

Dynamic Clustering in Active Colloidal Suspensions with Chemical Signaling

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In this Letter, we explore experimentally the phase behavior of a dense active suspension of self-propelled colloids. In addition to a solidlike and gaslike phase observed for high and low densities, a novel cluster phase is reported at intermediate densities. This takes the form of a stationary assembly of dense aggregates—resulting from a permanent dynamical merging and separation of active colloids—whose average size grows with activity as a linear function of the self-propelling velocity. While different possible scenarios can be considered to account for these observations—such as a generic velocity weakening instability recently put forward—we show that the experimental results are reproduced mathematically by a chemotactic aggregation mechanism, originally introduced to account for bacterial aggregation and accounting here for diffusiophoretic chemical interaction between colloidal swimmers.

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Active systems refer generically to collections of particles that consume energy at the individual scale in order to provide self-propelled motion. In assembly, these systems usually exhibit a wide variety of collective behaviors, structures, and patterns, which depart strongly from the classical equilibrium expectations [1–10]. In particular, there are many observations in nature of clusterlike phases in very different systems: flocks, schools, swarms of fishes, insects, or bacteria [11–16]. However, this apparent analogy, occurring over a broad range of scales, hides many different mechanisms in the propulsion and interactions. To disentangle the universal from the specific behaviors of those complex phases, a systematic experimental exploration of artificial active particle systems at high density is needed. Some experiments have been carried out on self-propelled walkers at high densities [17], but to our knowledge, active particles at the colloidal scale—involving natural Brownian noise and solvent-induced interactions—were only studied at low densities [18–21].

In this Letter, we explore experimentally the behavior of a two-dimensional dense active suspension of artificial self-propelled colloids (SPCs). We characterize the phase behavior of this active system under an external (gravity) field and observe the natural emergence of dynamic clustering at intermediate densities. The average size of the clusters grows with activity, in direct proportionality to the propelling velocity of an individual SPC. Several scenarios are discussed in order to rationalize these results, suggesting in particular a possible self-aggregation mechanism, in analogy to behavior of chemotactic systems.

Experimental description.—The active particles are homemade spherical gold colloids of radius $a \approx 1 \pm 0.1 \mu\text{m}$ half covered with platinum [22]. In the presence of hydrogen peroxide, the particles self-propel consuming H_2O_2 under a self-phoretic motion (a combination of diffusiophoresis and self-electrophoresis [20,23]). One key aspect here is

that the system does self-propel—with a velocity V around $3 \mu\text{m} \cdot \text{s}^{-1}$ —even at very low H_2O_2 concentrations, from 0.005 to 0.1%. This avoids the formation of O_2 bubbles even at high particle densities. For time scales longer than the rotational Brownian time of the particle, τ_r , the SPC performs a random walk with an effective diffusion coefficient $D_\rho \sim V^2 \tau_r / 6 \sim 15 \mu\text{m}^2 \cdot \text{s}^{-1}$ [20].

We confine those particles using a reduced gravity field: we let the colloids settle in a cell slightly tilted with an angle $\theta \sim 2 \times 10^{-3}$ rad. As the colloids are heavy (mass density $\sim 19 \text{g} \cdot \text{cm}^{-3}$), they quickly settle at the bottom of the cell forming a dense *two-dimensional* layer. We observe the system with an inverted optical microscope and a Hamamatsu Orca-ER camera. A MATLAB routine allows particle detection and tracking.

Sedimentation profile and phase behavior.—As observed in Fig. 1 (bottom left), nonactive SPCs in water exhibit, as expected, a solid phase at the bottom, above which a very low density gas phase can be distinguished. As soon as we introduce H_2O_2 , the particles become active and self-propel, leading after a few minutes of relaxation time to a strong change in the sedimentation profile [Fig. 1 (bottom right)]. A solid phase remains, but the top gas phase spreads to much higher heights [24]. In addition to these expected phases, particles tend to cluster for intermediate densities, a behavior that will be explored below.

