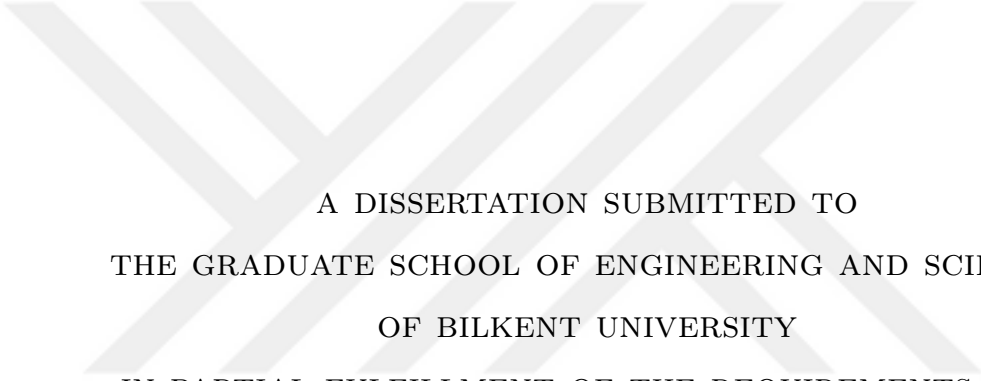


COMPLEX DYNAMICS OF SHEARED ACTIVE PARTICLE SUSPENSIONS



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By
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PENSIONS

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We certify that we have read this dissertation and that in our opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

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ABSTRACT

COMPLEX DYNAMICS OF SHEARED ACTIVE PARTICLE SUSPENSIONS

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Active systems, whether natural or artificial, have a unique ability to extract energy from their surroundings, driving themselves out of equilibrium. This capability gives rise to a variety of non-equilibrium phenomena such as swarming and clustering, creating potential uses for new materials and technologies. Among these active systems, we are particularly interested in the complex dynamics and the rheological behaviors of active colloidal suspensions and chiral active polymer chains when they are exposed to shear flow. In this sense, active Brownian dynamics (ABP), one of the most common computational methods, is used to study the complex dynamics of these active systems. In addition, the Multiparticle Collision Dynamics (MPCD) method is chosen to simulate in a computationally efficient way how the solvent dynamics, especially the resulting hydrodynamic effects, around these active systems behave.

Phase transitions and collective dynamics of active colloidal suspensions are fascinating topics in soft matter physics, particularly for out-of-equilibrium systems, which can lead to rich rheological behaviours in the presence of steady shear flow. The role of self-propulsion in the rheological response of a dense colloidal suspension is investigated by using particle-resolved Brownian dynamics simulations. First, the combined effect of activity and shear in the solid on the disordering transition of the suspension is analyzed. While both self-propulsion and shear destroy order and melt the system if critical values are exceeded, self-propulsion largely lowers the stress barrier needed to be overcome during the transition. We further explore the rheological response of the active sheared system once a steady state is reached. While passive suspensions show a solid-like behaviour, turning on particle motility fluidises the system. At low self-propulsion, the active suspension behaves in a steady state as a shear-thinning fluid. Increasing the self-propulsion changes the behaviour of the liquid from shear-thinning to shear-thickening. We attribute this to clustering in the sheared suspensions induced by motility. This new phenomenon of motility-induced shear thickening (MIST) can

be used to tailor the rheological response of colloidal suspensions.

Expanding the active Brownian dynamics simulation for particles of more complex shapes such as active polymers, we explore the complex formation of an active flexible polymer chain in linear shear flow in two spatial dimensions. The chiral head monomer is active and circling, while all other monomers are passive following both the motion of the head polymer and the shear flow. By the combination of activity, chirality and shear rate, a wealth of different states are found including the formation of a linear/complex folding and a spiralling state with both head-in and head-out morphologies. As the vorticity of the applied shear competes with the circling sense of the head, the chirality of the whole complex can be tuned by activity. Our results are relevant to characterize the response of living and artificial chiral active polymer chains to complex flow fields. These initial Brownian dynamics simulations of active polymer chains under shear flow did not account for hydrodynamic interactions (HI), which simplified the system to a dry environment influenced only by Gaussian-colored noises. Recognizing the potential impact of HI on the conformational and dynamical properties of these polymers, we advanced our study by incorporating shortly the hydrodynamic interactions using a hybrid Molecular Dynamics-Multiparticle Collision Dynamics (MD-MPCD) approach. In this way, we discuss the polymer dynamics and conformations for more realistic scenarios, observed in experiments. This hybrid approach is an improvement that captures the hydrodynamic effects of the solvent as well as thermal fluctuations. The swelling effect induced by HI is critical for these transitions, causing delayed conformational changes on the state diagram and preventing certain states already observed in the absence of HI. The results show that hydrodynamic interactions enhance linear folding and head-in spiraling states while suppressing complex folding and head-out spiraling. We could analyze simply the complex interplay between self-propulsion, shear, and hydrodynamics in active chiral polymer systems under shear flow, which will provide more realistic insights for future research and applications.

Keywords: Active matter, rheology, colloidal suspensions, polymers, chiral polymers.

ÖZET

AKTİF PARTİKÜL SÜSPANSİYONLARININ KESME AKIŞI ALTINDA KARMAŞIK DİNAMİKLERİ

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Aktif sistemler, doğal yada yapay, kendilerini denge dışına çıkarmak için çevrelerinden enerji çekme yetenekleriyle bilinirler. Bu yetenekleri sayesinde sürü ve kümelenme gibi çeşitli denge dışı olaylara yol açarak yeni aktif malzemeler ve teknolojiler tasarlamada potansiyel kullanımlar yaratır. Bu aktif sistemler arasında, özellikle aktif kolloidal süspansiyonların ve kiral aktif polimer zincirlerinin kayma akışına maruz kaldıklarında karmaşık dinamikleri ve reolojik davranışlarıyla ilgilendik. Bu anlamda, en yaygın hesaplama yöntemlerinden biri olan aktif Brownian dinamikleri (ABP), bu aktif sistemlerin karmaşık dinamiklerini incelemek için kullanıldı. Ayrıca, bu aktif sistemler etrafındaki çözücü dinamiklerinin, özellikle de ortaya çıkan hidrodinamik etkilerin nasıl davrandığını hesaplama açısından verimli bir şekilde simüle etmek için Çok Parçalı Çarpışma Dinamiği (MPCD) yöntemi seçilmiştir.

Aktif kolloidal süspansiyonların faz geçişleri ve kolektif dinamikleri, özellikle denge dışı sistemler için yumuşak madde fiziğinde ilgi çekici konulardır. Buna ek olarak bu sistemler sabit kesme akışının varlığında zengin reolojik davranışlara yol açabilir. Yoğun bir kolloidal süspansiyonun reolojik tepkisinde öz-itmenin rolü, parçacık-çözümlü Brownian dinamiği simülasyonları kullanılarak araştırıldı. İlk olarak, katıdaki aktivite ve kesmenin süspansiyonun düzensiz faza geçişi üzerindeki birleşik etkisi analiz edildi. Hem öz-itme hem de kesme düzeni bozar ve kritik değerler aşılsa sistemi eritirken, öz-itme geçiş sırasında aşılması gereken stres bariyerini büyük ölçüde düşürdüğü görüldü. Süspansiyon sabit bir duruma ulaşıldıktan sonra, aktif kesme sisteminin reolojik tepkisi araştırıldı. Pasif süspansiyonlar katı benzeri bir davranış gösterirken, parçacığın kendi aktif hareketliliğini açmak sistemi akışkanlaştırdığı görüldü. Düşük öz-itmede, sabit duruma geçmiş aktif kolloidal süspansiyon kesme inceltici bir akışkan gibi davranır. Kendiliğinden itmeyi artırmak, sıvının davranışını kayma incelmelerinden kayma kalınlaşmasına değiştirir. Bunu, hareketlilik tarafından tetiklenen

kayma süspansiyonlarındaki kümelenmeye bağlıyoruz. Bu yeni olay, hareketlilik kaynaklı kayma kalınlaşmasının (MIST), kolloidal süspansiyonların reolojik tepkisini ayarlamak için kullanılabilir.

Aktif Brown dinamiği simülasyonunu daha karmaşık şekilli parçacıklara, örneğin aktif polimerlere genişleterek, iki uzaysal boyutta doğrusal kayma akışında aktif esnek bir polimer zincirinin kompleks oluşturma durumunu inceledik. Kiral baş monomer aktiftir ve kiraliteden dolayı dairesel olarak hareket eder. Diğer monomerler ise pasiftir ve hem baş polimerinin hareketini hem de kayma akışını izleyerek hareket ederler. Aktivite, kiralite ve kayma hızının birleşimiyle, doğrusal/karmaşık katlanma ve hem baş içeri hem de baş dışarı morfolojilere sahip spiral gibi çok sayıda farklı durumlar ortaya çıkartır. Uygulanan kaymanın girdaplılığı başın kiral hareketi ile rekabet ettiği bu senaryoda, tüm kompleksin kiralitesi aktivite ile ayarlanabilir. Sonuçlarımız, canlı ve yapay kiral aktif polimer zincirlerinin karmaşık akış alanlarına tepkisini karakterize etmek için önemlidir. Kayma akışı altındaki aktif polimer zincirlerinin bu ilk Brown dinamiği simülasyonları, hidrodinamik etkileşimleri (HI) hesaba katmayarak sistemi Gauss renkli gürültüden etkilenen kuru bir ortama basitleştirmiştir. Fakat HI'nin bu polimerlerin konformasyonel ve dinamik özellikleri üzerindeki potansiyel etkisini fark ederek, çalışmamızı hidrodinamik etkileşimleri hibrit Moleküler Dinamik -Çok Parçacıklı Çarpışma Dinamiği (MD-MPCD) yaklaşımıyla dahil ederek ilerlettik. Böylece bu etkileşimlerin polimer dinamiklerini ve konformasyonlarını nasıl etkilediğine dair deneylerde gözlemlenen daha gerçekçi senaryolar için sonuçlar elde ettik. Bu hibrit yaklaşım ile, hem termal dalgalanmaları hem de çözücünün hidrodinamik etkilerini sisteme dahil ederek polimer dinamiklerinin daha doğru bir şekilde yorumladık. HI tarafından indüklenen şişme etkisinin bu konformasyonel geçişler için önemli etkilere sahip olduğunu gördük. Bu konformasyonel değişikliklerin durum diagramı üzerinde gecikmesine yol açtığını ve HI yokluğunda gözlemlenen belirli durumları engellediğini gözlemledik. Sonuçlar, hidrodinamik etkileşimlerin doğrusal katlanmayı ve baş-içeri spirallenme durumlarını desteklerken, karmaşık katlanmayı ve baş-dışarı spirallenmeyi bastırdığını göstermektedir. Aktif kiral polimer sistemlerinde kesme akışı altında kendi kendine tahrik, kesme ve hidrodinamik arasındaki karmaşık etkileşimi basitçe analiz ederek, gelecekteki araştırmalar ve uygulamalara ışık tutabilecek daha gerçekçi bilgiler elde etmiş olduk.

Anahtar sözcükler: Aktif madde, reoloji, kolloidal süspansiyonlar, polimerler, kiral polimerler.

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Chapter 1

Introduction

Active matter refers to systems composed of self-propelled entities, either natural or artificial, that continuously take energy from the environment and drive themselves out of equilibrium[4, 5]. This out-of-equilibrium state results in a range of unique phenomena, e.g. swarming and clustering, which are not possible to observe in equilibrium systems. The dynamics of active matter systems have gained substantial attention in recent years[6], both by academia and industry, due to not only their interesting non-equilibrium dynamics but also their prospective applications for designing novel smart devices and materials. Over the years, their study has evolved into a modern interdisciplinary research field nested between chemical physics, engineering, soft matter, robotics and biology[7, 8].

Originally, Reynolds and Vicsek et al. modeled the swarming behavior of the animals on a macroscopic scale using self-propelled particles[9, 10]. However, self-propulsion is also a common feature among microorganisms[11], allowing them to efficiently explore their environment for food or to escape predators and toxic substances. Bacteria like *Escherichia coli*[12] demonstrate a classic example of swimming behavior. On the other hand, recent advances in active matter have permitted the creation of artificial microswimmers and nanoswimmers that use a variety of propulsion systems to achieve self-propelling. Artificial self-propelled Brownian particles include Janus rods/spheres, chiral particles,

and vehicles. While passive Brownian particles move due to equilibrium thermal fluctuations caused by random collisions with the surrounding fluid molecules, self-propelled Brownian particles exhibit a combination of random fluctuations and active swimming[13, 14]. This drives them into a far-from-equilibrium state, which can only be understood through non-equilibrium physics. Therefore, they provide ideal (well-controlled) model systems for studying these non-equilibrium phenomena.

Self-propelled Brownian particles have a wide range of possible applications, with a focus on transport, sensing, and manipulation, etc. These microswimmers can complete tasks autonomously and selectively in specified locations. Despite the progress made in understanding active matter, the field is still full of open challenges in (i) understanding how active matter systems develop tunable behaviors that are not achievable by their equilibrium counterparts, and (ii) understanding the dynamics of active particles in real-life environments, such as within living tissues, where factors like randomness and crowding can either limit or boost the performance of biological and artificial microswimmers[5].

1.1 Active Colloidal Suspensions

Active colloids have been investigated [5] over the years since they provide a well-controlled testing ground for out-of-equilibrium systems. Experimentally, one among many realizations of active particles is active Janus colloids [5], which can show fascinating phenomena such as motility-induced phase separation [15, 16], vortex formation [17], clustering induced by hydrodynamic fluxes [18] or wall accumulation [19, 20, 21]. Dense suspensions of active particles have been realized and studied experimentally for Janus colloids[22], for vibrated active disks[23, 24] and theoretically [3, 25, 26]. Active particles that are in a glassy state [27] have given insights into random close packing [28] and it has been shown that shearing an active glass former leads to ordering [29]. However, the rheological properties of dense active colloids are largely unknown.

On the side of biological microswimmers, such as bacteria or microalgae, it has been shown that the presence of a small fraction of active swimmers in a fluid medium can fundamentally change the fluid’s rheological properties. It was found experimentally that pusher-type swimmers such as the bacterium *Escherichia coli* reduce the effective viscosity [30, 31, 32, 33, 34] while puller-type swimmers such as the microalgae *Chlamydomonas reinhardtii* can increase the viscosity [35]. This response to the swimming behavior has also been explained in theoretical and numerical studies [36, 37, 38, 39, 40, 41, 42, 43]. Further, the rheological properties of active fluids, that can model driven microtubules or active actin filaments, have been computed using field theoretical approaches [44, 45, 43, 46].

1.2 Active Polymers

Another big avenue of research in active matter systems is active polymers. Typical examples of active polymers[47, 48, 49] include living worms[50, 51, 52], filaments[53, 54, 55], artificial chains of granular[56] or colloidal particles[57, 58, 59, 60, 61, 62, 63] and flexible robots[64]. Many ubiquitous biological microswimmers, such as algae, bacteria, and sperm, are elongated structures, filamentous or polymer-like, exhibiting shape changes during movement[12, 4]. Additionally, some microswimmers, like *Bacillus subtilis* bacteria, organize into chain-like structures during the formation of biofilms[65]. Synthetic active particles have also been designed in various ways to function as artificial monomers. Phoretic effects due to the local gradients of, e.g., (i) electric fields (electrophoresis), (ii) concentration (diffusiophoresis) and (iii) temperature (thermophoresis) fields are used to activate these particles[66, 20, 67, 5].

In contrast to their passive counterparts, chains of active particles can serve as models for the integrated part of biological systems, *e.g.* bacterial swarms propelled by flagella. In these studies, activity is observed to play a crucial role in the formation of stable rotating spiral coils, as well as in controlling their folding and unfolding processes[68]. Other interesting new phenomena are activity-induced chain swelling[69, 70] and collapsing[69, 60] as well as the spontaneous

formation of spirals[71], and a change of the scaling exponents relative to passive polymers[72]. Moreover, although the influence of activity on stiff polymers is severe, it induces a transition from semiflexible-polymer behavior to flexible-polymer behavior, with increasing activity[73].

When passive polymers are exposed to shear flow, they start to tumble and the sense of the rotation of the whole chain is governed by the vorticity direction of the imposed shear field. The underlying physics is by now well understood[74, 75, 76, 77, 78, 79]. The behavior of sheared active polymer chains is more intricate and has been addressed only recently by theory and simulation[80, 81, 82, 83]. Novel properties of the polymer conformations induced by a combination of activity and shear have been reported including significant deviations from passive scaling laws. The combination of fluid-flow and active forces gives rise to fascinating phenomena in the swimming route of microorganisms, such as upstream swimming [84, 85] and vorticity migration[86]. Additionally, activity induces significant alterations in viscosity under shear flow, as observed in bacterial systems[32] and colloidal suspension[87]. This characteristic makes active polymers, or polymer-like structures, in natural life intriguing candidates as rheology modifiers.

1.3 Mesoscopic simulation of Active Polymers: Multiparticle Collision Dynamics (MPCD)

When considering practical scenarios, most experiments involving complex systems such as colloidal suspensions or polymer suspension are conducted in hydrodynamic environments[88, 89, 90]. In such environments, it is essential to account for hydrodynamics and hydrodynamic interactions (HI) between the particles in addition to the thermal fluctuations. The best way of doing that is to include the solvent effects explicitly in simulations. While hydrodynamic interactions are relatively trivial for static properties of particle systems at equilibrium, they become crucial for any dynamics in bulk or under confinement, especially in the

case of flow-induced structure formation.

However, it is generally computationally challenging to simulate these complex systems using traditional methodologies due to the coexistence of diverse lengths and time scales. For instance, colloidal or monomer particles are substantially larger (up to 10^{-6} m) than the atomic size of solvent molecules and, therefore, their relaxation time can be as long as 10 seconds, which is significantly longer than the solvent time scale (10^{-12} s)[91]. The use of a continuum description by the Navier-Stokes equation for these systems to encompass the hydrodynamics fails due to its lack of molecular details. On the other hand, atomistic molecular dynamics require resolving many microscopic degrees of freedom with extremely short time steps, making it impractical to study the long-timescale behaviour of the systems.

This difficulty has been addressed over the years by the development of mesoscopic simulation methods. In principle, these methods average out trivial microscopic details to increase the computational efficiency while retaining critical properties at relevant length scales of interest[92]. This technique simplifies the description of suspensions by adopting a coarse-grained model of solvent dynamics in which embedded (solute) macromolecules, such as polymers or colloids, are treated using traditional molecular dynamics simulations[93].

Although all the mesoscopic approaches for complex fluids are alternative ways of solving the Navier-Stokes equation and its generalization complemented by laws of mass, momentum and energy, among these models, such as lattice-Boltzmann methods[94, 95] and dissipative particle dynamics[96], Multiparticle Collision Dynamics (MPCD) is the most promising one. All these approaches are actually alternative solutions of the Navier-Stokes equation and its generalization. A particle-based mesoscopic simulation technique, Multiparticle Collision Dynamics was introduced by Malevanets and Kapral[1], which is well suited for studying complex fluids. It can be coupled to the dynamics of solute/embedded particles while taking into account both hydrodynamic interactions and thermal fluctuations[97, 98]. Another useful feature of the MPCD algorithm is the possibility of switching off the hydrodynamic interactions, allows us for straightforward

comparison of the system dynamics with and without long-ranged hydrodynamic interactions[92] in simulations. In addition, MPCD algorithm conserves energy locally as well as mass and momentum, enabling simulations in the microcanonical ensemble. Another significant feature of MPC algorithm is its well-defined dynamics for an arbitrary time step, Δt . Unlike other methods, such as molecular dynamics simulations or dissipative particle dynamics(DPD), which approximate the continuous-time dynamics of a system and require small time steps, MPC does not have this constraint. Additionally, the MPC algorithm can be modified easily to describe viscoelastic solvents/liquids by simply substituting the point particles of MPC with harmonic dumbbells, hence increasing its versatility and applicability to a broader range of systems[99].

The dynamical behaviour of macromolecules in solution is significantly influenced, or even dominated, by hydrodynamic interactions[100, 101, 102, 103]. While advances in experimental single-molecule techniques provide useful information about the dynamics of individual polymers, they also highlight the need for a quantitative theoretical framework to determine molecular parameters such as diffusion coefficients and relaxation times. Even, mesoscale hydrodynamic simulations can be used for validating these theoretical models. Even more, such simulations are particularly useful when analytical methods fail, such as in the case of more complicated molecules such as polymer brushes, stars, ultrasoft colloids, or semidilute solutions, in which hydrodynamic interactions are partially filtered in the system dynamics.

1.4 Thesis Layout

In Section 2, the mathematical model for active Brownian particles (ABPs) in a two-dimensional system is first described using stochastic differential equations, also known as Brownian dynamics equations. We briefly highlight the main differences between passive and active Brownian motion. Additionally, we illustrate their numerical solutions with a straightforward finite-difference algorithm, a first-order integration method that extends the Euler method to stochastic differential

equations. However, it is important to mention that higher-order algorithms can also be used. In the subsequent sections, we explain the use of the Brownian dynamics equations in detail for the specific active system under study. Afterwards, the mesoscopic approach, specifically Multiparticle Collision Dynamics (MPCD), used for explicit solvent is explained. This includes its version with the Anderson Thermostat (AT), which enables us to perform the simulations directly in the canonical ensemble. We discuss the validation of the simulation under flow conditions, employing both Poiseuille and Couette flows, and later we compare the resulting flow profiles from our simulations with the theoretical ones.

