

## Synthetic Chemotaxis and Collective Behavior in Active Matter

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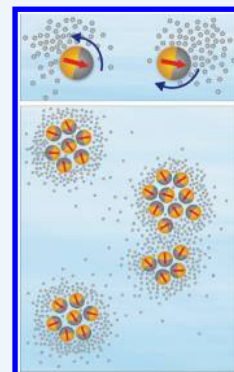
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**CONSPECTUS:** The ability to navigate in chemical gradients, called chemotaxis, is crucial for the survival of microorganisms. It allows them to find food and to escape from toxins. Many microorganisms can produce the chemicals to which they respond themselves and use chemotaxis for signaling, which can be seen as a basic form of communication, allowing ensembles of microorganisms to coordinate their behavior, for example, during embryogenesis, biofilm formation, or cellular aggregation. For example, *Dictyostelium* cells use signaling as a survival strategy: when starving, they produce certain chemicals toward which other cells show taxis. This leads to aggregation of the cells resulting in a multicellular aggregate that can sustain long starvation periods.

Remarkably, the past decade has led to the development of synthetic microswimmers, which can self-propel through a solvent, analogously to bacteria and other microorganisms. The mechanism underlying the self-propulsion of synthetic microswimmers like camphor boats, droplet swimmers, and in particular autophoretic Janus colloids involves the production of certain chemicals. As we will discuss in this Account, the same chemicals (phoretic fields) involved in the self-propulsion of a (Janus) microswimmer also act on other ones and bias their swimming direction toward (or away from) the producing microswimmer. Synthetic microswimmers therefore provide a synthetic analogue to motile microorganisms interacting by taxis toward (or away from) self-produced chemical fields.

In this Account, we review recent progress in the theoretical description of synthetic chemotaxis mainly based on simulations and field theoretical descriptions. We will begin with single motile particles leaving chemical trails behind with which they interact themselves, leading to effects like self-trapping or self-avoidance. Besides these self-interactions, in ensembles of synthetic motile particles each particle also responds to the chemicals produced by other particles, inducing chemical (or phoretic) cross-interactions. When these interactions are attractive, they commonly lead to clusters, even at low particle density. These clusters may either proceed toward macrophase separation, resembling *Dictyostelium* aggregation, or, as shown very recently, lead to dynamic clusters of self-limited size (dynamic clustering) as seen in experiments in autophoretic Janus colloids. Besides the classical case where chemical interactions are attractive, this Account discusses, as its main focus, repulsive chemical interactions, which can create a new and less known avenue to pattern formation in active systems leading to a variety of pattern, including clusters which are surrounded by shells of chemicals, traveling waves and more complex continuously reshaping patterns. In all these cases “synthetic signalling” can crucially determine the collective behavior of synthetic microswimmer ensembles and can be used as a design principle to create patterns in motile active particles.



### ■ INTRODUCTION

To find food and to avoid toxins, microorganisms are equipped with a remarkable navigation machinery, which allows them to sense (or “smell”) certain chemicals to which they respond by moving either up the chemical gradient (chemoattraction) or down it (chemorepulsion or negative chemotaxis). Besides chemotaxis, microorganisms show taxis also to many other gradients, such as temperature (thermotaxis),<sup>1</sup> light intensity (phototaxis),<sup>2,3</sup> or viscosity (viscotaxis).<sup>4,5</sup>

Remarkably, many microorganisms can produce the chemicals to which they respond themselves and use chemotaxis for signaling, allowing microorganisms (and cells) to coordinate their motion and gene expression. This is crucial for a large variety of biological processes: for example, it allows the sperm to find the egg, thus preceding mammalian life.<sup>6,7</sup>

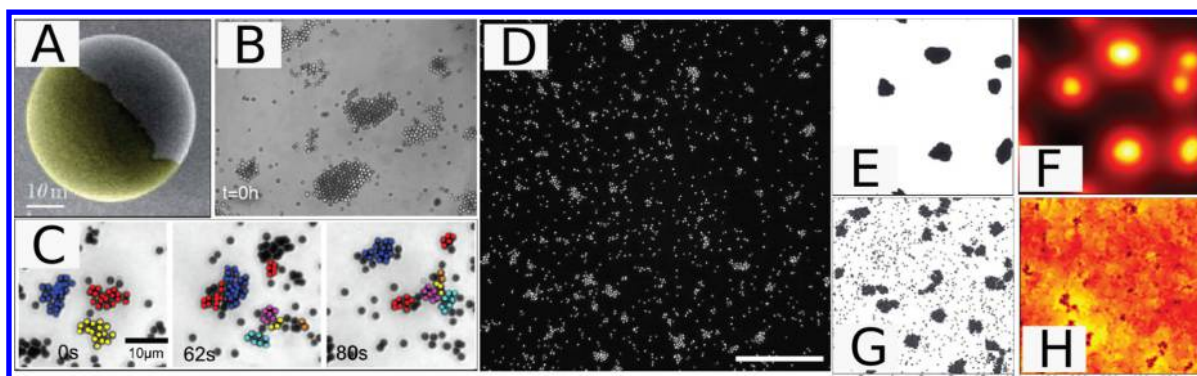
An example illustrating collective behavior based on signaling is provided by *Dictyostelium* cells; when starving,

they produce certain chemicals (cAMP) whose “smell” attracts other cells inducing a positive feedback loop: a local cell accumulation yields an enhanced chemical production, further enhancing the initial smell attracting other cells, etc. Overall, this results in a collapse of *Dictyostelium* cells followed by sporulation allowing the cells to survive long starvation periods;<sup>7,13,14</sup> see ref 15 for a recent model on signaling *Dictyostelium*. This mechanism is captured in the classical Keller–Segel model<sup>16,17</sup> and has recently been established also for *E. coli* bacteria showing positive chemotaxis to self-produced autoinducers.<sup>18</sup>

