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Stripes, clusters, and nonequilibrium ordering for bidisperse colloids with repulsive interactions

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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 [1]. Similar patterns can also arise for particles with strictly repulsive potentials that have a two-step form [2]. 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 [3]. 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 [4–6], moving Wigner crystals [7], and colloids [8]. 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 [4–8]. 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 [3], 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 $\mathbf{R}_{i(j)}$ is the position of colloid i (j), $R_{ij}=|\mathbf{R}_i-\mathbf{R}_j|$, $E_0=Z^{*2}/(4\pi\epsilon\epsilon_0 a_0)$, Z^* is the unit of charge, ϵ 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 [9]. Forces are measured in units of $F_0=E_0/a_0$. The dynamics of colloid i are given by the equation of motion

$$\eta\frac{d\mathbf{R}_i}{dt}=-q_i\sum_{j=1}^{N}q_j\nabla V(R_{ij})-\sum_{k=1}^{N_p}\nabla V_p(R_{ik})+\mathbf{F}_D+\mathbf{F}_i^T \quad (1)$$

where η is the damping term, $q_{i(j)}$ is the dimensionless charge of colloid i (j), $R_{ik}=|\mathbf{R}_i-\mathbf{R}_k|$, and $\mathbf{R}_k$ 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 $\mathbf{F}_D=F_D\hat{\mathbf{x}}$. A uniform drive of this type could be created electrophoretically [10]. Thermal effects are modeled by random Langevin kicks with $\langle F_i^T\rangle=0$ and $\langle F_i^T(t)F_j^T(t')\rangle=2\eta k_BT\delta_{ij}\delta(t-t')$. The initial colloid configurations are obtained using simulated annealing. We then set $F^T=0$ and gradually increase F_D in increments of $\delta F_D=0.001$ every τ

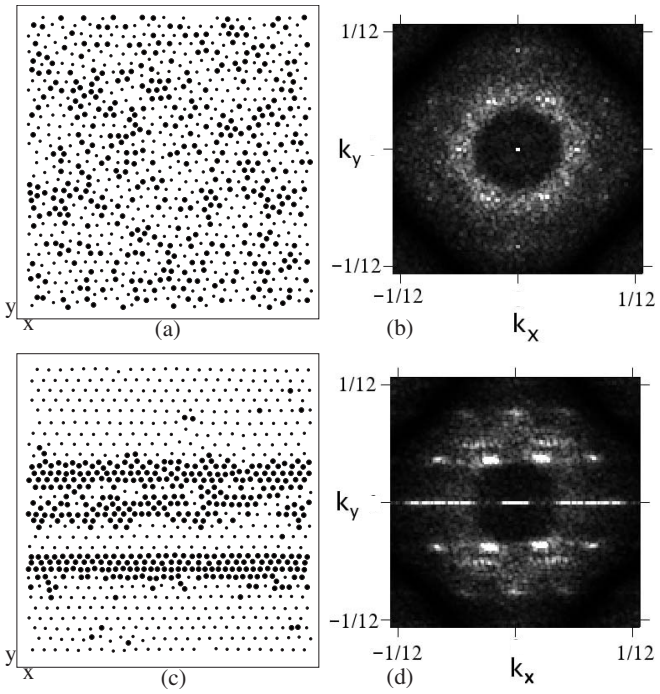

FIG. 1. Bidisperse system of colloids with $q_A/q_B=3$ and $n=0.385/a_0^2$. (a),(c) Real space colloid configurations. Small circles, species A; large circles, species B. (b),(d) Corresponding structure factor $S(\mathbf{k})$. (a),(b) Equilibrium state with no pinning or driving. (c),(d) Moving stripe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