Chapter 3 investigates the rheological properties of dense active colloids in two spatial dimensions. Note that these colloidal particles in our model are different from biological microswimmers, which typically use their limbs to swim via mechanical motion, giving rise to long-range hydrodynamic interactions. Colloidal particles are moving in a self-generated gradient and in many cases, their hydrodynamic interactions are much smaller[104]. Investigating the strain-stress curves shows that activity reduces and even destroys the stress barrier that a shear flow has to overcome to fluidise the system. In the steady state, the system's shear stress reveals that particle motility fundamentally changes the rheological properties of the system: at none or low activity the system is shear thinning, for intermediate activities it becomes Newtonian and at very high activity it is shear thickening Fig.3.1. The shear thickening behaviour is induced by particle clusters that stem from the active motion of the particles. Therefore, we refer to this new phenomenon as *motility-induced shear thickening* (MIST). In fact, MIST is somehow a consequence of motility-induced phase separation (MIPS) [15, 16] in the bulk which shows a pre-clustering in the one-fluid phase even before full phase separation is reached. These clusters are responsible for the shear-thickening under shear. The full rheological response is further well characterized using a Herschel-Bulkley model for the stress as a function of the shear rate, which shows the continuous transition from shear thinning to shear thickening as the activity is increased. Therefore the rheological behaviour can be tuned by activity.

In Chapter 4, we consider a single active polymer in shear flow that has an imposed chiral head monomer such that this monomer is moving on a circle[105,

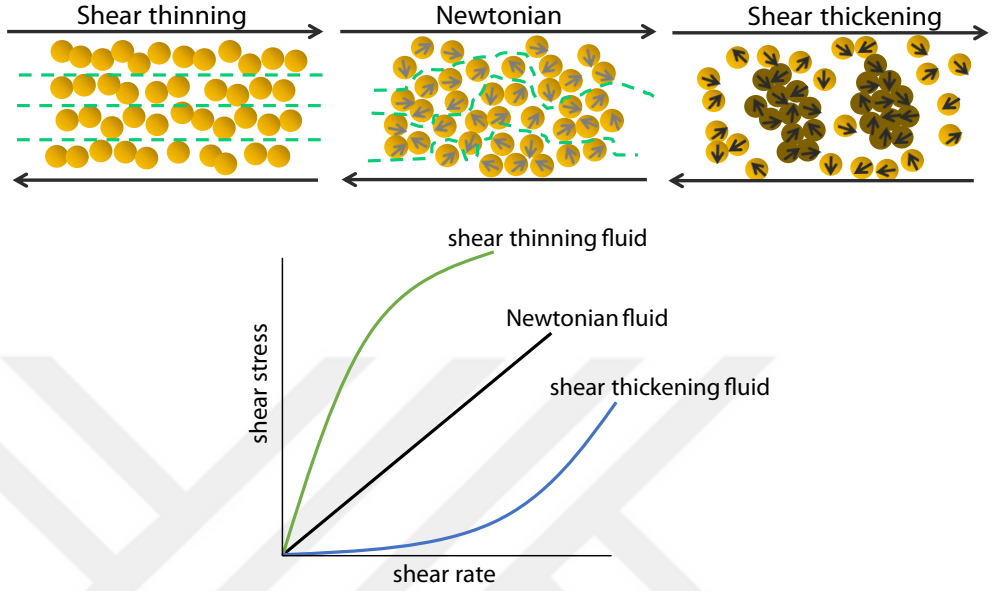


Figure 1.1: (a) Representation of the expected particle arrangements in different fluids and (b) shear stress-shear rate curve for different fluids.

106, 107, 108]. Here, we introduce the concept of chirality to a sheared active polymer. Instead of being self-propelled linearly leading to straight motion, active particles can also spin and circle[109]. There are two ways to connect chirality to active matter[110]: either already a single particle is chiral such that chirality is observed for the trajectories of individual particles[111, 112] or collections of non-chiral particles spontaneously self-organize into chiral structures[113, 114, 115, 71, 116]. In the first case, chirality is imposed, in the latter it is spontaneously emerging. The rest of the polymer chain is passive following the moving head but exposed to the shear flow. Therefore there is a combination and competition of activity, chirality and shear flow. Using monomer-resolved Brownian dynamics computer simulations in two dimensions, we explore the complex formation of such a flexible polymer chain. We find a plethora of different conformations including linear stretched complexes and spiralling states. The head monomer is either engulfed by the rest of the chain or rotating around the other monomers. As the vorticity of the applied shear competes with the circling sense of the head, the chirality of the whole complex can be tuned both by activity and the shear rate. Our results can be verified on artificial model granular or colloidal chiral chains exposed to shear and are of importance to characterize the response of

living chiral active polymers to complex flow fields.

After investigating the dynamics of dilute polymer suspension with a straightforward application of molecular dynamics simulations (MD) in Chapter 4, we also study the hybrid simulation, which combines the conventional molecular dynamics (MD) for monomers with Multiparticle Collision Dynamics (MPCD) for the solvent, in Chapter 5. In this hybrid approach, the MD simulations capture the solute-solute and solute-solvent interactions, while the MPCD method effectively models the solvent-solvent interactions, including both hydrodynamic interactions (HI) and thermal fluctuations. Our focus is on the dynamics of polymer chains in a sheared dilute solution, where the interactions between polymer chains are basically neglected, similar to a system already discussed in Chapter 4. In this chapter, we needed to expand the range of activities and shear rates for the analysis of the polymer chain conformations due to the revealed effect of hydrodynamics on the system dynamics. In this part of our study, we observe how HI affects the behaviour of polymer which promotes some conformations like linear folding and head-in spiraling while suppressing the head-out spiraling state. Additionally, we observe that the swelling effect induced by HI plays a critical role in the conformational transitions. The findings are illustrated by several state diagrams comparing the polymer conformations with and without HI, providing better understanding of the complex interplay between activity, shear rate, chirality and also hydrodynamic effects on the polymer dynamics and conformations.

The conclusion section of the thesis provide a final summary, including the main research objectives and our findings, providing connections from different chapters. We further highlight the potential contributions of our study to some fields and applications, including the suggestions for future research.

Chapter 2

General Models

2.1 Active Brownian Dynamics

Brownian dynamics is the most straightforward approach to studying the Brownian motion of real particles[117]. A particle immersed in a fluid undergoes diffusion because of the collisions with the surrounding fluid molecules. Each collision alters the velocity of the particle, which then drifts in a random direction until the next collision. After many such events, the direction and speed of the particle are effectively randomized. These interactions also ensure that the average kinetic energy of a particle remains at $k_B T/2$ for each degree of freedom, as stated by the equipartition theorem. The coefficients of diffusion (D) and friction (Γ) are closely connected to the average kinetic energy through the Einstein relation, expressed as $\Gamma D = k_B T$, where k_B is Boltzmann's constant and T is the temperature. The Langevin equation describing the motion of particles is:

$$m\ddot{\mathbf{r}}(t) = -\Gamma\dot{\mathbf{r}}(t) + \sqrt{2k_B T\Gamma}\mathbf{W}(\mathbf{t}) \quad (2.1)$$

where $\mathbf{r}$ is the particle position and m is its mass. The term on the left-hand side is the inertia term. The first on the right-hand side, $\Gamma\dot{\mathbf{r}}(t)$ is the friction term with a translational friction coefficient Γ . The second term $\sqrt{2k_B T\Gamma}\mathbf{W}(\mathbf{t})$ is fluctuating

force due to random impulses from the many neighboring fluid molecules, where $\mathbf{W} = [\mathbf{W}_x, \mathbf{W}_y, \mathbf{W}_z]$

Starting from this Langevin equation for the particle coordinates and discretizing the time into finite length steps Δt gives a first-order (Euler) update for the particle positions. Under the overdamped conditions, where the inertial term is dropped (e.g. $m = 0$) and in case more complex forces acting on particles, the equation (1) can be generalized to,

$$\dot{\mathbf{r}} = -\frac{1}{\Gamma} \mathbf{F}(r(t)) + \sqrt{2D} \mathbf{W}(t) \quad (2.2)$$

In the system of particles, particles interact via a potential U which gives rise to conservative forces $\mathbf{F}_i = -\frac{\partial U_{ij}}{\partial \mathbf{r}_i}$. This equation is then can be written as,

$$\dot{\mathbf{r}}_i = -\frac{1}{\Gamma} \sum_{i < j} \nabla_i U_{ij} + \xi_i \quad (2.3)$$

where ξ_i now denotes the Gaussian white noise mimicking the stochastic interactions with a thermal bath with a zero mean and variance $\langle \xi_i(t) \xi_j(t') \rangle = 2D_t \delta_{ij} \delta(t - t')$.

In passive Brownian dynamics, particles do not have any intrinsic motion and move only due to thermal fluctuations in the environment. Therefore, we can model the random and directed movements of Brownian particles by using the Equ.2.4.

Active Brownian dynamics, on the other hand, extends the concept of Brownian motion to active particles, those that consume energy taken from their environment to propel themselves[5, 118]. These particles exhibit self-propelled motion in addition to the random thermal forces present due to the solvent in passive systems. The active propulsion force is represented by an additional term (v_0) in the stochastic differential equations used in the active Brownian dynamics mathematical model. Brownian dynamics and active Brownian dynamics differ primarily in the following ways:

- Propulsion force: In active Brownian dynamics, particles are propelled in a specific direction by a propulsion force, which makes them move in a

more continuous and directed manner. Conversely, passive Brownian particles move due to random thermal forces, resulting in a more erratic and unpredictable motion.

- Persistent trajectories: Active particles, being self-propelled, tend to follow more persistent and directed paths. On the other hand, passive particles have completely random trajectories due to their lack of a driving force.
- Non-Equilibrium behavior: Active Brownian systems are always out of equilibrium because they constantly receive energy at the particle level. This leads to interesting phenomena like collective movement, swarming, and clustering. Passive Brownian systems, however, eventually reach thermal equilibrium and thus do not exhibit these types of collective behaviors.

Moreover, for active particles, a rotational equation of motion is necessary because they exhibit not only translational movement but also an additional inherent directionality due to self-propulsion. This directionality varies over time, and the rotational equation governs the orientation changes, ensuring accurate modeling of the self-propulsion in the simulations. Many active particles, like bacteria, periodically reorient themselves (known as tumbling) that change their direction in which they move. Understanding the complicated trajectories observed in experiments requires modeling these reorientation dynamics using a rotational equation[119, 120]. In general, active Brownian dynamics are more complex than passive Brownian dynamics because the equations of motion contain terms for both random thermal forces and active propulsion forces.

Additionally, the direction of active particles is frequently affected by their interactions with external fields, such as chemical gradients (chemotaxis) or light (phototaxis)[121]. These interactions are incorporated into the rotational equation of motion, which enables the modeling of directed movement in response to external stimuli. Rotational diffusion is caused by random rotational forces, η , which affect the orientation of active particles in a manner similar to how random thermal forces affect translational motion. A complete description of particle behavior is thus obtained by including these extra stochastic effects into the rotating

equation of motion.

Furthermore, the collective behavior of active particles, such as swarming, clustering, and pattern formation, are often resulted from the alignment and interaction of individual orientations. It is necessary to closely monitor particle orientations using the rotational equation of motion in order to accurately represent these interactions in the simulations. Therefore, to fully capture particle activity, including the direction and strength of their propulsion as well as their interactions and reactions to outside stimuli, rotational equation of motion is essential and must be included precisely.

Thereby, the overdamped translational and rotational equation of motion for active Brownian particles (ABPs) can be written by,

$$\dot{\mathbf{r}}_i = -\frac{1}{\Gamma} \sum_{i < j} \nabla_i U_{ij} + \xi_i + v_0 \mathbf{e}_i \quad (2.4)$$

$$\dot{\theta}_i = \eta_i(t) \quad (2.5)$$

The self-propulsion (or motility) has a constant magnitude of v_0 in the direction of a unit vector $\mathbf{e}_i = (\cos\theta_i(t), \sin\theta_i(t))$ [73, 60] for particle i . The orientation angle θ_i changes diffusively through η_i , which is a Gaussian white noise with zero mean $\langle \eta_i(t) \rangle = 0$ and variance $\langle \eta_i(t) \eta_j(t') \rangle = 2D_r \delta_{ij} \delta(t - t')$. The rotational diffusion coefficient D_r controls the strength of the rotational fluctuations.

Among numerical methods[122, 93], including simple finite-difference algorithms and more advanced techniques, Brownian dynamics provides a fundamental framework for understanding the random motion of particles due to thermal fluctuations, which are effectively described by stochastic differential equations[119]. Expanding this framework to active Brownian dynamics introduces an additional layer of complexity through the inclusion of self-propulsion forces (activity). However, active Brownian dynamics simulations is still the most commonly preferred tool, due to its relative simplicity, to explore the fascinating behaviors of active matter. It allows us to study their both transitional and rotational dynamics, revealing a rich variety of phenomena.

2.2 Multi- Particle Collison Dynamics(MPCD) for solvent dynamics

In this model, the solvent is represented by a large number N of point-like particles of mass m , without direct pairwise interaction, therefore they can overlap. This approach is commonly known as Stochastic Rotation Dynamics(SRD)[1], which is actually the initial version of the MPCD algorithm. The name of the algorithm is always based on its collision rule, which involves stochastic rotations of the relative velocities of the particles. However, there are various MPC algorithms, each characterized by different collision rules[92], and they are all named accordingly. Generally, the algorithm consists of two alternating steps describing the movement of the solvent particles: (i) *streaming* and *collision* steps, see in Fig.2.1. Mass, momentum and energy are transported by the streaming step and, then, the collision step redistributes these quantities among the particles to ensure the conservation of these quantities.

In the streaming step, all particles move ballistically and their positions are simultaneously updated according to Newton's equations of motion[1],

$$r_i(t + \Delta t_{MPC}) = r_i(t) + \Delta t_{MPC} v_i(t) \quad (2.6)$$

where r_i is the i th particle position and v_i is its velocity. Δt_{MPC} is the discretized time step.

In the subsequent step, the solvent undergoes multiparticle collisions. In order to achieve this, the particles are sorted into cells and interact only with the other particles within their cell. In our study, we use another version of MPCD, known as MPCD with Anderson Thermostat(MPC-AT), for the collision step since it offers several advantages over the standard SRD version. A key difference between SRD and MPC-AT is related to the relaxation times: in MPC-AT, the relaxation times generally tend to decrease as the number of particles per cell increases, whereas they increase in SRD. This characteristic of MPC-AT enables us to reach faster to the long-timescale system behaviors. The Anderson thermostat algorithm is already a robust thermostat via its collision step by replacing

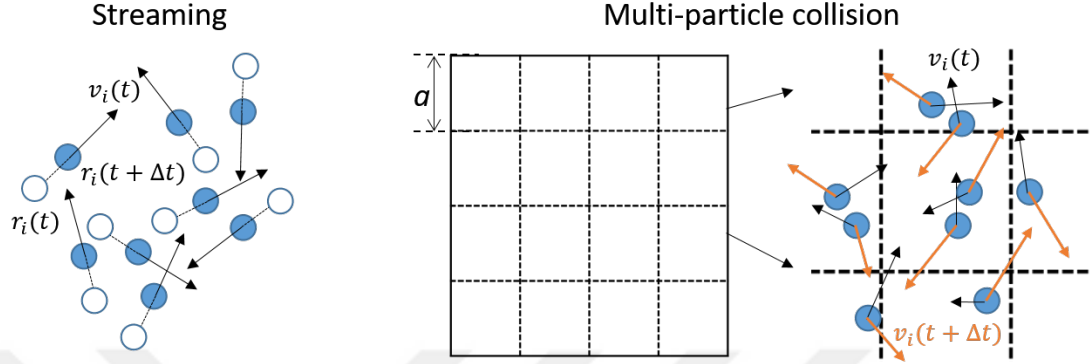


Figure 2.1: Schematic representation of Multiparticle Collision Dynamics (MPCD): streaming and collision steps, where r_i and v_i represent the particle positions and velocities, respectively, for particle i at any time t and $t + \Delta t$. Solvent particles are sorted into rectangular cells with a size a .

the term related to the relative velocities of particles in SRD algorithm with new Gaussian random numbers δv_i^{rand} generated at every time step with variance $\sqrt{k_B T/m}$. This is expressed by the following equation,

$$v_i(t + \Delta t_{MPC}) = u_{cm}(t) + \delta v_i^{rand} = u_{cm}(t) + v_i^{rand} - \frac{\sum_{j \in cell} v_j^{rand}}{N_c} \quad (2.7)$$

where $u_{cm}(t)$, is the center of mass velocity of all particles in a cell and N_c is the instantaneous number of particles in that collision cell at time t . Hence, MPC-AT functions both as a collision step and a thermostat, enabling simulations directly in the canonical ensemble without the need for additional velocity rescaling in non-equilibrium situations. Conversely, while SRD algorithm can be also used, it necessitates the application of an additional thermostat step at each time step, and the choice of thermostat can have a significant impact on the behaviour of the system. Previous studies comprising various thermostat schemes of SRD with MPC-Anderson thermostat have shown that Anderson thermostat performs well under all conditions[2, 123].

In our simulations, we adhere to commonly used simulation parameters as outlined in the literature[124, 2, 1, 125]. The total number of solvent particles, N , is determined based on the size of the rectangular domain (L^d) in a d -dimensional system. We ensure that the average number of particles per collision cell is $\rho = \Phi a^d/m = N(a/L)^d = 10$, where $\Phi = Nm/L^d$ is the mass density. Collision

cells are defined as unit cells with size a . We use $\tau = t\sqrt{k_B T / ma^2}$ and a as time and length scales, respectively, with the choice of $m = 1$, $a = 1$, $k_B T = 1$.

When the mean free path of fluid particles ($\lambda = \Delta t \sqrt{k_B T / m}$) is smaller than the collision cell size, the same particles may collide with each other many times within the same cell. This leads to correlated collisions, which is especially problematic especially at low temperatures or when using very small collision time steps. Therefore, because of these correlated collisions, the collision step of MPC can break Galilean invariance. To overcome this and restore Galilean invariance in the simulations, we shift particles by the same random vector with components uniformly distributed in the interval $[-a/2, a/2]$ before each collision step. This ensures uncorrelated collisions[126, 92, 127]. If λ is greater than $a/2$, the effect on Galilean invariance is minimal, and, therefore, this restoring procedure is unnecessary[2]. Furthermore, in the presence of solid walls, this shifting procedure causes an issue in which the solid boundaries do not align with the cell boundaries, resulting in partially empty cells near the walls. Lamura et al.[125] addressed this problem by adding virtual particles into these regions of the simulation domain. At each collision step, the required number of virtual particles is calculated simply by the difference between the mean number of particles and the actual number of particles in a cell, $N_{VP} = N_c - N_{remaining}$. Then, the velocities of virtual particles are generated from a Gaussian distribution with variance $k_B T / m$. There is no need to assign positions to these particles since they only participate in the collision step, and the positions are not relevant for this step.

We performed MPCD-AT simulations of solvent particles under two flow conditions, (i) Poiseuille and (ii) Couette flows. To validate our MPCD code under such conditions, we followed some studies in the literature[1, 2, 125] for the input parameters and then compared the simulation results with the analytical solutions of these flow profiles. In both cases, the analytical solution for the velocity profile is well-known.

2.2.1 Validation of MPCD simulations

2.2.1.1 Case 1: Poiseuille Flow

For Poiseuille flow between infinite parallel planes, we imposed a constant force g in the x direction and updated the streaming step accordingly. Streaming step in case of forced flow is given by,

$$r_i(t + \Delta t) = r_i(t) + \Delta t v_i(t) + \frac{g \Delta t^2}{2} \quad (2.8)$$

whereas the collision step remains unchanged. The analytical solution for Poiseuille flow is $v_x(y) = \frac{gy(L_y - y)}{2v}$, where L_y is the separation between the walls in the y -direction. Here, v is the kinematic viscosity which is calculated by the following equation and the simulation parameters used. It consists of a kinetic and collisional contribution as follows[128, 129, 130, 131] in d -dimensions,

$$v_{MPC-AT} = v_{MPC-AT}^{coll} + v_{MPC-AT}^{kin} = \frac{a^{d-1}(\rho - 1 + e^{-\rho})}{12\rho\Delta t} + \frac{k_B T \rho \Delta t}{\rho_m a^d} \left(\frac{\rho}{\rho - 1 + e^{-\rho}} - 0.5 \right) \quad (2.9)$$

Here, $\rho_m = 1/m$ is the mass density of the fluid.

For 2D validation, we followed the initial study of Malevanets et al.[1], simulating the flow within a rectangular domain of $L = 30a$. The bounce-back boundary conditions are employed due to the stationary nature of the solid walls, with the imposed force $g = 0.0013$. The collisional time step and the number of solvent particles are set to $\Delta t = 0.205\tau$ to match with the viscosity of the solvent and $N = 9000$ to ensure the mean number of particles per cell $\rho = 10$, respectively. Although this study is based on the SRD version, we are able to reproduce the correct flow profile in our simulations, as illustrated in Fig.2.2(a).

