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Active colloidal suspensions: Clustering and phase behavior

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ABSTRACT

We review recent experimental, numerical, and analytical results on active suspensions of self-propelled colloidal beads moving in (quasi-)two dimensions. Active colloids form part of the larger theme of *active matter*, which is noted for the emergence of collective dynamic phenomena away from thermal equilibrium. Both in experiments and computer simulations, a separation into dense aggregates, i.e., clusters, and a dilute gas phase has been reported even when attractive interactions and an alignment mechanism are absent. Here, we describe three experimental setups, discuss the different propelling mechanisms, and summarize the evidence for phase separation. We then compare experimental observations with numerical studies based on a minimal model of colloidal swimmers. Finally, we review a mean-field approach derived from first principles, which provides a theoretical framework for the density instability causing the phase separation in active colloids.

1. Introduction

In the past decade, active systems have gained enormous interest in the field of soft matter physics from both the experimental and the theoretical side, see Refs. [1–4] for recent general reviews. Motivated through not only macroscopic biological systems like flock of birds [5] and school of fish [6], but also microscopic systems like bacterial colonies [7,8], theoretical models of self-propelled particles have been developed that demonstrate the emergence of collective phenomena from simple idealized interactions [9,10]. Theoretical descriptions have mainly focused on hydrodynamic approaches describing the coarse-grained dynamics on large scales [11]. Coefficients are either treated as free parameters or are derived, e.g., from the microscopic modeling of collisions [12–14]. In these models, the crucial interaction mechanism responsible for collective behavior such as laning, swarming, and even active turbulence [15–17] is the alignment of velocities, or orientations. These interactions might be cognitive as in the case of birds, or physical due to, e.g., volume exclusion of granular rods [18] and disks [19].

More recently, experimental setups of artificial colloidal "swimmers" have been realized, the propulsion properties of which can be tuned. Directed phoretic motion of these colloidal particles is the hydrodynamic consequence of maintaining a local gradient of a molecular solvent, e.g. due to chemical reactions on the different surface areas of a particle in a hydrogen peroxide mixture [20–22], or the local demixing of a water–lutidine mixture at one side of the particle [23]. Moderately dense *active suspensions* of such artificial swimmers can be realized and studied [24,25], for a summary of the experiments see Fig. 1. Arguably the most interesting feature is that a clustering of particles is observed. These clusters are very dynamic, and particles join and leave as shown in Fig. 1(b). While the cluster size in these experiments seems to reach saturation, in another experiment [26] using the reversible demixing of a binary solvent evidence for phase separation into compact large clusters and a dilute gas phase of free swimmers has been presented.

Such a phase separation has also been observed in computer simulations of a minimal model [26–33]. In this model, disks are propelled with constant velocity along their orientations, which undergo free rotational diffusion. Moreover, disks interact via a purely repulsive pair potential. The existence of a collective phase transition is somewhat surprising given that this model lacks both attractions – leading to phase separation in passive suspensions – and an alignment mechanism. Still, the persistence of the directed motion in combination with volume exclusion forces leads to a self-trapping phenomenon, where particles get temporally "stuck" and block each other, which has also been shown for lattice models before [34,35]. Tailleur and Cates have shown theoretically for a model of run-and-tumble bacteria that indeed a locally reduced mobility is sufficient to give rise to a separation into dense *slow* regions, where directed motion is blocked, and a dilute gas of fast particles [36–38].

Instead of giving a general overview, in this article we focus on recent experimental and theoretical progress on the phase behavior of self-propelled colloidal particles in two dimensions without an alignment mechanism. First, we review results from three groundbreaking experimental setups that have realized (quasi-)two-dimensional systems of spherical swimmers with a controllable propelling speed v_0 of the order μm/s, where the correlation between the particle orientations, i.e., the direction of propulsion, appears to be negligible, see

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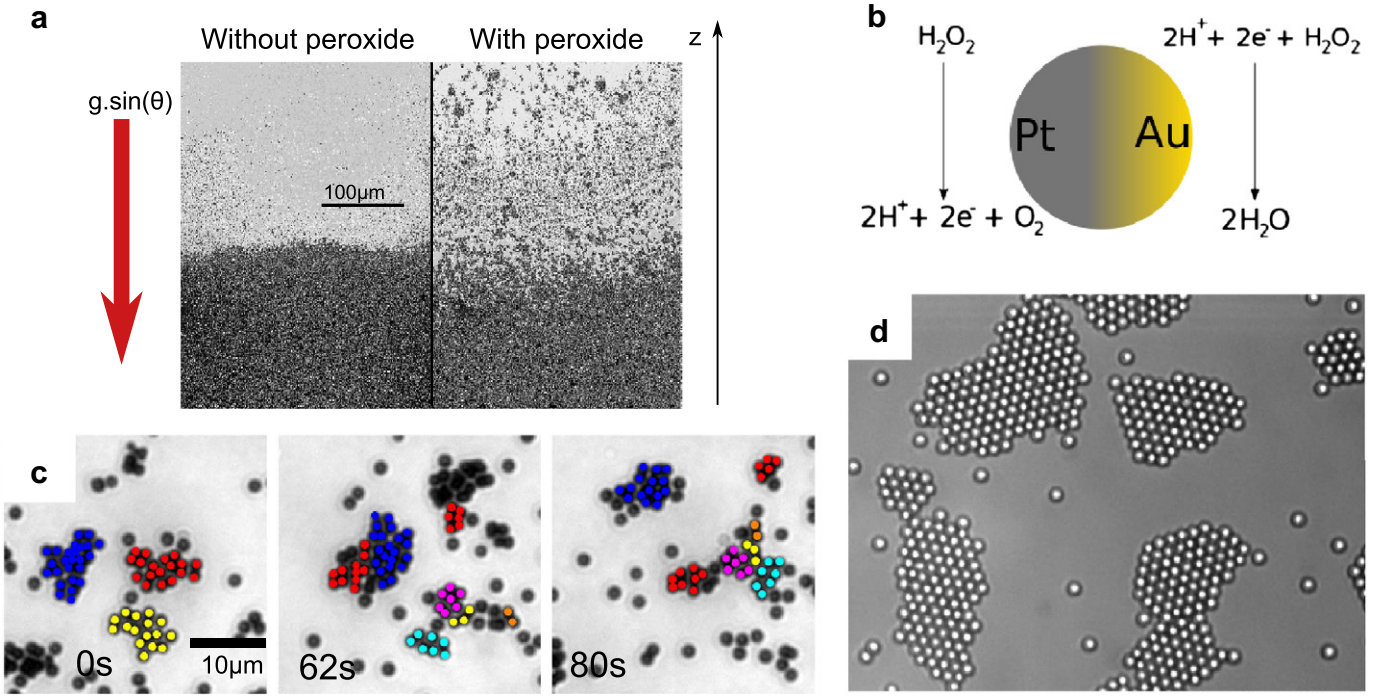

