The role of particle shape in active depletion

J. Harder$^1$, S. A. Mallory$^1$,*, C. Tung$^1$,*, and C. Valeriani$^2$ and A. Cacciuto$^1$†

$^1$Department of Chemistry, Columbia University
3000 Broadway, New York, NY 10027

and

$^2$Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Abstract

Using numerical simulations, we study how a solution of small active disks, acting as depletants, induces effective interactions on large passive colloids. Specifically, we analyze how the range, strength, and sign of these interactions are crucially dependent on the shape of the colloids. Our findings indicate that while colloidal rods experience a long-ranged predominantly attractive interaction, colloidal disks feel a purely repulsive force that is short-ranged in nature and grows in strength with the size ratio between the colloids and active depletants. For colloidal rods, simple scaling arguments are proposed to characterize the strength of these induced interactions.

* These three authors equally contributed to this work
† ac2822@columbia.edu
Introduction – Complex fluids and colloidal mixtures are some of the most ubiquitous substances on our planet. Aerosols, foams, emulsions, and gels have countless applications, and are the subject of intense scientific research across all disciplines. Recently, self-propelled or active colloidal systems have garnered considerable interest because of their exciting rheological properties and unusual phenomenological behavior. In contrast to traditional non-equilibrium systems, where directional driving forces emerge as a result of global changes of the thermodynamic variables or boundary conditions such as temperature and pressure, active systems are intrinsically out of equilibrium at the single particle level. The combination of this unique non-equilibrium driving force and the inherent stochastic nature of microscopic processes have endowed active systems with remarkable collective behavior. Self-propulsion is typically achieved by conversion of chemical or ambient free energy into consistent, directed motion. There are numerous examples of biological and synthetic active systems at the nanoscale, including the cytoskeleton of eukaryotic cells [1], bacterial suspensions, and catalytically activated colloidal particles [2–5]. In the latter case self-propulsion has been observed in platinum/gold and gold/nickel bi-laterally coated Janus nano-rods in the presence of H\textsubscript{2}O\textsubscript{2} [5–7], is also achieved in colloids where enzymatic reactions take place on one side of a particle [8], or can be driven by self-thermophoresis in defocused laser beams [9].

Although significant work has been carried out to understand the phenomenological behavior of self-propelled systems (for a recent review of the subject we refer the reader to reference [10]), we still have a poor understanding of how immersion into an active environment can affect the dynamic self-assembly pathways of large non-active bodies. This is a very important question in colloidal science where effective interactions (i.e. solvent mediated interactions) play a crucial role in stabilizing or driving self-assembly of colloidal particles.

One of the simplest ways of inducing a short range attraction among colloids is by taking advantage of the depletion effect which is an effective interaction achieved by the addition of numerous small, non-adsorbing components such as polymers (colloid-polymer mixtures) or colloids (asymmetric binary mixtures). The strength of this attraction increases linearly with the depletants’ concentration (the small particles) and the range is comparable to the depletants’ diameter. This attractive force is purely entropic and is due to an osmotic pressure difference when depletants are expelled from the region between two colloids [11].
In the simplest case where ideal polymers are used as depletants, this attraction takes the general form 
\[ F(r) = \pi \rho k_B T R^2 (1 - (r/2R)^2), \]
where \( r \) is the center-to-center distance between two colloids, \( R \) is the colloidal radius, \( \rho \) the density of depletant, and \( T \) is the system temperature. If \( \sigma \) is the diameter of the depletant, then the force between two colloids is present as long as \( r \leq (2R + \sigma) \). For sufficiently large attractions, usually controlled by the depletant’s concentration, phase separation will occur [12, 13]. The overall phase behavior as a function of polymer size and concentration has been thoroughly studied within the Oosawa-Asakura approximation [11, 14–16]. More recently there has also been an effort to characterize this force when the system is no longer in equilibrium [17].

