Structure and Dynamics of a Phase-Separating Active Colloidal Fluid

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We examine a minimal model for an active colloidal fluid in the form of self-propelled Brownian hard spheres that interact purely through excluded volume. Despite the absence of an aligning interaction, this system shows the signature behaviors of an active fluid, including anomalous number fluctuations and phase separation behavior. Using simulations and analytic modeling, we quantify the phase diagram and separation kinetics. The dense phase is a unique material that we call an active hexatic, which exhibits the structural signatures of a crystalline solid near the crystal-hexatic transition point, but the rheological and transport properties associated with a viscoelastic fluid.

Active fluids composed of self-propelled units occur in nature on many scales ranging from cytoskeletal filaments and bacterial suspensions to macroscopic entities such as insects, fish and birds [1]. From a physicist’s perspective, these constitute a class of novel materials that exhibit strange and exciting phenomena such as dynamical self regulation [2], clustering [3], anomalous density fluctuations [4], and strange rheological behavior [5–7]. Motivated by these findings, recent experiments have focused on realizing active fluids in nonliving systems, using chemically propelled particles undergoing self-diffusophoresis [8–10], Janus particles undergoing thermophoresis [11, 12], as well as vibrated monolayers of granular particles [13–15].

In this letter we explore a minimal active fluid model: a two-dimensional system of self-propelled smooth spheres interacting by excluded volume alone. Unlike self-propelled rods [16–20], these particles cannot interchange angular momentum and thus lack a mutual alignment mechanism. Recent simulation and experimental studies have shown that this system exhibits giant number fluctuations [21] and athermal phase separation [21, 22] that are characteristic of active fluids [4, 23, 24]. Here we employ extensive Brownian dynamics simulations to characterize the phase diagram of this system and its material properties. We find that the dense phase is a dynamic new form of material that we call an ‘active hexatic’. This material exhibits structural properties consistent with a 2D colloidal crystal near the crystal-hexatic transition point [25, 26], but is characterized by such anomalous features as superdiffusive transport at intermediate timescales and a highly heterogeneous and dynamic stress distribution (see Fig. (1)). We also map the system’s phase diagram over a large region of parameter space, develop an analytic model which captures its essential features, and draw an analogy between this athermal active phase separation and the behavior of equilibrium systems with attractive interactions. The experimental accessibility, tunable phase behavior, and unique material properties of this system make it an attractive starting point for the design of new active materials.

Model and Simulation Method: Our system consists of smooth spheres immersed in a Brownian solvent and confined to a plane. Each particle is self-propelled with a constant force, and interactions between particles result from isotropic hard-core repulsion only. We include no mechanism for explicit alignment or transmission of torques between particles.

The state of the system is represented by the positions and self-propulsion directions \( \{ \mathbf{r}_i, \theta_i \}_{i=1} \) of all particles.
Their evolution is governed by the coupled overdamped Langevin equations:

\[ \dot{r}_i = D\beta [\mathbf{F}_{\text{ex}}(\{r_i\}) + \mathbf{F}_p \mathbf{\nu}_i] + \sqrt{2D\eta_i^T} \]
\[ \dot{\theta}_i = \sqrt{2D_{r} \eta_i^R} \]

Here \( \mathbf{F}_{\text{ex}} \) is an excluded-volume repulsive force given by the WCA potential \( V_{\text{ex}} = 4k_B T \left( \frac{\sigma^12}{r^12} - \frac{\sigma^6}{r^6} \right) + k_B T \) if \( r < \frac{\sigma}{2} \), and zero otherwise [28], with \( \sigma \) the particle diameter. \( \mathbf{F}_p \) is the magnitude of the self-propulsion force, \( \mathbf{\nu}_i = (\cos \theta_i, \sin \theta_i) \), and \( \beta = \frac{1}{k_B T} \). \( D \) and \( D_r \) are translational and rotational diffusion constants, which in the low-Reynolds-number regime are related by \( D_r = \frac{3D}{\tau} \).

The \( \eta \) are Gaussian white noise variables with \( \langle \eta_i(t) \rangle = 0 \) and \( \langle \eta_i(t) \eta_j(t') \rangle = \delta_{ij}\delta(t - t') \).

We non-dimensionalized the equations of motion using \( \sigma \) and \( k_B T \) as basic units of length and energy, and \( \tau = \frac{\sigma^2}{D} \) as the unit of time. Simulations employed the stochastic Runge-Kutta method [29] with maximum timestep \( 2 \times 10^{-5} \tau \). Simulations mapping the phase diagram were run with 15,000 particles until time 100\( \tau \), while systems of 128,000 particles were used to explore kinetics and material properties. The simulation box was square with periodic boundaries, with side length chosen to achieve the desired density. The system is parametrized by two dimensionless values, the packing fraction \( \phi \) and the Péclet number \( \text{Pe} = \frac{v_p \tau}{\sigma} \), with the propulsive velocity \( v_p = D\beta F_p \). In this work, we varied \( \phi \) from near-zero to the close-packing value \( \phi_{cp} = \frac{2}{\sqrt{3}} \), and \( \text{Pe} \) from zero to 150.

**Phase Separation and Large Number Fluctuations:** We first show that our results are consistent with prior simulations [21] and confirm that this system, despite the absence of aligning interactions, shows the signature behaviors of an active fluid. In particular, the active spheres undergo nonequilibrium clustering (Fig. 1) and exhibit giant number fluctuations (Fig. 2b), similar to other model active systems [3, 19, 20, 30].