Recent advances in synthetic microswimmers<sup>19,20</sup> have revealed a remarkably close synthetic analogon to biological chemotaxis: phoretic Janus colloids, which are half-coated with

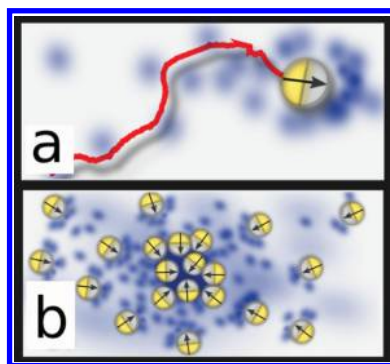
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**Figure 1.** Panel A shows an active Janus colloid that catalyzes a chemical reaction on part of its surface and swims by a phoretic mechanism in the self-produced chemical gradient. The same gradients also act on other colloids, leading to chemical cross-interactions probably underlying dynamic clusters commonly seen in low density ensembles of Janus colloids, panels B–D. Panels E–H show clusters seen in simulations of colloids with attractive (E,F) and (partly) repulsive (G,H) chemical cross-interactions, discussed later in the text. Panel A reproduced with permission from ref 8. Copyright 2011 Royal Society of Chemistry. Panel B reproduced with permission from ref 9. Copyright 2013 American Physical Society. Panel C reproduced with permission from ref 10. Copyright 2012 American Physical Society. Panel D reproduced with permission from ref 11. Copyright 2018 Nature. Panels E–H reproduced with permission from ref 12. Copyright 2017 American Physical Society.

a catalytic material like gold or platinum, catalyze chemical reactions in the solute surrounding them (Figures 1A, 2a).



**Figure 2.** (a) Self-propelled Janus colloid produces certain chemicals causing chemical self-interactions. (b) Keller–Segel instability for Janus colloids occurring due to chemical cross-interactions. Reproduced with permission from ref 60. Copyright 2016 Royal Society of Chemistry.

This results in a chemical gradient across the colloids' surfaces, driving them forward, for example, by diffusiophoresis. Interestingly, the self-produced chemical gradients decay slowly with increasing distance to a Janus colloid and act also on other Janus colloids, Figure 2b.

The analogy of chemically interacting Janus colloids and signaling microorganisms holds true even formally, yielding the same Keller–Segel equations for microorganisms<sup>21</sup> and (chemically interacting) Janus colloids.<sup>22–25</sup> However, synthetic signaling is not restricted to chemical interactions but can occur analogously in self-thermophoretic and self-electrophoretic colloids where particles interact via other self-produced phoretic fields (e.g., temperature, electric field), which they use for swimming.<sup>26–30</sup> We thus use the terms phoretic interactions and synthetic signaling interchangeably in the following.

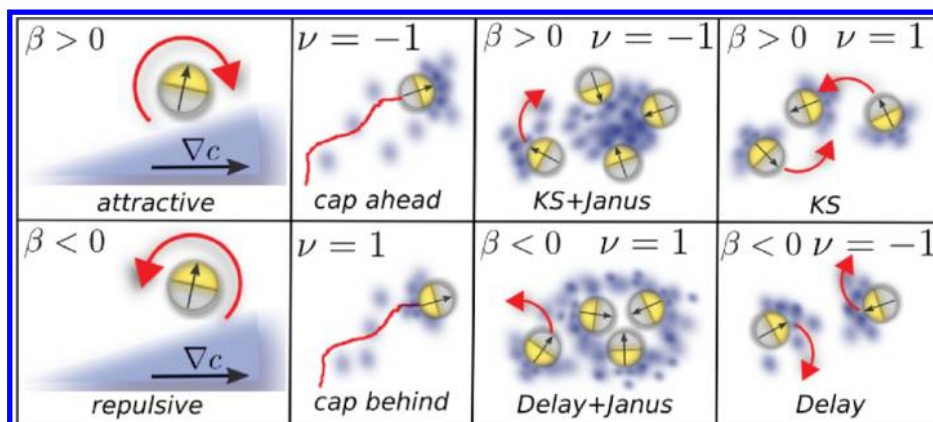
Remarkably, the “interaction fields” (chemicals, etc.) involved in synthetic signaling autonomously evolve in time and follow the motion of the Janus colloids noninstantaneously. This induces delay effects allowing particles to interact with their own past (they leave chemical trails behind), which

can induce pattern formation in repulsively signaling Janus colloids,<sup>25</sup> as we shall discuss below. Delay effects are also relevant in self-propelled oil droplets showing chemotaxis with respect to micellar surfactant gradients and to empty micelles, which they leave in their wake,<sup>31,32</sup> and to camphor boats<sup>33,34</sup> leaving slowly decaying chemical trails in their wakes.

