Dynamic assembly of active matter

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2021

Ma, Z. (2021). Dynamic assembly of active matter. Doctoral thesis, Nanyang Technological University, Singapore. <https://hdl.handle.net/10356/151042>

<https://hdl.handle.net/10356/151042>

<https://doi.org/10.32657/10356/151042>

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Dynamic Assembly of Active Matter

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School of Chemical and Biomedical Engineering

2021

Dynamic Assembly of Active Matter

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School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Doctor of Philosophy

2021

Statement of Originality

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Asst Prof. Ran Ni

Authorship Attribution Statement

This thesis contains material from 2 paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences and 1 paper under preparing in which I am listed as an author.

Chapter 2 is published as Zhan Ma, Mingcheng Yang, and Ran Ni, Dynamic Assembly of Active Colloids: Theory and Simulation, *Advanced Theory and Simulations*, **3**, 2000021 (2020). DOI: 10.1002/adts.20200021

The contributions of the co-authors are as follows:

- A/Prof Mingcheng Yang wrote chapter IV of the published paper which is not included in this thesis.
- I prepared the manuscript drafts of other chapters. The manuscript was revised by Asst Prof Ran Ni.

Chapter 5 is published as Zhan Ma#, Qunli Lei#, and Ran Ni, Driving dynamic colloidal assembly using eccentric self-propelled colloids, *Soft Matter*, **13**, 8940 (2017). DOI: 10.1039/C7SM01730H

The contributions of the co-authors are as follows:

- I found the demixing phenomena and performed simulations determining phase diagram. I also conducted simulations using effective pairwise potential extracted from radius distribution.
- Dr. Qunli Lei found the re-entrant mixing at high density.
- Asst Prof Ran Ni prepared the manuscript and revised by all of three authors.

Chapter 3 and 4 are partly included in Zhan Ma, and Ran Ni, Dynamical Clustering Interrupts Motility Induced Phase Separation in Chiral Active Brownian Particles, arXiv: 2104.11657

The contributions of the co-authors are as follows:

- I completed all theory work and conducted all simulations. And I prepared the manuscript draft.
- Asst Prof. Ran Ni revised the draft.

1 / Jun / 2021

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Acknowledgements

This work was carried out in the School of Chemical and Biomedical Engineering at Nanyang Technological University. And I would like to express my sincere appreciation for the support from many people during my PhD here.

First, I would like to acknowledge my thesis advisor, Asst Prof. Ran Ni, who offered me this unique opportunity to conduct research in the area of computational soft matter, when I had no experience in simulation. I offer my deepest gratitude for his time, patience, and assistance throughout this PhD. Aside from his scientific guidance, I appreciate his deep respect and trust for my independence.

I would like to thank the members in the Ran group. Postdoc Hao Hu and Qunli Lei advised me on technical problems and made it not too difficult to overcome the beginner barrier at the early stage of my PhD. Pablo and Aom made the environment more international and keep me open-minded.

Words cannot express how much I have been supported by the love from family. My mother has made tremendous sacrifices throughout my life, not only raising me up independently but also supporting me to be the best and happiest I could be. And in the coming years, I strive to do the same for her. Her optimism and resilience always mention me to be grateful in life. I hope my father be gratified and proud in heaven watching his daughter finishing PhD.

I would also like to thank my friends in Singapore. Thanks to Peng Bo, Xu Bo, and Cheng Weixia, their friendship is so important for life overseas. Sharing food and laughing, travelling around and enjoying the magnificent views of southeast Asia, these happy moments encourage me to overcome depression.

This work is supported by Nanyang Technological University Start-Up Grant M4081781.120; Academic Research Fund from Singapore Ministry of Education Grant M4011873.120; and Advanced Manufacturing and Engineering Young Individual Research Grant A1784C0018 by the Science and Engineering Research Council of Agency for Science, Technology and Research Singapore.

Abstract

Active matter refers to particles that can dissipate energy and drive their own motion. They display intriguing dynamic assembly phenomena as not restricted by equilibrium thermodynamics, including motility-induced phase separation (MIPS), collective motion, giant number fluctuation, and formation of complex patterns, etc. The study of dynamic assembly of active matter can help both understand the emergent behavior in living creatures and design dynamic materials.

Multiple models have been proposed to study active matters, such as active Brownian particles (ABPs) and Vicsek-like models. However, most of these models ignore the intrinsic trajectory curvature and chiral swimming pattern, which are widely observed in active matter systems.

This thesis focuses on the phase behavior of circle swimmers. We construct the circle active Brownian particles (cABPs) model by introducing the self-propulsion torque. Then we formulate a continuum theory for cABPs, and the fluctuation dispersion relation reveals two types of instabilities of the homogeneous state. Compared with simulations results, we verify that the type I instability leads to MIPS, while the type II instability, also called finite wave-number instability, results in a dynamic clustering state and interrupts the conventional MIPS. Besides, by measuring the self-intermediate scattering function, we reveal the dynamical property of this novel inhomogeneous state. Along with obtaining the full phase diagram of cABPs, we also study the phase transition between homogeneous state and dynamic clustering state in the context of percolation theory. Finally, we find the spontaneous demixing of circle swimmers and passive particles, which may have potential application in collecting and sorting passive colloids.

The introductory chapter provides an overview of experimental setups and simulation models for active units, and pays special attention to various circle swimmers, as how their trajectory curvature and the chirality element affect the dynamic assembly of active matter forms the main content of this thesis. Then in Ch. 2, we present a detailed review of the theoretical aspects of MIPS and collective motion, including effective thermodynamics established for ABPs and phase transitions under different symmetries in Vicsek-like models. In Ch. 3, we introduce our theoretical progress on circle swimmers, where a complete phase diagram is obtained by conducting instability analysis on homogeneous state, and we predict a novel finite-wavenumber instability state. In Ch. 4, we present the simulation results of the phase diagram along with structural and dynamical properties in each state. In Ch. 5, we report the spontaneous demixing of circle swimmers with passive colloids.

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Chapter 1

Introduction

1.1 Experiment and Simulation of Active Matter

Active matter refers to particles which can dissipate energy and drive their own motion. This field was first inspired by the biological objects such as bird flocks, fish schools, cell skeleton, and cell migration, etc. Later, various artificial active colloids were designed and synthesised, including Janus particles, nanorods, microrockets that can be propelled by effects like thermo-phoresis, local solvent demixing, gas bubble generation, along with magnetic particles controlled by magnetic-electronic field. In the following, we first overview the widely used wet and dry experimental setups, then introduce two main simulation models (ABPs and Vicsek-like models) which are successful in explaining the motility induced phase separation phenomena and collective motion observed in experiments, despite their simple dynamic rules.

1.1.1 Experimental Setup

Different from various biological active units, synthetic active colloids are easier to control and facilitate the study of phase behavior in active matter systems. Janus particles represent one of the general approaches to drive locomotion, where the different properties on opposite sides can induce particle moving towards a special direction. For example, in [1], setting the Si-Au Janus particle under laser illumination, the Au side has a higher temperature, then the self-thermophoresis effect (*i.e.*, the absorption of a laser at the metal-coated side of the Janus particle creates local temperature gradient which in turn drives the particle by thermophoresis) drives the particle moving towards Si side; merging such colloids in mixture solvent at a temperature a little lower than the critical temperature, illumination increases the temperature on the metal side and cause local demixing of the solvent, which drives moving towards the other side; in [2], Si-Pt Janus particles are merged in H_2O_2 , then the Pt side catalyses decomposition of solvent and generates H_2 and O_2 bubbles which propel the particles. These self-propulsion mechanisms are sketched in Fig. 1.1(a,b).

Above systems require merging colloids in solution thus their motion is highly coupled with hydrodynamic interactions, which can by itself cause complex assembly effects. Thus instead of these wet setup, vibrated disks systems are introduced, where

disks having two legs with different height or mechanical response put on a vibrated planner, the intrinsic polarity of disk can drive locomotion, as shown in Fig. 1.1(c), and this dry setup avoids hydrodynamic effects [3].

Figure 1.1: (a) Janus particle and its temperature distribution under laser illumination [1]. (b) Bubble driven microrocket [2]. (c) Polarity of vibrated disks with two different "legs". [3].

1.1.2 Simulation Models

Without considering hydrodynamic effects, various simulation models can be mainly categorized into two kinds depending on the interactions they account for: steric repulsion and self-propulsion direction alignment, represented by ABPs and Vicsek-like model, respectively.

Active Brownian Particles

Within the ABPs approach, the colloidal particles are modelled with a self-propulsion velocity v_p adding to normal Brownian motion, and the equation of motion can be described by using the overdamped Langevin equation:

$$\begin{aligned}\dot{\mathbf{r}}_i &= \frac{1}{\gamma} \mathbf{F}_{\text{in}} + v_p \hat{\mathbf{e}}_i + \sqrt{2D} \eta_i^T, \\ \dot{\theta}_i &= \sqrt{2D_r} \eta_i^R,\end{aligned}\tag{1.1}$$

where $\mathbf{r}_i$ represents its position and $\hat{\mathbf{e}}_i = [\cos \theta_i, \sin \theta_i]$ represents the propulsion orientation. γ is the friction coefficient, D and D_r are the translational and rotational diffusion constants, respectively, with η Gaussian white noise. $\mathbf{F}_{\text{in}}$ represents inter-particle interactions, and v_p is the self-propulsion velocity. One of the most striking phenomena observed in this system is the motility-induced phase separation (MIPS),

that for ABPs with large v_p at high packing fraction, the system spontaneously separates into a dilute gas phase and a dense liquid phase. The effective thermodynamic theory of MIPS is reviewed in the next chapter.

Vicsek-like model

Vicsek-like model represents a class of point models, where steric repulsive interactions are ignored and particles interact with explicit alignment mechanism. Their typical dynamics can be described as

$$\begin{aligned}\mathbf{r}_i^{t+1} &= \mathbf{r}_i^t + v\hat{\mathbf{e}}^t, \\ \theta_i^{t+1} &= \arg \left[\sum_{k \in \mathcal{N}_i} \exp(i\theta_k^t) \right] + \eta \zeta_i^t.\end{aligned}\tag{1.2}$$

The update of position $\mathbf{r}_i$ and orientation θ_i are in discrete time series. For the evolution of θ_i , the first term accounts for the alignment interaction, where $\mathcal{N}_i$ represents the neighbor regime of particle i . In the second term, ζ_i^t is Gaussian white noise, and η represent its strength intensity. Then for a fixed density, points move in disordered directions at large noise η , while align in a polar or nematic orientation and move collectively at small noise η . The detailed review of this order-disorder phase transition is presented in next chapter.

1.2 Circle Swimmers

Though the ABPs model and Vicsek-like model successfully account for the motility-induced phase separation and collective motion phenomena. The individual particle in these models moves along a straight line without thermal noise in the dilute limit, and thereby fails to take into account the effect of intrinsic trajectory curvature and chiral swimming pattern. However, the circular/helical swimming patterns are widely observed among microorganism like sperms [4, 5, 6, 7], algae [8], bacteria [9, 10, 11, 12, 13, 14, 15, 16] near surface or in strong chemical substance field, as a result of the symmetry of the propulsion mechanism, and also interactions with interfaces. Such motion patterns play important roles in microorganism living, e.g. feeding, gravitaxis motion, biofilm formation, pathogenic infection, etc. Besides, they can be conveniently introduced into a synthetic self-propulsion colloidal system by means like asymmetric shape, mass distribution, catalysis layer coating, applying external fields [17, 18, 19, 20]. In this section, we introduce mechanisms and design protocols for circle swimmers and their corresponding motility properties.

1.2.1 Microorganisms

In the following, we introduce two typical mechanisms inducing the circular swimming paths of microorganisms: one is the chiral rotation of bundled flagella, and the other one is the driving of strong chemical field.

Chiral rotation of flagella

Sperms, bacteria, and some algae with flagella are often observed to swim in circular or helical trajectories near surface. For example, as shown in Fig. 1.2(b), trapped in a microchannel, *E. coli* bacterium displays a preference to travel to the right path facing a junction instead of swimming straightly [11]. This intrinsic curvature results from the coupling between chiral rotation of flagella and the hydrodynamic effects near surface.

Figure 1.2: (a) Bacterium swims by a bundle of rotating helical flagella [21]. (b) *E. coli* cells prefer entering the right sidearm in microchannel [11]. (c) Model of cell swimming clockwise near a solid surface [12].

Fig. 1.2(a) shows the structure of a bacterium with multiple flagella. The rotary motors embedded in the cell wall drive flagella to rotate counter-clockwise, and the cell body rotates clockwise. When these flagella rotate in the same direction, they bundle and propel the cell forward (run event). The cell reorientates (tumble event) whenever one or more flagella motors reverse the sense of rotation and flagella unbundle [15]. The physical structural features of a bacterium with bundled flagella are sketched in Fig. 1.2(c), where it is modeled as a single, left-handed rigid helix attached to a spherical body. By using such model, in Ref. [12], the clockwise circular motion (when viewed from above the surface) and the swimming into the surface are found as a natural consequence of force-free and torque-free swimming, where the net velocity is obtained by balancing the propulsion force of the helical bundle with the viscous resistance on the whole bacterium, and the net rotation rate is found by the balance of viscous moments.

As the cell body is near the surface, when it rotates around the y -axis at a positive rate, there is a viscous force acting on the cell body in the positive x -direction. An intuitive way to think about this result is to picture a ball in a liquid film near a surface, pushing the ball along the surface will also make it rotate, and vice versa.

By contrast, when swimming near a liquid-air interface, the sense of rotation is found reversed [15]. Swimming speed increases with the distance from the boundary. As the motility is sensitive to the distance of the bacterium to the boundary surface, Brownian motion causing the distance fluctuation profoundly alters the bacterial swimming trajectory near the surface [14].

A special case of flagella-driven circular swimming is [8], where biflagellate alga *C. reinhardtii* take helical swimming trajectories as a result of asymmetric beating of two flagella. Where the flagella beat is not perfectly planar, so cells precess around their long axis. This rotation is critical for phototaxis.

Such circular swimming facilitates surface selection and attachment of microorganism, for example in [16], it is found that *vibrio cholerae* switch between straight and orbiting swimming, and only orbiting mode cells can attach irreversibly and form microcolonies. Besides, its high dependence on the hydrodynamic coupling to different types of interfaces could play an important role in the rectification phenomena recently observed in bacterial ratchet motors [22, 23, 24, 15].

Chemotaxis

Stimulating sperm by the chemoattractant elicits a turn in the trajectory followed by a period of straight swimming. In detail, it induces synchronized Ca^{2+} spikes in flagella, and a precise timing of Ca^{2+} spikes controls navigation. In [6], as shown in Fig. 1.3(a), they found when sperm swim in a concentration gradient of the attractant, the chemical field gives rise to repetitive loop-like movements.

Figure 1.3: (a) Ca^{2+} fluorescence signals from a single cell along its loop-like trajectory after stimulation by attractant [6]. (b) Simulated trajectories of Eq. 1.3 under strong attractive chemotaxis in deterministic and stochastic motion [25].

In [25], a brief simulation model was constructed to reproduce the circular pattern of microorganisms autochemotaxis motion, where cells swimming follows the gradient of a chemical field, and the dynamic equation for its angular momentum $\mathbf{L}$ is described as below

$$\frac{d}{dt}\mathbf{L} = -\gamma_R\Omega + \mathbf{M}_{\text{ext}} + \Gamma(t). \quad (1.3)$$

In Eq. (1.3), $\mathbf{M}_{\text{ext}} = \mathbf{e} \times \mathbf{E}$, where $\mathbf{E}$ is the chemotactic field detected at the surface of the microorganism, and its external product with propulsion orientation gives rise to the chemical torque. $\gamma_R > 0$ is the rotational friction coefficient, and the stochastic torque $\Gamma(t)$ is modeled as a Gaussian white noise. Then, this model simulates under strong attractive chemotaxis producing circular motion trajectories as shown in Fig. 1.3(b).

1.2.2 Synthetic Active Colloids

Various protocols can be applied to drive the circular motion of synthetic active colloids. And a general approach is introducing some asymmetric elements, including asymmetric shape, mass distribution, and catalysis coating, which are overviewed below.

Asymmetric colloidal shape

In [17, 18], Au is selectively deposited at the front side of the short arms of L-shaped particles as schematically in Fig. 1.4(A). These L-shaped particles are suspended in a homogeneous mixture solvent at a critical concentration kept several degrees below its lower critical temperature. When the sample cell is illuminated by light, the metal cap becomes slightly heated above the critical point inducing local demixing of the solvent, which propels the motion of particles in the direction vertical to the coated Au layer.

The viscous fluid drag force applies on its geometric center S , while the self-phoretic induced driven force does not across S as a result of the asymmetric shape. This inconsistency couples translational and orientational motion, by generating an additional torque depending on the lever arm l .

In experiments, pronounced circular motions are observed and their chiral trajectories are shown in Fig. 1.4(A:a,b). The torque is velocity dependent. Fig. 1.4(A:c,d,e) shows the distribution for angular difference between locomotion and driven direction shifting to large values as illumination intensity increases. And the trajectory properties are in full agreement with the theory of Brownian dynamics developed for asymmetric self-propelled particles.

In [26, 27], another kind of L-shaped like colloid is synthesized with driven layer on long arm, as shown in Fig. 1.4(B). And the rotation frequency is predicted to increase linearly with H_2O_2 concentration and parabolic with surface tension.

In some other experiments, self-driven rods were observed moving along circular orbits while no explicit asymmetric shape elements are designed [19, 28]. Though the physical origin is still not clear, as both clockwise (CW) and counterclockwise (CCW) orbits are observed with various radii depending on the individual rod, it is speculated that the asymmetric shape introduced by accident could be responsible for the observed circular orbiting motion instead of the straight-line propulsion.

In [20], the authors provided another design protocol, where the chemically fueled microswimmers are made of doublets of Janus colloidal beads with catalytic patches

Figure 1.4: (A) L -shaped particles swim in chiral patterns and torque is velocity dependent [17, 18]. (B) Near L -shaped particles with rotation frequency depending on "fuel" concentration and surface tension [26, 27].

that are positioned at a fixed angle relative to one another. Thus the rotation frequency, trajectory radii can be altered by the anisotropy of catalytic patches as shown in Fig. 1.5.

Asymmetric mass distribution

Aside from the asymmetric shape, in Ref. [29], it was found that with a sufficiently large mass anisotropy, even symmetric shaped self-propelled Janus particles can move along helical trajectories under gravity in 3D, whose axis is oriented either parallel or antiparallel (i.e., they show gravitaxis) to the direction of gravity. As a result of anisotropic mass density, the mass center is inconsistent with the geometric center, thus gravity induces a rotational torque on the geometric center. Fig. 1.6 shows its structure and experimental trajectory with constant translational propulsion speed but different self-propulsion angular velocity ω_a . At large ω_a , the particle has a helical trajectory with many loops, whereas, for small ω_a , the trajectory is elongated.

Asymmetric catalysis coating

Without explicit shape and mass asymmetry, in [30], the authors used glancing evaporation to introduce asymmetric coating and achieve controlled circular motion. Fig. 1.7(a-c) shows schematically the possible shadowing effects and important parameters for glancing angle metal evaporation. Catalyst evaporation for variable

Figure 1.5: (Left) Trajectories for a range of Janus doublets in solution: (a) pure water (b-f) H_2O_2 . (Right) Orientation versus time for the trajectories shown left, and example Janus particle doublet schematic configurations corresponding to each type of motion. [20]

Figure 1.6: (a) Schematic of a self-propelled gravitactic Janus sphere with asymmetric mass distribution in H_2O_2 solution (COM: center of mass). (b) Experimental trajectories of Janus spheres. [29]

glancing angles θ , crystal orientation α affect the perimeter shape of the deposited cap. Reducing θ is expected to considerably reduce the coverage of the deposited metal due to increase shadowing. Variations in α have a more subtle effect, changing the symmetry and position of the cusp-like features that define the cap perimeter.

Figure 1.7: (a-c) Glancing angle evaporation controlled by the glancing angle θ and crystal orientation α . (d, e) Representative plot trajectories. (f, g) Black points represent experimental measured MSD and the red line is fitting Eq. 1.4 to find ω and v . [30]

As the glancing angle decreases, an increasingly tight spiralling trajectory is induced (shown in Fig. 1.7(d,e)), suggesting an increasing amount of angular propulsive velocity which can still maintain a translational propulsive thrust.

The mean squared displacement (MSD) for free diffusing colloid producing both angular and rotational velocity is derived in [30] as

$$\Delta L^2(t) = 4Dt + \frac{2v^2 D_r t}{D_r^2 + \omega^2} + \frac{2v^2(\omega^2 - D_r^2)}{(D_r^2 + \omega^2)^2} + \frac{2v^2 e^{-D_r t}}{(D_r^2 + \omega^2)^2} [(D_r^2 - \omega^2) \cos \omega t - 2\omega D_r \sin \omega t]. \quad (1.4)$$

Here D and D_r represent translational and rotational diffusion constants, respectively, in addition to the translational and angular velocity v, ω . The experimentally measured MSD is well fitted by Eq. 1.4, as shown in Fig. 1.7(f,g). This fitting quantitatively extracts v, ω , and confirms that increasing glancing angle θ decreases angular velocity.

Chapter 2

Dynamic assembly of active colloids: theory and simulation

2.1 Introduction

Active matter is composed of the particles or objects, that are capable of converting ambient or stored energy into their self-propulsion, and they are intrinsically out of equilibrium. The original purpose of investigating active matter was to understand the emergent behaviour in nature, like bird flocks, bacteria colonies, tissue repair, and cell cytoskeleton [31]. Recent breakthroughs in particle synthesis have produced a spectacular variety of novel building blocks, which offers new possibilities to fabricate synthetic artificial active colloids, whose dynamics can be better controlled for investigating the emergent behaviour of non-equilibrium active matter [32]. Various active colloidal systems have been realized in experiments, such as colloids with magnetic beads acting as artificial flagella [33], catalytic Janus particles [34, 35, 36, 37], laser-heated metal-capped particles [38], light-activated catalytic colloidal surfers [39], and platinum-loaded stomatocytes [40]. In contrast to passive colloids undergoing Brownian motion due to random thermal fluctuations of the solvent, active colloids experience an additional force due to internal energy conversion. Although the long time dynamics of self-propelled particles is still Brownian, with a mean square displacement proportional to time [41], the self-propulsion has produced a variety of strikingly new phenomena, which were never observed in corresponding systems of passive particles [42], e.g., bacteria ratchet motors [24], mesoscale turbulence [43], living crystals [39], motility induced phase separation [44], emergent long range effective interactions [45, 46], hyperuniform fluids [47], etc. All these offered a new testbed for investigating non-equilibrium physics, in which theory and simulation have played an important role. Here we review the recent progress in understanding the emergent dynamic assembly of active colloids by using analytical mean field theories and computer simulations. Particularly, in Sec. 2.2, we first briefly review the recent progress in understanding the motility induced phase separation in systems of active repulsive spheres, which is arguably the “simplest” active colloidal systems. In Sec. 2.3, we show various dynamic patterns found in systems of anisotropic active colloids.

