An Active Approach to Engineering the Microscopic

Stewart A. Mallory

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences

COLUMBIA UNIVERSITY

2017
ABSTRACT

An Active Approach to Engineering the Microscopic

Stewart A. Mallory

Active colloids, which can be thought of as the synthetic analog of swimming bacteria, exhibit remarkable collective behavior. Using a combination of computer simulations and analytical theory, I have looked to provide quantitative answers to fundamental questions concerning the phase behavior and material properties of active suspensions. A primary focus of my Ph.D work has been devoted to developing novel techniques to exploit the active nature of these particles to manipulate and self-assemble matter at the colloidal scale. In the introductory chapter, I discuss recent advances in the self-assembly of self-propelled colloidal particles and highlight some of the most exciting results in this field. The remaining chapters are each self-contained and focus on a particular topic within active colloidal self-assembly. These chapters are ordered in terms of system complexity, and begins with characterizing the thermomechanical properties of an ideal active fluid. The next three chapters are centered around characterizing the effective interactions induced by an active suspension. The last two chapters focus on using self-propulsion as a tool to improve colloidal self-assembly, and understanding the interplay between self-propulsion and anisotropic pair interaction.
Contents

List of Figures iv

Acknowledgements xviii

1 Introduction to Active Colloidal Self-Assembly 1

1.1 Self-Assembly 1

1.2 Active Matter 3

1.3 Active Colloids 5

1.4 Self-assembly with ABPs 10

1.5 Can Activity Improve Self-Assembly? 24

1.6 Conclusions 29

2 Anomalous Thermomechanical Properties of a Self-propelled Colloidal Fluid 31

2.1 Introduction 31

2.2 Model 33

2.3 Discussion of Thermomechanical Properties 34

2.4 Applications: Effective Force from an Active Bath 45

2.5 Appendix: Analytical Calculation Details 47
<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>The Role of Particle Shape in Active Depletion</td>
<td>51</td>
</tr>
<tr>
<td>3.1</td>
<td>Introduction</td>
<td>51</td>
</tr>
<tr>
<td>3.2</td>
<td>Model</td>
<td>54</td>
</tr>
<tr>
<td>3.3</td>
<td>Numerical Results</td>
<td>57</td>
</tr>
<tr>
<td>3.4</td>
<td>Conclusions</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>Curvature Induced Activation of a Passive Tracer in an Active Bath</td>
<td>73</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction</td>
<td>73</td>
</tr>
<tr>
<td>4.2</td>
<td>Model</td>
<td>75</td>
</tr>
<tr>
<td>4.3</td>
<td>Numerical Results</td>
<td>77</td>
</tr>
<tr>
<td>4.4</td>
<td>Analysis of Tracer Motion</td>
<td>81</td>
</tr>
<tr>
<td>4.5</td>
<td>Conclusion</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Anomalous dynamics of an elastic membrane in an active fluid</td>
<td>90</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>90</td>
</tr>
<tr>
<td>5.2</td>
<td>Methods</td>
<td>93</td>
</tr>
<tr>
<td>5.3</td>
<td>Results</td>
<td>96</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusions</td>
<td>102</td>
</tr>
<tr>
<td>6</td>
<td>Activity-assisted self-assembly of colloidal particles</td>
<td>104</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>104</td>
</tr>
<tr>
<td>6.2</td>
<td>Additional simulation details</td>
<td>116</td>
</tr>
<tr>
<td>6.3</td>
<td>Derivation of MSD and Swim Pressure for oscillating Swimming Speed</td>
<td>119</td>
</tr>
<tr>
<td>7</td>
<td>Self-assembly of active amphiphilic Janus particles</td>
<td>122</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>7.1 Introduction</td>
<td>122</td>
<td></td>
</tr>
<tr>
<td>7.2 Model</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>7.3 Results</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>7.4 Discussion and conclusions</td>
<td>143</td>
<td></td>
</tr>
</tbody>
</table>

Bibliography 146
List of Figures

1.1 Macroscopic analogy for self-assembly. ........................................ 2

1.2 (a) Sketch of the propulsion mechanism for the active colloid synthesized by Howse et al. [35]. The platinum cap (shown in red) decomposes hydrogen peroxide into water (light blue) and oxygen (dark blue) resulting in an oxygen gradient across the particle. Panel a was adapted from ref [42] with permission from The Royal Society of Chemistry. (b) Typical trajectories of the active colloid synthesized by Howse et al. at various hydrogen peroxide fuel concentrations. Panel b reproduced with permission from American Physical Society. .......................................................... 7

1.3 Simulation snapshots of purely repulsive ABPs at two different volume fractions $\phi = 0.39$ (top row) and $\phi = 0.7$ (bottom row). The left column are snapshots from a system of passive particles while the right column shows the corresponding phase in the limit of very large self-propulsions. Particles are colored according to cluster size. Image reproduced with permission from American Physical Society from ref [102] . ............................ 12
1.4 (a) Top panel: Phase behavior of isotropically attractive ABPs at an area fraction $\phi = 0.4$ presented as a function of interparticle attraction strength $U$ and Peclet number $Pe = (v_p\sigma)/D$. The colors aid to distinguish the different phases: near-equilibrium gel states (green/upper-left), single-phase active fluids (red/center), and MIPS states (blue/right). (a) Bottom panel: Detailed snapshot at fixed interaction energy $U = 4k_B T$. At $Pe=4$ (left), the system forms a kinetically arrested attractive gel. At $Pe = 20$ (center), the attraction suppresses phase separation and produces a homogeneous fluid characterized by transient large density fluctuations. At $Pe = 100$ (right) MIPS is observed. (Panel reproduced with permission from American Physical Society from [119]. (b) Snapshots of spherical ABPs interacting via a short-range attractive and a long-range resulsive potential at two different volume fractions $\phi = 0.24$ (left) and $\phi = 0.55$ (right). From top to bottom: $Pe = 0, 10, 20$. At $Pe = 10$, meso-phases of living crystals are observed at lower densities, and living stripes are seen at higher densities. (c) Snapshots of self-propelled dumbbells interacting via a short-range attractive and a long-range resulsive potential at $\phi = 0.24$. From left to right we observe at $Pe = 0$ (static clusters), at $Pe = 5$ (rotating clusters), at $Pe = 15$ (living clusters) and at $Pe = 40$ (fluid phase). Panels $b$ and $c$ reproduced with permission from The Royal Society of Chemistry from [126]
1.5 (a) Dipolar Janus ABPs where both the sign and magnitude of the charge on each hemisphere can be controlled to impose different collective behavior. The sign of the charge (positive and negative) are color coded (red and blue), their relative magnitude is indicated by the respective dot size, and the black arrows indicate the propelling directions. Panels (b) to (d) show typical snapshots for the different phases, including (b) active chains, (c) swarms and (d) clusters. The white hemispheres represent the leading sides and the red hemispheres the trailing sides. The blue arrow in panel (c) marks the global direction of the swarm. Image reproduced with permission from Nature [141]. . .

1.6 Left panel: (A) Sketch of the assembly of OTS modified amphiphilic Janus ABPs from [142], with the hydrophobic OTS sides (in gray) facing one another. (B) Typical configurations (a—d) of a pair of amphiphilic Janus ABPs (Scale bar, 1 μm). (C) Typical assemblies of amphiphilic Janus ABPs triplet assemblies: (a—c) movement of triplet assemblies with different orientations (Scale bar, 1 μm). Reproduced with permission from the American Chemical Society from [142]. Right panel: Plot representing the angular speed of possible dimer conformations. The intensity of the shaded regions show counterclockwise (red) and clockwise (blue) rotations of the dimers. Reproduced with permission from American Physical Society from [143] . . . . . . . . . . . . . . . . .
1.7 Left panel: (a) Sketch of a triangular building block with two attractive sides.
   The white arrow indicates the direction of self-propulsion. (b) The target
   structure to be self-assembled is a hexagonal capsid composed of six colloidal
   building blocks. (c) Typical disordered aggregate formed when the attraction
   between the triangles is too strong. (d) Percent yield of target structure as
   a function of the strength of the attractive interaction for passive colloids.
   Right panel: Anti-aligned (top) and aligned (bottom) configurations of a pair
   of triangular particles. .................................................. 26

2.1 (a) Pressure in two-dimensional system as a function of temperature for sev-
   eral values of $|F_a|$. (b) The same curve as (a) for $T < 2$. (c) Pressure as a
   function of the box radius where $|F_a| = 20$ for several values of $T$. All solid
   lines are plotted using Eq. (2.8) and the corresponding system variables. ... 35

2.2 (a) Pressure in three-dimensional system as a function of temperature for sev-
   eral values of $|F_a|$. (b) The same curve as (a) for $T < 2$. (c) Pressure as a
   function of the box radius where $|F_a| = 20$ for several values of $T$. All solid
   lines are plotted using Eq. (2.8) and the corresponding system variables. ... 36

2.3 (a) Pressure in two-dimensional system as a function of $|F_a|$ for several values
   of $T$. (b) The same curve as (a) for $|F_a| < 50$. The solid lines in (a) and (b)
   correspond to Eq. (2.8). (c) The fraction of particles, $\beta$, that are within one
   particle radius from the boundary as a function of $|F_a|$ for various values of $T$. 38
2.4 Pressure in three-dimensional system as a function of $|F_a|$ for several values of $T$. (b) The same curve as (a) for $|F_a| < 50$. The solid lines in (a) and (b) correspond to Eq. (2.8). (c) The fraction of particles, $\beta$, that are within one particle radius from the boundary as a function of $|F_a|$ for various values of $T$. 39

2.5 Compressibility factor, $Z$, for three (a) and two (b) dimensional systems as a function of volume fraction, $\phi$, for different values of the active force, $|F_a|$, at $T = 1$. The dashed line indicates the non-active ideal case. 43

2.6 Distribution of the dot products between the propelling axis of a particle and the normal to the wall at the particle’s location for various volume fractions of interacting particles in both three (a) and two (b) dimensions. Only particles within a range of $\sigma$ from the wall are considered for this analysis. The log scale in the vertical axis has been chosen to better highlight the difference between the curves. The value of the active force is $|F_a| = 20$. 45

2.7 Non-monotonic behavior of the effective force, $\langle F_0 \rangle$, induced by an active gas on two plates held at fixed contact distance as a function of $T$. The value of the active force is $|F_a| = 25$. 46

3.1 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). 56
3.2 Radial distribution function \(g(r)\) of the large colloids for two different values of self-propulsion \(\beta F_0 \sigma\). In a passive bath (blue, solid) the expected peak signifies a short ranged attraction between colloids. In an active bath (dashed line), \(g(r)\) takes values which are less than 1, suggesting a repulsion between the colloids. This repulsion increases with the bath’s activity.

3.3 Effective rescaled forces \(\langle F/F_0 \rangle\) 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 \(\phi_b = 0.1\). Rescaling is only applied as long as \(\beta F_0 \sigma \neq 0\). 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.

3.4 (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 \(\beta F_0 \sigma = 50\). 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.[178]
3.5 Time averaged density maps of active particles for $\beta F_a \sigma = 50, \phi_b = 0.1$ 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).  

3.6 Effective force between two disks in contact and in the presence of active depletants as a function of self-propulsion $\beta F_a \sigma$ for disks of diameter $\sigma_c = 10\sigma$ and $20\sigma$, at $\phi_b = 0.1$ and box side length $L = 150\sigma$. The inset shows that for moderate active forces, an enhanced attraction is observed.  

3.7 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 particle persistence length $d/\sigma = \beta F_a \sigma/3$. 
3.8 Time averaged density maps of active particles around larger rods. (a) $\beta F_a \sigma = 0$ at rod separation $r = 4\sigma$, (b) $\beta F_a \sigma = 50$ at rod separation $r = 2\sigma$, (c) $\beta F_a \sigma = 50$ at rod separation $r = 4\sigma$, and (d) $\beta F_a \sigma = 50$ 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.

3.9 Effective force between two rods in contact with each other and in the presence of active depletants as a function of self-propulsion $\beta F_a \sigma$ for rods of length $\ell = 10\sigma$, at $\phi_b = 0.1$ 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. 3.4.

3.10 Effective force between two rods in contact with each other and in the presence of active depletants as a function of rod length for $\beta F_a \sigma = 50$, at $\phi_b = 0.1$ and box side length $L = 200\sigma$. A linear fit is also plotted, showing that our simulation results are consistent with Eq. 3.5.
4.1 (Color online) (a) Trajectories for tracers of various curvatures immersed in an active bath of volume fraction $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$. The trajectory for each tracer was taken over a duration of $5000\tau$ and each tracer was initially located at the origin. (b) Snapshot from simulation with $R = 8$, $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$ where both the laboratory and body-centered reference frames are shown. The orange half of a bath particle denotes the direction of propulsion. ................................. 78

4.2 (a) MSD for tracers of various curvatures immersed in an active bath of volume fraction $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$. (b) Mean displacement of the tracer along the $A$ axis in the body centered frame. (c) Sketch of the model and relative variables discussed in the paper. ................................. 79

4.3 Normalized time averaged active particle density for various tracers in an active suspension of $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$. ................................. 80

4.4 Rotational diffusion constants for tracer particles having different curvatures in an active suspension of $\phi = 0.005$ and $T = 1$. The data is plotted as a function of the active bath self-propelling force $|F_a|$. ................................. 81

4.5 (a) Effective force, $\langle F_A \rangle$, induced by the active particle on the tracer as a function of propulsion $|F_a|$ for various tracer curvatures. (b) Collapse of $\langle F_A \rangle$ as a function of $R$ for different values of $|F_a|$. The dashed line corresponds to Eq. (4.15) with a single fitting parameter $\kappa = 0.40(0)$ in the prefactor. ................................. 86
5.1 (Color online) Reference snapshots showing the various conformations taken by the membrane as the bath activity and bending rigidity is varied. (A) flat/extended, (B) bent, (C) single folded, and (D) multi-folded. .......................... 92

5.2 (Color online) The time average of the radius of gyration \( \langle R_g \rangle \) (left) and asphericity \( \langle A \rangle \) (right) as a function of \( Pe \) for membranes of different bending rigidities \( \kappa_b \). ................................................................. 95

5.3 (Color online) Probability distribution of the radius of gyration \( P(R_g) \) for membranes of increasingly large Peclet numbers. Different panels show the results for different bending rigidities of the membrane as indicated. The letters in parenthesis indicate the corresponding configurations as shown in Fig. 5.1. ................................................................. 96

5.4 (Color online) Probability distribution of the asphericity \( P(A) \) for membranes of increasingly large Peclet numbers. Different panels refer to different bending rigidities of the membrane as indicated. The letters in parenthesis indicate the corresponding configurations as shown in Fig. 5.1. .......................... 98

5.5 (Color online) Joint probability distribution of the membrane shape \( P(A, R_g) \) for a fixed Peclet number \( Pe = 50 \) and various bending rigidities. .......................... 100
6.1 (A) The colloidal building blocks have been functionalize such that two of the three faces exhibit a short range attraction. The white arrow indicates the direction of self-propulsion. (B) The target structure to be self-assembled is a hexagonal capsid composed of six colloidal building blocks. (C) Typical disordered aggregate formed when the attraction between colloids is too strong. (D) Percent yield of target structure as a function of the strength of the attractive interaction $\varepsilon$ for passive colloids ($F_a \sigma = 0 \ k_B T$).

6.2 Percent yield of the target structure as a function of time for binding energy $\varepsilon \approx 11 \ k_B T$ and several values of the self-propelling force $F_a$.

6.3 Percent yield of the target structure as a function of the binding energy $\varepsilon$ and the self-propelling force $F_a$. The white number at the center of the circle indicate the relative increase in the rate of the assembly process, $\nu_{SA}$, with respect to the best performing passive case that occurs for $\varepsilon \approx 16 \ k_B T$.

6.4 (A) Anti-aligned and (B) aligned binding configurations for this choice of colloidal building block. The introduction of self-propulsion stabilized the aligned configuration and destabilize the anti-aligned configuration.

6.5 Percent yield for colloids with a periodic self-propelling force. The self-propelling force $F_a \sigma = 25 \ k_B T$ is turned on for a time $\tau_{on}$ and then turned off for a time $\tau_{off}$. The interaction energy is fixed at $\varepsilon \approx 16 \ k_B T$. The white number at the center of the circle indicate the relative increase in speed of the assembly process $\nu_{SA}$.
7.1 Three patch coverages (in black) from left to right are $C = 0.25$, $C = 0.50$, and $C = 0.75$. The large arrow indicates the propulsion direction. The top row corresponds to patchy colloids propelled in the direction of the patch ($WP$), whereas the bottom row against the patch ($AP$).

7.2 (a) Snapshot of the stable trimer structure for passive suspension of APPs with patch coverage $C' = 0.25$. (b) Typical configuration observed for binding energy $\varepsilon = 20$.

7.3 (a) Average degree of aggregation $\langle \Theta \rangle$ as a function of $\varepsilon$ for passive suspension with $C = 0.25$. (b) Average degree of aggregation $\langle \Theta \rangle$ as a function of $v_p$ for active suspension with $C = 0.25$. Two different binding energies are considered: $\varepsilon = 12$ (light green) and $\varepsilon = 20$ (magenta). Solid lines correspond to the (WP) case, while the (AP) case is given by the dotted lines.

7.4 (a) Average degree of aggregation $\langle \Theta \rangle$ as a function of $\varepsilon$ for passive suspension with $C = 0.50$. (b) Average degree of aggregation $\langle \Theta \rangle$ as a function of $v_p$ for active suspension with $C = 0.50$. Two different binding energies are considered: $\varepsilon = 12$ (light green) and $\varepsilon = 20$ (magenta). Solid lines correspond to the (WP) case, while the (AP) case is given by the dotted lines.

7.5 Typical simulation snapshot for active patchy particles with patch coverage $C = 0.50$ and $\varepsilon = 12$. The passive reference system $v_p = 0$ is given at the top of the figure. The (WP) case is given in the left column while the (AP) case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.
7.6 Typical simulation snapshot for active patchy particles with patch coverage $C = 0.50$ and $\varepsilon = 20$. The passive reference system $v_p = 0$ is given at the top of the figure. The (WP) case is given in the left column while the (AP) case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.

7.7 Average radius of gyration $\langle R_g \rangle$ as a function of cluster size $S$ for binding energy $\varepsilon = 20$. The WP case shows a clear compaction of the clusters with increasing $v_p$, while the AP case exhibits reentrant behavior where clusters undergo an elongation before an eventual collapse as $v_p$ increases.

7.8 (a) Average degree of aggregation $\langle \Theta \rangle$ and average cluster size $\langle S \rangle$ for passive suspension of patchy particles with patch coverage $C = 0.75$ as a function of the binding energy $\varepsilon$. (b) Fraction of particles in clusters of a given size range as a function of the binding energy $\varepsilon$. (c) Simulation snapshots for various values of the binding energy $\varepsilon$.

7.9 Typical simulation snapshot for active APPs with patch coverage $C = 0.75$ and $\varepsilon = 12$. The passive reference system $v_p = 0$ is given at the top of the figure. The (WP) case is reported in the left column whereas the (AP) case in the right column. Each snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.
7.10 Typical simulation snapshot for active APPs with patch coverage $C = 0.75$ and $\varepsilon = 20$. The passive reference system $u_p = 0$ is given at the top of the figure. The $(WP)$ case is given in the left column while the $(AP)$ case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.

7.11 (a) Average degree of aggregation $\langle \Theta \rangle$ for all patch coverages considered in this study.
Acknowledgements

First and foremost, I would like to thank my thesis advisor Angelo Cacciuto. There are no proper words to convey my deep gratitude for his unwavering support. Over the past 5 years and through countless conversation, Angelo has imprinted on me the skill I value the most, which is the ability to think carefully and deeply about my scientific research. The atmosphere Angelo has cultivated in his group is truly one of a kind. It is not only intellectually stimulating, but an incredibly enjoyable place to work. In this moment of reflection, it is clear to me that attending Columbia was the right choice, and much of that can be attributed to the opportunity to work with Angelo. His approach to scientific research, limitless creativity and enthusiasm make him the kind of scientist I aspire to be.

My sincerest thanks to the members of my thesis committee: Professors Luis Campos, David Reichman, Kyle Bishop, Xavier Roy and Bruce Berne. Thank you for generously giving your time and valuable comments to improving my work. I am also grateful to my collaborators Chantal Valeriani and Yan Yu. Thank you for lending me your expertise and intuition. Chantal has also been a great host during my time at Universidad Complutense de Madrid, and I appreciate her continuing friendship and advice.

The Cacciuto group has been an amazing place to work these past five years. I would like to thank Andela Saric for her willingness to help me when I first entered the group.
I could have not asked for a better coworker and friend. I also owe a debt of gratitude to Clarion “The Chemist” Tung and Joseph ”J-Hard” Harder. I have spent nearly everyday over the last 5 years working and hanging out with you guys, and it is something I will miss deeply. Lastly, my friends at Columbia have made these past five years extremely bearable. They are too many to name but I would like to highlight a few who I could not have done without: Gaschner, Campos, Peter, Josh, Tim Su, Tim & Glen, and the SHP Crew. Thank you all for being my friend.

I want to express my sincere gratitude to my family for their unconditional love and support. I am especially grateful to my mother for her constant willingness to help me with just about anything. I would also like to thank my brothers: Aaron, Austin, Grant, John, and Phillip. You all continue to be a beacon of inspiration for me. Lastly, and most importantly I would like to thank my wife Jill. Without your love and support, none of this would have been possible. In the words of Kevin Durant, ”You’re the real MVP.”
For my wife Jill

“Obviously there is the scientific side to our journey, but what we are really chasing is the magical side, the demons, the new gods. This is the itinerary we have set for ourselves no matter how strange things may eventually get.”

— Werner Herzog, Into the Inferno
Chapter 1

Introduction to Active Colloidal Self-Assembly

In this introductory chapter, we discuss recent advances in the self-assembly of self-propelled colloidal particles and highlight some of the most exciting results in this field with a specific focus on dry active matter. We explore this phenomenology through the lens of the complexity of the colloidal building blocks. We begin by considering the behavior of isotropic spherical particles. We then discuss the case of amphiphilic and dipolar Janus particles. Finally, we show how the geometry of the colloids and/or the directionality of their interactions can be used to control the physical properties of the assembled active aggregates, and suggest possible strategies on how to exploit activity as a tunable driving force for self-assembly. The unique properties of active colloids lend promise for the design of the next generation of functional, environment-sensing microstructures able to perform specific tasks in an autonomous and targeted manner.

1.1 Self-Assembly

The way nature generates functional structures at the microscale is, in principle, extremely simple. This autonomous construction process is called self-assembly, and can be qualitatively understood with the following analogy (See Figure 1.1). Imagine placing a number of different LEGO bricks into a cardboard box. Now shake that box for a suf-
ficiently long time. Finally, open the box to find a perfectly assembled structure. This seemingly outrageous idea works at the micro and nano scale because, unlike the LEGO bricks which lay motionless unless an external force is applied (i.e. shaking), microscopic components freely and aimlessly diffuse via thermal motion across the space made available to them. Given enough time, they will eventually find each other. The process of self-assembly leverages this thermal motion to generate microstructures at practically no external cost. As such, this bottom-up approach to materials engineering is considered to be a major competitor to other more expensive top-down fabrication methods.

Unfortunately, the drawback of having to rely on random motion, as opposed to deliberate motion, is that microcomponents will indiscriminately find each other without necessarily matching to the correct partners to form the desired microstructure. This typically leads to a malformed final structure. For self-assembly to be successful, a very intricate game of labeling must be played. Each component must be encoded with its own local blueprint of where it will reside in the final structure. Clearly, the complexity of the rules (i.e. how the LEGO bricks should stick and fit together) increases with the complex-
ity of the desired final structure. As such, self-assembly is a rather delicate process, and the formation of defect-free structures is hardly achievable unless a careful design of the building blocks is performed beforehand.

1.2 Active Matter

In this introductory chapter, we discuss recent advances in the field of Active Matter with a specific focus on the self-assembly of active colloids. Throughout the chapter, we discuss ways in which self-propulsion can be exploited to form robust macroscopic and mesoscopic structures whose properties can be tuned by the degree of activity. Prior to diving into this topic, it is instructive to provide a brief overview of the field of Active Matter.

Over the past decade, Active Matter has transformed and energized the fields of Statistical Mechanics and Soft Condensed Matter. All active systems share the hallmark feature of being composed of self-driven units capable of converting stored or ambient energy into systematic movement. Examples of active systems permeate both the macroscopic and microscopic world and include: human crowds, flocks and herds of animals, living cells and tissues, active colloids and synthetic microswimmers. Active Matter represents a fundamentally new non-equilibrium regime within Statistical Mechanics. 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 these unique non-equilibrium driving forces and the
inherently stochastic nature of these systems have endowed active systems with remarkable collective behavior which ranges from bacterial turbulence [1, 2] to self-regulation [3] and, more generally, leads to large spatial correlations that are typically only observed near critical points in equilibrium systems. For a thorough discussion of these properties, we direct the reader to a number of comprehensive reviews recently written on the subject (see for instance [4–17, 17–19] and the references therein).