However, to validate our results also with the proper MPC-AT algorithm, we used the system in the extended study by Bolintineanu et al.[2] in 3D. Δt is set to 1.895τ , which corresponds to $v = 1.53a^2/\tau$. The system size of $L = 40a$ with the cell size of $2a$ and $N = 42240$ are used to ensure $\rho = 5.28$. For this case, the mean

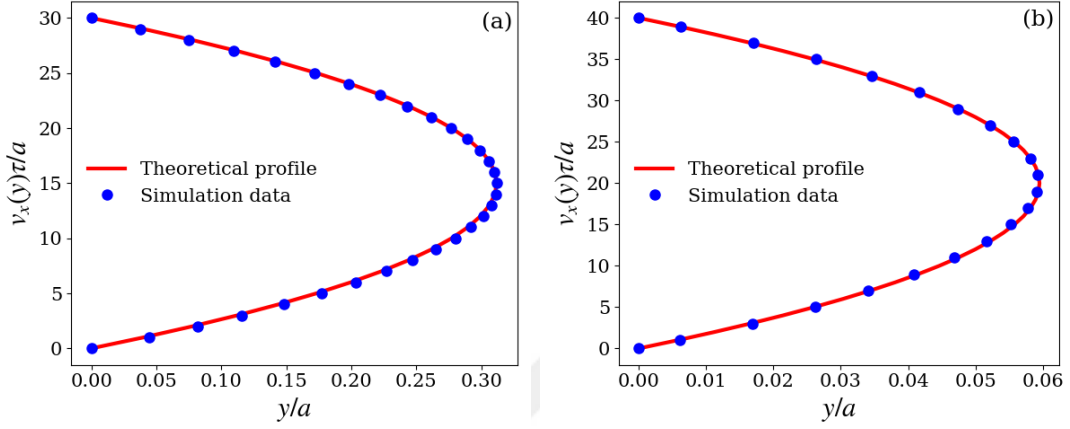


Figure 2.2: Validation of MPCD code for Poiseuille flow (a) in 2D ($g = 0.205$) [1] and (b) in 3D ($g = 0.0005$) [2]

free path of particles is sufficiently large ($\lambda > 0.6a$, therefore, the particle shifting procedure is not required. Consequently, we also reproduce the theoretical flow profile with this system and parameters (see Fig.2.2(b)).

2.2.1.2 Case 2: Couette Flow

As a next step, we focused on the Couette flow case due to the relevance of our shear flow studies in Chapters 3 and 4. The flow profile is implemented through the boundary conditions, with the top wall moving at a velocity of $v_{wall} = 0.5$ while the bottom wall remained stationary. Therefore, the streaming and collisional steps remained unchanged. the analytical solution for the velocity profile in this scenario is given by $v_x(y) = \frac{yv_{wall}}{L_y}$. For this case, we conducted the simulations in a rectangular box of $L = 30a$, and we turned on the particle shifting procedure in our simulations. We also used the same timestep ($\Delta t = 0.205$) of the 2D Poiseuille flow simulation. As a result, we obtained a Couette flow profile that precisely matched the analytical solution, as seen in Fig.2.3.

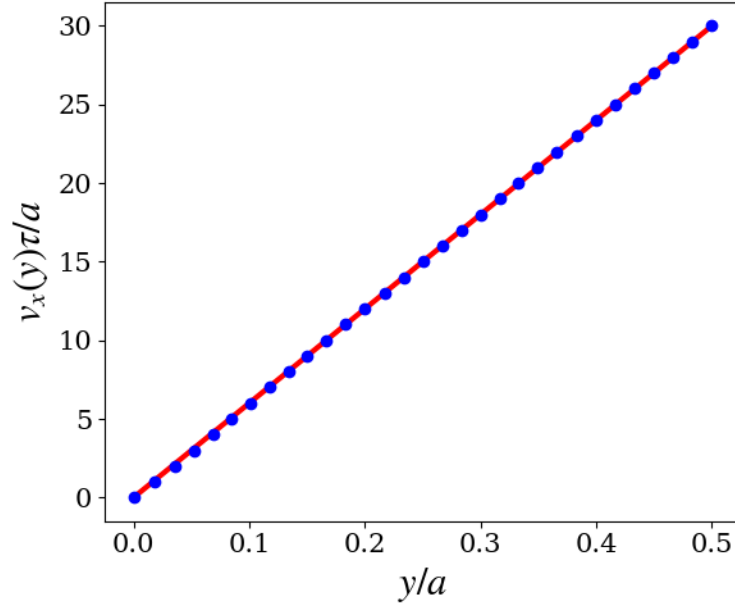


Figure 2.3: Validation of MPCD code for Couette flow in 2D ($v_{wall} = 0.5$).

Chapter 3

Motility-induced shear thickening in dense colloidal suspensions

We study a suspension of N self-propelled particles moving in two spatial dimensions under shear flow, Fig.3.1. In section 3.3.1, we introduce the model to be used for simulating this system, including the units and parameters used in it. We then describe in section 3.3.2 the observables that we measure in our simulation in order to analyse the phase and rheological response of the system for the different self-propulsion and shear forces. The results are then discussed in section 3.3.

3.1 Model

In two spatial dimensions, the over-damped dynamics of the colloids are modeled by active Brownian particles in the presence of a steady shear rate $\dot{\gamma}$ as,

$$\frac{d\mathbf{r}_i}{dt} = -\frac{1}{\Gamma} \sum_{i < j} \nabla_i U_{ij} + \xi_i + v_0 \mathbf{e}_i + \dot{\gamma} y_i(t) \mathbf{e}_x, \quad (3.1)$$

$$\frac{d\theta_i}{dt} = \eta_i(t) + \dot{\gamma}/2. \quad (3.2)$$

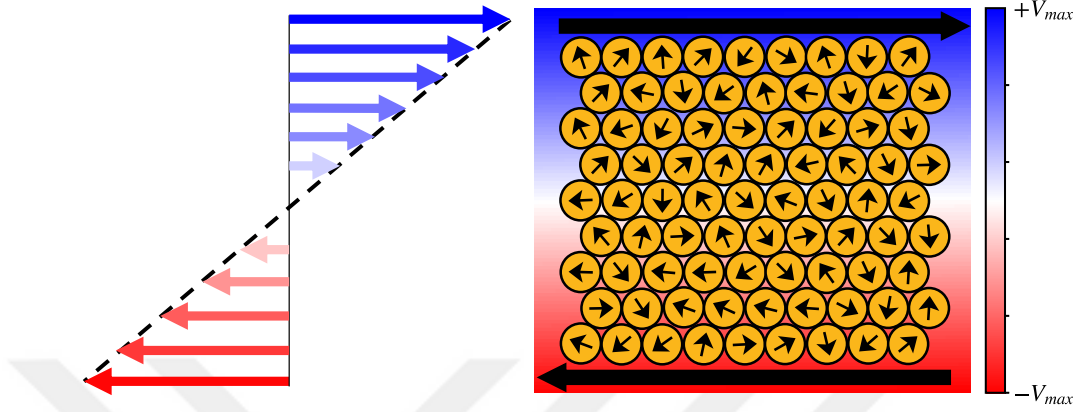


Figure 3.1: Schematic representations of the sheared active colloidal suspensions (the colour bar represents the distribution of shear force throughout the computational box)

Here, the second last term in Eq.(3.1) represents the imposed shear in the x direction (e_x is the unit vector pointing into the x direction) with respect to the position of particle i along the shear gradient direction y . Additionally, the second term on the right-hand side of Eq. 3.2 takes into account the effect of shear on the rotational motion of an isolated particle under shear flow[132]. Hydrodynamic interactions between the colloids are neglected.

The colloidal particles interact via a repulsive Yukawa potential

$$U(r_{ij}) = U_0 a \frac{\exp(-\lambda r_{ij}/a)}{r_{ij}}, \quad (3.3)$$

which is a potential commonly used in the case of charge-stabilized suspensions in two dimensions[133]. The screening parameter λ represents the range of the interaction between two limiting cases: (i) hard-core ($\lambda \rightarrow \infty$) and (ii) unscreened Coulomb ($\lambda \rightarrow 0$)[134] interactions. Moreover, $r_{ij} = |r_i - r_j|$ is the distance between two particle centers, a is a typical length scale taken as a unit of length determining the screening length as a/λ and U_0 is the bare potential strength.

We perform steady shear simulations for different number densities $\rho_N = N/\Omega$, the ratio of number of particles and the system area $\Omega = L_x L_y$, with periodic boundary conditions, schematically shown in Fig.3.1(a). The dimensions of the rectangular computational box are chosen as $L_x, L_y = (120a, 104a)$.

Three different numbers of particles $N = 14400, 10368$ and 8448 are used in the simulations corresponding to three different reduced number densities of $\rho_N a^2 = 0.68, 0.83, 1.15$. The bare potential strength is fixed to $U_0 = 800k_B T$ and the simulations are started from a hexagonal crystal configuration of the particles. Further, a soft potential with the screening parameter $\lambda = 3.5$ is chosen. The time step for the evolution of the particle positions is $\Delta t = 0.0001\tau_0$, with the natural unit of time $\tau_0 = a^2/D_0$. The colloid-colloid pairwise interactions are cut off at an inter-particle distance of $2a$ and the rotational diffusion coefficient is $D_r = 3.5\tau_0^{-1}$. After an initial relaxation time of $t = 0.4\tau_0$, shear is imposed.

3.2 Observables

3.2.1 Phase transition

The structural changes in the system are monitored by two-dimensional bond orientational order parameters[135],

$$\psi_\nu = \left| \frac{1}{N} \sum_{i=1}^N \frac{1}{\nu} \sum_{j \in \mathcal{N}(i)} e^{i\nu\theta_{ij}} \right|^2 \quad (3.4)$$

where $\mathcal{N}(i)$ is the set of ν nearest neighbour particles of the i th particle and θ_{ij} is the angle between the bond vector pointing from particle i to j and horizontal fixed axis.

Bond-orientational order describes how bonds between particles or atoms are arranged and oriented within a material. This concept is particularly useful for assessing the degree of order in particle systems, especially those in transient phases between solid and liquid states, such as liquid crystals, glasses, and certain colloidal systems[3, 136, 137]. Variations in their bond-orientational order parameter indicate the possible phase transition in these particle systems (see Fig.3.2). For $\nu = 6$ the order parameter is the hexatic order parameter ψ_6 , which is close to zero in the disordered phase (liquid-like) whereas it equals 1 in a perfect

hexagonal crystal (solid-like). Similarly, we also analyse the tetratic orientational order using ψ_4 .

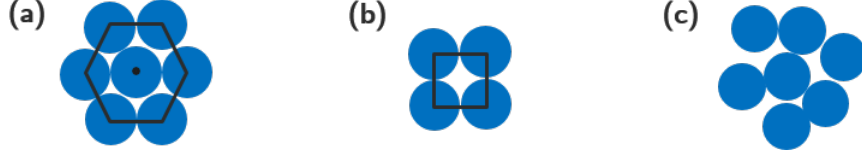


Figure 3.2: (a) Perfect hexagonal crystal ($\psi_6 = 1$), (b) perfect square crystal ($\psi_4 = 1$) and (c) disordered liquid ($\psi_{6,4} = 0$).

3.2.2 Rheology

The shear stress, which is the off-diagonal component of the stress tensor, is measured by

$$\sigma_{xy} = -\frac{1}{2\Omega} \sum_{i=1}^N \sum_{i>j} \frac{\partial U}{\partial r_{ij}} \frac{r_{ij}^x r_{ij}^y}{r_{ij}} \quad (3.5)$$

r_{ij}^x and r_{ij}^y are the distance between the centers of two particles i and j in direction of x and y , respectively. The stress is nondimensionalised by considering the thermal energy $k_B T$ and length scale a as $\sigma_{xy} a^3 / k_B T$, where k_B is the Boltzmann constant and temperature T with $k_B T = D_0 \Gamma$ resulting from the near-equilibrium fluctuation-dissipations relation. We note that the definition of shear stress in Eq.(3.5) is the generalization of the passive to the active case and therefore it is some kind of nonequilibrium effective shear stress. The dynamics of the system is controlled by two dimensionless numbers.

- (i) First, the imposed shear rate is given by *the shear Peclet number*, $Pe_s = \dot{\gamma} a^2 / D_0$, which measures the ratio of the shear force to thermal fluctuations.
- (ii) The second dimensionless number is *the active Peclet number*, $Pe_a = v_0 a / D_0$, which measures the ratio between the self-propulsion force (or the motility strength) and thermal fluctuations.

The typical magnitude of the dimensionless numbers considered here are $Pe_a \in [0, 150]$ for the active Peclet number and $Pe_s \in [0, 40]$ for the shear Peclet number. For each measured quantity, we collect the data from 12 independent runs for each free parameter (Pe_a, Pe_s) .

3.3 Results

3.3.1 Melting by the combined action of shear and activity

Our particular interest is the characterization of self-propelled particles in the dense regime, $\rho_N a^2 = 1.15$. We first analyze the instantaneous shear-stress-relation, i.e. the relation between σ_{xy} and the imposed strain ($\gamma = \dot{\gamma}t$), at a constant shear rate $Pe_s = 20$ for different self-propulsions. In parallel, we also monitor the bond-orientational order parameters of the system. We note that the results represented here show the system behaviour starting immediately from the time we impose the shearing force ($t = 0.4\tau_0$).

In the absence of particle motility ($Pe_a = 0$), the system starting out of the perfect hexagonal crystal stays in this solid-like phase during the relaxation, as documented in Fig.3.3 snapshot(1). When shearing is turned on thereafter, shear stress starts building up to a peak value, i.e., point (2) in Fig.3.3(a) which brings the system to the onset of melting. At this point, the system is not disordered yet and we discuss this structural transition in detail later on. Here, this nearly linear increase in the shear stress represents that the system response is nearly elastic at low strains. Further accumulation of the strain melts the crystal and, accordingly, causes a release of stress due to structural relaxation. This brings the system to a strain-independent plateau at higher strains. We can associate this best with the shear-induced disordering transition where the equilibrium melting transition is displaced by the imposed shear rate[138, 139, 140].

Moreover, the self-propulsion helps to cause a preliminary melting, which appears as a decrease in ψ_6 during the relaxation of the system. This fastens the hexagonal-liquid transition and consequently decreases the stress barrier, which is defined by the shear stress peak. Much higher activities ($Pe_a \geq 30$) melt the crystal entirely even before imposing the shear rate, thereby annihilating the stress barrier. After that, the colloidal suspension is disordered and its behaviour is liquid-like [in Fig.3.3 snapshot(3)]. In the latter case, the equilibrium melting transition is significantly displaced by self-propulsion and melting is thus expected for the parameters used to define the colloidal interactions [3, 141, 142, 143].

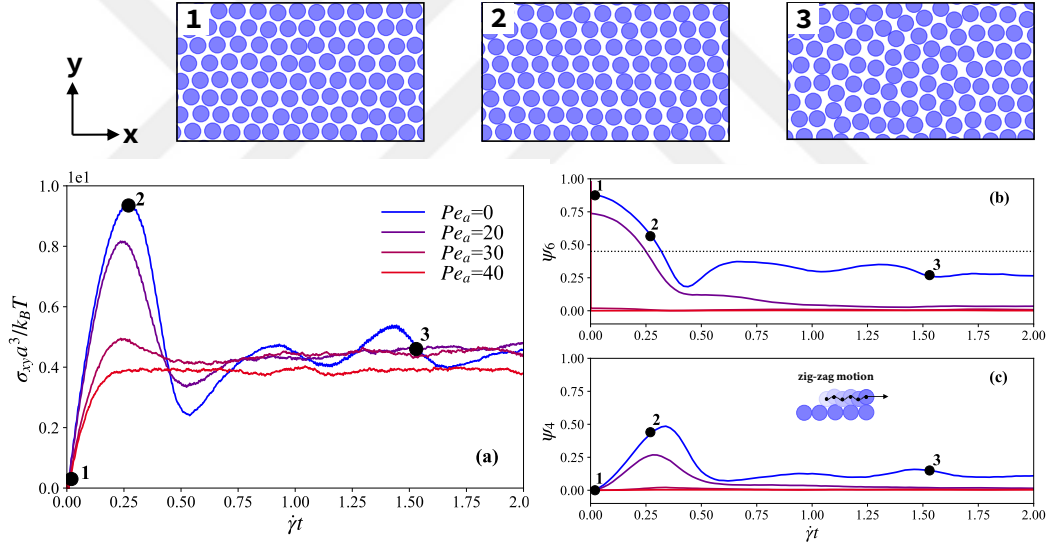


Figure 3.3: (top) Snapshots of particle configurations for (1) solid-like, (2) cubic-like and (3) liquid-like phases of the passive system, in which the system conditions correspond to the numbered black dots in the plots: (a) The instantaneous shear stress (σ_{xy}) with respect to strain ($\gamma = \dot{\gamma}t$) for passive ($Pe_a = 0$) and active systems ($Pe_a > 0$) at a constant shear rate $Pe_s = 20$. The corresponding structural changes throughout the bond orientational order parameters, ψ_6 (b) and ψ_4 (c). The black dotted-horizontal line defines the position of structural transition for the hexagonal configuration, $\psi_6 \approx 0.45$ [3]. The inset in (c) shows the representation of the zig-zag motion of a colloidal particle under shear. A colloidal particle follows a zig-zag-like trajectory (black dashed line) while moving to the right direction over the particle layer underneath due to the imposed shear.

Points (2) in Fig.3.3(a) and (b) together reveal that the stress peak appears just before the drop of ψ_6 below the structural transition, $\psi_6 = 0.45$ [3]. In fact, the

solid-to-liquid transition is not direct throughout this barrier but rather occurs via a structural rearrangement [Fig.3.3 snapshot(2)]. The zigzag motion of the particles, which emerges by their alternating motion in one layer between filling the grooves of the next layer and hopping up from there[144, 145], temporarily gives a rise in ψ_4 [see Fig.3.3 (c)]. We might expect this increase of ψ_4 at first sight when we look at the arrangement of particles in the snapshot (2). Additionally, even in the liquid regime below $\psi_6 < 0.45$, where the shear melts the crystal as a whole, some ordered regions show up at times due to this zig-zag motion of the particles in subsequent layers. This is similar to what was observed by Wu et. al.[146] in melting passive colloidal suspensions under shear. Although these ordered structures give rise to local increases in the hexagonal order parameter in the passive system below the structural transition line [see Fig.3.3(b)], the self-propulsion destroys these local ordered structures, resulting in zero ψ_6 .

Furthermore, we see that the subsequent melting first starts with local disruptions of the ordered structures, similar to the so-called interstitial defects[140] observed in purely shear-induced disordering. We located the position of defects by an analysis of the Voronoi cells. Voronoi cells with five or seven neighbour edges are indicative of defect positions. For the passive suspension at the shear rate $Pe_s = 20$, the defects appear due to the disordering effect of the shear (see Fig.3.4(a)). We see here that the suspension is able to restore the defect at one region while creating another one at another region. Therefore, the defects are not able to grow and the system stays in a solid-like regime. On the other hand, in an active suspension, there are two forces in the system for the hexagonal-to-liquid transition: (i) shear and (ii) self-propulsion. The presence of the self-propulsion inhibits the disappearance of the defects, creating also some additional defects at the same time. In this way, the interstitial defects can grow and spread around the domain as the activity increases, resulting at the end in the enhanced melting of the system. This scenario is confirmed by Fig.3.4(b), where the Voronoi diagram for $Pe_a = 20$ is illustrated.

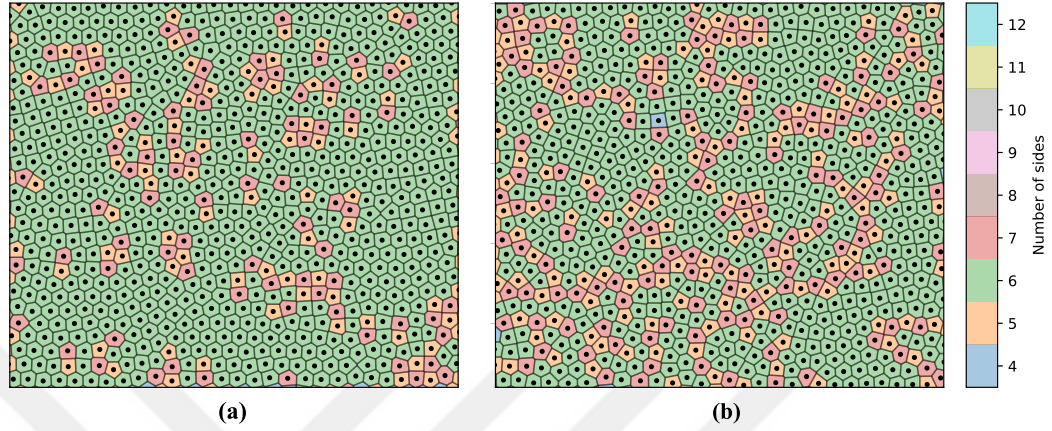


Figure 3.4: The Voronoi diagrams for the colloidal suspension at the same shear rate ($Pe_s = 20$) for (a) $Pe_a = 0$ (i.e, the passive case) and (b) $Pe_a = 20$. These diagrams illustrate the accumulation of disordered regions (symptoms of the presence of defects) with increasing activity, resulting in an enhanced melting of the colloidal suspension

3.3.2 Motility-induced shear thickening (MIST) and shear thinning

We now consider the liquid regime and discuss the time-averaged shear stress $\overline{\sigma_{xy}}$ with respect to the imposed shear rate $\dot{\gamma}$ [see in Fig.3.5(a)], which yields the rheology of the active colloidal suspensions. Note that the shear stress data are time averaged over the steady state time frame corresponding to the strain-independent plateau of the stress and the minimum shear rate is $Pe_s = 1$ in Fig.3.5(a).

