Active Brownian Particles Moving in Complex Environments

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In this thesis, the dynamics of a light-activated colloidal Janus particle are studied in a viscoelastic fluid under various spatial situations. These include the dynamics of a free active particle, its motion under additionally imposed spatial constraints e.g., flat walls, spherical obstacles, and cylindrical confinements. Opposite to a purely viscous fluid that remains in equilibrium to the imposed perturbation by a moving colloid, a viscoelastic fluid bath can not be considered in equilibrium. Because it develops transient stress in its microstructure against the motion of an active particle. The induced transient stress relaxes over the characteristic stress-relaxation time of a fluid which is typically of the order of a few seconds (i.e., a non-equilibrium bath). Consequently, the dynamical response of such an excited fluid couples to the motion of an active particle leading to very intriguing effects that are completely absent in a Newtonian fluid. In particular, striking features appear along the rotational dynamics of an active particle which include orders of magnitude enhancement of the rotational diffusion coefficient and even persistent circular motion. Such experimental observations are explained using a minimal non-Markovian Langevin model for active Brownian motion which considers the delayed response of the fluid (due to large relaxation time) with respect to the instantaneous orientation of an active particle. In addition, the presence of geometric constraints imposes long-range viscoelastic repulsion and torque to an active particle which further complicates its behavior. For instance, in comparison to pure thermal diffusion, such fluid-mediated interactions decrease the residence time of an active particle at a wall surface by orders of magnitude. Further, they have remarkable consequences on a strongly confined multi-active particle system. As observed, a multi-active particle confined in a cylindrical cavity displayed a transition to stable crystalline-like structures. Besides the molecular viscoelastic solvent, the dynamics of an active particle are also investigated in yet another type of viscoelastic background i.e., a dense suspension of colloidal rods. Even in this case, the orientational dynamics of the active particle are strongly enhanced. Therefore, this effect constitutes the central result of the present thesis. In contrast to the molecular viscoelastic solution, here, the observed enhancement of the rotational dynamics is found to stem from purely local mechanical interactions with the surrounding rods. The observations are further
corroborated by numerical simulations. Such a finding suggests that irrespective of its origin, the rotational dynamics enhancement of an active particle is a generic feature in viscoelastic media.
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Chapter 1

Introduction

Active colloids \textit{i.e.}, self-propelled particles have recently caught immense attention from people of various scientific disciplines since they share remarkable resemblance with living active matter \cite{1–8}. Opposite to their living counterparts \textit{i.e.}, motile microorganisms, they use much simpler propulsion schemes which render them ideal model systems for studying the rich physical phenomenon exhibited by living active matter \cite{9–11}. Since they respond to \textit{e.g.}, chemical \cite{12}, magnetic \cite{13}, acoustic \cite{14}, gravitational \cite{15}, and optical fields \cite{16, 17}, they can be operated under well-controlled conditions \cite{2}. In addition, they possess simple shapes and rigid structures which greatly reduces the complexities such as shape deformation, generally encountered in natural microswimmers \cite{18–21}. Consequently, they can reveal the exact role of the surrounding fluid medium on their swimming. So far, most of the studies involving active particles have been carried out in purely viscous fluids \textit{i.e.}, Newtonian fluids \cite{3, 22–24}. Such fluids relax quasi-immediately to the imposed deformation by an active colloid, thus, the surroundings behave as a faithful equilibrium bath \cite{25}. In contrast, very few have considered viscoelastic fluids \textit{i.e.}, depending on applied deformation rate they can behave as either elastic solids or viscous liquids \cite{26–30}. Unlike Newtonian fluids, viscoelastic fluids accumulate stress in their microstructure in response to an applied deformation which then takes rather large times (typically of the order of a few seconds) to relax \cite{26, 31–33}. Therefore, an active colloid while moving through a viscoelastic fluid drives it out of equilibrium. In consequence, the dynamical response of such an excited fluid can couple to the motion of the moving particle leading to striking different features such as orders of magnitude enhancement of the translational and rotational dynamics with no counterpart in Newtonian fluids \cite{26, 28, 34, 35}. Additionally, non-linear rheological effects of such fluids \textit{e.g.}, shear-thinning \cite{36–38}, and shear-thickening \cite{39} can have a profound impact on the swimmer’s directed motion \cite{40–44}. Besides, an active particle moving in a viscoelastic fluid represents a random walker in a non-equilibrium solvent which holds great fundamental relevance in non-equilibrium statistical physics \cite{32}. Moreover, most of the biological fluids such as mucus \cite{45},
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spermatozoa [46], blood [47], and the natural habitat of bacteria and cells are viscoelastic [48–50]. Therefore, investigating the behavior of active particles in such fluids is of major importance for biomedical applications [51–54] and for understanding intracellular motility [55,56].