The current rise in popularity of colloidal active matter is due in large part to the recent advances in colloidal synthesis. Through the pioneering work of synthetic chemists and material scientists, there is now a number of experimental realizations of synthetic microswimmers and active colloids. These active particles can be thought of as synthetic analogs of swimming bacteria. However, a major benefit of these synthetic variants is that, unlike bacteria, it is possible to systematically tailor inter-particle interactions and modulate their swimming velocity. For details about the growing library of synthetic microswimmers and their associated propulsion mechanisms, we direct the readers to several recent reviews on the subject [4, 5, 14, 17].

The functionality of these active colloids and synthetic microswimmers makes them the ideal tool to manipulate matter at the microscale. A synthetic microswimmer’s ability to autonomously navigate complex microfluidic environments conjures up a host of appealing applications, which include targeted drug delivery to specific cells [20], information storage and computation [21], clean-up and neutralization of environmental pollutants [22], self-propelled nanotools [23], and the massive parallel assembly of microscopic structures [24]. These potential applications are built around the unique self-driven nature of the microswimmers and their ability to manipulate, sense, and transport material
at the microscale.

Broadly speaking, it is fair to say that the field of self-assembly is still in its infancy. Many aspects of the process are still not well understood, and we have yet to reach the stage where we can make reliable robust predictions for materials engineering.[9, 25–34]. However, there is now clear evidence that the formation of defect-free structures in non-active systems is most probable when the rate of association of the particles from the bulk into the target aggregate is comparable to that of their dissociation from it, making the process tediously slow. Given the circumstances, the question of whether self-propulsion can be used as an extra handle to control and speed up the self-assembly of colloidal particles becomes extremely relevant. There are two open research areas within active self-assembly: finding ways to impart dynamic functionality to self-assembled structures and using activity to improve self-assembly. Here, we attempt to extract from the vast amount of phenomenology that has recently been reported, key features that may be important for improving self-assembly.

1.3 Active Colloids

At the microscale in the absence of external forces, the motion of a passive colloid is driven by equilibrium thermal fluctuations originating from the solvent. The dynamics can be described by the theory of Brownian motion, and much of the collective behavior can be explained within the framework of equilibrium Statistical Mechanics. In contrast, active colloids autonomously convert energy available in the environment, whether it be chemical [35], electromagnetic [36], acoustic [37], or thermal energy [27], into directed
mechanical motion. In this case, the swimming direction is not determined by an external force at a global level, but is an intrinsic local property of the individual swimmers. Thus, it is often noted that active fluids are driven out of equilibrium at the single particle level.

Active colloids, and more generally all colloidal particles, move in a low Reynold’s number environment, (i.e. viscous forces from the surrounding fluid dominate over any inertia forces) [38], making it very challenging to develop propulsion mechanisms for active colloids. Since inertia does not contribute to the motion of the colloid, a constant force must be applied to the colloid to maintain its swimming velocity. A common scheme to achieve this is creating and sustaining some sort of gradient across the colloid. This gradient driven motion is known as phoretic transport and the current belief is that if a particle can generate its own local field or gradient (whether it be chemical, electromagnetic, or thermal), then the particle will be propelled forward via ”self-phoresis” [17, 35, 39, 40].

Here, we briefly introduce one of the simplest propulsion mechanisms for active colloids. This particular type of active colloid is Janus in nature, i.e. the colloid itself is composed of two different materials. As shown in Fig.1.2a, the active colloid synthesized by Howse et al. [35] consists of a spherical polystyrene bead with a thin layer of platinum (Pt) deposited on one hemisphere. Platinum was chosen for the catalytic cap as it readily decomposes the aqueous hydrogen peroxide fuel source into water and oxygen. As the hydrogen peroxide is decomposed by the catalytic Pt cap, a concentration gradient of oxygen is generated and sustained across the colloid resulting in its self-propulsion. Although the exact details of the propulsion mechanism even in this simple case are not fully understood, and competing mechanisms of propulsion have been suggested[41], there is consensus that sustaining a gradient across the particle is required to propel these build-
ing blocks. For additional details on a variety of self-propelling mechanisms, we direct the reader to several comprehensive reviews in this field [4, 5, 12, 14, 17, 22].

![Diagram of Pt catalysis](image)

Figure 1.2: (a) Sketch of the propulsion mechanism for the active colloid synthesized by Howse et al. [35]. The platinum cap (shown in red) decomposes hydrogen peroxide into water (light blue) and oxygen (dark blue) resulting in an oxygen gradient across the particle. Panel a was adapted from ref [42] with permission from The Royal Society of Chemistry. (b) Typical trajectories of the active colloid synthesized by Howse et al. at various hydrogen peroxide fuel concentrations. Panel b reproduced with permission from American Physical Society.

**Active Brownian Particle Model**

Much of the existing work on Active Matter has relied on simplified or minimal models. One of the most heavily studied is the Vicsek model introduced by Tamas Vicsek [43]. The Vicsek model garnered considerable interest because of its applicability to a wide range of biological systems involving flocking, clustering and migration, see for instance references [6, 18, 44, 45]. With the recent proliferation of synthetic microswimmers, a new model, often referred to as the Active Brownian Particle (ABP) model, [4, 46–54], has recently achieved great popularity and will be the main focus of this review. In the context of the ABP model, active colloids are described as Brownian particles under the additional influence of a constant self-propelling force applied along a fixed particle axis.
While this simple representation captures many features of the basic motion of active particles, it neglects often crucial hydrodynamic interactions [38, 55–63]. Using previously introduced conventions [16, 64], the ABP model is a “dry” model of Active Matter, in contrast to “wet” models where the momentum exchanged between active particles and the surrounding solvent is considered explicitly.

A spherical active colloid in the APB model is described as a sphere of mass $m$ and diameter $\sigma$ that undergoes Brownian dynamics at a constant temperature $T$, and is subject to an axial propelling velocity of magnitude $v_p$. The dynamics of the ABP evolves following the coupled overdamped Langevin equations for the translational and rotational motion, respectively:

$$\dot{r}(t) = \frac{1}{\gamma} \mathbf{F}(\{r_{ij}\}) + v_p \mathbf{n} + \sqrt{2D}\xi(t) \quad (1.1)$$

$$\dot{\mathbf{n}}(t) = \frac{1}{\gamma_r} \mathbf{T}(\{r_{ij}\}) + \sqrt{2D_r}\xi(t) \times \mathbf{n} \quad (1.2)$$

Here $v_p$ is directed along a predefined orientation unit vector $\mathbf{n}$ which passes through the origin of each particle and connects its poles. The translational diffusion coefficient $D$ is related to the temperature $T$ and the translational friction $\gamma$ via the Stokes-Einstein relation $D = k_bT/\gamma$. It is typical to assume that the rotational diffusion coefficient $D_r$ satisfies the relation $D_r = (3D)/\sigma^2$, which holds true for spherical particles at low Reynolds’s numbers. The solvent induced Gaussian white-noise terms for both the translational and rotational motion are characterized by $\langle \xi_i(t) \rangle = 0$ and $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\delta(t-t')$. The con-
Conservative inter-particle forces and torques acting on the colloid are indicated as $\mathbf{F}(\{r_{ij}\})$ and $\mathbf{T}(\{r_{ij}\})$, respectively, and can be computed as

$$\mathbf{F}(\{r_{ij}\}) = \sum_j \mathbf{F}_{ij} = -\sum_j \frac{\partial U_{ij}}{\partial \mathbf{r}_{ij}}$$

(1.3)

and

$$\mathbf{T}(\{r_{ij}\}) = \sum_j \mathbf{T}_{ij} = -\sum_j \nabla_{\mathbf{n}_{ij}} U_{ij}$$

(1.4)

where $U_{ij}$ is the interaction potential between the colloids.

A very important length-scale in these systems is the persistence length of the active drive defined as $l_p = \frac{\nu_p \sigma}{D_r}$. This can be related to the Peclet number $Pe = \frac{\nu_p \sigma}{D} = \frac{1}{3} l_p$. For a passive colloid, the motion is completely Brownian and the mean square displacement in two dimensions is given by $\langle r^2(t) \rangle = 4Dt$. For an active colloid, the mean square displacement includes an additional term and is given by $\langle r^2(t) \rangle = 4Dt + 2l_p^2[D_r t + 1 - e^{-D_r t}]$ [65]. For sufficiently large $v_p$, the motion of the active colloid becomes increasingly ballistic at short time scales. However due to the colloid’s stochastic rotation, the motion is always diffusive at longer time scales. Typical trajectories of a single active colloid at different fuel concentrations are given in Fig.1.2b. Much of the interesting behavior in active systems arises when $l_p$ is significantly larger than the colloidal diameter. For instance, one of the most important features of active particles is their ability to exert a unique force or pressure on their surroundings. This is an area of research that has received considerable interest and a number of analytical, numerical, and experimental results have been published on the subject [12, 66–69, 69–75]. In fact, it has been shown
that active fluids not only can generate a pressure on a boundary, but they can also induce exotic (depletion-like) effective forces between passive particles (tracers) with range and strength controlled by $l_p$, that can be orders of magnitude larger than what expected for passive systems [73, 76–84]. These results suggest ways of designing microstructures to perform specific tasks when immersed in an active suspension. Most notably, work on how to drive microscopic gears and motors [85–88], on how to transport colloidal cargos [89], how to capture and rectify the motion of active particles [90–92], and how to use active suspensions to propel wedgelike carriers [93–97] has been carried out. In all these instances, the local geometry of these microdevices is crucial to effectively focus the random active motion of the colloids into directed mechanical work [67, 98–101].

1.4 Self-assembly with ABPs

In this section, we provide an overview of the various contributions to the field of active colloidal self-assembly. Special attention will be paid to the different types of colloidal interactions, and how they lead to a variety of ordered and disordered structures. Most of the discussion will be framed within the context of the Active Brownian Particle model, which was introduced in the previous section. The discussion will mainly be confined to two dimensional or quasi-two dimensional systems, as most experiments are performed under these conditions. The aim of this section is to provide some degree of insight into the interplay between activity and particle interactions, and how this relates to the successful self-assembly of a wide range of passive and active microstructures.

We begin by reviewing the self-assembly behavior of purely repulsive active colloids.
After that, we consider a few cases where active colloids interact via a generic isotropic attraction. We conclude this section by considering non isotropic potentials and by discussing recent work on the self-assembly of dipolar Janus ABPs and amphiphilic Janus ABPs.

**Isotropically purely repulsive ABPs**

Self-assembly of passive spherical colloids with short-range isotropic interactions is typically limited, in terms of structural variety, to closed packed hexagonal crystals. The isotropic nature of the interaction potential does not allow for any close control in either the relative location or orientation of the colloids in a particular aggregate, precluding the formation of more complex structures. The situation is even more drastic for colloids that interact solely through excluded volume interactions. In fact, at low densities a suspension of purely repulsive spheres exists only in the fluid phase, and when the density becomes sufficiently large an ordered phase develops as a result of an increased configurational entropy.

The behavior becomes much richer whenever some degree of activity is introduced. One of the most interesting and heavily studied phenomena, which appears to be ubiquitous in colloidal active systems, is giant, long-lived density fluctuations and anomalous clustering. A passive suspension of $N$ colloids in a volume $V$ exhibits number fluctuations that scale as $\Delta N \sim \sqrt{N}$ for $N \to \infty$. Interestingly, in a variety of active systems, $\Delta N$, can become very large and scales as $\Delta N \sim N^\alpha$, where $\alpha$ is an exponent predicted to be as large as one in two dimensions [6, 103]. This scaling prediction has been verified ex-
Figure 1.3: Simulation snapshots of purely repulsive ABPs at two different volume fractions $\phi = 0.39$ (top row) and $\phi = 0.7$ (bottom row). The left column are snapshots from a system of passive particles while the right column shows the corresponding phase in the limit of very large self-propulsions. Particles are colored according to cluster size. Image reproduced with permission from American Physical Society from ref [102].

experimentally [104–106] and in agent-based simulations [18, 107]. In these earlier works, the focus was on elongated active particles (inspired by swimming bacteria and animal flocking) and the associated giant number fluctuations were believed to be induced by the broken orientational symmetry of the particle. More recently, it has been shown that this is a more general phenomenon and has been observed in suspensions of purely repulsive
spheres with no alignment interaction [102, 108].

A related phenomenon observed in suspensions of purely repulsive ABPs is the existence of an athermal motility-induced phase separation (MIPS) [7, 10, 49, 109–115]. Here, the system is able to undergo a transition from a dilute fluid to a macroscopic dense phase, which takes place at densities much lower than those expected for the configurational-entropy-driven transition of the passive parent system. Figure 1.3 illustrates this novel phase transition in a simulation of purely repulsive ABPs. The discovery of MIPS has led to extensive theoretical, experimental, and numerical studies, which have culminated in a number of review articles on the subject [4, 7]. This phase transition differs significantly from the ordered states of nematic and polar active systems, which are intimately linked to the broken orientational symmetry of the particle, because spheres lack a mutual alignment mechanism and thus are unable to exchange angular momentum. This phase separation is strikingly similar to the vapor-liquid spinodal decomposition observed in many equilibrium systems, and there is now a significant amount of evidence supporting the hypothesis by Cates and collaborators [46, 110, 116–118] that MIPS is a generic features of systems that are driven out of equilibrium by a persistent local energy input that breaks detailed balance.

The physical mechanism responsible for giant number fluctuations and MIPS can be easily contextualized within a simple kinetic model [102, 108] which focuses on the local dynamics at the interface of a forming cluster. At any given time, the size of a cluster is determined by the flux balance of incoming and outgoing particles. The time required for an active colloid to leave the surface of a cluster is independent of the propelling velocity $v_p$ and is completely determined by its average rotational diffusion time $t_r \sim 1/D_r$, the
collision rate between free colloids and the forming cluster increases linearly with the particle density and propelling speed $v_p$[119].

By modulating the value of $D_r$, it is possible to control the size of the number fluctuations and retard or promote particles’ aggregation [120]. This is an often overlooked aspect of active system, but developing methods to systematically control the rotational dynamics of the active colloids has important implications for directed self-assembly. Interestingly, hydrodynamic interactions between active colloids have been shown to have major effects on the their rotational dynamics, and the local field inducing the particle’s propelling forces (pushers vs pullers) play a central role in MIPS [55, 57, 60, 121–125].

The notion that activity alone can generate giant number fluctuations and induce phase separation has important implications for self-assembly. In many colloidal self-assembly processes, the growth of a particular target structure requires the formation of a critical nucleus of a characteristic size. By introducing activity, it is then feasible to generate large density fluctuations that could be systematically exploited to extend the region in parameter space where self-assembly will successfully occur. In addition, self-propulsion will improve the kinetics of self-assembly as the local dynamics becomes inherently faster and, in more general, can make it easier for the system to escape local kinetic traps. These issues will be discussed in greater detail in a later section.

**Isotropically attractive ABPs**

The simplest extension over purely repulsive interactions is to consider spherical active colloids interacting via a short-ranged isotropic attraction. Interestingly, and to some
Figure 1.4: (a) Top panel: Phase behavior of isotropically attractive ABPs at an area fraction $\phi = 0.4$ presented as a function of interparticle attraction strength $U$ and Peclet number $Pe = (v_p \sigma)/D$. The colors aid to distinguish the different phases: near-equilibrium gel states (green/upper-left), single-phase active fluids (red/center), and MIPS states (blue/right). (a) Bottom panel: Detailed snapshot at fixed interaction energy $U = 4k_B T$. At $Pe=4$ (left), the system forms a kinetically arrested attractive gel. At $Pe = 20$ (center), the attraction suppresses phase separation and produces a homogeneous fluid characterized by transient large density fluctuations. At $Pe = 100$ (right) MIPS is observed. (Panel reproduced with permission from American Physical Society from [119].) (b) Snapshots of spherical ABPs interacting via a short-range attractive and a long-range repulsive potential at two different volume fractions $\phi = 0.24$ (left) and $\phi = 0.55$ (right). From top to bottom: $Pe = 0, 10, 20$. At $Pe = 10$, meso-phases of living crystals are observed at lower densities, and living stripes are seen at higher densities. (c) Snapshots of self-propelled dumbbells interacting via a short-range attractive and a long-range repulsive potential at $\phi = 0.24$. From left to right we observe at $Pe = 0$ (static clusters), at $Pe = 5$ (rotating clusters), at $Pe = 15$ (living clusters) and at $Pe = 40$ (fluid phase). Panels $b$ and $c$ reproduced with permission from The Royal Society of Chemistry from [126].

controversy [118], the interplay between attraction and self-propulsion gives rise to new phenomenological behavior not observed in the passive parent system or an active sys-
tem with purely repulsive interactions. In a recent article by [119], the authors consider a two dimensional suspension of attractive active particles at an area fraction of $\phi = 0.4$. The short ranged isotropic interaction is realized by allowing the ABPs to interact via a Lennard-Jones potential [127]. At this density, the phase diagram for this system exhibits reentrant behavior as a function of activity [119]. The phase diagram is given as a collection of simulation snapshots in Fig.1.4a. Self-propulsion can now either compete with the inter-particle attractions to suppress phase separation or act cooperatively to enhance it. At low levels of activity, the isotropic attraction between colloids dominates and the suspension phase separates in a similar manner to what expected in the parent equilibrium system. In this regime, self-propulsion has little to no relevance. At moderate levels of activity, the suspension melts into a single phase active fluid. As the activity is increased even further, phase-separation driven by the self-trapping mechanism of MIPS will occur. Here, energetic attractions act cooperatively with self-trapping to enable phase separation at lower propelling velocities than would be possible in the corresponding system with purely repulsive interactions.

Interestingly, experimental studies of active colloids [71, 114, 128, 129] at lower densities than the one discussed above [119], observe the formation of dynamic clusters (living crystals) were each finite-sized cluster continually breaks, merges, dissolves, and reforms. This peculiar finding has also been observed in two dimensional numerical simulations of self-propelled hard disks using kinetic Monte Carlo simulations [130], self-phoretic Active Brownian particles [131], and in a recent numerical study of a low density suspension of three dimensional attractive active colloids [120, 132]. These living aggregates appear to form whenever attractive and propelling forces are comparable in
magnitude. A recent study of attractive squirmers (which account for explicit hydrodynamic interactions) has also observed system coarsening or clustering depending on the ratio between attraction and propulsion strength[58].

Living clusters are a beautiful example of self-assembly into structures that can be active themselves. Unfortunately, it is not easy to control the size of these clusters using exclusively short range attractions, however, it is possible to overcome this problem by adding to each particle a weak, but long-range repulsion. This creates a pair of competing forces at different distances, and it is known to drive micro-phase separation into ordered structures of controllable size in passive suspension. A well-studied case is that of a short-range attraction (typically induced by depletion forces) coupled to a long-range repulsion (obtained, for instance, by giving the colloids a net charge). The result is the formation of a range of self-assembled structures whose morphologies depend on the balance between the attractive and repulsive interactions. At equilibrium and at relatively low densities, this interplay can lead to the formation of isotropic clusters arranged into hexagonal arrays (or stripes at larger densities) whose size is to some degree tunable with the interaction parameters [133–136].

As far as we are aware, there are no experimental realizations of active systems of this variety. Nevertheless, two recent theoretical studies of two dimensional suspensions of ABP interacting via a micro-phase separation-inducing long range potential have been carried out [126, 137]. The potential used consisted, apart from the excluded volume, of two generic parts: a short range attraction needed to induce clustering and a long range soft repulsion to guarantee micro-phase separation. These studies have shown that for the appropriate choice of the inter-particle interactions and for a range of active forces,
the living crystals of spherical ABP can be size-stabilized (See Fig. 1.4b). In the article by Tung et al. [126], the behavior of active dumbbells was also studied using the same inter-particle potential, and it was shown that it is possible to create mesoscopic crystalline structures that behave as micro-rotors (with definite, but tunable angular velocity). This occurs because of the particles’ geometry (See Fig.1.4c). The dumbbells tend to exhibit local nematic ordering upon aggregation causing the mesoscopic lattice sites to spin with a characteristic angular velocity. A similar behavior has been also observed in a two dimensional dilute suspension of self-propelled dumbbells interacting via a short-range attraction [138]

The above result allows us to make an interesting comparison between spherical and aspherical active colloids. For spherical colloids interacting through an isotropic potential, the aggregates that develop are intrinsically plastic, i.e. each particle within a structure is able to freely rotate, and this key feature is mainly responsible for the emerging active behavior of the resulting mesoscopic aggregates (e.g. living crystals). A rather different phenomenology is observed when considering particles endowed with directional interactions as was illustrated for the dumbbells in the previous example. These can develop either because of a non-spherical geometry of the particle or as a result of explicit anisotropic interaction potentials. A significant amount of work has been done on the former case, with specific focus on isotropic self-propelled rods. The literature on the subject is extensive and focuses heavily on the behavior of swimming bacteria and active nematics (see for instance [16] and references therein). In what follows, we review recent exciting results obtained on the self-assembly of spherical active Janus particles, which represent the simplest system with anisotropy in the inter-particle interactions.
Dipolar Janus ABPs

Dipolar Janus colloids consist of spherical particles coated with two oppositely charged hemispheres. The directional interactions between these particles depend on the salt concentration in solution and allow for self-assembly of complex structures. In a recent article Kaiser et al. [139] studied the clustering behavior of a small number of dipolar ABPs. The model considered by [139] is similar to the ABP model introduced in the previous section with the addition of a point dipolar potential at the center of each colloid aligned with the self-propelling axis. In this work, the authors allowed a small number of dipolar ABPs \((N = 1 - 5)\) to self-assemble under equilibrium conditions and then introduced self-propulsion to understand its effect on the clusters’ dynamics. This approach provides some intuition on how activity induces structural changes in small clusters.

A number of interesting features having potentially important applications in colloidal self-assembly have been observed. For instance, dynamic structures which are not stable at equilibrium develop when the particles are activated, and it is possible to both stabilize and destabilize particular configurations by the careful choice of the propelling velocity \(v_p\). Interestingly, the stability of the equilibrium clusters is dependent on the ramp rate at which the self-propelling force is applied. If self-propulsion is applied instantaneously, the clusters undergo a permanent fission process, where they either experience significant internal rearrangements or completely break. However, if self-propulsion is slowly ramped to its final value (adiabatic switching) no fission is observed and the equilibrium cluster configuration is retained. This sensitivity to the ramp rate offers a unique handle for modulating self-assembly. The authors illustrate a high level of control over the se-
lection of a particular cluster configuration by tuning both the system parameters and by selecting an adequate choice of how self-propulsion is applied to the particle. In a more recent paper the dynamical properties of these dipolar Janus ABP clusters were further characterized [140].

Using a combination of numerical simulations and experiments, Yan et al. [141] have shown how multiple modes of collective behavior can be encoded into Janus dipolar ABPs. In this work, each of the two hemispheres of the colloids carries its own electric charge and a colloid is propelled along the axis perpendicular to the particle’s equator. The experimental realization of this system consists of silica spheres with one hemisphere coated with a metal and then other covered with a thin $SiO_2$ protective layer. The two hemispheres of the colloid polarize differently when an AC electric field is applied perpendicular to system. This mismatched frequency-dependent dielectric response is exploited to both control the motility of the colloids and modulate colloid-colloid interactions. As shown in Fig.1.5, it is possible to self-assemble several distinct active structures by modulating magnitude and sign of the electric charge on each hemisphere of the colloid. When the charge on the two hemispheres has the same sign and magnitude, the system exhibits behavior similar to that of purely repulsive ABPs, and since the density considered is below the onset for the MIPS transition, the system remains in a fluid state (Fig.1.5a). More interestingly, when there is a charge imbalance between the two hemisphere, the system develops various forms of non-trivial self-organization. Particles with equal and opposite charges on the two hemispheres spontaneously assemble into active chains (Fig.1.5b). When a large charge imbalance between the two hemispheres is enforced, the colloids induce large torques on one another when coming in close proximity, and two distinct
Figure 1.5: (a) Dipolar Janus ABPs where both the sign and magnitude of the charge on each hemisphere can be controlled to impose different collective behavior. The sign of the charge (positive and negative) are color coded (red and blue), their relative magnitude is indicated by the respective dot size, and the black arrows indicate the propelling directions. Panels (b) to (d) show typical snapshots for the different phases, including (b) active chains, (c) swarms and (d) clusters. The white hemispheres represent the leading sides and the red hemispheres the trailing sides. The blue arrow in panel (c) marks the global direction of the swarm. Image reproduced with permission from Nature [141].

cases emerge. Case (1): when the propelling force is set to point towards the hemisphere with greater charge, the torques tend to aligns two colloidal swimmers in the same direction. This angular alignment produces large scale coherent swarms with phenomenology reminiscent of the Vicsek model (Fig.1.5c) [43]. Case (2): when the propelling force is set to point away from the hemisphere with greater charge, the induced torques tend to rotate the colloids so that the more charged hemispheres are pushed as far apart as pos-
sible from each other. In this case the colloids tend to align with their propelling axis facing one another resulting in the formation of jammed clusters with high local density (Fig.1.5d). These studies provide an excellent example of how angular interactions can be tuned to induce self-assembly of complex structures, and indicate how the interplay between the torques and the self-propelling forces can facilitate the formation of active aggregates.