In our previous work [18], we studied the thermomechanical properties of an active gas, and found that the force acting on two rods kept at a constant separation has an anomalous, non-monotonic dependence on the temperature — a notable deviation from the typical behavior of equilibrium systems. Two recent studies [19, 20] have further revealed that using active particles as depleting agents can give rise to behavior that is drastically different from that induced by passive depletants. In these works the forces induced by an active bath on two plates of a given length were measured, and layering effects and mid-to-long range interactions between plates were reported to develop when increasing the self-propulsion. Additionally, Angelani et al. [21] have recently shown that the depletion attraction alone cannot describe the effective interactions between passive colloids in a bath of active particles. In a way, it is therefore inaccurate to refer to these forces as active depletion, but we will nevertheless carry on with this nomenclature throughout the paper to keep the analogy with the parent equilibrium system.

In this paper, we go one step further and show how the strength, the sign and the range of this effective interaction can be controlled by tuning the geometry of the passive bodies in a way that is very different from what would be expected of their equilibrium counterparts. Specifically, we characterize how the effective interaction between two colloidal particles varies as a function of the magnitude of the self-propelling force of the depletant and the depletant-to-colloid size ratios. In addition, we highlight the strikingly different nature of the induced interaction when the colloids consist of rods or disks.

**Model** – We consider a two dimensional system of large, passive, colloidal particles of diameter \( \sigma_c \) immersed in a bath of smaller active particles of diameter \( \sigma \) and unit mass \( m \).
at a volume fraction $\rho_b$. Each active particle undergoes Langevin dynamics at a constant temperature, $T$, while self-propulsion is introduced through a directional force which has a constant magnitude $\vert F_a \vert$, along a predefined orientation vector, $n = [\sin(\theta), \cos(\theta)]$. The equations of motion of a bath particle are given by the coupled Langevin equations

$$
m \ddot{r} = -\gamma \dot{r} - \partial_r V(r) + \sqrt{2\gamma^2 D \xi(t)} + \vert F_a \vert n \quad \text{and} \quad \dot{\theta} = \sqrt{2D_r \xi_r(t)}$$

(1)

where $\gamma$ is the friction coefficient, $V$ the total conservative potential acting between any pair of particles, $D$ and $D_r$ are the translational and rotational diffusion constants, respectively (with $D_r = 3D/\sigma^2$). The typical solvent induced Gaussian white noise terms for both the translational and rotational motion are characterized by $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t) \cdot \xi_j(t') \rangle = \delta_{ij}\delta(t-t')$ and $\langle \xi_r(t) \rangle = 0$ and $\langle \xi_r(t) \cdot \xi_r(t') \rangle = \delta(t-t')$, respectively.

Bath particles are disks with diameter $\sigma$ which interact with each other via the Weeks Chandler Andersen (WCA) potential

$$U(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \frac{1}{4} \right]$$

(2)

with a range of interaction extending out to $r_{ij} = 2^{1/6} \sigma$. Here $r_{ij}$ is the center to center distance between any two particles $i$ and $j$, and $\epsilon$ is their interaction energy.

Suspended colloids are either rods or disks. The large colloidal disks interact with the bath particles through the same WCA potential defined above, with $\sigma_{ij} = (\sigma + \sigma_c)/2$, where $\sigma_c$ is the colloidal diameter. The rods are modeled as rectangular regions of width $\sigma_w = 2.5\sigma$ and vertical length $\ell$, and also repel the particles according to Eq. (2) where the separation $r_{ij}$ is the smallest distance between the particle the wall. Figure 1 shows a sketch of the model for disks. The strength of interaction for both the depletant-depletant interaction and the depletant-colloid interaction is chosen to be $\epsilon = 10k_B T$. The simulation box is a square with periodic boundary conditions, the Langevin damping parameter is set to $\gamma = 10\tau^{-1}$ (here $\tau$ is the dimensionless time), and the timestep to $\Delta t = 10^{-3}\tau$. Each simulation is run for a minimum of $3 \times 10^7$ iterations. All simulations were carried out using the numerical package LAMMPS [22].