We use the common Herschel-Bulkley model[147] to quantify the possible non-Newtonian behaviour where $\sigma_{xy} = \sigma_0 + K\dot{\gamma}^n$ with σ_0 representing the yield stress. A shear thinning liquid is characterized by power indexes $n < 1$, while for a shear thickening liquid $n > 1$. As a special case, $n = 1$ represents the classical Newtonian liquid. In Fig.3.5(b) we fit our stress-shear rate simulation data for different activities to this model. Thereby, we explore the effect of the self-propulsion on the rheological response of the system. Here, we analyse the active colloidal suspensions starting with $Pe_a \geq 40$ where the suspension is entirely in a

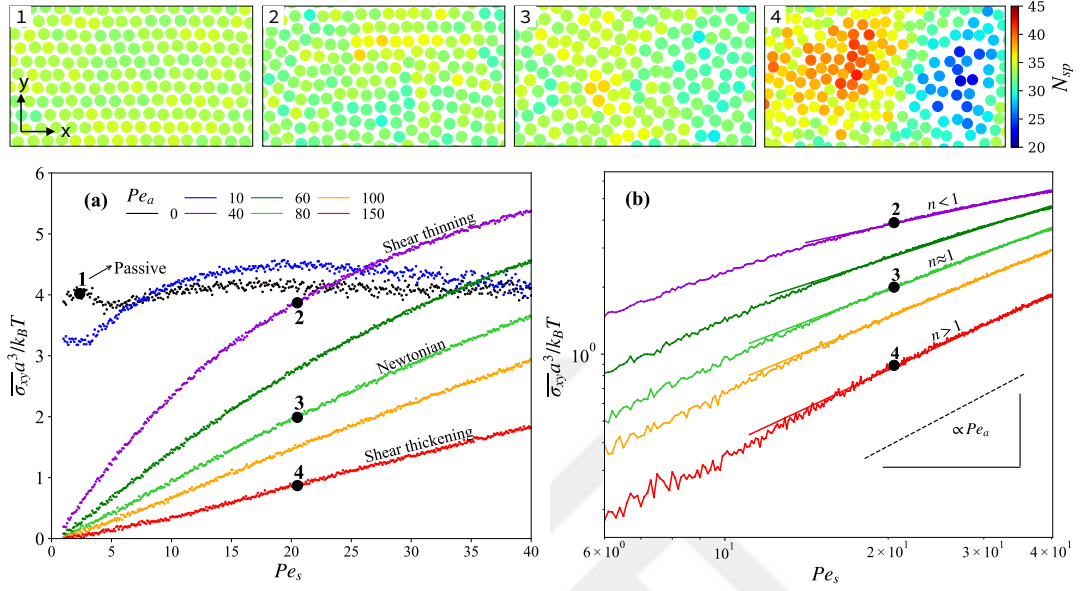


Figure 3.5: (top) Snapshots of particle configurations: (1) solid-like, (2) shear-thinning, (3) Newtonian and (4) shear-thickening, where the particles are coloured with respect to their number of surrounding particles (N_{sp}). (a) Nondimensional shear stress $\overline{\sigma_{xy}}$ - shear rate $\dot{\gamma}$ curves for $Pe_s \geq 1$ at different self-propulsion forces. (b) Liquid-like regime shown in log-log scale where the Herschel-Bulkley model-fitting has been applied is indicated by the fitting lines for different rheological behaviours with respect to the corresponding power indexes(n). The numbered black dots represent the conditions of the simulations where the snapshots are taken. The corresponding viscosity curves are shown in Fig.3.7.

liquid phase with $\psi_6 = 0$. For the passive and low activity (i.e., $Pe_a = 10$) cases, the suspension has still local crystals meaning that $\overline{\psi_6}$ cannot reach zero. In these cases, we cannot apply the Herschel-Bulkley model if $\overline{\psi_6} > 0$ since the rheology of the suspension becomes more complex, allowing plateau or non-monotonic behaviour in the shear stress versus strain rate curve. For this solid-like regime at the passive and weakly active suspensions, we simply reproduce Fig. 3(a) by indicating the corresponding time averaged hexagonal order parameter $\overline{\psi_6}$ of the colloidal suspension at different shear rates and self-propulsions. Looking at $\overline{\psi_6}$ values here in Fig.3.6, we see that the passive suspension and the low activity case (i.e., $Pe_a = 10$) cannot reach a fully liquid regime ($\overline{\psi_6} = 0$) over the shear range worked in this study. For these two cases, some ordered regions are still present in the suspension at different shear rates. The degree of order depends on the

dominant mechanism (either shear ordering or disordering) at the corresponding shear rate. Starting with $Pe_a > 0$, activity helps the shear in disordering the system, but it still cannot melt the suspension homogeneously until reaching $Pe_a \geq 40$. Therefore, we obtain a different rheological response for these two cases compared to the active suspensions with $Pe_a \geq 40$. On the other hand, the active suspensions ($Pe_a \geq 40$) homogeneously show liquid behaviour ($\overline{\psi}_6 = 0$) with a rheological response that can be modelled by using the Herschel Buckley constitutive relationship.

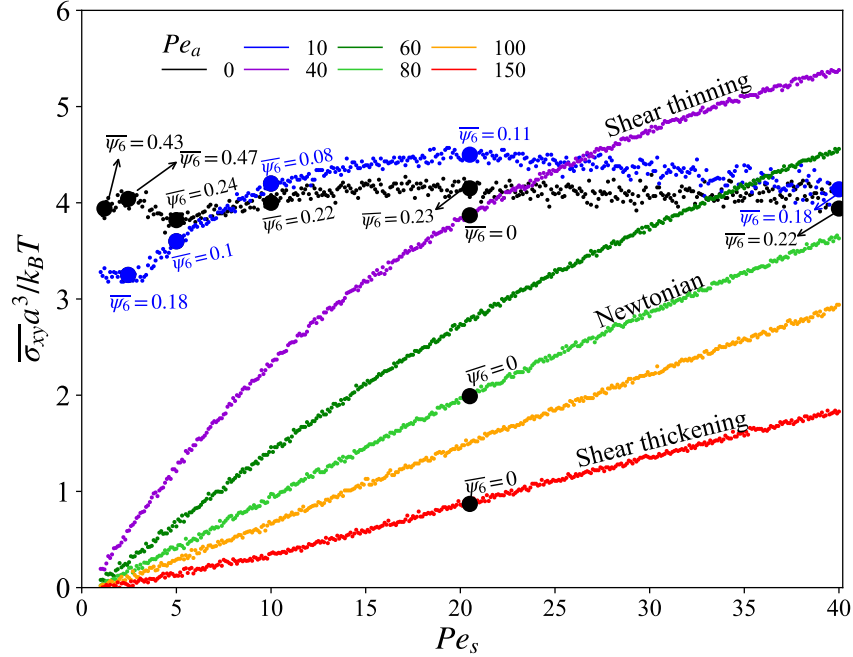


Figure 3.6: The nondimensional shear stress $\overline{\sigma_{xy}}$ - shear rate $\dot{\gamma}$ curves for the passive ($Pe_a = 0$) and self-propelled ($Pe_a > 0$) systems. Note that the shear rates are shown starting with $Pe_s \geq 1$. This figure is equivalent to Fig. 3a of the main manuscript but with adding the value of $\overline{\psi}_6$ found for different values of the shear rates.

Moreover, we follow up the structural changes by the number of surrounding particles N_{sp} , which is the number of particles counted inside the surrounding circle with a radius $r_{surr}/a = 3$ for every particle individually [see the top snapshots in Fig.3.5]. In this way, we better distinguish the occurrence of clustering and, accordingly, the onset of shear thickening in the system with increasing self-propulsion strength.

The passive system, initially in the crystalline phase, does not melt at very low shear rates ($Pe_s < 2.5$) and shows solid-like behaviour [Fig.3.5(1)] with non-zero yield stress $\sigma_0 a^3/k_B T \approx 4$, see Fig.3.5(a). This is in line with what Chen and Zukoski demonstrated for passive ordered suspensions[144]. Here, thermal fluctuations are responsible for the motion of colloids. At this solid regime, we see that turning on the activity diminishes the yield stress. In addition to weak activities, the hexagonal order in the system can be destroyed by more effective shearing, above the so-called critical shear rate[148, 140]. However, we note that in these weak activities, the phase transition of the suspension is not fully completed because shear can also induce ordering, which is known as a flow-induced crystallization phenomenon in colloidal suspensions[149, 150].

On the other hand, activities $Pe_a > 30$ eliminate the solid-like behaviour giving $\bar{\sigma}_0 = 0$, since the hexatic-to-liquid transition is already reached by activity [see again in Fig.3.3(b)]. Thereafter, the resulting melt starts behaving as a shear-thinning liquid which is a non-Newtonian behaviour characterized by the slopes lower than 1 ($n < 1$), see point (2) in Fig.3.5(b). Here, the shear force has control over the motion of the particles and yields sliding layers of particles aligned in the direction of shear flow [snapshot 2 in Fig.3.5]. Indeed, this layered flow, which is also discussed in Section 3.3.1, has been previously found as being intrinsic to the shear thinning behaviour of passive Brownian colloidal suspensions[144, 151, 152]. Moreover, local ordered regions are temporarily observed as a result of the zig-zag motion of colloids, which is also a shear-induced ordering phenomenon seen in 2D shear-thinning colloidal suspensions[153]. Although the shear thinning behaviour is relatively well understood in Brownian colloidal systems, the effect of self-propulsion has not been addressed. We observe that activities up to $Pe_a \approx 80$ assist only the shear in melting the system, while the resulting melt maintains the same shear-thinning behaviour observed for passive suspensions.

Interestingly, we find that increasing the self-propulsion force triggers the rheological response of the suspension and changes qualitatively the behaviour albeit in a smooth way. At moderate motilities, $Pe_a \approx 90$, the fluid behaviour is not shear-thinning, but Newtonian, corresponding to the curves (3) with an exponent

$n = 1$ in Fig.3.5(a,b). In this regime, self-propulsion degrades the stability of layered flow and the suspension becomes completely disordered, see snapshot (3) in Fig.3.5. Similar to the mechanism discussed in Section 3.3.1, some of the interstitial defects appeared in the shear-thinning liquid which spread with increasing self-propulsion, being responsible for the loss of thinning.

Above $Pe_a \approx 100$, we observe that the self-propulsion starts dominating over shear and reveals structural heterogeneities in the system, leading to transient cluster formation as shown by the snapshot (4) in Fig.3.5. In this case, the slope of shear stress- shear rate curves exceeds 1 [see (4) in Fig.3.5(b)], meaning that the suspension changes crossover from Newtonian to shear thickening behaviour. Here, we also observe that the colloidal suspension starts showing clusters even before imposing a shear to the system, which is expected for active particles in this parameter regime [154]. However, we found that these clusters enable the system to behave as a shear-thickening fluid when the system is forced to flow. Therefore, we refer to this behaviour as *motility-induced shear thickening* (MIST) in some analogy to motility-induced phase separation (MIPS). In fact, the cluster formation generating MIST is a precursor of MIPS, which has been seen starting at a critical self-propulsion of about $Pe_{a,cr} \approx 90$. Additionally, especially for this behaviour, we observe visually that the number of surrounding particles N_{sp} remarkably differs from region to region in the system [see snapshot (4) in Fig.3.5].

The shear thinning-to-thickening transition has been attained for years in passive colloidal suspensions with very high shear rates ($Pe_s > 100$), by underlining similar cluster formations in the shear-thickening fluid due to the hydrodynamic interactions and lubrication forces[155, 145, 156, 157]. In this study, instead, we could reach this transition by keeping the range of shear rate constant at relatively low values, while increasing the activity of colloids, with neglecting hydrodynamic interactions. In this work, the cluster formation is not triggered by shearing extremely the system, rather it is triggered by motility.

Additionally, the thinning-to-thickening transition in the fully liquid-like regime, we show here the apparent shear viscosity, $\eta = \overline{\sigma_{xy}}/\dot{\gamma}$, as a function of Pe_s for $Pe_a \geq 40$. As already illustrated by Fig.3.5(b), Fig.3.7 confirms that a

change in the regime between shear thinning and shear thickening occurs around $Pe_a = 90$.

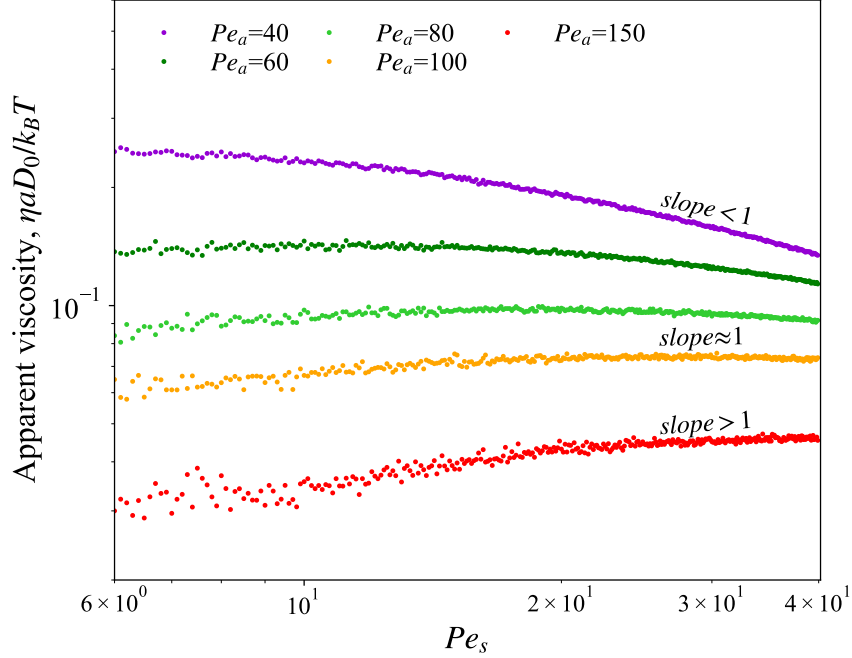


Figure 3.7: The apparent shear viscosity ($\eta = \overline{\sigma_{xy}}/\dot{\gamma}$) with respect to the shear rate $\dot{\gamma}$ at different self-propulsion strengths ($Pe_a \geq 40$).

3.3.3 The effect of particle density

Next, we analysed the stress-shear rate curves for the suspensions with two lower particle densities, a semi-dilute suspension $\rho_N a^2 = 0.83$, and a dilute suspension $\rho_N a^2 = 0.68$, respectively, achieved by lowering the number of particles in the simulation box while keeping all other parameters the same. Obviously, lowering the density creates more disorder in general. Thus, the solid behaviour is found as limited to very small parameter ranges. Consequently, a dilute suspension shows lower yield stresses compared to the dense case at the same activities. Fig.3.8 shows the effect of the particle density on the stress barrier during the melting of the passive colloidal suspensions in Fig. 3.8(a). We obtain a lower stress peak (or barrier) at the initial period of shearing in the dilute suspensions. This proves the tendency of the dilute system for disordering which makes the melting

process easier for the suspension. On the other hand, when we compare these two passive systems on the shear stress - shear rate plot [see Fig. 3.8(b)], they both show a solid-like behaviour, but with different yield stresses. Here, since the dilute system melts more easily than the dense one for the same parameters, its behaviour comes closer to the liquid-like regime.

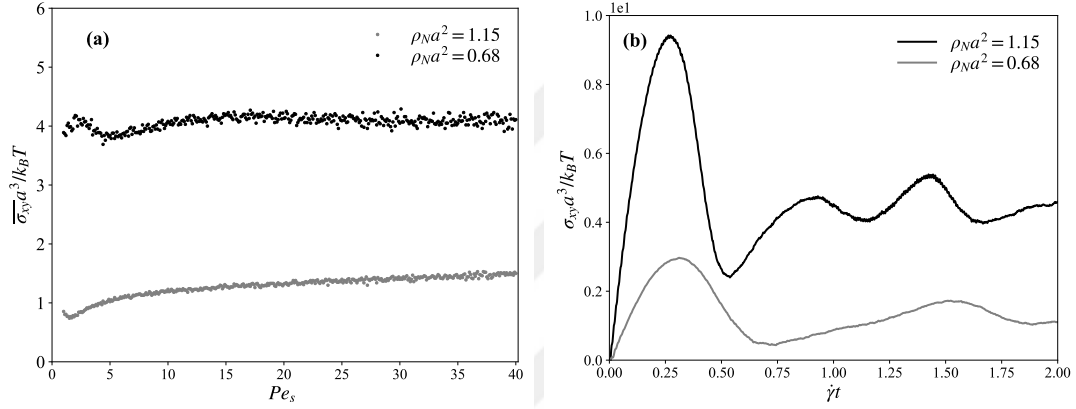


Figure 3.8: (a) The nondimensional shear stress $\overline{\sigma_{xy}}$ - shear rate $\dot{\gamma}$ curves for the passive ($Pe_a = 0$) systems and (b) the instantaneous shear stress (σ_{xy}) with respect to strain ($\gamma = \dot{\gamma}t$) at a constant shear rate $Pe_s = 20$ with different particle densities.

Accordingly, the system starts showing a shear thinning behaviour even with very low self-propulsion forces. Fig.3.9 summarizes the trend of the power index n with increasing self-propulsion for all cases. Here, again, the exponents are obtained by fitting the shear stress/shear rate data to the power law model for these two other densities, as done for the dense system in Section 3.3.2. The red line in this figure, which corresponds to the dense suspension case, starts at $Pe_a \approx 30$, since the system retains mostly solid-like behaviour below this value, followed by shear-induced disordering with increasing activity.

Regarding the liquid-like regime, it is evident that the critical self-propulsion ($Pe_{a,cr}$) for the shear thinning to thickening transition shifts to lower activities with decreasing particle density. In other words, dilute suspensions can thicken easier than dense ones. The underlying reason for this effect can be intuitively related to clustering. Keeping the particles very close to each other, as in a

dense system, obviously pronounces their collisions. Therefore, possible cluster formation becomes difficult in the system. Although some clusters are formed with these activities, they are not stable enough, such that they can be damaged by any strike from other particles around them. However, increasing the self-propulsion further promotes clustering and finally brings the system into a thickening regime. As we discussed previously, activity triggers the colloidal suspension to behave as a shear-thickening fluid.

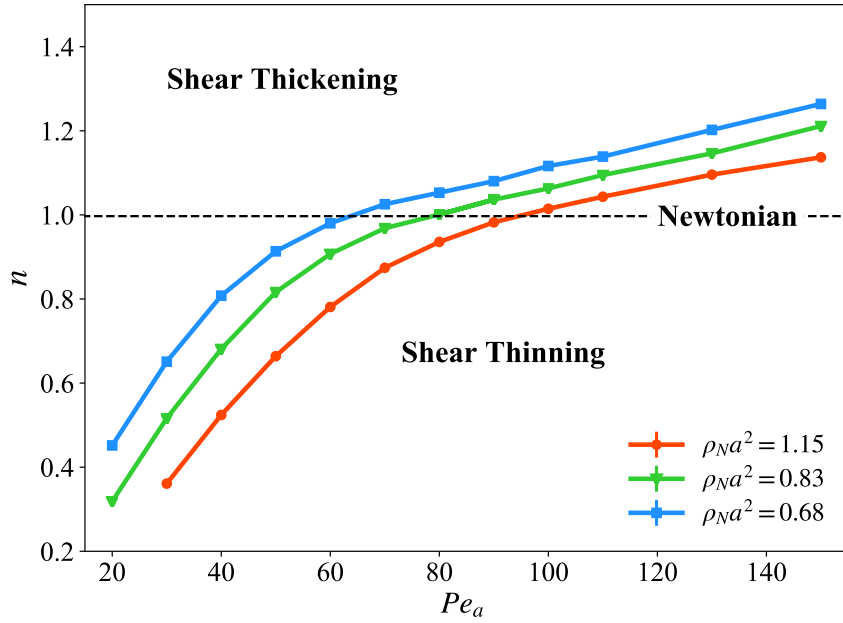


Figure 3.9: The power index n vs the active Peclet number Pe_a for different particle densities. The horizontal dashed line corresponds to the Newtonian case with a slope of 1 on a log-log scale.

Conversely, active colloids in a dilute environment can constitute more stable clusters even with low self-propulsion due to fewer repulsive collisions coming from particles around the clusters, accordingly undergoing this thinning-to-thickening transition earlier [see Fig.3.9].