**Amphiphilic Janus ABPs**

We now shift our focus to the self-assembly behavior of amphiphilic Janus ABPs. This type of Janus particle consists of two distinct hemispheres, one hydrophobic and the other hydrophilic. An experimental realization of an amphiphilic Janus ABPs consists of silica microspheres passivated with a hydrophobic ligand (octadecyltrichlorosilane, OTS), whose hemisphere is then covered by a Pt cap. These amphiphilic Janus ABPs experience a short ranged attraction between the hydrophobic domains, while the interaction between the Pt capped hemispheres is purely repulsive. In essence, the Pt cap restricts the inter-particle attraction to the hydrophobic hemisphere which gives rise to well defined assemblies (See Figure 1.6). By tuning the size of the hydrophobic domain and that of the Pt cap, it is possible to control the angular range of the interaction, and thus the number of colloids that can simultaneously stick to each other, and the degree of self-propulsion of the the colloid.

Gao et al. [142], investigated experimentally the formation and dynamics of small clusters of amphiphilic Janus ABPs. For a pair of colloids. They find that the motion is
Figure 1.6: Left panel: (A) Sketch of the assembly of OTS modified amphiphilic Janus ABPs from [142], with the hydrophobic OTS sides (in gray) facing one another. (B) Typical configurations (a—d) of a pair of amphiphilic Janus ABPs (Scale bar, 1 μm). (C) Typical assemblies of amphiphilic Janus ABPs triplet assemblies: (a—c) movement of triplet assemblies with different orientations (Scale bar, 1 μm). Reproduced with permission from the American Chemical Society from [142]. Right panel: Plot representing the angular speed of possible dimer conformations. The intensity of the shaded regions show counterclockwise (red) and clockwise (blue) rotations of the dimers. Reproduced with permission from American Physical Society from [143].

governed by the relative orientation of the two self-propelling force. Figure 1.6 enumerates the possible orientations for a pair of amphiphilic Janus ABPs. When the two propelling vectors are aligned with the interparicle axis, so that the particles directly push against each other, the pair becomes essentially passive. The two active forces cancel each other and the motion of the pair is purely Brownian. However, when the propelling vectors are both perpendicular to the interparticle axis, the pair behave as a colloidal rotor with a characteristic angular velocity determined by the magnitude of the self-propelling force. The self-propelling force in this case only contributes to the rotation of the pair. The translational dynamics of the pair are effectively Brownian when this configurations
is adopted. When the location of the Janus balance is altered so that the size of the hydrophobic patch becomes smaller, the rotational speed of the pair decreases and it revolves with a larger radius. While it is straightforward to estimate the degree of translational and rotational motion for a particular configuration of a pair of Janus amphiphilic ABPs (as shown in some detail in ref. [143]) the situations becomes much more complex when dealing with aggregates of a large number of particles.

One of the biggest challenges in active self-assembly is designing a building block where the interparticle interactions and the self-propulsion of the particles work in conjunction to bias the formation of a particular target structure. The next section in this review is dedicated to this topic.

### 1.5 Can Activity Improve Self-Assembly?

So far we have discussed some of the new exciting behavior observed in suspensions of active colloids with a specific focus on the new properties, morphological or dynamical, of the aggregates formed under the influence of propelling forces. In this last section, we shift the focus, and consider whether activity can be exploited to speed up the complex self-assembly dynamics of colloids designed to (passively) form desired target structures. For this purpose, we will consider activity as a new, tunable dimension in the colloidal parameter space. This new variable, self-propulsion, as already illustrated in the previous sections, can profoundly affect the dynamical behavior of a system. However, when implemented in a synergistic manner, it can be exploited to bias the formation of a particular desired microstructure against any malformed or competing microstructures.
As discussed in the introduction, it is quite clear that even when the interactions between building blocks are chosen so that a particular ordered structure is stable, the self-assembly of that structure may not be possible due to the presence of competing metastable states. Successful self-assembly usually requires a delicate balance between entropic and dispersion forces, and the formation of defect-free structures demands that the rate of association of the building blocks to the forming assembly to be comparable to the rate of dissociation from it, leading to rather slow time scales for the completion of the self-assembly process. Obviously, because of its enhanced translational motion, self-propelled particles can explore a given volume and find a large slow target (the assembly) much faster than their passive counterparts. However, the same propelling forces, when sufficiently large can alter the morphology, the structural properties, and even break down the target structure by exerting unbalanced inner forces and torques. In other words, if on the one hand self-propulsion will speed up the kinetics of particle association, on the other hand it can affect the stability of the desired target structure. As such, one should not expect that adding self-propulsion to any colloidal particle will necessarily be advantageous, unless the self-propelling forces themselves will organize within the target assembly in such a way that its stability is not compromised. This can be achieved by judiciously pairing the propelling forces and the inter-particle interactions.

As a simple illustration, we review the self-assembly of active triangular colloidal particles discussed in ref. [24]. Although there is nothing particularly special about the shape of this building block, the pathway associated to its self-assembly presents all the generic features observed in a typical self-assembly process: (1) there is a clearly defined target structure. Equilateral triangles with one side hard and the other two attractive
are designed to passively self-assemble into hexagonal structures of exactly six triangles (capsids) [see Fig.1.7a]. (2) There exist an ensemble of structures with a larger degree of orientational entropy [see Fig.1.7(c)] that can directly compete with the formation of the target structure as soon as the inter-particle interaction becomes sufficiently large. This high level of competition generates a scenario where the success of self-assembly of the hexagonal structures is highly dependent on the strength of attraction between colloids and is expected to only occur for a narrow energy range. (3) Starting from a low density suspension, the typical times required for self-assembly becomes exceedingly slow.

![Diagram of colloidal structures](image)

Figure 1.7: Left panel: (a) Sketch of a triangular building block with two attractive sides. The white arrow indicates the direction of self-propulsion. (b) The target structure to be self-assembled is a hexagonal capsid composed of six colloidal building blocks. (c) Typical disordered aggregate formed when the attraction between the triangles is too strong. (d) Percent yield of target structure as a function of the strength of the attractive interaction for passive colloids. Right panel: Anti-aligned (top) and aligned (bottom) configurations of a pair of triangular particles.

In Fig.1.7d, the percent yield of the target structure as a function of the strength of the attractive interaction is given. As expected, successful self-assembly in the passive
system is limited to a narrow range in the binding energy. In this window, the maximum yield observed is $\sim 90\%$. For smaller values of the binding energy, the colloids do no aggregate. For larger values, the formation of large disordered aggregates is favored [see Fig.1.7c]. How can one endow these particles with self-propulsion to improve the overall rate and yield of self-assembly?

The general strategy in implementing this approach is to design the colloidal building blocks such that the particle interactions and the direction of self-propulsion work in conjunction to form and stabilize the desired structure. In this simple example system, the solution is fairly straightforward. By choosing the direction of self-propulsion to be perpendicular to the repulsive face of the colloid as illustrated in Fig.1.7a, one can improve the stability of the final hexagonal aggregate. Furthermore, this choice biases the formation the target structure early on in the self-assembly process. Indeed, as illustrated in Fig.1.7(left panel), there are only two ways for a pair of colloids to bind to each other. In the first configuration, the propelling axes are anti-aligned, whereas in the second configuration the self-propelling axes are partially aligned. In the former case, activity tends to destabilize and separate the pair while in the latter case the bond between the two particles is strengthened by the contributions of the active force. Biasing the system away from binding configurations that lead to the formation of misaligned structures leads to a significant increase in the likelihood of a robust self-assembly process. Thus the selection of the final structure begins already at an early stage, as partially aligned configurations are favored and are compatible with the target geometry.

A critical requirement of the target microstructure is that the vectorial sum of the self-propelling forces in its interior is equal to zero. This creates a focal point in the cen-
ter of the compact aggregate where each colloid can exert a force that strengthens their mutual attractive interactions through the cooperative arrangement of the propelling forces. These emerging interactions stabilize the hexagonal structure even in the absence of explicit attractive forces and behave essentially as active bonds of tunable strength. Any compact aggregate for which this vectorial condition is not satisfied will experience large active torques and shear forces that can break them apart. One can think of self-propulsion in these systems as a very selective filter that only allows for the stabilization of certain structures. We believe that this strategy should work for all compact target structures satisfying the vectorial condition discussed above.

We should stress that this behavior also suggests ways of using activity as a tool to separate at once both time and energy scales in multi-stage self-assembly problems [144]. In fact, given that the aggregation rate and the strength of the active bonds are completely controlled by the particles’ self-propulsion, it is possible to use activity to quickly self-assemble compact structures with zero net propulsion, such as the hexagonal capsids described above, that would function as new passive mesoscopic building-blocks. These could then be made to slowly self-assemble even further exploiting standard dispersion or weak solvent-induced interactions. The ability to efficiently separate energy and time scale within the same sample can be greatly beneficial for the fabrication of evermore-complex microscopic architectures.

Although this strategy appears to be rather effective for compact but finite-sized structures, there is evidence [145] that it can also be applied to other systems. For instance, low levels of activity can be used to improve the self-assembly of macroscopic crystals and open lattice structures. It has been shown [146] that passive triblock Janus parti-
cles, which have two attractive patches located at the opposite poles of each particle, will spontaneously form macroscopic kagome lattices for sufficiently large patch areas and attraction strengths. Our preliminary results [145] indicate that the formation of the kagome lattice structure greatly benefits from the introduction of a small amount of self-propulsion along the pole-to-pole axis of these particles. The reason behind this is that the active forces in this case act to destabilize the competing elongated structures that tend to form early on in the self-assembly process. Clearly more work in this direction needs to be done to understand the intricacies of how activity may affect the stability or the dynamic pathway of the self-assembly process, nevertheless this is a very promising direction in the field.

## 1.6 Conclusions

In this chapter, we recapitulated some of the most exciting phenomenological behavior observed in suspensions of active colloids. We also discussed some of the strategies that can be deployed to exploit activity to more efficiently self-assemble target structures. To conclude, we would like to remark that apart from a few exceptions (see for instance [147, 148] and references therein), most of the work in this area has been carried out under the assumption that the active forces are constant with respect to time. However, the newest generation of active colloids, can be light activated [128, 149, 150] (i.e. their self-propulsion can be turned on and off by exposure to an external light source). This is achieved, for instance, by inserting a piece of hematite on one side of the colloids and shining light of a specific frequency on the suspension — it is only in these illuminated re-
regions that the hematite catalyzes the hydrogen peroxide [128]. This is an incredibly useful feature for self-assembly as it makes it feasible to create regions and sculpt patterns in the sample where particles become active (under light exposure) and regions where particles behave as purely Brownian objects. Another interesting feature of light-induced activity is that it allows the strength of the active forces to be easily modulated over time by either tuning the intensity of the light source or by switching it on and off at different frequencies. This simple feature opens the way to experimental studies of stochastic Brownian ratchets, and adds yet another handle that could be exploited to create new functional materials, allowing one to directly intervene and dynamically affect the pathway of structure formation.
Chapter 2

*Anomalous Thermomechanical Properties of a Self-propelled Colloidal Fluid*

We use numerical simulations to compute the equation of state of a suspension of spherical self-propelled nanoparticles in two and three dimensions. We study in detail the effect of excluded volume interactions and confinement as a function of the system’s temperature, concentration and strength of the propulsion. We find a striking non-monotonic dependence of the pressure with the temperature, and provide simple scaling arguments to predict and explain the occurrence of such anomalous behavior. We conclude this chapter by explicitly showing how our results have important implications for the effective forces on passive components suspended in a bath of active particles.

### 2.1 Introduction

The kinetic theory of gases proved to be one of the crowning achievements of 19th century physics. The seminal work of Bernoulli, Clausius, Maxwell and Boltzmann presented a definitive relationship between the internal structure of a gas and its thermomechanical properties, and thus provided unprecedented insight into the behavior of gaseous systems and set the foundation for the modern kinetic theory.
In recent years, active systems have been at the forefront of non-equilibrium statistical mechanics, as they show a range of exotic behavior not typically observed in their passive counterparts, including turbulence [2, 151–153], delayed crystallization [154], and self-regulation [3, 155–157]. (see references [8, 19] for recent reviews on the field). In spite of the great effort deployed to systematically quantify the individual and collective dynamics of synthetic and naturally occurring active nanocomponents, such as self-propelled colloidal particles and bacterial suspensions, our understanding of active systems still remains incomplete.

As an attempt to provide a better link between the microscopic properties and the resulting macroscopic behavior in actives systems, we consider a solution of spherical self-propelled nanoparticles (one of the simplest realizations of an active system) and determine what is typically one of the most fundamental properties of a solution: its equation of state. We show how self-propulsion leads to anomalous thermomechanical properties, and how these are affected by confinement and excluded volume interactions.

We also discuss, as an application of our results, how the effective interactions induced by an active ideal gas on two plates kept in close proximity present a new and unexpected behavior as a function of activity and temperature.

To understand the interplay between active and thermal forces, we begin our study with what is possibly the simplest thermodynamic system: a dilute suspension of non-interacting self-propelled particles — *the active ideal gas* — and we ignore any effective interaction between the particles that may arise, for instance as a result of gradients in fuel concentration or hydrodynamic interactions [158–161]. In our case, the pressure is determined solely by the average force that particles exert on an enclosing container.
2.2 Model

We implement a minimal model, inspired from recent experimental and theoretical work [49, 108, 129, 149, 162], of $N$ self-propelled particles in two and three dimensions modeled as spheres of diameter $\sigma$ confined within a circular/spherical container of radius $R$ centered at the origin of our coordinate system. Each ideal particle undergoes Langevin dynamics at a constant temperature $T$, and interacts exclusively with the wall via a truncated harmonic potential of the form

$$V_w(r) = \begin{cases} 
0, & \text{if } r - R < 0 \\
 k (r - R)^2, & \text{if } r - R \geq 0 
\end{cases}$$

where $r$ is the distance from the center of the container, $k = 800k_B T_0/\sigma^2$ is the spring constant, and $k_B T_0$ (with $T_0 = 1$) is the thermal energy at room temperature that will be used as the energy scale.

Self-propulsion is introduced through a directional force which has a constant magnitude, $|F_a|$, and is directed along a predefined orientation vector, $\mathbf{n}$, which passes through the origin of each particle and connects its poles. The equations of motion of an individual particle are given by the coupled Langevin equations

$$m\ddot{\mathbf{r}} = -\gamma \dot{\mathbf{r}} - \partial_r V_w + |F_a| \mathbf{n} + \sqrt{2\gamma D} \mathbf{\xi}(t)$$  \hspace{1cm} (2.1)

$$\dot{n} = \sqrt{2D} \mathbf{\xi_R}(t) \times \mathbf{n}$$ \hspace{1cm} (2.2)
where $m$ is the particle’s mass, $\gamma$ is the drag coefficient, and $D$ and $D_r$ are the translational and rotational diffusion constants, respectively. 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 $\langle \xi_{Ri}(t) \rangle = 0$ and $\langle \xi_{Ri}(t) \cdot \xi_{Rj}(t') \rangle = \delta_{ij}\delta(t - t')$, respectively. In the low Reynolds number regime the rotational and translation diffusion coefficients for a sphere satisfy the relation $D_r = (3D)/\sigma^2$.

All simulations were carried out in 2 and 3 dimensions using LAMMPS [163]. The mass of each particle is set to 1, the drag coefficient $\gamma = 10$, and the time step to $\Delta t = 10^{-3}$. The drag coefficient $\gamma$ was chosen to be sufficiently large such that the motion of the particles is effectively overdamped. Several of the simulations were repeated with larger values of $\gamma$ (e.g. $\gamma = 50, 100$), which produced no detectable differences in our results. Each simulation was run for a minimum of $3 \times 10^7$ time steps. The total number of particles ranged from $N = 10^2$ to $N = 3 \times 10^4$. The mechanical pressure was calculated as the average forces the particles exerts on the boundary divided by the area of the container $A$.

2.3 Discussion of Thermomechanical Properties

The zero-propulsion and zero-temperature limits are well understood. In the former, the system reduces to an ideal gas exerting a pressure $P = \rho k_B T$, while in the latter, all particles accumulate on the walls of the container and each contributes a persistent force of magnitude $|F_a|$. This result is due to a particle’s inability to rotate in the absence of thermal fluctuations, and after hitting the wall they slide across its surface until the tangential
component of the active force vanishes. The resulting pressure is trivially \( P = N|F_a|/A. \)

![Graph](image)

Figure 2.1: (a) Pressure in two-dimensional system as a function of temperature for several values of \( |F_a| \). (b) The same curve as (a) for \( T < 2 \). (c) Pressure as a function of the box radius where \( |F_a| = 20 \) for several values of \( T \). All solid lines are plotted using Eq. (2.8) and the corresponding system variables.

The interesting behavior emerges at finite temperatures and moderate activity where the rotational diffusion is able to derail the otherwise rectilinear trajectories of the particles. Figures 2.1(a) and 2.2(a) show how the pressure exerted on the wall depends on the temperature \( T \) for different values of the active force respectively in two and three dimensions. Strikingly, these curves show non-monotonic behavior. Specifically, for small values of \( T \), an increase of the temperature leads to a sharp decrease of the pressure,
Figure 2.2: (a) Pressure in three-dimensional system as a function of temperature for several values of $|F_a|$. (b) The same curve as (a) for $T < 2$. (c) Pressure as a function of the box radius where $|F_a| = 20$ for several values of $T$. All solid lines are plotted using Eq. (2.8) and the corresponding system variables.

whereas for large values of $T$, the system’s pressure re-establishes the ideal gas pressure-temperature dependence expected for non-active particles.

The behavior of the pressure at low temperatures (or large $|F_a|$) can be rationalized with the following argument: The two relevant time scales in the system are the decay of the rotational correlation time due to thermal fluctuations, this can be written for the specific cases of two and three dimensions as $\tau_r \simeq (d - 1)D_r^{-1}$ [164], where $d = 2, 3$ is the system dimensionality, and the time required for the particles to move across the
system. The latter time-scale at low $T$ is dominated by the active motion, and scales as $\tau_a \simeq R\gamma/|F_a|$. Therefore, as long as $\tau_a/\tau_r \ll 1$, i.e. the rotational motion does not decorrelate faster than the time required for the particle to cross the container, there will always be a net linear contribution to the pressure on the wall by the active force. A simple way of estimating the average pressure in this regime can be obtained by considering that a particle can be either on the wall pushing with a force proportional to $|F_a|$, or diffusing across the box generating no pressure on the wall. A particle on the wall will exert a force for a time of the order of $\tau_r \simeq (d - 1)D_r^{-1}$. The average time spent by the particle diffusing across the box without generating any pressure on the wall is $\tau_a \simeq R\gamma/|F_a|$. Hence, over the time $\tau_r + \tau_a$ the force exerted on the wall by a single active particle can be estimated as $\langle F \rangle \simeq (|F_a| \cdot \tau_r + 0 \cdot \tau_a)/(\tau_r + \tau_a) = |F_a|/(1 + \tau_a/\tau_r)$.

Multiplying by $N$ and dividing by the surface, one obtains the total pressure,

$$\langle P \rangle = \left( \frac{N}{A} \right) \frac{|F_a|}{1 + \frac{\tau_a}{\tau_r}},$$

and in the limit $\tau_a/\tau_r \ll 1$, this can be further simplified to

$$\langle P \rangle = \left( \frac{N}{A} \right) \frac{|F_a|}{1 + \frac{\tau_a}{\tau_r}} \simeq \frac{N|F_a|}{A} \left( 1 - \frac{\tau_a}{\tau_r} \right) \simeq \frac{N|F_a|}{A} e^{-\frac{\tau_a}{\tau_r}}$$

We expect that the exact numerical value of the pressure will be dependent on the specific geometry of the boundary, as the behavior of the particles on the surface is well known to be strongly sensitive to it [63]

, but the qualitative nonmonotonic behavior observed here should remain unaltered.
To account for this uncertainty, we introduce a geometric factor \( \alpha \) and Eq. (2.3) can be recast as

\[
\langle P \rangle = \left( \frac{N}{A} \right) \frac{|F_a|}{1 + \frac{\tau_a}{\tau_r}} = \left( \frac{R}{d} \right) \frac{\rho |F_a|}{1 + \alpha} \left( \frac{3(d-1)Rk_BT}{\sigma^2 |F_a|} \right)
\]  

(2.5)

where we have also used the appropriate Einstein relation \( D = k_B T / \gamma \) to introduce the proper temperature dependence.

Figure 2.3: (a) Pressure in two-dimensional system as a function of \( |F_a| \) for several values of \( T \). (b) The same curve as (a) for \( |F_a| < 50 \). The solid lines in (a) and (b) correspond to Eq. (2.8). (c) The fraction of particles, \( \beta \), that are within one particle radius from the boundary as a function of \( |F_a| \) for various values of \( T \).

The derivation of Eq. (2.5) assumes that particles spend a majority of their time at the boundary, which ceases to be true when \( \tau_a / \tau_r \gg 1 \). A simple expansion of Eq. (2.5) in this
Figure 2.4: Pressure in three-dimensional system as a function of $|F_a|$ for several values of $T$. (b) The same curve as (a) for $|F_a| < 50$. The solid lines in (a) and (b) correspond to Eq. (2.8). (c) The fraction of particles, $\beta$, that are within one particle radius from the boundary as a function of $|F_a|$ for various values of $T$.

limit gives $\langle P \rangle \simeq \left( \frac{4}{3} \right) \frac{|F_a|^2 \sigma^2}{3(d-1)k_B T}$ indicating that, as is typical for nonactive ideal gases, the pressure depends on the square of the particle velocities. Of course, such an expansion assumes that the particle velocities are proportional to the active force, but at large temperatures, one cannot neglect the contribution of thermal fluctuations to the motion of the particle. In this regime, we appeal to the insights of equilibrium statistical mechanics and make the assumption that the pressure is proportional to the average translational kinetic energy of the system. The introduction of self-propulsion when $\tau_a/\tau_r \gg 1$ can be
viewed as a perturbation of an ideal gas. One way to associate a pressure in this regime is to compute $\langle \dot{r}^2(t) \rangle$ from Eq. (1) (See Appendix A). For simplicity, we consider particles confined to two dimensions and only have a single degree of rotational freedom. Assuming the system reaches its steady state (i.e. $t \to \infty$ and $\langle F \rangle = 0$), we can write

$$\langle \dot{r}(t)^2 \rangle = \langle \dot{x}(t)^2 \rangle + \langle \dot{y}(t)^2 \rangle = \frac{2k_B T}{m} + \frac{|F_a|^2}{m(3k_B T / \sigma^2 + \gamma^2 / m)} \quad (2.6)$$

Measurements of $\langle \dot{r}(t)^2 \rangle$ in numerical simulations performed in two dimensions on a system with periodic boundary conditions are in good agreement with Eq. 2.6.

Assuming that in this limit we can write the pressure as $P / \rho = \frac{m}{2} \langle \dot{r}(t)^2 \rangle$, we obtain

$$P = \rho \left( k_B T + \frac{|F_a|^2}{6k_B T / \sigma^2 + 2\gamma^2 / m} \right) \quad (2.7)$$

where $\rho$ is the number density. The first term captures the ideal gas behavior, whereas the second term corrects for the increase of the velocity of the particles due to their propulsion. This correction is not a constant factor, but slowly decays with the temperature as the extent of the random thermal forces overwhelms (affecting both rotational and linear degrees of freedom) the role of the active ones. It is important to stress that, if the pressure/velocity relation that we used in Eq. (2.7) is indeed applicable to an active gas, it can only be valid for very high temperatures and large values of $R$.

Remarkably, we find that the equation obtained by simply adding the ideal gas limit $\rho k_B T$ to Eq. 2.5,

$$P = \rho k_B T + \left( \frac{R}{d} \right) \frac{\rho |F_a|}{1 + \alpha \left( \frac{3(d-1)Rk_B T}{\sigma^2 |F_a|} \right)} \quad (2.8)$$

40
provides the best description of the data observed in our simulations in both two and three dimensional systems in terms of all external parameters: the temperature (Fig. 2.1 and Fig. 2.2 panels (a) and (b)), the radius of the cavity (Fig. 2.1 and Fig. 2.2 panels (c)), and the strength of the activity (Figs. 2.3 and Fig. 2.4 panels (a) and (b)). The single fitting parameter for all curves in two and three dimensions is estimated to be $\alpha \simeq 0.89$. Our derivations of Eqs. 2.4 and 2.5 is based on simple scaling arguments, however, a recent detailed analysis of the dynamics of self-propelled particles under strong confinement near the boundary has been carried out by Fily et al. [99]. They found the analogous exponential decay we report in Eq. 2.4. In their calculations they predict that $\alpha = 1$, which is in good agreement with our numerical findings. The (c) panels on Fig. 2.3 and Fig. 2.4 also indicate how the average fraction of particles on the surface of a container, $\beta$, defined as the number of particles that are within a particle radius, $\sigma/2$, from the boundary divided by the total number of particles in the system, depends on $|F_a|$, for different values of the temperature. At low temperatures/large-propulsions the particles tend to accumulate at the surface, while for large-temperatures/weak-propulsions the particles are dispersed homogeneously within the container.

It should again be stressed that Eq. (2.8) suggests that the anomalous behavior of the pressure with the temperature is not solely to be found in highly confined gases, but should persist in the limit of large containers.

Taking the limit for $R \to \infty$ in Eq. (2.8) while keeping the density constant gives

$$P = \rho \left( k_B T + \frac{|F_a|^2 \sigma^2}{3 \alpha d (d-1) k_B T} \right) \quad d = 2, 3$$

(2.9)
which has the same limiting behavior for very high temperatures as Eq. 2.8. The location of the inflection point, $T^*$, whose value grows linearly with the strength of the active force and is independent of $R$, can then be easily computed to give

$$
T^* = \frac{|F_a|\sigma}{k_B\sqrt{3\alpha d(d - 1)}}
$$

(2.10)

Let’s now consider the behavior of an active gas when excluded volume interactions between the particles are no longer negligible. This is achieved in our simulations via the Weeks Chandler Andersen (WCA) potential

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

(2.11)

with a range of action extending up to $r_{ij} = 2^{1/6}$. Here $r_{ij}$ is the center to center distance between any two particles $i$ and $j$, and we set $\epsilon = 10k_B T_0$.