Motivated by this, the present thesis aims at addressing the influence of the viscoelastic medium on the dynamics of self-propelled colloidal spheres. Additionally, how their dynamics are affected by the presence of geometrical constraints such as flat walls, spherical obstacles, and cylindrical confinements are also explored. To show how distinct are the effects observed in viscoelastic environments, experiments under similar conditions are performed in the counterpart Newtonian fluid. Further, it is also demonstrated that the observed dynamics of active particles are not particular to the kind of viscoelastic fluid but are general features that occur in other kinds of viscoelastic fluids such as colloidal glasses.

The thesis is structured as follows:

Chapter 2 deals with the basic background knowledge required for the present thesis. In particular, the characterization of real fluids into Newtonian and viscoelastic. The passive and active Brownian motion of colloidal particles in both the Newtonian and viscoelastic fluids are also discussed.

Chapter 3 provides the detailed description of the experiments which includes the procedures of making Janus particles, the critical fluid mixture in which the colloids are suspended, the process of sample making, preparation of topographic patterns using photo-lithography, the experimental set-up to achieve self-propulsion of the colloids, and the methods to analyze their two dimensional (2D) motion.

In Chapter 4, the active motion of a single Janus particle is described in a viscoelastic fluid. It is observed that the coupling of the transient stress of underlying viscoelastic fluid to the motion of an active particle led to distinct rotational dynamics including orders of magnitude enhancement of the rotational diffusion coefficient and even persistent circular motion. The experimental observations are further rationalized using a minimal non-Markovian Langevin model for the active Brownian motion.

In Chapter 5, the orientational work fluctuations of an active particle in a viscoelastic fluid are explored in the context of the work fluctuation theorem. In this case, due to the non-linear coupling of the viscoelastic bath (non-Markovian bath) to the orientational motion of an active particle resulted in remarkable enhancement of its orientational diffusion. Consequently, the work fluctuation theorem is violated in the form of effective temperature. By replacing the bath temperature with the
effective temperature, the work fluctuation relation is re-established. Moreover, the work fluctuation theorem is exploited to measure the torque acting on an active particle undergoing pronounced circular motion.

In *Chapter 6*, the dynamics of active particles in a viscoelastic fluid are studied in presence of various geometrical constraints such as walls, obstacles, and, confinements. The main effect of the viscoelastic close to a solid surface is to induce an effective repulsion on an active particle. Further, such a surface imposes asymmetry to the motion of an active particle leading to a viscoelastic torque on the particle. It was observed that the magnitude of repulsive interactions depends strongly on the activity of an active particle. The combination of the activity-dependent viscoelastic repulsion and torque led to dramatic consequences on the dynamics of the confined multi-particle system as it exhibited a transition from a liquid-like state to a crystal-like ordered state.

*Chapter 7* describes the active Brownian motion of a colloid in a dense suspension of polydisperse colloidal rods. Even though the coupling mechanism of the active particle with the background is entirely mechanical compared to a molecular solvent, the rotational diffusion enhancement is still observed. The active particle picks up the fastest motion of the rods background *i.e.*, the fluctuations of rods along their long axis. The coupling mechanism is further resolved using Brownian dynamics numerical simulations.