2.2 Motility induced phase separation for active repulsive spheres

One of the most intriguing phenomena in active matter is the existence of the motility induced (gas-liquid like) phase separation (MIPS) without any attraction between particles [44], which was proven necessary to induce the gas-liquid transition in equilibrium [48]. The essential physics driving MIPS is the “self-trapping” effect first proposed by Tailleur and Cates using the model of run-and-tumble self-propelled particles in one dimension [49], which was observed in simulations [50, 51] and experiments [52] of two dimensional self-propelled colloidal systems. Recently, in three dimensional systems of active hard spheres, MIPS has also been confirmed [53]. For a comprehensive review on MIPS, please refer to Ref. [44], and in the following, we briefly review the recent progress on the theoretical understanding of MIPS.

2.2.1 Active Brownian particles

The most commonly used model for investigating MIPS is the system of active Brownian particles (ABPs), of which the physics can be also applied to some other self-propelled particle model systems, e.g., run-and-tumble particles [44]. Even though ABPs are driven and energy is continuously supplied to the system, the solvent is assumed to stay at a constant temperature T acting as a heat bath, and the equation of motion for particle i can be described via the overdamped Langevin equation:

$$\dot{\mathbf{r}}_i(t) = \gamma_t^{-1} [-\nabla_i U(t) + F_p \mathbf{e}_i(t)] + \sqrt{2k_B T / \gamma_t} \boldsymbol{\xi}_i^t(t), \quad (2.1)$$

$$\dot{\mathbf{e}}_i(t) = \sqrt{2k_B T / \gamma_r} \boldsymbol{\xi}_i^r(t) \times \mathbf{e}_i(t), \quad (2.2)$$

where $\mathbf{r}_i$ and $\mathbf{e}_i$ are the position of particle i and its self-propulsion orientation, respectively, and F_p is the strength of self-propulsion with k_B the Boltzmann constant. $\gamma_{t/r}$ is the translational/rotational friction coefficient. $\boldsymbol{\xi}_i^t(t)$ and $\boldsymbol{\xi}_i^r(t)$ represent Gaussian white noises with zero mean and unit variance. $U(t) = \sum_{i>j} U_{ij}$ is the potential of the system at time t , and the interaction between ABP i and j can be modelled as the hard-core interaction with diameter σ [54] or the Week-Chandler-Anderson (WCA) potential [51]:

$$U(r_{ij}) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & (r_{ij} < 2^{1/6}\sigma), \\ 0 & (r_{ij} \geq 2^{1/6}\sigma), \end{cases} \quad (2.3)$$

where r_{ij} is the center-to-center distance between particle i and j with $\epsilon \simeq k_B T$. It was recently confirmed that the soft repulsion in the WCA potential does not influence significantly the collective behaviour of ABPs [55]. In Ref. [51], a dimensionless Péclet number is defined as $\text{Pe} = F_p \sigma / k_B T$ to characterize the effect of self-propulsion. It was found that in a 2D system of ABPs, with increasing Pe above certain threshold, the system phase separates into a dense (dynamic clusters) and a dilute phase (Fig. 2.1a), and the probability distribution of local density becomes

bimodal (Fig. 2.1b). It was confirmed that the dynamic clusters merge into one single cluster in long enough simulations implying a first-order like phase separation [51]. As the interaction between ABPs is purely repulsive, the phase separation is solely induced by the motility of ABPs, i.e., motility induced phase separation. It has been confirmed that the thermal noise $\xi_i^t(t)$ on the translational degree of freedom does not qualitatively influence MIPS, and to investigate MIPS, $\xi_i^t(t)$ can be neglected [50].

To understand the intriguing phase separation in ABPs, Ref. [51] offers a kinetic theory to describe the steady state coexistence of dilute and dense phases, in which the dense phase is assumed to be close-packed. The orientations of particles in the dense phase evolve diffusively, while their positions are stationary. The dilute phase is treated as a homogeneous isotropic gas of density ρ_g , and if an ABP in the dilute phase collides with the dense phase, it gets absorbed immediately. Then one can write down the absorption rate of the particle with orientation θ with respect to the normal of dense phase surface as $k_{in}(\theta) = \frac{1}{2\pi}\rho_g F_p \gamma_t^{-1} \cos(\theta)$, which leads to the total incoming flux per unit length: $k_{in} = \frac{\rho_g F_p}{\pi \gamma_t}$. On the other hand, the evaporation rate of ABPs k_{out} from the dense phase is proportional to the rotational diffusion coefficient of ABPs D_r , and it can be written as $k_{out} = \frac{\kappa D_r}{\sigma}$ with a fitting parameter κ . In a steady-state coexistence, $k_{in} = k_{out}$, which leads to the prediction of fraction of particles in the dense phase:

$$f_c = \frac{4\phi\text{Pe} - 3\pi^2\kappa}{4\phi\text{Pe} - 6\sqrt{3}\pi\kappa\phi}, \quad (2.4)$$

where $\phi = N\pi\sigma^2/(4V)$ is the packing fraction of the coexisting system with N and V the number of ABPs and the volume of the system, respectively. The comparison of the theoretical prediction (Eq. 2.4) with the results measured in Brownian dynamics simulations are shown in Fig. 2.2, in which a quantitative agreement can be found.

Besides the kinetic theory, one of the major interests for MIPS in the past years has been developing an equilibrium-like mean field theory to explain MIPS. In equilibrium, the characterization of phase separation includes the boundary of binodal and spinodal, and the kinetic of coarsening and nucleation. The free energy of an equilibrium homogeneous state can be written as a function of density $F(\rho) = \int f(\rho) d\mathbf{r}$ with $f(\rho)$ the free energy density, and the phase separation requires $F(\rho)$ to have a concave shape. As the coexisting phases have the same pressure and chemical potential, the binodal boundary is determined by the common tangent construction on $f(\rho)$ with respect to ρ . The spinodal is obtained by the perturbation instability $\partial^2 f / \partial \rho^2 < 0$. From the kinetic perspective, the Cahn-Hilliard theory predicts a power law growth of the domain size $L(t) \sim t^\alpha$, and if the order parameter c_q indicating the domain follows the diffusive transport of chemical potential μ , i.e., $\partial c_q / \partial t = D_q \nabla^2 \mu$ with D_q the diffusion coefficient, $\alpha = 1/3$ is obtained [56]. Using the concepts in equilibrium phase separations, various methods have been developed to construct an effective free energy for ABP systems, with a special focus on the MIPS in repulsive ABPs.

Figure 2.1: (a) A typical snapshot for the system of ABPs beyond the critical density and activity levels that the ABP fluid separates into a dense and a dilute phase. (b) Observed density distributions for various Péclet numbers [51]. Reproduced with permission.[51] Copyright 2013, American Physical Society.

Figure 2.2: Left: contour map of cluster fraction $f_c(Pe, \phi)$ measured from simulations. The dashed curve marks the approximate location of the binodal. Right: cluster fraction as predicted by the kinetic theory (Eq. 2.4) [51]. Reproduced with permission.[51] Copyright 2013, American Physical Society.

Local density dependent effective bulk free energy

In Ref. [44], by coarsening the zeroth harmonic of dynamic $\psi(\mathbf{r}, \mathbf{u}, t)$ for individual particles, which is the probability of finding a particle at position $\mathbf{r}$ moving in the direction $\mathbf{u}$ at time t , the many body Langevin equation $\rho(\mathbf{r}, t)$ in the drift-diffusion form can be written as:

$$\begin{aligned}\dot{\rho} &= \nabla \cdot (\mathbf{V}[\rho]\rho - D[\rho]\nabla\rho + (2D\rho)^{1/2}\mathbf{\Lambda}), \\ \mathbf{V} &= \frac{-v\nabla v}{d(d-1)D_r}, \\ D &= \frac{v^2}{d(d-1)D_r} + D_t,\end{aligned}\tag{2.5}$$

where the functionals $v[\rho]$ and $D_{t,r}[\rho]$ of the individual particle define the many-body drift velocity $\mathbf{V}[\rho]$ and diffusivity $D[\rho]$ for the interacting particle system. Here d is the dimensionality of the system, and D_t is the translational diffusional constant induced by the thermal noise in the dilute limit, i.e., $\xi_i^t(t)$. $\mathbf{\Lambda}$ is a vector-valued unit white noise. For this drift-diffusion system, an effective free energy functional can be introduced for the steady state as:

$$F[\rho] = F_{ex}[\rho] + \int d\mathbf{r} \rho(\ln \rho - 1),\tag{2.6}$$

where $F_{ex}[\rho]$ is the effective excess free energy satisfying

$$\frac{\mathbf{V}([\rho], \mathbf{r})}{D([\rho], \mathbf{r})} = -\nabla \frac{\delta F_{ex}[\rho]}{\delta \rho(\mathbf{r})}.\tag{2.7}$$

With a local density-dependent velocity assumption, i.e., $v[\rho] = v(\rho)$, the local free energy density can be written as

$$f = \int_0^\rho ds \frac{1}{2} \ln [v^2(s)\tau + dD_t] + \rho(\ln \rho - 1).\tag{2.8}$$

For systems of ABPs, it has been found that the local velocity almost linearly decreases with increasing density, i.e., $v(\rho) = v_0(1 - \rho/\rho^*)$ with v_0 the velocity of a single isolated active particle, and ρ^* the nearly close-packed density of the system (Ref. [50, 51, 57, 58]), and the predicted phase boundary is shown in Fig. 2.3.

Beyond the effective bulk free energy

Ref. [59] studied the evolution of an initial perturbation for propulsion speeds $v_0 = v_c(1+\varepsilon)$ in the vicinity of the linear stability limit v_c . By expanding density fluctuation as $\delta\rho = \varepsilon c + \varepsilon^2 c^{(2)} + \dots$, the lowest order evolution $\dot{c}$ and an effective free energy $F[c]$ can be obtained as

$$\begin{aligned}\partial_t c &= \nabla^2 [\sigma_1 c - g c^2 + \kappa_1 c^3 - \nabla^2 c] = \nabla^2 \frac{\delta F}{\delta c}, \\ F[c] &= \int d\mathbf{r} \left[\frac{1}{2} |\nabla c|^2 + f(c) \right], \\ f(c) &= \frac{1}{2} \sigma_1 c^2 - \frac{1}{3} g c^3 + \frac{\kappa_1}{4} c^4,\end{aligned}\tag{2.9}$$

Figure 2.3: Phase diagrams of MIPS for $v(\rho)$ with (a) $v_0 = 5$ and (b) $D_t = 0.5, d = 2, \tau = 1, \rho^* = 0.8$ [44]. Reproduced with permission.[44] Copyright 2015, Annual Reviews.

where σ_1 , g and κ_1 are the coefficients depending on density with the assumption of effective velocity $v(\rho) = v_0 - \zeta\rho$ where ζ is a constant. As $f(c)$ is concave, a perturbation of propulsion velocity v_0 around the instability boundary induces a phase separation into densities $\rho + \varepsilon c_-$ and $\rho + \varepsilon c_+$ as shown in Fig. 2.4a. Perturbation analysis leads to the Clausius-Clapeyron equation

$$\frac{d\phi}{dv} = \frac{\phi}{v} c_-(\phi, v). \quad (2.10)$$

Approximating c_- by the inflection point $df^2(c)/dc^2|_{c_-} = 0$, one can obtain a spinodal boundary in the good agreement with simulation results as shown in Fig. 2.4b.

Figure 2.4: (a) Concave shape of bulk effective free energy $f(c)$ for $\sigma_1 < 0$; (b) Spinodal boundary of MIPS, and the colorbar indicates the fraction of particles that are part of the largest cluster [59]. Reproduced with permission.[59] Copyright 2014, American Physical Society.

Besides the spinodals being well predicted from the bulk free energy density $f(c)$, the bifurcation analysis obtains the correct phase transition type, i.e., a continuous

transition at high density and a discontinuous transition at low density, which are usually described as spinodal decomposition and nucleation and growth scenarios, respectively. This can be seen in Eq. 2.9, where the amplitude $a(q)$ of fluctuation $c(\mathbf{r}) = a \exp[i\mathbf{q} \cdot \mathbf{r}] + c.c.$ shows two types of bifurcations at the boundary of linear stable wave mode q_0 as shown in Fig. 2.5, and the supercritical bifurcation leads to a continuous transition, while the subcritical bifurcation results in a discontinuous transition.

Figure 2.5: (a) Growth rate as a function of the wave vector q for the linearly unstable and linearly stable regimes; (b) Bifurcation diagram for the supercritical and (c) the subcritical case, where λ is defined by $q^2 = q_0^2 - \lambda \varepsilon^2$, and q_0 is the instability boundary wavemode in dispersion relation [59]. Reproduced with permission.[59] Copyright 2014, American Physical Society.

Nonintegrable gradient term

In Eq. 2.8, by neglecting the contribution of D_t , as generally it is tiny compared with the propulsion term, the chemical potential can be written as

$$\mu_0 \equiv \frac{\delta F[\rho]}{\delta \rho} = \ln \rho + \ln v[\rho]. \quad (2.11)$$

In Ref. [57], beyond the local $v(\rho)$ assumption made in Sec. 2.2.1, a gradient term is introduced to the velocity functional $v(\hat{\rho})$, where $\hat{\rho}(\mathbf{r}) = \rho + \gamma^2 \nabla^2 \rho$, so that it samples ρ on a non-local length scale $\gamma(\rho) = \gamma_0 \tau_r v(\rho)$ depending on the orientational relaxation time τ_r with the coefficient γ_0 . Substituting $v(\hat{\rho})$ into Eq. 2.11, one can

obtain a modified chemical potential

$$\begin{aligned}\mu &= \mu_0 - \kappa(\rho) \nabla^2 \rho + \mathcal{O}(\nabla^4 \rho), \\ \kappa(\rho) &= -\gamma_0^2 \tau_r^2 v(\rho) \frac{dv(\rho)}{d\rho}.\end{aligned}\tag{2.12}$$

However, such modification of the chemical potential breaks the detailed balance (DB), as it can not be integrated into any effective free energy functional. Meanwhile, using similar ideas, one can introduce the density dependent surface tension parameter $\kappa(\rho)$ directly into the free energy density and obtain the corresponding chemical potential recovering DB

$$\begin{aligned}f[\rho] &= f_0(\rho) + \frac{\kappa(\rho)}{2} (\nabla \rho)^2, \\ \mu &= \mu_0 - \kappa(\rho) \nabla^2 \rho - \frac{d\kappa(\rho)}{d\rho} \frac{(\nabla \rho)^2}{2}.\end{aligned}\tag{2.13}$$

Then the corresponding continuum model can be written as

$$\partial_t \phi = \nabla \cdot \left\{ \phi(1 - \phi)^2 \nabla \mu - \sqrt{2\phi(1 - \phi)^2 N_0^{-1} \mathbf{\Lambda}} \right\},\tag{2.14}$$

where $\phi(\mathbf{r}) \sim \rho(\mathbf{r})$ is the local packing fraction and $v(\phi) = v_0(1 - \phi)$ [57]. Here N_0 is the number of ABPs in the cell of side D_t/v_0 .

The comparison between computer simulations of ABPs and the numerical solution of the continuum models (Eq. 2.14) with (Eq. 2.13) and without DB (Eq. 2.12) is shown in Fig. 2.6, including both the obtained binodal (Fig. 2.6a) and the coarsening dynamics (Fig. 2.6b). Here the coarsening length scale is defined as $L(t) = 2\pi \frac{\int S(k,t) dk}{\int k S(k,t) dk}$, where $S(k, t)$ is the structure factor of the system at time t . Interestingly, even though the DB violation enters this model via the gradient term in the effective free energy, which is generally related with the interface formation, it has little influence on the coarsening dynamics, while marginally improve agreement of coexistence densities with ABPs [57].

2.2.2 Binodal of MIPS

In the previous section, we reviewed the progress in mapping the dynamics of ABPs to equilibrium systems via $\dot{\rho} \sim \nabla \cdot (\nabla \frac{\delta F}{\delta \rho})$ [44], which has obtained a good estimation of the spinodal, phase transition types, and coarsening dynamics [59, 57] for MIPS. However, as shown in Fig. 2.6a, the predicted binodal is still significantly different from the measurements in computer simulations [57], and the thermodynamic pressure $p = \partial F / \partial V$ was found unequal across the interface between coexisting phases [60]. These violation suggests that the steady state of ABPs does not correspond to the extrema of thermodynamic free energy $F[\rho]$. This is not surprising as part of the free energy budget is dissipated, and the detailed balance is broken.

In Ref. [61, 62], by defining a one-to-one mapping $R(\rho)$, generalized thermodynamic principles are developed for the dynamics $\dot{\rho} \sim \nabla \cdot (\nabla \frac{\delta \mathcal{G}}{\delta R})$, where $\mathcal{G} =$

Figure 2.6: (a) Probability distribution $P(\phi)$ of the local area fraction ϕ ; (b) Time-dependent coarsening length $L(t) \sim t^\alpha$, where the fitted exponents are $\alpha = 0.27(9)$ (ABPs), $\alpha = 0.28(7)$ (continuum model without DB), $\alpha = 0.27(9)$ (continuum model with DB) [57]. Reproduced with permission.[57] Copyright 2013, American Physical Society.

$\int d\mathbf{r} (\Phi(R) + \Phi_1[R])$ is the generalized free energy with $\Phi(R)$ and $\Phi_1[R]$ free energy densities. Then the violations mentioned above are reasonable as the steady state is at the extrema of $\mathcal{G}$ instead of F . Like in equilibrium, two intensive quantities are found equal in coexisting phases of MIPS, namely the generalized chemical potential $g_0(R) = \frac{d\Phi}{dR}$ and the generalized pressure $h_0(R) = R \frac{d\Phi}{dR} - \Phi$, so that the common tangent of $g_0(R)$ and the equal-area Maxwell construction of $h_0(1/R)$ can be employed to determine the binodal of MIPS.

To apply this generalized thermodynamics into ABPs, the hydrodynamic description of conserved density $\partial_t \rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}$ is obtained by integrating the probability density distribution function of particle $\psi(\mathbf{r}, \theta, t)$ at position $\mathbf{r}$ with orientation θ , and

$$\mathbf{J} = v_0 \mathbf{m} + \mathbf{I}^{(0)} - D_t \nabla \rho, \quad (2.15)$$

with $\mathbf{m}(\mathbf{r}) = \int d\theta \mathbf{u} \psi$ the polarization field, which is the first harmonic of ψ with $\mathbf{u} = (\cos \theta, \sin \theta)$, and $\mathbf{I}^{(0)}(\mathbf{r}) = -\int d\mathbf{r}' u_t \nabla V(|\mathbf{r} - \mathbf{r}'|) \langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle$ the pairwise interaction density, where $u_t = 1/\gamma_t$ is the mobility, and $V(\cdot)$ is the pair potential between ABPs. $\dot{\mathbf{m}}$ depends on the second harmonic $\mathbb{Q} = \int d\theta (\mathbf{u} \cdot \mathbf{u} - \mathbb{I}/2) \psi$ (nematic order field), and $\dot{\mathbb{Q}}$ depends on the higher order harmonic $\Theta[\psi]$. To close Eq. 2.15, one can make the quasi-stationary assumption $\dot{\mathbf{m}} = \dot{\mathbb{Q}} = \dot{\Theta} = 0$, since they are fast modes compared with $\rho(\mathbf{r}, t)$ [62, 63].

For the expression of flux in Eq. 2.15, instead of constructing a $\mathbf{J} \sim \nabla \frac{\delta \mathcal{G}}{\delta R}$ and predicting the binodal using the first principle approach, in Ref. [64] a stress tensor $\boldsymbol{\sigma}$ is found so that $\mathbf{J} \sim \nabla \cdot \boldsymbol{\sigma}$, and the generalized pressure is defined as the diagonal term

$$\begin{aligned} h &\equiv -\sigma_{xx} \\ &= \frac{D_t}{u_t} \rho + P^A(x) + P^D(x) + \frac{v_0^2}{u_t D_r} \mathbb{Q}_{xx} - \frac{D_t v_0}{u_t D_r} \partial_x m_x. \end{aligned} \quad (2.16)$$

Here P^A and P^D are “active” and “direct” passive-like part pressures, respectively, which have explicit mechanical definitions [65] discussed in detail in Sec. 2.2.3.

The flux-free steady state sets the first restriction to coexisting homogeneous phases

$$h_0(\rho_\ell) = h_0(\rho_g) = \bar{h}, \quad (2.17)$$

where $\bar{h}$ is the coexisting pressure. The generalized pressure h is splitted into a local term and an interfacial contribution: $h = h_0(\rho) + h_1[\rho]$. To predict binodals, we need one more restriction, as no explicit $R(\rho)$ is obtained, and the equal-area Maxwell construction for the equation of state (EOS) $h_0(1/R)$ cannot be applied. Instead, Solon *et al.* measured the violation of Maxwell construction for $h_0(1/\rho)$ numerically in a slab simulation box [62]

$$\int_{\nu_\ell}^{\nu_g} (h_0(\nu) - \bar{h}) d\nu = \int_{x_g}^{x_\ell} h_1 \partial_x \nu dx \equiv \Delta A, \quad (2.18)$$

where $\nu = 1/\rho$. The integration in Eq. 2.18 goes through the interface separating the coexisting gas and liquid-like phases along the x axis of the simulation box. Then for a given ΔA , coexisting phases were determined on the EOS $h_0(\nu)$ as schematic in Fig. 2.7a, and the phase diagram obtained fit well with simulation result Fig. 2.7b.

Figure 2.7: (a) Modified Maxwell construction: for EOS $h_0(\nu)$, $h_0(\nu_\ell) = h_0(\nu_g)$ and $A_1 - A_2 = \Delta A$ are used to determine $\nu_{\ell,g}$. (b) Phase diagram of ABPs, modified (red) and the equal-area (blue) Maxwell constructions, compared with numerically measured binodals (black). Dashed lines correspond to the spinodals $h'_0(\rho) = 0$ [62]. Reproduced with permission.[62] Copyright 2018, IOP Publishing.

2.2.3 Pressure

The generalized pressure defined in Eq. 2.16 coincides with the mechanical pressure in the isotropic homogeneous state of ABPs [65].

The “active” contribution to pressure is

$$P^A = \frac{v_0^2}{2u_t D_r} \rho + \frac{v_0}{u_t D_r} \mathbb{I}_{xx}^{(1)}, \quad (2.19)$$

which is also called “swim” pressure proposed by Brady and coworkers [66, 67], and

$$\mathbb{I}_{\alpha\beta}^{(1)} = - \int d\mathbf{r}' u_t \partial_\beta V(|\mathbf{r} - \mathbf{r}'|) \langle \rho(\mathbf{r}') m_\alpha(\mathbf{r}) \rangle \quad (2.20)$$

describes the pairwise interaction density projected on the self-propulsion direction. Therefore, the physical interpretation of P^A is the transport of propulsion forces [65]. Assuming short-range repulsions between ABPs, P^A can be estimated as $P^A = v_0 v(\rho) \rho / (2u_t D_r)$ with $v(\rho) = v_0(1 - \rho/\rho^*)$ [50, 51, 57]. When neglecting the contribution of D_t , Solon *et al.* defined a Péclet number as $\text{Pe} = 3v_0/D_r\sigma$ [62], and it was found that at small Pe regime, i.e., $< \text{Pe}_c$, the system remains in a homogeneous state. Here Pe_c is the critical Péclet number, above which MIPS occurs. For fixed v_0 , by changing D_r , $P_0^A \propto \text{Pe}$, which was numerically confirmed in Fig. 2.8a, where the subscription 0 means in a homogeneous state.