In analogy with non-active gases, the deviations from the ideal (non-interacting) case are estimated by $Z \equiv P/P_0$, where $P$ and $P_0$ are, respectively, the pressures of the non-ideal and ideal active systems at the same $V$, $T$ and $|F_a|$. The conventional understanding of this factor for non-active systems is intimately linked to the virial expansion of the pressure at low densities: when $Z \approx 1$, the system has nearly ideal behavior and molecular interactions are negligible, $Z > 1$ is the signature of a positive second virial coefficient pointing to an effectively repulsive nature of the interactions between the particles, and $Z < 1$ would point to an effective attraction that under the appropriate conditions would lead to phase separation. The compressibility factor as a function of volume frac-
tion $\phi = \pi \rho \sigma^3 / 6$ at several values of $|F_a|$ is shown in Fig. 2.5. As expected, for small values of $|F_a|$, the purely repulsive nature of the interparticle interactions leads to $Z > 1$, for the range of volume fractions considered in these simulations. Strikingly, as the activity is increased, $Z$ shows non-monotonic behavior. Specifically, there exist values of $Z$ smaller than one which appear for a range of low densities until excluded volume interactions eventually take over at larger $\phi$ to restore the expected $Z > 1$. It is tempting to associate the value of $Z < 1$ with an effective attraction among the particles leading to a

![Graph](image)

**Figure 2.5:** Compressibility factor, $Z$, for three (a) and two (b) dimensional systems as a function of volume fraction, $\phi$, for different values of the active force, $|F_a|$, at $T = 1$. The dashed line indicates the non-active ideal case.
phase separation between the high density layers on the surface and the low density in the bulk, however, it is not clear that a simple relation between the virial coefficients and the sign of the interaction between the particles also holds for active non-ideal gases. Nevertheless, phase separation of spherical self-propelled particles has been recently observed and predicted in two and three dimensional systems with periodic boundary conditions.

To understand this behavior it is instructive to consider how the active force (the dominant term in the large $|F_a|$ limit) generates a pressure on the wall. For an ideal active gas, particles accumulating at the walls can freely slide across its surface until they align their propulsion axis parallel to the normal of the wall, thus each contributing the maximal force $|F_a|$ (when $T = 0$) to the pressure. For a non-ideal active gas, excluded volume interactions between the particles hinder the particles’ ability to reach these optimal configurations. Clearly, this becomes more of a problem as the volume fraction is increased, and the particles begin to form layers at the surface of the container. The net result is a smaller average force per particle relative to the one generated by the ideal gas and a compressibility factor $Z < 1$. This effect is highlighted in Fig. 2.6 where we plot the angular distribution $P(\cos \alpha)$ for all the particles in contact with the boundary for various volume fraction in two and three dimensions. As density increases, the angular distribution broadens, and a fraction of the particles are anti-aligned to the normal at the boundary, indicating that the second layers of particles can cage particles in the first layer leading to a broadening of the angular distribution.
Figure 2.6: Distribution of the dot products between the propelling axis of a particle and the normal to the wall at the particle’s location for various volume fractions of interacting particles in both three (a) and two (b) dimensions. Only particles within a range of $\sigma$ from the wall are considered for this analysis. The log scale in the vertical axis has been chosen to better highlight the difference between the curves. The value of the active force is $|F_a| = 20$.

2.4 Applications: Effective Force from an Active Bath

We briefly conclude with an important application of the nontrivial thermomechanical properties of an active gas reported in this paper. We compute the strength of the effective force felt by two parallel plates immersed in a two dimensional suspension of non-ideal active particles. For the sake of simplicity, we consider a two-dimensional system, where each plate has a length of $10\sigma$ and a width of $\sigma$, and are fixed at a center to center distance $\sigma$ such that the faces of the plates are in contact. All particles in the system have a diameter of $\sigma$ and interact via the potential in Eq. (5.5) with $\varepsilon = 10\ k_B T_0$. The plates are made to be purely repulsive and interact with the particles in the system via a WCA potential with cutoff, $\sigma_R$, where $\sigma_R$ is the shortest distance between the center of the particle and the edge of the plate. The strength factor is kept consistent with the interparticle strength factor and is set to $\varepsilon_R = 10\ k_B T_0$. In addition, the simulation box is setup to be a square of
area $A$ with periodic boundary conditions at a fixed particle concentration $\rho = N/A = 0.1$ with $N = 188$ particles. The strength of the effective attractive force between the plates, $\langle F_0 \rangle$ is computed from the mean force acting on the plates when held in place.

![Graph](image)

Figure 2.7: Non-monotonic behavior of the effective force, $\langle F_0 \rangle$, induced by an active gas on two plates held at fixed contact distance as a function of $T$. The value of the active force is $|F_a| = 25$.

The well known result for non-active systems is that the strength of the induced attractive potential (depletion force) is proportional to the local pressure imbalance $\rho k_B T$ (in the ideal gas approximation) that develops when the plates are at a surface-to-surface distance smaller than $\sigma$. The expectation for non-active particles is therefore that the interaction strength should increase monotonically with $T$ and $\rho$. Fig. 2.7 shows how instead the strength of the force between the plates presents a non-monotonic behavior with temperature when the depletant is activated by a sufficiently large propelling force, $|F_a| = 25$ in our two dimensional simulations. This counterintuitive result becomes immediately obvious when considering the anomalous pressure/temperature dependence discussed in this paper. We anticipate that other anomalies will appear when computing the full potential of mean force between the plates as a function of distance, as also ob-
served by Angelani et al.[80] for the case of active rod-like particles and spherical colloids.

2.5 Appendix: Analytical Calculation Details

In the high temperature limit where $\tau_a/\tau_r \gg 1$, the average pressure exerted by a single active particle can be readily computed using two different methods. For simplicity, we consider a particle confined to two dimensions with a single rotational degree of freedom.

The first approach is simply to assume the pressure is proportional to the average squared velocity of the particle and thus $P/\rho = m\langle \dot{r}^2 \rangle /2$ where $\rho$ is the number density. A more rigorous approach is to directly compute the correlation function $\langle \mathbf{r} \cdot \mathbf{F}_e \rangle$ where $\mathbf{F}_e$ is the net force exerted on the particle. For a system of ideal particles, it is relatively straightforward to prove $P/\rho = -\langle \mathbf{r} \cdot \mathbf{F}_e \rangle$. In the long time limit, both approaches give the same expression for the pressure, and thus we choose to illustrate the former method for its computational convenience and simple interpretation. The equation of motion of an active Brownian particle of mass $m$ and self-propelling force $|F_a(\theta(t))|$ are given by the coupled Langevin Equations:

\begin{align}
    m\ddot{\mathbf{r}} &= -\gamma \dot{\mathbf{r}} + |F_a| \mathbf{n} + \sqrt{2D}\xi(t) \\
    \dot{\theta} &= \sqrt{2D_r} \xi_R(t)
\end{align}

(2.12)

(2.13)

Using a similar approach to that given in [164] and references therein, the x-
component of the velocity is given by

\[ \dot{x}(t) = \dot{x}_0 e^{-\frac{\gamma}{m}t} + \frac{e^{-\frac{\gamma}{m}t}}{m} \int_0^t \left[ |F_a| \cos(\theta(s)) + \sqrt{2D\xi(s)} \right] e^{\frac{\gamma}{m}s} ds \] (2.14)

where \( \dot{x}_0 = \dot{x}(0) \). It follows that

\[ \dot{x}(t)^2 = \dot{x}_0^2 e^{-\frac{2\gamma}{m}t} + \frac{2\dot{x}_0 e^{-\frac{\gamma}{m}t}}{m} \int_0^t \left[ |F_a| \cos(\theta(s)) + \sqrt{2D\xi(s)} \right] e^{\frac{\gamma}{m}s} ds \]

\[ + \frac{e^{-\frac{2\gamma}{m}t}}{m^2} \left[ \int_0^t \left[ |F_a| \cos(\theta(s)) + \sqrt{2D\xi(s)} \right] e^{\frac{\gamma}{m}s} ds \right]^2 \] (2.15)

which readily simplifies to

\[ \dot{x}(t)^2 = \dot{x}_0^2 e^{-\frac{2\gamma}{m}t} + \frac{2\dot{x}_0 e^{-\frac{\gamma}{m}t}}{m} \int_0^t \left[ |F_a| \cos(\theta(s)) + \sqrt{2D\xi(s)} \right] e^{\frac{\gamma}{m}s} ds \]

\[ + \frac{|F_a|^2 e^{-\frac{2\gamma}{m}t}}{m^2} \int_0^t \int_0^t \cos(\theta(s)) \cos(\theta(s')) e^{\frac{\gamma}{m}(s+s')} ds' ds \] (2.16)

\[ + \frac{2De^{-\frac{2\gamma}{m}t}}{m^2} \int_0^t \int_0^t \xi(s)\xi(s') e^{\frac{\gamma}{m}(s+s')} ds' ds \]

Using the equipartition theorem (\( \langle \dot{x}_0^2 \rangle = k_B T/m \)) and taking the ensemble average of \( \dot{x}(t)^2 \) we are able to further simplify the above expression to

\[ \langle \dot{x}(t)^2 \rangle = \frac{k_B T}{m} e^{-\frac{2\gamma}{m}t} + \frac{2De^{-\frac{2\gamma}{m}t}}{m^2} \int_0^t e^{\frac{\gamma}{m}s} ds \]

\[ + \frac{|F_a|^2 e^{-\frac{2\gamma}{m}t}}{m^2} \int_0^t \int_0^t \langle \cos(\theta(s)) \cos(\theta(s')) \rangle e^{\frac{\gamma}{m}(s+s')} ds' ds \] (2.17)

To evaluate the integral in the last term, it is important to note that
\( \langle \cos(\theta(t)) \cos(\theta(t')) \rangle_{t' > t} = e^{-D_r(t-t')/2} \). It follows that

\[
\frac{|F_a|^2 e^{-\frac{2\pi t}{m}}}{m^2} \int_0^t \int_0^s \langle \cos(\theta(s)) \cos(\theta(s')) \rangle e^{\frac{\pi}{m} (s+s')} ds' ds
\]

\[\begin{align*}
&= \frac{|F_a|^2 e^{-\frac{2\pi t}{m}}}{2m^2} \left( \int_0^t \int_0^s \langle \cos(\theta(s)) \cos(\theta(s')) \rangle e^{\frac{\pi}{m} (s+s')} ds' ds + \int_0^t \int_s^t \langle \cos(\theta(s)) \cos(\theta(s')) \rangle e^{\frac{\pi}{m} (s+s')} ds' ds \right) \\
&= \frac{|F_a|^2 e^{-\frac{2\pi t}{m}}}{2m^2} \left( \int_0^t e^{-(D_r-\frac{\pi}{m})s} \left[ \int_0^s e^{(D_r+\frac{\pi}{m})s'} ds' \right] ds + \int_0^t e^{(D_r+\frac{\pi}{m})s} \left[ \int_s^t e^{-(D_r-\frac{\pi}{m})s'} ds' \right] ds \right) \tag{2.18}
\end{align*}\]

The integral in the second term of Eq. 2.17 is straightforward and the final result is

\[
\langle \dot{x}(t)^2 \rangle = \frac{k_B T}{m} + \frac{|F_a|^2}{2m^2} \left( \frac{1}{D_r + \alpha} \left[ \frac{1}{2\alpha} \left[ 1 - e^{-2\alpha t} \right] + \frac{1}{D_r - \alpha} \left[ e^{-(D_r+\alpha)t} - e^{-2\alpha t} \right] \right] \right.
\]

\[\left. + \frac{1}{D_r - \alpha} \left[ \frac{1}{2\alpha} \left[ 1 - e^{-2\alpha t} \right] - \frac{1}{D_r + \alpha} \left[ 1 - e^{-(D_r+\alpha)t} \right] \right] \right) \tag{2.19}\]

where \( \alpha \equiv \frac{\pi}{m} \). In the limit that \( t \to \infty \),

\[
\langle \dot{x}(t)^2 \rangle = \frac{k_B T}{m} + \frac{|F_a|^2}{2m^2 \alpha (D_r + \alpha)} \tag{2.20}
\]

A similar computations can be carried out to show that \( \langle \dot{y}(t)^2 \rangle = \langle \dot{x}(t)^2 \rangle \) and thus the
pressure is given by

\[
P/\rho = \frac{m}{2} \langle \dot{r}(t)^2 \rangle = \frac{m}{2} (\langle \dot{x}(t)^2 \rangle + \langle \dot{y}(t)^2 \rangle) \\
= m \langle \dot{x}(t)^2 \rangle = k_B T + \frac{|F_a|^2}{2\gamma (D_r + \gamma/m)} \\
= k_B T + \frac{|F_a|^2}{6k_B T/\sigma^2 + 2\gamma^2/m}
\] (2.21)
Chapter 3

The Role of Particle Shape in Active Depletion

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 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.

3.1 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 [165], bacterial suspensions, and catalytically activated colloidal particles [39, 162, 166, 167]. 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 H₂O₂ [167–169], and it is also achieved in colloids where enzymatic reactions take place on one side of a particle [170], or can be driven by self-thermophoresis in defocused laser beams [171].

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 [16]), 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 [172]. 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 [49, 102]. The overall phase behavior as a function of polymer size and concentration has been thoroughly studied within the Oosawa-Asakura approximation [172–175]. More recently there has also been an effort to characterize this force when the system is no longer in equilibrium [176], and a few studies have considered the phase behavior of active particles in a system of passive depletants [161].

In our previous work [68], we studied the thermomechanical properties of an active gas, and found that the force acting on two rods kept at a constant separation in the presence of active depletants has an anomalous, non-monotonic dependence on the temperature – a notable deviation from the typical behavior of equilibrium systems. Two recent studies [73, 78, 79] 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. [80] 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.

### 3.2 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 $\phi_b$. 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 $F_a$, along a predefined orientation vector, $\mathbf{n} = [\sin(\theta), \cos(\theta)]$. The equations
of motion of a bath particle are given by the coupled Langevin equations

\[ m \ddot{r} = -\gamma \dot{r} - \partial_r V(r) + \sqrt{2\gamma^2 D(t)} + F_a n \quad \text{and} \quad \dot{\theta} = \sqrt{2D_r \xi_r(t)} \quad (3.1) \]

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 \( \langle \xi_r(t) \rangle = 0 \) 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

\[ V(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} + \frac{1}{4} \right] \quad (3.2) \]

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. 5.5, where the separation \( r_{ij} \) is the smallest distance between the particle the wall. Figure 3.1 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 $\varepsilon = 10 \, k_B \, T$. The simulation box is a square with periodic boundary conditions, the Langevin damping parameter is set to $\gamma = 10 \tau_0^{-1}$ (here $\tau_0$ is the dimensionless time), and the timestep to $\Delta t = 10^{-3} \tau_0$. Each simulation is run for a minimum of $3 \times 10^7$ iterations. All simulations were carried out using the numerical package LAMMPS [163], and throughout this work we use the default dimensionless Lennard Jones units as defined in LAMMPS, for which the fundamental quantities mass $m_0$, length $\sigma_0$, epsilon $\epsilon_0$, and the Boltzmann constant $k_B$ are set to 1, and all of the specified masses, distances, and energies are multiples of these fundamental values. In our simulations we have $T = T_0 = \epsilon_0 / k_B$, $m = m_0$, $\sigma = \sigma_0$, and $\tau_0 = \sqrt{\frac{m_0 \sigma_0^2}{\epsilon_0}}$.

![Diagram](image)

Figure 3.1: 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).
3.3 Numerical 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 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 \( \beta F_a \sigma = 0 \) \( (\beta \equiv (k_B T)^{-1}) \), 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 \( U(r) = -k_B T \log[g(r)] \) [177]. 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 volume fraction \( \phi_b = 0.1 \), and the simulation box is a periodic cube with box length \( 150\sigma \). The resulting radial distribution functions are shown in Fig. 3.2. Each simulation was run for over \( 10^8 \) time-steps.

In the passive system with \( \beta F_a \sigma = 0 \), the \( g(r) \) presents a large peak at the colloid contact separation as expected for this system which is characterized by a strong deple-
tion 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 \( \phi_b = 0.1 \). 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. 3.3.

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. 3.4(a)) as the half circle which lies closer to the center of the other colloid, and the outer surface
Figure 3.2: Radial distribution function $g(r)$ of the large colloids for two different values of self-propulsion $\beta F_a \sigma$. In a passive bath (blue, solid) the expected peak signifies a short ranged attraction between colloids. In an active bath (dashed line), $g(r)$ takes values which are less than 1, suggesting a repulsion between the colloids. This repulsion increases with the bath’s activity.

(Region I Fig. 3.4(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. 3.4(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 a wall. The active particle will continue to exert a force into a barrier until its propulsion
axis begins to rotate, upon which the particle will slide along the wall. For a given strength of self-propulsion, the duration of a collision is controlled by the rotational diffusion, which is governed by thermal fluctuations, and has a strong dependence on the local
environment. During collisions, active particles remain in contact with the surface of the larger colloids for some amount of time before sliding off or rotating away. The duration of contact is in large part determined by the geometry of the colloids.

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 [179] 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. 3.4(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. 3.5).
Figure 3.5: Time averaged density maps of active particles for $\beta F_a \sigma = 50, \phi_b = 0.1$ 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).

As 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.

We also measure the net force between two disks at contact as a function of the active force for $\sigma_c = 10\sigma$ and $\sigma_c = 20\sigma$, this is shown in Fig. 3.6. In the absence of activity, we recover the expected depletion attraction for equilibrium systems, and in the limit of large active forces, we observe the repulsive behavior discussed above. However, for intermediate values of $\beta F_a \sigma \in [1, 10]$, we observe a strengthening of the attraction between the colloids as a function of $F_a$. These results suggest that as long as $F_a$ is sufficiently small, the main effect of the propelling force is that of an effective higher temperature of the bath, leading to a strengthening of the depletion interactions. It should be noted that,
for this range of active forces, the persistence length of the trajectory traced by a single active particle, estimated as \( d \approx (F_a/\gamma)D_r^{-1} = (\beta F_a\sigma^2)/3 \), is significantly smaller than the colloidal diameter used in these simulations. One possible interpretation of this result is that as long as \( d \ll \sigma_c \) the colloids always experience an attractive interaction. To see whether this is true, we repeated our simulations for the same range of active forces for two larger colloids with twice the diameter \( \sigma_c = 20\sigma \), placed in contact with each other. Surprisingly, the sign of the interaction switches over at approximately the same value of \( F_a \) as for the smaller colloids (see Fig. 3.6 inset). If the \( d \ll \sigma_c \) argument were correct, the attraction should persist to larger values of \( F_a \) for the larger colloids, but we find that this is not the case. One reason for this could be due to the fact that larger colloidal diameters also correspond to larger regions where particles can be trapped. This leads to an enhanced repulsion between the colloids that competes with the strengthened attraction. This enhanced repulsion is easily seen when comparing the two plots in Fig. 3.3 showing that larger colloids experience overall 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
Figure 3.6: Effective force between two disks in contact and in the presence of active depletants as a function of self-propulsion $\beta F_a \sigma$ for disks of diameter $\sigma_c = 10\sigma$ and $20\sigma$, at $\phi_b = 0.1$ and box side length $L = 150\sigma$. The inset shows that for moderate active forces, an enhanced attraction is observed.

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 [73], 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. 3.7(a)). Surprisingly, at larger separations (Fig. 3.7(b)), a large long-ranged attraction is induced between the rods. In agreement
with [73] 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 \( d/\sigma = (\beta F_a \sigma)/3 \). The inset of Fig. 3.7(b) shows the linear dependence of the interaction decay length \( \ell_p \) as a function of the particle persistence length \( d/\sigma = \beta F_a \sigma/3 \).

![Graph](image)

Figure 3.7: 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 particle persistence length \( d/\sigma = \beta F_a \sigma/3 \).

Further insight can be obtained by looking at the time-averaged density map of the depletants for different rod separations (Fig. 3.8.) 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.

In principle, this “shadowing” effect leading to a long-range attraction extending up to \( \ell_p \) should also be observed for colloidal disks. However, in this case, partial layers of active particles form on the perimeter of the disks and can easily diffuse around it. This leads to a uniform density of active particles along the disk perimeter, which balances the forces acting on the colloids’ inner and outer sides. In simulations with ideal active particles, where no layering can develop, long-range attractive forces are observed for colloidal disks. This suggests that an equilibrium distance in the effective colloidal interactions will develop for sufficiently low concentrations of active particles.

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 [99], have shown that for large self-propelling forces the typical time \( t_1 \) a particle remains in contact with a rod scales as \( t_1 \sim \left( \frac{s}{F_a} \right)^2 \left( \frac{1}{D} \right)^{1/4} \). 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 \( t_2 \sim \frac{L^2 \gamma}{\ell F_a} \), which accounts for the probability of finding the rod when moving at a speed \( v_a = F_a/\gamma \) across the box. Alternatively, one can think of \( 1/t_2 \) as the average collision rate between an active particle and the rod. So that \( 1/t_2 = (1/L^2)Cv_a \), where \( C = \ell \) is the cross section of the rod.

During this time the particle will exert no force on the rod. The net average force can then be estimated as \( \langle F \rangle \sim \frac{N E_o t_1}{t_1 + t_2} \), \( (N \) is the number of active particles) and for sufficiently large systems, \( t_2 \gg t_1 \), it can be simplified to \( \langle F \rangle \sim NF_a t_1/t_2 \), leading to the
Figure 3.8: Time averaged density maps of active particles around larger rods. (a) $\beta F_a \sigma = 0$ at rod separation $r = 4\sigma$, (b) $\beta F_a \sigma = 50$ at rod separation $r = 2\sigma$, (c) $\beta F_a \sigma = 50$ at rod separation $r = 4\sigma$, and (d) $\beta F_a \sigma = 50$ 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.

scaling behavior

$$
\langle F \rangle \simeq \rho \left( \frac{F_a^{4.65}}{\gamma D_r} \right)^{\frac{1}{3}}
$$

where $\rho$ is the number density. 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

\[
\langle F \rangle \simeq \rho F_a \ell^2 \quad (3.4)
\]

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 \( \langle \theta^2 \rangle = (\pi/2)^2 = 2D_r t_1^{\max} \) as the upper bound. In this limit the average force should scale as

\[
\langle F \rangle \simeq \frac{F_a^2 \ell}{\gamma D_r} \quad (3.5)
\]

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 3.9 and 3.10 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 volume fraction \( \phi_b = 0.1 \), 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. 3.4 should give the most appropriate description for the effective force. This is consistent with Fig. 3.9, 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 \( F_a \) will contribute to the average force a quadratic (thermal-like) term corresponding to an enhanced velocity of the particles [68].

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 \( t_1 \sim \left( \frac{\gamma \ell}{F_a} \right)^\frac{2}{3} \left( \frac{1}{D_r} \right)^\frac{1}{3} \) (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. 3.5 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. 3.3 to hold, but at $\phi_b = 0.1$, all these effects become relevant. We therefore expect a combination of Eq. 3.4 and Eq. 3.5 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 $\ell$.

### 3.4 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 [95].

Finally, as discussed above, we expect these interactions to be quite sensitive to the concentration of the active particles. Furthermore, we anticipate that many body effects play an important role in these systems, as the conditions leading to long-range attractive forces are strongly dependent on the specific arrangements of colloids.
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.
Chapter 4

Curvature Induced Activation of a Passive Tracer in an Active Bath

We use numerical simulations to study the motion of a large asymmetric tracer immersed in a low-density suspension of self-propelled particles in two dimensions. Specifically, we analyze how the curvature of the tracer affects its translational and rotational motion in an active environment. We find that even very small amounts of curvature are sufficient for the active bath to impart directed motion to the tracer, which results in its effective activation. We propose simple scaling arguments to characterize this induced activity in terms of the curvature of the tracer and the strength of the self-propelling force. Our results suggest new ways of controlling the transport properties of passive tracers in an active medium by carefully tailoring their geometry.

4.1 Introduction

In recent years, the behavior and dynamics of microstructures and colloidal particles immersed in an active fluid (e.g. bacteria, self-propelled nanoparticles, artificial microswimmers, etc.) have drawn considerable interest. The inherently non-equilibrium driving forces and stochastic nature of an active fluid give rise to phenomenological behavior
that is quite remarkable including anomalous diffusion [84, 180–184], tunable effective interactions between suspended microcomponents [52, 80, 82, 185], and targeted delivery of colloids [89, 186]. In addition, there has recently been an effort to understand the dynamics, phase behavior, and self-assembly properties of suspensions of deformable [187, 188] and/or irregular shaped active particles [98, 189]. An emerging area in this field is designing microstructures to perform specific tasks when immersed in an active suspension, most notably driving microscopic gears and motors [86, 87], the capture and rectification of active particles [92, 155, 190–192], and using active suspensions to propel wedge-like carriers [97, 193]. The geometry of these microdevices is a crucial component to being able to effectively convert the energy from the active environment into mechanical work. Interestingly, Angelani and Di Leonardo [97] showed that chevron shaped micro-shuttles immersed in a bacterial suspension undergo directed motion along their axis of symmetry. A similar observation was made experimentally by Kaiser et al. [193] who showed that chevron shaped particles can be set into rectified motion along their wedge cusp when immersed in a high density bacterial suspension. Given these results, it is well established that asymmetric tracers with locally concave regions (e.g. wedge, chevron, lock and key colloids, etc.) are able to undergo rectified motion in an active fluid, while spherical tracers only undergo enhanced isotropic diffusion [84, 181, 184]. Intriguingly and in stark contrast to a tracer in a passive environment, the transport properties of a tracer immersed in an active fluid are strongly dependent on its underlying geometry. In short, a tracer in an active environment can be made active in its own right by simply altering its shape.