In this thesis, the numerical simulations provided *Chapter 7* are performed by Meike F. Bos who working as a Ph.D. student in the group of Dr. Joost de Graaf at the Utrecht University, The Netherlands. The present thesis focuses mainly on the experimental part, the simulations are referred with only brief details to further rationalize the experimental findings.

Parts of the present work are already published:


- N. Narinder, S. Paul, and C. Bechinger. Work fluctuation relation of an active
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Chapter 2

Fundamentals

The present thesis aims at understanding the passive and active Brownian motion of a colloidal particle in a Newtonian as well as in a viscoelastic fluid. This chapter provides a brief introduction to the basic background knowledge and related concepts. To this, first, the classification of fluids into Newtonian and viscoelastic is introduced by demonstrating their response to an external shear. Later a detailed description of the dynamics of a passive and an active colloidal particle both in a Newtonian and in viscoelastic fluids are discussed.

2.1 Newtonian and viscoelastic fluids

Depending on the response to an external shear stress or force, real fluids can be broadly characterized into Newtonian and non-Newtonian fluids. In the following, a distinction is drawn between a Newtonian and a non-Newtonian fluid by describing their response in a simple shear experiment as sketched in Fig. 2.1, where a volume of a fluid under investigation is placed between the two parallel plates which are separated by a distance $h$. Now, dragging the upper plate with surface area $A$ with a constant velocity $v$ while keeping the bottom plate at rest, leads to a shear flow. Under this condition, the imposed shear rate $\dot{\gamma} = dv/dh$ would lead to the development of a shear stress $\sigma = F/A$, defined as force $F$ per unit area $A$. Such a rheological investigation generally provides the measure of the viscosity of a fluid $\eta_f$ as the ratio of the induced stress and the applied strain rate. Mathematically,

$$\eta_f = \frac{\sigma}{\dot{\gamma}} \quad (2.1)$$

Therefore, depending on the properties of an enclosed fluid between the plates, it would exhibit a distinct response. For instance, when the enclosed fluid is a Newtonian fluid, the applied step-like shear rate $\dot{\gamma}$, would generate a stress $\sigma$ quasi-instantaneously as depicted in Fig. 2.2. Further, upon removal of the applied $\dot{\gamma}$, a Newtonian fluid would also relax back almost immediately. Therefore, such purely
viscous liquids follow Newton’s law \( i.e., \sigma = \eta_f \dot{\gamma} \propto v \) and hence, they are referred as the Newtonian fluids. Furthermore, the viscosity of such a fluid \( \eta_f \) remains independent of the applied shear rate.

This response, however, changes dramatically when the enclosed fluid between the plates is replaced by a non-Newtonian fluid\(^1\), say a viscoelastic fluid. In this case, in response to the applied \( \dot{\gamma} \), the stress \( \sigma \) will not develop immediately, rather it will take some finite time \( \tau_0 \). In addition, upon removal of the applied \( \dot{\gamma} \), it will also take \( \tau_0 \) to relax back. This is sketched in Fig. 2.3 for an applied step-like

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\(^1\) Broadly, there are two types of non-Newtonian fluids \( i.e., \) viscoelastic and inelastic [57, 58]. However, here only viscoelastic is considered for discussion, as it is only relevant for the present thesis.
Hence, on short times after the applied strain rate, it responds like an elastic solid and on long timescales, it behaves as a viscous fluid and therefore, known as viscoelastic fluid. The above described simple shear experiment measures the time-dependent response of an enclosed fluid and provides bulk or average flow patterns. The field is called bulk rheology or macrorheology. As the very name suggests, the term is derived from Greek where \( \text{rheo} \) stands for flow and \( \text{logos} \) is the study of. This approach is derived from the principles of continuum mechanics [59]. Based on this approach, nowadays, commercial rheometers use much more sophisticated rotational geometries which can provide precise measure of the average properties of a fluid [59,60].