Results – We first present the results for disk-shaped colloids. To understand the effective interactions induced by active bath particles on the suspended colloids, we proceed in two
FIG. 1. Schematic representation of two colloidal disks in a bath of active particles. The smaller, active components move according to Eq.1. The persistent force $|F_a|$ acts along a defined axis (as shown by the arrow as well as the colors, where red corresponds to the back of the particle and yellow the front).

ways: (1) We measure the radial distribution function $g(r)$ for a suspension of passive colloidal disks in the presence of the active depletants. In this case the large colloids move according to the Langevin dynamics in Eq.1, but with $|F_a| = 0$, and without the rotational component. (2) We calculate the effective force between two colloids by directly measuring the mean force acting on the particles when they are frozen in place as a function of the bath activity, colloidal shape (disks and rods), and colloid separation $r$.

For non-active equilibrium systems, the reversible work theorem provides a simple relationship between the potential of mean force and the radial distribution function, namely $U(r) = -k_B T \log [g(r)]$ [23]. Unfortunately, such a relation does not necessarily hold in the presence of an inherently out-of-equilibrium active bath. Nevertheless, from the $g(r)$ it is possible to extract qualitative information about the sign, strength and range of the interaction. To determine the $g(r)$, simulations were carried out with 100 colloidal disks of diameter $\sigma_c = 5\sigma$ immersed in an active bath at a density $\rho_b = 0.1$. The resulting radial distribution functions are shown in Fig. 2. Each simulation was run for over $10^8$ time-steps.

In the passive system with $|F_a| = 0$, the $g(r)$ presents a large peak at the colloid contact separation as expected for this system which is characterized by a strong depletion attraction. In other words, this peak indicates a significant likelihood of finding two colloids in contact with each other. When the bath is active, however, the radial distribution function is smaller than 1 for small colloid separations, which strongly suggests that there is an effective repulsion between the colloids.
To provide a more quantitative measurement of this repulsion and to better understand its nature, we proceed by performing simulations where two colloids are frozen in place and the force between them is measured directly from their interactions with the active bath particles. All results presented below are obtained at a constant volume fraction $\rho_b = 0.1$. The net force exerted on the two disks by the bath along the inter-colloidal axis was evaluated for two different colloidal sizes $\sigma_c = 5\sigma$ and $\sigma_c = 10\sigma$. The results are shown in Fig. 3.

FIG. 2. Radial distribution function $g(r)$ of the large colloids for three different values of self-propulsion $|F_a|$. In a passive bath (blue, solid) the expected peak signifies a short ranged attraction between colloids. In an active bath (dashed/dotted lines), $g(r)$ takes values which are less than 1, suggesting a repulsion between the colloids. This repulsion increases with the bath’s activity.

In a passive bath, the interaction between two large colloids is well understood and is given by the depletion attraction previously discussed. Surprisingly, as the bath becomes increasingly active, the effective interaction between the colloids becomes purely repulsive. This result is consistent with the observed behavior of the $g(r)$. The introduction of activity results in a repulsive force much larger than the depletion attraction observed in passive systems, and grows with the extent of the activity. Notice however, that the range of the interaction is rather insensitive to the propulsion strength, and extends to a distance of roughly half the colloidal diameter.

To better understand this phenomenon, we examine the duration of collisions between bath particles and the colloidal disks as well as where along the colloids’ surface these collisions take place. Here, we define the inner surface of a colloid (Region II Fig. 4(a))
FIG. 3. Effective rescaled forces $\langle F \rangle/|F_a|$ experienced by two colloidal disks as a function of separation for different values of depletant’s activity. (a) Shows the result for $\sigma_c = 5\sigma$ and (b) for $\sigma_c = 10\sigma$. For both sets of simulations $\rho_b = 0.1$. Rescaling is only applied as long as $|F_a| \neq 0$. Positive values correspond to a repulsion, which clearly dominates any depletion driven interaction when the bath is active. The larger the active force and the larger the colloid-to-depletant size ratio is, the stronger the repulsion.