In typical active matter systems, phoretic interactions compete with steric short-range repulsions and hydrodynamic interactions, making it important to understand which interactions dominate the collective behavior:<sup>35</sup> from the exploration of minimal active matter models, it is known that the combination of steric short-range repulsions and motility alone can lead to spontaneous aggregation of particle ensembles<sup>36</sup> (“motility induced phase separation”). However, this requires packing fractions  $\gtrsim 30$ –40% to occur spontaneously from a uniform phase<sup>37</sup> or a large nucleation seed.<sup>38</sup> Similarly, hydrodynamic interactions are known to often play an important role not only for microorganisms<sup>39</sup> but also for the collective behavior of colloids at moderate to high density.<sup>40,41</sup> Particularly at low density, where many experiments with Janus colloids are performed, chemical (phoretic) interactions seem to be dominant in many cases.<sup>35,42,43</sup> These interactions generically destabilize the uniform phase in Janus colloids (and dimers) even at low area fraction<sup>12,35,44,45</sup> and can lead to clusters of self-limited size<sup>25,35,46,47</sup> as in experiments.<sup>9–11,42</sup> On the experimental side, attractive phoretic interactions have been measured in Janus colloids forming dynamic clusters<sup>42</sup> and microgears<sup>48</sup> and in low density active–passive mixtures.<sup>43</sup> Finally, experiments in  $\text{Ag}_3\text{PO}_4$  microparticles, which lead to schooling patterns and allow for transitions to patterns involving large exclusion zones, seem to be also dominated by phoretic interactions.<sup>49,50</sup>

### Organization of the Article

After briefly discussing chemical signaling in isotropic particles, we will focus on active particles with an intrinsic self-propulsion direction, which changes in response to chemical gradients. Here, we will discuss the *Phoretic Brownian Particle* (PBP) model, which leads to a wealth of patterns not only for attractive signaling but, remarkably, also for the less studied repulsive case.



**Figure 3.** Classification of Janus colloids and the instabilities to which they can lead in the PBP model. Here, KS represents the Keller–Segel instability, and Janus and Delay stand for the Janus instability and the delay induced instability discussed in the text. Reproduced with permission from ref 12. Copyright 2017 American Physical Society.

## CHEMOTAXIS IN ISOTROPIC PARTICLES

### One Particle

Consider an isotropic overdamped Brownian particle with center of mass coordinate  $\mathbf{r}_1$  that couples to the gradient of a field  $c(\mathbf{r}, t)$ , yielding the Langevin equation

$$\dot{\mathbf{r}}_1(t) = \beta_D \nabla c(\mathbf{r}_1(t), t) + \sqrt{2D} \boldsymbol{\xi}(t) \quad (1)$$

Here, we call  $c$  the “chemical field” for concreteness but keep in mind that  $c$  may also represent, for example, a temperature or light intensity field, depending on the type of taxis we consider.  $\beta_D$  is the (chemo)tactic coupling coefficient,  $\boldsymbol{\xi}(t)$  represents Gaussian white noise of zero mean and unit variance, and  $D$  is the diffusion coefficient of the particle. If  $\beta_D > 0$ , the particle moves toward high chemical concentration and shows *chemoattraction* (or positive chemotaxis); if  $\beta_D < 0$ , the particle moves down the chemical gradient representing *chemorepulsion* (or negative chemotaxis).

As we have discussed above, many microorganisms self-produce the chemical to which they respond, say with a rate  $k_0$ . This is called (positive or negative) *autochemotaxis*. We describe the corresponding chemical dynamics by a diffusive evolution equation with a source representing chemical production by the particle

$$\dot{c}(\mathbf{r}, t) = D_c \Delta c(\mathbf{r}, t) + k_0 \delta(\mathbf{r} - \mathbf{r}_1) - k_d c(\mathbf{r}, t) \quad (2)$$

where  $D_c$  is the chemical diffusion coefficient. The sink term, led by the rate coefficient  $k_d$ , represents chemical evaporation, occurring, for example, due to secondary chemical reactions taking place in the underlying solvent. For autochemoattraction ( $\beta_D > 0$ ), where the particle produces a chemical to which it is attracted, eqs 1 and 2 can lead to self-trapping in one and two dimensions (but not in three),<sup>51</sup> which can be permanent ( $k_d = 0$ <sup>51</sup>) or transient ( $k_d > 0$ <sup>52,53</sup>) and is opposed by noise.<sup>54</sup> Conversely, autochemorepulsion ( $\beta_D < 0$ ) can lead to self-avoidance.<sup>52,53</sup> A system of two chemotactic particles, A and B, where A is attracted by the chemical released by B, and B is repelled by the chemical produced by A has been explored in ref 55 and forms a close analogue to a predator–prey system featuring nonreciprocal interactions. For more details on single and two-particle chemotaxis, we refer the reader to ref 56. Here, we mainly focus on collective behavior.