Apart from macrorheology, another technique which characterizes the local rheological properties of a fluid, called microrheology, is developed [60–67]. It is based on the principles of statistical mechanics. Opposite to macrorheology, this technique measures the local rheological properties of a fluid. This is done typically by measuring the trajectories of an embedded colloidal particle (generally a sphere) in a fluid of interest. Depending on whether the embedded particle is passive or driven, it is termed as passive microrheology or active microrheology, respectively. In the following of this chapter, the passive Brownian motion of an embedded colloid both in a Newtonian as well as in a viscoelastic fluid are described where the dynamics are explicitly shown to have a link with the rheological properties of the surrounding fluid. In particular, the expression for one of the central quantity i.e., mean squared
displacement (MSD) is derived for both kinds of fluids. Since in the present thesis work, the fluids are characterized only by the passive microrheology technique, therefore, the discussions remained limited to it. For active microrheology the reader can refer to the following Refs. [66,68–78] and the literature within.

2.2 Passive Brownian motion

The Brownian motion is an erratic motion of colloids (∼ 1 nm − 1 μm) i.e., particles larger than the surrounding molecules, in a fluid [79]. The motion is named after a botanist named Robert Brown (1773-1858), who first reported the random motion of pollen grains immersed in a liquid. This erratic motion stems from the random impacts between the atoms or molecules of a fluid and a suspended colloidal particle. The energy is not permanently transferred to the colloid but there is an energetic equilibrium between the suspended colloid and the surrounding fluid through viscous dissipation which can be expressed by fluctuation-dissipation theorem [80]. Although the Brownian motion of a suspended colloid is not the molecular motion in itself but it can be inferred to provide an indirect access to the properties of the surrounding fluid.

2.2.1 Translational Brownian motion in a Newtonian fluid

The two dimensional (2D) passive translational motion of a colloidal particle (mass \( m \)) characterized by its position \( \mathbf{r} = (x, y) \) in a Newtonian fluid can be described by the Langevin equation [81,82]

\[
\frac{d\mathbf{r}}{dt} = \mathbf{v}; \quad m\frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v} + \mathbf{F}(t).
\] (2.2)

where \( \mathbf{F}(t) \) is a stochastic force which mimics the thermal fluctuations and \(-\gamma \mathbf{v}\) is the viscous friction. As pointed in Ref. [82], the stochastic force \( \mathbf{F}(t) \), should be Gaussian distributed with independent components having \( \delta \)-correlated time dependence as

\[
\langle \mathbf{F}(t) \rangle = 0; \quad \langle F_i(t)F_j(t') \rangle = 2D_p\delta_{i,j}\delta(t-t'); \quad i, j = x, y
\] (2.3)

The components \( F_i(t) \) have intensity \( D_p \) and are referred to as white Gaussian noise. The noise strength \( D_p \) (for momentum \( p \)) is related to the noise strength \( D_T \) (for velocities \( v \)) by the relation: \( D_p = m^2D_T \). In addition, the fluctuation-dissipation theorem states [80]

\[
D_p = m^2D_T = k_BT\gamma
\] (2.4)

where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. Therefore, Eqn. 2.2 can be written as

\[
\frac{d\mathbf{v}}{dt} = -\frac{\gamma}{m} \mathbf{v} + \sqrt{2D_T}\xi(t),
\] (2.5)
where $\xi(t)$ follows

\[
\langle \xi(t) \rangle = 0; \quad \langle \xi_i(t)\xi_j(t') \rangle = \delta_{i,j}\delta(t-t'); \quad i, j = x, y
\] (2.6)

