Comment on "Which interactions dominate in active colloids?" [J. Chem. Phys. 150, 061102 (2019)]

M. N. Popescu, A. Domínguez, W. E. Uspal, et al.

View Online   Export Citation   CrossMark

Comment on "Which interactions dominate in active colloids?" [J. Chem. Phys. 150, 061102 (2019)]

View Online   Export Citation   CrossMark

M. N. Popescu,[1,a] (iD) A. Domínguez,[2,b] (iD) W. E. Uspal,[3,c] (iD) M. Tasinkevych,[4,d] (iD) and S. Dietrich[1,5,e]

AFFILIATIONS

[1] Max-Planck-Institut für Intelligente Systeme, Heisenbergstr. 3, D-70569 Stuttgart, Germany
[2] Física Teórica, Universidad de Sevilla, Apdo. 1065, 41080 Sevilla, Spain
[3] Department of Mechanical Engineering, University of Hawai'i at Manoa, 2540 Dole Street, Holmes 302, Honolulu, Hawaii 96822, USA
[4] Centro de Física Teórica e Computacional, Departamento de Física, Faculdade de Ciências, Universidade de Lisboa, Campo Grande P-1749-016, Lisboa, Portugal
[5] IV. Institut für Theoretische Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany

[a] Electronic mail: popescu@is.mpg.de
[b] Electronic mail: dominguez@us.es
[c] Electronic mail: uspal@hawaii.edu
[d] Electronic mail: mtasinkevych@fc.ul.pt
[e] Electronic mail: dietrich@is.mpg.de

https://doi.org/10.1063/1.5095716

Chemically active colloids (CAC) achieve motility by promoting, on catalytic parts of their surface, chemical reactions involving molecular species from the surrounding solution. Recently, they have been the subject of extensive research (see, e.g., the reviews in Refs. 1–3). The issue of the collective dynamics of such particles is a particularly difficult problem not only due to the intrinsic nonequilibrium character of the system but also due to the complex nature of the effective interactions—generically anisotropic—between the self-propelled CAC. This topic has been the subject of several experimental and numerical studies (see, e.g., Refs. 4–9), and recently it is receiving significantly increased theoretical interest (see, e.g., Refs. 10 and 11).

In this context, in Ref. 12, which deals with chemically active Janus colloids in unbounded suspensions, Liebchen and Löwen (LL) surprisingly claim "to demonstrate that phoretic interactions are generically important in active colloids ... and often seem to be the dominant far-field interactions," and "to derive a minimal description of these often neglected interactions."[12] Here, we demonstrate that their claim, that in the far field the phoretic interactions *generically* ("*often seem to*") dominate the

hydrodynamic ones, is flawed on account of the points detailed below. In addition, we point out that, contrary to the opinion of LL that such aspects have been neglected in the literature, the importance of the phoretic interactions is well known for more than a decade[13–15] and a number of systematic studies of systems with phoretic interactions only have been published.[16–21]

Our arguments are as follows:

(i) *In contrast to the claim by LL, the model of self-phoresis considered by them typically involves hydrodynamic interactions with precisely the same far-field decay as the unscreened phoretic ones; only in an exceptional case, the phoretic interactions are dominant in the far field.*

We set aside the issue of "screened" (i.e., exponentially decaying) phoretic interactions because asymptotically they cannot dominate the algebraically decaying hydrodynamic ones. (We note that, as discussed in Ref. 22, also in this case the far-field hydrodynamic flow exhibits, generically, a decay $\propto 1/r^2$.) In the case of unscreened phoretic interactions (i.e., with an inverse decay length $\kappa = 0$), LL use the conceptually simple model of self-diffusiophoresis of a particle as proposed in Ref. 23 and analyzed further in, e.g., Refs. 13, 24, and 25.

For this model, the behavior of the number densities of the chemical species and of the hydrodynamic field, associated with the chemically active character of the particle, is well understood. In spatial dimension three (i.e., in unbounded suspensions), the number densities decay as r^{-1} and thus the phoretic interactions, which are proportional to the gradient of the number densities, depend asymptotically on the distance r from the particle as r^{-2}.

As far as the hydrodynamic interactions are concerned, the model mentioned above implies that a spherical Janus particle immersed in a three-dimensional unbounded suspension induces a hydrodynamic flow decaying as r^{-2} (stresslet), where r is the distance from the particle (as pointed out in Ref. 13, and subsequently analyzed thoroughly in Ref. 25); this holds because a Janus particle has two hemispheres with different surface properties. Only in the *very special* case that the two faces (here denoted by "c"atalytic and "i"nert, respectively) of the Janus particle have exactly the same phoretic mobility coefficient, $\mu_c = \mu_i$, and that these are spatially constant over the corresponding hemisphere, the hydrodynamic flow field changes qualitatively to one which decays faster, i.e., $\propto r^{-3}$.