As the half circle which lies closer to the center of the other colloid, and the outer surface (Region I Fig. 4(a)) as the half circle which is further away from the other colloid. When a bath particle strikes the outer surface of either of the large disks a force is generated with a net component, $F_I$, which pushes the disks toward each other. When a particle strikes the inner surface of either disk it generates a force with components, $F_{II}$, which pushes the disks away from each other (see Fig. 4(a) for a sketch of these forces). The effective force experienced by the two disks is determined by the number of particles at the surface of each region as well as by the average duration of a collision event.

Unlike equilibrium systems for which one expects a particle to bounce off a wall upon collision, the collision of an active particle with a wall is similar to that of a car driving into
FIG. 4. (a) Sketch showing the effective forces exerted on the disks by the active particles in the two different regions. (b) Snapshot from a simulation of two colloidal disks of diameter $\sigma_c = 10\sigma$, at $|F_a| = 50$. The two large disks experience a net repulsion due to the trapping of active bath particles. As in (a), the yellow portions of the particles indicate the direction along which the propulsive force is applied.

When the colloids are far apart, active particles have equal probability of striking either their inner or outer surfaces, leading to a zero net effective force between them. When the colloids are in contact, they form an object characterized by regions of both positive and negative curvature. The outer surfaces have positive curvature, and colliding particles can slide off rather quickly. The inner surfaces have negative curvature and can create a trap [24] for the active particles, greatly increasing the duration of a collision. The result is a net gradient in particle concentration along the colloidal surface, leading to the effective repulsion reported in our simulations (See Fig. 4(b) for a snapshot from our numerical simulations).

To determine the surface concentration gradient of bath particles, we compute a density map of the active particles around the disks at large and small separations (Fig. 5). As
FIG. 5. Density maps of active particles for $|F_a| = 50, \rho_b = 0.1$ around two colloidal disks of diameter $\sigma_c = 10\sigma$ at a center-to-center distance of $10\sigma$ (a), and $15\sigma$ (b). In both cases, it is clear that active particles aggregate on the colloid surfaces. When the colloids are in contact, a region of high active particle density can be seen near the effectively concave surface between the colloids. The scale bar corresponds to the density of the bath particles, and goes from a minimum of zero in the space occupied by the colloids to a maximum value near the point where the colloids meet in (a).

expected, when the disks are sufficiently far apart, there is no significant difference between the particle density on the inner and outer region. When the surface-to-surface separation between the disks is of the order of $2\sigma$ however, the inner density is significantly larger than the outer one resulting in the observed repulsion.

When disks are immersed in a passive bath, their attractive interactions increase with their diameter, this is simply due to the corresponding increase of the size of the excluded area. When active depletants are considered, a larger $\sigma_c$ implies a larger region where particles can be trapped. The net effect is therefore an enhanced repulsion between the colloids which can be seen by comparing the two plots in Fig. 3 showing that larger colloids experience larger repulsive forces. Finally, it should be noticed that the range of the interaction between disks is not very sensitive to the strength of the propelling force, and does not extend to separations much further than a fraction of the colloidal diameter.

We now turn our attention to the case of two colloidal rods. A system composed of two such rods was one of the earliest to be studied in the context of the depletion attraction. As was the case for disks, two rods in a bath of smaller particles experience an entropic attractive force which depends on the size of the excluded area, as well as the size and density of the depletants, and the temperature. This force can be large when compared
to that between two suspended disks due to the relatively larger excluded area when rods are in contact. Unlike colloidal disks, rods have no curved surfaces, so active bath particles which come into contact with the surface of a rod are effectively confined to move along this surface until they rotate away or slide to the end of the rod.

When the separation between the rods is small, we observe an oscillating attractive and repulsive force. As also reported in [20], this behavior is due to a competition between the forces exerted by the active particles on the outer surfaces, and the buildup of ordered layer of particles between the rods. (see Fig. 6(a)). Surprisingly, at larger separations (Fig. 6(b)), a large long-ranged attraction is induced between the rods. In agreement with [20] this attractive effective interaction can be well fit to an exponential and the range of the interaction is controlled by the effective persistence length of the path traced by the active particles (which should scale as $|F_a|/(\gamma D_r)$.) The inset of Fig. 6(b) shows the linear dependence of the interaction decay length $\ell_p$ as a function of activity $|F_a|$.