The “direct” contribution to the pressure

$$P^D = -\sigma_{xx}^{\text{IK}}, \quad (2.21)$$

with

$$\sigma_{\alpha\beta}^{\text{IK}}(\mathbf{r}) = \frac{1}{2} \int d\mathbf{r}' \frac{r'_\alpha r'_\beta}{|\mathbf{r}'|} \frac{dV(|\mathbf{r}'|)}{d|\mathbf{r}'|} \int_0^1 d\lambda \langle \rho(\mathbf{r} + (1-\lambda)\mathbf{r}') \rho(\mathbf{r} - \lambda\mathbf{r}') \rangle, \quad (2.22)$$

representing the density of pairwise forces acting across a plane [65], and it is passive-like and independent with Pe in a homogeneous phase (Fig. 2.8a). As $h_0(\rho) = P_0^A + P_0^D$, the EOS of phase separated state at high Pe can be constructed following the scale rule

$$h_0(\rho, \text{Pe}) = P_0^A(\rho, \text{Pe}_0) \left(\frac{\text{Pe}}{\text{Pe}_0} \right) + P_0^D(\rho, \text{Pe}_0), \quad (2.23)$$

where $\text{Pe}_0 < \text{Pe}_c$ (Fig. 2.8b).

The modified Maxwell construction in Eq. 2.18 results from the fact that the integration of nonlocal contribution $h_1[\rho] = P_1^A[\rho] + P_1^D[\rho] + \frac{v_0^2}{u_t D_r} \mathbb{Q}_{xx} - \frac{D_t v_0}{u_t D_r} \partial_x m_x$ at interface does not vanish, where the subscription 1 indicates the interfacial contribution, and the contribution of each term can be numerically measured for a flat interface in a slab simulation box (Fig. 2.9a). The nonlocal contribution of “active” pressure P_1^A is negative, while the “direct” pressure P_1^D is positive, which is due to the more intensive collision events occurring at the interface. Overall, this leads to a negative interfacial tension (Fig. 2.9b), which is also observed in Ref. [68].

Moreover, apart from the derivation of a generalized EOS $h_0(R)$ from the generalized free energy $\mathcal{G}$ as discussed in Sec. 2.2.2, the existence of an EOS in systems

Figure 2.8: (a) P_0^A (black) scales linearly with Pe and P_0^D (red) is independent with Pe . (b) Empirical EOS (lines) $h_0(\rho) = P_0^A + P_0^D$ constructed by scale rules of Pe based on numerically measured EOS (dots) at homogeneous state [62]. Reproduced with permission.[62] Copyright 2018, IOP Publishing.

of torque-free ABPs was also confirmed via mechanical approaches [69, 70]. It was found that for torque-free ABP systems, there is an effective conservation of momentum in the steady state, which leads to a mechanical pressure depending solely on bulk quantities [69]. A local stress expression for ABPs using the virial theorem derived in Ref. [70] also underlines the existence of an EOS, and opens up the possibility to calculate stresses even in inhomogeneous systems.

Need to be notice, though the properties of MIPS in bulk phase is well captured by free-energy-like descriptions as we have reviewed, special boundaries can induce more complex emergent behavior of active colloids and may challenge such description. Such as collective directed motion of self-propulsion particles along the racetrack, which breaks down time-reversal symmetry macroscopically [71, 72], and rectification effect in patterned substrate [73].

2.3 Anisotropic active colloids

Different from the system of active spherical particles, in which MIPS was one of the major research focuses in the past, in systems of anisotropic self-propelled particles, the coupling between the intrinsic shape anisotropy and the self-propulsion results in effective alignments, which have produced more emergent dynamic phases like swarming, turbulent, lane and oscillation states. In Sec. 2.3.1, we summarize recent simulations on self-propelled rods (SPRs) interacting with steric repulsion in two-dimensions, and we also discuss systems of active particles with more complex shape in Sec. 2.3.2, where the chirality plays an important role in assembly. Further, in Sec. 2.3.3, we compare with point polar particle systems with explicit alignment interactions, which are more convenient for theoretical analysis, and various modified models are designed to bridge them with the SPR systems. Finally, in Sec. 2.3.4, we summarize useful properties of density fields, orientational fields and swirling flows

Figure 2.9: (a) Flat interface between phase-separated state in slab simulation box. (b) Nonlocal terms contribute to generalized pressure at the flat interface [62]. Reproduced with permission.[62] Copyright 2018, IOP Publishing.

to characterize various phases and phase transitions.

2.3.1 SPR model and phase diagrams

Self-propelled rigid chains of repulsive disks are one of the most commonly used models for investigating the dynamic assembly of SPRs in two-dimensions. As shown in Fig. 2.10a, $\mathbf{x}_i$ and θ_i are the position of the center of mass and the orientation of the long axis of the rod, respectively. The equation of motion for the SPR i is

$$\begin{aligned}\dot{\mathbf{x}}_i &= \boldsymbol{\mu} [-\nabla U_i + F \mathbf{V}(\theta_i) + \boldsymbol{\Lambda}_i(t)], \\ \dot{\theta}_i &= \frac{1}{\zeta_\theta} \left[-\frac{\partial U_i}{\partial \theta_i} + \xi_i(t) \right],\end{aligned}\tag{2.24}$$

where $\boldsymbol{\mu}$ is the mobility tensor defined as $\zeta_\parallel^{-1} \mathbf{V}(\theta_i) \mathbf{V}(\theta_i) + \zeta_\perp^{-1} (\mathbf{I} - \mathbf{V}(\theta_i) \mathbf{V}(\theta_i))$, with $\zeta_{\parallel, \perp, \theta}$ the friction coefficients and $\mathbf{V}(\theta_i) = (\cos \theta_i, \sin \theta_i)$. Here the interaction between two SPRs is simplified as the summation of the pair interactions between all disks, and $U_{ij} = \sum_{\alpha, \beta} u_{i,j}^{\alpha, \beta}$, where $u_{i,j}^{\alpha, \beta}$ is the potential between disk α of the i th rod and disk β of the j th rod. $\boldsymbol{\Lambda}$ and ξ are the vectorial and scalar Gaussian white noises, respectively. The excluded volume interaction between discs induces a torque, which leads to an effective nematic alignment between SPRs as shown in Fig. 2.10. ℓ and σ represent rod length and disc diameter respectively.

Control parameters: aspect ratio a and packing fraction ϕ

Using the effective packing fraction $\phi = N [\sigma(\ell - \sigma) + \pi\sigma^2/4] / V$ and the length-to-width ratio $a = \ell/\sigma$ as control parameters, a phase diagram for SPRs is obtained as shown in Fig. 2.10 [43, 74], which features the following phases.

Active jamming: For small aspect ratio a , increasing ϕ results in a sharp drop of the mobility of SPRs, which marks the onset of jamming transition. The boundary highly depends on the shape anisotropy of SPRs.

Figure 2.10: Top: Sketch of two interacting rods in the SPR model . Forces and torques resulting from the interaction lead to effective alignment (right panel) [75]. Reproduced with permission.[75] Copyright 2015, American Physical Society. Bottom: Schematic non-equilibrium phase diagram of the 2D SPR model at variable aspect ratio a and effective filling fraction ϕ [74]. Reproduced with permission.[74] Copyright 2012, IOP Publishing.

Turbulent: For intermediate a , the significant increase of enstrophy density defined as $\Omega = \frac{1}{2} \langle |w(\mathbf{r}, t)|^2 \rangle$ marks the transition to a turbulent phase, where particles collectively swirl. The scalar vorticity field is defined as $w(\mathbf{r}, t) = [\nabla \times \mathbf{v}(\mathbf{r}, t)] \cdot \hat{\mathbf{e}}_z$, where $\mathbf{v}(\mathbf{r}, t)$ is the velocity field, and $\hat{\mathbf{e}}_z$ is the unit vector perpendicular to the 2D plane. We note that with increasing ϕ , the system experiences a crossover from the

state of inhomogeneous density distribution with giant number fluctuation (GNF) to a homogeneous turbulent state.

Swarming: In systems of slender SPRs, at low to moderate density, particles tend to form large compact flocks with coherent motion indicated by the relatively long velocity correlation length.

Laning: For extremely large a at high density, the divergence of the correlation length with increasing ϕ marks the transition to the laning phase, where flocks start to span the entire system and self-organize into lanes moving in opposite directions.

The results above provide a schematic phase diagram of SPRs, while in another similar disc-chains model, an “aggregate” phase was found [75], of which the phase diagram is shown in Fig. 2.11. The “clusters” phase in Fig. 2.11 is similar to the “swarming” phase in Fig. 2.10, while slightly increasing density makes those flocks with local polar order aggregate into a giant cluster, of which the size increases linearly with the system size and the global orientation order vanishes. For larger aspect ratio, there is a broad “unstable” regime of density, where the system oscillates between clusters and giant aggregates states. Comparing the difference between the two models, even though the former employs the Yukawa potential, which is steeper than the harmonic potential used in the latter model, they both achieve an effective velocity alignment in pairwise rod collision events. The difference is that the SPR model in Fig. 2.10 neglects both the translational and rotational thermal noises so that it is deterministic but the disc-chain model in Fig. 2.11 considers the rotational thermal noise. Besides, the SPR model employs a mobility tensor depending on aspect ratio, while $\zeta_{\parallel,\perp,\theta}$ is fixed in the disc-chain model, and in the investigated regime of aspect ratio, the mobility of SPRs in the former model (Fig. 2.10) is much smaller than that in the latter (Fig. 2.11). The most significant difference may be that the self-propulsion velocity along long-axis in the SPR model investigated in Fig. 2.10 is much larger than the disc-chain in Fig. 2.11. All these break the large swarming clusters in the SPR model into smaller polar clusters in the disc-chain model, so that the giant clusters formed in a “traffic jammed” scenario is possible in the disc-chain model.

Control parameters: packing fraction ϕ and Pe

Different from the studies above focusing on the control parameters aspect ratio a and packing fraction ϕ , in Ref. [76], the aspect ratio is fixed at $a = 40$ and the phase behaviour of the system in the parameter space of ϕ, Pe was investigated in Fig. 2.12. At the passive limit $Pe = 0$, with the increasing ϕ , the system transforms from an isotropic fluid to a nematic and finally to a crystalline phase. With increasing the self-propulsion, a flock phase appears, which is characterized by the collective motion of dense aligned clusters, indicated by the peaks in the pair distribution function and the emergence of the polar orientational correlation that persists over the length scale of typical cluster-size. Here the flock phase is essentially the same as the swarming phase defined in Ref. [74]. The transition from a nematic phase to a flock phase has a strong hysteresis.

The normalized structure factor time correlation functions for nematic-laning and

Figure 2.11: Left: Phase diagram of the 2D disk-chain model at variable aspect ratio κ and effective filling fraction η , where κ and η are the same as a and ϕ in Fig. 2.10. Right-top: Snapshots of a percolate polar cluster. Right-bottom: Giant aggregate state [75]. Reproduced with permission.[75] Copyright 2015, American Physical Society.

Figure 2.12: (a) Phase diagram of the 2D SPR model with aspect ratio 40 at variable packing fraction ϕ and Pe . (b) Structure factor peak correlation as a function of time for $Pe = 160$ in the laning ($\phi = 0.44$) and flocking ($\phi = 0.34$) state. (c) Stress-tensor correlation as a function of time for $Pe = 160$, inset, zoomed view of long-time tail [76]. Reproduced with permission.[76] Copyright 2015, American Physical Society.

flocking phases are shown in Fig. 2.12b, and one can see that the nematic-laning phase exhibits an exponential decay, while the flocking state shows a power-law decay, which indicates slow structural relaxation at the length scale of typical cluster-size in the flocking state. Besides, the long-lived non-zero plateau in the correlation function of the internal stress tensor suggests a slow mechanical relaxation. These imply that the transition from nematic-laning to flocking is glassy.

In experimental systems like actin filaments propelled by molecular motors, active units are penetrable, which significantly affects the phase behavior, as the motility is not restricted in two-dimensions. In Ref. [77], a separation-shifted Lennard-Jones potential is employed so that the SPRs have certain probability to penetrate each other. At the fixed aspect ratio $a = 18$, for intermediate ϕ , with increasing Pe , the

system first forms a flocking phase similar to Fig. 2.12, while further increasing Pe breaks up the polar clusters and the system becomes homogeneous, indicated by the density probability distribution changing from unimodal to bimodal finally again to a broader unimodal distribution.

Because of the energy dissipation in active nematics, the defect-free alignment in liquid crystal system is destabilized. And the excitation, annihilation and transportation of topological defects play import role in controlling the nonequilibrium dynamics of active nematics. In 2D, activity leads to the spontaneous motility of $+1/2$ disclinations, and lowers the defect-unbinding transition temperature [78, 79]. In 3D, the large space of possible defect configurations has previously hindered the study of topological dynamics. Recently, [80] suggests a framework for analyzing the topological dynamics in 3D active nematics, where excitation mode is dominated by emerging of topological neutral loops.

2.3.2 Chirality and oscillation state

Beyond the SPR model, if the shape of active particles is asymmetric, e.g. L-shaped, the eccentric self-propulsion induces an extra torque, which makes the active particle swim in a chiral circular fashion [81, 17]. In Fig. 2.13a, the L-shaped model is sketched, where α is the ratio between the length of long and short arms, and β is the angle between the two arms. With an active force and torque, an isolated particle swims in a circular trajectory with the period T_0 increasing with α and β , so does the chirality. In Ref. [82], an oscillation state was found with increasing the chirality, which is characterized by the periodic change of local density.

2.3.3 Explicit alignment model

One of the major differences between SPRs and self-propelled spheres is that the steric effect leads to the effective alignment of propulsion direction via collision events between SPRs. Therefore, models of point like particles with explicit alignment interactions were applied to investigate the alignment effect, which are known as Viscek-like models. Besides the steric hindrance, the aligning interactions may have other origins, like hydrodynamic interaction in systems of bacteria and actin filaments, and more complex for bird flocks or fish schools. In this section, we summarize the phase behaviour of these explicit alignment models.

One basic active particle model with alignment interaction is the Viscek model (VM), where particles were represented by points without steric interaction, which was first introduced to study the collective motion of self-propelled particles [83]. Based on the symmetry of alignment and self-propulsion, the self-propelled point models can be categorized into four kinds: polar point (PP/VM), polar rod (PR), apolar rod (AR, also called active nematics), Viscek-shake (VS). General equations of motion for them are

$$\begin{aligned}\mathbf{r}_j^{t+1} &= \mathbf{r}_j^t + v_{\pm} \mathbf{e}_{\theta_j}^t, \\ \theta_j^{t+1} &= F_j(\theta, \mathbf{r}) + \eta \xi_j(t),\end{aligned}\tag{2.25}$$

Figure 2.13: (a) Sketch of chiral L-shaped particle model and its circular motion. (b) Local number density as a function of time in the chiral rod system (top) and the achiral rod system (bottom). (c) Phase diagram with varying α and β at packing fraction $\phi = 0.2$ [82]. Reproduced with permission.[82] Copyright 2019, Royal Society of Chemistry.

where $\mathbf{r}_j^t$ and θ_j^t are the position and orientation of particle j at time t , and $\mathbf{e}_{\theta_j}^t$ is the unit vector pointing to the direction of θ_j^t . Here $t' = t$ is backward difference and $t' = t + 1$ is forward difference, and for VM there is no significant differences between the two methods [84]. $\xi_j(t)$ is a Gaussian white noise with zero mean and unit variance, and η is the strength of noise. PP and PR are polar driven, and $v_{\pm} = v_0$ is a constant propulsion velocity, while AR and VS are apolar driven, and $v_{\pm} = \pm v_0$ is chosen with equal probability; the function $F_j(\theta, \mathbf{r})$ indicates polar (PP, VS) and

nematic (PR, AR) alignment interaction:

$$\begin{aligned} \text{PP, VS: } F_j(\theta, \mathbf{r}) &= \arg \left[\sum_{k \in S_j} e^{i\theta_k(t)} \right], \\ \text{PR, AR: } F_j(\theta, \mathbf{r}) &= \arg \left[\sum_{k \in S_j} \text{sign}[\cos(\theta_k(t) - \theta_j(t))] e^{i\theta_k(t)} \right], \end{aligned} \quad (2.26)$$

where S_j contains all the neighbours of particle j . As a result of the balance between alignment and noise, decreasing η leads to a disorder-order transition in all these four models indicating by the increase of macroscopic mean velocity. Because of different symmetries, these models exhibit various ordered states and phase transitions, which have been widely employed to study the collective motion of bird flocks, fish schools, bacteria, vibrated granular rods, microtubule-molecular motor suspensions, etc.

Table 2.1: Emergent phases in Viscek-like models.

Model	States (Decrease noise)	Homogeneous ordered phase		Transition
		Orientalional Order	GNF exponent	
Polar Points [83, 85, 84, 86]	I: disordered homogeneous II: travelling bands (L-G coexistence) III: ordered homogeneous	Long range polar	~ 1.6	I-II: 1st order transition II-III: 1st order transition
Polar Rods [87]	I: disordered homogeneous II: disordered unstable band III: ordered bands IV: ordered homogeneous	Long range nematic		I-II: 1st order transition
Viscek-shake [88]	I: disordered homogeneous II: ordered homogeneous	Quasi-long range polar	$\sim 1.73(3)$	2nd order transition
Apolar Rods [89, 90]	I: disordered homogeneous II: disordered unstable bands III: ordered homogeneous	Quasi-long range nematic	~ 2.0	Berezinskii-Kosterlitz-Thouless transition

Table. 2.1 shows the states observed in the four different models. For the PP model, decreasing the noise strength η induces a phase transition from disordered homogeneous state to an ordered traveling bands state. Further decreasing η leads to a long-range (LR, or global) polar ordered homogeneous phase with GNF, and the finite-size analysis suggests the disorder-order transition is discontinuous [83, 85, 84]. Instead of focusing on the disorder-order transition of the global orientational order, Ref. [86] suggested that it is better to understand this transition as a gas-liquid transition, while the band solution is in a coexistence region, supported by the band fraction being proportional to excess density, which is consistent with the lever rule. For the PR model, decreasing η leads the disordered homogeneous state first to an unstable band state without global orientational order, further to a band state with long range nematic order, and finally to a homogeneous nematic ordered state with GNF [87]. Similarly, for the AR model, decreasing η induces a chaotic disordered state, finally to a homogeneous quasi-long-range (QLR) nematic order state with GNF [89, 90]. For the VS model [88], the instability of homogeneous disordered phase is absent, decreasing η directly leads to a homogeneous ordered phase, which exhibits a QLR polar order.

Even through these Viscek-like models consider basic symmetry factors and facilitate theoretical works, there are still significant difference between the Viscek-like

models and the realistic active particle models, which exhibit more complex phase behaviours as in Sec. 2.3.1. To bridge between these two different types of models, point particles with density dependent motility [91] and lattice models, where each node can be occupied by at most one particle [92], were introduced to mimic the steric hindrance. In the models above, a number of new patterns were found, and they partially recover the phases observed in steric models, which are absent in point models, e.g., the polar ordered [91] and glider states [92] resembling the swarming phase [74], and the aster [91] and traffic jam states [92] resembling the aggregate state [75] to some extent. Most significantly, in the Vicsek model, the particles move perpendicular to the band, but in Ref. [91, 92], the band state recovers the parallel orientation as in volume excluded models. Especially in Ref. [91], the similarity of phase boundary between the homogeneous ordered phase and the disordered cluster phase obtained by simulation and linear instability analysis in continuum theories suggests that the cluster instability is determined by the effective “pressure term” $-\frac{1}{2}\nabla(v(\rho)\rho)$. This is similar to the MIPS scenario and mostly steric effect [49, 50, 51, 91]. In contrast, in the point model, adding a repulsive interaction by introducing an anti-alignment rotation to nearby particles inside a repulsion zone instead of the explicit excluded volume effect only leads to the conventional order-disorder transition [93]. A simple explanation for the differences observed in explicit alignment and steric models is that, in the latter, the traffic jam can trap particles and lead to denser disordered aggregates, while in the former, only the ordered region can sweep more and more particles leading to denser groups.

2.3.4 Order parameter and phase characterization

Density field

Different from the MIPS observed in spherical ABP systems, the density field in SPR systems exhibits a signature of GNF, which was first predicted by continuum theories [94]. The number fluctuation of particles in a finite box of length l is defined as $\sigma_l^2 = \langle N_l^2 \rangle - \langle N_l \rangle^2$. According to the central limit theorem, $\sigma_l^2 \sim \langle N_l \rangle^\alpha$ with the exponent $\alpha = 1$ for randomly distributed particles. In contrast, $\alpha > 1$ is called GNF indicating the existence of long-range correlation in the system. Other properties that can be used to characterize the density field include the coarse-grained density probability distribution $P(\rho_l)$, the spatial density-density correlation function $C(\mathbf{r}, t) = \langle \rho(\mathbf{0}, t)\rho(\mathbf{r}, t) \rangle$, and the structure factor $S(\mathbf{k}) = \frac{1}{N} \sum_i |\exp(-i\mathbf{k} \cdot \mathbf{r}_i)|^2$. In the steric SPR model [74], the incoherent phase at low ϕ has $\alpha \simeq 1.2$ a little larger than the criterion of GNF, and the swarming phase at low ϕ and large a exhibits significant GNF with $\alpha \simeq 1.8$, while other high density phases, i.e., jammed, turbulent and laning phases, have $\alpha \simeq 0.6$, as shown in Fig. 2.14.

Ref. [96] discussed the relationship between GNF exponent, $C(r)$ and $S(k)$ for different Vicsek-like models. In general, the number fluctuation information is embedded in the density correlation function $C(r)$, and

$$\sigma_l^2(t) = l^d \int_0^l d^d \mathbf{r} [C(\mathbf{r}, t) - \langle \rho \rangle^2]. \quad (2.27)$$

Figure 2.14: (a) Number fluctuation of different phases for 2D steric SPR model [74], and here $\gamma = \alpha/2$. Reproduced with permission.[74] Copyright 2012, IOP Publishing. (b, c) Two kinds of cluster size distribution at two sides of critical weight of coagulation vs fragmentation P_c [95]. Reproduced with permission.[95] Copyright 2013, IOP Publishing.

The results are summarized in Table. 2.2. For PP and PR models, which are both polar driven, $S(k, t)\mathcal{L}^2(t)$ consists of two distinct power-law scalings for small and large $k\mathcal{L}(t)$, where $\mathcal{L}(t)$ is a macroscopic length scale over which enhanced clustering exists. The small k part corresponds to the long range density correlation tail $C(\mathbf{r}) \sim |\mathbf{r}|^{-\eta}$ for $r/\mathcal{L} \geq 1$, where $\eta = 0.8$. According to Eq. 2.27, the GNF is dominated by the integration near upper bound and has $\alpha = 2 - \eta/d = 1.6$ with d the dimensionality of the system. While for the apolar-driven rod (AR) model, there is no long power law tail in $C(r)$, so the integration is dominated by the cusp $C(r) \sim a - b|r/\mathcal{L}|^{\beta_1}$ in the range $r \ll \mathcal{L}$, which leads to the number fluctuation following $\sigma_l^2 \sim a_1 \langle N \rangle^2 - \frac{b_1}{\mathcal{L}^{\beta_1}} \langle N \rangle^{\beta_1/d+2} + \dots$, where a_1 , b_1 and β_1 are positive constants.