### Collective Behavior: Keller–Segel Model

We now consider ensembles of diffusive particles interacting via self-produced chemical fields (signaling). Here, the dynamics of each particle couples to the chemicals produced by *all*  $N$  particles in the system. Formally, to describe collective behavior, we can replace  $\mathbf{r}_1(t)$  with  $\mathbf{r}_i(t)$  ( $i = 1, \dots, N$ ) in eq 1 and  $k_0 \delta(\mathbf{r} - \mathbf{r}_1(t))$  with  $\sum_{i=1}^N k_0 \delta(\mathbf{r} - \mathbf{r}_i(t))$  in eq 2. It is convenient to describe collective behavior using a particle density field  $\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i(t))$  coupled to the chemical density. The exact Smoluchowski equation for  $\rho$  coupled to an evolution equation for  $c$  reads

$$\dot{\rho} = -\nabla \cdot (\beta_D \rho \nabla c) + D \nabla^2 \rho \quad (3)$$

$$\dot{c} = D_c \nabla^2 c + k_0 \rho - k_d c \quad (4)$$

These equations represent the classical Keller–Segel model (see ref 21 for variants of this model). One obvious solution is  $(\rho, c) = (\rho_0, k_0 \rho_0 / k_d)$  representing a uniform disordered phase. Performing a linear stability analysis of this phase predicts a criterion for the onset of structure formation, which reads:

$$k_0 \rho_0 \beta_D > D k_d \quad (5)$$

This is the Keller–Segel instability, which occurs for chemoattraction ( $\beta_D > 0$ ) and is based on a positive feedback between particle aggregation and chemical production. Following the instability criterion (eq 5) and strong overall chemical production ( $\sim k_0 \rho_0$ ), strong response to the chemical ( $\sim \beta$ ) supports the emergence of an instability, whereas fast evaporation (decay) and fast particle diffusion oppose it. The Keller–Segel instability, typically leads to clusters (Figure 1E) and collocated chemical clusters (F), which both coarsen (and coalesce) and lead to one dense macrocluster at late times, resembling a gravitational collapse.<sup>51,57,58</sup> For weak chemotactic coupling such a collapse can be prevented by reproduction processes, which are naturally present in microorganisms, but not for strong coupling.<sup>59</sup>

## CHEMOTAXIS IN ACTIVE PARTICLES

### Active Particles in Imposed Gradients

When exposed to a chemical gradient, anisotropic particles, such as self-propelled Janus colloids, may both displace (change of velocity) and align with or against the chemical gradient (change of self-propulsion direction), that is,



effectively, they experience both a force acting on their center of mass and a torque. It is convenient to describe the motion of an overdamped chemotactic particle self-propelling with a velocity  $v_0$  (independently of chemotaxis) in a direction  $\mathbf{p} = (\cos \theta, \sin \theta)$  in two dimensions by the following evolution equations

$$\dot{\mathbf{r}}(t) = v_0 \mathbf{p} + \beta_D \nabla c(\mathbf{r}(t), t) + \sqrt{2D} \boldsymbol{\xi}(t) \quad (6)$$

$$\dot{\theta}(t) = \beta \mathbf{p} \times \nabla c(\mathbf{r}(t), t) + \sqrt{2D_r} \eta(t) \quad (7)$$

where  $\mathbf{a} \times \mathbf{b} = a_1 b_2 - a_2 b_1$  represents the 2D cross-product. Here, the chemotactic drift,  $\beta_D \nabla c$ , changes the speed of the particle in response to the imposed chemical gradient and the alignment term,  $\beta \nabla c$ , changes the particle orientation (swimming direction): when  $\beta > 0$ , the particle (i.e., its swimming direction) turns up the chemical gradient (chemoattraction), whereas for  $\beta < 0$ , the particle turns down the gradient (chemorepulsion); see the left two columns in Figure 3. This alignment occurs in competition with rotational Brownian diffusion due to collisions with solvent molecules, described by the rotational diffusion coefficient  $D_r$  and Gaussian white noise  $\eta$  with zero mean and unit variance.

Synthetic taxis of active particles has first been observed for microrods in imposed chemical gradients<sup>61</sup> and later also for Janus colloids in temperature gradients<sup>28,62</sup> and light gradients.<sup>63</sup> An active version of *autochemotactic* particles interacting with their own trails has been discussed in refs 64 and 65, and typical trajectories of two (and more) of these walkers have been discussed in ref 66.

### Collective Behavior: The Phoretic Brownian Particle Model

We now discuss the Phoretic Brownian Particle (PBP) model,<sup>12</sup> which is based on equations of motion for  $N$  chemotactic swimmers, each described by eqs 6 and 7, coupled to each other via a self-produced chemical field, which evolves following the chemical diffusion equation. To define the PBP equations, we consider the following simplifications of eqs 6 and 7.

- (i) Since “active diffusion” dominates over passive diffusion, that is,  $\sim v_0^2/D_r \gg D$ , we set  $D \rightarrow 0$  in eq 6.
- (ii) For simplicity, we also neglect the chemotactic drift ( $\beta_D \rightarrow 0$ ), allowing us to capture most aspects of chemically interacting microswimmers in a simplified way. (Physically, drift effects are also important for typical Janus colloids<sup>35</sup> but can to some extent be absorbed in the alignment effects we discuss here.)