In an effort to characterize this unique phenomenon, we systematically distort the
geometry of a rod shaped tracer and study the resulting dynamics in an active medium. Our goal is to understand the transition from isotropic to directed motion as a function of tracer geometry. In previous studies, the rectification of the random motion of the bacteria is caused by polar ordering and trapping of bacteria inside the cusp regions of the tracer. We however consider a low-density suspension of non-aligning active particles. This choice is motivated by the recent developments in the design and synthesis of artificial self-propelled particles [25, 128, 129, 149], as well as to eliminate the polar ordering and trapping which is typical of high density bacterial suspensions, and be able to focus exclusively on the effect of the particle activity disregarding collective effects that may ensue due to excluded volume interactions at larger concentrations. Our results show that directed motion of the tracer can be obtained under a much more general set of geometric constraints and explain how it can be easily controlled by the curvature of the tracer alone. In other words, independently of the local ordering of the particles, induced activity can be imparted by local density gradients around the tracer, which can be tuned and enhanced by manipulating the curvature of the tracer.

4.2 Model

We consider a two dimensional model where a single asymmetric tracer is immersed in a bath of \( N \) spherical active particles of diameter \( \sigma \). Each active bath particle has mass \( m \), and undergoes Langevin dynamics at a constant temperature \( T \). Self-propulsion is introduced through a directional force of constant magnitude \( |F_a| \) and is directed along a predefined orientation vector \( \mathbf{n} = (\cos \theta, \sin \theta) \) which passes through the origin of each
particle and connects its poles. The equations of motion of an individual particle are given by the coupled Langevin equations

\[ m\ddot{r} = -\gamma \dot{r} + |F_a| \mathbf{n} - \partial_r V + \sqrt{2\gamma^2 D} \xi(t) \]  
\[ \dot{\theta} = \sqrt{2D_r} \xi_r(t) \]

where \( \gamma \) is the translational friction and \( V \) the interparticle potential acting on the particle. The translational and rotational diffusion constants are given by \( D \) and \( D_r \), respectively. 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. The translational diffusion constant \( D \) is related to the temperature \( T \) via the Stokes-Einstein relation \( D = k_B T / \gamma \).

In the low Reynolds number regime, the rotational and translation diffusion coefficients for a sphere satisfy the relation \( D_r = (3D) / \sigma^2 \).

Each tracer is modeled as a bent rod characterized by its arc length \( \ell = 25\sigma \) and radius of curvature \( R \) (Fig. 4.1(b) and Fig. 4.2(c)). For practical purposes, the rods are discretized into \( N_T = 21 \) equidistant and overlapping spherical particles of diameter \( \sigma_T = 2.5\sigma \). A suitably large number of spheres were chosen to accurately reproduce the shape of the particle and to make the surface sufficiently smooth. The tracer itself undergoes over-damped Langevin dynamics at a constant temperature \( T \) and the equations of motions are the rigid body analogs to Eqs. (1) and (2) where \( |F_a| = 0 \) since the tracer itself is non-active.
All interactions between the particles in the systems are purely repulsive and are given by the Weeks-Chandler-Andersen (WCA) potential

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

(4.3)

with a range of action extending up to \( r_{ij} = 2^{1/6}\sigma \). Here \( r_{ij} \) is the center to center distance between any two particles \( i \) and \( j \), \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \) where \( i = 1, 2 \) corresponding to an active particle or a tracer particle, respectively, and \( \epsilon = 10k_B T \) is the interaction energy. Using the numerical package LAMMPS [163], all simulations were carried out in a periodic box of dimension \( L = 200 \) with \( T = m = \sigma = \tau = 1 \) and \( \gamma = 10\tau^{-1} \) (here \( \tau \) is the dimensionless time). Each simulation was run for a minimum of \( 5 \times 10^8 \tau \) time steps. The drag coefficient \( \gamma \) was chosen to be sufficiently large such that the motion of the particles is effectively overdamped. Several of the simulations were repeated with larger values of \( \gamma \) (e.g. \( \gamma = 50, 100 \)), which produced no detectable differences in our results. All quantities in this investigation are given in reduced Lennard-Jones units.

4.3 Numerical Results

As a way of illustrating our main result we show in Fig. 1(a) typical trajectories (particle traces) for tracers having different radii of curvature \( R \) at constant arc length \( \ell \) immersed in an active suspension of volume fraction \( \Phi = 0.005 \) and propelling force \( |F_a| = 100 \). A sufficiently large propelling force was chosen to illustrate the curvature induced activation of a tracer. In addition, a typical snapshot from a simulation is given in Fig. 4.1(b),
Figure 4.1: (Color online) (a) Trajectories for tracers of various curvatures immersed in an active bath of volume fraction $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$. The trajectory for each tracer was taken over a duration of $5000\tau$ and each tracer was initially located at the origin. (b) Snapshot from simulation with $R = 8$, $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$ where both the laboratory and body-centered reference frames are shown. The orange half of a bath particle denotes the direction of propulsion.

which details the different reference frames used in the subsequent analysis. The typical mean square displacement (MSD) of the center of mass $Q$ for various tracers in the laboratory frame is shown in Fig. 4.2(a). All tracers undergo ballistic behavior at short times, and eventually crossover to a diffusive regime at longer times. As the curvature of the tracer increases, the super-diffusive regime persists for longer times prolonging the eventual crossover to the purely diffusive regime. In the body-centered frame, the mean displacement of the tracer along its main axis of symmetry $A$ is given in Fig. 4.2(b). For a straight tracer (i.e. $R = \infty$), there is no net displacement along the main axis of the tracer, which is obvious from symmetry considerations. However, as soon as the symmetry of the tracer is broken by introducing any amount of curvature, the tracer undergoes net directed motion in the positive $A$ direction leading to a nonzero mean displacement in the body-centered frame. As the tracer becomes increasingly curved (Fig. 4.2(b)), this effective propelling force becomes larger.
The directed motion of the tracer can be understood by looking at the time averaged local density of active particles in the system (Fig. 4.3). The average local density is homogeneous across the system, except along the surface of the tracer, where it shows a significant increase. Specifically, the density is larger on the concave side of the tracer when compared to its convex side, and this difference becomes even larger for tracers with higher degrees of curvature. As demonstrated in reference [99], the positive curvature of a surface can act as a restoring force against random thermal rotations, and drives active

![Graphs and diagrams]

Figure 4.2: (a) MSD for tracers of various curvatures immersed in an active bath of volume fraction $\Phi = 0.005$, $T = 1$, and $|F_a| = 100$. (b) Mean displacement of the tracer along the $A$ axis in the body centered frame. (c) Sketch of the model and relative variables discussed in the paper.
Figure 4.3: Normalized time averaged active particle density for various tracers in an active suspension of $\Phi = 0.005$, $T = 1$, and $|F_\alpha| = 100$.

particles towards a stable orientation where the propelling axis becomes parallel to the surface normal. This stabilizing effect greatly increases the time required for a particle to escape from the side of the surface with positive curvature. The side of the tracer with negative curvature behaves in the opposite way and destabilizes the axial angle of the particle from the surface normal upon any amount of thermal rotations, which results in a significantly shorter escape time. The combination of these two mechanisms produces the measured density gradient across the tracer that results in its net directed motion.

Due to the symmetry of the system, the average tangential force as well as the average
torque will be equal to zero, and indeed we find that the mean squared angular displace-
ment of the tracer $\langle \Omega^2 \rangle$ is diffusive for almost all observed times (i.e. $\langle \Omega^2 \rangle = D_\Omega t$ where
$D_\Omega$ is the rotational diffusion constant of the tracer). We find that the rotational diffusion
constant $D_\Omega$ increases with the strength of the active force as well as with the curvature
of the tracer for large self-propelling forces (Fig. 4.4). We however defer a full char-
acterization of the rotational dynamics to a later publication, as it is a highly non-trivial
problem that truly deserves its own in-depth analysis. The remainder of this work focuses
on developing a scaling theory for the curvature induced activation of the tracer.

![Graph showing $D_\Omega$ vs $|F_a|$](image)

**Figure 4.4:** Rotational diffusion constants for tracer particles having different curvatures
in an active suspension of $\phi = 0.005$ and $T = 1$. The data is plotted as a function of the
active bath self-propelling force $|F_a|$.

## 4.4 Analysis of Tracer Motion

The directed motion of the curved tracer emerges when the persistent length of an active
particle becomes much larger than the dimension of the tracer. In this regime, a simple
way of estimating the net force exerted on the tracer can be obtained by considering that
a bath particle can either be on the surface of the tracer pushing with a force proportional to $|F_a|$ or diffusing across the system and applying no force. As previously mentioned, the amount of time an active particle spends on the surface of the tracer is highly dependent on the side it is located and characterized by a residence time $\tau_n$ or $\tau_p$ for the side of the tracer with negative or positive curvature, respectively. Given these quantities and the average time an active particle spends in the bath between collision with the tracer, which we denote by $\tau_0$, the net average force exerted by an ideal gas of $N$ active particles along the $A$ axis of the tracer can be estimated as $\langle F_A \rangle = N(\langle F_p \rangle - \langle F_n \rangle)$, where $\langle F_p \rangle$ and $\langle F_n \rangle$ are the average forces exerted on the positive and negative sides of the tracer. In the low density and small tracer limit (i.e. $\tau_0 \gg \tau_n$ and $\tau_0 \gg \tau_p$),

$$\langle F_A \rangle \simeq N \langle F \rangle \left( \frac{\tau_p - \tau_n}{\tau_0} \right) \quad (4.4)$$

where $\langle F \rangle \simeq |F_a|\langle \cos(\phi) \rangle$ is the average force an active particle exerts along the $A$ axis of the tracer. For simplicity, we assume that the particle axis is predominantly parallel to the surface normal at that point [99].

Given the geometry of the system and assuming that an active particle can diffuse anywhere on the surface of the tracer with equal probability (where the angular range spans $[-\frac{\phi_m}{2}, \frac{\phi_m}{2}]$ (Fig. 4.2(c)), it follows than an approximation for $\langle F \rangle$ is given by

$$\langle F \rangle = \frac{2|F_a|}{\phi_m} \sin\left(\frac{\phi_m}{2}\right) \quad (4.5)$$

In order to estimate $\tau_p$ and $\tau_n$, we use a similar approach to that proposed by Fily et al. [99]. In the limit of large activity, it is fair to assume that the active particles can
only leave the surface of the tracer (once they are in contact with it) by sliding out. This sliding motion is driven by the angle between the self-propelling axis and the boundary which results in tangential forces along the tracer, and can be described with the coupled overdamped Langevin equations

\[
\dot{\phi} = \frac{v_a}{R} \sin(\theta - \phi) \tag{4.6}
\]
\[
\dot{\theta} = \sqrt{2D_r} \xi_r(t) \tag{4.7}
\]

where \(\theta\) is the angle of the active axis, and \(\phi\) is the angular position of the active particle with respect to the osculating circle of the tracer (see Fig. 4.2(c)). Here \(v_a = |F_a|/\gamma\) is the particle active velocity, and for simplicity, we neglected the thermal noise in \(\phi\) as for large forces it gives only a small contribution to the sliding motion of the particle. We define \(\alpha \equiv \theta - \phi\) to be the angle between the self-propelling axis and the boundary normal. By taking the difference between the two equations, we have

\[
\dot{\alpha} = -\frac{v_a}{R} \sin(\alpha) + \sqrt{2D_r} \xi_r(t) \simeq -\frac{v_a}{R} \alpha + \sqrt{2D_r} \xi_r(t) \tag{4.8}
\]

for a particle facing the concave side of the tracer. In the large activity regime, Fily et al. [99] have demonstrated that the small angle approximation in Eq. (4.8) is valid for sufficiently curved surfaces. The equation for a particle on the convex side is obtained by replacing \(R \rightarrow -R\).
This equation can be readily solved to give

\[
\langle \alpha^2(t) \rangle = \frac{RD_r}{v_a} \left( 1 - e^{-2\frac{v_a}{R}t} \right)
\]  \hspace{1cm} (4.9)

Notice that in this derivation we ignored the contribution due to \( \alpha(0) \) (the initial angle of impact of a particle with the tracer). This is justified because the time spent on the tracer by an active particle with a large value of \( \alpha(0) \) is typically small and so is its contribution to the net force on the tracer. Furthermore, we find that the probability that a particle hits the tracer with a large angle with respect to the surface normal is exponentially small (data not shown). Nevertheless the contribution from \( \alpha(0) \) becomes critical in the limit of very short tracers, when the active particles slide off before any significant rotational diffusion can take place.

Since \( \langle \alpha^2 \rangle = \langle \phi^2 \rangle + \langle \theta^2 \rangle - 2\langle \phi \theta \rangle = \langle \phi^2 \rangle - \langle \theta^2 \rangle + 2\langle \alpha \theta \rangle \) where \( \langle \theta^2 \rangle = 2D_r t \) and

\[
\langle \alpha \theta \rangle = 2D_r \int_0^t dt_1 \int_0^t dt_2 \langle \xi(t_1) \xi(t_2) \rangle e^{-\frac{v_a}{R}(t-t_1)} = \frac{2RD_r}{v_a} (1 - e^{-\frac{v_a}{R}t}),
\]

we can solve explicitly for \( \langle \phi^2 \rangle \)

\[
\langle \phi^2 \rangle_p = 2D_r t + \frac{RD_r}{v_a} \left[ \left( 1 - e^{-2\frac{v_a}{R}t} \right) - 4 \left( 1 - e^{-\frac{v_a}{R}t} \right) \right]
\]  \hspace{1cm} (4.11)

Equation (4.11) gives the MSD of an active particle along the concave surface of the tracer (positive curvature). The analogous equation for the convex side of the tracer (negative curvature) is

\[
\langle \phi^2 \rangle_c = 2D_r t + \frac{RD_r}{v_a} \left[ \left( 1 - e^{-2\frac{v_a}{R}t} \right) - 4 \left( 1 - e^{-\frac{v_a}{R}t} \right) \right]
\]

This equation can be readily solved to give

\[
\langle \alpha^2(t) \rangle = \frac{RD_r}{v_a} \left( 1 - e^{-2\frac{v_a}{R}t} \right)
\]  \hspace{1cm} (4.9)

Notice that in this derivation we ignored the contribution due to \( \alpha(0) \) (the initial angle of impact of a particle with the tracer). This is justified because the time spent on the tracer by an active particle with a large value of \( \alpha(0) \) is typically small and so is its contribution to the net force on the tracer. Furthermore, we find that the probability that a particle hits the tracer with a large angle with respect to the surface normal is exponentially small (data not shown). Nevertheless the contribution from \( \alpha(0) \) becomes critical in the limit of very short tracers, when the active particles slide off before any significant rotational diffusion can take place.

Since \( \langle \alpha^2 \rangle = \langle \phi^2 \rangle + \langle \theta^2 \rangle - 2\langle \phi \theta \rangle = \langle \phi^2 \rangle - \langle \theta^2 \rangle + 2\langle \alpha \theta \rangle \) where \( \langle \theta^2 \rangle = 2D_r t \) and

\[
\langle \alpha \theta \rangle = 2D_r \int_0^t dt_1 \int_0^t dt_2 \langle \xi(t_1) \xi(t_2) \rangle e^{-\frac{v_a}{R}(t-t_1)} = \frac{2RD_r}{v_a} (1 - e^{-\frac{v_a}{R}t}),
\]

we can solve explicitly for \( \langle \phi^2 \rangle \)

\[
\langle \phi^2 \rangle_p = 2D_r t + \frac{RD_r}{v_a} \left[ \left( 1 - e^{-2\frac{v_a}{R}t} \right) - 4 \left( 1 - e^{-\frac{v_a}{R}t} \right) \right]
\]  \hspace{1cm} (4.11)

Equation (4.11) gives the MSD of an active particle along the concave surface of the tracer (positive curvature). The analogous equation for the convex side of the tracer (negative curvature) is

\[
\langle \phi^2 \rangle_c = 2D_r t + \frac{RD_r}{v_a} \left[ \left( 1 - e^{-2\frac{v_a}{R}t} \right) - 4 \left( 1 - e^{-\frac{v_a}{R}t} \right) \right]
\]
curvature) is again obtained by replacing $R \to -R$, and gives

$$\langle \phi^2 \rangle_n = 2D_r t + \frac{RD_r}{v_a} \left[ \left( e^{\frac{v_a}{R} t} - 1 \right) - 4 \left( e^{\frac{v_a}{R} t} - 1 \right) \right]$$

(4.12)

In the long time limit ($t \to \infty$), the particles facing the concave side of the traces will undergo standard diffusive behavior $\langle \phi^2 \rangle_p = 2D_r t$, whereas those facing the convex side will have an exponentially growing angular dependence.

The expression for the MSD on the concave side of the tracer (Eq. (4.11)) does indeed confirm that the positive curvature acts as a restoring force which greatly increases the time required for a bath particle to escape, while (Eq. (4.12)) clearly reveals that the side of the tracer with negative curvature destabilizes the propelling axis of an active particle away from the surface normal giving rise to a faster escape time. Expanding Eqs. (4.11) and (4.12) for small times, we obtain

$$\langle \phi^2 \rangle_{p/n} \approx \frac{2}{3} D_r \left( \frac{v_a}{R} \right)^2 t^3$$

(4.13)

For the case of particles on the concave surface, we verified these results numerically by explicitly measuring the diffusion of an active particle confined inside a circular cavity.

We define $\tau_p$ and $\tau_n$ to be the times required for the particles facing respectively the concave and the convex sides of the tracer to cover the same arc length $\langle \phi^2 \rangle_p = \langle \phi^2 \rangle_n = \left( \frac{\ell}{R} \right)^2$. We first discuss the limit of large $R$ or small $\ell$, for which $\tau_p \gtrsim \tau_n$. Carrying out the expansion of Eqs. (4.11) and (4.12) to the fourth order and taking the difference of the two
Figure 4.5: (a) Effective force, \( \langle F_A \rangle \), induced by the active particle on the tracer as a function of propulsion \( |F_a| \) for various tracer curvatures. (b) Collapse of \( \langle F_A \rangle \) as a function of \( R \) for different values of \( |F_a| \). The dashed line corresponds to Eq. (4.15) with a single fitting parameter \( \kappa = 0.40(0) \) in the prefactor.

expressions gives

\[
\frac{2}{3} \left( \frac{v_a}{R} \right)^2 (\tau_p^3 - \tau_n^3) = \frac{1}{2} \left( \frac{v_a}{R} \right)^3 (\tau_p^4 + \tau_n^4).
\]

(4.14)

For sufficiently large \( R \), we can write \( \tau_p - \tau_n = \varepsilon \), where \( \varepsilon \) is a small but positive number.

We can then further expand Eq. (4.14) in \( \varepsilon \) by writing \( \tau_p^3 - \tau_n^3 \approx 3\tau_n^2\varepsilon \) and \( \tau_p^4 + \tau_n^4 \approx 2\tau_n^4 \), to get \( \varepsilon = \frac{1}{2} \left( \frac{v_a}{R} \right)^2 t_n^2 \). Using Eq. (4.13), with \( \langle \phi^2 \rangle = \left( \frac{\xi}{R} \right)^2 \), we finally get \( \tau_n^2 = \left( \frac{2\varepsilon}{2D_R v_a^2} \right)^{\frac{2}{3}} \), and thus \( \varepsilon = \tau_p - \tau_n = \frac{1}{2R} \left( \frac{3}{2D_R} \right)^{\frac{2}{3}} \xi^{\frac{2}{3}} v_a^{\frac{1}{3}} \).

The average collision rate between a single bath particle and the tracer can be es-
imated by $1/\tau_0 = (1/L^2)Cv_a$ where $C$ is the collision cross section of the tracer. A reasonable approximation for the collision cross section is either the length of the tracer $l$ for relatively straight tracers or the radius of curvature $R$ for highly curved tracers.

Using Eq. (4.4), and taking $1/\tau_0 \simeq (1/L^2)\ell v_a$, we finally obtain

$$\langle F_A \rangle \simeq \frac{\rho \ell^\frac{2}{3} |F_a|^\frac{2}{3}}{(D_r \gamma)^\frac{2}{3}} \sin \left( \frac{\ell}{2R} \right)$$

(4.15)

where $\rho = N/L^2$. We find that this functional form properly accounts for all of our data. This is shown in Fig. 4.5 where Eq. (4.15) has been used to fit the data both in terms of the radius of curvature $R$ and the strength of activity $|F_a|$ with a single fitting parameter in the prefactor given by $\kappa = 0.40(0)$.

We expect deviations from this law to appear for long and highly curved tracers, where in general a significant amount of diffusive sliding occurs before the particles leave the tracer. In this case, the small $R$ limit of Eqs. (4.11) and (4.12) is more appropriate, and $\tau_p$ can be approximately written as $\tau_p \simeq \frac{1}{2D_r} \left( \frac{\ell}{R} \right)^2$. In this limit $\tau_p \gg \tau_n$ and $1/\tau_0$ can be written as $1/\tau_0 \simeq (1/L^2)Rv_a$ resulting in

$$\langle F_A \rangle \simeq \frac{\rho \ell |F_a|^2}{\gamma D_r} \sin \left( \frac{\ell}{2R} \right)$$

(4.16)

It is important to stress that in both cases we have the same curvature dependence of the effective active force, and that curvature is the crucial parameter for the activation of the tracer with a dependence given by $\langle F_A \rangle \sim 1/R$. 

87
4.5 Conclusion

Using a combination of numerical simulations and analytical theory, we have demonstrated how a tracer can be made effectively active when immersed in a suspension of active particles. We have analyzed how the speed of this effective motion can be enhanced with the curvature of the tracer, and proposed simple theoretical arguments to quantify the induced activity as a function of the strength of the bath activity and the tracer curvature. Our results are most valid in the low density limit, where the residence time of the active particles on the surface of the tracer is much smaller than the typical time required for the particles in the bulk to find the tracer. Clearly whenever, the two timescales are of the same order a crossover from a super-linear to a linear dependence of the effective force on $|F_a|$ should be expected, at least in the ideal gas limit. In fact, at higher densities, when significant clustering on the concave side of the surface occurs, excluded volume interactions become important and will act to weaken the overall force exerted on the wall as explained in our previous work [68]. Indeed, the spherical shape of the active particles will not produce any cooperative alignment (at least as long as hydrodynamic interactions are not considered), but will prevent optimal ordering of the particles propelling axes along the normal to the surface.

In principle, one could improve our estimates for the calculation of $\langle F_A \rangle$ by modifying $\langle F \rangle$ in Eq. (5) to also include the average over the small deviations of the active particle axis away from the normal to the surface. This gives

$$\langle F \rangle = 2|F_a| \frac{\sin(\phi_m/2)}{\phi_m} \exp \left( -\frac{\gamma R D_r}{|F_a|} \right)$$
but for large forces and sufficiently curved tracers, this would only add a sub-leading term to our estimates.

It should be finally noted that in all our simulations we considered the friction coefficient of the tracer $\gamma_t$ to be independent of the particle curvature. Clearly this is an approximation as we expect this value to be dependent on $R$. Unfortunately, evaluating an explicit formula for $\gamma_t(R)$ is not trivial, but any curvature dependence could be easily incorporated.
Chapter 5

Anomalous dynamics of an elastic membrane in an active fluid

Using numerical simulations, we characterized the behavior of an elastic membrane immersed in an active fluid. Our findings reveal a nontrivial folding and re-expansion of the membrane that is controlled by the interplay of its resistance to bending and the self-propulsion strength of the active components in solution. We show how flexible membranes tend to collapse into multi-folded states, whereas stiff membranes fluctuate between an extended configuration and a singly folded state. This study provides a simple example of how to exploit the random motion of active particles to perform mechanical work at the micro-scale.

5.1 Introduction

Suspensions of bacteria and synthetic active particles offer a novel approach to manipulating matter at the micro-scale. Not only do passive micro-components in an active fluid display unusual transport properties [1, 5, 81, 95, 157, 181–184, 194–201], but active fluids can mediate a new set of effective interactions between passive elements [73, 79, 80, 83, 193, 202, 203], providing an extra handle in material design. In addition, active fluids have been used to power primitive micro-machines [85–87, 89, 90, 161]. The origin of this phenomenology is derived from the unique pressure (or stress) gradients
generated by active fluids [66, 68–71, 99, 204–206].