$=5000$ simulation time steps. After each drive increment, once the system has reached a stationary state we measure the average velocity $\langle V_x\rangle=\langle(1/N)\Sigma_{i=1}^{N}\mathbf{v}_i\cdot\hat{\mathbf{x}}\rangle$, where $\mathbf{v}_i$ is the velocity of colloid i. The depinning threshold F_C corresponds to the value of F_D at which $\langle V_x\rangle=0.04$. As an example, for $a_0=0.6$ μm, $\epsilon=2$, 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 $S(\mathbf{k})=(1/N)|\Sigma_{i=1}^{N}\exp(-i\mathbf{k}\cdot\mathbf{R}_i)|^2$. In Fig. 1(b), $S(\mathbf{k})$ 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 sixfold-coordinated colloids P_6 obtained from a Voronoi construction, $P_6=(1/N)\Sigma_{i=1}^{N}\delta(z_i-6)$, where z_i is the coordination number of colloid i. In a triangular lattice all the colloids have $z_i=6$, giving $P_6=1.0$. 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 $S(\mathbf{k})$ and P_6. In general, for stronger quenched disorder the system becomes more disordered, producing increased smearing in the ring structure of $S(\mathbf{k})$ 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 $F_p=0$ (light line), and for a system with traps of

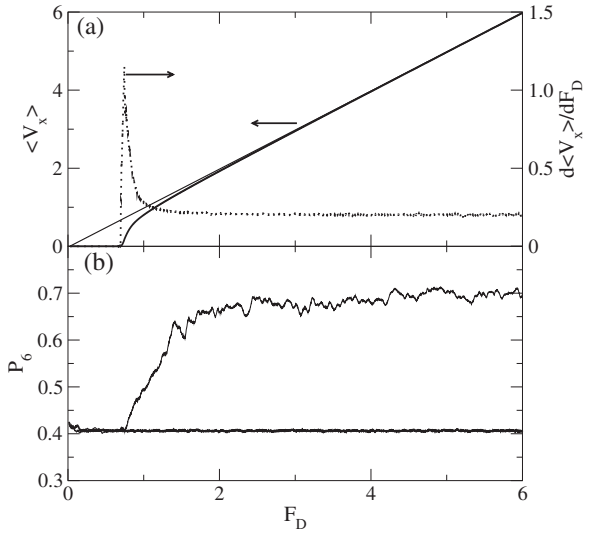

FIG. 2. (a) Average velocity $\langle V_x\rangle$ vs applied drive F_D for the system in Fig. 1. Light upper line, sample with $F_p=0$; dark lower line, sample with $F_p=1.0$; dashed line, $d\langle V_x\rangle/dF_D$ for the $F_p=1.0$ case. (b) P_6 vs F_D for the same system. Upper curve, $F_p=1.0$; lower curve, $F_p=0$.

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 [5,7,8], 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 around the trapped colloids. For $F_D>2.0$, P_6 saturates at $P_6\approx 0.7$. This result indicates that the moving system with quenched disorder is more ordered than the equilibrium system without quenched disorder. To illustrate the nature of this order, in Fig. 1(c) we show the colloid configuration for the system with $F_p=1.0$ at $F_D/F_C=3.0$, and we plot the corresponding $S(\mathbf{k})$ in Fig. 1(d). Here a stripe ordering occurs where the species have partially segregated. Complete segregation is prevented since this would produce a strong charge inhomogeneity in the system. Local triangular order appears within each stripe. 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