Consider  $N$  self-propelled particles moving with identical self-propulsion velocities  $v$  in directions  $\mathbf{p}_i = (\cos \theta_i(t), \sin \theta_i(t))$ ,  $i = 1, \dots, N$ , which change due to rotational diffusion and chemical torques.

$$\dot{\mathbf{r}}_i = v_0 \mathbf{p}_i \quad (8)$$

$$\dot{\theta}_i = \beta \mathbf{p}_i \times \nabla c(\mathbf{r}_i) + \sqrt{2D_r} \xi_i(t); \quad i = 1, \dots, N \quad (9)$$

To account for possible anisotropic chemical production, occurring, for example, for Janus colloids, we slightly generalize the evolution equation for the chemical:

$$\begin{aligned} \dot{c}(\mathbf{r}, t) = & D_c \nabla^2 c(\mathbf{r}, t) - k_d c(\mathbf{r}, t) \\ & + \sum_{i=1}^N \oint d\mathbf{x}_i \delta(\mathbf{r} - \mathbf{r}_i(t) - R_0 \mathbf{x}_i) \sigma(\mathbf{x}_i) \end{aligned} \quad (10)$$

The integral is over the 3D surface of the (spherical) particles with radius  $R_0$  and  $\sigma(\mathbf{x}_i)$  is the (nonuniform) production rate density on the particle surface. Specifically for Janus colloids, we have  $\sigma(\mathbf{x}_i) = k_0/(2\pi R_0^2)$  on the catalytic hemisphere and zero elsewhere. Since we are mainly interested in understanding the onset of pattern formation at low densities, we neglect steric short-range repulsions among the particles for simplicity (but will include them in particle based simulations).

**Limit of Fast Chemical Dynamics and the Active Attractive Alignment Model.** Seemingly, for large  $D_c$ , we may treat  $c$  as a fast variable and set  $\dot{c} \rightarrow 0$  in eq 2. This approach leads to the Active Attractive Alignment model (when accounting also for drift effects), which has recently been developed in ref 35 for attractive phoretic interactions and leads to dynamic clustering at low density, in accordance with experiments.<sup>9–11,42</sup> In general, however, the limit of fast chemical diffusivity is dangerous for Janus colloids, since the chemical coupling coefficients  $\beta$  (and  $\beta_D$ ) turn out to be proportional to  $D_c$ .<sup>12</sup> Thus, delay effects may be important even for large  $D_c$ , particularly for repulsive phoretic interactions as we will discuss below in detail.

### Field Theory of the Phoretic Brownian Particle Model

To understand the collective behavior of phoretically interacting active particles, we now coarse grain the PBP model. Since active particles are nonisotropic, a field theory for their collective behavior naturally involves both the particle density field,  $\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i(t))$ , and the polarization density,  $\mathbf{w}(\mathbf{r}, t)$ , defined as  $\mathbf{w} = \sum_{i=1}^N v_i \mathbf{p}_i \delta(\mathbf{r} - \mathbf{r}_i(t))$ . Its magnitude is a measure for the number of aligned particles around position  $\mathbf{r}$ , and its direction describes the average self-propulsion direction. Following ref 47, for moderate deviations from isotropy, we obtain

$$\dot{\rho} = -\text{Pe} \nabla \cdot \mathbf{w} \quad (11)$$

$$\begin{aligned} \dot{\mathbf{w}} = & -\mathbf{w} + \frac{B\rho}{2} \nabla c - \frac{\text{Pe}}{2} \nabla \rho + \frac{\text{Pe}^2}{16} \nabla^2 \mathbf{w} - \frac{B^2 |\nabla c|^2}{8} \mathbf{w} \\ & + \frac{\text{Pe}B}{16} (3(\nabla \mathbf{w})^T \cdot \nabla c - (\nabla c \cdot \nabla) \mathbf{w} - 3(\nabla \cdot \mathbf{w}) \nabla c) \end{aligned} \quad (12)$$

$$\dot{c} = \mathcal{D} \nabla^2 c + K_0 \rho + \nu \frac{K_0}{2} \nabla \cdot \mathbf{w} - K_d c \quad (13)$$

Here, we have introduced time and space units as  $t_u = 1/D_r$  and  $x_0 = R_0$ , leading to the following six dimensionless control parameters: (i) the Peclet number,  $\text{Pe} = v_0/(R_0 D_r)$ ; (ii)  $B = \beta/(D_r R_0^4)$ ; (iii)  $K_0 = k_0/D_r$ ; (iv)  $K_d = k_d/D_r$ ; (v)  $\mathcal{D} = D_c/(R_0^2 D_r)$ ; (vi) the dimensionless quasi-two-dimensional density,  $\rho_0 = x_u^2 N/L^2$ . Finally,  $\nu$  determines the anisotropy in the chemical production; we have  $\nu = 0$  for isotropic chemical production, and specifically for Janus colloids, we have  $\nu = 1$  for those moving with the catalytic cap in the back and  $\nu = -1$  for Janus swimmers moving cap-ahead; compare Figure 3.