For suspended colloids in a solvent, the typical momentum relaxation time $m/\gamma$ is of the order of $\sim \mu s$, whereas, the typical measurement times are of the order of $\sim ms$. Therefore, the inertial effects can be ignored i.e., overdamped limit. When ignoring inertial effects, Eqn. 2.5 can be integrated to obtain the mean squared displacement (MSD) in 2D which characterizes the diffusive dynamics of a colloid as

\[
\langle |r(t) - r(0)|^2 \rangle = 4D_T t
\] (2.7)

where $D_T$ is the translational diffusion coefficient of a colloid and is given by $D_T = k_B T/\gamma$ i.e., Stokes-Einstein relation [83]. Hence, the MSD of a passive colloid in a Newtonian fluid undergoes linear growth. Indeed, the MSD from an experimentally measured trajectory (Fig. 2.4(a)) of a colloid with mean diameter $2a = 7.75 \mu m$ in a Newtonian fluid is linear in time as plotted in Fig. 2.4(b). A linear fit to the MSD determines the translational diffusion coefficient to be $D_T = 0.0041 \mu m^2 s^{-1}$. By equating the value of $D_T$ to the Stokes-Einstein relation gives the viscosity $\eta_f$ of the fluid as

\[
\eta_f = \frac{k_B T}{6\pi a D_T} = 0.014 \text{ Pas}
\] (2.8)

Thus, the thermally excited motion of an embedded colloid in a fluid provides rheological information of the fluid. The same can also be inferred from the rotational

**Figure 2.4:** (a) Trajectory (solid line) of a passive Janus colloid with diameter $2a = 7.75 \mu m$ in a Newtonian fluid comprised of water and propylene glycol $n-$propyl ether measured over 1000 s. The arrows denote the instantaneous orientation $\mathbf{n}$ of the colloid. Inset: Optical image of a Janus particle $2a = 7.75 \mu m$ with labeled orientation vector $\mathbf{n}$ pointing from its capped side (darker side) to its uncapped side, defined by the angle $\theta$. (b) Mean squared displacement $\langle \Delta r(t)^2 \rangle$ for the translational particle motion as a function of time.
dynamics of a colloidal particle. The orientation in 2D of a colloid can be tracked, for instance, for a Janus particle (Inset Fig. 2.4 (a)) whose one hemisphere is coated with carbon film which provides an optical contrast for tracking the orientation. This is dealt in the following subsection.

2.2.2 Passive rotational motion in a Newtonian fluid

Similar to the translational Brownian motion, one can write the corresponding Langevin equation governing the orientational dynamics of a suspended colloid. The orientation vector \( \mathbf{n} = (\cos \theta, \sin \theta) \), in 2D can be defined for a Janus sphere (see inset Fig. 2.4 (a)) as a unit vector pointing perpendicularly from the capped side to the uncapped side. The Langevin equation for the orientational motion becomes

\[
\frac{d\theta}{dt} = \omega; \quad I \frac{d\omega}{dt} = -\gamma_\theta \omega + T(t)
\]

where \( I \) is the moment of inertia of a colloid, \( \gamma_\theta \) is the rotational frictional coefficient and, \( T(t) \) is the erratic torque acting on a suspended colloidal particle due to collisions with the solvent molecules. Similar to the properties of the stochastic force \( F(t) \) in Eqn. 2.3, the stochastic torque \( T(t) \) follows

\[
\langle T(t) \rangle = 0; \quad \langle T_i(t)T_j(t') \rangle = 2k_B T \gamma_\theta \delta_{i,j} \delta(t - t')
\]

Again, due to overdamped dynamics, inertial terms can be neglected to obtain the angular mean squared displacement (AMSD)

\[
\langle (\theta(t) - \theta(0))^2 \rangle = 2\frac{k_B T}{\gamma_\theta} t = 2D_\theta t
\]

where \( D_\theta \) is the rotational diffusion coefficient. Using Stokes-Einstein relation, \( D_\theta \) can be expressed as

\[
D_\theta = \frac{k_B T}{8\pi \eta_f a^3}.
\]

The experimentally measured orientation \( \theta(t) \) of a colloidal particle (diameter \( 2a = 7.75 \mu m \)) as a function of time and its corresponding AMSD are plotted in Figs. 2.5 (a) and 2.5 (b), respectively.