Fig. 1. Suspensions of catalytic Janus particles close to a surface: (a) Snapshots of platinum coated gold particles without (left) and with "fuel" (right) in the experiments of Theurkauff et al. [24]. Particles have sunk to the bottom of a tilted cell, where they accumulate at the bottom. In the active suspension (right), a smeared interface between a dense phase at the bottom and a dilute gas phase at the top is observed. (b) Cluster formation in the dilute phase in the experiment of Theurkauff et al. Colors indicate membership of a cluster at $t = 0$ and demonstrate how clusters evolve. (c) The platinum acts as a catalyst for the decomposition of hydrogen peroxide. The actual swimming mechanism is still somewhat debated, see text. (d) Formation of large clusters, "living crystals", in a related experiment performed by Palacci et al. [25] using colloidal particles with an embedded hematite cube. The catalytic activity of the hematite is controlled externally through light.
Figure adapted from Refs. [24,25].

Supplementary Material of Ref. [26]. A minimal model is then described, which nevertheless captures the relevant ingredients of the experiments. We discuss numerical results based on this model and compare them to experimental results. We briefly discuss the influence of hydrodynamic interactions as well as freezing of active systems at high densities. Finally, we introduce a mean-field approach leading to evolution equations for the density and the orientational field of an active suspension [30]. The crucial role in this theory is played by a single parameter, the force imbalance due to an anisotropic pair distribution. We then conclude and outline possible directions for further research in this rapidly evolving field.

2. Experimental evidence

2.1. Clustering of catalytic swimmers

For colloidal particles to "swim" autonomously, at least the following two conditions need to be met: (i) besides the colloidal solute and the solvent, there is a molecular solute and (ii) the distribution of this molecular solute is kept asymmetric.[1] Two practical schemes have been realized for the study of (moderately) dense active suspensions: the decomposition of water peroxide [41] and the reversible, spinodal demixing of a binary water–lutidine solvent [42].

While aggregation of catalytic swimmers has been observed before [21], clusters of active colloids have been characterized the first time in experiments performed by Theurkauff et al. [24]. They prepared the so-called Janus particles consisting of two surfaces with different physical properties. In this particular experiment they used spherical gold particles with one hemisphere coated with platinum. Immersing these particles in a solvent containing hydrogen peroxide H_2O_2, the particles are propelled along their symmetry axis. The propulsion is realized due to the different chemical properties of platinum and gold, leading to different rates of H_2O_2 consumption, see Fig. 1(c). The mechanism that is actually responsible for the propulsion (diffusiophoresis, electrophoresis, or a combination of both) is still somewhat debated, see Ref. [43] for a more detailed account for polystyrene-Pt swimmers. At sufficient low concentrations of hydrogen peroxide, the propelling speed is proportional to the H_2O_2 concentration. Of course, at some point, the swimming velocity saturates due to the finite number of active sites on the particle surface [44]. The swimming motion of a single particle, as measured by the mean-squared displacement, fits excellently with the prediction of a simple theoretical model [22,45,46], which is discussed in Section 3.1. The experiment can even be performed at high densities since particles do self-propel at H_2O_2 concentration below 0.1 %, which, in addition, prevents the creation of unfavorable O_2 bubbles.

In order to realize different density regimes, Theurkauff et al. have confined particles in a slightly tilted cell, which creates a reduced gravity field. The resulting sedimentation profile is more stretched compared to the equilibrium case, giving the possibility to study the system at different densities corresponding to different heights in one single sample, see Fig. 1(a). At low to intermediate densities, the suspension shows the formation of several clusters, cf. Fig. 1(b). Once clusters are formed, particles do not stay in their initial cluster but are continuously exchanged between clusters, see Fig. 1(b). For a better understanding of this cluster phase, the structure factor has been measured, which shows that clusters are highly ordered with pronounced peaks at values of the wave vector k corresponding to the hexagonal lattice. Simultaneously, an apparently diverging behavior for $k \to 0$ is observed, which has been the first experimental indication of density

[1] Thermophoresis could in principle also work [39,40], but the required high illumination powers induce optical forces, which, in the context considered here, are less desirable.