Although, much of the effort in this field has focused on the interaction of active fluids with rigid, passive micro-components, there has been some work on the behavior of flexible objects. For instance, the behavior of fluid membranes immersed in a variety of active environments have been studied [8, 207–209]. Both flexible[81, 82] and semi-flexible polymers[82] confined to a two-dimensional active bath have been shown to exhibit dynamic and scaling behavior that is much richer than that expected for polymers in a thermal bath. Fully flexible polymers[81] display a non-universal Flory scaling behavior as well as an anomalous chain swelling, while semi-flexible polymers[82] display a dynamic collapse and re-expansion when immersed in an active bath at different values of the propelling forces. These results suggest that the driven nature of an active fluid can be used to control the shape of flexible micro-components. This can be thought of as a microscopic joint or clamp where the mechanical action (folding) of stiff fibers can be induced by increasing the self-propulsion of the active components in solution.

Much of the phenomenological behavior observed for polymers is, however, specific to two-dimensional (or quasi-two dimensional) systems, where active particles can be confined with relative ease within the bends of a polymer, and generate significant pressure gradients capable of driving its collapse. The scaling behavior and statistical properties of a polymer, when embedded in a three-dimensional active fluid, do not differ significantly from those of a polymer in a thermal bath. This would not be the case when replacing the polymer with a flexible two dimensional surface, which is the subject of this work.

Here, we study the behavior of an extended elastic membrane, a natural generalization of a linear polymer chain to an intrinsically two-dimensional structure, suspended in a
three dimensional active bath. Physical examples of such materials include graphite-oxide and graphene sheets[210–213], cross-polymerized biological membranes[214], and the cytoskeleton of red blood cells[215, 216]. Polymerized membranes have been studied intensively in the last few decades (see [217] and references therein for a review on the subject) and display a phenomenological behavior that is far richer in complexity than that observed in linear polymers.

Using numerical simulations, we explore the mechanical properties and conformational behavior of an elastic membrane immersed in an active fluid for different strengths of the bath activity and for different values of its bending rigidity. Our findings reveal a nontrivial folding and re-expansion of the membrane that is controlled by the interplay of its resistance to bending and the self-propulsion strength of the active components in solution. We show how flexible membranes tend to collapse into multi-folded states, whereas stiff membranes fluctuates between an extended configuration and a singly folded state.

Figure 5.1: (Color online) Reference snapshots showing the various conformations taken by the membrane as the bath activity and bending rigidity is varied. (A) flat/extended, (B) bent, (C) single folded, and (D) multi-folded.
5.2 Methods

The elastic membrane is modeled using a standard triangulated mesh with hexagonal symmetry [218]. The mesh is composed of $N_m$ nodes which are arranged in a circular geometry with diameter $d$. Self-avoidance of the surface is imposed by placing a purely repulsive particle of diameter $\sigma$ and mass $m$ at each node of the mesh. Every particle on the surface is bonded to its first neighbor via a harmonic potential

$$U_{\text{stretching}} = \kappa_s (r - r_0)^2$$  \hspace{1cm} (5.1)

where $\kappa_s$ is the spring constant, $r$ the distance between two neighboring particles, and $r_0 = 2^{1/6}\sigma$ the equilibrium bond length between two particles. The bending rigidity of the membrane is implemented using a dihedral potential between adjacent triangles of the mesh:

$$U_{\text{bending}} = \kappa_b (1 + \cos \phi)$$  \hspace{1cm} (5.2)

where $\phi$ is the dihedral angle between opposite vertices of any two triangles sharing an edge and $\kappa_b$ is the bending constant.

Each active bath particle is a sphere with mass $m$, diameter $\sigma$, and undergoes overdamped Langevin dynamics at a constant temperature $T$. Self-propulsion is introduced through a directional force of constant magnitude $|F_a|$ and is directed along a predefined orientation vector $\mathbf{n}$ which passes through the origin of each particle and connects its poles. The equations of motion of an individual particle are given by the coupled Langevin
\[
\begin{align*}
\dot{\mathbf{r}} &= -\gamma \dot{\mathbf{r}} - \partial_r U + |F_a| \mathbf{n} + \sqrt{2\gamma^2 D} \xi(t) \\
\dot{\mathbf{n}} &= \sqrt{2D_r} \mathbf{x}_R(t) \times \mathbf{n}
\end{align*}
\] (5.3)

where \( \gamma \) is the drag coefficient, \( U \) the conservative inter-particle potential, and \( D \) and \( D_r \) are the translational and rotational diffusion constants respectively, satisfying the relation \( D_r = (3D)/\sigma^2 \). The translational diffusion constant \( D \) is related to the temperature \( T \) via the Stokes-Einstein relation \( D = k_B T/\gamma \). 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 \( \langle \xi_{Ri}(t) \rangle = 0 \) and \( \langle \xi_{Ri}(t) \cdot \xi_{Rj}(t') \rangle = \delta_{ij} \delta(t - t') \), respectively. Each node of the membrane also undergoes over-damped Langevin dynamics at a constant temperature \( T \) where the equations of motion are given by Eqs. (3) and (4) while letting \( |F_a| = 0 \). The interactions between any two particle in the systems (membrane nodes or active components) are purely repulsive and are given by the Weeks-Chandler-Andersen (WCA) potential

\[
U(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right]
\] (5.5)

with a range of action extending up 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 the interaction energy.

Using the numerical package LAMMPS [?], all simulations were carried out in a
periodic box of dimension $L = 100$ with $T = \epsilon = m = \sigma = \tau = 1$ and $\gamma = 10\tau^{-1}$ (here $\tau$ is the dimensionless time). The drag coefficient $\gamma$ was chosen to be sufficiently large such that the motion of the particles is effectively over-damped. The number of active particles considered in our simulations was $N = 10,000$ giving an active particle density of $\rho = N/V = 0.01$. While, the number of nodes in the membrane was set to $N_m = 1700$ resulting in a membrane with diameter $d \approx 46\sigma$. For each simulation, the membrane was initialized in a flat configuration and the simulation was run for a minimum of $1 \times 10^8 \tau$ time steps. All quantities in this investigation are given in reduced Lennard-Jones units and for convenience, we refer to the activity of the bath in terms of the dimensionless Peclet number $Pe = |F_a|\sigma/(\gamma D) = |F_a|\sigma/(k_B T)$.

![Graph](graph.png)

Figure 5.2: (Color online) The time average of the radius of gyration $\langle R_g \rangle$ (left) and asphericity $\langle A \rangle$ (right) as a function of $Pe$ for membranes of different bending rigidities $\kappa_b$. 

95
Figure 5.3: (Color online) Probability distribution of the radius of gyration $P(R_g)$ for membranes of increasingly large Peclet numbers. Different panels show the results for different bending rigidities of the membrane as indicated. The letters in parenthesis indicate the corresponding configurations as shown in Fig. 5.1.

### 5.3 Results

To characterize and quantitatively differentiate between the different conformations of the membrane, we employ two well established shape parameters: the membrane asphericity $A$ and its radius of gyration $R_g$. Following Rudnick et al. [219], we define asphericity as the rotational invariant

$$A = \frac{\sum_{i \neq j} (\lambda_i - \lambda_j)^2}{(\sum_i \lambda_i)^2} \quad (5.6)$$
where $\lambda_i, \lambda_j$ are the $i$th and $j$th eigenvalues of the inertia tensor

$$I_{\alpha\beta} = \frac{1}{2N_m} \sum_i \sum_j (r_{i,\alpha} - r_{j,\alpha})(r_{i,\beta} - r_{j,\beta})$$ (5.7)

where $r_i$ is the position of the $i$th node in the membrane. A fully symmetric object such as a sphere (i.e. $\lambda_1 = \lambda_2 = \lambda_3$), will have a value of asphericity equal to zero. At the opposite extreme, a thin rod (i.e. $\lambda_1 > 0, \lambda_2 = \lambda_3 = 0$) will have an asphericity equal to one. We are predominately concerned with a planar circular membrane whose conformation fluctuates between an extended state ($A \approx 0.25$), a singly folded state ($A \approx 0.5$), and an ensemble of multi-folded crumpled states (that are the most symmetric) which are characterized by the smallest values of $A$. Representative snapshots of these configurations are shown in Fig. 5.1. The second configurational parameter, the radius of gyration of the membrane, is simply the trace of the inertia tensor given by

$$R_g^2 = \sum_i \lambda_i$$ (5.8)

We begin by considering the time average of the shape descriptors $\langle A \rangle$ and $\langle R_g \rangle$ for different values of the Peclet number. In the limit of low bath activity ($Pe \to 0$), the membrane is found in a characteristically extended state with $\langle A \rangle \approx 0.22 - 0.25$ and the radius of gyration at a maximum $\langle R_g \rangle \approx 16 - 17\sigma$, with the larger values associated with the stiffer membranes. Notice that, unlike its one-dimensional counterpart (the polymer), an elastic membrane exhibits an overall extended state even in the limit for $\kappa_b = 0$, which makes the dependence of $R_g$ with $Pe$ rather different than what was observed for fully
Figure 5.4: (Color online) Probability distribution of the asphericity $P(A)$ for membranes of increasingly large Peclet numbers. Different panels refer to different bending rigidities of the membrane as indicated. The letters in parenthesis indicate the corresponding configurations as shown in Fig. 5.1.

Flexible polymers confined to two dimensions[81, 82]. In fact, as shown in Fig. 5.2, as the bath activity is increased, $R_g$ systematically decreases to smaller values until a plateau is reached. Stiffer membranes require larger $Pe$ before $R_g$ begins to decrease and the value it decays to increases with the strength of the active force. The behavior of the average asphericity as a function of $Pe$, suggests a more complex structural landscape. While the asphericity for the fully flexible membrane is relatively well behaved where it undergoes an initial decreases followed by a gradual increase for larger $Pe$, the typical conformations acquired by the rigid membranes are strongly dependent on the value of the bending rigidity and $Pe$, as illustrated by the sharp changes in $\langle A \rangle$ particularly for intermediate active forces.
To gain additional insight into the shape of the membrane as a function of the active forces, we analyze the underlying probability distributions of the asphericity $P(A)$ and radius of gyration $P(R_g)$. The results are given in Fig. 5.3 and Fig. 5.4, respectively. For small active forces, as discussed above, the membrane is nearly flat and as expected the distributions for $P(A)$ and $P(R_g)$ are sharply peaked around the corresponding values of $R_g$ and $A$. In this low $Pe$ limit, the distributions become increasingly sharper as the bending rigidity is increased. For larger values of $Pe$, both $P(R_g)$ and $P(A)$ broaden and shift towards smaller values for flexible membranes, indicating that the membrane is on average more compact, but it can also access a variety of conformations across the spectrum of possible shapes. More interestingly, for large bending rigidities distinct multiple peaks appear at specific values of $A$, which is a clear indications that the membrane breathes dynamically between a restricted number of partially stable conformations. Specifically, at large bending rigidities and intermediate values of $Pe$, the membrane mainly interconverts between a bent configuration (Fig. 5.1B) characterized by $A \approx 0.2$, and a configuration displaying a single fold along the center of the membrane (Fig. 5.1C) $A \approx 0.48$. Visualization of the membrane trajectory (provided in the supporting materials) reveals a continuous folding and unfolding of the membrane over time. For more flexible membranes, the dynamic behavior is similar, however, the most compact shape the membrane obtains is a multi-folded configuration as shown in Fig. 5.1D. The larger degree of flexibility allows for a broader range of shape deformations under the forces generated by the active particles. This is clearly observed in Fig. 5.5 where we plot the joint probability distribution $P(A, R_g)$ for a fixed Peclet number $Pe = 50$ and various bending rigidities. A flexible membranes explores a wide range of configurations with different $R_g$ and $A$. 

99
Figure 5.5: (Color online) Joint probability distribution of the membrane shape \( P(A, R_g) \) for a fixed Peclet number \( P_e = 50 \) and various bending rigidities.

but as the stiffness of the membrane is increased the explorable landscape of shape conformations becomes more and more localized.

All of the conformations active particles induce on the membrane surface are the result of their tendency to localize near regions with large/positive curvature. The reasoning behind this phenomenon has been discussed in detail here [95, 99, 100, 205]. A rigid membrane is nearly flat in the absence of active particles. When active particles are introduced, they tend to accumulate on the surface of the membrane. An initial bend of the membrane occurs once a sufficiently large asymmetry in the number of active particles develops on either side of its area. This leads to an instability because the region of the membrane with higher/positive curvature will further stabilize the active particles residing on it, while the ones on the outer surface can more easily escape. The net result is an increasing density gradient of particles on the surface. Similarly to the mechanism driving the formation of hairpins in polymers [81, 82], particles accumulating within the creased region of the membrane act as a dynamic fulcrum by which the sides of the membrane can pivot and
fold onto one another. Because no direct attractive interactions are present in our system, any folded or multi-folded configuration of the membrane will eventually unfold, resulting in the membrane perpetually folding and unfolding. The rate and the degree to which the membrane is folded increases with the flexibility of the membrane (see supplemental material.)

Two limits are worthy of a more detailed discussion. The first case concerns the large Peclet number limit. In this limit, the probability distribution $P(A)$ associated to rigid membranes become comparable with that of their fully flexible counterparts. This is because larger active forces are able to fold the membrane simultaneously at different locations, leading to the formation of more compact multi-folds and to an overall softening of the bending rigidity. Thus at large $Pe$ the dynamical behavior of a rigid membrane is nearly analogous to that of a flexible membrane. The second limit concerns the case in which the membrane is sufficiently rigid that the active forces are not strong enough to drive the formation of a single fold. Here, the membrane adopts partially bent configurations (Fig 5.1B), and the surface acts as a sail able to trap a significant number of active particles preferentially on the side of the membrane with positive curvature. The net result is a active motion of the surface that is modulated by the propelling forces. The mechanism behind how an active fluid can induce an active transport on curved micro-components as been discussed in our previous work [95].
5.4 Conclusions

In this paper we studied the behavior of a deformable elastic membrane in the presence of a low density suspension of active particles as a function of the mechanical parameters of the membrane and the strength of the bath activity. We find that as soon as the collective strength of the active forces becomes sufficiently large compared to the bending energy of the membrane a repeating sequence of folding and re-expansion transitions of the surface takes place. While flexible membranes tend to collapse into multi-folded states, stiff membranes fluctuates between an extended configuration and a singly folded state. Interestingly, in the large activity-limit, the behavior of rigid membranes resembles that of fully flexible ones, indicating that strong active forces can soften the modes of deformation of the membrane. Furthermore, we find that bent or partially folded membrane configurations act as sails or nets capable of trapping active particles on the positive curvatures of their surface and become actively transported through the medium. Unlike what had been suggested in previous studies on fluid surfaces [209, 220], we do not believe that in our system the activity can be described as an effective temperature of the membrane. This is because the bi-stable behavior observed in our system does not have an analog in the passive system. Although, one could feasibly define an effective temperature in the limit of small activities and large bending rigidities, (i.e. prior to the collapse of the membrane), this mapping cannot be done for the whole range of system parameters.

We expect the number density of active particles to play an important role in determining the exact values of $Pe$ driving the collapse of the membrane at a given bending rigidity. However, it is not clear how the membrane will behave at very high densities,
where clustering and possibly phase separation of the active fluid occurs.

The work presented in this paper is complementary to our previous study on rigid filaments [82], and suggests ways of exploiting the random motion of active particles to perform mechanical work at the micro-scale. The system we considered here consisted of a simple isotropic membrane in a bath of spherical particles; it is feasible to imagine that further control over the mechanical response of flexible micro-components such as the ones discussed here and in our previous work can be achieved by introducing judicious amount of anisotropy either on the elastic properties of the surface or on the interactions between active particles and surface.
Chapter 6

*Activity-assisted self-assembly of colloidal particle*

We outline a basic strategy of how self-propulsion can be used to improve the yield of a typical colloidal self-assembly process. The success of this approach is predicated on the thoughtful design of the colloidal building block as well as how self-propulsion is endowed to the particle. As long as a set of criteria are satisfied, it is possible to significantly increase the rate of self-assembly, and greatly expand the window in parameter space where self-assembly can occur. In addition, we show that by tuning the relative on/off time of the self-propelling force it is possible to modulate the effective speed of the colloids allowing for further optimization of the self-assembly process.

### 6.1 Introduction

The colloidal self-assembly of a well defined micro-structure is a complex process that is difficult to control with any degree of precision. Most modern approaches to this problem revolve around tailoring the morphology of the individual colloids. By either altering the shape of the colloid or introducing highly selective interactions, it is possible to drive the mono-disperse self-assembly of a specific colloidal cluster. This approach has been particularly fruitful and some of the more prominent examples include: patchy particles [26, 30–32, 221–225], lock and key colloids [25, 29, 33, 226–229], and DNA decorated col-
loids [230–232]. Nevertheless, it is well known that high yield self-assembly only occurs for very specific particles shapes and interaction strengths, making the search for the self-assembly window in parameter space rather cumbersome. This is typically due to the presence of large kinetic and entropic barriers, and in many cases it is only possible to obtain a meaningful yield of the target structure after waiting a significant amount of time.

Recent advances in colloidal chemistry have led to the reliable synthesis of self-propelled or active colloids [14, 41, 71, 114, 128, 129, 150, 167, 171, 233–235]. These particles can be thought of as the colloidal analog of swimming bacteria and are characterized by inherently non-equilibrium, directional forces that can propel them at velocities of tens of microns per second. Recent experimental and numerical studies have considered a myriad of objects immersed in these suspensions of self-propelled colloids, which are often referred to as active fluid [73, 79–83, 86, 89, 94–97, 97, 121, 139, 159, 181–184, 193, 196–199, 201, 203, 236–238]. It has been shown by multiple investigators that active fluids exhibit unique thermo-mechanical properties [48, 68–72, 102, 141, 205, 239] and are a powerful medium for mediating the effective interactions between suspended passive colloids and polymers. In addition, active fluids have proven to be a useful tool for powering primitive micro-machines and controlling the transport properties of passive tracers. In this work, we explore how self-propulsion can be used as an extra handle for colloidal self-assembly. By introducing a new dimension in the parameter space, we show how it is possible to bias the selection of a particular micro-structure and greatly improve the overall yield and rate of the assembly process. The main idea behind this approach is to use the self-propelling forces generated by the colloids to reinforce the sta-
Figure 6.1: (A) The colloidal building blocks have been functionalize such that two of the three faces exhibit a short range attraction. The white arrow indicates the direction of self-propulsion. (B) The target structure to be self-assembled is a hexagonal capsid composed of six colloidal building blocks. (C) Typical disordered aggregate formed when the attraction between colloids is too strong. (D) Percent yield of target structure as a function of the strength of the attractive interaction $\varepsilon$ for passive colloids ($F_{a}\sigma = 0 k_{B}T$).

ability of the desired micro-structure while simultaneously destroying any malformed or competing micro-structures. This technique not only expedites the rate of self-assembly, but broadens the window in parameter space where self-assembly is actually possible.

As our colloidal building blocks we functionalize equilateral triangles with the aim of self-assembling capsid like structures. The design of the colloidal building block and the target structure are shown in Figs. 6.1A and 6.1B, respectively. The formation of the capsid is driven by both the shape of the colloid and an anisotropic interaction between colloids. Each colloid is patterned such that two of the three faces exhibit a short range
attraction. There are three reasons for choosing this particular shape and surface interaction. The first being that there is a clearly defined target structure. Given the tailored nature of the interaction between colloids, one can readily expect them to self-assemble into finite-sized closed hexagonal aggregates. The second reason is that there exist an ensemble of structures with a larger degree of orientational entropy (see Fig. 6.1C) that can directly compete with the formation of the target structure. This high level of competition generates a scenario where the success of self-assembly is highly dependent on the strength of attraction between colloids and is expected to only occur for a narrow range of parameters. Lastly, we have chosen these specific building blocks because the vectorial sum of the colloids’ propelling axes in the target structure is equal to zero (see Fig. 6.1B), and they all point towards the center of the aggregate. This will turn out to be a crucial requirement if self-propulsion is to improve the self-assembly process.

The model and simulation technique implemented here are similar to the the work of Zhang et al. [222] where they studied the self-assembly behavior of a similarly shaped patchy particle. A complete description of the simulation details is included in Appendix A. To summarize, each colloid is confined to move in two dimensions, has mass $m$, and undergoes translational and rotational Langevin dynamics at a constant temperature $T$. Self-propulsion is introduced through a directional force of constant magnitude $F_a$ and is directed along a predefined orientation vector $n$ which passes through the center of mass of each particle and is perpendicular to the purely repulsive face of the colloid as illustrated in Fig. 6.1A. The edge length of the colloid is fixed at $2\sigma$, where $\sigma$ is the unit length in our simulations. Here, we define the Péclet number of an individual colloid as $Pe = v_0 \frac{\tau_D}{\sigma} = \frac{F_a \sigma}{k_B T}$, where $\tau_D = \sigma^2 / D$ is the particle self-diffusion time, $D = \frac{k_B T}{\gamma}$ is the
linear translational diffusion constant, and \( v_0 \) is the swim velocity of the colloid, which is related to the propelling force via \( v_0 = F_a / \gamma \) where \( \gamma \) is the friction coefficient. The attraction between the faces of the colloid is quantified in terms of the binding energy when a pair of colloids have their attractive faces fully aligned and in contact which we denote by \( \varepsilon \). The attraction is quite short ranged and decays to zero within a distance \( 0.5\sigma \) from the face of the colloid. (See supplement for full details). Using the numerical package LAMMPS [163], all simulations were carried out in a periodic box of dimension \( L \) with \( T = m = \sigma = \tau = 1 \). All quantities in this investigation are given in reduced Lennard-Jones units.

We begin our analysis by identifying the range of binding energies \( \varepsilon \) for which passive colloids successfully self-assemble into the target structure. A series of numerical simulations for different values of \( \varepsilon \) were carried out in the absence of any self-propelling force \( (F_a \sigma = 0 \text{ } k_B T) \). In each simulation, the total number of colloids is fixed at \( N = 600 \) with an overall volume fraction of \( \phi = 0.1 \). We restrict our study to this dilute regime as it predisposes hexagonal assembly over the formation of disordered aggregates. Each simulation is run for a minimum of \( 10^8 \tau \). In the case of perfect self-assembly, we would expect to form 100 capsid structures. We define the yield of the process as the average number of successfully self-assembled structures out of the theoretical maximum number of target structures. Figure 6.1D shows the percent yield of hexagonal structures as a function of the strength of the attractive interaction. As expected, only a narrow range of \( \varepsilon \) returns a respectable yield, with a maximum of 90% at around \( \varepsilon \approx 16 \text{ } k_B T \). For values of \( \varepsilon \) smaller than this range, the colloids do no aggregate and the system remains in the fluid phase. For larger values of \( \varepsilon \), the formation of large disordered aggregates is favored.
(see Figure 6.1C).

![Graph showing percent yield vs time for different values of $F_a\sigma$.]

Figure 6.2: Percent yield of the target structure as a function of time for binding energy $\varepsilon \approx 11 \, k_B T$ and several values of the self-propelling force $F_a$. 

A similar set of simulations were also carried out where a self-propelling force $F_a$ was applied to each colloid. In Figure 6.2, we plot typical trajectories of the percent yield as a function of time for several values of the self-propelling force $F_a$. To illustrate the beneficial effects self-propulsion can have on self-assembly, we consider the case where the attraction between colloids ($\varepsilon \approx 11 \, k_B T$) is too weak to drive a significant aggregation in the absence of active forces. In this instance, the yield never rises above about 5%. By introducing a small amount of self-propulsion to the colloids ($F_a\sigma = 2.5 \, k_B T$ and $F_a\sigma = 5.0 \, k_B T$), it is possible to dramatically improve self-assembly. For both of these values the yield increases at a rapid rate before plateauing at around 60%. The yield does however begin to rapidly decreases if the activity of the colloids is increased any further (i.e. $F_a\sigma > 7.5 \, k_B T$). For these larger values of $F_a$, the forces exerted by a single active colloid swimming in the bulk are able to destroy a fully formed target structure. The rate of formation of the target structure is self-regulated by these errant colloids eventu-
ally leading to a steady state condition where the percentage of target structures formed fluctuates about some fixed value. This study suggests that a) it is possible to significantly improve the self-assembly of these colloids by introducing a judicious amount of self-propulsion even in regions of parameter space where passive colloids wouldn’t spontaneously self-assemble, b) the overall dependence of the yield on the self-propelling force is non-monotonic (i.e. there is a range of self-propelling forces for which the maximum yield can be obtained, but above which a strong decline is expected).

![Diagram](image)

Figure 6.3: Percent yield of the target structure as a function of the binding energy $\varepsilon$ and the self-propelling force $F_a$. The white number at the center of the circle indicate the relative increase in the rate of the assembly process, $\nu_{SA}$, with respect to the best performing passive case that occurs for $\varepsilon \approx 16 \ k_B T$.

Figure 6.3 summarizes all our results into a two dimensional plot where we report the equilibrium yield as a function of the binding energy $\varepsilon$ and the self-propelling force $F_a$. Crucially, the size of the region in parameter space where self-assembly takes place is now
much wider for self-propelled systems. In many instances, the self-propelled systems can achieve yields comparable or greater than those obtained for the optimal passive case. We find that respectable yields of the target structure are typically obtained when the self-propelling force is slightly weaker than the binding energy between two colloids (i.e. \((F_a \sigma)/\varepsilon \lesssim 1\)). As a measure of the rate of the self-assembly process, we measure \(\tau_{\frac{1}{2}}\), defined as the time required for the yield to reach 50\% of the possible maximum yield, and then compute the relative self-assembly rate \(\nu_{SA} = \tau_{\frac{s}{2}} / \tau_{\frac{1}{2}}\), where \(\tau_{\frac{s}{2}}\) corresponds to the \(\tau_{\frac{1}{2}}\) obtained for the best performing passive system (\(\varepsilon \approx 16 k_B T\)). Remarkably, it is possible to significantly increase the rate of self-assembly without compromising the yield by using the largest possible values of \(F_a\) and \(\varepsilon\) for which \((F_a \sigma)/\varepsilon \lesssim 1\). In other words, fast and sticky colloids give the overall best self-assembly results in terms of speed and yield (at least within the range of parameters considered in this work).