This scenario is also confirmed by Fig.3.10, where we report the standard deviation of the time averaged number of surrounding particles $\sigma_{\bar{N}_{sp}} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\bar{N}_{sp,i} - \langle \bar{N}_{sp} \rangle)^2}$ (in which $\langle \bar{N}_{sp} \rangle = \frac{1}{N} \sum_{i=1}^N \bar{N}_{sp,i}$) vs the active Peclet

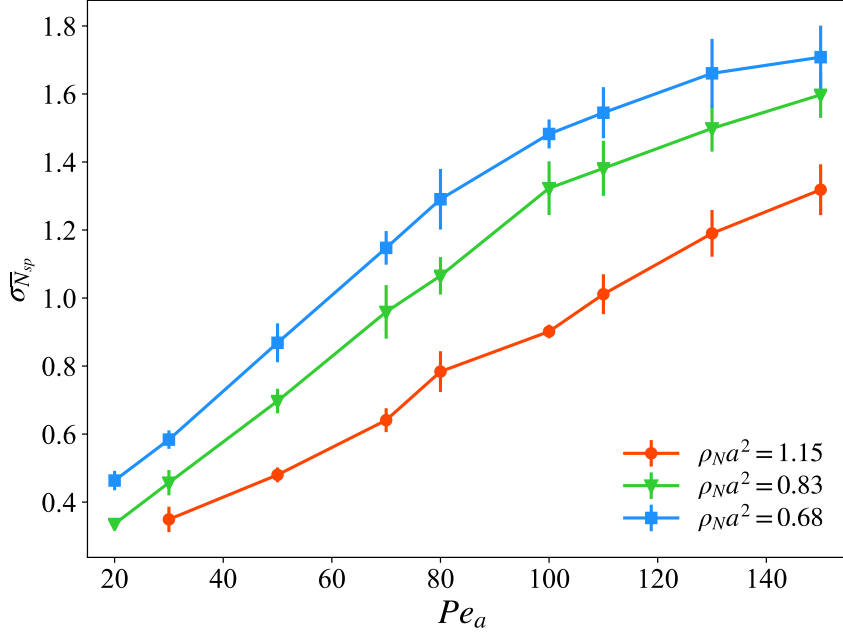


Figure 3.10: Standard deviation of the time averaged number of surrounding particles, $\sigma_{\overline{N}_{sp}}$, vs the active Peclet number Pe_a for different particle densities, $\rho_N a^2 = 1.15$ (circle), $\rho_N a^2 = 0.83$ (triangle) and $\rho_N a^2 = 0.68$ (square) at $Pe_s = 30$.

number Pe_a for the three different densities. Here, to quantify the cluster formation in the liquid regime, we use N_{sp} since the parameters ψ_4 and ψ_6 are more connected to the ordered structures of the solid crystals. Typically there are more fluctuations in the surrounding particle density for dilute systems, also for weak self-propulsion forces. However, here the activity enhances dramatically (i) the local density inhomogeneities, as revealed by the strong increase of $\sigma_{\overline{N}_{sp}}$ with Pe_a , and (ii) the gap in $\sigma_{\overline{N}_{sp}}$ between dilute and dense systems. The motility-induced local density inhomogeneities correspond to pre-clustering which provides evidence that this is the underlying reason for the shear-thickening behaviour consistent with snapshot (4) in Fig.3.5. Since this pre-clustering is more pronounced for dilute systems, the MIST transition occurs earlier in these systems confirming our previous intuitive explanation.

Chapter 4

Dynamics of an active chiral polymer in shear flow

After exploring the effect of self-propulsion on the rheological response of the dense colloidal suspensions under steady shear by Brownian dynamics simulations [87], we extend our simulation to particles of more complex shape than spheres; active polymers. In this section, we study an active polymer chain with a chiral head under linear shear flow, as schematically illustrated in Fig. 4.1 with blue arrows indicating the flow gradient in the y -direction. In Section 4.1, we explain the model employed to simulate this system and the description of the simulation parameters utilized in the system simulation. Here, the active Brownian dynamics equations of motion include different terms for passive and active particles.

4.1 Model

We use Brownian dynamics to model a linear polymer chain, described as a sequence of N_m coarse-grained spring beads in two spatial dimensions. We label each monomer by an integer index i where the active head monomer has $i = 1$ and all other passive monomers are indexed with $i = 2, 3, \dots, N_m$. In the presence

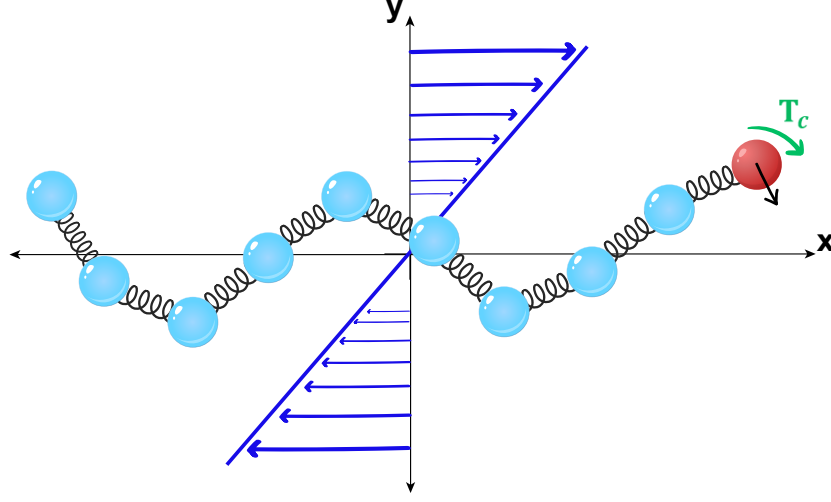


Figure 4.1: Schematic of an active bead-spring polymer with a chiral head (red monomer) in the linear flow. The blue monomers are passive. The black arrow on the head monomer represents the direction of the active force and the green arrow depicts the direction of head chirality. The flow is imposed along the x -axis and the gradient is in the y -direction whose variation is shown by blue arrows.

of a steady shear rate $\dot{\gamma}$, the translational motion of the passive monomers ($i \neq 1$) in the overdamped limit is given by

$$\dot{r}_i = -\frac{1}{\Gamma} \sum_{\substack{j=1 \\ j \neq i}}^{N_m} \nabla_i U_{ij} + \dot{\gamma} r_{i,y} \mathbf{e}_x, \quad (4.1)$$

and the motion of the active head monomer is described by

$$\dot{r}_1 = -\frac{1}{\Gamma} \sum_{j=2}^{N_m} \nabla_1 U_{1j} + \dot{\gamma} r_{1,y} \mathbf{e}_x + v_0 \mathbf{e}_h, \quad (4.2)$$

where $r_i = (r_{i,x}, r_{i,y})$ denotes the position vector of the i -th monomer. The second term on the right-hand side of the equations is the uniform linear *shear flow* imposed in the x -direction with unit vector $\mathbf{e}_x$ such that the shear gradient is along the y -axis. Since the chiral head monomer ($i = 1$) is active, it moves additionally with the constant active speed v_0 in the direction described by the unit vector $e_h = (\cos\theta_h, \sin\theta_h)$ [73, 60] which we refer to as *activity*. Here θ_h denotes its orientational angle with the x -axis. Then its translational equation

of motion can be written as Eq. 4.2. The orientation of the head monomer is governed by the rotational equation of motion[158],

$$\dot{\theta}_h(t) = -\frac{\dot{\gamma}}{2} - T_c. \quad (4.3)$$

In this study, the subscript h is used in the rotational equation of motion to distinguish the head monomer from other monomers. Again, $\dot{\gamma}/2$ denotes the shear torque the shear flow creates on the head monomer. T_c is an additional torque that is intrinsic to the head monomer which we refer to as the head *chirality*. This torque controls how fast the orientation of the head monomer does change and, consequently, it can set the whole complex into overall rotation. It can be realized experimentally in various ways. For instance, the head monomer can carry a dipole moment and brought into rotation either by a rotating magnetic field[159, 160, 161] or by circularly polarized light[162].

The first term on the right-hand-side of Eqs. (1) and (2) accounts for all the conservative forces acting on the i -th monomer, including the excluded-volume and bond interactions. The excluded-volume interactions between the monomers are described by a smooth repulsive Weeks-Chandler-Andersen (WCA) potential[163],

$$U_{WCA}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon, & r \leq 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma. \end{cases} \quad (4.4)$$

Here, σ is the diameter of the monomers and ϵ is the interaction strength. The spring connection of neighboring monomers is introduced via a FENE (finitely extensible nonlinear elastic) potential[164, 60],

$$U_{FENE}(r) = -\frac{1}{2}KR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], \quad (4.5)$$

where i and j are the neighboring beads with their distance being $r_{ij} = |r_i - r_j|$. The spring constant is $K = 27\epsilon/\sigma^2$, while the maximum allowed bond length is $R_0 = 1.5\sigma$. The FENE potential has distinct characteristics of a maximal extension/compression than harmonic potential, although they yield similar outcomes at a specific distance denoted as R_0 . Additionally, when combining the FENE potential with the WCA (Weeks-Chandler-Andersen) potential, it ensures that a

polymer chain does not intersect itself or any other chains in systems with multiple polymers. This approach allows for an accurate representation of a crucial property of polymers[165].

In the Brownian dynamics simulations, we use σ and ϵ as our units of length and energy, respectively, while we measure time in units of the characteristic time $\tau_0 = \Gamma\sigma^2/\epsilon$. The number of monomers in the polymer is set to $N_m = 20$. The overdamped equations of motion, Eqs. (4.1-4.3), have been integrated with a small finite time step $\Delta t = 10^{-4}\tau_0$, assuming periodic boundary conditions. The dimensions of the computational box are chosen as $L_x, L_y = (80\sigma, 40\sigma)$. The dimensionless activity is $v_0\tau_0/\sigma$, which varies in the range of $[0.1, 100]$, while the dimensionless shear rate $\dot{\gamma}\tau_0$ is chosen in the range of $[0.01, 50]$. Additionally, positive values of both the dimensionless shear rate and the external torque in Eq. (4.3) rotate the head monomer clockwise, as shown in Fig.1 but we also use negative values of the dimensionless shear rate for the analyses in Section 4.2.4. Even in the absence of noise, the system runs into a dynamical state which does not depend on the initial conditions, it is this state which we shall analyze in the sequel.

4.2 Results

Equipped with a chiral head, the active flexible polymer chain exhibits various conformational states under shear flow. The shear triggers the translational motion of the chain by affecting similarly all the monomers. Thus, the polymer chain tends to move aligned with the flow. Since the chiral head monomer is active, its rotational motion is also affected by the vorticity created by the shear, so that it circles due to both shear torque and its head chirality. Although shear vorticity may also affect the passive monomers, this influence is countered by the spring-like connections within the chain. The resulting conformation of the polymer chain under the combined action of shear and head chirality remains dependent on the active speed of the head monomer.

This section elucidates the conformational states of an active polymer chain, their dependence on the head chirality and the interplay between shear vorticity and head chirality. We also address the rheological properties. In Sections 4.2.1-4.2.5, we analyze the system in the case of vanishing translational and rotational diffusion coefficients, while in Section 4.2.6, we consider a more practical scenario for the active polymer chain by including environmental fluctuations.

4.2.1 Combined effect of head activity and shear rate on the polymer conformation

We examine a flexible polymer chain that has an active head with a constant clockwise chirality of $T_c/\tau_0 = 2$. While the chiral head circles, all other passive monomers both (i) follow the head monomer via the connecting polymer bonds and (ii) flow with the shear. We demonstrate the various states of the polymer chain that are observed in response to both head activity and shear flow.

We identify two main regimes: *folding* and *spiralling* for the shear-dominated and activity-dominated cases, respectively, which are observable only when the head monomer is active. Here, the activity leverages the chiral motion of the head, thereby controlling the polymer regimes under shear flow (see Fig. 4.2). Applicable to all states, we observe a range of conformational diversity as activity increases at the same shear rate. However, the diversity remains consistent with increasing shear rates along the same activity line.

In the range of low ratios of $v_0/\dot{\gamma}\sigma$ up to intermediate values, we observe the shear-dominated regime, in which the chain folds into two distinct forms: *linear folding* and *complex folding*. In the linear folding regime, a weak activity can only initiate a subtle clockwise rotation, aligned with the chirality of the head monomer. Subsequently, the head monomer is entrained by the negative flow field beneath the centerline, inducing movement of the chain along the flow. This results in the folding of the chain (depicted by ► in Fig. 4.2), where the further rotation of the head monomer halts by the passive tail.

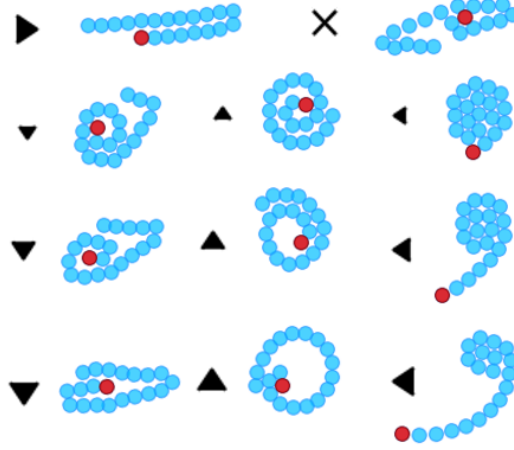
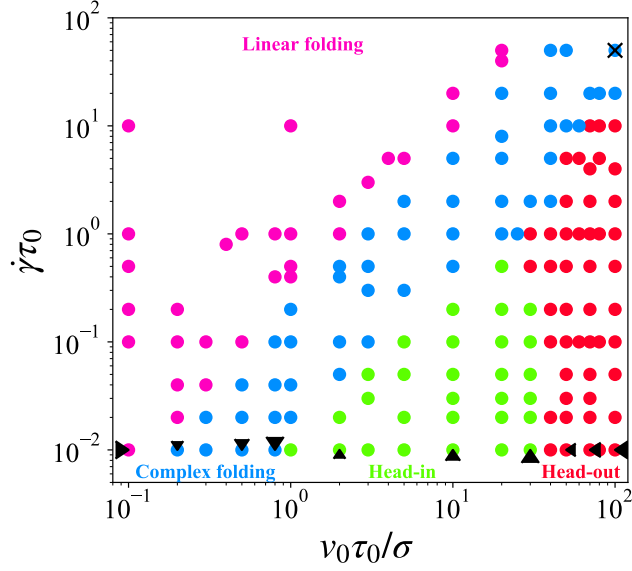


Figure 4.2: State diagram of the active polymer chain conformations as a function of activity $v_0\tau_0/\sigma$ and shear rate $\dot{\gamma}\tau_0$ when the chirality of the head monomer is set to $T_c/\tau_0 = 2$: linear folding (magenta), complex folding (blue), head-in spiralling (green) and head-out spiralling (red). The conformational diversity of the states is demonstrated underneath the diagram and their positions are marked by black symbols in the state diagram.

As the activity increases, reaching intermediate ratios of $v_0/\dot{\gamma}\sigma$, the swirling motion of the head monomer becomes more intense, exerting greater influence over the entire chain. In this case, when the head folds the chain once, the rotation of the head is not blocked by the passive monomers it encounters along its path. Instead, the head monomer pushes and rearranges the passive monomers around itself, leading to the formation of a complex folding pattern (indicated by all ▼ in Fig. 4.2). Here, the head monomer becomes surrounded by the passive monomers, forming an inner cavity that encapsulates itself. However, the shear flow compresses the chain conformation in the shear gradient direction and stretches the cavity from its corners to align it along the flow direction. At high activity and shear rate within this regime, the motion of the chain fastens, while the shear also stretches the bonds and aligns the conformation along the flow direction (see × in Fig. 4.2). This shear-induced conformation of an active chain due to stretching/alignment in the flow direction and compression in the gradient direction is similar to what is observed previously in the case of all monomers being active[166]. In fact, the blue region, representing the complex folding regime in Fig. 4.2, serves as a kind of transitional zone between folding and spiralling conformations.

For increasing activity, the head enables the spiralling of the entire chain. Depending on the level of activity, the polymer chain adopts two spiral modes, *head-in* and *head-out*. For moderate activity, the head continues its enclosed rotations within the cavity, akin to complex folding. Differently here, the chain activity overcomes the compression and alignment effects of the shear flow on the chain conformation and achieves a perfect circular form, referred to as head-in spiralling (indicated by ▲ in Fig. 4.2). At the same time, the shear vorticity also causes the entire chain to rotate as a bulk unit. In the range of head-in spiralling state, increasing the head activity widens the diameter of the circling, creating a larger inner cavity.

On the other hand, the size of the inner cavity is constrained by the length of a polymer chain. When the head monomer rotates with a diameter larger than the maximum diameter achievable by the chain's length, it escapes from the cavity and, in turn, encapsulates the passive monomers (see all ◀ in Fig. 4.2). We denote

this motion of the chain as head-out spiraling. At the initial stage of the head-out spiralling regime, the head encapsulates all the passive monomers. As the activity increases, the size of encapsulated passive monomers decreases. Generally, in both spiralling regimes (head-in and head-out), the activity drives the encapsulation process, while the shear flow instigates the rolling of the polymer chain as a bulk along the flow direction. Applicable to all states, we observe a range of conformational diversity as activity increases, while remaining at the same shear rates. However, the diversity remains consistent with increasing shear rates along the same activity line.

4.2.2 Conformational properties of an active flexible polymer chain

The conformational properties of the active polymer are characterized by the radius of gyration tensor[164, 167, 166],

$$G_{\alpha\beta} = \frac{1}{N_m} \sum_{i=1}^{N_m} \Delta r_{i,\alpha} \Delta r_{i,\beta}, \quad (4.6)$$

where $\alpha, \beta \in \{x, y\}$. Here, Δr_i is the position of i^{th} monomer in the polymer center-of-mass reference frame, $(r_i - r_{cm})_{\alpha,\beta}$ with $r_{cm} = \sum_{i=1}^{N_m} r_i$. The mean square radius of gyration is then calculated by summing up the diagonal elements of the gyration tensor as $\overline{R_g^2} = \overline{G_{\alpha\alpha}} + \overline{G_{\beta\beta}}$. The overline denotes a time average.

Fig.4.3a-d show the change in radius of gyration of four different conformational states over time, where the active polymer chain undergoes either folding or spiraling in a cyclic fashion. In Fig.4.3a, the observed plateaus correspond to the linear extension of the chain between each folding event. For the linear folding conformation, the mean radius of gyration fluctuates around the size of the polymer chain. Specifically, R_g^2 exceeds the chain size due to the stretching of the chain during its linear extension, while R_g^2 decreases below that during the subsequent linear folding. The duration of these plateaus in R_g^2 indicates the extent of chain stretching: longer plateaus correspond to greater stretching of the chain by shear. Comparing the linear and complex folding regimes, depicted

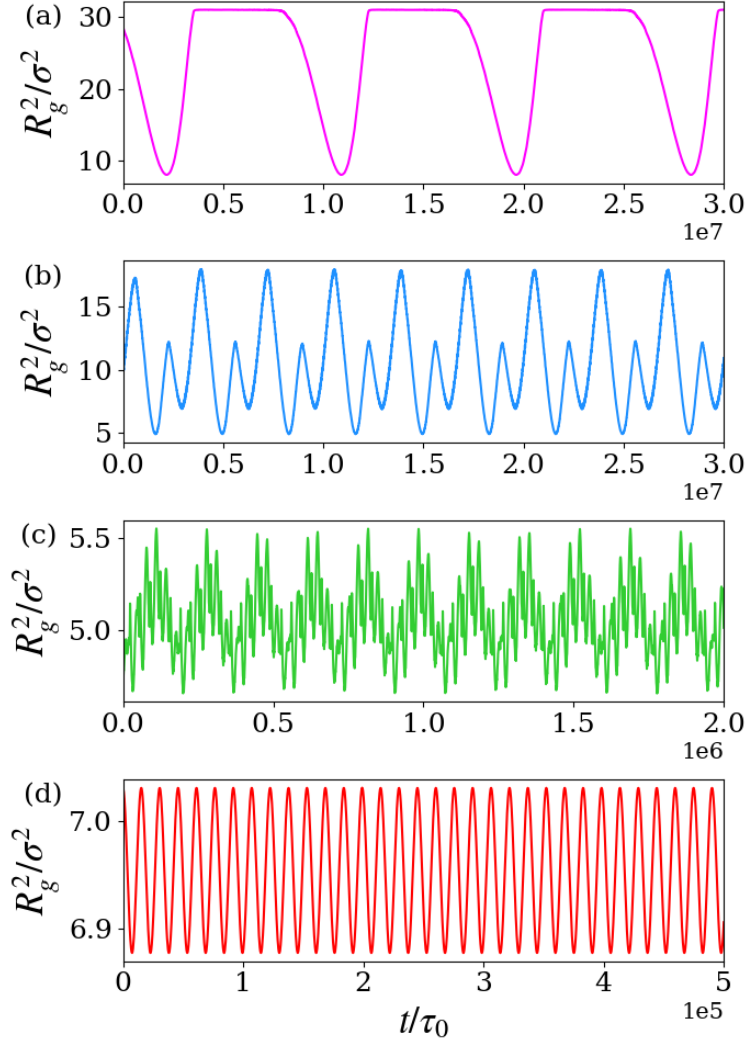


Figure 4.3: Square of the radius of gyration R_g^2 as a function of reduced time t/τ_0 in the steady state: (a) linear folding ($v_0\tau_0/\sigma = 0.1, \dot{\gamma}\tau_0 = 0.1$), (b) complex folding ($v_0\tau_0/\sigma = 1, \dot{\gamma}\tau_0 = 0.1$), (c) head-in spiralling ($v_0\tau_0/\sigma = 20, \dot{\gamma}\tau_0 = 0.1$) and (d) head-out spiralling ($v_0\tau_0/\sigma = 80, \dot{\gamma}\tau_0 = 0.1$). The colors are used to match the responses with the states, as in Fig.4.2.

in Fig.4.3a and b, respectively, we observe that the encapsulation of the head monomer produces an secondary peak characterizing the head rotation within the cavity. In the head-in spiralling regime (Fig.4.3c), we observe multiple peaks while in the head-out spiralling state, since the polymer chain rotates as a bulk unit, a single oscillation is dominating again and the changes in the radius of gyration are small (Fig.4.3d).

In Fig.4.4a-d we plot the corresponding Fourier spectra of $R_g^2(t)$. In the folding states, Fig.4.4a and b, the two primary peaks have different relative weights. For the head-in spiralling state, the frequency of the head swirling is as the activity starts dominating in the system. This results in shifting the swirling peaks in the spectrum Fig.4.4c to higher frequencies compared to Fig.4.4a and b and the peak related to the bulk chain folding becomes trivial. On the other hand, in the head-out spiraling state, we observe a single peak in the Fourier spectrum, in line with Fig.4.3d.