The difference between passive and active particles can also be clearly seen on the surface density profile ρ of the colloids; see Fig. 1 top (right). These density profiles are obtained after a binarization of the 500 movie frames (taken at 1 fps) and averaged over the horizontal direction. The experimental profiles exhibit an enlargement of the “intermediate zone” between the solid and gas phases when the particles are made active. We finally note that the situation is *reversible*, which means that when we

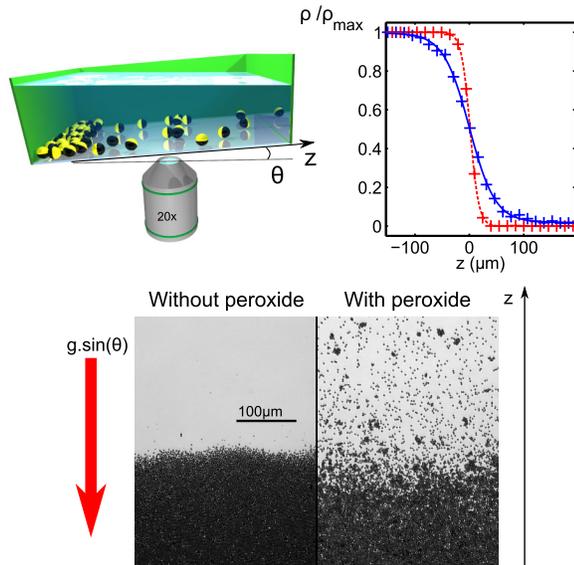


FIG. 1 (color online). Top: (left) Schematic representation of the experimental system and (right) normalized surface density profiles ρ/ρ_{\max} as a function of the position z along the cell—with (blue line) and without (red dotted line) H_2O_2 . Solid lines are fits with a tangent hyperbolic function. Bottom: picture of the 2D sedimented particles: left, passive colloids in water; right, active colloids (SPCs) in a solution of 0.1% of H_2O_2 . The effective gravity, $g \sin\theta \approx 2 \times 10^{-2} \text{ m} \cdot \text{s}^{-2}$, is indicated by the arrow.

replace the H_2O_2 with water, this intermediate zone disappears to recover the nonactive sedimentation profile.

We then measure the structure factors of the system for various zones in the sedimentation profile; see Fig. 2. The 2D structure factor is defined as $S(k) = \frac{1}{N} \langle \rho_k \rho_{-k} \rangle$, where N is the number of particles in the region of interest, k is

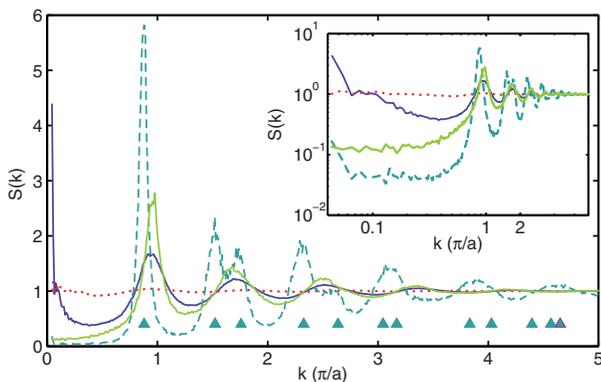


FIG. 2 (color online). Structure factors $S(k)$: Nonactive SPCs in water in the solid phase are indicated by the dashed line. The bottom arrows point to the first vectors in the reciprocal space for a triangular lattice. Active SPCs (in $\text{H}_2\text{O}_2 = 0.1\%$) for the solid phase (light green line), the intermediate zone (dark blue line), and the gas phase (red dotted line). Inset: same plots in logarithmic scales, zooming in on the small k behavior.

the in-plane wave vector, and ρ_k is the Fourier transform of the instantaneous number density of SPCs. For the SPC without activity—in water—we report $S(k)$ in the bottom solid phase only (dashed line). It exhibits a strong ordering characteristic of a solid phase but is, however, not perfectly crystalline due to the size polydispersity of the colloids. For the active SPCs, we have measured $S(k)$ in three zones arbitrarily defined as a solid phase for $\rho/\rho_{\max} > 0.8$, a gas phase for $\rho/\rho_{\max} < 0.05$ [25], and an “intermediate zone” in between [26]. As seen in Fig. 2, while a high ordering remains in the solid phase of SPCs, the amplitude of the first peak decreases strongly, and activity is observed to destabilize the crystalline phase, in line with recent simulations [10]. The intermediate “cluster” phase is particularly interesting: it exhibits a strong ordering, but also shows a strong increase of the structure factors when $k \rightarrow 0$. This points to a strong compressibility of the system, reminding us of a critical behavior and large fluctuations. Altogether, the introduction of H_2O_2 modifies the interactions between colloids and the experimental observations of (i) the formation of clusters, (ii) a small ordering in the low density phase (up to 3 peaks can be identified), and (iii) a shift in the position of the first peak of $S(k)$ in the solid phase towards higher density, all suggesting an apparent kinetic attraction between SPCs. This attraction can be interpreted in terms of *diffusiophoresis*, which is the motion of a particle induced by gradients of solutes or chemicals [27,28]. Here, diffusiophoresis would be induced by the chemical gradients associated with the chemical reaction powering the SPC, in particular, H_2O_2 and O_2 [23].