Therefore, the generic case is the one in which hydrodynamic and phoretic interactions decay equally $\propto r^{-2}$. Only in the rather exceptional case $\mu_i = \mu_c$ (exceptional because a Janus particle has two sides with *different* coatings), i.e., when $\mu_r := (\mu_i - \mu_c)/(\mu_i + \mu_c) = 0$ in the notation of LL, one can disregard the hydrodynamic interactions within a far-field approximation.

(ii) *Equation (9) in Ref. 12 is incompatible with the model [Eqs. (1), (3), and either (5) or (8) therein] if $\mu_r \neq 0$.*

The analysis discussed in Ref. 12 invokes a phoretic rotational response of the particle [see the second part of Eq. (5) or (8), respectively, depending on whether screened or unscreened phoretic interactions are considered]. Such a quantity can contribute only if $\mu_r \neq 0$. This implies, in accordance with the discussion in (i), the occurrence of a stresslet hydrodynamic field decaying $\propto r^{-2}$.

Consequently, Eq. (9) in Ref. 12 is incompatible with the remaining part of the self-phoretic Janus particle model. The model, claimed by the authors to be "generic," is actually internally inconsistent.

(iii) *It is an ad hoc procedure to discard, within a far-field theory and based on the analysis of their relative amplitudes (Sec. V in Ref. 12), one of the two contributions (phoretic or hydrodynamic), both of which exhibit the same far-field power law decay.*

Irrespective of their amplitudes, the two contributions can exhibit competing effects or, worse, decoupled ones. Based on a rigorous linear stability analysis concerning the isotropic and uniform density steady state of a dilute suspension of basically the same model CAC as considered by LL, Refs. 26–28 have shown precisely such a decoupling of the hydrodynamic and phoretic effects. The solutions of the corresponding eigenvalue problem consist of two subsets, the first one being "purely phoretic," i.e., exhibiting the same eigenvalues as one would have obtained by neglecting hydrodynamic interactions altogether and the second one being "purely hydrodynamic," i.e., the same as one would have obtained by neglecting phoretic interactions altogether. Accordingly, each of the phoretic and the hydrodynamic interactions induces its own set of stable or unstable perturbations, irrespective of the relative amplitudes

of the two contributions. There is no possibility of, e.g., canceling a linear instability of one type by a linear stability of the other type.

Finally, we briefly note that, because the experimental realizations of suspensions of CAC usually deal with particles sedimented near a wall, it may be the case that a "screening" of the hydrodynamic interactions occurs. While such effects are well understood for *driven* particles, the case of the "force- and torque-free" self-propelled CAC may be different and more involved (see, e.g., the recent discussion in Ref. 10). Irrespective of whether such a confinement-induced screening of hydrodynamic interactions occurs or not, the issue remains that the model proposed by LL builds upon Eqs. (1)–(9) in Ref. 12, the form of which holds only for unbounded suspensions. Accordingly, any extrapolation of such a model to be valid even in the case of confinement-induced screened hydrodynamic interactions gives rise to inconsistencies and leads solely to a heuristic, *ad hoc* mathematical formulation which is disconnected from the actual physical system.

REFERENCES

[1] J. Elgeti, R. G. Winkler, and G. Gompper, "Physics of microswimmers—Single particle motion and collective behavior: A review," Rep. Prog. Phys. **78**, 056601 (2015).

[2] C. Bechinger, R. Di Leonardo, H. Löwen, C. Reichhardt, G. Volpe, and G. Volpe, "Active particles in complex and crowded environments," Rev. Mod. Phys. **88**, 045006 (2016).

[3] J. L. Moran and J. D. Posner, "Phoretic self-propulsion," Ann. Rev. Fluid Mech. **49**, 511 (2016).

[4] J. Palacci, S. Sacanna, A. P. Steinberg, D. J. Pine, and P. M. Chaikin, "Living crystals of light-activated colloidal surfers," Science **339**, 936 (2013).

[5] I. Buttinoni, J. Bialké, F. Kümmel, H. Löwen, C. Bechinger, and T. Speck, "Dynamical clustering and phase separation in suspensions of self-propelled colloidal particles," Phys. Rev. Lett. **110**, 238301 (2013).