### Active Keller–Segel Model

One interesting limiting case of eqs 11–13 is obtained for quasi-instantaneous alignment of the particles to the chemical gradients ( $\dot{\mathbf{w}} \rightarrow 0$ ) when neglecting nonlinear terms and second order gradients in eq 12, that is,  $\mathbf{w} \approx B\rho \nabla c/2 - \text{Pe} \nabla \rho/2$ . Plugging this expression into eq 11 yields the Keller–Segel eqs 3 and 4 for isotropic production ( $\nu = 0$ ), now applying to active particles and written in dimensionless units. Thus, the

apparent similarity between signaling microorganisms and synthetic microswimmers holds true also formally. The formal analogy allows us to immediately write down the instability criterion as

$$\frac{K_0 \rho_0 B}{K_d \text{Pe}} > 1 \quad (14)$$

It can be shown<sup>12</sup> that despite the approximations that we have used here, this instability criterion holds true exactly for eqs 11–13. The Keller–Segel instability leads to clusters of active particles and colocated clusters of the self-produced chemical that grow in the course of the time due to coarsening and cluster coalescence (see Figure 1E,F). In physical units, the instability criterion translates to  $k_0 \rho_0 \beta / (k_d \nu_0) > 1$  showing that strong production and alignment of chemical gradients favors instability of the uniform phase. However, it also suggests that self-propulsion opposes the instability, which seems paradoxical but will be resolved in the next paragraph.

### Parameter Collapse and Universality

As discussed in the Introduction, phoretic microswimmers move by catalyzing certain chemical reactions in a bath on part of their surface only, which drives them forward. The same gradients also act on other phoretic swimmers and bias their swimming direction. It has been shown that this situation allows us to express the (dimensionless) phoretic cross coupling coefficient,  $B$ , through parameters determining the single-particle swimming speed<sup>12</sup> as

$$B \approx \frac{4\pi s \text{Pe} \mathcal{D}}{K_0} \quad (15)$$

where  $s = 1$  represents chemoattraction and  $s = -1$  represent chemorepulsion. This expression for  $B$  can now be used to strongly simplify the Keller–Segel instability for active particles. Combining eq 15 with eq 14 yields the instability criterion  $6\mathcal{D}\rho_0/K_d > 1$  or with the quasi-2D area fraction  $f = \pi\rho_0$  ( $f = \pi R_0^2 \rho_0$  in physical units):

$$6\mathcal{D}f > K_d \quad (16)$$

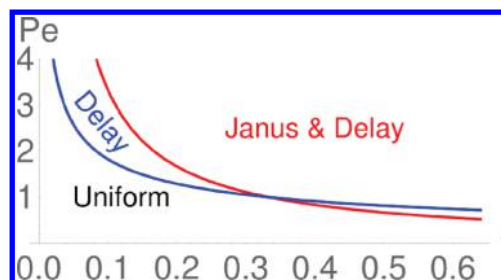
In physical units, criterion 16 can be written as  $D_c/(R_0^2 k_d) > 1/(6f)$  where<sup>35</sup>  $D_c/(k_d R_0^2) \approx 1-10$ , suggesting that the Janus instability might occur at low area fractions of a few percent only. In real Janus colloids with attractive phoretic interactions, drift effects further support this instability.

### Chemorepulsive Route to Pattern Formation

Remarkably, not only attractive signaling but also repulsive signaling can destabilize the disordered uniform phase, which, in fact, creates a proper route to pattern formation leading to a large variety of possible structures including clusters and wave patterns. A general linear stability analysis of eqs 11–13 for  $K_d \ll 1$  leads, together with eq 15, to the following instability criterion of the uniform phase for  $B < 0$

$$3\text{Pe}f\left(\frac{\nu}{2} + \text{Pe}\right) \gtrsim 1 \quad (17)$$

Note that eq 17 represents a massive collapse of the parameter space of the PBP model. From originally six dimensionless parameters, it depends only on two parameters  $\text{Pe}$  and  $f$  (and  $\nu$ , which is of order 1) allowing one to compare the phase diagram of the PBP model (Figure 4) with that of the widely used active Brownian particle model. Since we have  $\text{Pe} \approx 20-200$  for typical autophoretic Janus swimmers,<sup>9,10,42</sup> this



**Figure 4.** Phase diagram of the Phoretic Brownian Particle model for  $\beta < 0$  (repulsive phoretic interactions) and  $k_d = 0$ . See ref 12 for details. Reproduced with permission from ref 12. Copyright 2017 American Physical Society.

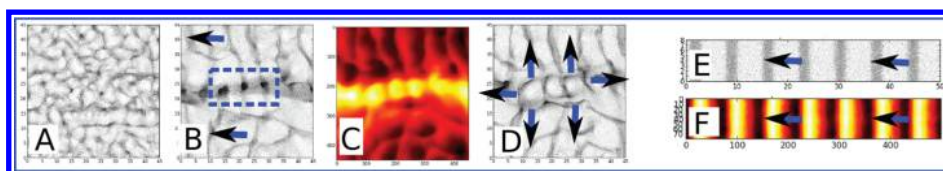
criterion shows that not only attractive chemical interactions but also repulsive ones generically destabilize the uniform phase in autophoretic microswimmers. Thus, the very fact that Janus colloids swim obliges them to form patterns, even at very low density,<sup>12</sup> where the active Brownian particle model predicts stability of the uniform phase only but experiments show dynamic clustering.<sup>9-11,42</sup> (This remains true in the presence of chemical evaporation ( $K_d \neq 0$ ), up to  $K_d \approx \text{Pe}^2 f$ .)