Emergence of dynamic clustering.—A key observation in the snapshots (see Fig. 3 and movies [29]) is the ap

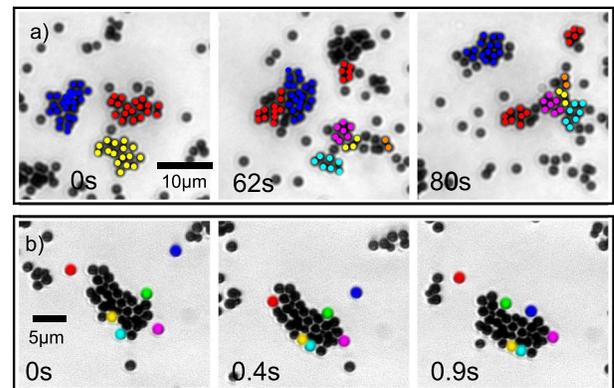


FIG. 3 (color online). Dynamic clusters of SPCs observed in a horizontal geometry for $\phi \approx 5\%$ and $C_{\text{H}_2\text{O}_2} = 0.1\%$. The images are obtained in the transmission mode with a $63\times$ objective. For the chronophotography of the clusters, see the Supplemental Material [29] for movies. (a) Illustration of the dynamics between clusters. (b) Dynamics inside a cluster. Marked particles show exchanges between clusters, a dynamic exchange of SPCs between the gas phase and the cluster, and internal reorganization of the cluster.

pearance of clustering for active SPCs in the regime of intermediate densities, corresponding typically to a surface fraction ϕ in the range of 3%–50%. In order to better characterize this “cluster phase,” we use a nontilted cell and start with a homogeneous suspension of particles in water, with surface fraction $\sim 5\%$. Upon addition of H_2O_2 , we observe after a few seconds the appearance of clusters coexisting with a gas phase. These clusters are not immobile but exhibit a slow, randomlike dynamics, with typical speeds of $0.1 \mu\text{m} \cdot \text{s}^{-1}$ compared to $V \sim 3 \mu\text{m} \cdot \text{s}^{-1}$, the typical velocity of the SPC. Another striking point is that the clusters are dynamic, with particles going in and out over time, and clusters *permanently* merging and dissociating, as highlighted in Fig. 3 and corresponding movies [29].

More quantitatively, we measure the average size of clusters versus the activity of the system, i.e., the amount of fuel added. At each H_2O_2 concentration, we measure the activity by tracking the individual SPC in the gas phase and extracting the mean velocity V [30]. We count the number of colloids forming each cluster in the stationary state. A cluster is defined as an assembly of at least three colloids that remains connected for at least one second. For each H_2O_2 concentration, we count more than 150 different clusters. As shown in Fig. 4, we measure that the average cluster size N^* is a linear increasing function of the mean velocity V of the individual SPC in the gas phase. This is a counterintuitive result, as it shows that clustering is enhanced for the larger effective temperature of SPCs (as $T_{\text{eff}} \sim V^2$ [20]).