Cluster size distribution (CSD) is another property used to study the density field. Ref. [97, 95] constructed a kinetic clustering equation for SPRs based on the control parameter P , which is the relative weight of coagulation with respect to fragmentation. It was found that there is a critical P_c where the power law CSD $p(m; P_c) \sim m^{-\gamma}$, with m the cluster size, separates an individual and a collective (clustering) phases. For $P < P_c$, CSD can be well fitted with $p(m, P) \sim m^{-\gamma} \exp(-m/\tilde{m}(P))$ with $\tilde{m}(P)$ the characteristic cluster size at P , while for $P > P_c$, CSD is non-monotonic and has a bump for relatively large cluster size, as shown in Fig. 2.14. Similar CSD behaviors below, at and above transition threshold are observed in various experimental [98] and simulation [99, 84, 100, 93] works of spherical ABP and SPR systems. Besides, the phase with a fat tails in the CSD appears always leading to GNF, while GNF does not always produce a fat tail. Thus a solid connection between GNF and the

Table 2.2: Relation between $C(r)$, $S(k)$ and σ_l^2 in active matter systems [96]. Reproduced with permission.[96] Copyright 2012, American Physical Society.

Model	Align	Driven	$S(k)$	$C(r)$	σ_l^2
Polar Point	Polar	Polar		$C(r) \sim r ^{-\eta}$ $\frac{r}{\mathcal{L}} \geq 1$	$\alpha = 2 - \frac{\eta}{d}$
Polar Rod	Nematic	Polar
Apolar Rod	Nematic	Reversal		$C(r) \sim a - b \left \frac{r}{\mathcal{L}} \right ^{\beta_1}$ $r \ll \mathcal{L}$	$\sigma_l^2 \sim a \langle N \rangle^2 - \frac{b}{\mathcal{L}^{\beta_1}} \langle N \rangle^{\beta_1/d+2} + \dots$

fat tails in the CSD remains to be established [95].

Orientalional field

The order parameter of orientational field is defined as $S_n = \langle |\exp(in\theta_j)| \rangle_t$, and the orientational spatial correlation function is defined as $g_n(r) = \langle \cos\{n[\theta(0) - \theta(r)]\} \rangle$, where n is a positive integer, and $n = 1$ and 2 for polar and nematic orders, respectively. The increase of S_n implies the change from a disordered state to an ordered state. And whether the ordered state has long-range order (LRO) or quasi-long-range-order (QLRO) can be studied from the finite size scaling of $\langle S_n \rangle$, the decay of $g_n(r)$ and whether the probability distribution of order parameter $P(S_n)$ converge to the Bramwell-Holdsworth-Pinto (BHP) distribution [90, 101, 102].

For ordered phases in PP and PR models, the finite size scaling of S_n decays slower than a power law and approaches a finite asymptotic value S^* as shown in Fig. 2.15a, suggesting a LRO. For the VS and AR models, the finite size scaling of S_n shows a crossover of effective exponent $\zeta(\eta, N) = -\frac{d \ln S}{d \ln N}$ from a small finite value towards $1/2$, suggesting a fully disordered state at $N \rightarrow \infty$ (Fig. 2.15b), which resembles the QLRO in an equilibrium XY model. Besides, the $g_2(r) \sim r^{-1/4}$ at the threshold η_c in VS and AR models is also similar with the scaling of XY model. Furthermore, as L increases, the order parameter distribution $P(S_n)$ converges to BHP distribution, as shown in Fig. 2.15d, which also suggests a QLRO [90].

Both in the steric hindrance models and explicit alignment models, finite size analysis of the orientational order is necessary for determining the type of ordered

Figure 2.15: (a) Long-range nematic order phase of PR model: nematic order parameter decays with system size slower than power law and approaches an asymptotic value S^* . [87] Reproduced with permission.[87] Copyright 2010, American Physical Society. (b-d) Quasi-long-range nematic order phase of AR model: (b) the nematic order parameter decreases algebraically with system size $\langle S \rangle \sim N^{-\zeta(\eta)}$, with ζ increasing continuously with η , and crossover to fully disordered phase characterized by $\zeta = 1/2$ at large-enough sizes [89]; (c) orientational correlation function $g_2(r) \sim r^{-1/4}$ at critical η_c [89]; Reproduced with permission.[89] Copyright 2006, American Physical Society. (d) rescaled distribution $P(S)$ at different system size converge to BHP distribution. Inset: $\langle S \rangle \times L^{-\zeta}$ vs L [90]. Reproduced with permission.[90] Copyright 2014, American Physical Society.

states and disorder-order phase transitions. For example, in Ref. [75], a global polar order is observed for relatively smaller system size N . However, when N reaches $\sim 10^5$, S_1 decreases with N (Fig. 2.16a) while the average cluster size keeps increasing linearly with N (Fig. 2.16b). In the PP model, at small L , the order-disorder phase transition appears to be continuous, which can be seen in the continuous change of $\langle \varphi \rangle$ (same as S_1) and the crossover of Binder cumulant $G(\eta) = 1 - \frac{\langle \varphi^4 \rangle}{3\langle \varphi^2 \rangle^2}$ at a critical noise strength η_c for different L . However, with increasing L , $\langle \varphi \rangle$ change sharply

at certain threshold (Fig. 2.16c) and G drops towards a negative value (Fig. 2.16d), which both indicate the discontinuous feature of the transition [84].

Figure 2.16: (a-b) Finite size scaling of polar order parameter and average cluster size in self-propelled rods with steric interaction, where global polar order perishes at relative large N while aggregate size keep increasing linearly with N [75]. Reproduced with permission.[75] Copyright 2015, American Physical Society. (c-d) Order-disorder phase transition in PP model shows continuous and discontinuous manners at small and large L , respectively [84]. Reproduced with permission.[84] Copyright 2008, American Physical Society.

Vortical states and turbulence

In experiments, collective swirling motion of active units and vortical patterns have been observed in various systems, e.g., mixtures of actin or microtubules and motor proteins [103], swimming bacteria [104, 43, 105], vibrated rods [106], etc. In computer simulations of SPRs, the turbulent state was qualitatively recovered [107, 74]. In biological systems, the turbulent state optimizes fluid mixing, and the corresponding optimal aspect ratio of rods found in SPR simulations fall in the range of typical

bacterial cells [43]. The turbulent state is characterized by using properties like velocity field structure, enstrophy density, and energy spectrum.

Velocity structure Velocity correlation (VC) is defined as $g_v(r) = \langle (\mathbf{v}(0) \cdot \mathbf{v}(\mathbf{r}) - \langle v \rangle^2) \rangle / (\langle v^2 \rangle - \langle v \rangle^2)$, where the minima of VC reflects a typical vortex size R_v , and the non-monotonic decrease of $g_v(r)$ with negative correlations represents more pronounced vortical motion (Fig. 2.17a). More detailed structure can be revealed by different moments of transverse velocity structure functions $S_{\perp}^n(\mathbf{R}) = \langle (\mathbf{v}_{\perp}(\mathbf{R}, t) - \mathbf{v}_{\perp}(\mathbf{0}, t))^n \rangle$ with n the order of moments, where the maxima of the even transverse structure $S_{\perp}^{2n}$ also signals R_v (Fig. 2.17b). In agent based simulations, it is found that $g_v(r)$ is insensitive to the bulk density and aspect ratio of particles [74], which suggests the possible existence of a universal vortical structure.

Vorticity In 2D systems, the enstrophy per unit area is defined as $\Omega = \frac{1}{2} \langle |w(\mathbf{r}, t)|^2 \rangle$, which measures the kinetic energy associated with the local vortical motion. For slender rods, the mean enstrophy exhibits a pronounced maximum in the turbulent state. Besides, in hydrodynamic models, the probability distribution of velocity follows a Gaussian distribution, while for vorticity, as it is the function of the velocity gradient, its probability distribution is different from the Gaussian distribution due to the spatial correlation [108].

Energy spectrum To compare with classical 2D turbulence, the energy spectrum is obtained through the Fourier transform of velocity correlation: $E(k) = \frac{k}{2\pi} \int d\mathbf{r} \exp^{-i\mathbf{k} \cdot \mathbf{r}} \langle \mathbf{v}(0, t) \cdot \mathbf{v}(\mathbf{r}, t) \rangle$, which is supposed to follow a power-law decay with $k^{-5/3}$ at large k predicted by the Kolmogorov-Kraichnan scaling theory [109, 110]. In contrast, for SPRs, energy is injected from microscopic length scale and a different $E(k)$ behavior is expected. In both experiment and continuum model, an exponent of $-8/3$ is observed [43], but in agent-based SPR model simulation an approximate $-5/3$ exponent is observed [74] (the blue dashed line in Fig. 2.17c). Besides, the 2D SPR model and 3D experimental systems show the intermediate plateau region indicating that kinetic energy is more evenly distributed over a range of length scales.

Figure 2.17: (a) Velocity correlation of SPR [74]. Reproduced with permission.[74] Copyright 2012, IOP Publishing. (b) Second moment of transverse velocity correlation [43]. (c) Energy spectrum of turbulent states in experiment(2D, 3D), SPR model and continuum model [43]. Reproduced with permission.[43] Copyright 2012, National Academy of Sciences.

Chapter 3

Hydrodynamics of circle active Brownian particles

In this chapter, we first describe the simulation model used to study the collective motion of circle swimmers with steric repulsive interaction. Then we formulate the hydrodynamic description from the microscopic dynamics based on mean-field approximation. Finally, we analyse the linear stability of homogeneous state to fluctuations.

3.1 Model

We consider N circle active Brownian particles (cABPs) in two-dimensions interacting via the repulsive, pairwise additive, WCA potential:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon, \quad (3.1)$$

with an upper cut-off at $r_c = 2^{1/6}\sigma$, beyond which $V = 0$. Here σ is the nominal particle diameter, ϵ determines the interaction strength, and r is the center-to-center separation between two particles. Particle i evolves in two dimensions, with periodic boundary conditions in both directions, according to the Langevin equations:

$$\begin{aligned} \dot{\mathbf{r}}_i &= -\mu \sum_j \nabla_i V(|\mathbf{r}_i - \mathbf{r}_j|) + v_0 \mathbf{e}_i + \sqrt{2D_t} \boldsymbol{\xi}_i, \\ \dot{\theta}_i &= \omega_0 + \sqrt{2D_r} \eta_i. \end{aligned} \quad (3.2)$$

Here, $\mathbf{r}_i$ is the particle position. μ is the translational mobility and fixed to 1. v_0 is the magnitude of the self-propulsion velocity, and $\mathbf{e}_i = (\cos \theta_i, \sin \theta_i)$ indicates the direction of self-propulsion. The Gaussian white noise $\boldsymbol{\xi}_i$ models the interactions with the solvent, $\langle \xi_i^\alpha(t) \xi_j^\beta(t') \rangle = \delta_{\alpha\beta} \delta_{ij} \delta(t - t')$, and as the translational diffusion effect is much smaller compared with that of the self-propulsion, we set $D_t = 0$. To model the circular motion of active particles, the orientation θ_i displays a drift of constant angular velocity ω_0 and is also subject to orientational Brownian motion characterized by the rotational diffusion coefficient D_r , with η_i the unit Gaussian white noise.

Then, there are three characteristic time scales for this system: rotational diffusion $\tau_r = 1/D_r$, circular motion $\tau_\omega = 2\pi D_r/\omega_0$ and ballistic motion $\tau_b = 1/(v_0\sqrt{\rho})$. In the dilute and deterministic limit, particle conducts circular motion with revolution radial $R = v_0/w_0$.

The full phenomenology of this model requires scanning a four-parameter phase diagram, parametrized for instance by the Péclet number $Pe = v_0/(\sigma D_r)$, dimensionless angular velocity $\Gamma = \omega_0/D_r$, the potential stiffness $\kappa = \mu\epsilon/(v_0\sigma)$, and the area fraction $\phi = \pi\sigma^2 N/(4L^2) = \rho_0\pi\sigma^2/4$, where L is the side length of the simulation box, and ρ_0 is the average density. In practice, we set $\sigma = 1$, $\mu = 1$, and fix $1/\kappa = v_0/\epsilon \equiv 24$, so that two head-to-head collision cABPs reach the dynamic balance between their self-propulsion and pairwise interaction.

According to Ref. [81, 20, 111], the mean-square displacement (MSD) of single circle swimmer can be written as

$$\begin{aligned} \langle |\Delta \mathbf{r}(t)|^2 \rangle = & 4D_t t + \frac{2v_0^2 D_r t}{D_r^2 + \omega_0^2} + \frac{2v_0^2(\omega_0^2 - D_r^2)}{(D_r^2 + \omega_0^2)^2} \\ & + \frac{2v_0^2 e^{-D_r t}}{(D_r^2 + \omega_0^2)^2} [(D_r^2 - \omega_0^2) \cos(\omega_0 t) - 2\omega_0 D_r \sin(\omega_0 t)]. \end{aligned} \quad (3.3)$$

So at the long time scale, the dynamics crosses over to a purely diffusive regime with the effective single particle diffusion coefficient

$$D_{\text{eff}} = D_t + \frac{v_0^2 \tau_r}{2[1 + (\omega_0 \tau_r)^2]}. \quad (3.4)$$

Neglecting D_t , it can be rewritten as $D_{\text{eff}} = v_0^2 \tau_{\text{er}}/2$, with effective rotational diffusion time $\tau_{\text{er}} = D_r/(D_r^2 + \omega_0^2)$.

3.2 One-particle Distribution

In this section, we derive the one-particle distribution based on the mean-field assumption following Ref. [112, 59, 113]. The time evolution of the normalized joint probability distribution $\psi_N(\{\mathbf{r}_i, \theta_i\}; t)$ is governed by the N-body Smoluchowski equation

$$\partial_t \psi_N = \sum_{i=1}^N \nabla_i \cdot \left[(\mu \nabla_i (\sum_{j>i} V(r_{ij})) - v_0 \mathbf{e}_i) \psi_N \right] + \sum_{i=1}^N \frac{\partial}{\partial \theta_k} \left[(-\omega_0 + D_r \frac{\partial}{\partial \theta_k}) \psi_N \right]. \quad (3.5)$$

The projected probability density of a single particle is

$$\psi_1(\mathbf{r}_1, \theta_1; t) = \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \int d\theta_2 \cdots d\theta_N N \psi_N. \quad (3.6)$$

Performing the integration, Eq. (3.5) becomes

$$\partial_t \psi_1 = -\nabla \cdot (\mathbf{F} + v_0 \mathbf{e}_1 \psi_1) - \omega_0 \frac{\partial}{\partial \theta_1} \psi_1 + D_r \frac{\partial^2}{\partial \theta_1^2} \psi_1, \quad (3.7)$$

with mean force density

$$\begin{aligned}\mathbf{F} &= \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \int d\theta_2 \cdots d\theta_N (-\nabla_1 (\sum_{j=2} V(r_{1j}))) N \psi_N \\ &= - \int d\mathbf{r}' V'(|\mathbf{r} - \mathbf{r}'|) \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \psi_2(\mathbf{r}, \theta, \mathbf{r}'; t)\end{aligned}\quad (3.8)$$

exerted by the surrounding particles onto the tagged particle. Here, $\psi_2(\mathbf{r}, \theta, \mathbf{r}'; t)$ is the two-body density distribution function to find another particle at $\mathbf{r}'$ (with arbitrary orientation) together with the tagged particle at $\mathbf{r}$ with orientation θ . Following this scheme leads to the well-known BBGKY hierarchy of coupled equation.

The two-body density distribution $\psi_2(\mathbf{r}, \theta, \mathbf{r}'; t)$ can be decomposed in the following way

$$\psi_2(\mathbf{r}, \theta, \mathbf{r}'; t) = \psi_1(\mathbf{r}, \theta; t) \bar{\rho} g(|\mathbf{r} - \mathbf{r}'|, \varphi | \mathbf{r}, \theta; t), \quad (3.9)$$

where $\bar{\rho}$ is the average density, and $g(|\mathbf{r} - \mathbf{r}'|, \varphi | \mathbf{r}, \theta; t)$ is the conditional probability of finding another particle at $\mathbf{r}'$, and φ is the angle enclosed by the vector $\mathbf{r}' - \mathbf{r}$ and the orientation $\mathbf{e}$.

Then, we decompose the mean force in the basis spanned by the orientation $\mathbf{e}$ and the density gradient $\nabla \psi_1$ (non-orthogonal). Inserting Eq. (3.9) into Eq. (3.8), the projection of the mean force on the orientation reads $\mathbf{e} \cdot \mathbf{F} = -\bar{\rho} \psi_1 \zeta$ with the coefficient

$$\zeta = - \int_0^\infty dr r V'(r) \int_0^{2\pi} d\varphi \cos \varphi g(r, \varphi), \quad (3.10)$$

by adopting approximation $g(r, \varphi | \mathbf{r}, \theta; t) \approx g(r, \varphi)$, meaning that ζ does not depend on the position and orientation of the tagged particle, which is equivalent to assuming that the system is homogeneous and isotropic. Besides, time dependence is also neglected. For the $\nabla \psi_1$ component, with the approximation to its linear order

$$\mathbf{F} = (\mathbf{e}_1 \cdot \mathbf{F}) \mathbf{e}_1 - D \nabla \psi_1 + \mathcal{O}(|\nabla \psi|^2), \quad (3.11)$$

where $D = -\mathbf{F} \cdot [\nabla \psi_1 - (\mathbf{e}_1 \cdot \nabla \psi_1) \mathbf{e}_1] / |\nabla \psi_1|$. Hence, Eq. (3.7) now reads

$$\partial_t \psi_1 = -\nabla \cdot [(v_e \mathbf{e}_1 - D \nabla) \psi_1] - \omega_0 \frac{\partial}{\partial \theta} \psi_1 + D_r \frac{\partial^2}{\partial \theta^2} \psi_1, \quad (3.12)$$

with the effective swimming speed $v_e(\bar{\rho}) = v_0 - \bar{\rho} \zeta$. In the following, we assume that D is a constant coefficient that does not depend on the position of the tagged particle. It thus corresponds to the long-time diffusion coefficient of the passive suspension ($v_0 = 0$).

Above mean-field effective speed and diffusion descriptions reveal the following physical picture: as shown in Fig. 3.1(a,b), the persistent motion leads to an anisotropic pair distribution $g(r, \varphi)$, *i.e.*, particles are rich in the front zone, and sparse in the behind zone. The effective swimming speed $v_e(\bar{\rho})$ is then reduced by the dense front zone, as particles block each other due to the repulsive interactions. The projection coefficient ζ quantifies how strongly the tagged particle is slowed down by

its neighbors as a function of the particle density $\bar{\rho}$. The effective velocity can be rewritten as

$$v_e(\phi) = v_0(1 - \phi/\phi^*), \quad (3.13)$$

with ϕ^* the packing fraction damped v_e to zero.

Figure 3.1: (a,b) Anisotropic pair distribution function $g(r, \varphi)$ in homogeneous state for a tagged particle (white sphere) at the origin with its orientation pointing along the x -axis. $D_r = 0.5$, $v_0 = 24$ (a) $\phi = 0.37$, $\omega_0 = 8.0$, (b) $\phi = 0.40$, $\omega_0 = 0.12$. (c) Effective velocity at different packing fraction, $D_r = 0.1$, $v_0 = 24$. Different colors indicate ω_0 .

Through such mean-field theory originally proposed for ABPs [50, 57, 58, 53, 114, 44], we verify it in the simulation of cABPs systems. Fig. 3.1(a, b) show the pair distribution function $g(r, \varphi)$ for large and small chirality, respectively. The anisotropic dense and sparse regions are observed exactly at the front and behind zones, and it is worth noting that $g(r, \varphi)$ keeps symmetric to φ even for large chirality Fig. 3.1(a), where $R = 3.0\sigma$. So that even the circular motion introduces chirality on individual particle level, it does not significantly show up on the pair distribution. The effective velocity is measured as the average of instantaneous velocities of all particles projected onto their self-propulsion direction $\mathbf{e}_i$

$$v_e = \langle (\mu \mathbf{F}_i + v_0 \mathbf{e}_i) \cdot \mathbf{e}_i \rangle, \quad (3.14)$$

where the $\langle \cdot \rangle$ represents both time and ensemble average. The formula of $v_e(\phi)$ in Eq. (3.13) is verified in Fig. 3.1(c) for a wide range of ω_0 , and fitted with $\phi^* = 0.91$.

3.3 Hydrodynamic Equation

3.3.1 Hierarchy Equation

The density field is defined as $\rho(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$, and polarization field $\mathbf{W}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \mathbf{e}_i$. To derive the evolution of above hydrodynamic fields, we adopt the angular momentum decomposition method, where $f_k = \int \psi_1 e^{ik\theta} d\theta$, and $\psi_1 = (1/2\pi) \sum_k f_k e^{-ik\theta}$. Then the density field is the zeroth order harmonic $\rho = \int \psi_1 d\theta = f_0$, and the polarization field $\mathbf{W} = (w_x, w_y) = \int \mathbf{e} \psi_1 d\theta$ is related with the first order harmonic $f_1 = w_x + iw_y$. Eq. (3.12) can be decomposed into infinite hierarchy

equations

$$\begin{aligned}
\sum_k \partial_t f_k e^{-ik\theta} = & -\frac{v_e}{2} \left[\sum_k \partial_x f_k e^{-i(k-1)\theta} + \sum_k \partial_x f_k e^{-i(k+1)\theta} \right] \\
& -\frac{v_e}{2i} \left[\sum_k \partial_y f_k e^{-i(k-1)\theta} - \sum_k \partial_y f_k e^{-i(k+1)\theta} \right] \\
& + \frac{\zeta \partial_x f_0}{2} \left[\sum_k f_k e^{-i(k-1)\theta} + \sum_k f_k e^{-i(k+1)\theta} \right] \\
& + \frac{\zeta \partial_y f_0}{2i} \left[\sum_k f_k e^{-i(k-1)\theta} - \sum_k f_k e^{-i(k+1)\theta} \right] \\
& + D(\partial_x^2 + \partial_y^2) \sum_k f_k e^{-ik\theta} + \omega_0 \sum_k ik f_k e^{-ik\theta} - D_r \sum_k k^2 f_k e^{-ik\theta}.
\end{aligned} \tag{3.15}$$

3.3.2 Hydrodynamic Fields

Zeroth order f_0 of Eq. (3.15) gives the mass conservation law straightforward

$$\partial_t \rho + \nabla \cdot (v_e \rho \mathbf{P}) = D \nabla^2 \rho. \tag{3.16}$$

To obtain the polarization field evolution, truncation is needed to close the hierarchy equations. Truncating Eq. (3.15) by $f_{k \geq 2} = 0$ gives

$$\dot{\mathbf{W}}_I = -\frac{1}{2} \nabla(\rho v_e) + (D \nabla^2 - D_r) \mathbf{W} + \boldsymbol{\omega}_0 \times \mathbf{W}, \tag{3.17}$$

$\boldsymbol{\omega}_0 = \omega_0 \hat{\mathbf{z}}$. Otherwise, we can truncate at higher order by $\dot{f}_2 = 0$, $f_{k \geq 3} = 0$, then

$$\dot{\mathbf{W}}_{II} = -\frac{1}{2} \nabla(\rho v_e) + \frac{1}{4} (\alpha \mathbf{S} - \beta \mathbf{z} \times \mathbf{S}) + (D \nabla^2 - D_r) \mathbf{W} + \boldsymbol{\omega}_0 \times \mathbf{W}, \tag{3.18}$$

where $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$

$$\begin{aligned}
\mathbf{S}_1 = & v_e (\nabla^2 v_e) \mathbf{W} + |\nabla v_e|^2 \mathbf{W}, \\
\mathbf{S}_2 = & v_e \left[v_e \nabla^2 \mathbf{W} + (\nabla \cdot \mathbf{W}) (\nabla v_e) + (\nabla v_e \cdot \nabla) \mathbf{W} \right. \\
& \left. + (\nabla v_e \times \nabla) \times \mathbf{W} + (\nabla \times \mathbf{W}) \times (\nabla v_e) \right],
\end{aligned} \tag{3.19}$$

and

$$\alpha = \frac{D\Delta - 4D_r}{(D\Delta - 4D_r)^2 + 4\omega_0^2}, \quad \beta = \frac{2\omega_0}{(D\Delta - 4D_r)^2 + 4\omega_0^2}. \tag{3.20}$$

As Eq. (3.18) is too complex for analysis, in the following, we adopt the lower order truncation $\dot{\mathbf{W}} = \dot{\mathbf{W}}_I$.

