1}^{N} \delta(z_i - 6)$, where $z_i$ is the coordination number of colloid $i$. In a triangular lattice all the colloids have $z_i = 6$, giving $P_6 = 1$. For the configuration shown in Fig. 1(a), $P_6 = 0.41$, indicating that a large fraction of the colloids have $z_i \neq 6$. If we anneal in the presence of quenched disorder, we find a similar disordered state as measured by $S(k)$ and $P_6$. In general, for stronger quenched disorder the system becomes more disordered, producing increased smearing in the ring structure of $S(k)$ and reducing $P_6$ to $P_6 = 0.3$.

In Fig. 2(a) we plot the dynamic response of the system given by the average colloid velocity $\langle V_x \rangle$ versus external drive $F_D$ for $P_6 = 0$ (light line), and for a system with traps of strength $F_p = 1.0$ and density $n_p = 4.0/a_0^2$ (heavy line). For $F_p = 0$, the velocity response is strictly linear. In the presence of traps, there is a clear depinning threshold $F_C = 0.7$ for colloid motion followed by a nonlinear regime which crosses over to an ohmic regime at higher $F_D$. For $F_p = 1$, Fig. 2(a) shows that $d\langle V_x \rangle/dF_D$ has a peak in the nonlinear regime at $F_D = 0.75$ and flattens in the ohmic region for $F_D > 2.0$. These features in the velocity-force curves are the same as those previously observed for monodisperse systems with quenched disorder \[\text{[4, 18]}\], where the onset of the ohmic response was correlated with a dynamical reordering of the system into a moving smectic state.

In Fig. 2(b) we plot the corresponding $P_6$ versus $F_D$ curves for the systems with and without quenched disorder. For $F_p = 0$, $P_6 = 0.41$ for all $F_D$. For $F_p = 1.0$, we still find $P_6 = 0.41$ in the pinned region at $F_D/F_C < 1$. Above the depinning transition, $P_6$ increases over the same range of $F_D$ where there is a nonlinear response in the velocity force curves, as seen in Fig. 2(a). Here, the system moves plastically with portions of the colloids remaining temporarily trapped while other colloids move

FIG. 1: A bidisperse system of colloids with $q_A/q_B = 3$ and $n = 0.385/a_0^2$. (a,c) Real space colloid configurations. Small circles: species A; large circles: species B. (b,d) The corresponding structure factor $S(k)$. (a,b) Equilibrium state with no pinning or driving. (c,d) Moving stripe state for $F_p = 1.0$, $n_p = 4.0/a_0^2$, and $F_D/F_C = 3.0$.

FIG. 2: (a) Average velocity $\langle V_x \rangle$ vs applied drive $F_D$ for the system in Fig. 1. Light upper line: sample with $F_p = 0$; dark lower line: sample with $F_p = 1.0$; dashed line: $d\langle V_x \rangle/dF_D$ for the $F_p = 1.0$ case. (b) $P_6$ vs $F_D$ for the same system. Upper curve: $F_p = 1.0$; lower curve: $F_p = 0$. 
FIG. 3: (a) The different regimes for the system in Fig. 1 at $n = 0.385/a_0^2$ and $n_p = 4.0/a_0^2$ as a function of $F_D$ and $F_p$. I: pinned regime; II: moving disordered regime; III: plastic flow regime; IV: moving stripe regime, as in Fig. 1(c). Circles: the pinned regime; II: moving disordered regime; III: plastic flow (b) The different regimes for plastic flow state (region III) appears above depinning. 

The structure factor has a smecticlike form, indicative of the presence of stripes, as well as second order peaks at smaller scales resulting from the in-stripe triangular ordering.

We next show that sufficiently strong quenched disorder must be present for the stripe patterns to occur. In Fig. 3(a) we outline the four distinct regimes that we find as a function of driving force $F_D$ and pinning force $F_p$ for a system with $n = 0.385/a_0^2$ and $n_p = 4.0/a_0^2$. At all $F_D$, the colloids are pinned in region I for $F_D < F_C$. As $F_D$ is increased above $F_C$, we find that for $F_p < 0.4$, the system never orders into a stripe state. Instead, the disordered mixture depins with little or no plastic deformation, and the moving state, marked region II in Fig. 3(a), retains the same disordered configuration as the pinned state. We have tested different values of $\delta F_D$ and find no change in the location of region II. For $F_p \geq 0.4$, a plastic flow state (region III) appears above depinning.

The moving stripe state forms when the quenched disorder is strong enough to induce plastic deformations in the colloid configuration. The effective pinning force from the substrate decreases for increasing colloid-colloid interactions in a monodisperse system. In a bidisperse system, local clustering of colloid species occurs, as seen in experiments. Clusters of the weakly charged colloid species B experience a stronger effective pinning force than clusters of the more strongly charged colloid species A. If the quenched disorder is sufficiently strong and dense, the two species will move at different average velocities even though they both couple to the external drive in the same way. Stripes form as the faster moving species begins to collect together. In a co-moving reference frame, this state resembles a system of bidisperse colloids.
We now address the effect of the polydispersity on the moving regimes by varying $q_A/q_B$. A system with the same parameters as in Fig. 2(a) and $F_p = 1.0$ acts like a monodisperse sample for $1 < q_A/q_B < 1.3$, where it reorders into a moving smectic (MS) state as observed in previous simulations [3, 4, 8]. For $1.4 < q_A/q_B \lesssim 10$ the system forms a moving stripe state (region IV), and for $q_A/q_B \gtrsim 10$ we observe a moving clump (MC) state. The onset of these different states appears in Fig. 2(a) where we plot $P_0$ versus $q_A/q_B$ at $F_D/F_C = 3$. In the moving smectic state, $P_0 \approx 0.82$, in the moving stripe state $P_0 \approx 0.7$, and in the moving clump state $P_0$ is sharply reduced. The real space configuration of the moving clump state is illustrated in Fig. 2(b), and the corresponding structure factor $S(k)$ in Fig. 2(c) has a multiple ring structure characteristic of a disordered system containing more than one length scale. Here, the different length scales are associated with the triangular ordering of the higher charge $q_A$ species and the inter-clump distance. Similar to the moving stripe state, the moving clump state requires sufficient quenched disorder to form. As $q_A/q_B$ increases, the size of the individual clumps decreases.

In summary, we have shown that a bidisperse system of repulsively interacting colloids driven over quenched disorder can form moving smectic, moving stripe, and moving clump states. The moving states are in general more ordered than the equilibrium states that form in the absence of quenched disorder, in contrast to a monodisperse system. The stripe state arises when the disorder is strong enough to induce different average velocities for the two species, leading to a laning instability similar to that seen for particles driven in opposite directions. In our system, the velocity difference is due entirely to the quenched disorder, and not to different drives on the different colloids. Physical systems in which this model could be realized include driven bidisperse colloidal assemblies with charge or magnetic interactions driven over optical pinning or a rough wall, electron systems with co-existing single and multiple electron bubble states, and superconductors with mixtures of Abrikosov and Josephson vortices.

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