Topics in soft and active matter physics

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November 1, 2016

I have chosen to look at the paper *Self-assembly of active colloidal molecules with dynamic function* [5], discussed with Ramin Golestanian.

1 Key achievements

Summarize in 500 words or fewer the key achievements of the paper you have chosen.

This paper looked at the self-assembled structures that emerge in a dilute mixture of a certain class of active colloids, which are analogous to molecules. The kind of active colloids studied are isotropic catalytic spherical colloids. These are colloidal spheres with an isotropic coating that catalyzes a chemical reaction that produces certain products. Unlike anistropically coated catalytic colloids, these particles do not self-propel, as there is no self-produced tangential gradient of product concentration.

However, such a gradient can be present due to the concentration profile produced by other catalytic colloids, providing a mechanism for the interaction of the active colloids. This concentration profile, formed by diffusion, decays with distance as $1/r$. Therefore, its gradient (and thus the diffusiophoretic velocity) decays as $1/r^2$. This interaction is analogous to an electrostatic interaction. A crucial difference, as the paper highlights, is that due to the independence of the material properties that control the rate of catalysis (the *activity*), and the phoretic response to a gradient (the *mobility*), the force exerted by particle 1 on particle 2, say, is generally different from that exerted by particle 2 on 1. As an intuitive picture, one can imagine how a homing missile can be "attracted" to a fighter jet, while the jet need not be attracted to it (in fact, quite the opposite). This action-reaction asymmetry is indicative of nonequilibrium, that can sustain currents at stationarity (often by frustrated situations, like the above analogy).

By simulating binary systems of such particles, where like particles repel, and unlike attract (although with different intensities), the authors find that several self-assembled structures can form. Furthermore, these can exhibit interesting dynamic behavior (or *function*, if one is looking at applications), which they theoretically analyze using a dissipative version of d'Alembert's principle. In particular, they find a configuration which sustains stable oscillations with a well defined frequency in a certain parameter regime. This is interesting, among other reasons, because it demonstrates a way nonequilibrium systems can form "clocks" even in an overdamped environment (low Reynolds number).

They also find a molecule which (in some parameter regime) has two stable configurations, such that one (the T isomer) is asymmetric and has net self-propulsion, while the other (the Y isomer) is asymmetric and does not self-propel. These stable configurations have an effective potential barrier that is overcome by thermal fluctuations once every mean residence time, on average. This is analogous to the run-and-tumble behavior observed in real bacteria (like *E. Coli*), with the T and Y configurations corresponding to the run and tumble phases, respectively. The tumbling may be due to actual rotational diffusion, or due to the symmetry of the configuration making three run directions equally probable. From a dynamical systems perspective, the parameter dependence of the calculated phase portraits for the conformations of these molecules show interesting bifurcations.

To conclude they remark that more complex structures should be possible, and they give an example of a self-assembled swimmer that breaks time-reversal symmetry, as done by some real biological micro-swimmers.

2 Importance in the scientific literature

Explain in 500 words or fewer why the paper turned out to be an important work in the scientific literature.

This paper is still very recent, and its importance can not be fully assessed yet. However, it has shown a very promising future direction of research that may lead to the realization of artificial systems that perform many of the functions of life. Biological systems are active systems that need to convert chemical and other forms of energy into useful work to perform their functions. Thus it is not surprising that active systems may be the most promising area for biomimetic goals.

Several active systems have been explored, including DNA machines [1], magnetically actuated robotic microswimmers [2], and artificial cilia [6]. However, this paper is (as far as I know), one of the first to look at very specific examples of dynamic function emerging from a system of active colloids. One of the advantages of active colloids is that they are relatively easy to experimentally realize and measure. Among the things the paper manages to highlight is that the "structure determines function" paradigm in protein biology may persist in designing artificial active systems.

