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Activity-Induced Phase Separation and Self-Assembly in Mixtures of Active and Passive Particles

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We investigate the phase behavior and kinetics of a monodisperse mixture of active (i.e., self-propelled) and passive isometric Brownian particles through Brownian dynamics simulations and theory. As in a purely active system, motility of the active component triggers phase separation into a dense and a dilute phase; in the dense phase, we further find active-passive segregation, with “rafts” of passive particles in a “sea” of active particles. We find that phase separation from an initially disordered mixture can occur with as little as 15% of the particles being active. Finally, we show that a system prepared in a suitable fully segregated initial state reproducibly self-assembles an active “corona,” which triggers crystallization of the passive core by initiating a compression wave. Our findings are relevant to the experimental pursuit of directed self-assembly using active particles.

Understanding the collective behavior of systems composed of self-propelled (“active”) constituents is of great importance both from a fundamental physics perspective and for understanding many biological systems, such as bacterial suspensions, fish schools, and bird flocks [1]. One example of such collective behavior is seen in so-called active Brownian particles—self-propelled particles whose propulsion direction relaxes through rotational diffusion—which have been shown to phase separate into a dense and a dilute phase even in the absence of attractive or aligning interactions [2–12]. The driving force behind this phase separation is a positive accumulation feedback triggered by a slow down of particles due to collisions, which can be represented by a propulsion speed $v(\rho)$ that decreases with the local particle density $\rho$ [5,15,16]. The phase behavior of such systems is controlled by the total average particle packing fraction $\phi_0$ and the Péclet number $Pe = 3v_0\sigma_r/\sigma$, which essentially controls the ratio between motility and diffusion, where $v_0$ is the propulsion speed of an isolated particle, $\tau_r$ is its rotational relaxation time, and $\sigma$ is its diameter.

Experimentally, it is very challenging to reach the high packing fractions ($\phi_0 \approx 0.5$) required for phase separation using only active particles [17]. Therefore, the phase-separation behavior of suspensions where the microswimmers are mixed with regular passive colloidal particles is of great practical interest. To date, most studies on active-passive mixtures have focused on the motion of individual passive tracer particles in swimmer suspensions [18–21]. Only a small number of investigations have addressed the behavior of dense mixtures of active and passive agents; these have found interesting novel phenomena including active-passive segregation between rodlike particles [22], crystallization of hard-sphere glasses [23], emergence of flocking and turbulence [24], and a facilitation of attraction-induced phase separation [25].

In this Letter, we provide a comprehensive numerical study of the complex phase behavior of mixtures of monodisperse isometric repulsive active Brownian particles and their passive counterparts in two dimensions. First, we show that a mixture prepared in a uniform phase is unstable to activity-induced phase separation, even when the fraction of active particles $x_A$ is modest. We also find that the clusters formed are not homogeneous, but are predominantly active at the periphery and passive in their interior (see Fig. 1). Compared to the dynamics of the purely active case, the dynamics of active-passive mixtures shows enhanced fluctuations, with frequent fission and fusion of clusters. Most strikingly, we show that, by carefully choosing our initial condition, the mixture self-assembles into a disk-shaped core of passive particles surrounded by an active shell; the active particles further stimulate a compression wave that induces crystallization of the passive component.

In our two-dimensional Brownian dynamics simulations, all particles (active as well as passive) are treated as monodisperse repulsive disks interacting through a truncated and shifted Lennard-Jones potential $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] + \epsilon$ with an upper cutoff at $r = 2^{1/6}\sigma$, beyond which $U = 0$. Here, $\epsilon$ determines the interaction strength as well as the Lennard-Jones time scale $\tau_{LJ} = \sigma^2/(\epsilon\beta\sigma^2)$; $r$ is the center-to-center distance between two particles, and $\beta = 1/(k_B T)$ is the inverse thermal energy. We studied this model by solving the overdamped Langevin equations (thus neglecting hydrodynamic interactions between particles)

$$\partial_t r_i = \beta D_1 (F_i + F_A p_i) + \sqrt{2D_1 \Lambda_r},$$

$$\partial_t \theta_i = \sqrt{2D_1 \Lambda_r},$$

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where \( \mathbf{r}_i(t) \) is the position and \( \theta_i(t) \) is the orientation of the \( i \)th particle at time \( t \) [26], in a box with periodic boundary conditions. \( \mathbf{F}_i \) is the total conservative force on particle \( i \), which results from \( U(r) \), \( F_A \) is the constant magnitude of the self-propulsion force \( F_{Ap} \) on particle \( i \) (\( F_A = 24\epsilon/\sigma \) for active and \( F_A = 0 \) for passive particles, see Ref. [7] for details), and \( \mathbf{p}_i = (\cos \theta_i, \sin \theta_i) \) is its direction. Furthermore, \( D_t \) and \( D_r = 1/\tau_r = 3D_t/\sigma^2 \) denote the translational and rotational diffusion coefficients of the particles, respectively; \( \Lambda_t(t) \) and \( \Lambda_r(t) \) are unit-variance Gaussian white-noise terms [27].