Fig.4.5a displays the mean radius of gyration $\overline{R}_g^2$ with increasing activity for several shear rates. Here, the chain states are marked by different symbols to recognize the transitions between them. In the linear folding regime, $\overline{R}_g^2$ is highest but decreases with increasing activity during the linear and complex folding states. A polymer chain in a linear folding regime exhibits the highest $\overline{R}_g^2$. Later, a descending trend is observed as the activity increases, corresponding to linear and complex folding states. This suggests that higher activity leads to more effective chain folding. Chains with the same activity exhibit larger $\overline{R}_g^2$ due to a greater stretching under higher shear flows. Additionally, for the chains with the same activity but under different shear flows, we observe larger $\overline{R}_g^2$ values when the chain experiences a greater stretching due to the higher shear flows. At the transition to the head-in spiralling state, the descending trend of $\overline{R}_g^2$ shifts in an ascending direction. This transition occurs at lower activities at low shear, as it becomes easier for activity to dominate. Within the activity range of the head-in spiralling, the mean radius of gyration keeps increasing due to the expansion of an inner cavity further by the higher activity of the head monomer, as observed on the state diagram in Section 4.2.1. For $\dot{\gamma} = 1$, the head-in spiralling state is absent and the chain translates directly to the head-out spiralling state (see also

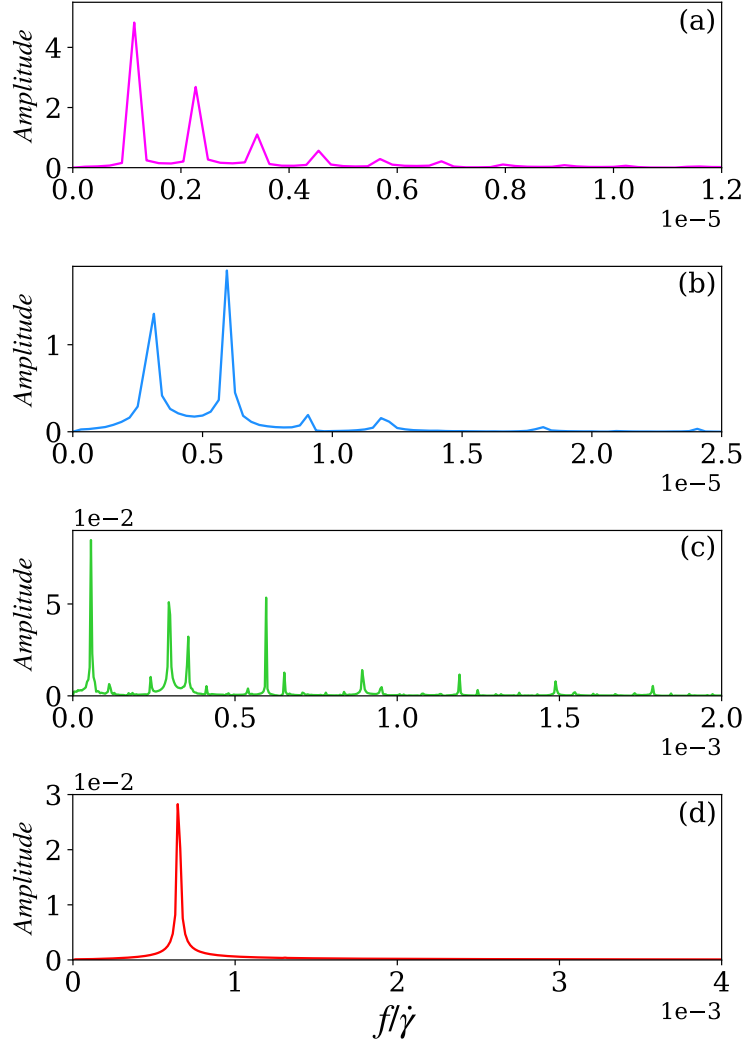


Figure 4.4: Fourier spectra of $R_g^2(t)$ (in arbitrary units) as a function of reduced frequency $f/\dot{\gamma}$: (a) linear folding, (b) complex folding, (c) head-in spiralling and (d) head-out spiralling states, indicating the characteristic frequency peaks related to the polymer state. The colors match the different states corresponding to Fig.4.2.

the state diagram in Fig.4.2).

In the head-out spiralling state, $v_0\tau_0/\sigma > 30$, the mean radius of gyration becomes independent of the shear rate and the chain conformation depends only on activity. Initially, $\overline{R}_g^2$ decreases due to unstable conformations at the beginning of the full wrapping of all the passive monomers (the smallest $\blacktriangleleft$ in Fig. 4.2). Here, the head monomer intermittently attempts to leave the encapsulated monomers. The stabilization of the head-out state occurs at activities $v_0\tau_0/\sigma \sim 60$, where the minimum $\overline{R}_g^2$ is reached in Fig.4.5a. Subsequently, as the size of the encapsulated passive monomers decreases with activity (as illustrated by $\blacktriangleleft$ symbols in Fig.4.2), $\overline{R}_g^2$ begins to increase again.

Fig.4.5b shows the frequency of the highest amplitude peak at the Fourier spectra, i.e., the highest frequency peak f_c , normalized by the corresponding shear rates $\dot{\gamma}$, plotted as a function of activity. The folding frequency is lower than that of spiralling states and increases slightly as activity increases. Later, the onset of the head-in spiralling state is identified by the jump observed in the non-dimensional frequencies. After this jump, the characteristic frequency of the head-in spiralling state remains constant with activity. However, this plateau occurs at higher frequencies for lower shear rates. This again underscores the predominance of the activity, which can further increase the frequency of the head circling within the cavity when the shear is weaker. For $\dot{\gamma} = 1$, again, the head-in spiralling state is absent, we lose the first jump in the normalized frequencies is missing. Moreover, the transition to the head-out state is then identified by the second jump of the normalized frequencies. Similar to the head-in state, the head-out state shows a constant characteristic frequency that remains unaffected by activity.

After all, Figs.4.5a and b provide evidence of regime transitions, particularly from the linear folding to the spiralling states and from head-in to head-out spiralling states, respectively. Additionally, they demonstrate how the size of the conformation and the folding/spiralling frequencies are tuned by (i) the activity of the chain and (ii) the imposed shear flow. Similar to the active polymer chain composed solely of active monomers[166, 55], we note a consistent trend in $\overline{R}_g^2$

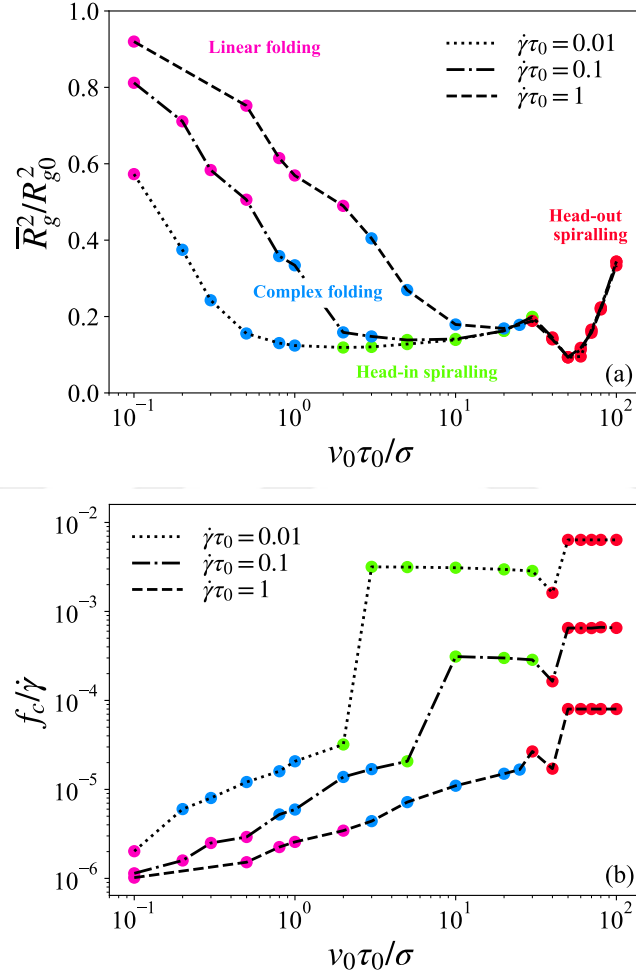


Figure 4.5: (a) The nondimensional mean-square radius of gyration $\overline{R}_g^2/\sigma^2$ and (b) the normalized characteristic frequency f_c obtained from the Fourier spectra of R_g^2 -time data, as a function of activity $v_0\tau_0/\sigma$ for $\dot{\gamma}\tau_0 = 0.01, 0.1$ and 1 . The color code denotes the state of the active polymer chain at the corresponding states: linear folding (magenta), complex folding (blue), head-in spiralling (green) and head-out spiralling (red).

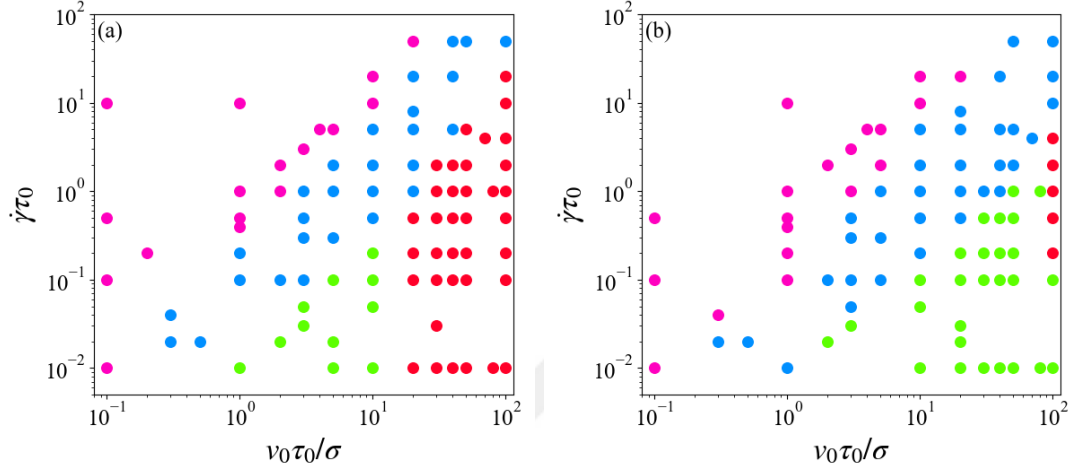


Figure 4.6: The state diagrams of the active polymer chain as a function of activity $v_0\tau_0/\sigma$ and shear rates $\dot{\gamma}\tau_0$ when the chirality of the head monomer is set to (a) $T_c/\tau_0 = 1$ and (b) $T_c/\tau_0 = 5$. The colorcode represents different states: linear folding (magenta), complex folding (blue), head-in spiralling (green) and head-out spiralling (red).

with increasing activity $v_0\tau_0/\sigma < 30$. However, beyond this activity threshold, we observe that the combination of activity and chirality of the head monomer reveals a distinct spiralling state unique to active polymer chains with a chiral head.

4.2.3 Shifting on the state diagram due to the head chirality, T_c , of the polymer chain

In this section, we present the results illustrating the effect of the chirality of the head monomer on the conformational states of an active polymer chain. The head chirality of the polymer chain is adjusted by modifying the term T_c in Eq.4.3. Up to this point, the conformational states have been discussed primarily for the case where $T_c/\tau_0 = 2$ (see Fig.4.2). Now, in Fig.4.6, we address two cases, a lower ($T_c/\tau_0 = 1$) and a higher ($T_c/\tau_0 = 5$) head chirality.

The folding states are not significantly affected by the head chirality strength. This is simply because the folding states arise from the shear dominance in the

system and the head chirality term T_c is not directly linked to the shear rate, as seen in Eq.4.3. On the other hand, the chiral motion of the polymer chain depends on its activity via the active speed term v_0 . This relationship is confirmed by the simulations that the head chirality (different values of T_c) causes a change in the spiralling states on the state diagram. Comparing Figs.4.2 and 4.6a, we observe that a weaker chirality shifts the head-out spiralling transition to lower activities by limiting the head-in spiralling region. Conversely, a polymer chain with stronger chirality requires a large $\nu_0\tau_0/\sigma$ to reach the head-out spiralling state, as seen in Fig.4.6b. This indicates that the chirality of the head monomer determines the encapsulation route of the polymer chain at the spiralling state, allowing us to reach the desired state not only by tuning the activity but also the chirality. In other words, one can prefer to work with less chiral polymer at lower activities while others may prefer a more chiral polymer at higher activities.

Although both folding states are not influenced directly as T_c changes, the shifting of spiralling states to higher activity regions mildly extends the region of complex folding state observed on the state diagram. This analysis sheds light on the unique effect of the combination of activity and chirality. Specifically, the head-in spiralling regime emerges as a distinctive feature of an active polymer chain with a chiral head. This conclusion is further corroborated by simulations conducted under conditions where the chirality parameter T_c/τ_0 is set to zero (see Fig.4.7). In this setup, the orientation of the head monomer is solely affected by the vorticity of the shear flow. In such cases, the head-in spiralling state completely vanishes, affirming its existence due to the presence of head chirality, and parts of the head-out spiralling are also disrupted for certain parameters. Moreover, while the folding states merge on the state diagram, they remain distinguishable based on the level of activity.

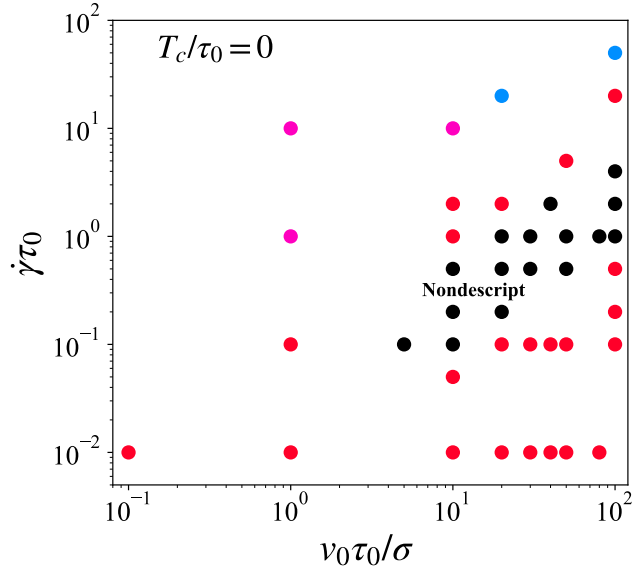


Figure 4.7: The state diagrams of the active polymer chain as a function of activity $v_0\tau_0/\sigma$ and shear rates $\dot{\gamma}\tau_0$ when the chirality of the head monomer is set to zero. The colorcode represents different states: linear folding (magenta), complex folding (blue), head-out spiralling (red) and nondescript (or destroyed) state (black).

4.2.4 Competition between shear torque and head chirality

After exploring the impact of head chirality of the head monomer on the state diagram, we shift our focus to the competition between two torques, the shear torque $\dot{\gamma}/2$ and the torque T_c by head chirality, in determining the final direction of both folding and spiralling conformations. To do that, these torques should be applied countercurrently which are also tunable directed forces in the system. In this way, the response of the active polymer is better understood under different operating conditions (for instance, different shear flow directions or head's monomer spin directions), which helps for the experimental realization of this system in the future.

The state diagram in Fig.4.2 illustrates the chain states when both torques are imposed in a clockwise (CW) direction. Here, the same active polymer with a

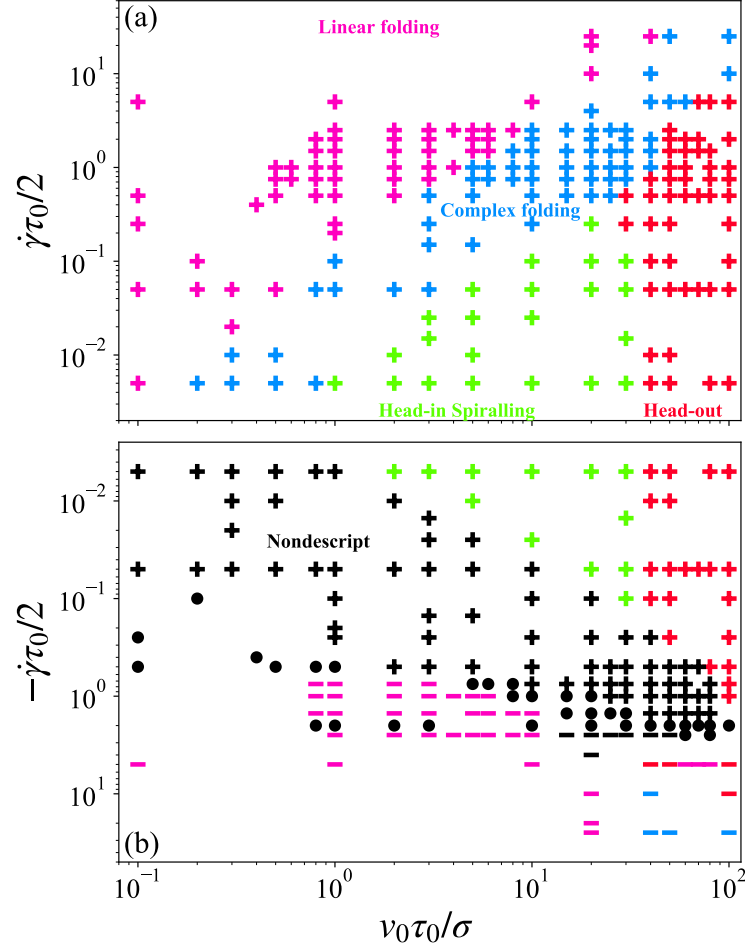


Figure 4.8: (a) The state diagram when both torques cause clockwise rotation of the head monomer, $\dot{\gamma}/2 > 0$ and $T_c > 0$. (b) The state diagram when the shear flow creates a CCW shear torque on the monomer, $\dot{\gamma}/2 < 0$, while the head chirality resists the CW rotation with $T_c > 0$. The colorcode represents different states: linear folding (magenta), complex folding (blue), head-in spiralling (green), head-out spiralling (red) and nondescript state (black). Symbols correspond to clockwise (+), counter-clockwise (-) and hesitant (•) rotations. The dotted black line denotes the neutralization of the countercurrent torques on the head monomer.

CW head chirality is simulated under the shear reversed flow field ($\dot{\gamma} < 0$ used in Eqs.4.1-4.3). This time, the negative flow gradient is instead located in the upper region, unlike Fig.4.1. Consequently, the resulting shear torque exerted on the head monomer becomes counterclockwise (CCW).

Fig.4.8 shows the conformational state diagrams where both torques are CW in (a) and the opposite case (i.e., shear torque CCW vs chiral torque CW) in (b). In Fig.4.8a, the active polymer chain forms the conformational states consistently in the CW direction, as previously observed (see Fig.4.2). In the case of a negative shear rate, where the shear torque CCW, we obtain a completely different state diagram, see Fig.4.8b. When the activity dominates in the system, the head chirality of the head monomer prevails over the shear torque, allowing the head-in and head-out spiralling states to persist mostly on the state diagram. However, as the shear flow increases or the polymer activity decreases, the shear torque resists more the head chirality, destroying the complex folding state. Despite the head monomer's overall tendency to rotate the polymer chain CW, the competition results in a nondescript conformation of the active polymer chain. At a point, the head monomer also loses CW rotational tendency, leading to dynamic fluctuations without settling into a definitive conformation, which we refer to as a hesitant state. Around this hesitancy on the state diagram, the head monomer keeps attempting to rotate the chain in the CW direction (+) on the activity dominant regions of the state diagram, while in the CCW(-) direction on the shear dominant regions. However, the hesitant state arises due to the balanced effects of shear and activity wherein the polymer remains linear, except for a slight up and down motion of head monomer.

When the magnitudes of two countercurrent torques become exactly equivalent, such that $\dot{\gamma}\tau_0/2 = -2$ and $T_c/\tau_0 = 2$, the active polymer chain remains always linear without any directional preference of the head monomer over the range of activities. Consequently, it can only translate with the shear flow. In fact, the two torques cancel each other out in Eq.4.2. Below this torque neutralization line on the state diagram in Fig.4.8b, the shear prevails in the system, meaning that the shear torque $\dot{\gamma}/2$ surpasses the head chirality T_c . As a result, either the shear-dominant or hesitant states emerge in the CCW direction.

4.2.5 Viscosity

The rheological response of the active polymer chain with a chiral head is characterized by the shear viscosity, η , which is calculated similarly to Sec.4.2.2 via shear stress according to,

$$\sigma_{xy} = -\frac{1}{\Omega} \sum_{i=1}^{N_m} \sum_{i>j} \frac{\partial U}{\partial r_{ij}} \frac{r_{ij,x}}{r_{ij,y}} r_{ij}, \quad (4.7)$$

where $r_{ij,x}$ and $r_{ij,y}$ are the distance between the centers of two particles i and j in the direction of x and y , respectively, while $\Omega = L_x L_y$ is the system area. Differently from Equ.3.5, here, we consider the average stress contribution of monomer particles in the chain to obtain the rheological behavior of the polymer chain. The shear stress is nondimensionalized by considering the energy and length scales, ϵ and σ , of the system. The shear viscosity is then calculated as $\eta = \bar{\sigma}_{xy} / \dot{\gamma}$.

Fig.4.9a displays the shear stress as a function of activity for various shear flows, highlighting the contribution of different polymer conformations to the shear stress. Here, the change in the shear stress is plotted for increasing activity similar to previous analyses in Section 4.2.2.