The physical system in the paper is also relevant to explore the collective behavior of systems interacting with forces that break action-reaction symmetry. In addition, just like passive colloids have been a great model system to study certain simple condensed matter phases (like crystals), active colloids, like those proposed in the paper, can be model systems for more complicated phases of matter, like plasmas, or self-gravitating systems. These analogies are explored in a previous paper for the case of anisotropic (self-propelling) active colloids [4].

3 Shortcomings and limitations

Are there any significant shortcomings or limitations of the approach presented? (500 words or fewer).

There is a number of approximations and simplifications in the paper. These are clearly stated and are justified by either empirical facts of the models of interest, or by arguing that the neglected effects would only affect the results quantitatively, and not qualitatively (which is the aspect of interest in the paper).

To begin with, the catalytic activity of the colloids are simplified to be a net production or consumption of chemicals at specified rates. More realistically, the production and consumption rates will depend on the substrate and product concentrations and will follow the Michaelis-Menten rule. Depending on the reaction, the reaction kinetics may be more complicated. They also take the substrate concentration to be constant during the simulation time, which is a good approximation, as long as they are in the dilute limit.

The next assumption is that the Péclet number is small. The Péclet number measures the relative effect of advection and diffusion, and is $\mathrm{Pe} = V\sigma/D$, where V is the velocity of the colloid, σ is its diameter, and D is the diffusion coefficient of the solute molecules. This assumption means that the solute concentration profile relaxes very quickly to a comoving cloud when a colloidal particle moves. Empirically, it is found that for many active colloidal systems the Péclet number is indeed small, making this a good approximation. This also means that we can ignore the spontaneous symmetry breaking (spontaneous autophoretic motion of isotropic particles) that can happen at large Pe. They also do not consider the anomalous superdiffusion at relatively short time scales.

Another approximation is that the concentration fields are assumed to be far-field. Near-field fields would have to be calculated by solving the diffusion equation, and the resulting forces will in general not be pairwise additive. However, the near-field forces retain the action-reaction asymmetry, and it is thus argued that their effect would affect the dynamics only quantitatively. This approximation,

together with the inclusion of short-range steric forces (so the colloids can't overlap) makes their model an extension of the restricted primitive model of charged colloids. Furthermore, to reduce computational load, the Brownian dynamic simulation is done so that the colloids are constrained to move in 2D (while the diffusing particles diffuse in 3D, so the concentration still decays as $1/r$).

Finally, hydrodynamic interactions (which can contribute to both the far and near field) are ignored, but their effect is again argued in the paper to just change the dynamics quantitatively (and not qualitatively).

All these effects should potentially be included to quantitatively predict the behaviour of the a real experimental implementation of the system. This is a significant limitation of their results; however, the focus of the paper was on qualitative features, plus they clearly outline how to extend their treatment to make it more physically relevant.

4 Unanswered questions

What questions remained unanswered after this work? (500 words or fewer).

The first evident questions that remain unanswered regard the effect of the neglected mechanisms and approximations described above. They acknowledge that the dynamical function of the particular examples presented in the paper may not survive the inclusion of these effects. However, because the crucial property making these functions possible, the action-reaction symmetry breaking, will be retained, they say we should find configurations with similar functions. Still, the question of how these will actually arise in the more complete treatment remains unanswered. Of course, an experimental realization and study of the system would also be worth doing.

Probably the most interesting open question regards what kinds of more complex structures may be possible in this system. As I said, they show an interesting example of a tail-beating swimmer. It will be interesting to see which other kinds of functional structures are possible.

The self-assembly of other types of active colloids, in particular self-propelling (for instance, by asymmetric catalytic coating) colloids is an interesting extension not looked at, in this paper. Collective behavior of these types of particles is explored in other articles [4, 3]. The possibility of forming low-weight colloidal molecules from self-propelling colloids, is still unaddressed in this work.

Finally, the possible applications of this work remains an open question. Its potential to perform complex dynamical functions probably makes it relevant in some biomimetic systems. More generally, the ideas could be applicable in nanotechnology design, and have potential applications to medicine, microfluidics, materials science, and other disciplines where complex function is required at micro and nano scales.

References

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