FIG. 6. Measured force (scaled by the active force) felt by two rods in a bath of active particles as a function of their separation for different strengths of self-propulsion. (a) Shows the behavior for small separations, ($r \sim \sigma$) while (b) shows the curve for large separations ($r \gg \sigma$). The inset in (b) shows how the decay length $\ell_p$ of the fitted exponential curves in the limit of large separations (a measure of the interaction range) grows linearly with the strength of the self-propulsion.

Further insight can be obtained by looking at the density map of the depletants for different rod separations (Fig. 7.) In the passive case, the density of bath particles is uniform throughout the simulation box. However, when the bath particles are active, they aggregate on the surfaces of the rods and there is a marked difference in local density on the different
rod surfaces. Specifically, once the rods are separated by more than $\sim 4\sigma$, there are more bath particles on the outer surfaces than on the inner ones, resulting in an attractive force between the rods. When the rods are at a smaller separation, the situation is the opposite.

![Density maps of active particles around larger rods.](image)

**FIG. 7.** Density maps of active particles around larger rods. (a) $|F_a| = 0$ at rod separation $r = 4\sigma$, (b) $|F_a| = 50$ at rod separation $r = 2\sigma$, (c) $|F_a| = 50$ at rod separation $r = 4\sigma$, and (d) $|F_a| = 50$ at rod separation $r = 6\sigma$. In the passive case (a), the bath particle density is uniform across the simulation box, resulting in no long range interaction between the rods. (b) shows the bath particle density profile around two rods in contact. (c) shows particles getting trapped in between the rods and giving rise to a net repulsion. In (d), the density of bath particles on the outside of the rods is greater than that inside, leading to the observed long-ranged attraction. As before, the scale bar shows the particle density, and goes from a minimum in the regions excluded by the rods to a maximum at points near the rod surfaces.

An estimate of how the force exerted on two rods at contact scales with their length and with the strength of the bath activity can be obtained with the following simple argument. In the diffusive limit (i.e. when the length of the rods is sufficiently large such that the particles can diffuse over their surface before sliding off) Fily et. al [25], have shown that for large self-propelling forces the typical time $t_1$ a particle remains in contact with a rod scales as $t_1 \sim \left( \frac{\gamma \ell}{|F_a|} \right)^{\frac{3}{2}} \left( \frac{1}{D_r} \right)^{\frac{5}{2}}$. During this time the particle will exert an average force on the
rod, that to leading order scales like $|F_a|$. The time required for a particle in a container of lateral size $L$ to find the rods can be estimated as $t_2 \sim \frac{L^2}{\ell} \frac{\gamma}{|F_a|}$, which accounts for the probability of finding the rod when moving at a speed $|F_a|/\gamma$ across the box. During this time the particle will exert no force on the rod. The net average force can then be estimated as $\langle F \rangle \simeq \frac{N|F_a|t_1}{t_1 + t_2}$, ($N$ is the number of active particles) and for sufficiently large systems, $t_2 \gg t_1$, it can be simplified to $\langle F \rangle \simeq N|F_a|t_1/t_2$, leading to the scaling behavior

$$\langle F \rangle \simeq \rho \left( \frac{|F_a|}{\gamma D_r} \right)^{\frac{1}{3}}$$

(3)

In the non-diffusive limit, when the rods are short and the force is so large that an active particle slides off of the surface before any diffusion can occur, $t_1 \sim \ell \gamma/|F_a|$, the average force should scale as

$$\langle F \rangle \simeq \rho |F_a| \ell^2$$

(4)

For long rods or weak propelling forces, the residence time of the particles on the surface is simply controlled by the rotational diffusion $t_1 = 1/D_r$. In fact, in these cases a particle leaves the surface as soon as its axis turns away from the surface’s normal, with $\langle \theta^2 \rangle = (\pi/2)^2 = 2D_r t_{1,\text{max}}$ as the upper bound. In this limit the average force should scale as

$$\langle F \rangle \simeq \rho \frac{|F_a|^2 \ell}{\gamma D_r}$$

(5)

Finally, whenever $t_1 \gg t_2$ (for sufficiently high densities) one should expect to first order $\langle F \rangle \simeq |F_a|(1 - \frac{t_2}{t_1})$.