The continuum theory composed of Eq. (3.16) (3.17) suggests the following scenario: in cABPs fluid, current is driven with density dependent velocity $v_e(\rho)$, and its orientation rotates with angular speed ω_0 . Inspired by Eq. (3.4), at long time scale,

Figure 3.2: $D_r = 0.1$, $v_0 = 24.0$ (a) Mean square displacements for $\phi = 0.30$, colors indicate ω_0 . (b) For fixed ω_0 , $\tau_{er} = 2D_p/v_e^2$ keeps constant in homogeneous states. (c) τ_{er} fitted with the effective rotational diffusion time derived for non-interacting cABPs.

the phenomenological diffusion constant is expected to be $D_p = v_e^2(\rho_0)\tau_{er}/2 + D$. In simulation, we measure MSD for various ω_0 as shown in Fig. 3.2(a), and D_p is determined at long time scale by $\langle \Delta r(t)^2 \rangle = 2D_p t$. Fig. 3.2(b) shows D_p/v_e^2 keeping constant at low packing fraction, and the measured τ_{er} is well fitted by the formula of effective rotational diffusion time derived for non-interacting cABPs as shown in Fig. 3.2(c). These results verify the physical scenario revealed by the continuum theory at the hydrodynamic limit.

3.3.3 Linearized Equation

For Eq. (3.16) (3.17), obviously, the isotropic homogeneous steady state with $\rho = \rho_0$ and $\mathbf{W} = 0$ is a solution. To study the linear stability of the homogeneous steady state, we examine the dynamics of spatially inhomogeneous fluctuations $\delta\rho = \rho - \rho_0$ and $\delta\mathbf{W} = \mathbf{W}$. The linearized dynamics of fluctuations are

$$\begin{aligned}\partial_t \delta\rho &= -\bar{v}_e \nabla \cdot \mathbf{W} + D \nabla^2 \delta\rho, \\ \partial_t \mathbf{W} &= -\eta \nabla \delta\rho + (D \nabla^2 - D_r) \mathbf{W} + \boldsymbol{\omega}_0 \times \mathbf{W},\end{aligned}\tag{3.21}$$

where $\bar{v}_e = v_0 - \zeta\rho_0$ is the average effective velocity, and the parameter $\eta = (\bar{v}_e - \zeta\rho_0)/2$ serves like an effective compressional modulus. Intuitively, positive η leads the polarization to avoid dense zone, while negative η results in polarization pointing to dense zone.

Fourier transform Eq. (3.21) in space and time $\tilde{f}(\mathbf{q}, \omega) = \int dt \int d\mathbf{r} f(\mathbf{r}, t) e^{-i(\mathbf{q}\cdot\mathbf{r} - \omega t)}$. For compactness, we introduce a vector with elements $\tilde{\boldsymbol{\phi}} = [\tilde{\delta\rho}, \tilde{w}_\parallel, \tilde{w}_\perp]^T$, where $\tilde{w}_\parallel = \tilde{\mathbf{W}} \cdot \mathbf{q}/|\mathbf{q}|$ is the polarization fluctuation longitudinal to $\mathbf{q}$, and $\tilde{w}_\perp = |\tilde{\mathbf{W}} - \tilde{w}_\parallel \mathbf{q}/|\mathbf{q}||$ the transversal polarization fluctuation. Then the linearized hydrodynamic equation is written as $M(\mathbf{q}, \omega) \cdot \tilde{\boldsymbol{\phi}} = 0$, where

$$M(\mathbf{q}, \omega) = \begin{bmatrix} s + \Gamma_\rho & i\bar{v}_e q & 0 \\ i\eta q & s + \Gamma_r & \omega_0 \\ 0 & -\omega_0 & s + \Gamma_r \end{bmatrix},\tag{3.22}$$

with $s = -i\omega$ and damping rates $\Gamma_\rho = Dq^2$, $\Gamma_r = Dq^2 + D_r$. The relaxation of density fluctuation is coupled to the longitudinal component $\tilde{w}_\parallel$, while the transversal

component $\tilde{w}_\perp$ cannot be decoupled from other two modes as in normal fluid due to the convection induced by intrinsic torque ω_0 .

3.4 Hydrodynamic Modes

3.4.1 Dispersion Relations

The non-trivial solution of Eq. (3.22) leads to the dispersion relation $s(q)$ for wave mode $\exp(st + i\mathbf{q} \cdot \mathbf{r})$ which is restricted by

$$(s + \Gamma_\rho) [(s + \Gamma_r)^2 + \omega_0^2] + \gamma q^2 (s + \Gamma_r) = 0, \quad (3.23)$$

where $\gamma = \bar{v}_e \eta = v_0^2 (\frac{\phi}{\phi^*} - 1) (\frac{\phi}{\phi^*} - \frac{1}{2})$. Since the hydrodynamic description is only valid in the long-wavelength limit, it is sufficient to calculate $s(q)$ to low q order. Expand to q^2 order, the perturbation diffusive mode is $s_d(q) = \beta_d q^2 + \mathcal{O}(q^4)$ with

$$\beta_d = -D - \frac{\gamma D_r}{\omega_0^2 + D_r^2}, \quad (3.24)$$

and two inversely transported propagation modes $s_p(q) = \Gamma_p(q) \pm i n_p(q) + \mathcal{O}(q^4)$ with

$$\begin{aligned} \Gamma_p(q) &= -D_r + \left[\frac{\gamma D_r}{2(\omega_0^2 + D_r^2)} - D \right] q^2 + \mathcal{O}(q^4), \\ n_p(q) &= \omega_0 + \frac{\gamma \omega_0}{2(\omega_0^2 + D_r^2)} q^2 + \mathcal{O}(q^4). \end{aligned} \quad (3.25)$$

Eq. (3.25) suggests the propagation speed is dominated by the intrinsic torque at small q , while by local compression at large q .

According to Eq (3.24) (3.25), the spectrum of density fluctuations is supposed to consist of three components: the Rayleigh line centred at $\omega_R = 0$ with half peak width about $\beta_d q^2$, and two Brillouin lines at $\omega_B = \pm n_p(q)$ with half peak width about $\Gamma_p(q)$ [115].

In simulation, we measure the self-intermediate scattering function (sISF)

$$F_s(\mathbf{q}, t) = \frac{1}{N} \sum_{i=1}^N \langle \exp(i\mathbf{q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]) \rangle, \quad (3.26)$$

where $\langle \cdot \rangle$ represents the ensemble average. Then the Fourier transform of sISF gives the self dynamic structure factor (sDSF)

$$S_s(\mathbf{q}, \omega) = \int_0^T F_s(\mathbf{q}, t) e^{i\omega t} dt, \quad (3.27)$$

which represents the density fluctuation spectrum.

Fig. 3.3(a,c) show sDSF for homogeneous state. As predicted, both Rayleigh line and Brillouin line are observed. Extract the peak position of shifted mode as position

Figure 3.3: Homogeneous states at $D_r = 0.1$, $v_0 = 36.0$. (a,c) Self dynamic structure factor, color indicates n_q ($q = n_q \frac{2\pi}{L}$). a: $\phi = 0.40, \omega_0 = 0.72$, c: $\phi = 0.20, \omega_0 = 0.18$ (b,d) Dispersion of the Brillouin peak $\omega_B(q)$. The points are measured results, dashed lines are $\omega_B = \omega_0$. b: $\phi = 0.40, \omega_0 = 0.72, 0.96$, d: $\phi = 0.20, 0.25, \omega_0 = 0.18$.

of Brillouin line ω_B , its dispersion relation is shown in Fig. 3.3(b,d). For $\phi = 0.40$, ω_B shows a plateau around ω_0 (Fig. 3.3(b)) as predicted in Eq (3.25) that $n_p(q) \simeq \omega_0$ for small q , while for larger q , ω_B is q related. For $\omega_0 = 0.18, \phi = 0.20, 0.25$ (Fig. 3.3(d)), as the ϕ is far from the phase transition packing fraction and leads to a relative large value of γ , so that $n_p(q)$ in Eq. 3.25 is dominated by the q^2 term, and no plateau is observed.

These observations qualitatively verify the hydrodynamic modes predicted, even through the exact q dependent form of ω_B is difficult to study, on the one hand as q increases, the peak becomes too flatten to determine $\omega_B(q)$, and on the other hand multiple approximations are introduced in deriving the hydrodynamic modes, including the mean-field assumption, linear dynamic approximation and the cut off of higher q terms.

3.4.2 Two Types of Instabilities

Stable wave modes require that the fluctuation decays along time, so that the dispersion relation $\text{Re}[s(q)] < 0$. By analyzing the solution of Eq. 3.23 in Appendices. A, we find the control parameter space $[\phi, v_0, \omega_0]$ can be separated into three regions: stable homogeneous state, type I and type II instability, as sketched in Fig. 3.4(a, b), and corresponding $\text{Re}[s(q)]$ demonstrated in Fig. 3.4(c).

For small ϕ and v_0 , $\text{Re}[s(q)] \leq 0$ for all q , indicates that homogeneous isotropic state is stable. For small torque $\omega_0 < D_r$, by increasing ϕ and v_0 , $\text{Re}[s(q)] > 0$ starts

Figure 3.4: (a) Phase boundaries for control parameter $[\phi, v_0, \omega_0]$ at $D_r = 0.1$, with phenomenological mean-field parameter $D = 15.1$, $\phi^* = 0.63$. Blue plane separates stable homogeneous state with type I instability. Red plane separates stable homogeneous state with type II instability, and cyan is pseudo separation plane for type I and II instability. (b) Cross section at $v_0 = 24.0$. (c) Dispersion relation $s(q)$ for stable homogeneous state (s), type I instability (t), type II instability (o).

from $q = 0$, which is generally called type I instability [116], and suggests the fluctuation is unstable at the hydrodynamic limit. While for large torque $\omega_0 > D_r$, by increasing ϕ and v_0 , $\text{Re}[s(q)] > 0$ starts from finite q , called type II instability, suggesting the fluctuation mode has certain characteristic length scale. The theoretical boundaries are

$$\omega_0 = \begin{cases} \sqrt{-\gamma D_r/D - D_r^2} & (\omega_0 < D_r), \\ -\gamma/2D & (\omega_0 > D_r), \end{cases} \quad (3.28)$$

or rewritten as

$$v_0 = \begin{cases} \sqrt{D(\omega_0^2 + D_r^2)/D_r h(\phi)} & (\omega_0 < D_r), \\ \sqrt{2D\omega_0/h(\phi)} & (\omega_0 > D_r), \end{cases} \quad (3.29)$$

where $h(\phi) = (1 - \phi/\phi^*)(\phi/\phi^* - 1/2)$.

Chapter 4

Dynamic clustering and motility-induced phase separation

In this chapter, we present the full phase diagram of cABPs in Sec. 4.1 obtained by large-scale simulation of the model described in Sec. 3.1, and compare the phase boundaries with the theoretical prediction. Then in Sec. 4.2, we study the density fluctuations in two inhomogeneous states by sub-block analysis, revealing their differences in the scale of correlation length. In Sec. 4.3, we further study the density fields by measuring the cluster size distribution, and its finite size scaling confirms that the particle aggregation in inhomogeneous states occurs at two different length scales. We also study the critical behavior below the phase transition threshold to dynamical clustering state, and discuss its similarities and differences with the percolation transition. In Sec. 4.4, we present the hydrodynamic field by coarse graining, and discuss how they result in two types of inhomogeneous states intuitively. Finally, in Sec. 4.5, we study the dynamical properties of cABPs by discussing the potential energy fluctuations and the intermediate scattering function.

4.1 Dynamic Patterns and Instabilities

In Sec. 3.4.2, we predict two types of instability for the homogeneous isotropic state depending on the relative magnitude of ω_0 and D_r : type I instability with unstable wavemode starting from $q = 0$ for $\omega_0 < D_r$, and type II instability or finite-wavenumber instability for $\omega_0 > D_r$. These different types of instability are generally supposed to result in different dynamic patterns. In Brownian dynamics simulation, we indeed observe two inhomogeneous states in corresponding parameter space, *i.e.*, the motility-induced phase separation (MIPS) and dynamic clustering state.

Fig. 4.1(a) shows the typical snapshots for $D_r = 0.1$, with fixed $v_0 = 36.0$ and using the control parameter $[\phi, \omega_0/D_r]$. Homogeneous state remains stable at low packing fraction, while with increasing ϕ , there are two types of phase transitions depending on the value of ω_0/D_r . For small torque, *i.e.*, $\omega_0 < D_r$, increasing ϕ leads to MIPS, and the phase parameter region corresponds to the type I instability predicted by the hydrodynamic theory. While for large torque, *i.e.*, $\omega_0 > D_r$, increasing ϕ leads to

Figure 4.1: $D_r = 0.1, v_0 = 36.0$ (a) Typical snapshots of three states. Color of particles indicates the orientation. (b) Phase diagram, blue dot represents the homogeneous state (h), black square the MIPS (p) and red triangle the dynamic clustering state (c). The red/cyan dashed line is predicted phase boundary between stable homogeneous and type II/I instability, with fitting parameter $\phi_a^* = 0.58$, $D_a = 46.1$.

the dynamic clustering state, which corresponds to the type II instability. Fig. 4.1(b) shows the phase boundaries predicted by Eq. (3.28), with fitting parameter $\phi_a^* = 0.58$, $D_a = 46.1$. The green dot marks $\omega_0 = D_r$, above which, the red dashed line separates homogeneous state with type II instability, and fits well with the dynamical clustering state phase boundary. Below the green dot, the cyan line representing phase boundary of type I instability deviates from the observed MIPS phase boundary in simulation, as a result of the large hysteresis loop in MIPS. The MIPS phase boundaries shown in the phase diagram are obtained by turning on activity from homogeneous initial configurations.

To eliminate the suspicion that the dynamic clustering state is a metastable or near-critical region of phase separation, we further explore the control parameter space $[\phi, v_0]$, increasing ϕ and v_0 to the highly supersaturated region for $\omega_0/D_r < 1$ and > 1 , separately. In Fig. 4.2(a), fixed $\omega_0/D_r = 0.5$, increasing ϕ and v_0 leads to a single giant stable dense cluster. Once the cluster formed, it keeps stable and does not disassemble. The condensation and evaporation only occur at the interface. The shape of cluster is nearly circular, and the boundary is smoother compared with that in dynamical clustering state. While at fixed $\omega_0/D_r = 2.4$, increasing ϕ and v_0 leads to multiple highly dynamical clusters. These clusters keep to aggregate, merge, break and disappear, but they never form a stable dense bulk phase. Even for large $\phi = 0.40$, where the dynamical clustering state already emerges at $v_0 = 24.0$, with increasing v_0 by a factor of 5, these clusters still remain highly dynamic instead of merging into a stable giant cluster as in MIPS. This observation that increasing ϕ and v_0 cannot leads to MIPS for $\omega_0 > D_r$, suggests that the dynamical clustering

Figure 4.2: $D_r = 0.1, \phi = 0.40$ Typical snapshots for (a) $\omega_0/D_r < 1$ and (b) $\omega_0/D_r > 1$. X -axis represents ϕ , Y -axis represents propulsion velocity v_0 .

should be a new dynamical state, instead of near-critical region of MIPS.

Figure 4.3: Typical snapshots at $D_r = 0.3, \phi = 0.40$, X -axis represents ω_0/D_r , Y -axis represents propulsion velocity v_0 .

The two types of inhomogeneous states separated to opposite sides of $\omega_0 = D_r$ are shown in the control parameter plane $[\omega_0/D_r, v_0]$ in Fig. 4.3 for fixed $\phi = 0.40, D_r = 0.3$. We explore a wide range of v_0 , and for $\omega_0/D_r < 1$, the homogeneous state transforms into MIPS by increasing v_0 , while into dynamical clustering state for $\omega_0/D_r > 1$. Even at extremely large v_0 , the dynamic clustering state does not blur with MIPS.

To further check the phase boundary predicted in our hydrodynamic theory, we derive the slope of phase boundary between homogeneous and dynamical cluster state

Figure 4.4: Typical snapshots at $D_r = 0.1, v_0 = 120.0$, X -axis represents ϕ , Y -axis represents ω_0/D_r . Phase boundary between homogeneous state and dynamic clustering state becomes nearly vertical for large v_0 .

in parameter space $[\phi, \omega_0]$ from Eq. (3.28)

$$\frac{\partial \omega_0^{\text{II}}}{\partial \rho_0} = \frac{v_0^2}{4D\rho^*} \left(3 - 4\frac{\rho_0}{\rho^*}\right). \quad (4.1)$$

Eq. 4.1 suggests that the slope of the phase boundary increases with v_0 . Then we simulate cABPs for $v_0 = 120.0$ at $D_r = 0.1$, and show typical snapshots in Fig. 4.4. Compared with Fig. 4.1(a), we indeed observe that the slope of phase boundary ($\phi^{\text{pb}}, \omega_0^{\text{pb}}$) increases significantly by increasing v_0 from 36.0 to 120.0, where the phase separation curve changing from gentle incline to nearly vertical.

4.2 Density Fluctuations

We study the density fluctuations in two inhomogeneous states by sub-block analysis, which can reveal the scale of correlation length. The distribution of local density ρ_{L_b} is obtained by coarse graining the simulation box into sub-blocks with length scale L_b , and $\langle \Delta \rho^2 \rangle$ represents its variance. Define ξ as the correlation length, then if $\xi \ll L_b \ll L$, the probability distribution $P(\rho_{L_b})$ is nearly a Gaussian distribution leading to $\langle \Delta \rho^2 \rangle \propto L_b^{-d}$. However, as NVT ensemble is employed, $\langle \Delta \rho^2 \rangle \rightarrow 0$ when $L_b \rightarrow L$, because the scaling function depends on L_b/L instead of L_b/∞ . So that when $\xi \rightarrow L$, the algebraic dependence of $\langle \Delta \rho^2 \rangle$ on L_b disappears. Therefore, in the following, we present only the decay of $\langle \Delta \rho^2 \rangle$ for $L_b < L/4$.

Fig. 4.5 shows the density fluctuation changing across the phase boundary between homo-MIPS and homo-dynamic clustering, respectively. The $\langle \Delta \rho^2 \rangle_r$ represents $\langle \Delta \rho^2 \rangle (L_b/L)$ normalised by its value at smallest L_b . For uniform randomly distributed particles in 2-dimension, the density fluctuation is supposed to decrease with the sub-block size $\langle \Delta \rho^2 \rangle \propto L_b^{-2}$, indicated by the dashed line.

Fig. 4.5(a) plots the density fluctuations for low torque $\omega_0/D_r = 1$ at $D_r = 0.1$, with increasing the packing fraction ϕ crosses the homogeneous-MIPS phase boundary between 0.30 – 0.31. For the homogeneous state, the algebraic relation is well fitted for L_b larger than several σ , suggesting an extremely small correlation length $\xi <$

Figure 4.5: The normalized density fluctuation $\langle \Delta \rho^2 \rangle_r$ decrease versus subbox side length L_b for $D_r = 0.1, v_0 = 36.0$ (a) $\omega_0 = 0.10$, homogeneous state transits to MIPS by increasing ϕ larger than 0.30. (b) $\omega_0 = 0.36$, homogeneous state transits to dynamical clustering state by increasing ϕ larger than 0.32. Colors indicate different packing fraction. The dashed line indicates $\langle \Delta \rho^2 \rangle_r \propto L_b^{-2}$.

$0.05L$. While for MIPS at large packing fraction, the density fluctuation nearly keeps constant for $L_b < L/4$. This indicates that the sub-blocks are mostly settled in the bulk liquid and gas phase, suggesting the length scale of the giant cluster is larger than $L/4$. And once transforming into the MIPS state, increasing ϕ from 0.31 to 0.40 causes little change of the curve. Fig. 4.5(b) shows the density fluctuation for large torque $\omega_0/D_r = 3.6$ at $D_r = 0.1$, with increasing the packing fraction ϕ crosses the homogeneous-dynamic clustering phase boundary between 0.32 – 0.34. In the dynamic clustering state, for $\sigma \ll L_b \ll L$, the density fluctuation deviates significantly from the algebraic decay, nor keeps constant as in MIPS. It decays with an intermediate exponent, suggesting a correlation length $\xi \gg \sigma$. And ξ increases abruptly as ϕ increasing beyond a threshold value, marking a phase transition to the dynamic clustering state. After crossing the phase boundary, increasing ϕ leads to a slightly slower decay of the curve, suggesting that ξ increases gradually with ϕ .

4.3 Cluster Properties

4.3.1 Cluster Size Distribution

Criteria of cluster is defined by using the cut-off of WCA potential $r_c = 2^{1/6}\sigma$. In this section, s is used to represent the size of clusters, instead of the definition of wave mode $\exp(st + i\mathbf{q} \cdot \mathbf{r})$ in other chapters. For cluster containing s particles, $\langle \mathcal{N}(s; N) \rangle$ is the average cluster size frequency, where $\langle \cdot \rangle$ represents the time average. Then normalised by the number of particles in the system, we obtain the cluster size distribution (CSD) or cluster number density distribution $n(s) = \langle \mathcal{N}(s; N) \rangle / N$. In this notation, $sn(s)$ is the probability that a given particle belongs to an s -cluster.