The instability criterion, eq 17, is a sum of two terms representing independent physical mechanisms:<sup>12,25</sup>

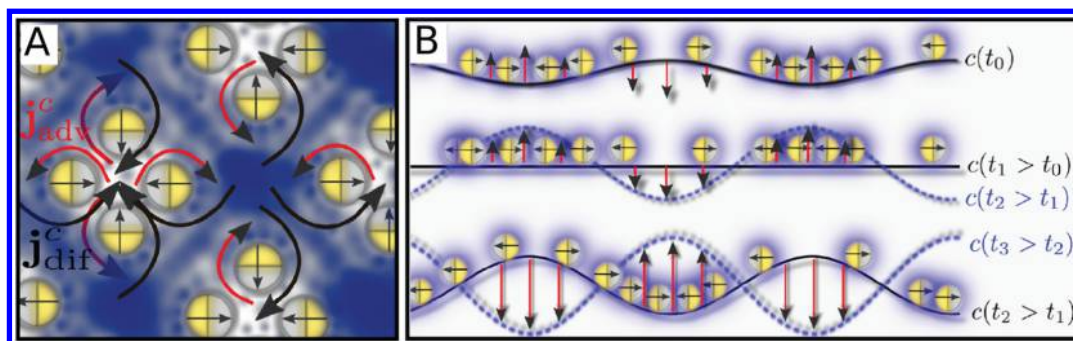
- **Janus instability:** The first part of the criterion reads  $3\text{Pe}f\nu > 2$ . Since  $\nu = 0$  for isotropic chemical production on the surface of the particles, this criterion can only be fulfilled for anisotropic chemical production; hence it is called, the *Janus instability*. The Janus instability leads to clusters of finite size. The underlying physical mechanism is illustrated in Figure 5A.
- **Delay-induced instability:** The second criterion,  $3\text{Pe}^2 f > 1$ , in eq 17 represents an oscillatory instability and creates wave patterns. The underlying delay-induced instability mechanism is detailed in Figure 5B.

The Janus and the delay-induced instabilities create a rich panorama of patterns. In most cases, the delay-induced instability dominates over the Janus instability and leads to continuously evolving patterns.<sup>12,25</sup> A typical example is shown in Figure 6. It involves colloidal waves pursued by self-produced phoretic waves. When these waves collide frontally, the pursuing phoretic waves act as cages for the chemorepulsive particles and morph them into a cluster (Figure 6B). The high particle density within such a cluster induces an enhanced chemical production resulting in colocated phoretic clusters (C), which in turn expel the chemorepulsive colloids. This expulsion may occur rather suddenly and may initiate new colloidal ring waves leaving low density regions at the locations of the former clusters (D). These waves continue colliding, creating new clusters, and so on. At very late times, these waves may settle down into a regular pattern of traveling waves (E) pursued by cotraveling chemical waves (F). When two waves collide laterally rather than frontally, they often create moving clusters as discussed in some detail in ref 12. Recent experiments in ensembles of thermophoretic active colloids<sup>30</sup> find corresponding traveling clusters, which might have a similar origin.

While these patterns mainly hinge on the delay-induced instability, a variant of the PBP model where particles produce a chemical on one hemisphere and consume it at the same rate on the other one (zero net production) allows us to explore patterns resulting from the Janus instability. This variant leads



**Figure 5.** Simulations of the PBP model for repulsive signaling including additional short-ranged steric repulsions among the particles. The figure shows colloidal waves (A) pursued by self-produced phoretic waves caging the colloids in dense clusters (B); these clusters act as enhanced phoretic producers leading to phoretic clusters (C), which drive colloids away and induce escape waves (D). At late times, these wave patterns may settle into regular moving bands of colloids closely followed by phoretic waves (E,F). Reproduced with permission from ref 12. Copyright 2017 American Physical Society.



**Figure 6.** Instability mechanisms for repulsive signaling: (A) The Janus instability is based on anisotropic chemical production of colloids on their surface leading to clusters of self-limited size that are surrounded by self-produced shells of high chemical density, which keeps the particles in the cluster together. (B) Delay induced instability. Chemorepulsive colloids accumulate in the minima of a weak initial fluctuation of the uniform chemical field (upper panel). Chemical production by the colloids opposes the original fluctuation (middle panel) but does not stop at uniform chemical density but overshoots, due to a finite response time of the colloids. This reverses the original profile and may amplify (lower panel) triggering an oscillatory instability. Reproduced with permission from ref 25. Copyright 2015 American Physical Society.

to dynamic clusters with a finite self-limited size, shown in Figure 1G,H.