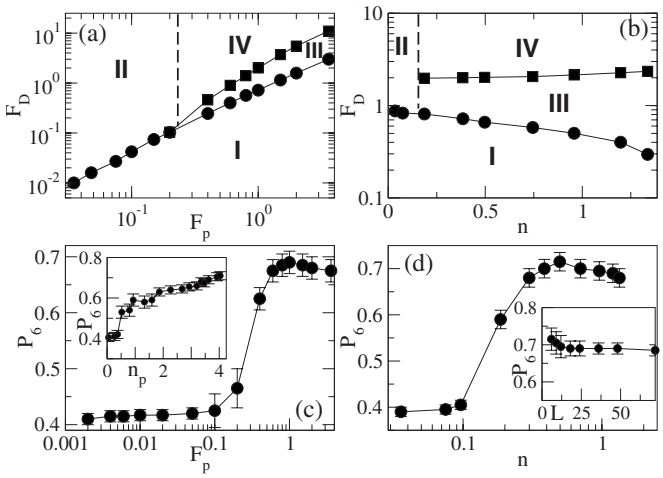

FIG. 3. (a) Different regimes for the system in Fig. 1 at $n=0.385/a_0^2$ and $n_p=4.0/a_0^2$ as a function of F_D and F_p. I, pinned regime; II, moving disordered regime; III, plastic flow regime; IV, moving stripe regime, as in Fig. 1(c). Circles, the depinning threshold F_C. Squares, stripe formation threshold. (b) Different regimes for F_D vs density n at fixed $F_p=1.0$ and $n_p=4.0/a_0^2$. Symbols are the same as in (a). (c) P_6 versus F_p for $n=0.385/a_0^2$ and $n_p=4.0/a_0^2$ at $F_D/F_C=3.0$. Inset: P_6 versus pinning density n_p for fixed $F_p=1.0$ and $n=0.385/a_0^2$ at $F_D/F_C=3.0$. (d) P_6 versus n for fixed $F_p=1.0$ and $n_p=4.0/a_0^2$ at $F_D/F_C=3.0$. Inset: P_6 versus system size L for fixed $F_p=1.0$, $n=0.385/a_0^2$, $n_p=4.0/a_0^2$, and $F_D/F_C=3.0$.

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_p, 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 δF_D and find no change in the location of region II. For $F_p \geqslant 0.4$, a plastic flow state (region III) appears above depinning. Here the colloids are repeatedly trapped and escape from the traps but stripes do not completely form. Finally, for high enough values of F_p and F_D we find region IV, the moving stripe state. In Fig. 3(c) we plot P_6 as a function of F_p for the same system in Fig. 3(a) at fixed $F_D/F_C=3.0$. For $F_p>0.4$, P_6 saturates near 0.7 and the moving stripe state forms. In contrast, for $F_p<0.4$ the moving state has $P_6=0.41$, the same value measured in the pinned state. This indicates that there is a critical disorder strength that is necessary for the formation of the stripe state to occur.

In Fig. 3(b) we plot the locations of the four regimes as a function of F_D versus colloid density n for fixed $F_p=1.0$ and $n_p=4.0/a_0^2$. The depinning threshold F_C marking the end of the pinned region I drops to lower values of F_D as n increases since the colloid-colloid interactions become stronger relative to F_p, making the traps less effective at pinning the colloids. A reordering into the moving stripe state (region IV) occurs only for $n \geqslant 0.2/a_0^2$; for smaller values of n, we find the moving disordered region II at high drives. This is confirmed by Fig. 3(d), which shows P_6 versus n for the same system in Fig. 3(b) at fixed $F_D/F_C=3.0$. For $n<0.2/a_0^2$ in the moving region, $P_6 \sim 0.4$. Here the system does not reorder since at low densities the colloids are far enough apart that they interact only weakly and remain in a disordered state. The pinning density n_p also plays a role in determining whether the moving stripe state can form. In the inset of Fig. 3(c) we plot P_6 versus n_p for a system with fixed $F_p=1.0$ and $n=0.385/a_0^2$ at $F_D/F_C=3.0$. For $n_p<0.5/a_0^2$, P_6 remains low, indicating that the system does not reorder into the stripe state. This result shows that a critical amount of quenched disorder, as well as a critical strength of disorder, is necessary for the moving system to form the stripe state. To show that there are no finite size effects for the appearance of the four regions, in the inset of Fig. 3(d) we plot P_6 vs system size L at $F_D/F_C=3.0$ in the moving stripe state. There is a slight increase in P_6 for the smallest values of L since the small systems form fewer stripes, resulting in a lower number of topological defects at the interfaces between any two stripes. We find that P_6 saturates for $L>20$, well below the size studied throughout this work.