The homogeneous, MIPS, and dynamic clustering states show three different types

Figure 4.6: Cluster size distribution and typical snapshots for three states: (a) homogeneous; (b) MIPS; (c) dynamic clustering. $D_r = 0.1$, $v_0 = 24.0$, and color indicates ω_0 . Dashed line represents $\propto s^{-1.9}$.

of CSD as shown in Fig. 4.6. For the homogeneous state, Fig. 4.6(a) shows a CSD approximately in the form

$$n(s) \propto s^{-\alpha} \exp(-(s/s_\zeta)), \quad (4.2)$$

which is generally observed before the percolation transition. Here s_ζ is the “characteristic” cluster size, signalling the onset of the rapid decay. For cluster size $s < s_\zeta$, the decay of CSD is dominated by a power-law, while for $s > s_\zeta$, CSD decays exponentially. Fig. 4.6(b) shows the scenario for the phase separated state, where a dot separated from the continuous distribution is observed which represents the single giant cluster. While for dynamic clustering state shown in Fig. 4.6(c), the distinctive feature is a pronounced bump in the distribution before it decays rapidly. And the center of bump is at an intermediate size $s \sim 10^3 - 10^4$, different with the extremely large cluster size $s \rightarrow N$ indicated by the isolated dot in MIPS $n(s)$.

4.3.2 Finite Size Scaling

To verify the length scale of the single giant cluster and dynamic clusters, we perform the finite size scaling by increasing particle number N from 1×10^4 to 8×10^4 .

Fig. 4.7(a) shows the CSD at different system size for MIPS, where the size of the giant cluster $s_{\max}$ increases with system size N . And Fig. 4.7(c) shows more clearly that the maximum cluster size increases linearly with system size $s_{\max} \propto N$ at small ω_0 where MIPS occurs. These confirm that the phase separation occurs at the macro-length scale for MIPS. For a relatively large torque, where the dynamic clustering state is observed, Fig. 4.7(b) shows the cluster size distribution curves collapse for various system sizes. Increasing the system size 8 times leads to no significant change to the position or width of the bump. This finite size scaling behavior differs significantly from the phase separation scenario. The characteristic length scale in the dynamic clustering state is independent with the system size N , but completely determined by its self-propulsion parameters.

The scaling of dynamic clustering state is different from most models where a bump distribution in CSD is observed. For example, in [95], a kinetic model is

Figure 4.7: Finite size scaling for cluster size distribution. $D_r = 0.1, v_0 = 24.0, \phi = 0.40$. (a) $n(s)$ at $w_0 = 0.024$ for different number of particles indicated by colors. (b) $n(s)$ at $w_0 = 0.24$. (c) Maximum cluster size $s_{\max}$ scale with system size N , colors indicate w_0 . Red dashed line indicate $\propto N$, and black dashed line represents constant.

proposed to study the non-equilibrium clustering of self-propelled particles, where they constructed a phenomenological control parameter P representing the relative weight of cluster fragmentation with respect to coagulation. For P smaller than a critical value P_c , which indicates the speed of cluster disassembly is faster than aggregation, the cluster size distribution follows Eq. (4.2). For critical point $P = P_c$, a bump of $n(s)$ is observed at the end of distribution in finite system, looks similar with Fig. 4.6(c) and Fig. 4.7(b). But as N approaching infinity, the bump position shift upwards and finally disappears leading to a pure power law distribution. So the bump at critical P_c is a result of finite size effect. For $P > P_c$, the position and width of bump are observed to scale with N , indicating the characteristic aggregation size is system size dependent. Similar scenario was also observed in the avalanches distribution in BTW model, where the phase transition is studied in the percolation theory context [117].

In our system, the bump in CSD neither shifts upwards approaching a power law nor separates into an isolated peak as system size increases. The fixed bump position scenario strongly supports the argument that the dynamic clustering state is a dynamical phase where the circular swimming results in a characteristic cluster size. Fig. 4.7(c) shows $s_{\max}$ increases much slower than $\propto N$ for dynamic clustering state at large w_0 , confirming that the cluster size is not at the macroscopic length scale. That $s_{\max}$ does not keep exactly constant may result from that the fluctuation of characteristic cluster size has higher probability to reach a larger size with increasing the system size.

4.3.3 Scaling Function and Data Collapse

The similarity between CSD of cABPs and percolation models inspires us studying the scaling function and critical behavior in the context of percolation theory.

Fig. 4.8(a,b) shows the cluster size distributions approaching homogeneous-dynamic clustering phase boundary with increasing v_0 and ϕ , respectively. With the control parameter approaching transition boundary, the characteristic cluster size s_ζ increases

Figure 4.8: Data collapse of the cluster number densities for homogeneous state for (a,b) $D_r = 0.3, \phi = 0.35, \omega = 0.48$, color indicates different v_0 , and (c,d) $D_r = 0.1, \omega = 0.48, v_0 = 24.0$, color indicates different ϕ .

and the CSD approaches a power-law decay.

To be more accurate for various percolation models, a general scaling ansatz for CSD is proposed slightly different from Eq. (4.2) by replacing the exponential decay with a general scaling function $\mathcal{G}(s/s_\zeta)$

$$n(s, \phi, v_0) \propto s^{-\alpha} \mathcal{G}(s/s_\zeta) \quad \text{for} \quad \phi, v_0 \rightarrow \phi_c, v_{0,c}, s \gg 1. \quad (4.3)$$

The characteristic cluster size is expected to diverge like a power-law in terms of the distance of ϕ, v_0 from $\phi_c, v_{0,c}$

$$s_\zeta(\phi, v_0) \propto |\phi - \phi_c|^{-1/\sigma} |v_0 - v_{0,c}|^\zeta \quad \text{for} \quad \phi, v_0 \rightarrow \phi_c, v_{0,c}. \quad (4.4)$$

Explicitly, the scaling function in Eq.4.3 can be rewritten as

$$\mathcal{G}(s/s_\zeta) \propto s^\alpha n(s, \phi, v_0) \quad s \gg 1. \quad (4.5)$$

Fig. 4.8(c,d) show the collapse of rescaled curves with $\alpha \simeq 1.9$ and s_ζ fitted from Eq. (4.2). The quality of the collapse improves with proximity to the critical point ϕ_c or $v_{0,c}$. For $s/s_\zeta \ll 1$, the scaling function $\mathcal{G}(s/s_\zeta)$ is approximately constant, and for $s/s_\zeta \gg 1$ it decays rapidly. The crossover is marked by $s/s_\zeta \approx 1$, and this result confirms that the s_ζ is extracted from CSD properly.

4.3.4 Critical Behavior

Inspired by the critical behavior near percolation transition described in Eq. (4.3), we study the scaling rule near homo-dynamic clustering phase transition. In Sec. 4.3.3, we already show the characteristic cluster size s_ζ extracted properly from CSD. Additionally, we measure the average cluster size defined as

$$\chi = \frac{\sum s^2 n(s)}{\sum s n(s)}. \quad (4.6)$$

The divergences of the characteristic cluster size $s_\zeta(\rho)$ and the average cluster size $\chi(\rho)$ are supposed to be described by the critical exponents γ and σ respectively,

$$s_\zeta(\phi) \propto (\phi_c - \phi)^{-1/\sigma}, \quad \chi(\phi) \propto (\phi_c - \phi)^{-\gamma}, \quad (4.7)$$

and in percolation theory they are related by the scaling relation $\gamma = (3 - \alpha)/\sigma$.

Fig. 4.9(a,b) shows the power-law scaling fitted for $s_\zeta(\phi)$ and $\chi(\phi)$ near the homo-dynamic clustering phase transition boundary ϕ_c at $D_r = 0.1, v_0 = 24.0, \omega_0 = 0.48$. The fitting of characteristic cluster size $s_\zeta(\phi)$ gives the critical packing fraction $\phi_{c,s_\zeta} = 0.369$ and critical exponent $\sigma = 0.70$, and the fitting result of average cluster size $\chi(\phi)$ is $\phi_{c,\chi} = 0.371$ and $\gamma = 1.07$. The critical packing fractions determined by two properties are very close. However, the critical relation has some deviation from the percolation theory $\gamma\sigma \simeq 0.75 < (3 - \alpha) \simeq 1.1$. The deviation may partly result from the fitting error of critical exponents α , as the power law decay $n(s) \propto s^{-\alpha}$ is only valid for large cluster sizes, while s is in a relatively small range for homogeneous

Figure 4.9: The characteristic cluster size $s_\zeta(\phi)$ and average cluster size $\chi(\phi)$ versus $\phi_c - \phi$, the distance of ϕ from critical packing fraction ϕ_c , at $D_r = 0.3, v_0 = 24.0$ for (a,b) $\omega_0 = 0.48$ and (c,d) $\omega = 0.36$.

state, so that α is underestimated. The fitting for $\omega_0 = 0.36$ shown in Fig. 4.9(c,d) gives smaller ϕ_c and robust σ, γ values.

The data collapse of rescaled cluster size distribution in Sec. 4.3.3 and the critical scaling of cluster properties near phase boundary discussed in this section suggest that the homo-dynamical clustering transition resembles the percolation problem below the transition threshold. However, instead of diverging into an infinite percolated graph, it is disrupted by the finite-wavenumber instability. Thus short-wavelength fluctuations lead into a dynamical clustering state instead of the macroscopic bulk phase separation.

4.3.5 Geometric Properties

Figure 4.10: The distribution $n(s)$ and gyration radius R_g versus cluster size s for dynamic clustering state at $D_r = 0.1, v_0 = 24.0, \omega_0 = 0.24, \phi = 0.40$. The black dashed line indicates $R_g \propto \sqrt{s}$.

The giant cluster in phase separated state is close packed with a smooth and nearly circular boundary, while the dynamical clusters are branched and stretched into fractal shape with rough boundaries. To quantify the geometric properties of dynamical clusters, we measure its fractal dimension. Assume that the positions of all particles in a given s -cluster are denoted by $\mathbf{r}_i, i = 1, \dots, s$. The centre of mass of the cluster is defined as $\mathbf{r}_{cm} = \sum \mathbf{r}_i / s$, and its squared radius of gyration is defined as the average square distance to the centre of mass

$$R_g^2(s) = \frac{1}{2} \sum_{i=1}^s |\mathbf{r}_i - \mathbf{r}_{cm}|^2. \quad (4.8)$$

For compact circular giant cluster $s \propto R_g^2$ is expected, while for fractal clusters, $s \propto R_g^D$ defines the fractal dimension $D < d$. Fig. 4.10 plots the CSD and corresponding

gyration radius versus the cluster size for a typical dynamic clustering state. For most part of $R_g(s)$ curve, the slope is slightly larger than the calibration curve $\sqrt{s}$, indicates $D < 2$, and reveals the branched structure of cluster.

4.4 Hydrodynamic Field

Figure 4.11: Snapshots (upper) and hydrodynamic fields (bottom) of three states: (a) homogeneous state, (b) MIPS, (c) dynamic clustering state. Color of particle in snapshots indicate the orientation of self-propulsion. Colorbar of hydrodynamic fields represents the relative local packing fraction, and black arrows represent the driven velocity field.

By coarse graining, Fig. 4.11 shows the density field and driven velocity field for three different states. For corresponding snapshots on the upper panel, the colorbar of lower panel indicates the relative local packing fraction $\phi_l(\mathbf{r})/\phi_0$, and black arrows demonstrate the direction and scale of driven velocity field $\mathbf{v}_{0,l}(\mathbf{r})$. For the homogeneous state, density field is nearly uniform, and the driven velocity is smeared out by coarse graining as its correlation length is small. For MIPS, a dense droplet is formed, and driven velocity field only exists on the droplet boundary, no static driven velocity exists inside the bulk phase. While for the dynamic clustering state, driven velocity field does not vanish in the bulk dense phase, suggesting the correlation length is larger than the coarse graining length. This correlation can also be observed in the snapshots. In MIPS, the orientation of $\mathbf{v}_0$ is uniformly distributed in bulk phase, while in the dynamic clustering state, the clusters are composed by several collective

moving flocks, inside which, particles with same color indicating their driven velocities are correlated. The hydrodynamic field reveals that the dynamic clustering state is a result of the “traffic jamming” of these polarized flocks. As the driven velocity field dose not disappear, it finally leads to the fragmentation of clusters.

4.5 Dynamical Properties

4.5.1 Potential Fluctuation

Figure 4.12: Fluctuation of individual particle potential energy E_p versus time t for $D_r = 0.1$, $\phi = 0.35$, $v_0 = 36.0$, color indicates different torques, and from upper to bottom $\omega_0/D_r = 0.5, 1.0$ (MIPS), $1.8, 2.4, 3.6$ (dynamical clustering), 7.2 (homogeneous).

We measure the average individual particle potential energy $E_p = \sum_{ij} V(r_{ij})/N$ fluctuating with time t for different ω_0 , as shown in Fig. 4.12. From bottom to top, ω_0 decreases and the system transforms from a homogeneous to a dynamical clustering state, and finally to MIPS. The bottom line for homogeneous state at $\omega_0/D_r = 7.2$ has both low average E_p and fluctuation scale. Decreasing ω_0 to the dynamic clustering state, the average E_p increases slightly, while the fluctuation scale increases significantly. Further decrease $\omega_0 \leq D_r$ into MIPS state, the average E_p increase abruptly, while the fluctuation scale keeps similar as in the dynamic clustering state.

4.5.2 Intermediate Scattering

To illustrate the dynamic behavior of the system, we measure the self intermediate scattering function (sISF)

$$F_s(\mathbf{q}, t) = \frac{1}{N} \sum_{i=1}^N \langle \exp(i\mathbf{q} \cdot [\mathbf{r}_i(t) - \mathbf{r}_i(0)]) \rangle, \quad (4.9)$$

where $\langle \cdot \rangle$ represents the ensemble average. The sISF reflects the persistent swimming, circular motion and enhanced effective diffusion at different spatiotemporal regimes.

Figure 4.13: $D_r = 0.1$, $\phi = 0.40$, $v_0 = 36.0$. Upper: Snapshots for ω_0 increasing from left to right. Bottom: $q = 2\pi n_q/L$, left: $n_q = 1$ (dashed line suggests exponential decay), right: $n_q = 5$, color indicates Γ and inside bracket is τ_w/τ_r .

Fig. 4.13 shows sISF and corresponding snapshots for various ω_0 ranging from phase separation, to dynamic clustering and homogeneous states. And the sISF is measured at different wavenumber $q = n_q \frac{2\pi}{L}$. For small $\omega_0 = 0.01, 0.10$ corresponding to MIPS, $F_s(\mathbf{q}, t)$ decays in much slower manner than larger ω_0 in both $n_q = 1$ and $n_q = 5$, which suggests that the persistent swimming is suppressed as particles are frozen in a stable dense droplet. For larger ω_0 at $n_q = 1$, the oscillations around finite plateau suggests the chiral swimming pattern of individual particle is partly preserved in dynamic clustering state and homogeneous state. For large ω_0 at $n_q = 5$, the oscillations of $F_s(\mathbf{q}, t)$ around zero reflects the persistent swimming at corresponding length scales. As ω_0 increases, the oscillation amplitude increases and finally saturates, suggesting that the velocity damping effect in dynamic clustering

state decreases with ω_0 and then disappears in homogeneous state. From the sISF, we calculate the self dynamic structure factor (sDSF), which has been discussed in theoretical part Sec. 3.4.1.

4.6 Discussion

In this section, we first show that dynamical clustering state results from the combination of the standard MIPS cohesion, and the circulating current caused disintegration. Then we demonstrate that the non-vanishing current in steady states microscopically originates from the motility "relieved" by fast enough rotation. Finally, we also discuss the relation with other works on assembly of circle swimmers.

4.6.1 Cohesion and Disintegration

As shown in linearised hydrodynamics Eq. (3.22), density and longitudinal polarization fluctuation evolutions are coupled by the average effective velocity $\bar{v}_e$ and the effective compressional modulus η . Usually, MIPS instability in linear model is usually intrigued by $\partial v_e / \partial \rho < 0$ and $\eta < 0$, suggesting that particles mobility slows down by the steric repulsion from its neighbours, and particles tend to accumulate where they move slower [62]. Such slowdown-accumulation feedback loop provides effective cohesion for phase separation, and we verify here that this mechanism is also preserved in chiral swimmers. However, the transversal component $\tilde{w}_\perp$ cannot be decoupled from the other two modes at linear order as in normal fluids due to the convection induced by automatic rotation ω_0 .

As the conventional MIPS cohesion effect is preserved in the linear order hydrodynamic of chiral swimmers, to form dynamic clusters, there should be a disintegration mechanism. Thus, we explore the steady state current, which vanishes in equilibrium systems as a result of the balance of chemical potential and pressure everywhere. For slowly varying fields, we neglect the temporal derivative as well as the viscosity term in Eq. (3.21) to obtain the adiabatic solution of polarization field

$$\mathbf{W}_{\text{ad}} = -\frac{1}{2(D_r^2 + \omega_0^2)} \begin{bmatrix} D_r & -\omega_0 \\ \omega_0 & D_r \end{bmatrix} \nabla j(\rho), \quad (4.10)$$

where $j(\rho) = \rho v_e(\rho)$ represents the scalar strength of effective current. As $\mathbf{J}_{\text{ad}} = v_e \mathbf{W}_{\text{ad}}$, we found a not curl free current in steady state of chiral swimmers, $\nabla \times \mathbf{J}_{\text{ad}} = \omega_0 \eta [\zeta |\nabla \rho|^2 - v_e \nabla^2 \rho] / (D_r^2 + \omega_0^2)$, resulted from the automatic rotation. The emergence of such circulating current $\mathbf{J}_c$ breaks the detailed balance at continuum level, and no effective free energy function $\mathcal{F}(\rho)$ satisfies $\mathbf{J} = -\nabla(\delta \mathcal{F} / \delta \rho)$. The effect of $\nabla \times \mathbf{J} \neq 0$ was studied in Active Model B+ (AMB+) which resulted in a reversal Ostwald process and leads to the cluster/bubbly phase separation [118]. Our work provides a realistic model for the phenomenon predicted in field theory. More intuitively, such system spanning circulating current can continuously disassemble the dynamic clusters.

4.6.2 Current “Relieved” by Rotation

To understand the microscopic origin of circulating current, we look at the sISF as shown in Fig. 4.13, which reveals dynamic patterns at different spatiotemporal regimes. First, in the large time and length scale, diffusive-like behavior is expected, as persistent swimming is smeared out by frequent particle collisions (in the parameter region used in simulation, $\tau_b/\tau_r \simeq 0.4$). Thus the correlation follows a near-exponential decay fashion $\exp(-D_{\text{eff}}q^2t)$ at $t \gg \tau_b$ and small n_q (the dashed line in Fig. 4.13 (a)). Whereas in MIPS at slow rotation $\Gamma \lesssim 1$, $F_s(q, t)$ relaxes in a much slower manner than the diffusive motion, reflecting particles frozen inside the stable dense droplet, confirming the particle exchange is only interface process in bulk phase separation case. Second, to observe the circular motion, one should look at large enough wavelength $\lambda = L/n_q \gtrsim R$, thus we choose $n_q = 1$. Intriguingly, for fast rotation $\Gamma \gtrsim 1$, $F_s(q, t)$ oscillations around finite plateau at time scale around τ_w , suggesting that the chiral swimming pattern of individual particle is partially preserved in dynamical clustering, even dense liquid droplets are formed. Finally, at large wave number $n_q = 5$, the oscillations of $F_s(q, t)$ around zero within τ_r indicates a pure persistent motion $|\Delta \mathbf{r}(t)| = v_{\text{eff}}t$ at short wavelength, till for longer times rotational diffusion washes out the oscillations. The oscillation amplitude increases with Γ indicating less velocity damping effect, and it finally saturates when further increase Γ into homogeneous state. We notice that the instantaneous effective swimming velocity v_e is independent with ω_0 , while the time averaged persistence velocity v_{eff} increases with ω_0 as shown in the sISF. This inconsistency reflects that fast enough rotation can “relieve” trapped particles from temporal fluctuations before being smeared out by the rotational diffusion, thus preserves the chiral swimming pattern and gives rise to the system spanning circulating current.

4.6.3 Significance

The emergent behaviour of circle swimmers with explicit alignment was studied by generalizing the Vicsek model, where slow rotations enhance the polarization in macroflocks, while fast rotations induce secondary instabilities leading to phase synchronized microflocks [119]. However, these flocks are integrated by phase-lock mechanism and suffer from strong fluctuations once including excluded volume interactions, which occur naturally among typical circle swimmers [120]. In simulations of purely steric repulsive circle swimmers, significant suppression of MIPS, antiwise rotation of macrodroplet at some optimal slow rotation frequency [121] and collective oscillation of density under strong chirality [82] were observed. Those emergent behaviours were explained in phenomenological manners and until recently, a field theory quantitatively accounting for the suppression of MIPS was proposed [122]. However, as they consider the effect of self-propel torque using an effective rotational diffusion coefficient, this framework is only valid in slow rotation region. In contrast, non-equilibrium hyperuniform fluids were found in a deterministic model [47, 123], in which the active rotation rate can be seen as extremely fast, as the rotational noise is zero. Therefore, the unified understanding of the collective assembly of chiral active

swimmers remains unknown.

In this Letter, we formulate a hydrodynamic description from the microscopic dynamics of circle active Brownian particles (cABPs), and it is valid both at slow and fast rotations. Thereby, we find a short wavelength instability leading to a dynamic clustering state at fast rotation, and the phase boundary predicted from theory well agrees with computer simulations. By discussing the hydrodynamic matrix, we propose a novel instability mechanism originating from the combination of conventional MIPS cohesion and the circulating current caused disintegration. The current with non-zero curl was found in field theories responsible for reversal Ostwald process resulting in a cluster/bubbly phase [118], while our results show that the non-zero curl current can be induced by the automatic rotation in cABPs. We also verify that the system spanning circulating current originates from the motility “relieved” by fast rotation from temporal fluctuations. Our results may help understand the general mechanism of self-limiting size cluster formation without introducing explicit alignment to synchronize phases [119] or chemical signalling [124, 125]. More generally, non-vanishing current in steady states is a distinct feature of non-equilibrium systems, as not restricted by the thermodynamic balance. Therefore, the dynamical clustering state differs from MIPS, where detailed balance is usually restored [44, 61].

Chapter 5

Driving dynamic colloidal assembly using eccentric self-propelled colloids

Designing protocols to dynamically direct the self-assembly of colloidal particles has become an important direction in soft matter physics because of the promising applications in fabrication of dynamic responsive functional materials. Here using computer simulations, we found that in the mixture of passive colloids and eccentric self-propelled active particles, when the eccentricity and self-propulsion of active particles are high enough, the eccentric active particles can push passive colloids to form a large dense dynamic cluster, and the system undergoes a novel dynamic demixing transition. Our simulations show that the dynamic demixing occurs when the eccentric active particles move much faster than the passive particles such that the dynamic trajectories of different active particles can overlap with each other while passive particles are depleted from the dynamic trajectories of active particles. Our results suggest that this is in analogy to the entropy driven demixing in colloid-polymer mixtures, in which polymer random coils can overlap with each other while deplete the colloids. More interestingly, we find that by fixing the passive colloid composition at certain value, with increasing the density, the system undergoes an intriguing re-entrant mixing, and the demixing only occurs within certain intermediate density range. This suggests a new way of designing active matter to drive the self-assembly of passive colloids and fabricate dynamic responsive materials.