The value of \( D_\theta \) obtained by linear fitting the computed AMSD is \( 6.28 \times 10^{-4} \text{ rad}^2/\text{s} \) which gives the fluid viscosity \( \eta_f \approx 0.004 \text{ Pa s} \). In comparison to the bulk value of viscosity of the fluid i.e., \( \eta_f = 0.004 \text{ Pa s} \) [84], the value obtained from the translational MSD is 3.1 times higher. This is due to the presence of presence confining walls of the sample cell which lead to a higher translational friction coefficient compared to that in the bulk. A detailed description of the sample cell is provided in Chapter 3.
2.2 Passive Brownian motion

Figure 2.5: (a) Time evolution of the orientation $\theta$ of a passive colloid having diameter $2a = 7.75 \, \mu m$ in a Newtonian fluid comprised of water and propylene glycol $n$-propyl ether. (b) Angular mean squared displacement $\langle \Delta \theta(t)^2 \rangle$ of the orientational particle motion as a function of time.

2.2.3 Translational Brownian motion in a viscoelastic fluid

In this subsection, the Brownian motion of a colloid suspended in a viscoelastic fluid is discussed. The obtained expression for the MSD is then shown to provide the rheological parameters of the surrounding viscoelastic fluid. Unlike the Newtonian case, here, due to finite memory effects of the fluid, the translational motion of a suspended colloid (sphere of radius $a$) is described by the overdamped generalized Langevin equation (GLE) as \[31, 32, 35, 85\]

$$-\int_{-\infty}^{t} \Gamma_T(t - t')\dot{r}(t')dt' + \xi(t) = 0$$

(2.13)

where $\Gamma_T(t) = 6\pi a G(t)$ is the translational memory friction kernel and $G(t)$ is the stress relaxation modulus of the fluid and, $\xi(t)$ is the Gaussian-distribution correlated thermal noise with zero mean and autocorrelation $\langle \xi(t)\xi(t') \rangle = 2k_B T \Gamma_T(t - t')$ \[86\]. The stress-relaxation modulus $G(t)$ which nicely describes the relevant parameters for most of the semi-dilute polymer solutions is the three-parameter Jeffrey’s model \[87, 88\]

$$G(t) = 2\eta_\infty \delta(t) + \left( \frac{\eta_0 - \eta_\infty}{\tau_0} \right) \exp \left( -\frac{t}{\tau_0} \right)$$

(2.14)

where $\eta_\infty$ is the viscosity contribution of the molecular solvent and, $(\eta_0 - \eta_\infty)$ is the viscosity of the polymer network, $\tau_0$ corresponds to the stress-relaxation time of a viscoelastic solution. Physically, it describes that the solvent part of the solution exhibits an immediate relaxation and therefore, modelled by the Dirac delta function $\delta(t)$ whereas the polymer part which provides viscoelastic properties to the solution,
displays an exponentially decaying response with a time constant $\tau_0$. Eqn. 2.13 in the frequency domain can be written as

$$0 = i\omega \Gamma(\omega) r(\omega) + \xi(\omega).$$

(2.15)

This gives the particle position $r(\omega)$ in the frequency space

$$r(\omega) = -\xi(\omega)/i\omega \Gamma(\omega) r(\omega).$$

(2.16)

Straightforwardly, from Eqn. 2.16, one can obtain the power spectrum density (PSD) $\langle r(\omega)r^*(\omega) \rangle$ of the particle as

$$\langle r(\omega)r^*(\omega) \rangle = \frac{4k_B T}{6\pi \eta_\infty a} \frac{\left(\frac{(1+\frac{\eta_0-\eta_\infty}{\eta_\infty})}{\frac{\eta_0}{\tau_0}} + \omega^2\right)}{\omega^2 + \left(\frac{1+\frac{\eta_0-\eta_\infty}{\eta_\infty}}{\tau_0}\right)^2}. \quad (2.17)$$