Deviations from this simple scaling are also expected at moderate and large densities due to the excluded volume interactions between particles. Figures 8 and 9 show how the force between the rods scales with the strength of the activity and with the length of the rods in our simulations. Our numerical data have been taken at density $\rho_b = 0.1$, which is sufficiently low to prevent any bulk phase separation or aggregation of the active particles, yet, it is large enough to give non-negligible excluded volume effects. The relatively short length of the rods, $\ell = 10\sigma$, in these simulations implies that Eq. 4 should give the most appropriate description for the effective force. This is consistent with Fig. 8, that shows a linear dependence of the force with $|F_a|$ in the large propulsion limit. When $|F_a|$ is small, we expect $\langle F \rangle$ to depend quadratically on $|F_a|$. In fact, in this case the rotational diffusion is fast enough to limit the persistence-time of the particles on the colloidal surface, thus
FIG. 8. Effective force between two rods in contact with each other and in the presence of active depletants as a function of self-propulsion $|F_a|$ for rods of length $\ell = 10\sigma$, at $\rho_b = 0.1$ and box side length $L = 77\sigma$. The dashed line is a linear fit to the net force at high bath activity and shows that our simulation results are consistent with Eq. 4.

$|F_a|$ will contribute to the average force a quadratic (thermal-like) term corresponding to an enhanced velocity of the particles [18].

The analysis for the dependence on the length of the rods is a bit more complicated. The problem is that the short $\ell$ limit is characterized by a short residence time that is inversely proportional to the self-propulsion, it grows linearly with $\ell$, and for which clearly $t_2 \gg t_1$. As $\ell$ becomes larger (up to $\ell = 80\sigma$), $t_1$ should scale as $t_1 \sim (\gamma\ell |F_a|^{\frac{2}{3}})(\frac{1}{D_e})^{\frac{1}{3}}$ (as long as...
$t_1 < 1/D_r$), however, as the particles’ residence time becomes longer, the average number of particles at contact becomes larger, and for moderate volume fractions, the assumption that $t_2 \gg t_1$ becomes less adequate. To complicate matters even further, for large $\ell$, excluded volume interactions begin to matter, and local self-trapping of the particles may effectively increase of $t_1$ to values larger than $1/D_r$, so that the time to rotationally diffuse away from the surface may become faster than the time required to slide off the surface edge; making Eq. [5] more appropriate in this regime. This phenomenon is quite visible in our simulations for the longest rods ($\ell = 80\sigma$), where diffusive correlated motion of linear clusters of active particles over the rod surfaces takes place. At significantly lower densities than the ones considered in this paper, we would have expected Eq. [3] to hold, but at $\rho_b = 0.1$, all these effects become relevant. We therefore expect a combination of Eq. [4] and Eq. [5] to provide a good approximation to our data. Indeed, in the long rod limit the average force seems to be well fitted by a linear dependence on $\ell$.

Conclusions – In this paper, we have studied the effective interactions induced by small active components on large passive colloidal particles as a function of the strength of the propelling force of the active bath and of the geometry of the colloids. Our results indicate that the induced colloidal interactions are crucially dependent on their shape, and that while a long ranged, predominantly attractive interaction is induced between rods, disks undergo a purely short range repulsion that grows in strength with the size ratio between the colloid and the active component. Crucial to this difference is the role of curvature, which determines whether passive bodies act as traps or as efficient scatterers of active particles. For instance, we have recently shown how curvature can be exploited to activate C-shaped passive bodies, by creating density gradients across the colloids [26].