5.1 Introduction

Active matter comprises the particles capable of converting chemical and/or biological energies to drive their motion, of which the study originates from the purpose of understanding the collective self-organization phenomena in nature, like bird flocks, bacteria colonies, tissue repair, and cell cytoskeleton [31]. In recent decades, thanks to the breakthrough of particle synthesis, a number of artificial active self-propelled colloidal systems have been realized in experiments [33, 34, 35, 36, 37, 38, 39, 40],

in which the dynamics and interaction between particles can be better controlled to understand the physics of the emergent phenomena in active matter. Different from passive colloids undergoing Brownian motion due to random thermal fluctuations of the solvent, active self-propelled colloids experience an additional force due to internal energy conversion, which is random in long time with short time memories [41]. Because of the special dynamics of active particles, they produced a number of interesting dynamic phenomena never observed in corresponding equilibrium passive matter systems, such as bacteria ratchet motors [24], meso-scale turbulence [43], motility induced phase separation [50, 51, 57, 112, 126, 53, 60, 52, 59, 66] and mediating emergent long range interactions [45, 46]. Although recently it has been shown that active colloids can serve as a medium to tune the effective interaction between passive particles [45, 46], it requires the large diffusivity difference between the active and passive particles, and directing the collective assembly of passive particles using active particles remains challenging, which limits the application of using active particles in the fabrication of functional materials.

So far, most of the studies on the collective assembly of active colloids have concentrated on the spherical or rodlike active particles, of which the self-propulsion goes through the mass center of the particle, and the dynamics is well described by a persistent random walk [34]. However, due to the inhomogeneity of activity surface modification or shape anisotropy of the particle [127, 128, 129, 130] the random self-propulsion on active particles can be eccentric, and it was found that the eccentric self-propulsion, due to the shape anisotropy of active swimmers, can significantly change the dynamics of single active particle, such as inducing the circular-like active motion [17] and gravitaxis [18, 131]. Here we found that if one put these eccentric active particles into the suspension of passive colloids, the eccentric active particles can collectively push the passive colloids together to form a dense large cluster, and the system demixes. More interestingly, we find that with certain active-passive compositions, by increasing the density of the system, the active-passive mixture undergoes an intriguing re-entrant mixing transition, and the demixing only occurs within some intermediate density range. The re-entrant behaviour offers new possibilities of using active colloids to help the fabrication of responsive functional materials.

5.2 Model

In experiments, eccentric active colloids are typically anisotropic [18, 17], while one can make the particles highly charged such that the interaction between them does not affect the orientation [132]. Therefore, focusing on the effect of eccentricity, we consider a 2D binary mixture of $N = N_p + N_a$ colloidal hard spheres with N_p and N_a the number of passive and active particles, respectively. As shown in Fig. 5.1a, the eccentric self-propelled hard sphere is modelled as an eccentric active Brownian particle (EABP) with a spherical diameter σ , and a constant self-propulsion acting on the colloidal surface, which has an eccentric angle θ from the center of the particle. This eccentric self-propulsion induces a constant torque $\mathbf{\Omega}_i$ on particle i given by

$$\mathbf{\Omega}_i = f_i \cdot \mathbf{d}_i \times \mathbf{u}_i, \quad (5.1)$$

Figure 5.1: **Illustration of the binary passive-EABP mixture.** (a) The schematic illustration of EABPs (blue) and passive particles (red) in the system. (b,c) The radial distribution $g(r)$ of EABPs and passive particles (mass center) with respect to the instant center of circular trajectory of the reference EABP in the infinitely dilute limit for $\theta = 4.5^\circ$ (b) and 30° (c) with $f\sigma/k_B T = 10$ and 200 .

where $\mathbf{d}_i$ is the vector connecting the mass center of the particle and the location of the self-propulsion with f_i and $\mathbf{u}_i$ the strength and orientation of the self-propulsion on particle i , respectively. Here we use $|\mathbf{d}_i| = \sigma/2$. For passive particles, $f_i = 0$. The strength of the active torque is $|\boldsymbol{\Omega}_i| = f_i |\mathbf{d}_i| \sin \theta$, and we define θ as the eccentricity of the self-propulsion. In our 2D system, $\boldsymbol{\Omega}_i$ is a constant vector always pointing towards the inside or outside of the plane, and for the sake of simplicity we choose $\theta > 0$ and $\boldsymbol{\Omega}_i$ points to the inside of the plane. Even though the particles are driven and energy is continuously supplied to the system, we assume the solvent to be at an equilibrium temperature T . The motion of particle i with position $\mathbf{r}_i$ and orientation $\mathbf{u}_i$ is described via the overdamped Langevin equation given by

$$\dot{\mathbf{r}}_i(t) = \frac{D_0}{k_B T} [-\nabla_i U(t) + f_i \cdot \mathbf{u}_i(t)] + \sqrt{2D_0} \xi_t(t), \quad (5.2)$$

$$\dot{\mathbf{u}}_i(t) = \left[\frac{D_r \boldsymbol{\Omega}_i}{k_B T} + \sqrt{2D_r} \xi_r(t) \right] \times \mathbf{u}_i(t), \quad (5.3)$$

where D_r is the rotational diffusion constant of the particle with k_B the Boltzmann constant. According to the Stoke-Einstein relationship [54], we assume $D_r = 3D_0/\sigma^2$ with D_0 the short-time translational self-diffusion coefficient of the sphere. $\xi_t(t)$ and $\xi_r(t)$ are Gaussian thermal noises with zero mean and unit variance. For a given θ , without the thermal noises, the EABP performs circular motion with a radius $R = |\mathbf{r}|/|\dot{\mathbf{u}}| = 2\sigma/(3\sin \theta)$. Here R reaches the minimal value of $2\sigma/3$ at $\theta = \pi/2$, and it is due to the fact that the torque is induced by the eccentricity of the self-propulsion, which is true for shape anisotropic active swimmers in experiments. U is the total potential energy of the system, which is the sum of all pairwise interactions $U(r_{ij})$ given by the Weeks-Chandler-Andersen (WCA) potential to mimic the colloidal

Figure 5.2: **Phase behavior of the 2D passive-EABP mixtures with various eccentricity.** Typical snapshots (upper panels) and the reduced probability distribution of local density $P(\rho_a, \rho_p)/P_{\max}$ (lower panels) in the binary mixture of passive particles (red) and EABPs (blue) at $\rho\sigma^2 = 0.891$, $x_p = 0.4$, and $f\sigma/k_B T = 200$ with various eccentricity: (a) $\theta = 0$ ($R = +\infty$); (b) $\theta = 14.5^\circ$ ($R = 8/3\sigma$); (c) $\theta = 30^\circ$ ($R = 4/3\sigma$); (d) $\theta = 90^\circ$ ($R = 2/3\sigma$). Here ρ_a and ρ_p are the local density of EABPs and passive particles, respectively, with $P_{\max}$ the maximal probability in $P(\rho_a, \rho_p)$. The arrows indicate the direction of rotation of the passive particle cluster.

hard-sphere interaction [133]

$$\frac{U(r_{ij})}{k_B T} = \begin{cases} 4 \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 + \frac{1}{4} \right] & (r_{ij} < 2^{1/6}\sigma) \\ 0 & (r_{ij} > 2^{1/6}\sigma) \end{cases} \quad (5.4)$$

where r_{ij} is the center to center distance between particle i and j .

5.3 Results

We first study the infinitely dilute mixture of passive and EABPs with different f and θ , in which we simulate two particles and the system size is large enough to exclude any effect of the periodic boundary condition. In Fig. 5.1b,c, we plot the radial distribution functions $g_{A'A(P)}(r)$ of the system, in which r is the distance between the instant center of the circular trajectory of a reference EABP and the mass center of another EABP (passive) particle. One can see that when the eccentricity is small, i.e. $\theta = 4.5^\circ$, $g_{A'A}(r)$ and $g_{A'P}(r)$ are very similar to each other and do not change much with increasing f , and both EABPs and passive particles can enter the circular trajectories of other EABPs. With increasing the eccentricity to $\theta = 30^\circ$, $g_{A'A}(r)$ becomes larger than $g_{A'P}(r)$ at distance $r < R + \sigma$, and the difference becomes more substantial with increasing f . This implies that compared to EABPs, passive

particles are more depleted from the zone within the circular trajectories of other EABPs, which effectively induces an “extra short range repulsion” between EABPs and passive particles.

To further investigate the effect of eccentricity on the collective assembly of the system, we simulate a binary mixture of EABPs and passive particles with the overall density $\rho\sigma^2 = 0.891$ and composition $x_p = N_p/(N_a + N_p) = 0.4$, where the self-propulsion of EABPs is fixed at $f\sigma/k_BT = 200$, and eccentricity varies from $\theta = 0$ to 90° . As shown in Fig. 5.2a, when $\theta = 0$, the system recovers the conventional binary mixture of passive and active Brownian particles [134], and phase separates into a high density liquid-like phase and a low density gas-like phase, whose densities can be obtained from the location of two peaks in the reduced probability distribution of local density in the lower panel of Fig. 5.2a similar to Ref. [135, 134]. When increasing the eccentricity to $\theta = 14.5^\circ$, the gas-liquid like phase separation disappears, and the bimodal probability distribution of local density merges into a single peak in Fig. 5.2b suggesting a homogeneous phase. Interestingly, as shown in Fig. 5.2c, with further increasing the eccentricity to $\theta = 30^\circ$, a different bimodal probability distribution of the local density appears, and the system forms a dense cluster of pure passive particles with density $\rho_p\sigma^2 \simeq 1.2$ surrounded by a binary fluid mixture with $(\rho_a\sigma^2, \rho_p\sigma^2) \simeq (0.6, 0.3)$. This implies the demixing of passive particles from the passive-EABP mixture. Moreover, as the system is in 2D, the cluster of passive particles formed in the system spontaneously rotates towards the opposite rotating direction of EABPs. By further increasing the eccentricity to $\theta = 90^\circ$, one can observe a more pronounced passive-EABP demixing in the system, which almost completely phase separates into a high density phase of passive particles and a low density phase of EABPs.

By locating the peaks in the probability distribution of local density, like in Fig. 5.2a,b, we construct the phase diagram for the motility induced gas-liquid like phase separation in mixture of passive and EABPs with weak eccentricity (symbols in Fig 5.3). One can see that when θ is zero, the phase diagram features a gas-liquid like phase separation of two phases with similar passive particle densities and different active particle densities. By adding passive particles to the mixtures, the density difference between the co-existing phases becomes smaller, and the co-existing phase envelope eventually closes at the high enough density of passive particles, which agrees with Ref. [134]. With slightly increasing the eccentricity θ , the binodal of non-equilibrium gas phase increases dramatically, and the gas-liquid like phase envelope becomes smaller, which almost completely disappears at $\theta > 0.76^\circ$. To understand the disappearance of the motility induced gas-liquid like phase separation in the system, we build up a phenomenological theory following the kinetic model in Ref. [51, 134]. In 2D, we assume that the gas-liquid interface consists of close packed EABPs [134], and the orientation of an EABP ψ satisfies the Langevin equation:

$$\frac{d\psi}{dt} = \frac{D_r\Omega}{k_BT} + \sqrt{2D_r}\xi_r, \quad (5.5)$$

by solving which we obtain the orientation correlation function $\langle \cos \Delta\psi(t) \rangle = \cos(2\pi\omega t)e^{-D_rt}$ with $\Delta\psi(t) = \psi(t) - \psi(0)$ and $\omega = D_r\Omega/2\pi k_BT = fD_r\sigma \sin \theta/4\pi k_BT$. When $\theta \rightarrow 0$,

Figure 5.3: **Motility induced phase separation in passive-EABPs mixtures.** Phase diagrams of the 2D binary mixture of passive and EABPs with $f\sigma/k_B T = 200$ and weak eccentricity θ in the $\rho_a - \rho_p$ representation. The dashed lines are the theoretical prediction in Eq. 5.6.

we have $D_r \gg \omega$ and $\langle \cos \Delta\psi(t) \rangle \simeq e^{-D_r t}$, in which the characteristic time for an active particle on the gas-liquid interface escaping to the gas phase is $\tau_{out} = 1/D_r$. On the other hand, when the eccentric torque on the active particle is very large, i.e. $D_r \ll \omega$, the characteristic time for an active particle to escape from the surface can be approximated as $\tau_{out} = 1/4\omega$, which is the time that the orientation correlation function first becomes zero. Therefore, generally, as the first approximation, we assume $\tau_{out} = 1/(D_r + 4\omega)$, and the flux of EABPs per unit length on the gas-liquid interface escaping from the liquid phase $k_{out} = \kappa/(\sigma\tau_{out})$ with $\kappa = 4.5$ obtained from the fitting in Ref. [51]. Similarly, we also obtain the flux of active particles per unit length on the phase boundary entering the liquid phase as $k_{in} = \rho_g^a v_p / \pi$, where ρ_g^a is the density of active particles in the non-equilibrium gas phase with velocity $v_p = fD_0/k_B T$. By equating $k_{out} = k_{in}$, we obtain the binodal of the gas phase

$$\rho_g^a = \frac{\pi\kappa(D_r + 4\omega)}{v_p \sigma}, \quad (5.6)$$

of which the dependence on θ is shown as the vertical dashed lines in Fig. 5.3. One can see that by slightly increasing θ , the binodal of gas phase increases significantly, which qualitatively agrees with the phase boundary obtained from simulations. Essentially, this implies that the disappearance of the gas-liquid like motility induced phase separation in the passive-EABP mixture is due to the decreased orientation relaxation time by the active torque Ω , which is similar to the effect of increasing D_r on the motility induced phase separation [136].

Figure 5.4: **Dynamic demixing in passive-EABP mixtures.** (a) Phase diagram of the 2D binary passive-EABP mixtures in the $f - \theta$ representation with $\rho\sigma^2 = 0.891$ and $x_p = 0.4$, where the black squares are the demixing phase boundary. The insets are typical snapshots of the mixed and demixed systems, where red and blue spheres are passive and eccentric active particles, respectively. The background represents the value of τ_c/τ_B according to the color bar on the right. (b,c) Typical snapshots of the binary system of quasi-A (blue) and quasi-P (red) particles at $\rho\sigma^2 = 0.891$ and $x_p = 0.4$ (same as in Fig. 5.2d), and the pair interactions used are shown in the insets. Pair interactions in (b) are obtained from simulations of infinitely dilute binary passive-EABP mixtures with $f\sigma/k_B T = 200$ and $\theta = 90^\circ$, based on which those in (c) are modified by including an excluded volume effect between the A-A interaction.

Additionally, as shown in Fig. 5.1c and d, with further increasing the eccentricity to 30° and 90° , the system undergoes a new dynamic demixing by forming a large dense cluster of passive particles surrounded by non-equilibrium binary fluids. By using the quaternion-based Rotational Brownian Dynamics algorithm [137], we confirm that the demixing also occurs in the 3D binary passive-EABP mixtures, where the orientation of the active torque on each EABP performs free Brownian rotation. To understand the essential physics driving this intriguing demixing in the passive-EABP mixture, we simulate the system with different combinations of f and θ at $\rho\sigma^2 = 0.891$ and $x_p = 0.4$. To identify the critical f and θ for the demixing, we calculate the demixing order parameter $\langle\alpha\rangle = \frac{1}{A_a}\langle(1-x_p)[\sum_{i=1}^{N_a}(n_i^a - n_i^p)/6N_a + 2x_p - 1]\rangle + \frac{1}{A_p}\langle x_p[\sum_{i=1}^{N_p}(n_i^p - n_i^a)/6N_p - 2x_p + 1]\rangle$, where $n_i^{a/p}$ is the number of EABP/passive particle neighbours in the 6 nearest neighbours of particle i . A_a and A_p are the normalization factors, which are chosen such that $\langle\alpha\rangle = 1$ when EABPs and passive particles are fully demixed, and $\langle\alpha\rangle = 0$ when the two types of particles are miscible. As a single large cluster forms when $\langle\alpha\rangle \simeq 0.2$, we use $\langle\alpha\rangle > 0.2$ as the criteria of demixing, and the resulting phase boundary is plotted in Fig. 5.4a. We can see that with increasing the strength of self-propulsion, the critical eccentricity for driving the demixing decreases significantly. When $f\sigma/k_BT \simeq 80$, the critical eccentricity for demixing is around $\theta \simeq 90^\circ$, while θ drops to about 30° for $f\sigma/k_BT \simeq 200$. In the binary mixture, there are essentially two different dynamic time scales for the motion of passive particles and EABPs, respectively: (i) $\tau_B = \sigma^2/4D_0$ the average time for a passive particle diffusing for the distance of σ ; (ii) $\tau_c = 4\pi\sigma k_BT/(3fD_0 \sin\theta)$ the period of circular motion of an EABP. We superpose the ratio between these two dynamic time scales τ_c/τ_B on the phase boundary in Fig. 5.4a. We can see that the system demixes at small τ_c/τ_B , in which the EABPs perform circular-like motion much faster than the Brownian diffusion of passive particles. As seen from our simulation of dilute systems, when EABPs move much faster than passive particles, passive particles are depleted from the dynamic trajectories of EABPs, which effectively creates a “repulsion” between the dynamic trajectories and passive particles. At the meanwhile, as EABPs are all moving on the same time scale, their dynamic trajectories can overlap with each other such that the “repulsion” between the dynamic trajectories of active particles is weaker. This is similar to the system of colloid-polymer mixtures, in which polymer random coils can to some extent overlap with each other but not with the colloidal particles inducing an stronger repulsion between colloid and polymer than that of polymer-polymer interaction. When the density is high enough, the colloid-polymer mixture demixes due to the entropy maximization of the system [138], and in our non-equilibrium system of passive-EABP mixtures, similar demixing also occurs.

To test the picture of entropy driven demixing, we assume the circular-like dynamic trajectory of an EABP as a quasi-particle, namely A particle, whose center is the instant center of the circular trajectory, and passive particles can be seen as another type of particles, namely P particles. From the simulation of infinitely dilute passive-EABP mixtures, we can extract the effective pair potentials among A and P particles, which are used as input for equilibrium simulation of the system at high

densities. From the obtained pair potentials in the inset of Fig 5.4b, one can see that the repulsion between A-A particles is softer than that between A-P particles, which is similar to the colloid-polymer mixtures [139]. The equilibrium Brownian dynamic simulation follows the same overdamped Langevin dynamics as Eq. (5.2), except without the active term. However, as shown in Fig. 5.4b, the equilibrium simulation at high density, i.e. $\rho\sigma^2 = 0.891$ and $x_p = 0.4$, does not show a demixing seen in the corresponding passive-EABP mixture in Fig 5.2d. From the snapshot of the equilibrium simulation, we can see that many A particles overlap with each other due to the potential well between A-A particles at the short distance $r \lesssim 0.5\sigma$, and most of the blue spots are occupied by at least 4 A particles in Fig. 5.4b. This is the artefact of the effective pair potential, as in our simulation of passive-EABP mixtures, dynamic trajectories of two EABPs can overlap and share the circular center with $R = 2/3\sigma$, while because of the hard-core interaction between EABPs, it is not possible to have more than 3 active particles sharing the same circular trajectory, and this number can increase at the larger R . Therefore, this suggests that there should be a multi-body excluded volume term in the effective interaction among A-A particles. If we just add an excluded volume effect at short distance, i.e. $r \lesssim 0.5\sigma$, to the A-A interaction (Fig. 5.4c inset), the demixing between A and P particles occurs as shown in Fig. 5.4c. This suggests that the multi-body excluded volume effect induced by the non-equilibrium dynamics is important for the dynamic demixing of the system at high density, and by including proper excluded volume effects between dynamic trajectories of EABPs, i.e. A particles, one can indeed use effective interaction obtained from low density passive-EABP systems to qualitatively reproduce the dynamic demixing at high density. It is worth noticing that as shown in Fig. 5.4a, when $f \rightarrow \infty$, the phase boundary is approaching certain threshold θ , e.g. about 30° in Fig. 5.4a, depending on the density and stoichiometry of the system, and this can not be explained by using the ratio between two dynamic time scales τ_c/τ_B , which approaches zero at $f \rightarrow \infty$. Therefore, the physics of this threshold of θ at $f \rightarrow \infty$ remains interesting for further investigation.

Furthermore, we construct the demixing phase diagram for the binary mixture of passive particles and EABPs of $f\sigma/k_B T = 200$ with various eccentricity θ as shown in Fig. 5.5a, in which we simulate the system of $N = N_a + N_p = 5,000 \sim 10,000$ particles to ensure the system size large enough to eliminate the finite size effect. When $\theta \gtrsim 14.5^\circ$, the dynamic demixing occurs in the system. One can see that with increasing the eccentricity θ , the EABP rich phase boundary significantly moves to the lower fraction of passive particles, while the composition in the passive particle rich phase once formed is almost independent with eccentricity. We also varies the passive particle composition x_p in the system to ensure that similar to equilibrium demixing, the obtained phase boundary is independent with x_p and the lever rule still holds. More interestingly, as shown in Fig. 5.5a, the density of passive particles in the EABP rich phase changes non-monotonically with increasing the density of EABPs ρ_a , and develops a minima. Therefore, as shown in Fig. 5.5b-d, by fixing the passive particle composition at $x_p = 0.15$ with $\theta = 90^\circ$, and increasing the density of the binary mixture from $\rho\sigma^2 = 0.38$ to 1.27, the system undergoes an interesting re-entrant mixing, which demixes at the intermediate density, i.e. $\rho\sigma^2 = 0.76$. This re-

Figure 5.5: **Dynamic demixing phase diagram.** Phase diagram of the 2D binary passive-EABP mixtures with $f\sigma/k_BT = 200$ and various eccentricity θ in the $\rho_a - \rho_p$ representation, where x_p is fraction of passive particles in the simulated systems, and the dashed line indicates the close packing obtained. (b-d): Typical snapshots of the 2D binary mixture of passive particles and EABPs with $f\sigma/k_BT = 200$ and $x_p = 0.15$ at different densities: $\rho\sigma^2 = 0.38$ (b), 0.76 (c), and 1.27 (d). Here the blue and red spheres are EABPs and passive particles, respectively.

entrant mixing at high density is due to the fact that the system is too crowding such that EABPs can not perform proper circular-like motion, and the dynamic entropy driven demixing picture breaks down.