The underlying mechanism responsible for improving self-assembly can be understood with simple geometric arguments. As mentioned above, a critical requirement of the target micro-structure is that the vectorial sum of the self-propelling forces pointing in its interior is equal to zero. This creates a focal point in the center of the compact aggregate where each colloid can exert a force \(F_a\) that strengthen their mutual attractive interactions. Also, any aggregate for which this vectorial condition is not satisfied, will experience large active torques and shear forces that can break them apart. One can think of self-propulsion in these systems as a very selective filter that only allows for the stabilization of certain structures. We believe that this is a general feature of this approach and should work for all compact target structures satisfying the vectorial condition discussed above.
It should also be stressed that self-propulsion not only stabilizes the final hexagonal aggregates, but it also biases the formation of specific pair interactions early on in the self-assembly process. As illustrated in Fig. 6.4, there are two ways for colloids to bind to each other. In the first configuration, the propelling axes are anti-aligned, whereas in the second configuration the self-propelling axes are partially aligned. In the former case, activity tends to destabilize and separate the pair by creating a shear along the contact edge, in the latter case the bond between the two particles is strengthened and they will move as a pair at a reduced speed whose value depends essentially on the geometry of the particles. Thus the selection of the final structure begins already at an early stage as the partially aligned configuration is favored and is compatible with the target structure.

Figure 6.4: (A) Anti-aligned and (B) aligned binding configurations for this choice of colloidal building block. The introduction of self-propulsion stabilized the aligned configuration and destabilize the anti-aligned configuration.

One particularly appealing aspect of active colloids is that in many cases the self-propulsion mechanism can be turned on and off by an external light source. [114, 150, 186, 233]. In what follows, we study how the self-assembly process is affected when allowing the self-propelling force of the particles to change over time. Specifically, we considered a
periodic step function where the self-propelling force is turned on for a time $\tau_{on}$ and then turned off for a time $\tau_{off}$ for a total period of $\tau_0 = \tau_{on} + \tau_{off}$. For this particular form of the self-propelling force, it is possible to compute exactly the mean square displacement and the swim pressure of an active Brownian particle. These calculations are included in Appendix B. In the limit for $\tau_0 \to 0$, 

$$\langle x^2(t) \rangle \simeq \left[ 2D + \frac{1}{D_r} \left( \frac{v_0 \tau_{on}}{\tau_0} \right)^2 \right] t \quad (6.1)$$

$$\frac{\Pi^{Swim}}{\rho} \simeq \frac{\gamma}{D_r} \left( \frac{v_0 \tau_{on}}{\tau_0} \right)^2 \quad (6.2)$$

where $v_0 = F_a/\gamma$ is the bare swimming speed of the colloid, $\gamma$ is the friction coefficient, and $\rho$ is the colloid density. Both expressions have the functional form of a brownian active particle with a constant propelling force of effective strength equal to

$$F_{eff} = \frac{\tau_{on} F_a}{\tau_{on} + \tau_{off}} = \frac{\tau_{on} F_a}{\tau_0} \quad (6.3)$$

which is simply the time averaged force within a single period. This result is significant as it shows that by tuning the relative on/off time of the self-propelling force it is possible to modulate the effective speed of the colloids. In practical terms, this protocol can be used to modulate the speed of the colloid which would otherwise be exclusively controlled by the chemical details of the propulsion mechanism.

As our example case, we consider a self-propelling force $F_a \sigma = 25 \ k_B T$ and interaction energy $\varepsilon \approx 16 \ k_B T$. For this set of parameters the behavior of the system is highly dynamic and the target structures are continually being destroyed by errant
free swimming colloids. The yield reaches a maximum value of about 20% when the self-propelling force is constant. When setting $F_a \sigma = 0 \ k_B T$, we obtain the best passive yield of about 90%. In Figure 6.5, we plot the percent yield for different pairings of $\tau_{on}$ and $\tau_{off}$. We first discuss the effects of a symmetric periodic step function, i.e. $\tau_{on} = \tau_{off}$. For large values of $\tau_{on}$ and $\tau_{off}$, which in our simulations corresponds to $\tau_{on} = \tau_{off} = 40 \ \tau_D$, the system gives a yield that is comparable with that obtained for a constant self-propelling force $F_a \sigma = 25 \ k_B T$. At the opposite extreme, for very fast switching times, $\tau_{on} = \tau_{off} = 0.4 \ \tau_D$, we obtain a yield consistent with a constant self-propelling force of half its original value (i.e. $F_a \sigma = 12.5 \ k_B T$). This result is in agreement with our theoretical expectations concerning the effective self-propelling force given in
Eq. (6.3). We find the best yields are obtained when $F_a$ is turned on for $\tau_{on} = 0.4 \tau_D$ and then turned off for $\tau_{off} = 2 \tau_D$, or greater. This is in good agreement with our data in Fig. 6.3, for which a constant propelling force $F_a\sigma \approx 5 k_B T$ gives the best yield for $\varepsilon \approx 16 k_B T$. These results further bolster our argument that the effective force of the colloid can be modulate to its optimal value by tuning $\tau_{on}$ and $\tau_{off}$ for sufficiently small $\tau_0$. Since $\varepsilon \approx 16 k_B T$ is the optimal condition for the passive case, larger values of $\tau_{off}$ effectively decreases the strength of the effective force slowly moving the system towards the passive limit with a roughly constant yield but decreasing $\nu_{SA}$. Finally, we observe that by moving along the diagonals of Fig. 6.5 (points for which $\tau_{on}/\tau_{off} = \text{const}$) the best yield is obtained for the smallest values of $\tau_0$, (i.e. in the limit where Eq. 6.3 becomes more accurate). In general, increasing $\tau_0$, while keeping the ratio $\tau_{on}/\tau_{off}$ fixed, decrease the overall yield, but may lead to faster rates of self-assembly.

In summary, we have discovered that a judicious use of self-propulsion can greatly benefit the colloidal self-assembly of a certain class of target micro-structures. In simple terms, we show that fast and sticky colloids can successfully self-assemble more than one order of magnitude faster than their passive counterparts without sacrificing the overall yield. We also demonstrate how tuning the relative on/off time of the self-propelling force (i.e. by using quick bursts of activity rather than a constant force) it is possible to modulate the effective speed of the colloids allowing for further optimization of the self-assembly process. This result also suggests that quickly toggling the self-propelling force is a simple method to control the microscopic speed of the colloids and it is not always necessary to tinker with the chemical details of the propulsion mechanism.

Although we study this problem through the lens of a simple minimal model, we
believe that the general approach and methodology discussed here can be successfully applied to other colloidal systems with different building blocks as long as the necessary criteria are satisfied. We don’t believe that the vectorial constraint discussed above needs to be strictly satisfied, and aggregates whose propelling axes sum up to a sufficiently small value would still see an improvement in self-assembly. For instance small clusters of Janus particles in three dimensions, should be amenable to this approach. More work in this direction is needed.

Finally, we should stress that at low densities, hydrodynamic interactions can lead to long range forces mediated by the surrounding fluid. In this work, we haven’t explicitly considered this effect, however, we expect it to lead mostly to quantitative and not qualitative changes in the phase behavior as long as hydrodynamic interactions do not break the stable aggregates. Recent work [57] indicates that hydrodynamics has a crucial role on the rotational dynamics of spheres inside living crystals, however, in our case the anisotropic nature of the direct interparticle interactions and their excluded volumes forbids them to rotate once assembled, which negates this effect. Additional work is needed to understand how hydrodynamics interactions may affect the self-assembly pathway in active systems.

### 6.2 Additional simulation details

For computational efficiency, each colloid is discretized into $N_T = 30$ equidistant, partially overlapping, and rigidly connected spherical subunits of diameter $\sigma_T = 0.25\sigma$, where $\sigma$ is the unit length in our simulations. The edge length of the colloid is fixed at $2\sigma$. 
A suitably large number of spheres was chosen to accurately reproduce the shape of the colloid and to make the surface interaction sufficiently smooth. All particle interactions in the systems are given by a Lennard-Jones potential

\[
V(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_T}{r} \right)^{12} - \left( \frac{\sigma_T}{r} \right)^{6} \right]
\]  

(6.4)

The spherical subunits that make up the colloid come in two different varieties: type A and type B, and the \(i\) and \(j\) indices refer to them. Type A particles are responsible for the attractive interaction while type B only account for volume exclusion. The distinguishing characteristic between these two particle types is the potential cutoff distance. The cutoff distance between type A particles is set to \(r_c = 2.5\sigma_T\). Type A particles are in essence Lennard-Jones particles and exhibit a weak, short range attraction, which is modulated by the interaction energy \(\varepsilon_{AA}\). The cut off distance for the remaining pair interactions (type A-type B and type B-type B) is set to \(r_c = 2^{1/6}\sigma_T\) making these interactions purely repulsive in nature. The interaction energy for these volume excluding pair interactions is fixed at \(\varepsilon_{BB} = \varepsilon_{AB} = 1\). In both cases the potential is shifted after truncation so that \(V(r_c) = 0\).

Each colloid is confined to move in two dimensions, has mass \(m\), and undergoes Langevin dynamics at a constant temperature \(T\). At each time-step, both the total force and torque on each rigid body is computed as the sum of the forces and torques on its constituent particles. The coordinates, velocities, and orientations of the particles in each body are then updated so that the body moves and rotates as a single entity. Self-propulsion is introduced through a directional force of constant magnitude \(F_0\) and is di-
rected along a predefined orientation vector $\mathbf{n}$ which passes through the center of mass (COM) of each particle and is perpendicular to the purely repulsive face of the colloid as illustrated in Fig. 1A of the main text. The equations of motion of an individual colloid are given by the coupled Langevin equations

$$
 m\ddot{r}_i = -\gamma \dot{r}_i + F_a \mathbf{n}_i - \nabla_i V(r_{ij}) + \sqrt{2\gamma^2 D} \xi_i 
$$

(6.5)

$$
 \mathbf{n}_i = -\frac{D_r}{k_B T} \nabla_i V(r_{ij}) + \sqrt{2D_r} \xi_{r,i} \times \mathbf{n}_i 
$$

(6.6)

where $\gamma$ is the translational friction and $V$ the total interparticle potential acting on the particle. The translational and rotational diffusion constants are given by $D$ and $D_r$, respectively. 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 $\langle \xi_i(t) \cdot \xi_j(t') \rangle = \delta_{ij} \delta(t - t')$, $\langle \xi_r(t) \rangle = 0$ and $\langle \xi_r(t) \cdot \xi_r(t') \rangle = \delta(t - t')$. The translational diffusion constant $D$ is related to the temperature $T$ via the Stokes-Einstein relation $D = k_B T / \gamma$. All quantities in this investigation are given in reduced Lennard-Jones units. The friction coefficient $\gamma$ was chosen such that the translational and rotational motion of the colloid is overdamped.
6.3 Derivation of MSD and Swim Pressure for oscillating Swimming Speed

For simplicity, we consider an active Brownian particle in one dimension where the $\xi$ and $\xi_r$ correspond to the gaussian distributed translational and rotational random noises with $\langle \xi(t) \rangle = 0$, $\langle \xi(t) \cdot \xi(t') \rangle = \delta(t - t')$ and $\langle \xi_r(t) \rangle = 0$, $\langle \xi_r(t) \cdot \xi_r(t') \rangle = \delta(t - t')$, respectively. The propelling velocity $v_o(t)$ has the functional form of a asymmetric periodic step function $v_o(t) = v_0 \Xi[t]$ with

$$
\Xi(t) = \begin{cases} 
1 & \text{if } n(\tau_{on} + \tau_{off}) \leq t \leq n(\tau_{on} + \tau_{off}) + \tau_{on} \\
0 & \text{Otherwise}
\end{cases}
$$

(6.7)

with period $\tau_0 = \tau_{on} + \tau_{off}$, $n = 0, 1, 2, 3, ..., t/\tau_0$, and $\theta(t)$ is the angle between the $x$ axis and the propelling axis of the particle. Clearly, $\tau_{on}$ is the time the propelling velocity is active and $\tau_{off}$ is the time off, and $v_0$ is the bare propulsion speed of the particle. To draw comparison with our simulations of the triangular colloids $v_o = F_o/\gamma$. We can now directly compute the mean square displacement of the particle

$$
\langle x^2(t) \rangle = v_0^2 \int_0^t \int_0^t \Xi(t)\Xi(t') \\
\times \langle \cos[\theta(t)] \cos[\theta(t')] \rangle \, dt \, dt' + 2Dt
$$

(6.8)
where \( \langle \cos[\theta(t)] \cos[\theta(t')] \rangle_{t > t'} = \frac{1}{2} e^{-D_r(t-t')} \). It follows that

\[
\langle x^2(t) \rangle = 2Dt + \frac{v_0^2}{2} \left[ \int_0^t ds \, e^{-D_r s} \Xi(s) \int_0^s dp \, e^{D_r p} \Xi(p) + \int_0^t ds \, e^{D_r s} \Xi(s) \int_s^t dp \, e^{-D_r p} \Xi(p) \right]
\]

(6.9)

We begin by evaluating the first double integral on the right hand side of the equation above. The integral over \( p \), which we define as \( G_1(s) \) can be rewritten as a geometric series

\[
G_1(s) = \int_0^s dp \, e^{D_r p} \Xi(p) = \frac{\left(e^{D_r \tau_0} - 1\right)}{D_r} \sum_{n=0}^{\tau_0 - 1} e^{nD_r \tau_0} = \frac{\left(e^{D_r \tau_0} - 1\right)}{D_r} \frac{1 - e^{D_r s}}{1 - e^{D_r \tau_0}}
\]

(6.10)

By substituting this expression for \( G_1(s) \) we are able to integrate the complete double integral which we define as \( Q_1(t) \)

\[
Q_1(t) = \int_0^t ds \, e^{-D_r s} \Xi(s) G_1(s) = \frac{\left(e^{D_r \tau_0} - 1\right)}{D_r(1 - e^{D_r \tau_0})} \int_0^t ds \, (e^{-D_r s} - 1) \Xi(s)
\]

(6.11)

\[
= \frac{(1 - e^{D_r \tau_0})}{D_r(1 - e^{D_r \tau_0})} \left[ \frac{\tau_0}{D_r} t + \frac{(e^{-D_r \tau_0} - 1)}{D_r} \sum_{n=0}^{\tau_0 - 1} e^{-nD_r \tau_0} \right]
\]

\[
= \frac{(1 - e^{D_r \tau_0})}{D_r(1 - e^{D_r \tau_0})} \left[ \frac{\tau_0}{D_r} t + \frac{(e^{-D_r \tau_0} - 1)(1 - e^{-D_r t})}{D_r(1 - e^{-D_r \tau_0})} \right]
\]

In a similar fashion we can compute the second double integral on the right hand side of
Eq. 6.9 which we define as $Q_2(t)$

$$Q_2(t) = \frac{(1 - e^{-D_r \tau_{on}})}{D_r (1 - e^{-D_r \tau_0})} \left[ \frac{\tau_{on}}{\tau_0} t + \frac{(e^{D_r \tau_{on}} - 1)}{D_r (1 - e^{D_r \tau_0})} (1 - e^{-D_r t}) \right] \quad (6.12)$$

The expression for the mean square displacement can now be rewritten as

$$\langle x^2(t) \rangle = 2Dt + \frac{v_0^2}{2} [Q_1(t) + Q_2(t)] \quad (6.13)$$

In the diffusive limit ($t \to \infty$) with a short total period ($\tau_0 \to 0$), we find apart from a constant

$$\langle x^2(t) \rangle \simeq \left[ 2D + \frac{1}{D_r} \left( \frac{v_0 \tau_{on}}{\tau_0} \right)^2 \right] t \quad . \quad (6.14)$$

In the ballistic limit ($t \to 0$) with a short total period ($\tau_0 \to 0$), we find

$$\langle x^2(t) \rangle \simeq \left( \frac{v_0 \tau_{on}}{\tau_0} \right)^2 t^2 \quad . \quad (6.15)$$

In both cases, when $\tau_{on} = \tau_0$ one recovers the well known results for a constant self-propelling force. It is now possible to obtain the swim pressure from the stress $\Pi = -\text{Tr} \ \sigma^{\text{swim}} / 3$ by simply computing $\sigma^{\text{swim}} = -\langle x F^{\text{swim}} \rangle$. In the diffusive limit the swim pressure is

$$\frac{\Pi^{\text{Swim}}}{\rho} = \frac{\gamma}{D_r} \left( \frac{v_0 \tau_{on}}{\tau_0} \right)^2 \quad (6.16)$$

where $\rho$ is the colloid density.
Chapter 7

*Self-assembly of active amphiphilic Janus particles*

In this article, we study the phenomenology of a two dimensional dilute suspension of active amphiphilic Janus particles (APPs). We analyze how the morphology of the aggregates emerging from their self-assembly depends on the strength and the direction of the active forces. We systematically explore and contrast the phenomenologies resulting from particles with a range of attractive patch coverages. Finally, we illustrate how the geometry of the colloids and the directionality of their interactions can be used to control the physical properties of the assembled active aggregates and suggest possible strategies to exploit self-propulsion as a tunable driving force for self-assembly.

### 7.1 Introduction

Active matter continues to be one of the most exciting new fields in statistical mechanics and materials engineering. Whether one focuses on the chaotic dynamics of human crowds or the peculiar swarming of swimming bacteria, a common feature of all active systems is their ability to convert environmental or internal energy into systematic movement. The inherent self-propulsion or activity at the “single particle level” in these systems gives rise to a remarkable range of different collective behaviors. For a number of examples and a thorough discussion on the topic, we direct the reader to a number of
comprehensive reviews (see for instance [4–17, 17–19] and the references therein). In this work, we are predominately concerned with colloidal active systems, and developing new methods to use activity as a tool to optimize colloidal self-assembly. Synthetic microswimmers are expected to fill an important void within the material science community as they possess the rather unique ability of being able to manipulate, sense, and transport material at the micro-scale. The potential applications are far reaching and include: targeted drug delivery [20], information storage and computation [21], and the clean-up and neutralization of environmental pollutants [22]. These applications are all built around the unique self-driven nature of the microswimmers and in many ways, active colloids look to serve as the perfect building blocks for the self-assembly of the next generation of functional, environment-sensing microstructures able to perform specific tasks in an autonomous and targeted manner.

Through the groundbreaking work of synthetic chemists and material scientists, there is now a continually growing library of synthetic microswimmers and active colloids. These active particles are the synthetic analogs of swimming bacteria. However, a major benefit of these synthetic variants over swimming bacteria is that both the inter-particle interactions and the swimming velocity can be systematically controlled. For details about the growing variety of synthetic microswimmers and their associated propulsion mechanisms, we direct the readers to several recent reviews [4, 5, 14, 17]. The majority of the published work on colloidal active matter focuses on suspensions of active particles which interact via an isotropic potential (whether it be attractive [119, 132, 161, 240], or purely repulsive [49, 50, 109, 110, 113, 114, 129]). Only recently, has the field branched out to explore the interplay between activity and anisotropic pairwise interactions. We are
only now developing a systematic understanding of how active forces can be exploited in conjunction with anisotropic pair interactions to design macroscopic assemblies with desired structural properties (see [24, 143, 241–245] and references therein).

The inspiration and motivation for this work was derived from the recent experimental synthesis of active colloids with directed anisotropic interactions. By altering the surface chemistries of an active colloid, it is possible to introduce a number of different directed anisotropic interactions. In a recent publication, Yan et al. [141] presented a general strategy, that exploits electrostatic imbalance between the two hemispheres of an active dipolar Janus particle, to reconfigure their assembly into a number of different collective states. Several research groups [139, 140] have also begun to probe the clustering behavior of a small number of dipolar Janus particles with a specific focus on analyzing how the structural properties of the self-assembled clusters are affected by the introduction of self-propelling forces. An alternative approach to introducing directed anisotropic interactions is to pattern the hydrophobic region on the surface of the active colloid [142]. Unlike dipolar active Janus particles that consists of two hemispheres of opposite charge, amphiphilic active patchy particles (APPs) consist of a polar and a hydrophobic region. A recent experimental realization of an active amphiphilic patchy particle consists of silica microspheres passivated with a hydrophobic ligand (octadecyltrichlorosilane, OTS), whose hemisphere is then covered by a Pt cap. These active APPs experience a short ranged attraction between the hydrophobic domains, while the interaction between the Pt capped hemispheres is purely repulsive. In essence, the Pt cap restricts the inter-particle attraction to the hydrophobic region which gives rise to well defined assemblies. By tuning the size of the hydrophobic domain and that of the Pt cap, it is possible to control the
angular range of the interaction, and thus the number of colloids that can simultaneously stick to one another.

In this paper, we report the self-assembly dynamics of a two dimensional dilute suspension of active APPs and study the structural and morphological properties of the aggregates that spontaneously form in the presence of active forces. We consider active APPs with different sizes of the hydrophobic regions spanning from 25%, 50% and 75% of the total area of the particle, and for two different propelling directions: one that is in the same direction as the hydrophobic patch and one that is in the opposite direction of the hydrophobic patch. Our results unveil a nontrivial morphological dependence of the self-assembled structures on the active forces and hydrophobic coverage.

7.2 Model

We simulate a two dimensional dilute suspension of $N = 2000$ amphiphilic patchy particles (APPs) at an area fraction of $\phi = 0.1$. Each APP is modeled as a disk with mass $m$, diameter $\sigma$, and undergoes Brownian dynamics at a constant temperature $T$ according to the coupled translational and rotational equations:

$$\dot{\mathbf{r}}(t) = \frac{1}{\gamma} \mathbf{F}({\{r_{ij}\}}) + v_p \mathbf{\eta}(t) + \sqrt{2D} \mathbf{\xi}(t) \quad (7.1)$$

$$\dot{\mathbf{\eta}}(t) = \frac{1}{\gamma_r} \mathbf{T}({\{r_{ij}\}}) + \sqrt{2D_r} \mathbf{\xi}(t) \times \mathbf{\eta}(t) \quad (7.2)$$

Activity or self-propulsion is introduced through a directional propelling velocity of con-
Figure 7.1: Three patch coverages (in black) from left to right are $C = 0.25$, $C = 0.50$, and $C = 0.75$. The large arrow indicates the propulsion direction. The top row corresponds to patchy colloids propelled in the direction of the patch $(WP)$, whereas the bottom row against the patch $(AP)$.

A constant magnitude $v_p$ and is directed along a predefined orientation vector $\eta$ centered at the origin of each particle. The translational diffusion coefficient $D$ is related to the temperature $T$ and the translational friction $\gamma$ via the Stokes-Einstein relation $D = k_B T / \gamma$. We make the typical assumption that the rotational diffusion coefficient $D_r = k_B T / \gamma_r$ satisfies the relation $D_r = (3D) / \sigma^2$. The solvent induced Gaussian white-noise terms for both the translational and rotational motion are characterized by $\langle \xi(t) \rangle = 0$ and $\langle \xi_i(t) \xi_j(t') \rangle = \delta_{ij}\delta(t - t')$. The conservative inter-particle forces and torques acting on each colloid are given by $\mathbf{F}(\{r_{ij}\})$ and $\mathbf{T}(\{r_{ij}\})$ respectively, and can be computed as

$$\mathbf{F}(\{r_{ij}\}) = \sum_j \mathbf{F}_{ij} = -\sum_j -\nabla r_{ij} U_{ij} \quad (7.3)$$
and
\[ T(\{r_{ij}\}) = \sum_j T_{ij} = -\sum_j \nabla r_j U_{ij} \] (7.4)

where \( U_{ij} \) is the interaction potential between colloids. The anisotropic pair potential is given by

\[ U_{ij}(r_{ij}, \theta_i, \theta_j) = U_{rep}(r_{ij}) + U_{att}(r_{ij})\phi(\theta_i)\phi(\theta_j) \] (7.5)

where

\[ U_{rep}(r_{ij}) = \begin{cases} 
4\varepsilon_{rep} \left( \frac{\sigma}{r_{ij}} \right)^{12} & r_{ij} \leq 1.5\sigma \\
0 & r_{ij} > 1.5\sigma 
\end{cases} \] (7.6)

and

\[ U_{att}(r_{ij}) = \begin{cases} 
4\varepsilon \left[ \left( \frac{\sigma/2}{r_s + \sigma/2 \times 2^{1/6}} \right)^{12} - \left( \frac{\sigma/2}{r_s + \sigma/2 \times 2^{1/6}} \right)^6 \right] & r_{ij} \leq 1.5\sigma \\
0 & r_{ij} > 1.5\sigma 
\end{cases} \] (7.7)

Here \( \varepsilon \) is the binding energy, \( r_{ij} \) is the distance between the centers of particles \( i \) and \( j \), while \( r_s = |r_{ij} - \sigma| \) is the distance between the particles surfaces. The angular interaction \( \phi(\theta_i) \) is given by

\[ \phi(\theta_i) = \begin{cases} 
1 & \theta_i \leq \theta_{max} \\
\cos^2 \left( \frac{\pi(\theta_i - \theta_{max})}{2\theta_{tail}} \right) & \theta_{max} \leq \theta_i \leq \theta_{max} + \theta_{tail} \\
0 & \text{otherwise}
\end{cases} \] (7.8)
where \( \theta_i \) is defined as the angle between the patch unit vector \( \mathbf{n}_i \) and the inter-particle vector \( \mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i \) (similarly \( \theta_j \) is the angle between patch vector \( \mathbf{n}_j \) and inter-particle vector \( \mathbf{r}_{ij} = -\mathbf{r}_{ji} \)). The corresponding expression for \( \phi(\theta_j) \) is also given by Eq. 8. The angular potential \( \phi \) is a smooth step function that modulates the angular dependence of the potential and is equal to 1 within the region \( \theta_i < \theta_{max} \) and decays to zero following the expression above. The particular value of \( \theta_{tail} = 25 \) degrees has been selected to generate a sufficiently smooth potential at the Janus interface. This potential was adapted from the model introduced by Miller & Cacciuto [246], and is appropriate to describe the behavior of patchy particles at high salt concentration. In this case, the charge on the hydrophilic side of the colloid is well screened and short ranged [247]. In our simulations \( \sigma \) and \( k_B T \) are used as the basic units of length and energy, while \( \tau = \sigma^2 / D \) is our unit of time. All simulations were run for a minimum of \( 10^7 \) steps with time step \( \Delta t = 10^{-5} \tau \).