Although our study has been performed in two dimensions, the essence of our results should be easily extendable to three dimensions when considering colloidal rods and spheres. Our work further highlights the many differences between the effective forces induced by small active components and those produced by the corresponding equilibrium system, and suggests that active depletion can have dramatic consequences on both the phase behavior and the self-assembly of differently shaped colloids, with possible applications in material engineering and particle sorting.
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[1] B. Alberts, A. Johnson, J. Lewis, M. Raff, K. Roberts, and P. Walter, Molecular Biology of the Cell, 5th ed. (Garland Science, New York & Oxford, 2008).
[2] J. Gibbs and Y. Zhao, Frontiers of Materials Science 5, 25 (2011).
[3] R. Golestanian, T. B. Liverpool, and A. Ajdari, Phys. Rev. Lett. 94, 220801 (2005).
[4] J. Palacci, B. Abécassis, C. Cottin-Bizonne, C. Ybert, and L. Bocquet, Phys. Rev. Lett. 104, 138302 (2010).
[5] W. F. Paxton, P. T. Baker, T. R. Kline, Y. Wang, T. E. Mallouk, and A. Sen, J. Am. Chem. Soc. 128, 14881 (2006).
[6] R. F. Ismagilov, A. Schwartz, N. Bowden, and G. M. Whitesides, Angew. Chem. Int. Ed. 41, 652 (2002).
[7] S. Fournier-Bidoz, A. C. Arsenault, I. Manners, and G. A. Ozin, Chem. Commun. 41, 441 (2005).
[8] N. Mano and A. Heller, J. Am. Chem. Soc. 127, 11574 (2005).
[9] H. R. Jiang, N. Yoshinaga, and M. Sano, Phys. Rev. Lett. 105, 268302 (2010).
[10] M. C. Marchetti, J. F. Joanny, S. Ramaswamy, T. B. Liverpool, J. Prost, M. Rao, and R. A. Simha, Rev. Mod. Phys. 85, 1143 (2013).
[11] S. Asakura and F. Oosawa, J. Polym. Sci. 33, 183 (1958).
[12] Y. Fily and M. C. Marchetti, Phys. Rev. Lett. 108, 235702 (2012).
[13] J. Stenhammar, D. Marenduzzo, R. J. Allen, and M. E. Cates, Soft Matter 10, 1489 (2014).
[14] M. Dijkstra, J. M. Brader, and R. Evans, J. Phys.: Condens. Matter 11, 10079 (1999).
[15] M. Dijkstra, R. van Roij, and R. Evans, Phys. Rev. E 59, 5744 (1999).
[16] M. Dijkstra, R. van Roij, R. Roth, and A. Fortini, Phys. Rev. E 73, 041404 (2006).
[17] J. Dzubiella, H. Löwen, and C. N. Likos, *Phys. Rev. Lett.* **91**, 248301 (2003).

[18] S. A. Mallory, A. Šarić, C. Valeriani, and A. Cacciuto, *Phys. Rev. E* **89**, 052303 (2014).

[19] D. Ray, C. Reichhardt, and C. J. Olson Reichhardt, arXiv:1402.6372.

[20] R. Ni, M. A. Cohen Stuart, and P. G. Bolhuis, arXiv:1403.1533.

[21] L. Angelani, C. Maggi, M. L. Bernardini, A. Rizzo, and R. Di Leonardo, *Phys. Rev. Lett.* **107**, 138302 (2011).

[22] S. Plimpton, Journal of Computational Physics **117**, 1 (1995).

[23] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford University Press, 1987).

[24] E. J. Marsden, C. Valeriani, I. Sullivan, M. E. Cates, and D. Marenduzzo, *Soft Matter* **10**, 157 (2014).

[25] Y. Fily, A. Baskaran, and M. F. Hagan, *Soft Matter* **10**, 5609 (2014).

[26] S. A. Mallory, C. Valeriani, and A. Cacciuto, arXiv:1407.3418.