Performing the inverse Fourier transformation of PSD gives the position autocorrelation function (ACF) $\langle r(t)r(0) \rangle$ in the time domain as

$$\langle r(t)r(0) \rangle = \frac{2k_B T}{6\pi \eta_\infty a} \left[ \tau_0 \left(\frac{\eta_\infty}{\eta_0}\right)^2 \exp \left(-\frac{\eta_\infty}{\eta_0 \tau_0} t\right) - \frac{\eta_\infty t}{\eta_0}\right]. \quad (2.18)$$

The ACF is related to the mean squared displacement (MSD) as

$$\langle \Delta r(t)^2 \rangle = 2[\langle r(0)^2 \rangle - \langle r(t)r(0) \rangle]. \quad (2.19)$$

Substituting the expression of ACF from Eqn. 2.18 into Eqn. 2.19 gives MSD as

$$\langle \Delta r(t)^2 \rangle = \frac{4k_B T}{6\pi \eta_\infty a} \left[ t + \left(1 - \frac{\eta_\infty}{\eta_0}\right) \tau_0 \left(1 - e^{-\frac{t}{\tau_0}}\right)\right]. \quad (2.20)$$

The MSD on short timescales \textit{i.e.}, $t \approx (\eta_\infty/\eta_0)\tau_0$, exhibits a sub-diffusive behavior because of the caging effects of the surrounding polymer network around the probe. However, on sufficiently long timescales \textit{i.e.}, $t >> (\eta_\infty/\eta_0)\tau_0$, it displays diffusive translational dynamics. As a matter of fact, the MSD of a colloid (diameter $2a = 7.75 \mu m$) embedded in a viscoelastic fluid comprised of water with added propylene glycol $n-\text{propyl ether with added 0.05\% wt. polyacrylamide}$ is very well described by the Eqn. 2.20, as shown by the solid line in Fig. 2.6 (b). Fitting the experimental data to Eqn. 2.20 determines the parameters $\eta_\infty$, $\eta_0$ and, $\tau_0$ to 0.13 Pas, 0.69 Pas and, 17 s, respectively. Therefore, this demonstrates the importance of the Brownian motion of a colloid in inferring the rheological parameters even for a complex fluid.
2.2 Passive Brownian motion

Figure 2.6: (a) Trajectory (solid line) of a passive Janus colloid of diameter $2a = 7.75 \mu m$ in a viscoelastic fluid comprised of water and propylene glycol $n$-propyl ether with added polyacrylamide (0.05% wt.). The arrows denote the instantaneous particle orientation $\mathbf{n}$. (b) Mean squared displacement $\langle \Delta r(t)^2 \rangle$ of the translational particle motion as a function of time. The solid black line is the fit according to Eqn. 2.20.

2.2.4 Rotational Brownian motion in a viscoelastic fluid

Quite similar to the passive translational motion, one can describe the rotational motion of a suspended colloid in a viscoelastic fluid using the corresponding GLE as

$$- \int_{-\infty}^{t} \Gamma_R(t-t') \dot{\theta}(t') dt' + \zeta(t) = 0$$

where $\Gamma_R(t) = 8\pi a^3 G(t)$ is the rotational memory friction kernel for a sphere of radius $a$ and $G(t)$ is the stress-relaxation modulus of the fluid as described in Eqn. 2.14 and, $\zeta(t)$ is the Gaussian-distribution correlated thermal noise with zero mean and autocorrelation $\langle \zeta(t)\zeta(t') \rangle = 2k_B T \Gamma_R(t-t')$. Following the same steps as done for the translational equation of motion (Eqn. 2.13), the expression for the AMSD can be obtained as

$$\langle \Delta \theta(t)^2 \rangle = \frac{2k_B T}{8\pi \eta_0 a^3} \left[ t + \left( 1 - \frac{\eta_\infty}{\eta_0} \right) \tau_0 \left( 1 - e^{-\frac{t}{\tau_0 \eta_\infty}} \right) \right].$$