The two folding states of the polymer chain demonstrate distinct contributions to the shear stress. Generally, any folding of the chain leads to an increase in the shear stress compared to the linear polymer chain simply flowing under the shear flow[168]. Here, the chain in the linear folding state (magenta) increases the shear stress until crossing to a complex folding form (blue). Immediately after this crossover, the chain reaches the maximum stress, allowing us to discriminate between the folding states on the shear stress plot. At subsequent activities, the chain in the complex state initiates a decreasing shear stress trend.

By comparing the lowest and highest shear flow cases in Fig.4.9a, $\dot{\gamma}\tau_0 = 0.01$ and $\dot{\gamma}\tau_0 = 1$, the shear stress contribution of the polymer chain in the complex folding state tends to remain more constant with the activity, especially when

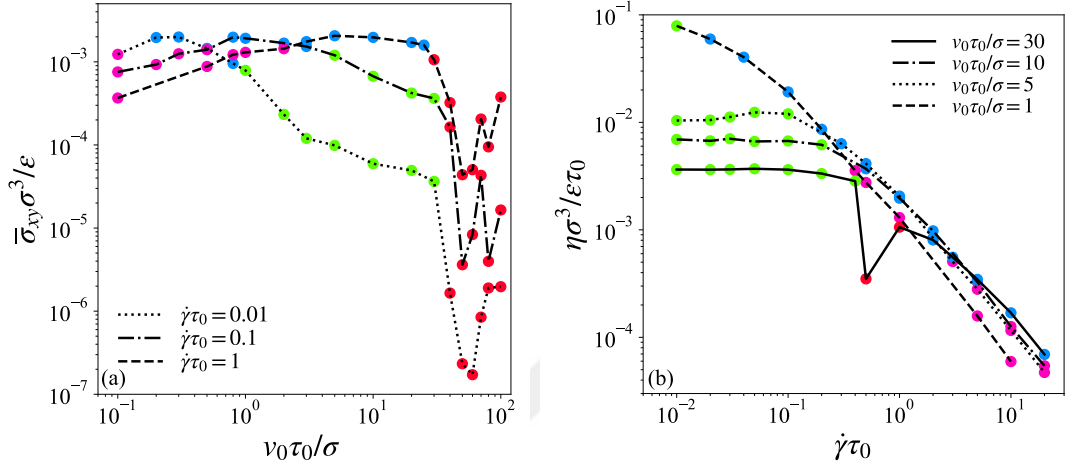


Figure 4.9: (a) Nondimensional shear stress $\sigma_{xy}\sigma^3/\epsilon$ as a function of chain activity $v_0\tau_0/\sigma$ for various shear rates, $\dot{\gamma}\tau_0 = (0.01, 0.1, 1)$. (b) Nondimensional shear viscosity $\eta\sigma^3/\epsilon\tau_0$ as a function of shear rate $\dot{\gamma}\tau_0$ for the polymer chain activities $v_0\tau_0/\sigma = (30, 10, 5, 1)$. The colors denote the state of the active polymer chain at the corresponding states: linear folding (magenta), complex folding (blue), head-in spiralling (green) and head-out spiralling (red).

the head-in spiralling regime (green) is absent. For $\dot{\gamma}\tau_0 = 1$, where the head-in spiraling state does not appear, there is a monotonic stress behavior due to the balance between activity and shear. This observation is evident for $\dot{\gamma}\tau_0 = 1$, where the head-in spiralling state does not appear across the entire activity range. Here, the competition between the activity and the shear within their ranges leads to a monotonic stress behavior. When the activity-induced forces on the chain surpass the shear forces, the chain directly translates into a more relaxed state, namely head-out spiralling (red), causing a significant decrease in shear stress. Conversely, when the head-in spiralling state is present on the state diagram at lower shear flows, such as $\dot{\gamma}\tau_0 = 0.01$ and $\dot{\gamma}\tau_0 = 0.1$ on Fig.4.9a, the shear stress initially decreases smoothly with increasing activity before the transition from folding to spiralling occurs. In both cases, during this transition, the activity assists the polymer chain in relaxing the stress, enabling it to flow with shear as a bulk unit.

Fig.4.9(b) presents the shear viscosity as a function of the shear rate for different chain activities. We observe that the activity severely affects the intrinsic

viscosity of the polymer. At low activity $v_0\tau_0/\sigma = 1$, the polymer chain consistently behaves as a shear thinning fluid, wherein the viscosity decreases with increasing shear rate. This behaviour is observed when the chain exhibits mainly folding conformations (corresponding to magenta and blue). Through the moderate activities, $v_0\tau_0/\sigma = 5 - 10$, the polymer behaves as a Newtonian fluid at low shear rates $\dot{\gamma}\tau_0 < 0.1$, showing shear rate-independent viscosity. In this range, the chain predominantly adopts the head-in spiralling state (depicted by green symbols). However, as the shear rate rises, the chain behavior turns into a shear-thinning, as the chain enters the folding state (red). This decrease in η reflects the alignment and the stretching of the polymer chain in the folding states, due to the shear dominance, hence resulting in a more pronounced viscosity change. In general, a higher shear rate in the system or lower activity of the chain intensifies the stretching of the chain in alignment with the shear flow, hence promoting the shear thinning behaviour. These results with an active chiral polymer chain show agreement with the previous simulations conducted on chain composed only of active monomers[166].

On the other hand, for a more active polymer chain, $v_0\tau_0/\sigma = 30$, a smooth transition from Newtonian to shear thinning behavior is disrupted by an unstable head-out spiralling conformation of the chain observed around $\dot{\gamma}\tau_0 = 0.4$. The head-out spiralling state appears between head-in spiralling and complex folding states on the state diagram Fig.4.2, indicating weaker resistance to the flow of the head-out spiralling state, despite its unstable conformation in this parameter range.

In general, we observe that the rheological transition from Newtonian to shear-thinning behavior of the chain occurs at higher shear rates when the chain activity increases. The folding polymer chain exhibits shear-thinning behavior, whereas the head-in spiralling polymer chain behaves as a Newtonian fluid. The further activity induces a kind of shrinkage effect on the spiralling polymer chain conformation by weakening the importance of excluded-volume interaction among the monomers and the shear flow, leading to a more shear-independent viscosity response.

4.2.6 The effect of fluctuations

In this section, we investigate the existence of the same polymer conformational states when including fluctuations in the environment (shown in Fig. 4.10). To do that, we include the Gaussian random processes (ξ_i) and (η_h) via non-zero translational (D_t) and rotational (D_r) diffusion coefficients in the overdamped equations of motion as follows,

$$\dot{r}_i = -\frac{1}{\Gamma} \sum_{\substack{j=1 \\ j \neq i}}^{N_m} \nabla_i U_{ij} + \dot{\gamma} r_{yi}(t) \mathbf{e}_x + \xi_i, \quad (4.8)$$

$$\dot{r}_1 = -\frac{1}{\Gamma} \sum_{j>2}^{N_m} \nabla_1 U_{1j} + \dot{\gamma} y_1(t) \mathbf{e}_x + \xi_1 + v_0 \mathbf{e}_h, \quad (4.9)$$

$$\dot{\theta}_h(t) = \eta_h(t) - \frac{\dot{\gamma}}{2} - T_c. \quad (4.10)$$

We have considered the different ratios between the translational and rotational diffusion coefficients, $D_t/D_r\sigma^2$ in the simulations to regulate the strength of Gaussian noise terms,

1. ξ_i , describing the thermal fluctuations affecting all monomers in the system with zero mean $\langle \xi_i(t) \rangle = 0$ and variance $\langle \xi_i(t) \xi_j(t') \rangle = 2D_0 \delta(t - t')$.
2. η_h , accounting for the fluctuations in the orientation of the head monomer caused by the environment, with zero mean $\langle \eta_h(t) \rangle = 0$ and variance $\langle \eta_h(t) \eta_h(t') \rangle = 2D_r \delta_1 \delta(t - t')$.

The two extreme states, i.e., (i) the linear folding state under shear dominance and (ii) the highly active polymer in the head-out spiralling state, are unmodified to all fluctuations from the environment (see Figs. 4.10a and b). The linear folding state stands out due to the strong shear effects while the combined action of activity and head chirality is responsible for ensuring the consistency of the head-out spiralling state. Notably, in the case of linear folding, thermal fluctuations in the environment alter the linear trajectory of folding since it affects both

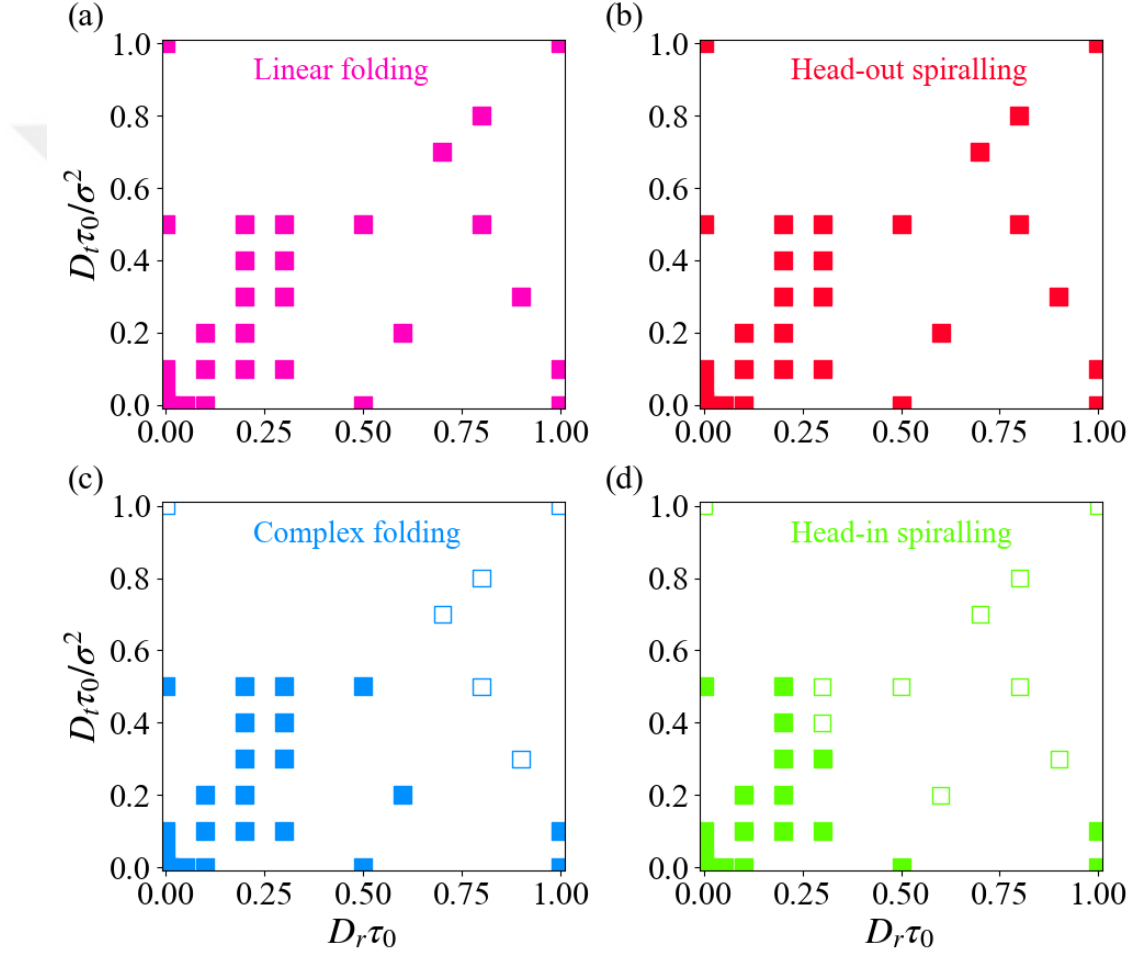


Figure 4.10: The appearance of the conformational states of the active polymer chain in the presence of translational and rotational fluctuations. The colorcode represents the different states, matching with the state diagrams. The closed (■) and open (□) symbols denote the appearance and disappearance of the corresponding states, respectively.

active and passive monomers similarly, giving rise occasionally to a new folding phase, S-like folding.

Fig.4.11 demonstrates the potential folding states of the active polymer chain in the presence of thermal fluctuations induced by the solvent particles in its vicinity. Here, we outline two possible folding routes of the chain based on the cumulative direction of these stochastic kicks to the tail monomer. Figs.4.11 a-b and c-d show the scenarios when the tail monomer is kicked towards the negative and positive flow fields, respectively.

In the first scenario, Fig.4.11(a), the resulting kicks from the solvent particles propel the tail monomer towards the negative flow field, while the head monomer initiates the linear folding of the chain as usual. Although the shear flow attempts to entrain the passive tail monomer to direct it toward the negative x -direction, this effect is largely mitigated by the polymer bonds and the overall tendency of the chain to follow the head monomer. Consequently, we observe the typical linear folding state, accompanied by the stretching of several tail monomers due to the shear flow, see in Fig.4.11(b).

Fig.4.11(c-d) illustrates the mechanism behind the S-like folding observed when the resulting kicks propel the tail monomer into the positive flow field. In this scenario, the direction of the shear flow does not attempt to pull the tail monomer away from the rest of the chain, allowing it to be entrained to flow with the shear (Fig.4.11(c)). Therefore, it induces a second folding in addition to the usual folding caused by the head monomer, as shown in Fig.4.11(d), due to the combined action of chirality and shear torque. Notably, this secondary folding is solely attributed to the shear torque acting on the passive monomers. In addition, such an S-folding state can also occur in reverse such that the head monomer initiates folding to the top while the tail folds the chain to the bottom.

In the complex folding state, Fig. 4.10c, where shear- and activity- induced forces are commensurable, the chain state begins to be disrupted by fluctuations. At this point, it is worth noting that if the chain state persists for more than half of the total simulation time despite environmental fluctuations, we deem it to exist

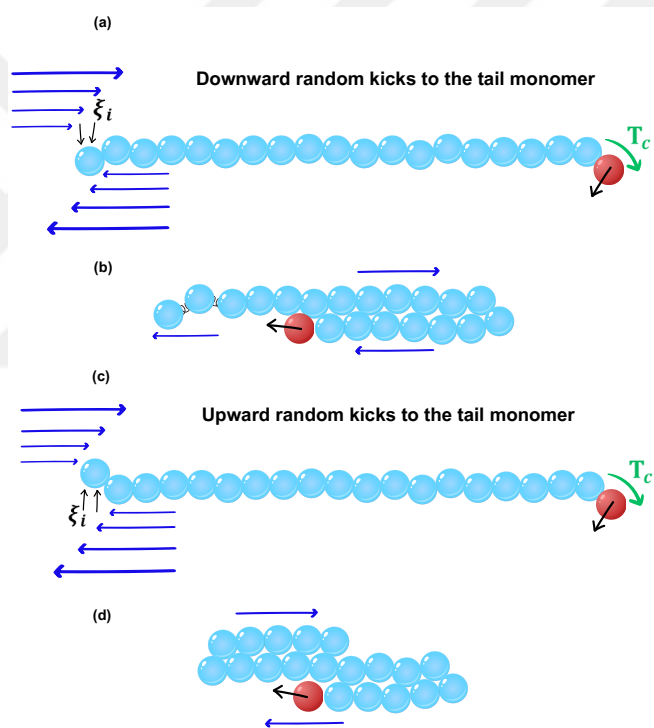


Figure 4.11: (a-b) The linear folding mechanism of the chain when the tail monomer is kicked into the negative flow field and (c-d) The S-folding mechanism of the chain when the tail monomer is into the positive flow field by environmental fluctuations in its vicinity.

under such conditions. Here, the chain state becomes sensitive to the fluctuations above $D_t\tau_0/\sigma^2 \approx 0.2$ - $D_r\tau_0 \approx 0.5$. The heightened sensitivity stems mostly from the competition between the shear flow and the thermal fluctuations. While the shear flow triggers the folding of the chain and aligns the passive monomers in the shear flow direction, the thermal fluctuations cause their motions to become randomized again. On the other hand, strong rotational noise randomizes the head orientation of the chain. However, this does not affect much the complex folding state, since this state is predominantly triggered by the shear.

As the activity of the head monomer increases, the chain enters the head-in spiralling state Fig.4.10d, becoming more susceptible also to fluctuations, below $D_r\tau_0 \approx 0.5$. In particular, at $D_t\tau_0/\sigma^2 = 0.2$ and $D_r\tau_0 \approx 0.6$ in Fig.4.10d, we observe that the fluctuations significantly disrupt the orientation of head monomer. Indeed, at certain parameters, the active chain still exhibits a kind of spiralling motion, albeit lacking an explicit head-in conformation.

Moreover, upon comparing the two spiralling states (Fig.4.10b and d), we discern that not only the high activity but also the shear terms in Eqs. 4.8-4.10 may contribute to the existence of the head-out spiralling against the fluctuations. In summary, these results suggest that the head chirality of the head monomer can overcome the rotational fluctuations due to its activity if the shear torque also induces sufficient further rotation. However, in the case of relatively weaker activities, the shear effects are precluded by all fluctuations, resulting in the disappearance of one of the activity-induced states, the head-in spiralling conformation.

4.2.7 The effect of chain length

Furthermore, we investigate the effect of the polymer chain length on the state diagram. By doubling the number of monomers in the chain ($N_m = 40$), we observe in Fig.4.12 a notable shift in the conformational states at high activities compared to the existing one ($N_m = 20$). Although we include also the normalization by the number of monomers for the nondimensional activity on the

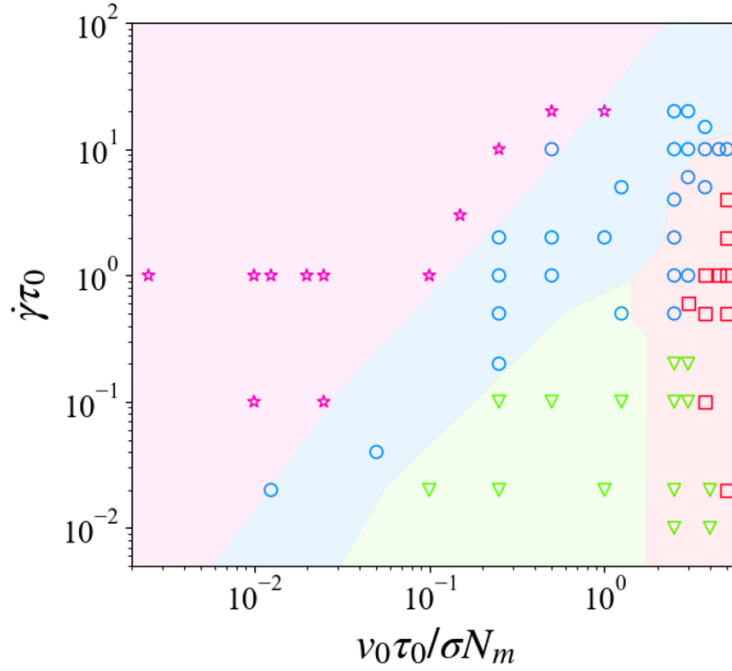


Figure 4.12: The state diagram normalized by the number of monomers, N_m , for the active polymer chains composed of $N_m = 20$ (represented by colored background) and $N_m = 40$ (closed symbols). The colorcode represents different states: linear folding (magenta), complex folding (blue), head-in spiralling (green) and head-out spiralling (red).

x -axis, a longer polymer chain exhibits a wider region corresponding to the head-in spiralling state. As discussed in Section 4.2.1, the transition from head-in to head-out spiralling state is determined by the maximum cavity size formed by the chain, which is directly related to the chain length. However, one can anticipate this size effect to diminish with the normalization by N_m on the state diagram. The discrepancies in the state diagram point out the role of the chain bonds, which allow for further extension of the chain. Consequently, the active chain can continue forming a larger cavity in the head-in spiralling state with increasing activity, thereby shifting the transition to the head-out spiralling states to higher activity levels compared to its shorter polymer counterpart.

Chapter 5

Hybrid MPCD- MD simulation approach for an active chiral polymer in shear flow

In this section, we combine full molecular dynamics (MD) simulations (in Section 4) of solute (in this case, monomer particles) motion with Multiparticle Collision Dynamics of solvent, which was introduced earlier in Section 2.2. Here, molecular dynamics describes the solute-solute and solute-solvent interactions while multiparticle collision dynamics is responsible for solvent-solvent interactions (Fig. 5.1). We aim to achieve the nature of their interactions better with this mesoscale treatment of solvent. Hence, we analyze the effect of solvent dynamics on solute motions in more detail, including the hydrodynamics. With this hybrid scheme, it is relatively easier to include the hydrodynamic interactions, particularly for polymers, due to the easy coupling algorithm between solvent particles and monomers.