Figure 1 (see also movies in the Supplemental Material [28]) shows the late-time local area fractions \( \phi_A \) and \( \phi_P \) of active (\( \phi_A \)) and passive (\( \phi_P \)) particles in initially homogeneous mixtures with \( N \approx 760000 \) particles as well as the corresponding probability distributions \( P(\phi_A, \phi_P) \) for active-particle fractions \( x_A \in \{0.25, 0.5, 0.75\} \). For all \( x_A \) the mixture phase separates into a dense “liquid” phase and a dilute “gas” phase. The probability plots also suggest that (i) the area fraction \( \phi_{A,g} \) of active particles in the gas phase remains essentially constant as \( x_A \) is varied (unlike the corresponding passive area fraction \( \phi_{P,g} \) which varies markedly), and (ii) the total area fraction \( \phi_{A,l} + \phi_{P,l} \) in the liquid phase remains constant and close to unity as indicated by the diagonal straight lines in \( P(\phi_A, \phi_P) \).

From the snapshots in Fig. 1 it is also apparent that the distribution of active and passive particles within the dense phase is inhomogeneous, with the active particles being significantly enriched at the boundaries of the dense domains. The interfacial layer remains essentially purely active for all \( x_A \). Since the flux balance between this layer and the gas determines \( \phi_{A,g} \), this corroborates our finding that \( \phi_{A,g} \) remains constant as \( x_A \) is varied. However, even in the interior of the dense phase, there is clearly an inhomogeneous distribution of the two species, with the passive particles agglomerating into domains. As can be seen from Fig. S1 and movies in the Supplemental Material [28], the domain size of these “passive rafts” inside the “active sea” initially increases with time and eventually reaches a (noisy) steady-state plateau value of approximately 20\( \sigma \). Such spontaneous segregation between otherwise identical active and passive particles has only been observed before in the context of rodlike particles [22]; our results suggest that it is the result of activity alone and occurs also for mixtures of isometric particles (see further information in the Supplemental Material [28]). This phenomenon may be seen as a manifestation, at a larger density and with equal-sized particles, of the effective attraction observed between passive colloids [29] and between hard walls [30,31] in a bacterial bath.

We also note that the overall dynamics of active-passive mixtures is very different from that of the corresponding purely active systems [5] (see movies in the Supplemental Material [28]). Most importantly, the dynamics of phase-separating mixtures is much more violent, with clusters constantly moving, fissioning, and merging.

Figure 2 shows phase diagrams in the \( \text{Pe}-x_A \) and \( \text{Pe}-\phi_0 \) planes, where \( \phi_0 \) is the total particle area fraction and \( 0 \leq x_A \leq 1 \) is the fraction of the particles that are active. Interestingly, spontaneous phase separation occurs with \( x_A \) values as small as 0.15, or equivalently with \( \phi_A = 0.09 \) [see Fig. 2(a)]. Such area fractions should be easily achievable in experiments, although the corresponding

**FIG. 1** (color online). Left and center columns: Density plots of the local area fractions of active (\( \phi_A \)) and passive (\( \phi_P \)) particles for \( \text{Pe} = 300 \), \( \phi_0 = 0.6 \), and three different values of the fraction \( x_A \) of active particles, obtained at late times (\( t = 5000\tau_{LJ} \)) after a quench from a random initial configuration. The box size is \( 1000\sigma \times 1000\sigma \), corresponding to \( N \approx 760000 \) particles. Right column: Two-dimensional probability distribution \( P(\phi_A, \phi_P) \) obtained by averaging the corresponding simulations over the time window \( 4500\tau_{LJ} \leq t \leq 5000\tau_{LJ} \).