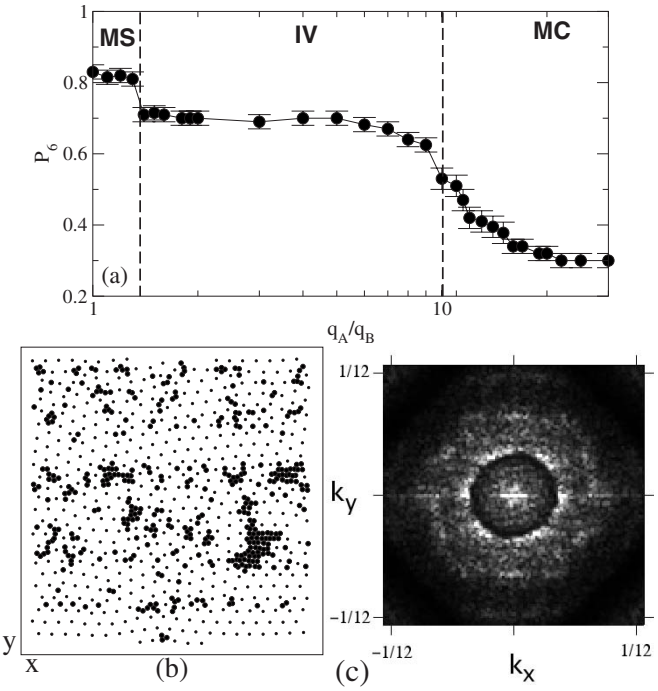

FIG. 4. (a) P_6 versus q_A/q_B for $F_p=1.0$, $n=0.385/a_0^2$, $n_p=4.0/a_0^2$, and $F_D/F_C=3.0$. MS, moving smectic region; IV, moving stripe (region IV); MC, moving clump region. (b) Real space colloid configuration for the moving clump state at $q_A/q_B=11$. Small circles, species A; large circles, species B. (c) Corresponding structure factor $S(\mathbf{k})$.

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 [3]. 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 comoving reference frame, this state resembles a system of bidisperse colloids moving in opposite directions, where a laning instability has been shown to occur [11]. In Ref. [11], the two species were driven in opposite directions with no quenched disorder; here, the disparity in velocity between the two species is induced entirely by the quenched disorder. If the quenched disorder is weak, the colloid configuration moves elastically and no velocity difference between the two species occurs, so that no stripes can form. We have verified that the average velocity distribution for the two different species (not shown) is different in region III but the same in region II. The stripe phases show less ordering than would occur in a system with only a single species since topological defects form at the boundaries between the phases.

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 [5,7,8]. 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. 4(a) where we plot P_6 versus q_A/q_B at $F_D/F_C=3$. In the moving smectic state, $P_6\approx 0.82$, in the moving stripe state $P_6\approx 0.7$, and in the moving clump state P_6 is sharply reduced. The real space configuration of the moving clump state is illustrated in Fig. 4(b) and the corresponding structure factor $S(\mathbf{k})$ in Fig. 4(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 interclump 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 coexisting single and multiple electron bubble states, and superconductors with mixtures of Abrikosov and Josephson vortices.

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[1] M. Seul and D. Andelman, Science **267**, 476 (1995).
[2] G. Malescio and G. Pellicane, Nat. Mater. **2**, 97 (2003).
[3] N. Hoffmann, F. Ebert, C. N. Likos, H. Lowen, and G. Maret, Phys. Rev. Lett. **97**, 078301 (2006).
[4] L. Balents, M. C. Marchetti, and L. Radzihovsky, Phys. Rev. Lett. **78**, 751 (1997); P. Le Doussal and T. Giamarchi, Phys. Rev. B **57**, 11356 (1998).
[5] A. E. Koshelev and V. M. Vinokur, Phys. Rev. Lett. **73**, 3580 (1994); K. Moon, R. T. Scalettar, and G. T. Zimányi, *ibid.* **77**, 2778 (1996); C. J. Olson, C. Reichhardt, and F. Nori, *ibid.* **81**, 3757 (1998); A. B. Kolton, D. Domínguez, and N. Grønbech-Jensen, *ibid.* **83**, 3061 (1999).
[6] F. Pardo *et al.*, Nature (London) **396**, 348 (1998).
[7] C. Reichhardt, C. J. Olson, N. Grønbech-Jensen, and F. Nori, Phys. Rev. Lett. **86**, 4354 (2001).
[8] J. Chen, Y. Cao, and Z. Jiao, Phys. Rev. E **69**, 041403 (2004).
[9] M. F. Hsu, E. R. Dufresne, and D. A. Weitz, Langmuir **21**, 4881 (2005).
[10] N. Garbow *et al.*, J. Phys.: Condens. Matter **16**, 3835 (2004); J. Kim *et al.*, Langmuir **21**, 10941 (2005); F. Strubbe, F. Beunis, and K. Neyts, J. Colloid Interface Sci. **301**, 302 (2006).
[11] J. Dzubiella, G. P. Hoffmann, and H. Löwen, Phys. Rev. E **65**, 021402 (2002); J. Chakrabarti, J. Dzubiella, and H. Löwen, *ibid.* **70**, 012401 (2004).