[6] I. Theurkauff, C. Cottin-Bizonne, J. Palacci, C. Ybert, and L. Bocquet, "Dynamic clustering in active colloidal suspensions with chemical signaling," Phys. Rev. Lett. **108**, 268303 (2012).

[7] B. Liebchen, D. Marenduzzo, I. Pagonabarraga, and M. E. Cates, "Clustering and pattern formation in chemorepulsive active colloids," Phys. Rev. Lett. **115**, 258301 (2015).

[8] M.-J. Huang, J. Schofield, and R. Kapral, "Chemotactic and hydrodynamic effects on collective dynamics of self-diffusiophoretic Janus motors," New J. Phys. **19**, 125003 (2017).

[9] M. Wagner and M. Ripoll, "Hydrodynamic front-like swarming of phoretically active dimeric colloids," Europhys. Lett. **119**, 66007 (2017).

[10] E. Kanso and S. Michelin, "Phoretic and hydrodynamic interactions of weakly confined autophoretic particles," J. Chem. Phys. **150**, 044902 (2019).

[11] N. Yoshinaga and S. Yabunaka, "Chapter 14. Theory of active particles and drops driven by chemical reactions: The role of hydrodynamics on self-propulsion and collective behaviours," in *Self-organized Motion: Physicochemical Design Based on Nonlinear Dynamics* (The Royal Society of Chemistry, 2019), pp. 339–365.

[12] B. Liebchen and H. Löwen, "Which interactions dominate in active colloids?," J. Chem. Phys. **150**, 061102 (2019).

[13] R. Golestanian, T. B. Liverpool, and A. Ajdari, "Designing phoretic micro- and nano-swimmers," New J. Phys. **9**, 126 (2007).

[14] W. E. Uspal, M. N. Popescu, S. Dietrich, and M. Tasinkevych, "Self-propulsion of a catalytically active particle near a planar wall: From reflection to sliding and hovering," Soft Matter **11**, 434 (2015).

[15] J. Simmchen, J. Katuri, W. E. Uspal, M. N. Popescu, M. Tasinkevych, and S. Sánchez, "Topographical pathways guide chemical microswimmers," Nat. Commun. **7**, 10598 (2016).

[16]S. Saha, R. Golestanian, and S. Ramaswamy, "Clusters, asters, and collective oscillations in chemotactic colloids," Phys. Rev. E **89**, 062316 (2014).

[17]O. Pohl and H. Stark, "Dynamic clustering and chemotactic collapse of self-phoretic active particles," Phys. Rev. Lett. **112**, 238303 (2014).

[18]O. Pohl and H. Stark, "Self-phoretic active particles interacting by diffusio-phoresis: A numerical study of the collapsed state and dynamic clustering," Eur. Phys. J. E **38**, 93 (2015).

[19]J. A. Cohen and R. Golestanian, "Emergent cometlike swarming of optically driven thermally active colloids," Phys. Rev. Lett. **112**, 068302 (2014).

[20]R. Golestanian, "Collective behavior of thermally active colloids," Phys. Rev. Lett. **108**, 038303 (2012).

[21]R. Soto and R. Golestanian, "Self-assembly of active colloidal molecules with dynamic function," Phys. Rev. E **91**, 052304 (2015).

[22]S. Y. Reigh, M.-J. Huang, J. Schofield, and R. Kapral, "Microscopic and continuum descriptions of Janus motor fluid flow fields," Philos. Trans. R. Soc., A **374**, 20160140 (2016).

[23]R. Golestanian, T. B. Liverpool, and A. Ajdari, "Propulsion of a molecular machine by asymmetric distribution of reaction products," Phys. Rev. Lett. **94**, 220801 (2005).

[24]S. Michelin and E. Lauga, "Phoretic self-propulsion at finite Peclét numbers," J. Fluid Mech. **747**, 572–604 (2014).

[25]M. N. Popescu, W. E. Uspal, Z. Eskandari, M. Tasinkevych, and S. Dietrich, "Effective squirmer models for self-phoretic chemically active spherical colloids," Eur. Phys. J. E **41**, 145 (2018).

[26]C. Hohenegger and M. J. Shelley, "Stability of active suspensions," Phys. Rev. E **81**, 046311 (2010).

[27]E. Lushi, R. E. Goldstein, and M. J. Shelley, "Collective chemotactic dynamics in the presence of self-generated fluid flows," Phys. Rev. E **86**, 040902 (2012).

[28]E. Lushi, R. E. Goldstein, and M. J. Shelley, "Nonlinear concentration patterns and bands in autochemotactic suspensions," Phys. Rev. E **98**, 052411 (2018).