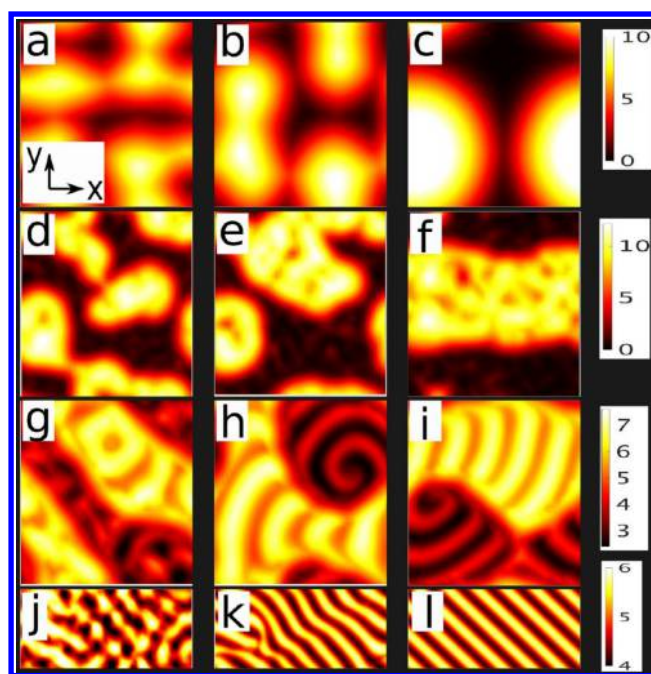
### ■ BEYOND THE ACTIVE BROWNIAN PARTICLE MODEL: CHIRALITY

Many active particles are chiral and swim in circles. Phoretic interactions creating an effective torque in such particles lead to a competition between intrinsic rotations and phoretic alignment. Specifically for chiral particles that synchronize their orientations due to alignment interactions, a simplified model<sup>60</sup> unveils traveling wave patterns and spiral patterns (Figure 7). Besides the case where particles are (completely) synchronized, most aspects of chemically interacting chiral active matter remain to be studied.

So far, we have mainly focused on chemotactic alignment. Generally, however chemotactic drift effects should be also important. In particular, chemoattractive drifts alone,<sup>35</sup> as well as their combination with alignment (taxis) down the chemical gradient, can lead to dynamic clustering.<sup>35,46</sup> The opposite case of a repulsive drift and a chemotactic alignment toward (up) the chemical gradient can lead to an oscillating state between a collapse and its dissolution.<sup>24</sup>

While we have focused here on one chemical field representing an effective combination of the fuel chemical and the product species, the case of two chemical species has been explicitly discussed in ref 23, providing a catalogue of possible instabilities of the uniform phase, which can lead, for example, to clustering and collective oscillations.

The case of two different colloidal species producing chemicals can lead to nonreciprocal interactions<sup>67</sup> among the colloids,<sup>68</sup> which can result in the formation of “active molecules”.<sup>69</sup> These molecules consist of non self-propelled



**Figure 7.** Patterns in chemically interacting (signaling) chiral active particles. Each row corresponds to a different set of parameters and shows the particle density field,  $\rho(\mathbf{r}, t)$ , at three consecutive points in time. Reproduced with permission from ref 60. Copyright 2016 Royal Society of Chemistry.

colloids, which interact nonreciprocally via self-produced (chemical) fields, leading to propulsion of the pair. Active molecules have recently been demonstrated experimentally in ref 70 based on ion exchange particles interacting via charge-



neutral ionic gradients with colloids and in a light-controllable setup based on colloids<sup>71</sup> leading to stators, rotators, spinners, and linear swimmers.<sup>71</sup>

The influence of hydrodynamic interactions has been studied only in a few cases, yielding a “mixed phase” for chemotactic run and tumble bacteria<sup>72</sup> and to finite clusters<sup>73</sup> and swarm-like structures<sup>74</sup> in colloids.

While showing remarkably close analogies to signaling among cells and microorganisms, research on synthetically signaling active particles may shed new light on biological phenomena. One recent example is<sup>75</sup> applying a variant of the field theory of the PBP model<sup>12,25</sup> to growing bacterial colonies.

## CONCLUSIONS AND OUTLOOK

We have reviewed the collective behavior of active systems showing synthetic chemotaxis with a focus on the Phoretic Brownian Particle (PBP) model and corresponding field theories. As we have seen, there is now significant evidence that synthetic chemotaxis is responsible for much of the collective behavior seen in experiments with active colloids and other active systems like camphor and droplet swimmers. However, we are still at the beginning of understanding synthetic signaling in detail. Open problems include a detailed characterization of the properties of patterns occurring in systems with repulsive chemical interactions using, for example, amplitude equations, structure factors, etc., and a detailed understanding of the evaporation rate of the chemical field ( $k_d$ ) and of phoretic near field effects as well as fuel depletion, leading to a coupling of the self-propulsion velocity to the chemical field. Further important open points include boundary and dimensionality effects, as well as a general understanding of the interplay of phoretic and hydrodynamic interactions regarding the large scale collective behavior of autophoretic swimmers. Short-range repulsions among the colloids, so far included in simulations but not in theoretical calculations based on the PBP model, could be described, for example, in the framework of dynamical density functional theory.<sup>76,77</sup> Similarly, dynamical density functional theory could also be used to describe interactions among the chemicals perhaps leading to interesting phenomena, for example, if the chemical has a tendency to phase separate. Finally, further interesting problems concern the role of phoretic interactions in chiral autophoretic swimmers without explicit alignment interactions and a detailed study of ionic contributions to signaling.<sup>78</sup>

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### Notes

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Since 2017, he is a postdoctoral researcher at the University of Düsseldorf. He works on (active) soft matter and nonlinear dynamics using theoretical descriptions and computer simulations.

**Hartmut Löwen** studied physics at the University of Dortmund, Germany. In 1987, he received his Ph.D. degree in physics from Dortmund University on phase transitions in polaron systems. He then moved to the Ludwig-Maximilians-Universität München where he worked on surface melting and classical density functional theory. During a postdoctoral stay in Lyon (France), he started to do research on colloidal dispersions. Since 1995, he is full professor for Theoretical Physics at the University of Düsseldorf (Germany). His research concerns theoretical descriptions and computer simulations of soft matter systems.

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