**FIG. 2.** (a) Phase diagram in the \( \text{Pe}-x_A \) plane for \( \phi_0 = 0.6 \). (b) Phase diagram in the \( \text{Pe}-\phi_0 \) plane for \( x_A = 0.5 \). Filled symbols denote phase-separated systems, as determined by visual inspection, and open symbols denote homogeneous systems. All results were obtained by a quench from random initial configurations, using systems of size \( 150\sigma \times 150\sigma \), corresponding to \( N \approx 150000 \) particles for \( \phi_0 = 0.6 \). The dashed lines indicate phase boundaries predicted by Eq. (3) with \( \kappa = 4.05 \).
Pécel number required for phase separation is relatively high (≈500 according to our simulations, as opposed to ≈60 for a purely active system [5]).

Figure 2(a) also shows that the phase boundary between the uniform and the phase-separated region closely follows a fit to the function \( x_A \sim 1/\text{Pe} \) (dashed line). To understand this behavior, we start from the observations of Fig. 1 that \( \phi_{A,g} \) is approximately independent of \( x_A \) and that the total density of the dense phase is close to the close-packing density \( \phi_0 = \pi/(2\sqrt{3}) \approx 0.907 \) (this is also true for the corresponding purely active system [3]). Following the kinetic model developed by Redner et al. in Ref. [3], we equate the incoming and outgoing fluxes \( k_{in} \) and \( k_{out} \) of active particles at the interface of a dense cluster. The use of \( k_{in} = 4\phi_{A,g}v_0/(\pi^2\sigma^2) \) and \( k_{out} = k\rho f_{df}/\sigma \), where \( k \) is a dimensionless parameter introduced to take into account the fact that particles leave the dense phase in bursts [3], yields \( \phi_{A,g} = 3\pi^2k/(4\text{Pe}) \). In the purely active case, the binodal is given by the relationship \( \phi_0 = \phi_{A,g} \). In the case of active-passive mixtures, the condition is instead \( \phi_0 x_A = \phi_{A,g} \), leading to the following expression for the binodal:

\[
\phi_0 x_A = \frac{3\pi^2 k}{4\text{Pe}}. \tag{3}
\]

The dashed lines in Fig. 2 show Eq. (3) with \( k \approx 4.05 \), close to the value found for \( x_A = 1 \) [3]. For the case of constant \( \phi_0 \) and varying \( x_A \) [see Fig. 2(a)], the agreement is excellent, showing that the basic kinetic assumptions made above (and originally proposed to describe a purely active system) provide a workable model for active-passive mixtures with \( x_A \) as low as 0.15 and for a significantly larger range of Pécelt numbers than studied previously [3]. For the case of constant \( x_A = 0.5 \) and varying \( \phi_0 \), the agreement between simulation results and Eq. (3) is good down to \( \phi_0 \approx 0.45 \), below which point the simulated systems stop phase separating altogether [see Fig. 2(b)]. This discrepancy arises because the approximations inherent in Eq. (3) are known to be inappropriate as \( \text{Pe} \rightarrow \infty \), where phase separation does not occur if the decrease of \( v(\rho) \) with \( \rho \) is not steep enough [5,8,15,16]. This also explains why in practice there exists a lower value of \( x_A \) required for spontaneous phase separation, while in principle Eq. (3) predicts phase separation to occur even for \( x_A \rightarrow 0 \) as \( \text{Pe} \rightarrow \infty \).

To describe this lower “spinodal line” it is therefore necessary to extend the continuum theories developed in Refs. [6,16] towards active-passive mixtures. While we postpone the detailed treatment of this problem to a future study [32], we show in the Supplemental Material [28] that the simple assumption of a linear dependence of the propulsion speed \( v \) on each of the area fractions \( \phi_A \) and \( \phi_P \), i.e., \( v = v_0(1 - a\phi_A - b\phi_P) \) with constant parameters \( a \) and \( b \), together with the assumption that \( \phi_P \) remains uniform during the initial spinodal instability, leads to the spinodal condition \( \phi_0 > 1/\{2a\phi_A + b(1 - x_A)\} \) [33]. Simulations in the one-phase region of the phase diagram confirm the linear dependence of \( v \) on both area fractions and yield the approximate values \( a = 1.08 \) and \( b = 1.21 \) (see the Supplemental Material [28]). For \( x_A = 0.5 \), this gives a spinodal density \( \phi_0 = 0.59 \), in reasonable agreement with the value \( \phi_0 = 0.45-0.50 \) observed in Fig. 2(b); the slight mismatch can be attributed to the fact that spontaneous phase separation will occur slightly outside the spinodal due to the high noise level.