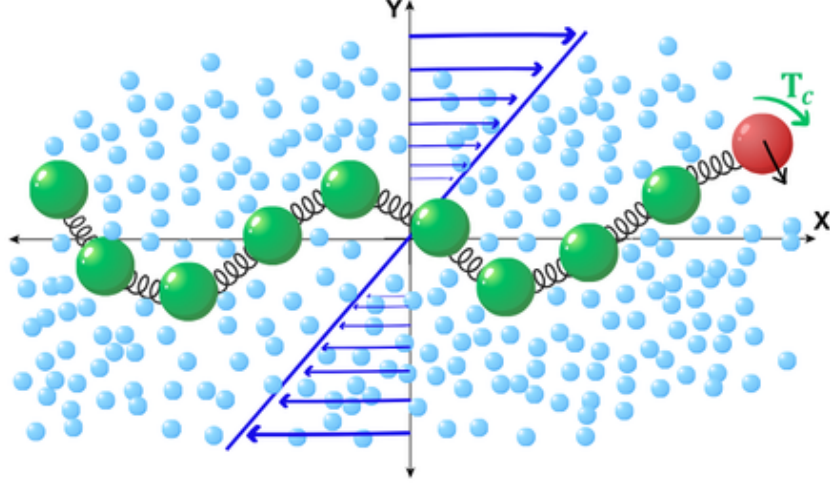


Figure 5.1: Schematic of an active bead-spring polymer with a chiral head (red monomer) in the linear flow. The green monomers are passive. The black arrow on the head monomer represents the direction of the active force and the green arrow depicts the direction of head chirality. Blue particles are solvent particles that are simulated by Multiparticle collision dynamics (MPCD). The flow is imposed along the x -axis and the gradient is in the y -direction whose variation is shown by blue arrows.

5.1 Model

The molecular dynamics of an active chiral polymer chain under shear flow is given by,

$$\dot{R}_i(t) = V_i(t), \quad (5.1)$$

$$M\dot{V}_1 = - \sum_{j=2}^{N_m} \nabla_1 U_{1j} + v_0 \mathbf{e}_h, \quad (5.2)$$

$$M\dot{V}_{i>1} = - \sum_{\substack{j=2 \\ j \neq i}}^{N_m} \nabla_i U_{ij}, \quad (5.3)$$

where $R_i = (R_{i,x}, R_{i,y})$ and $V_i = (V_{i,x}, V_{i,y})$ are the position and the velocity vectors of monomers. M is the monomer mass. Similar to 4.1, the chiral head

monomer ($i = 1$) is active, therefore, Eq. 5.3 includes self propulsion term, $v_0 \mathbf{e}_h$. Its direction is also changed by Eq. 4.10, including the noise term $\eta_h(t)$, the shear torque term $\dot{\gamma}/2$ and the head chirality T_c . For Eq. 5.1 and 5.2, the interactions between the monomers are considered via WLA and FENE potentials, similarly as in Section 4.1. Shear flow is applied through solvent dynamics MPCD.

In this MPCD- MD hybrid scheme (see the representation in Fig. 5.1), the molecular dynamics of a polymer chain is simulated by Eqs. 5.1, 5.2, 5.3 which are integrated using the time-reversible velocity Verlet algorithm, employing a time step Δt_{MD} . The solvent dynamics are simulated by using Eqs. 2.6 and 2.7 with time step Δt_{MPC} , including the shear flow. In MPCD, we account for numerous real collisions of N -point solvent particles with mass m through free streaming and multi-collision steps.

We utilize one of the coupling procedures between MD and MPCD, proposed for the systems when the embedded particles are polymers [97, 89]. This approach is known to be well for studying the dynamics and hydrodynamics effects of short, flexible polymers in dilute solutions. In our study, an active chiral polymer chain is embedded in MPCD solvent to capture accurately the hydrodynamic behaviour of the system. In this scheme, every monomer in the polymer chain participates in the collision step of MPCD as a point-like particle with a mass M in their cells, which is $M = \rho m$ where m is the mass of a solvent particle. Therefore, the center of mass velocity of the cell is then determined as follows,

$$u_{cm}(t) = \frac{\sum_{i=1}^N m v_i(t) + \sum_{i=1}^{N_m} M V_i(t)}{mN + MN_m} \quad (5.4)$$

The velocities of monomers are then updated according to Eq.2.7 after each collision step. In this context, the velocities of monomer particles are those resulting from the molecular dynamics simulations, not simply the velocities carried over from the previous collision step. This coupling allows fluid particles to freely penetrate solute particles (monomers). Therefore, while the hydrodynamic interactions are accurately reproduced using this coupling scheme, lubrication forces are not accounted for[169].

In this study, we examine the same active chiral polymer chain with $N_m = 20$

subjected to different shear rates $\dot{\gamma}$ within a computational box of dimensions $L_x, L_y = (80a, 40a)$. We assume an average of 10 solvent particles per cell, giving a particle density $\rho = 10$. Consequently, the mass of a colloidal particle M is equal to the average mass of solvent particles per cell, *i.e.*, $M = m\rho$. Given the system size, the total number of solvent particles is $N = 8000$ for a cell size of $2a$. We scale length and time by using the cell size a , $\hat{a} = x/a$ and characteristic time $\tau_0 = t\sqrt{k_B T / ma^2}$, respectively, with $k_B T = 1$, $m = 1$ and $a = 1$. The interaction strengths are scaled with $\epsilon/k_B T = 1$ for the potentials. The time steps for the two dynamics are chosen as $\Delta t_{MPC} = 0.01\tau_0$ and $\Delta t_{MD} = 0.002\tau_0$. The rotational diffusion coefficient (D_r) is set to $0.1\tau_0^{-1}$ to use in Eq. 4.3. The translational diffusion coefficient D_t is extracted from the relation $D_t = k_B T / 6\pi\eta R$, where R is the radius of the monomers. The initial velocities of particles are drawn from Gaussian distributions with zero mean and variances $k_B T / m$ for solvent particles and $k_B T / M$ for monomers.

5.2 Results

We investigate the possible conformational behaviour of an active chiral polymer chain ($T_c = 2\tau_0$) in shear flow, similar to analysis in Chapter 4, Section 4.2.1. This time, the solvent is modelled explicitly to account for hydrodynamic interactions (HI) as well as the thermal fluctuations. First, we obtain a state diagram across the different ranges of activity and shear rate. It is important to note that, in Chapter 4, Section 4.2.6, the existence of conformations was assessed only for the specific ranges used in the state diagram 4.2, with the presence of thermal fluctuations. In contrast, we here extended the range of activity and shear rate in the state diagram presented in Fig. 5.2. The inclusion of HI causes a shifting in the states by pronouncing the linear folding state. This is expected, as HI generally enhances the stretching of the polymer chain in the direction of the flow [164, 126, 170].

In Fig. 5.2, we observe that the presence of hydrodynamic interactions in the system annihilates the head-out spiralling state. Additionally, the extent of the

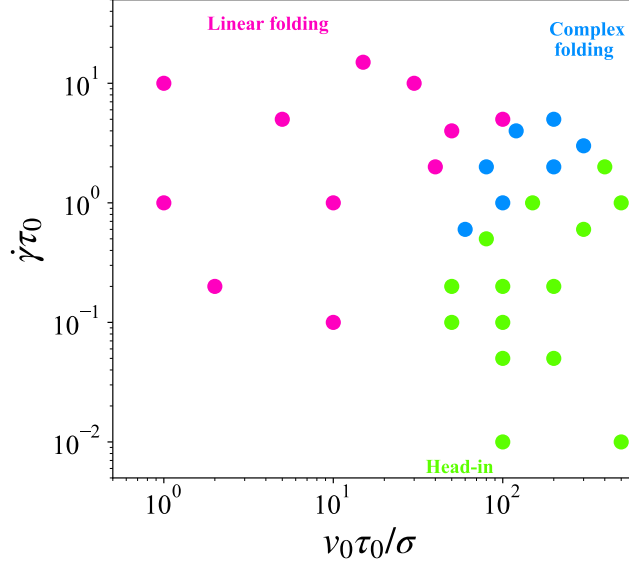


Figure 5.2: State diagram of the active polymer chain conformations as a function of activity $v_0\tau_0/\sigma$ and shear rate $\dot{\gamma}\tau_0$ when the chirality of the head monomer is set to $T_c/\tau_0 = 2$ in the presence of thermal fluctuations and hydrodynamic interactions: linear folding (magenta), complex folding (blue) and head-in spiralling (green).

remaining three conformational behaviors is altered. Both the linear folding and head-in spiralling states become more pronounced due to the effects of HI, while the complex folding conformation of the polymer chain is suppressed. This is primarily attributed to the swelling of the chain, as hydrodynamic interactions are known to cause the polymer chain to swell compared to cases where HI is neglected. In the presence of shear flow, this swelling restricts the maximum shear rate that can be applied. Above $\dot{\gamma} = 20$, the combined effect of shear flow and HI causes such significant elongation of the chain that it leads to the breakage of the polymer.

In the linear folding state, we observe that the polymer chain continuously swells and contracts (Fig. 5.4). During the swelling, the linear chain folds by forming several lines of wrinkles. Therefore, the passive monomers cannot surround the head monomer, blocking the complex folding. Moreover, due to this swelling effect, elongation times of the chain observed between each folding event, get longer than those observed in the system without HI, corresponding to the

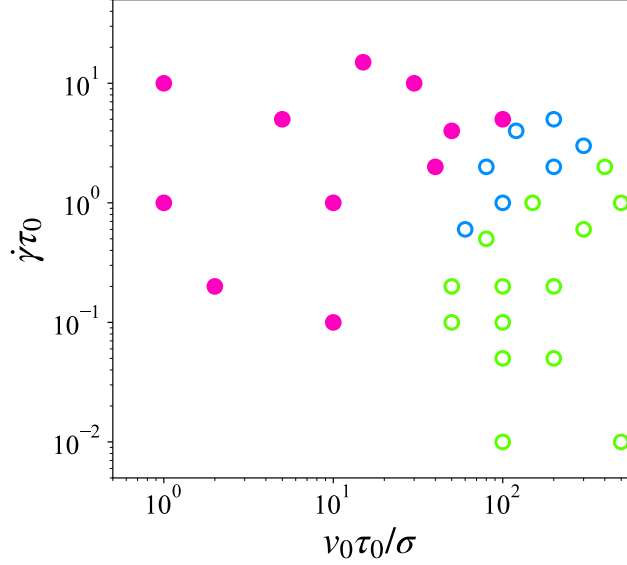


Figure 5.3: State diagram comparing the polymer chain including thermal fluctuations in the system, with and without hydrodynamical interactions (HI). Empty and filled symbols denote the disappearance/appearance of the states when the system is without and with HI, respectively. Colors denote the states: linear folding (magenta), complex folding (blue) and head-in spiralling (green).

plateaus in Fig.4.3. Although the polymer chain occasionally exhibits S-folding behavior —initially observed with thermal effects included (Fig. 4.11)- the swelling induced by hydrodynamic interactions transforms this S-folding behavior (Fig.5.4) into a motion resembling a somersault motion[78].

Moreover, the swelling of the polymer chain in activity-dominant states hinders the transition from a head-in to head-out spiralling state. This transition is typically driven by the activity of the head monomer and its circling diameter. It is also constrained by the chain size, as discussed in Section 4.2.1. However, the swelling of the chain in the head-in spiralling state, particularly passive segments surrounding the active head monomer, prevents the head monomer from escaping the inner cavity. Consequently, the head-out spiralling state is not observed.

Comparing the conformational states observed with only thermal fluctuations (Fig.4.10) to those observed with both thermal fluctuations and HI, it is evident that HI leads to the reappearance of the complex folding and head-in spiralling

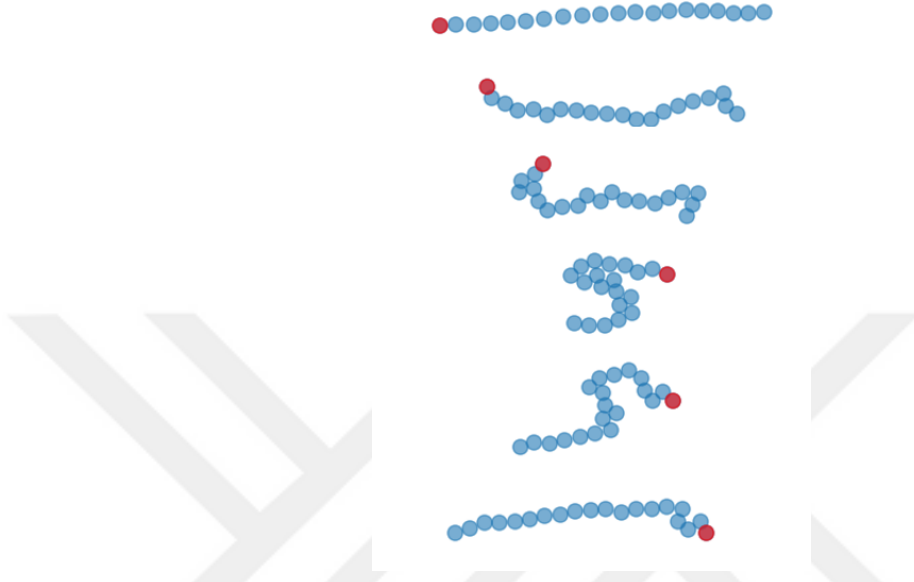


Figure 5.4: Representation of Somersault-like motion of an active chiral polymer chain in the linear folding state where the chain continuously swells and contracts while rotational flipping around its axis. Red monomer is the active-chiral head, while blue monomers are the passive monomers.

states. Fig. 5.3 illustrated the states observed with HI and without HI at the different levels of activity and shear rate. The state least affected by HI remains the most shear-dominant state: linear folding. Notably, the regions corresponding to complex folding and head-in spiralling states in the presence of HI align with the head-out spiralling states observed in the absence of HI. Overall, HI enhances the tumbling and tank-treading-like motions of the polymer chain in the presence of shear flow, effectively transforming head-out spiraling states into head-in or complex folding states in the state diagram.

Moreover, we compare the results of our base simulation (without fluctuations and HI) with those of the final hybrid simulation (with fluctuations and HI) in Fig.5.5. Firstly, we find that HI causes a delay in the occurrence of the complex folding and head-in spiralling ($v_0\tau_0/\sigma = 10, \dot{\gamma}\tau_0 = 0.1$) states by pronouncing the linear folding state. Secondly, the swelling effect caused by HI does not allow the chain to evolve into head-out spiralling with increasing activity by trapping the head monomer within the swollen trap of passive monomers around

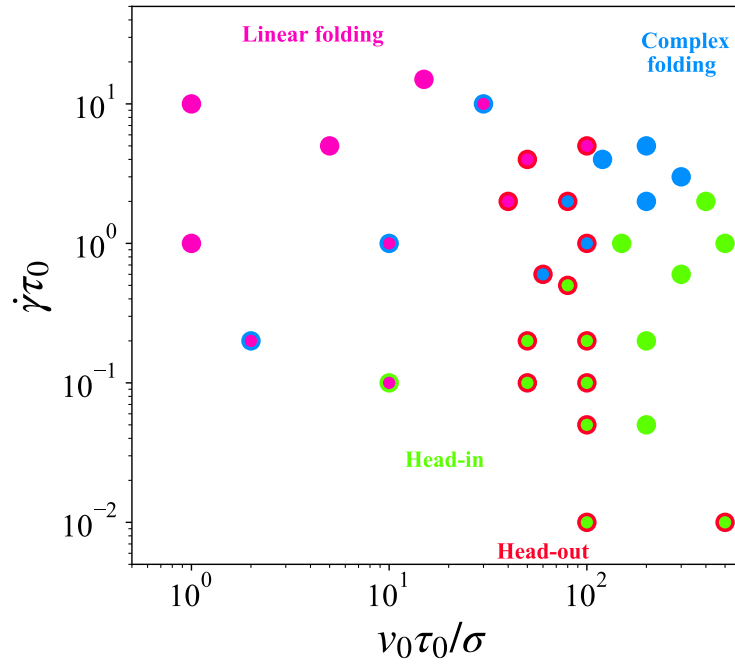


Figure 5.5: State diagram of the active polymer chain conformations as a function of activity: linear folding (magenta), complex folding (blue) and head-in spiralling (green). The edge color of the symbols represent the state of the chain without thermal fluctuations and HI, while the face colors are the states when thermal fluctuations and HI are included in the system.

it. Consequently, we never observe head-out spiralling state, even with increased activity, which only leads to the breakage of the head monomer away from the rest of the chain. Instead, we observe the head-in spiralling state at the parameter ranges where the head-out spiralling state was previously observed.



Chapter 6

Conclusions and Future work

In this section, we summarize the key findings of our study on active colloidal and polymer systems under shear flow and conclude by suggesting potential future research directions that could further advance our understanding of these complex systems.

In the third chapter, we have explored the effect of self-propulsion on the rheological response of the dense colloidal suspensions under steady shear by using Brownian dynamics simulations. First, the solid-to-liquid transition of the suspension was characterized, showing that activity helps to melt the systems, as shown before in literature[3, 88]. When melting, the self-propulsion of the colloids reduces the stress barrier that the system has to overcome in order to transition from the solid to the liquid state. Self-propulsion is not only responsible for assisting the shear in melting the colloidal suspension but also introduces a transition in the rheology of the melted suspension. Depending on the activity of colloids in the suspension, different fluid behaviours are found: shear thinning, Newtonian and shear-thickening. The underlying reason behind this response is a well-known dynamical mechanism of active colloidal particles: activity-induced clustering. When the self-propulsion is sufficiently strong to prevail against the shear, or even before shearing, a cluster formation is observed. The existence of these clusters creates additional resistance to flow when the suspension is exposed

to shear, causing it to behave as a shear-thickening fluid. We referred to this as motility-induced shear-thickening in this article.

The shear-thinning to thickening transition reported here is different from the transition observed in passive colloidal systems. Passive colloids tend to stick together by hydrodynamic and lubrication forces at high shear rates [171, 156], while active colloids cluster due to their motility (akin to motility-induced phase separation). The simulations presented here were performed in the absence of hydrodynamic interactions. Including hydrodynamics and lubrication forces would be an interesting future avenue since hydrodynamics suppress the tendency for active particles to form clusters [136, 90, 172], while on the other hand, hydrodynamics lead to clusters of sheared passive colloids. Additionally, the rheological behaviour of the colloidal suspension at low activities is very promising and requires more detailed analyses in future work with possibly using constitutive relationships more complex than Hershel-Buckley. Further, it would be interesting to test the response in a three-dimensional set-up or to include inertia to the active particles motion [173, 174]. Experimentally, the shear thinning to thickening transition could be tested using active colloids in a "washing-machine" set up [175]. Finally, it would be interesting to extend our simulation to particles of more complex shape than spheres such as active polymers or active filaments [60, 83], where new rheological behaviour due to active entanglements can be expected in dense solutions.

In the fourth chapter, we have extended our simulations to a flexible polymer chain in shear flow which exhibits some kind of chirality since the head monomer is dragging the rest of the monomers along a prescribed circle. The combination of activity, shear and chirality leads to a rich morphology of polymer complexes which includes both folding and spiralling states. The sense of rotation of the whole complex results from a competition between chirality and shear vorticity and can be tuned by activity and shear. Furthermore, we have demonstrated various physical properties of the active polymer chain such as the radius-of-gyration tensor and the shear viscosity to characterize these morphological states. Particularly, active chiral polymer chains in folding states exhibit shear-thinning

behavior, attributed to shear-induced stretching and alignment in the shear direction. Spiraling active chiral polymers disrupt the shear thinning character due to the robust activities of the head monomer, resulting in a Newtonian behavior of the chain. Moreover, working with the polymer chain at medium activity levels introduces the tunability of the polymer’s rheological properties by varying shear rates. Thus, the resulting combination and competition of activity, shear rate and chirality modify the rheology of the active polymer chain through distinct conformational states.

Our work builds the first basic step towards a monomer-resolved understanding of the rheological behavior of chiral active polymers and this model can be generalized and extended in various directions. First of all the role of fluctuations should be explored in the future. These can be both thermal and non-thermal ones induced by an active bath[69, 176, 70, 112]. Second, the collective effects of many interacting active polymers in shear flow can be studied leading possibly to distorted worm-blob-like configurations[48, 50]. Moreover, it would be interesting to expose active polymers with chirality to confinement[177] or to complex environments such as porous media[178, 179] or periodic pillars[180] to see whether chirality can enhance long-time diffusion significantly. The insights gained from the presented work can contribute to developing future applications, where the active systems are integrated into new technologies.

We remark that our Brownian dynamics simulations currently do not incorporate the hydrodynamic interactions (HI) for the sake of simplicity, serving as an initial reference to a dry system influenced by Gaussian noises. However, theoretical expectations suggest that HI could influence both the conformational and dynamical characteristics of the active polymer chain, contingent upon the nature of the activity. Therefore, as a next step, we focused on the multiparticle collision dynamics to simulate the solvent explicitly, including the hydrodynamical interactions. We study the same polymer chain with an active chiral head under shear flow, but this time the system is simulated by a hybrid algorithm: Molecular dynamics- Multiparticle Collision Dynamics (MD-MPCD). Our code of MPCD is first validated for several flow conditions, Poiseuille and Couette, and then is combined with the conventional molecular dynamics. This approach

allowed us to capture the polymer response in a more realistic environment considering the mesoscale dynamics of the solvent phase, which includes both thermal fluctuations and hydrodynamics. Our findings show that including the HI has an impact on the conformational states of a polymer chain. In particular, HI promotes linear folding and head-in spiraling states, while it reduces the occurrence of complex folding and eliminates completely the head-out spiraling state. The swelling effect induced by HI alters the transition dynamics between these states by leading to a delay in their occurrence on the state diagram. Hence, we could shortly highlight the importance of including hydrodynamic interactions in the simulations to comply with more realistic scenarios of the 2D experiments (e.g. particles on a quasi-two-dimensional substrate[15]), providing a further complex interplay between activity, shear, and chirality under such a condition. However, we note that HI scales differently in 2-dimensional and 3-dimensional systems, therefore these results might not be applied directly to more realistic 3D cases. It may open up exciting new directions for active matter systems in investigating the effects of fluctuations/hydrodynamics and how confinement and complex environments influencing active chiral polymers[177, 7, 85, 181, 182].

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