In this manuscript, we consider three different attractive patch coverages, \( C \), defined as the ratio between the area of the hydrophobic patch and the total area of the particle. In Figure 7.1, we illustrate from left to right the different attractive patch coverages: \( C = 0.25 \), \( C = 0.50 \), and \( C = 0.75 \). The large arrow in the figure indicates the direction of self-propulsion with respect to the attractive patch. The top row corresponds to APPs that are propelled in the same direction as the patch, \( \eta_i = \mathbf{n}_i \), or with the patch, which we abbreviate as \( WP \). The bottom row corresponds to APPs propelled against the attractive patch, \( \eta_i = -\mathbf{n}_i \), which is abbreviated as \( AP \). In Fig 7.1, the black portion of the particles correspond to the attractive patches, and we use yellow and blue to differentiate between the \( WP \) and \( AP \) cases, respectively. For each patch coverage, we will first study the behavior of the passive counterpart at the same density, represented as green (repulsive
7.3 Results

Dilute suspension of active APPs with patch coverage \( (C = 0.25) \)

![Snapshot of the stable trimer structure for passive suspension of APPs with patch coverage \( C = 0.25 \). (b) Typical configuration observed for binding energy \( \varepsilon = 20 \).](image)

We begin by considering the bulk properties of a low density suspension of passive APPs with a small attractive patch. For all patch coverages, the passive system serves as a reference to the equilibrium behavior. In the passive system at \( C = 0.25 \), the maximum number of attractive interactions or bonds a given APP can form is limited to two, resulting in clusters of three APPs at most. In this configuration the APPs arrange into equilateral triangles with the attractive patch oriented toward the barycenter of the triangle as shown in Fig. 7.2(a). A snapshot of a typical configuration at large binding energy \( (\varepsilon = 20) \) is given in Figure 7.2(b). As one would expect, the binding energy determines the clustering behavior of these suspensions, and the shape of the largest possible stable
cluster is determined by the geometric constraints imposed by the shape of the attractive patch: a trimer in this small patch case \( C = 0.25 \).

To study how these particles self-assemble, we compute the average degree of aggregation \( \langle \Theta \rangle \) of the system defined as in Ref.\,[132, 240]:

\[
\langle \Theta \rangle = 1 - \frac{\langle N_c \rangle}{N} = 1 - \frac{1}{\langle S \rangle}
\]  

(7.9)

where \( \langle N_c \rangle \) is the average number of clusters in the system and \( \langle S \rangle \) is the average number of APPs in a cluster. For a system, that has aggregated into a single cluster \( \langle \Theta \rangle = 1 \), and conversely a system composed of single particle clusters will give a value \( \langle \Theta \rangle = 0 \). In Figure 7.3(a), we show how the average degree of aggregation \( \langle \Theta \rangle \) depends on the binding energy \( \varepsilon \). For small binding energies the system mainly consists of monomers and dimers, while for large \( \varepsilon \) it almost exclusively consists of trimers. For the largest binding energy, we find that \( \langle \Theta \rangle \simeq 0.66 \), which is consistent with the theoretical maximum value of \( \langle \Theta \rangle = 2/3 \) occurring when all aggregates are trimers.

Figure 7.3: (a) Average degree of aggregation \( \langle \Theta \rangle \) as a function of \( \varepsilon \) for passive suspension with \( C = 0.25 \). (b) Average degree of aggregation \( \langle \Theta \rangle \) as a function of \( \nu_p \) for active suspension with \( C = 0.25 \). Two different binding energies are considered: \( \varepsilon = 12 \) (light green) and \( \varepsilon = 20 \) (magenta). Solid lines correspond to the (WP) case, while the (AP) case is given by the dotted lines.
With an understanding of the equilibrium behavior, we now turn our attention to the effect of self-propulsion. Specifically, we consider the two cases where APPs are either propelled in the direction of the attractive patch (WP) or in the opposite direction (AP). For these active suspensions, we only consider two different values of the binding energy, \( \varepsilon = 12 \) and \( \varepsilon = 20 \), and a range of activities up to \( v_p = 50 \). Fig. 7.3(b) summarizes the results of this study for \( C = 0.25 \). Interestingly, the clustering behavior of active APPs is highly sensitive to the direction of self-propulsion relative to the attractive patch. At the smaller binding energy \( \varepsilon = 12 \), thermal fluctuations in the passive case are able to easily break the bond between two APPs. As a result, \( \langle \Theta \rangle \) in the passive system is quite small and takes a value of \( \langle \Theta \rangle = 0.3 \). As we introduce self-propulsion in the (WP) direction, we observe an increase in \( \langle \Theta \rangle \) to values above \( \langle \Theta \rangle = 0.50 \). Here activity stabilizes the formation of dimers and trimers structures. Whereas the opposite occurs when the propulsion is in the (AP) direction, where we observe \( \langle \Theta \rangle \) rapidly dropping to nearly zero where even small clusters quickly break into unpaired monomers. This behavior is even more pronounced at higher binding energies. At \( \varepsilon = 20 \), the system mainly consists of trimers for the (WP) direction. Interestingly, since in this configuration, the net sum of the active forces is zero, these trimers are essentially inert, resulting in a low density fluid where each trimer undergoes Brownian diffusion. Once more, in the (AP) direction we observe \( \langle \Theta \rangle \) dropping to nearly zero (even though slower than in the \( \varepsilon = 12 \) case).

This behavior is particularly interesting as it further reinforces the notion that activity in the (WP) direction can be used to strengthen particle-particle interactions and significantly improves self-assembly of compact structures [145]. It is worth pointing out, however, that the small lowering in \( \langle \Theta \rangle \) for the largest activities at \( \varepsilon = 12 \) is due to either
collisions of a trimer with fast moving unpaired APPs, or the formation of unstable configurations where the vectorial sum of the propelling axes in the trimer deviates sufficiently from zero to generate internal torques able to break the trimer. These destructive events are very rare for $\varepsilon = 20$ as most APPs occupy a stable configuration within a trimer, and thus we observe no significant decline with increasing $v_p$ (at least within the range of velocities considered in this study). These trimer destroying events occur more frequently at lower binding energies, as there are more unpaired APPs and the interaction energy is not as effective at maintaining fairly strict angular orientations within the trimer.

Although, it is tempting to think of the role of activity in this system as having the simple effect of shifting the strength of the inter-particle interactions as $\varepsilon_{\text{eff}} = \varepsilon \pm \alpha v_p$, with the plus or minus corresponding to the $(WP)$ and $(AP)$ directions respectively, and where $\alpha$ is a phenomenological constant, the reality is more complicated. In fact, while on the one hand, self-propulsion can either strengthen or weakens the interaction energy of the particles in a cluster, on the other hand self-propulsion increases the translational velocity of the unpaired particles in the bulk (that one could think of as an effective "temperature"), which makes a straightforward mapping to an effective equilibrium system rather nontrivial.

**Dilute suspension of active APPs with patch coverage ($C = 0.50$)**

We now consider the behavior of APPs with patch coverage $C = 0.50$. For this patch coverage, the maximum number of bonding interactions for a given APP is limited to four. For this reason, unlike the $C = 0.25$ case, there isn’t a simple compact structure
Figure 7.4: (a) Average degree of aggregation $\langle \Theta \rangle$ as a function of $\varepsilon$ for passive suspension with $C = 0.50$. (b) Average degree of aggregation $\langle \Theta \rangle$ as a function of $v_p$ for active suspension with $C = 0.50$. Two different binding energies are considered: $\varepsilon = 12$ (light green) and $\varepsilon = 20$ (magenta). Solid lines correspond to the (WP) case, while the (AP) case is given by the dotted lines.

determining the maximum cluster size for a given set of system parameters (i.e. density, binding energy, temperature, etc). In the passive system, the most stable local configuration is achieved when each APP is located at the vertices of a parallelogram with the attractive patches oriented inward toward one another. This results in the most abundant macrostructures being two-particle thick, rigid chain-like clusters, whose length is controlled by the binding energy $\varepsilon$ (see top panels in Figures 7.5 and 7.6). For small values of $\varepsilon$ (top panel of Fig. 7.5), clustering is limited to the dynamic assembly and disassembly of chain like clusters. In this regime, predominately linear chain structures are observed and the typical number of APPs in a single cluster is on the order of 20. As expected, the length of these chains increases with increasing binding energy. However, as the binding energy increases to large values, branches and kinks develop along the chain backbone (top panel of Fig. 7.6). For the largest binding energies considered, we observe the formation of large branched networks spanning the size of the system. This qualitative description of the behavior of the passive system can be represented quantitatively with average degree of aggregation $\langle \Theta \rangle$ shown in Fig 7.4(a).
Figure 7.5: Typical simulation snapshot for active patchy particles with patch coverage $C = 0.50$ and $\epsilon = 12$. The passive reference system $\nu_p = 0$ is given at the top of the figure. The (WP) case is given in the left column while the (AP) case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.
Figure 7.6: Typical simulation snapshot for active patchy particles with patch coverage $C' = 0.50$ and $\varepsilon = 20$. The passive reference system $v_p = 0$ is given at the top of the figure. The (WP) case is given in the left column while the (AP) case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.
The effects of self-propulsion are not as simple to unravel as in the $C = 0.25$ case, where self-propulsion can either stabilizes or destabilizes a cluster depending on the direction of self-propulsion relative to the attractive patch. In Figure 7.4(b), we show the average degree of aggregation $\langle \Theta \rangle$ as a function of activity for both binding energies considered. In both cases, $\langle \Theta \rangle$ decreases as $v_p$ is increased, and in both cases, the $(AP)$ direction experiences a significantly faster decay of $\langle \Theta \rangle$. Thus, one would naively concluded that the main effect of activity is that of reducing the average size of the aggregates in solution until a fluid state is recovered for very large $v_p$. This line of thought also suggests that larger active forces are necessary in the $(WP)$ direction to break the clusters with respect to the $(AP)$ direction. However, this is not the entire story: a closer look at the evolution of the different configurations that develop in the two propelling directions reveals a complex structural behavior. Figures 7.5 and 7.6 present steady-state snapshots of typical structure that develop as activity $v_p$ is increased for $\varepsilon = 12$ and $\varepsilon = 20$, respectively.

A binding energy of $\varepsilon = 12$ is somewhat ideal for the passive system, as the APPs self-assemble into long linear aggregates with only a sporadic formation of kinks along the chain (Fig. 7.5). No branching of the chains is observed at these binding energies. When activity is introduced in the $(AP)$ direction (right column of Figure 7.5), the length of the structures decreases with increasing $v_p$, and the formation of kinks becomes less probable. The system eventually devolves into a hot fluid for even larger values of $v_p$. When activity is introduced in the $(WP)$ direction (left column of Figure 7.5), patchy particles feel a stronger attraction when in the condensed phase. This leads to the more frequent formation of kinks along the chain, but simultaneously internal torques develop
at the location of the kinks that act as pivots around which the chain can fold. A comparison of the structures for $v_p = 25$ in the $(WP)$ and $(AP)$ directions is quite revealing (lowest panels in Fig. 7.5). In the $(WP)$ direction most of the particles are involved in the formation of small, rigid and compact clusters, while in the $(AP)$ direction most particles are in a fluid phase. This is consistent with the data shown in Fig. 7.4(b).

A much more dramatic illustration of this effect can be observed for $\varepsilon = 20$. Here, large branched clusters develop in the passive case (Fig. 7.6, top panel). As activity is introduced either in the $(AP)$ (right column) or in the $(WP)$ direction (left column), we observe an overall collapse of the structures. The collapse or folding points in these structure are those locations where kinks or branching exist. The kink portions of the structure act as a fulcrum, and the two linear segments surrounding this fulcrum generate a force imbalance leading to the compaction and folding of the structure. However, while these structures, regardless of the direction of the active force, tend to become more compact for small values of $v_p$, at intermediates values of $v_p$, we observe diverging structural behaviors. In both WP and AP cases the large branched aggregates systematically break down into smaller chuckucks. This is because kinks and branching points are the structural weak points of these assemblies and thus more susceptible to be unraveled by the active forces. However, when considering the $(WP)$ direction, we observe small compact structures where multiple linear pieces merge together into activity-stabilized open-mesh clusters, whereas in the $(AP)$ direction, we observe a suspension of linear chains. This phenomenon is most evident as soon as the active forces become comparable in strength to the dispersion forces $v_p \simeq 20$.

This diverging structural behavior for the two propelling directions can be more quan-
Figure 7.7: Average radius of gyration $\langle R_g \rangle$ as a function of cluster size $S$ for binding energy $\varepsilon = 20$. The WP case shows a clear compaction of the clusters with increasing $v_p$, while the AP case exhibits reentrant behavior where clusters undergo an elongation before an eventual collapse as $v_p$ increases.

...tatively expressed by measuring the average radius of gyration of the clusters formed by particle in the AP and WP directions. This analysis is shown in Figs. 7.7, where the average radius of gyration $\langle R_g \rangle$ is given as a function of clusters size $S$ for $\varepsilon = 20$ at different propelling velocities $v_p$. Figure 7.7(a) refers to the data for the (WP) direction and illustrates how $R_g$ systematically decreases when going from the passive case, $v_p = 0$ (blue curve), to the largest activity considered, $v_p = 50$ (red lowest curve). The (AP) direction is given in figure. 7.7(b) and shown how $\langle R_g \rangle$ initially slightly decreases when compared to the passive reference system, but eventually moves up to larger values for sufficiently large activities (already for $v_p = 20$). Unfortunately, it is very hard to obtain these data with sufficient statistics and for large enough clusters to extract a reliable size exponent. Nevertheless the two trends are quite clear. Structurally speaking, apart from the decreasing overall size of the clusters with the increase of $v_p$, one can think of the aggregates formed by the (WP) particles as polymers in a bad solvent with a linear persistence length of about 10 particles, and of the aggregates formed by the (AP) particles,
at least beyond the re-entrant point, as semiflexible polymers in a good solvent. Lastly, it is also worth noting, that the activation of the APPs in the (AP) direction has a practical application as a method to wash away unwanted kinks and branches from a configuration of passive particles assembling with interactions that are too sticky.

**Dilute suspension of active APPs with patch coverage** \((C = 0.75)\)

![Graphs](image)

Figure 7.8: (a) Average degree of aggregation \(\langle \Theta \rangle\) and average cluster size \(\langle S \rangle\) for passive suspension of patchy particles with patch coverage \(C = 0.75\) as a function of the binding energy \(\varepsilon\). (b) Fraction of particles in clusters of a given size range as a function of the binding energy \(\varepsilon\). (c) Simulation snapshots for various values of the binding energy \(\varepsilon\).

We conclude this study by analyzing the bulk properties of a low density suspension of APPs with patch coverage \(C = 0.75\). At this large patch coverage, the geometry of the interaction is wide enough that each APP can accommodate more than 4 other APPs, leading to the formation of more isotropic aggregates. In Fig. 7.8(a), we show \(\langle \Theta \rangle\) as a function of the binding energy \(\varepsilon\) for the passive system. The system fully aggregates into a single cluster for any \(\varepsilon\) greater than about 10, and for smaller values of \(\varepsilon\) we observe small isotropic clusters with overall hexagonal symmetry. At \(\varepsilon = 12\), we observe thick crystalline branched structures. See top panels of Fig. 7.9 for a typical conformations
of the passive suspension with $C = 0.75$ and $\varepsilon = 12$. Figure 7.8(b) shows the average degree of aggregation $\langle \Theta \rangle$ as a function of activity for binding energies $\varepsilon = 12$ and $\varepsilon = 20$. Notably, when compared to the two smaller patch geometries considered in this study the difference in $\langle \Theta \rangle$ between the $(AP)$ and $(WP)$ directions is far less dramatic. For both binding energies, $\langle \Theta \rangle$ decrease monotonically with increasing self-propelling velocity $v_p$.

Figure 7.9: Typical simulation snapshot for active APPs with patch coverage $C = 0.75$ and $\varepsilon = 12$. The passive reference system $v_p = 0$ is given at the top of the figure. The $(WP)$ case is reported in the left column whereas the $(AP)$ case in the right column. Each snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.

One of the most compelling features of the clusters formed both at $\varepsilon = 12$ and at $\varepsilon = 20$ is the change in cluster shape as soon as activity is introduced. Unlike the typical branched structures formed by the passive system, clusters formed by active APPs imme-
diately collapse into truly two dimensional objects with a size exponent equal to $1/2$. This is due in large part to the increased degree of rotational freedom of an APP allowing for more efficient folding of the cluster. Figures 7.9 (lower panels) and 7.10 (lower panels) show the typical aggregates formed for binding energy $\varepsilon = 12$ and $\varepsilon = 20$, respectively. Apart from the slightly faster decay in $\langle \Theta \rangle$ for the $(AP)$ direction with respect to the $(WP)$ direction, there aren’t significant structural differences across the range of active velocities considered in this study.

![Figure 7.10: Typical simulation snapshot for active APPs with patch coverage $C = 0.75$ and $\varepsilon = 20$. The passive reference system $v_p = 0$ is given at the top of the figure. The $(WP)$ case is given in the left column while the $(AP)$ case is given in the right column. Each system snapshot is accompanied by an enlarged snapshot highlighting the local cluster geometry.](image)

What is, however, more significant, is the dynamical nature of the clusters themselves.
In fact, the clusters that form are active in their own right, and they exhibit "living" behavior where they "move, break apart and form again" over the life-time of the simulations. The behavior here is reminiscent of the behavior observed in experiments with attractive colloidal swimmers [128]. The main difference between our work and active spherical particles interacting via an isotropic attractive potential is that in our case, the axis of propulsion of the particles in the condensed phase is essentially frozen, and thus patchy particles in the cluster do not rotate significantly. This is in stark contrast with the isotropic attractive case where active particles undergo rotational Brownian motion. For APPs, what drives these clusters unusual dynamics is their orientational and translational frustration. In fact, far from being hexagonal, these clusters are frozen into rather disordered configurations with frequent gaps within the structure and with the presence of several tetramers with square symmetry organized in such a way that the hydrophilic, rather than the hydrophobic sides of the particles, are in contact. The large torques and forces that develop within these clusters can therefore easily destabilize them as soon as they grow to a sufficiently large size, or, as we often observe, as soon as a small cluster in solution binds to it forcing orientational re-arrangements of the particles that can destabilize their already precarious balance of forces. Finally, it is worth mentioning that while living crystals observed for $C = 1.00$ are typically in dynamic equilibrium with a fluid of unpaired particles, at low velocities, we observe fluids of active clusters, with no unpaired APPs, where clusters either break upon interacting with other clusters, or after large and slow internal cluster re-arrangements.
7.4 Discussion and conclusions

Figure 7.11: (a) Average degree of aggregation $\langle \Theta \rangle$ for all patch coverages considered in this study.

In this paper, we analyzed how active forces can be used to stabilize or destabilize aggregates formed by active amphiphilic patchy particles (APPs). We study the phase behavior of dilute suspensions of these patchy particles for three different hydrophobic patch coverages: $C = 0.25$, $C = 0.50$, and $C = 0.75$. We also considered explicitly the role of the direction of the active forces with respect to the placement of the attractive patch, i.e. with the patch $(WP)$ and against the patch $(AP)$ for a range of different swimming velocities $v_p$ and hydrophobic attractions $\varepsilon$. Figure 7.11 nicely summarizes all of our results concerning how the average degree of aggregation $\langle \Theta \rangle$ depends on the swimming velocity $v_p$ for two different values of $\varepsilon$. The left column shows results for the $(WP)$ direction while the right column corresponds to the $(AP)$ direction. For completeness
we also added to these plots the data corresponding to the fully hydrophobic particles (isotropic attraction) for which $C = 1.00$.

Our study illustrates how the geometry of the interactions between the particles plays a pivotal role in how active forces affect the stability of self-assembled aggregates. In fact, unlike the very special case of spherical active particles interacting with an isotropic potential, where the rotational degrees of freedom of each particle aren’t lost when in the condensed phase, using active APPs with a tunable size of the hydrophobic region enables us to systematically control the parameters responsible for their rotational dynamics. Interestingly, we find that under strong angular confinement — condition that leads to the formation of small finite size clusters — it is possible to increase the particle’s aggregation yield by aligning the active forces in the direction of the patch ($WP$). We have also shown how, when only half of the particle is covered by a hydrophobic patch, it is possible to break apart and either compactify or wash away branches from large branched networks of particles. In doing so we highlighted the significant role played by the direction of the propelling forces for particle with 50% hydrophobic coverage. Finally, we discussed the remarkable behavior of the isotropic active clusters that self-assemble when 75% of the particle area is covered by a hydrophobic patch, and point out how frustration of the frozen active forces within the clusters leads to their dynamic behavior. One can think of these aggregates as being in between those formed by active attractive rods, and those formed by isotropic active Lennard Jones particles. In fact, in clusters formed by rods (or dumbbells), particles are unable to rotate even when a second cluster merges with it. This leads to the formation of ever growing macroscopic aggregates that have a net rotational speed that depends on the details of the particle’s relative orientations,
and that decreases with the cluster size [161]. In clusters formed by spherical particles, as mentioned above, the colloids are completely free to rotate within the clusters, and for a range of active forces and for sufficiently low densities, this leads to the formation of living clusters which do not seem to grow beyond a certain size [128]. Active APPs with 75% coverage form clusters where the directions of the active forces of the particles is mostly frozen when in isolation, leading to rotating clusters with a net rotational speed, but the propelling forces can undergo significant re-arrangements when interacting with another cluster, leading to cluster fractures, large global re-arrangements and eventual disassembly.

Hydrodynamic interactions may play an important role on the phase behavior and structural properties of the assemblies formed by these particles. Extensive work on the subject is currently underway and it will be published elsewhere.
Bibliography


[201] Daisuke Takagi, Jeremie Palacci, Adam B. Braunschweig, Michael J. Shelley, and

Phase Behavior of Active Swimmers in Depletants: Molecular Dynamics and Integral 

[203] Ryan C. Krafnick and Angel E. García. Impact of hydrodynamics on effective 
interactions in suspensions of active and passive matter. *Phys. Rev. E*, 91(2):022308, 
February 2015.

[204] Alexander Y Grosberg and Jean-François Joanny. Activity induced phase separa-

[205] Xingbo Yang, M. Lisa Manning, and M. Cristina Marchetti. Aggregation and segre-


Proteins Induces Magnification of Shape Fluctuations of Lipid Membranes. *Phys. 

[209] Eyal Ben-Isaac, YongKeun Park, Gabriel Popescu, Frank L. H. Brown, Nir S. Gov, 
and Yair Shokef. Effective Temperature of Red-Blood-Cell Membrane Fluctuations. 


[211] Sasha Stankovich, Dmitriy A Dikin, Geoffrey HB Dommett, Kevin M Kohlhaas, 
Eric J Zimney, Eric A Stach, Richard D Piner, SonBinh T Nguyen, and Rodney S 

[212] Xin Wen, Carl W Garland, Terence Hwa, Mehran Kardar, Etsuo Kokufuta, Yong 
Li, Michal Orkisz, and Toyoichi Tanaka. Crumpled and collapsed conformation in 

2870, November 1994.

[214] Janos H Fendler and Pietro Tundo. Polymerized surfactant aggregates: characteri-


[243] Dhruv P. Singh, Udit Choudhury, Peer Fischer, and Andrew G. Mark. Non-

[244] Yirong Gao, Fangzhi Mou, Yizheng Feng, Shengping Che, Wei Li, Leilei Xu, and
Jianguo Guan. Dynamic Colloidal Molecules Maneuvered by Light-Controlled
2017.

[245] Mingfeng Pu, Huijun Jiang, and Zhonghuai Hou. Reentrant phase separation
behavior of active particles with anisotropic Janus interaction. *Soft Matter*,

2009.

[247] Liang Hong, Angelo Cacciuto, Erik Luijt, and Steve Granick. Clusters of Am-