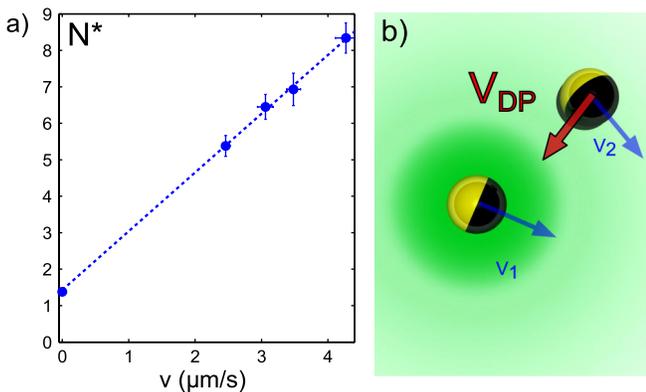


FIG. 4 (color online). (a) Mean cluster size N^* vs the average velocity of the particles in the gas phase, measured in the experiments (with SPC surface fraction 5%). The point at $V = 0$ is measured for zero activity. The dashed line is a linear fit, $N(V) = 1.6V + 1.4$ (V in $\mu\text{m} \cdot \text{s}^{-1}$). (b) Schematic representation of the aggregation mechanism (top view): two SPCs, moving with phoretic velocity \vec{V}_1 and \vec{V}_2 , create a monopole of concentration c (for instance, H_2O_2 , O_2) around them. This gradient induces a diffusiphoretic motion of the SPCs toward each other with a drift velocity $V_{DP} \propto \nabla c$. For the sake of simplicity, only the gradient of chemical for the bottom SPC is represented.

Tentative scenarios for the dynamic clustering.—The theoretical literature offers various predictions for clustering in active matter, which involve a variety of ingredients and mechanisms [1–3,5,6]. We thus try to discriminate between various possible scenarios, allowing us to rationalize the emergence of clustering in our active SPC, especially for surface fraction as low as a few percent. It is, accordingly, important to first recall some facts about our SPCs: (i) they are janus spherical particles, which lead only to a negligible anisotropy in the steric interaction between particles, and would *a priori* discard modelization of the observed behavior in terms of couplings between density and short-range orientational ordering; (ii) self-propulsion takes its origin in our case in the self-phoretic motion of the colloids, leading to a perturbation of the hydrodynamic velocity field around a SPC decaying as $\sim 1/r^3$ [27], in contrast to pusher-puller systems which behave as a force dipole with a longer $1/r^2$ decay. As for phoretic motion in general, hydrodynamic interactions are accordingly not expected to play a dominant role in our system. In contrast, chemical interactions are susceptible to act as a novel ingredient for our SPCs, since, due to the chemical origin of the motion, the consumption of fuel and associated production of “waste” species lead to long range chemical gradient ∇c around SPCs [23]—with concentration fields decaying here like $1/r$ [31]. Such gradients are expected to induce diffusiphoretic interactions between particles, taking the form of a relative drift induced by chemical concentration gradients [27], as we discuss below.

Among the exhaustive zoology of aggregation behavior discussed in theoretical literature, many of the interpretations are difficult to reconcile with our observations:

Flocking behavior, i.e., a group of orientationally ordered particles moving in the same direction [1,5]: in our case, SPC clusters do not exhibit directed motion. This discards the interpretation in terms of a nematic ordering of the SPCs, in line with the expected weak anisotropy of their steric interaction.

Adhesive clustering: one may not *a priori* discard a mechanism based on a simple adhesion between particles, by analogy to the structure of simple adhesive colloids [32]. However, the observed SPC clusters are reversible and strongly kinetic by nature. This scenario is also difficult to reconcile with the observation that the size of the SPC clusters increases with the activity of the particles.

Surface-generated attraction between particles induced by slip flows: such a scenario, previously described for thermophoresis [33,34], was shown to induce two-dimensional crystallization of colloids at the surfaces. This is, however, quite in disagreement with the present observation of kinetically alive clusters, reaching quickly a steady state, stable over hours.

While those scenarios do not provide a convincing framework for our observations, we highlight two alternative views which account better for our experimental results.

First, in a recent numerical study, Fily *et al.* [35] have shown that self-propelled particles with no alignment mechanism can exhibit an intrinsic clustering instability, though at much higher density, typically $\geq 40\%$ in volume fraction. They interpret their results in terms of a generic instability, taking its origin in the density-weakening dependence of the particle velocities, in line with predictions obtained in a 1D model of run and tumble [7]. Many features of our experiments are reproduced in their simulations. However, at this stage, neither a prediction for the present linear dependence $N^*(V) \sim V$ nor an explanation for the appearance of cluster at very low volume fraction is proposed.