We next establish that this clustering is indeed athermal phase separation by measuring the density in each phase at different parameter values (Fig. 2a). We identify a critical point near \( (\text{Pe} = 50, \phi = 0.7) \) beyond which the system separates into two phases whose densities are independent of overall system density and are determined by the strength of activity alone. The result resembles the binodal curve of an equilibrium system of mutually attracting particles undergoing phase separation, with Pe playing the role of an attraction strength. The physical mechanism underlying this phenomenon is a density-dependent suppression of the self-propulsion velocity (see Fig. S7 in [27]), leading to a negative correction to the macroscopic diffusion coefficient [21, 24, 31].

**The Phase-Separated Steady State:** To characterize the steady state, we measured the fraction of particles in the dense phase at time 100\( \tau \) (Fig. 3). In contrast with recent work [21] which reported a single critical density, we observe that this cluster fraction is a nontrivial function of the system parameters \( f_c(\text{Pe}, \phi) \). To understand this relationship we develop a minimal model in which this function can be found analytically. Let us assume the steady state contains a macroscopic cluster which we take to be close-packed. Particles in the cluster are stationary in space but their \( \theta_i \) continue to evolve diffusively. We treat the gas as homogeneous and isotropic, and assume that a particle colliding with the cluster surface is immediately absorbed. This model captures the physics of the density-dependent propulsion velocity [21, 24, 31] in a tractable manner (see Fig. S7 in [27]).

Within this model, we can write the rate of absorption of particles of orientation \( \theta \) from the gas phase as \( k_{\text{in}}(\theta) = \frac{1}{\pi \rho_g v_p} \cos \theta \), where \( \rho_g \) is the gas number density. Integrating yields the total incoming flux per unit
Dynamics in the Dense Phase: Within the active hexatic material, self-propulsion forces continuously evolve by rotational diffusion, breaking local force balance and leading to defect formation and migration (see S4 in [27]). A compelling way to view the motion produced by this athermal process is a simulated FRAP experiment [35], in which particles within a contiguous region are tagged, making subsequent mingling of tagged and untagged particles visible (see S3 in [27]). To quantify this behavior, we measured the mean square displacement (MSD) of particles in the cluster interior. As shown in Fig. (1), we observe subdiffusive motion on short timescales, followed by a superdiffusive regime, returning to diffusive motion on long timescales. The exponents of the subdiffusive and superdiffusive motion ($\frac{1}{2}$ and $\frac{3}{2}$, respectively) are well-conserved across a wide range of propulsion strengths.

The observed dynamics within the active hexatic can be viewed in two ways. First, note that an isolated self-propelled particle will exhibit diffusive, ballistic and diffusive behavior on time scales $t < \frac{1}{D_i}$, $\frac{1}{D_i} < t < \frac{1}{D_{out}}$ and $t > \frac{1}{D_{out}}$, respectively (see Fig. S5 in [27]). These dynamical regimes are modified by the active hexatic environment; in particular, the ballistic regime is modulated by “sticking” events as the particle is localized in crystal domains, resulting in the observed Lévy flight like behavior [36, 37]. Second, treating the observed MSD behavior as a window into the material’s rheology [38] enables us to use the relationship between the shear modulus and particle MSD in Laplace space, $G(s) = \frac{k_B T}{\pi \sigma_0^2 \Delta r^2(s)}$, to see that a) at short time scales (high frequency), the effective viscosity
Kinetics of Phase Separation: Despite the athermal origins of phase separation in this system, simulations quenched from a homogeneous state to parameters where clustering occurs move through familiar nucleation, growth, and coarsening stages (Fig. (5)). However, in the coarsening regime we find surprisingly that the mean cluster size scales as $t^{1/2}$, with a corresponding length scale $\xi(t) \sim t^{1/2}$ (Fig. (5) inset, also see S8 in [27]). This differs from the standard 2D coarsening exponents, but matches recent simulation results for the Vicsek model and related active systems [39]. Our results should be viewed as preliminary due to the limited range of our data, but nevertheless this unexpected similarity between the coarsening of point-particles with polar alignment and that of hard spheres with no alignment suggests a deep relationship between these very different types of systems. Future work is needed to uncover the origins of these scaling exponents and their implications for universality in active fluids.

Discussion: A fluid of self-propelled colloidal spheres exhibits the athermal phase separation that is intrinsic to active fluids and is a primary mechanism leading to emergent structures in diverse systems [2, 24]. We have shown that the physics underlying this phase behavior can be understood in terms of microscopic parameters. From a practical perspective, our simulations show that the active hexatic dense phase exhibits a combination of structural and transport properties not achievable in a traditional passive material. Further development of experimental realizations of this system (e.g. Ref. [22]) will advance the development of materials whose phase behavior, rheology, and transport properties can be precisely controlled by activity level.

Acknowledgments: This work was supported by NSF-MRSEC-0820492 (GSR, MFH, AB), as well as NSF-DMR-1149266 and NSF-1066293 and the hospitality of the Aspen Center for Physics (AB). Computational support was provided by the Brandeis HPC.

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FIG. 5. (color online) Examples of phase separation kinetics. Left: A system with $Pe = 100$, $\phi = 0.45$ in which a delayed nucleation event leads quickly to steady-state. For shallowly-quenched systems, the nucleation time can be long enough that artificial seeding is needed to make nucleation computationally accessible. Right: A system with $Pe = 80$, $\phi = 0.6$ where spinodal decomposition leads to a coarsening regime which slowly evolves towards steady-state (see S1 in [27]). Inset shows mean cluster size scaling approximately as $t^{1/2}$, (see S8 in [27]).
[27] See supplemental material for movies and additional figures.