FIG. 3 (color online). Density plots showing the local area fractions of active (\( \phi_A \)) and passive (\( \phi_P \)) particles at different times after a quench, starting with a fully segregated initial configuration. The system parameters are as in Fig. 1 with \( x_A = 0.5 \).
component on the passive one can be lumped into a  

stand this scaling, we assume that the effect of the active  

initial position of the active-passive interface. To under-

velocity  

lead to the propagation of a compression wave, whose  

functions and hexagonal order parameters shown in Fig.4(b)  

Supplemental Material[28]). Finally, the pair-distribution  

with what we observe in the simulations (see movies in the  

Supplemental Material[28]).

We now note that the total mass \( M \) of the slab segment is  

proportional to the total area swept by the wave front,  

\[ M(t) = m \rho_s L [x(t) - x_0], \]  

where \( m \) is the mass of a single particle. Inserting this  

expression into Eq. (4) yields the differential equation  

\[ \dot{x}(t) = \frac{P_a \rho_1}{\rho_1 - \rho_2} \frac{F_a}{M(t) \gamma}, \]  

(4)  

where \( F_a = LP_a \) is the active force acting on a slab  

segment of length \( L \), \( M(t) \) is the total mass of the particles  
carried along by this segment of the wave front, \( \gamma \) is the  
damping rate (in units of inverse time) of the implicit  
solvent, and \( \rho_1 \) and \( \rho_2 \) denote the number densities of the  
dense and dilute phases, respectively. The prefactor  

involving the densities takes into account the relative velocities of  
the front and the back of the wave and can be derived  
through a straightforward mass conservation argument (see  
the Supplemental Material[28]).

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proportional to the total area swept by the wave front,  
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where \( m \) is the mass of a single particle. Inserting this  
expression into Eq. (4) yields the differential equation  
\[ \dot{x}(t) = \frac{P_a \rho_1}{m \gamma \rho_2 (\rho_1 - \rho_2)} (x - x_0), \]  
(5)  

with the solution  
\[ x(t) = x_0 + \left( \frac{2 P_a \rho_1}{m \gamma \rho_2 (\rho_1 - \rho_2)} \right)^{1/2} t^{1/2}. \]  
(6)  

The fitting parameter \( P_a \) for the solid line in Fig. 4(a)  
corresponds to \( P_a \approx 120 \varepsilon / \sigma^2 \). With the single-particle  
propulsion force \( F_a = 24 \varepsilon / \sigma \), this means that the pressure  
during the compression is comparable to about five layers of  
active particles compressing the slab, in broad agreement  
with what we observe in the simulations (see movies in the  
Supplemental Material[28]). Finally, the pair-distribution  
functions and hexagonal order parameters shown in Fig. 4(b)  
clearly show that the final state of the two-dimensional  
passive suspension is a crystalline one. These results suggest  
that judicious mixing with active particles can be used as a  
tool to control self-assembly of passive colloids, at least in  
two dimensions.

In this Letter, we have presented a systematic study of  
mixtures of active and passive Brownian particles with  
varying composition and density. Apart from being of  
fundamental interest from a nonequilibrium physics  
perspective, understanding such mixtures is a prerequisite for  
experiments intended to create novel materials through active  
phase separation and self-assembly. We have shown that  
activity-induced phase separation is indeed possible for a  
wide range of system parameters and for active-to-passive  
ratios as small as 1:6, as long as the Péclet number is large  
enough. This is encouraging from an experimental viewpoint  
given the difficulties associated with the manufacturing and  
fuel supply of large quantities of active colloids[17]. We  
have further shown that the choice of appropriate initial  
conditions, where the two species are segregated, leads to a
remarkable directed assembly process, whereby the active particles drive a compression wave through the passive phase, which leads to the creation of a passive colloidal crystal. The active particles then coalesce and form a highly fluctuating wetting layer around the crystal. These results call for a future experimental exploration of active-passive mixtures and open up new potential routes to directed assembly using active particles.

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[26] Further technical details about the simulations can be found in Appendix B of Ref. [7].
[27] We use the same noise terms for the active particles as for the passive ones, which is a common approximation for active-particle simulations [3,5].
[32] R. Wittkowski et al. (to be published).
[33] Note that for $\lambda = 1$ this condition reduces to the one for a purely active system with propulsion speed $v(\phi_A) = v_0(1 - \epsilon \phi_A)$ obtained in Ref. [16].
[34] Note that this active pressure is distinctly different from the “thermodynamic” active pressure studied in Ref. [11]. It is, however, closely related to the mechanical pressures studied in the context of active particles in Refs. [35–37].