A second possibility can be also drawn, which is directly related to the chemical interactions mentioned above. The role of chemical sensing has already been studied in the context of patterns and clusters formation of bacteria [13,14,36,37]. In a pioneering work, Keller and Segel (KS) rationalized such behaviors on the basis of a mean-field description, taking into account the diffusion of bacteria, a drift induced by chemical sensing, and the production and diffusion of a chemoattractant [36,37]; its extension to thermotactic SPCs was proposed recently [38]. In our context, a direct mathematical analogy may be drawn. The chemotactic drift is played here by diffusio-phoresis, the motion of particles induced by solute gradients [27,28]. Indeed, due to the propulsion mechanism, each SPC creates a solute concentration gradient ∇c (H_2O_2 and O_2) around it and induces a corresponding diffusio-phoretic drift of the other SPCs: $V_{DP} = \mu \nabla c$ with μ the diffusio-phoretic mobility [23]. Such a mechanism, sketched in Fig. 4, allows us to rationalize the various observations of dynamic attraction quoted above for active SPCs under self-generated chemical gradients. The spatio-temporal dynamics of the active particle population can then be described at a mean-field level in terms of a (here, 2D) particle density ρ and a global chemoattractant field c , using a KS description:

$$\begin{aligned} \partial_t \rho &= D_\rho \nabla^2 \rho - \nabla(\rho V_{DP}) = D_\rho \nabla^2 \rho - \nabla(\mu \rho \nabla c), \\ \partial_t c &= D_c \nabla^2 c + \alpha \rho, \end{aligned} \quad (1)$$

with D_ρ the effective diffusion coefficient of the SPC, D_c the ‘‘chemoattractant’’ diffusion coefficient, and α the chemical rate of the powering chemical reaction occurring at the surface of each colloid.

An interesting feature of the KS equations is that they exhibit singular solutions, leading to a ‘‘chemotactic collapse’’ of the structure into a single or many dense aggregates [37]. This phenomenon introduces a threshold ‘‘Chandrasekhar’’ number, N_c , above which the bacteria population clusterizes, while below it remains homogeneous. The expression for N_c is (in 2D): $N_c = 4D_\rho D_c / \mu \alpha$. Furthermore, as discussed in [37], $N^* \approx N_c$ is also expected to fix the typical size of a cluster [39].

Here, in order to connect this size to the experimentally measured velocity V of the SPC, we first note that V is itself a function of these parameters. Indeed, the motion is driven by the chemical reaction at the surface of the colloids and following [23,31], one expects typically $V \sim \mu \alpha / a D_c$, so that $\mu \alpha \sim V a D_c$ and $D_\rho \propto V^2 \tau_r$ [20]. Altogether, this yields

$$N^* \sim \frac{V \tau_r}{a} \sim \text{Pe}, \quad (2)$$

where $\text{Pe} = Va/D_0$ is a Peclet number characterizing the SPC (D_0 the bare diffusion coefficient), which can be also interpreted in terms of a persistence number [41]. This prediction is in good agreement with the experimental result in Fig. 4, $N^*(V) \propto V$, with furthermore a predicted prefactor given by an inverse velocity $\tau_r/a \sim \mu \text{m}^{-1} \cdot \text{s}$, also in agreement with the experiments.

This KS chemotactic scenario points to the basic ingredients for the chemically powered SPC particles and proposes a consistent and predictive explanation for clustering. The real mathematical description may be more complex as nonlinear mechanisms, such as a possible dependency of D_ρ or μ with chemical concentration c (e.g., a decrease of D_ρ with a decrease in c), were not considered here but would anyway act as second order corrections which do not modify the basic instability. Such refinements would require further mathematical developments, as in Ref. [42]. As a coarse-grained and mean-field description, KS cannot describe the detailed kinetics of the aggregate formation and distribution, which remain to be studied theoretically in more detail. It would also be desirable to explore further the relative dynamic stability between a collection of clusters versus the relaxation toward a single cluster. Recent simulations of a chemotactic model have shown results similar to the one experimentally observed here with ‘‘hot clusters’’ coexisting and fluctuating in time [41].

To conclude, we have explored the high density phase behavior of suspension of active particles at the colloidal scale. We have observed the formation of a dynamical ‘‘cluster phase’’ with a typical cluster size increasing linearly with a Peclet, or persistence, number characterizing the self-propelled colloids. Our results can be interpreted in the context of a chemotactic aggregation scenario first introduced to explain clustering observed for bacterial populations [13,36]. It suggests that chemical interactions between SPCs can mimic, on a purely physical basis, chemoattractivity and its consequences.

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