5.4 Conclusions

In conclusion, by performing computer simulations for binary mixtures of passive and eccentric active particles, we find that with increasing the eccentricity of the active particles, the gas-liquid like motility induced phase separation disappears, and the system undergoes a new dynamic demixing transition, in which active particles push passive particles forming a large cluster. In [140], demixing phenomenon was also observed in a mixture of clockwise (+) and counter-clockwise (−) concave spinners. But the concave shape plays essential role for the phase transition, as we have simulated similar binary mixture with spherical shape disks, and find no phase separation between + and − disks. Besides, in [141] which was published later than the work presented here, similar spontaneous demixing between passive and circle swimmers was studied. However, there is a difference with model we simulated. All circles swimmers rotate at the same phase in [141], while our model is more general, with rotation phase of particles setting randomly. Intriguingly, in this later paper, the demixing is proposed to be driven by the composition-dependent diffusion constant. And by bridging the relation between enhanced diffusion and nonconservative forces in mixed state, the phase boundary is predicted and also agree well with simulation. The relation between these two demixing mechanism deserves further study. We argue that the new dynamic demixing is due to the interplay between two different dynamics in the binary mixture. The circular-like trajectories of fast moving eccentric active particles, which can overlap with each other, deplete the slow moving passive particles, and when the density is high enough, to maximize the “entropy”, the system demixes in analogy to the colloid-polymer mixtures [138, 142, 143, 144]. However, we find that the multi-body excluded volume effect between dynamic trajectories of active particles is very important, without which the demixing can not be reproduced in equilibrium using the obtained pair effective interaction. This makes the quantitative prediction on the dynamic demixing highly challenging and interesting for future study. Moreover, we construct the phase diagram for the demixing of passive and eccentric active particles, and we find that the composition on the phase boundary of active rich phase changes non-monotonically with increasing the density of the system, which induces an intriguing re-entrant mixing with increasing the density of the system at certain fixed active-passive compositions. Here we focused on the effect of eccentricity of active particles on the dynamic assembly of the system, and neglected hydrodynamic effects that would be interesting for future experimental and theoretical studies [145]. However, the results of this work can be also realized experimentally in the system of active granular matter, in which the hydrodynamic effect is neglectable, and the eccentricity of active particles can be better controlled [146, 3]. Therefore, our results open up a new way in designing active particles to collectively drive the assembly of passive matter [45, 147, 148, 54].

Chapter 6

Conclusion

This thesis aims to study the dynamic assembly of active matter, especially focusing on circle swimmers. Continuum theories are applied to study possible dynamic states, then the predicted heterogeneous states and phase boundary are verified by simulation. Finally, we study the spontaneous demixing of circle swimmers with passive particles, which may have potential application in sorting passive colloids.

In Ch 2, two most intriguing phenomena in active matter system were reviewed, *i.e.*, motility induced phase separation (MIPS) and collective motion. For MIPS, an effective free energy functional was derived from microscopic dynamics of the active Brownian particle model, and quantitatively predicts many aspects of phase separation, including pressure of bulk phase, spinodal, binodal, discontinuous/continuous phase transition, and coarsening dynamics. The non-equilibrium character endows the MIPS special features like breaking common tangent construction, unequal area Maxwell construction, and negative surface tension, etc. For collective motion, the transition to ordered flocking phase is due to the explicit alignment of motility orientation, and Vicsek-like models count both the motility and alignment interaction. The dynamic states, phase transitions, and density fluctuations in homogeneous state in various Vicsek-like models with different motility and interaction symmetries were summarized.

In Ch 3, dynamic states in circle swimmers are studied theoretically. By mean-field approximation, we constructed continuum equation for density and polarization field, then obtained dispersion relation by linear instability analysis of homogeneous state. Two types of instabilities were found, the first type instability starts from zero wavenumber corresponding to the infinite length scale in real space, and the second type instability starts from finite wavenumber, which are supposed to related to fluctuations at microscopic length scale.

In Ch 4, Brownian dynamics simulation of circle active Brownian particles (cABPs) are conducted. As predicted by instability analysis, two heterogeneous states are observed: dynamic clustering and MIPS. The different correlation length scales of two instabilities are verified, and phase boundaries fit prediction qualitatively. Along with obtaining the full phase diagram of cABPs, we also studied the homo-dynamic clustering phase transition in the context of percolation theory, by measuring the scaling of cluster size distribution. The density and polarization field obtained by

coarse-graining gives an intuitional explanation for the formation of dynamic clustering state. Finally, the intermediated scattering functions were studied to reveal the different dynamic properties in the three phases.

In Ch 5, spontaneous demixing of circle swimmers and passive particles were found. The complete phase diagram including MIPS and demixing was obtained, and phase boundaries of MIPS in the mixture was qualitatively fitted by a phenomenological theory. Besides, effective pairwise interactions were extracted from the radial distribution but cannot recover demixing in the counterpart passive system, which suggests the necessary role of multi-body effect in this phenomenon. Finally, the demixed passive colloids clusters are found to rotate in opposite direction of individual circle swimmers, so that this demixing phenomenon may have potential application in sorting passive colloids and building micro-machines.

With respect of further directions of research, in the pure cABPs system, we expect that the dynamical clustering state can serve as a good platform to examine the generalization of effective thermodynamic concepts (temperature, pressure, etc) previously developed in MIPS context. Besides, in such a simple model, there are two significantly different heterogeneous states: the MIPS restores detailed balance at continuum level, while dynamical clustering breaks time reversal symmetry even at macroscopic scale. Thus, we are curious about to what extent the active transitions is distinct from equilibrium ones. Two probable approaches are measuring the fluctuation-dissipation relation and large deviation. Similar approaches can also be applied to the passive-EABP binary system, to further understand the dynamic “entropy” which drives the demixing.

Appendices

Appendix A

Instability Analysis

A.1 Introduction

While in Sec. 3.4.1, the dispersion relations $s_{d/p}(q)$ for diffusion and propagation modes are discussed in perturbation theory, in this part, we discuss their stability accurately. In the first section, starting from Eq. 3.23, the dispersion relation $s(q)$ for wave mode $\exp(st + i\mathbf{q} \cdot \mathbf{r})$ is restricted to be roots of a cubic equation; second part Sec. A.3 introduces general skills used in solving cubic equation; third part Sec. A.4 discusses coefficients of the cubic equation in detail to support the overall discussion of roots structure, however, as this part is too tedious to follow, it may be helpful to be skipped first, and come back when read Sec. A.5 following the reference link; fourth part Sec. A.5 provides a workflow for the instability analysis which combines various criteria mentioned in Sec. A.4; fifth part Sec. A.6 applies results from Sec. A.5 and draw the phase diagram in control parameter plane $[\omega_0, \phi]$.

A.2 Dispersion relationship

The expansion of Eq. 3.23 gives the restriction for dispersion relation $s(q)$ of wave mode $\exp(st + i\mathbf{q} \cdot \mathbf{r})$

$$f_q(s) = \mathbf{a}s^3 + \mathbf{b}s^2 + \mathbf{c}s + \mathbf{d} = 0, \quad (\text{A.1})$$

in which parameters are

$$\begin{aligned} \mathbf{a} &= 1, \\ \mathbf{b} &= 3Dq^2 + 2D_r, \\ \mathbf{c} &= 3D^2q^4 + (4DD_r + \gamma)q^2 + (D_r^2 + \omega_0^2), \\ \mathbf{d} &= D^3q^6 + (2D^2D_r + \gamma D)q^4 + [D(D_r^2 + \omega_0^2) + \gamma D_r]q^2. \end{aligned} \quad (\text{A.2})$$

For dispersion relation $s(q)$, positive solution of s indicates unstable wave mode, as the fluctuation increases as time evolve, inversely, negative s solution indicates stable wave mode, where fluctuation decays with time.

A.3 General roots structure of cubic equation

The quadratic term in a general cubic equation $f(y) = y^3 + by^2 + cy + d = 0$ can be cancelled by substitution $x := y + b/3$, then the equation transfers as

$$F(x) = x^3 - 3mx + 2n = 0, \quad (\text{A.3})$$

for which determination function can be constructed as

$$\mathbf{D} := n^2 - m^3, \quad (\text{A.4})$$

where $m = (b^2 - c)/9$, $n = (2b^3 - 9bc + 27d)/54$. Then

1)if $\mathbf{D} > 0$, there are one real root and two conjugated complex roots,

$$\begin{aligned} x_1 &= u + v, \\ x_2 &= -\frac{u+v}{2} + i\frac{\sqrt{3}}{2}(u-v), \\ x_3 &= \bar{x}_2, \end{aligned} \quad (\text{A.5})$$

where

$$\begin{aligned} u &= \sqrt[3]{-n + \sqrt{\mathbf{D}}}, \\ v &= \sqrt[3]{-n - \sqrt{\mathbf{D}}}. \end{aligned} \quad (\text{A.6})$$

2)if $\mathbf{D} = 0$, there are two real roots (one of them is repeated);

3)if $\mathbf{D} < 0$, there are three real roots,

$$\begin{aligned} x_k &= 2\sqrt{m} \cos\left(\frac{\theta + 2\pi k}{3}\right) \quad k = 0, 1, 2, \\ \theta &:= \arccos\left(\frac{-n}{m\sqrt{m}}\right), \end{aligned} \quad (\text{A.7})$$

and easy to prove x_0 is the largest.

There is another way to define determination function as

$$\Delta = 18abcd - 4b^3d + b^2c^2 - 4ac^3 - 27a^2d^2, \quad (\text{A.8})$$

and it determines the roots structure in an opposite manner to $\mathbf{D}$.

A.4 Discussion of dispersion relation

A.4.1 Cancel square term

For the convenience of writing, adopting shorthand to Eq. A.1 and A.2,

$$\begin{aligned} \beta &= \omega_0, \\ \kappa &= \frac{D_r}{\omega_0}, \\ z &= q^2, \end{aligned} \quad (\text{A.9})$$

where $\gamma < 0$, $\beta, \kappa, z > 0$. According to Eq. A.3, change variable $x := s + b/(3a)$, so that

$$s = x - (Dz + \frac{2}{3}\beta\kappa), \quad (\text{A.10})$$

then $f_q(s) = 0$ converts as

$$G_z(x) = x^3 - 3mx + 2n = 0, \quad (\text{A.11})$$

where

$$\begin{aligned} m &= -\frac{1}{9}[3\gamma z + \beta^2(3 - \kappa^2)], \\ n &= \frac{1}{54}[9\gamma z - 2\beta^2(9 + \kappa^2)]. \end{aligned} \quad (\text{A.12})$$

Then the determination function of $G_z(x)$ is

$$\mathbf{D}(z) = \frac{1}{108}[4\gamma^3 z^3 + \gamma^2 \beta^2(12 - \kappa^2)z^2 + 4\gamma\beta^4(3 - 5\kappa^2)z + 4\beta^6(1 + \kappa^2)^2], \quad (\text{A.13})$$

A.4.2 Discussion of $\mathbf{D}(z)$ and roots structure

The sign of $\mathbf{D}(z)$ determines roots structure of $G_z(x)$ and so that $f_q(s)$. For the convenience of discussion of sign of Eq. A.13, let $\hat{D}(z) = 108\mathbf{D}(z)$, and noticing the cubic term has negative coefficient, while constant term is always positive, so that in the range $z \in [0, +\infty)$, $\hat{D}(z)$ have single root or three roots, and these two types $\hat{D}(z)$ are sketched in Fig. A.1

Figure A.1: Sketch of two kinds of $\mathbf{D}(z)$.

Differentiation of $\hat{D}(z)$ is a square function

$$\hat{D}'(z) = 2[6\gamma^3 z^2 + \gamma^2 \beta^2(12 - \kappa^2)z + 2\gamma\beta^4(3 - 5\kappa^2)]. \quad (\text{A.14})$$

If $\mathbf{D}(z)$ satisfies type I, $\Delta_{\hat{D}} > 0$ (three real roots) and the extreme point of $\hat{D}'(z)$ defined as z_0 should be positive. The first condition gives

$$\Delta_{\hat{D}} = 16\gamma^6 \beta^4 2\kappa^4 (\kappa^6 - 81\kappa^4 + 2187\kappa^2 - 19683) > 0, \quad (\text{A.15})$$

where numerical solution gives $\kappa > \kappa^* = 5.196\dots$. While the second condition gives

$$z_0 = -\frac{\gamma^2 \beta^2 (12 - \kappa^2)}{12\gamma^3} > 0, \quad (\text{A.16})$$

then $\kappa^2 < 12$, which contradicts with Eq. A.15, so that $D(z)$ must take type II.

In summary, $\mathbf{D}(z) > 0$ for $z \in [0, z^*)$, while $\mathbf{D}(z) < 0$ for $z \in (z^*, +\infty)$, which means as long as $\gamma < 0$, $\beta, \kappa > 0$ satisfied, $f_q(s) = 0$ have one real roots and two complex roots for $q < \sqrt{z^*}$, and three real roots for $q > \sqrt{z^*}$.

A.4.3 Discussion of $f_{q=0}(s)$

Fix $q = 0$, then Eq. A.1 becomes

$$f_{q=0}(s) = s[(s + D_r)^2 + \omega_0^2] = 0, \quad (\text{A.17})$$

and solutions are

$$\begin{aligned} s_1(q=0) &= 0, \\ s_{2,3}(q=0) &= -D_r \pm i\omega_0. \end{aligned} \quad (\text{A.18})$$

A.4.4 Discussion of complex roots

In Eq. A.12, as $\gamma < 0$, it is obvious that $n < 0$ for positive z . Then substitute negative n into Eq. A.6, easy to get $u > 0$ and $|u| > |v|$, so that $(u+v) > 0$. Considering roots structure in Eq. A.5, it suggests the real part of complex roots for Eq. A.11 is always negative, written as $\text{Re}[x_{2,3}] < 0$. Then substitute into Eq. A.10, obviously, the real part of complex roots for dispersion relation $f_q(s) = 0$ follows

$$\text{Re}[s_{2,3}] < -(Dz + 2/(3\beta\kappa)) < 0, \quad \text{for } \text{Im}[s_{2,3}] \neq 0. \quad (\text{A.19})$$

In summary, to find positive $s(q)$, we only need to consider real roots.

A.4.5 Discussion of $f_q(s=0)$

Define $f_q(s=0) := z h(z)$, then

$$h(z) = D^3 z^2 + (2\beta\kappa D^2 + \gamma D)z + [D\beta^2(\kappa^2 + 1) + \gamma\beta\kappa]. \quad (\text{A.20})$$

Obviously, $h(z)$ is a quadratic function and the coefficient of the quadratic term is positive, and the determination function is

$$\Delta_h = D^2(\gamma^2 - 4D^2\beta^2). \quad (\text{A.21})$$

The extreme point of $h(z)$ is at

$$\hat{z}_0 = -\frac{b_h}{2a_h} = -(2\beta\kappa D + \gamma), \quad (\text{A.22})$$

Figure A.2: Sketch of four kinds of $h(z)$.

and roots for $h(z) = 0$ are

$$\hat{z}_{1,2} = \frac{-(2\beta\kappa D + \gamma) \mp \sqrt{\gamma^2 - 4D^2\beta^2}}{2D^2}. \quad (\text{A.23})$$

Then four possible types of $h(z)$ can be classified and are sketched in Fig. A.2.

1) Type I is classified with criteria $h(z=0) < 0$, requiring

$$D < -\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, \quad (\text{A.24})$$

in which case

$$f_q(s=0) \begin{cases} \leq 0 & q \in [0, \sqrt{\hat{z}_2}], \\ > 0 & q \in (\sqrt{\hat{z}_2}, +\infty). \end{cases} \quad (\text{A.25})$$

2) Type II is classified with criteria $h(z=0) > 0$ and $\Delta_h < 0$, requiring

$$D > \max\left\{-\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, -\frac{\gamma}{2\beta}\right\} = -\frac{\gamma}{2\beta}, \quad (\text{A.26})$$

in which case $f_q(s=0) \geq 0$ for $q \geq 0$.

3) Type III is classified with criteria $h(z=0) > 0$, $\Delta_h > 0$ and $\hat{z}_0 < 0$, requiring

$$\max\left\{-\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, -\frac{\gamma}{2\beta\kappa}\right\} < De < -\frac{\gamma}{2\beta}. \quad (\text{A.27})$$

Here involves an implicit condition $-\gamma/(2\beta\kappa) < -\gamma/(2\beta)$, which requires

$$\begin{aligned} \kappa &> 1, \\ D &\in \left(-\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, -\frac{\gamma}{2\beta}\right), \end{aligned} \quad (\text{A.28})$$

in which case $f_q(s=0) \geq 0$ for $q \geq 0$.

4) Type IV is classified with criteria $h(z=0) > 0$, $\Delta_h > 0$, and $\hat{z}_0 > 0$, requiring

$$-\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1} < De < \min\left\{-\frac{\gamma}{2\beta}, -\frac{\gamma}{2\beta\kappa}\right\}, \quad (\text{A.29})$$

and involves the implicit condition $-\gamma\kappa/[\beta(\kappa^2 + 1)] < -\frac{\gamma}{2\beta\kappa}$, which requires

$$\begin{aligned} \kappa &< 1, \\ D &\in \left(-\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, -\frac{\gamma}{2\beta}\right). \end{aligned} \quad (\text{A.30})$$

In this case

$$f_q(s=0) \begin{cases} \geq 0 & q \in [0, \sqrt{\hat{z}_1}] \cup [\sqrt{\hat{z}_2}, +\infty) \\ < 0 & q \in (\sqrt{\hat{z}_1}, \sqrt{\hat{z}_2}). \end{cases} \quad (\text{A.31})$$

In summary, how the shape of $f_q(s=0)$ depends on parameters γ , β , κ and D is sketched in Fig. A.3.

Figure A.3: Sketch of $f_q(s=0)$.

A.4.6 Discussion of reflection points of $f_q(s)$

The reflection points of cubic function $f_q(s)$ are defined as the roots $s_{1,2}^*(q)$ of its derivative function $f'_q(s) = 0$, where

$$\begin{aligned} f'_q(s) &= 3s^2 + 2(3Dz + 2\beta\kappa)s + g(z), \\ g(z) &= 3Dz^2 + (4D\beta\kappa + \gamma)z + \beta^2(\kappa^2 + 1), \\ s_{1,2}^* &= \frac{-(3Dz + 2\beta\kappa) \mp \sqrt{-3\gamma z + \beta^2(\kappa^2 - 3)}}{3}. \end{aligned} \quad (\text{A.32})$$

Here we only consider the case where real $s_{1,2}^*$ exists.

Obviously, $s_1^* < 0$, so the sign of s_2^* is opposite to the sign of $g(z)$ ($f'_q(s)$ is a quadratic function with positive quadratic and linear term coefficients). Then a detailed discussion of quadratic function $g(z)$ gives the result that

$$\begin{cases} \kappa < \sqrt{3} & s_2^* < 0, \\ \kappa > \sqrt{3} & \begin{cases} D > -\frac{\gamma}{4\beta\kappa} & s_2^* < 0, \\ D < -\frac{\gamma}{4\beta\kappa} & \begin{cases} z \in [0, \tilde{z}_1) \cup (\tilde{z}_2, +\infty) & s_2^* < 0, \\ z \in (\tilde{z}_1, \tilde{z}_2) & s_2^* > 0, \end{cases} \end{cases} \end{cases} \quad (\text{A.33})$$

where $\tilde{z}_{1,2}$ are roots for $g(z) = 0$,

$$\begin{aligned} \tilde{z}_{1,2} &= \frac{-(4\beta\kappa D + \gamma) \mp \sqrt{\Delta_g}}{6D^2}, \\ \Delta_g &= \gamma^2 + 4\beta^2(\kappa^2 - 3)D^2 - 8\gamma\beta\kappa D. \end{aligned} \quad (\text{A.34})$$

A.5 Instability of dispersion relation

According to Sec. A.2, positive $\text{Re}[s]$ corresponds to unstable wave mode. According to Eq. A.19, the real part of complex root is always negative, so that we only need to consider real roots, which is convenient to discuss by sketch of $f_q(s)$. Applying the property that the coefficient of cubic term is positive, we can classify the shape of $f_q(s)$ and so that the roots structure as below

$$f_q(s=0) > 0 \begin{cases} q < q^* & (1) \text{ no positive root} \\ q > q^* \begin{cases} s_2^* > 0 & (2) \text{ two positive roots} \\ s_2^* < 0 & (3) \text{ no positive root} \end{cases} \end{cases}, \quad (\text{A.35})$$

$$f_q(s=0) < 0 \begin{cases} q < q^* & (4) \text{ one positive root} \\ q > q^* \begin{cases} s_1^* < 0 & (5) \text{ one positive root} \\ s_1^* > 0 & (6) \text{ three positive roots} \end{cases} \end{cases}, \quad (\text{A.36})$$

where sign of $f_q(s=0)$ is discussed in Sec. A.4.5; q^* is the critical point separates cases one real root plus two complex roots and three real roots, which is discussed in Sec. A.4.2; $s_{1,2}^*$ are reflection points of $f_q(s)$, which is discussed in Sec. A.4.6.

Then we analyse the existence condition for each cases. According to Sec. A.4.6, $s_1^* < 0$ satisfied as far as it exists, so Eq. A.36-(6) cannot exist, which also indicates as far as $f_q(s=0) < 0$, there exists one positive root.

Next, considering case Eq. A.35-(2), assuming $s_2^* > 0$, according to Eq. A.33, it requires $\kappa > \sqrt{3}$, $D < -\gamma/(4\beta\kappa)$ and $q \in (\tilde{q}_1, \tilde{q}_2)$. The domain of κ and D make sure $f_q(s=0)$ satisfying Eq. A.25, so that $f_q(s=0) > 0$ requires $q > \hat{q}_2$, however, according to Eq. A.23 and Eq. A.34, $\hat{z}_2 > \tilde{z}_2$ leads to blank domain for q therefore Eq. A.35-(2) cannot exist, which indicates as far as $f_q(s=0) > 0$, there is no positive root.

In summary, the number of positive roots only depends on sign of $f_q(s=0)$, where $f_q(s=0) > 0$ corresponds no positive root, and $f_q(s=0) < 0$ corresponds one positive root. Besides, how $f_q(s=0)$ depends on various parameters is illustrated in Fig. A.3.

A.6 Phase diagram

Recalling the physical background of the dispersion relation Eq. A.1, if a positive solution $s(q)$ is obtained in the domain $(0, q_c)$, it suggests an instability at infinite length scale which are supposed to result in MIPS. However, if positive solution $s(q)$ requires $q > q_c$ where $q_c > 0$, it suggests a fluctuation at finite length scale and corresponds to the dynamic clustering state. Lastly, no positive $s(q)$ suggests a stable homogeneous phase.

In this section, we fix $D = 28$, $D_r = 0.3$, applying results of Sec. A.5, exploring phase boundary consisted of ω_0 and ϕ , and using first order expansion of $\bar{v}_e$, then

$$\gamma = v_0^2 \left(1 - \frac{\phi^*}{2\phi_c}\right) \left(1 - \frac{\phi^*}{\phi_c}\right), \quad (\text{A.37})$$

and sketch result with parameters $v_0 = 24.0$, $\phi_c = 0.32$

As shown in Fig. A.3, no matter $\kappa < 1$ or $\kappa > 1$, the MIPS boundary is defined as

$$\begin{aligned} D &< -\frac{\gamma}{\beta} \frac{\kappa}{\kappa^2 + 1}, \\ \Rightarrow \omega_0 &< \sqrt{-\frac{\gamma D_r}{D} - D_r^2}. \end{aligned} \quad (\text{A.38})$$

However, finite wavenumber instability only exists for $\kappa < 1$ ($D_r < \omega_0$), thus requiring $D \in (-\gamma\kappa/[\beta(\kappa^2 + 1)], -\gamma/(2\beta))$, which corresponds to

$$\omega_0 \in \left(\sqrt{-\frac{\gamma D_r}{D} - D_r^2}, -\frac{\gamma}{2D}\right). \quad (\text{A.39})$$

Then we can draw the phase diagram as Fig. A.4, and show typical dispersion relations $s(q)$ inside three state, at boundaries and triple point.

Figure A.4: Phase diagram and corresponding dispersion relation.

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