In Fig. 2.7 (b), the expression for the AMSD (Eqn. 2.22) is fitted to an experimentally measured orientational AMSD of a colloid of diameter 7.75 $\mu m$ in a viscoelastic solution composed of mixture of water and propylene glycol $n$--propyl ether with added 0.05% wt. polyacrylamide. The fitting demonstrates that the above obtained expression for the AMSD excellently describes the orientational dynamics of a colloid in a viscoelastic medium. Similar to the translational motion, the orientation of the particle also subjected to the caging effects of the surrounding polymer network. As
observed, at short times \((t \approx (\eta_\infty/\eta_0)\tau_0)\) the AMSD shows sub-diffusive behavior which becomes diffusive at later times \((t >> (\eta_\infty/\eta_0)\tau_0)\).

Figure 2.7: (a) Time evolution of the orientation of a passive colloid having diameter \(2a = 7.75 \, \mu m\) in a viscoelastic fluid composed of a mixture of water, propylene glycol \(n\)-propyl ether, and polyacrylamide. (b) Angular mean squared displacement \(\langle \Delta \theta(t)^2 \rangle\) of the orientational particle motion shown in (a), as a function of time. The solid line is the fit to Eqn. 2.22.

2.3 Active Brownian motion

In the previous section, the passive Brownian motion of a colloid is discussed in detail, where the system remains energetically in equilibrium. However, when we look out in nature almost all the phenomena and processes involve a net flow of matter or energy and, therefore, are out of equilibrium. Even systems as small as a single cell which is the most basic unit of life involves a net flow of energy, matter and information to perform crucial tasks such as intracellular transport and positioning of compartments etc., and hence, are non-equilibrium systems [56,90–92]. Swimming of microorganisms is also non-equilibrium process since it involves constant energy input for propulsion [18–21,93,94]. Such systems are of great fundamental significance to understand and develop non-equilibrium statistical physics [95,96]. Synthetically, these can also be realized with colloidal particles by imparting distinct physical or chemical properties to their surfaces which enable them to undergo anisotropic interactions with their surroundings [2,97]. In the following subsections, the translational and rotational dynamics of an active colloid are discussed in both a Newtonian and a viscoelastic fluid.
2.3 Active Brownian motion

2.3.1 Translational dynamics of an active colloid in a Newtonian fluid

The Langevin description for the passive motion of a colloid (mass \( m \)) mentioned in Eqn. 2.2 can be extended for an active Brownian particle by including an additional force term \( F_v \) which accounts for the self-propulsion force as \[98\]

\[
\frac{dr}{dt} = \mathbf{v}; \quad m \frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v} + \mathbf{F}_v + \sqrt{2D_T \mathbf{\xi}(t)} \tag{2.23}
\]

where \( F_v \) can be simply assumed to always act in the direction of particle orientation vector \( \mathbf{n} \) \[98\]. Mathematically,

\[
\mathbf{F}_v = \gamma v \mathbf{n} \tag{2.24}
\]

Ignoring inertial effects \( i.e., \) the overdamped limit, analytically the expression for the MSD of an active Brownian particle can be obtained as \[22,99\]

\[
|\mathbf{r}(t) - \mathbf{r}(0)|^2 = 4D_T t + v^2 \tau_\theta^2 \left[ \frac{2t}{\tau_\theta} + e^{-(2t/\tau_\theta)} - 1 \right] \tag{2.25}
\]

where \( \tau_\theta = 1/D_\theta \) is the rotational diffusion time of the particle. This suggests, for timescales much smaller than the rotational diffusion time \( i.e., \) \( t \ll \tau_\theta \), Eqn. 2.25 reduces to

\[
|\mathbf{r}(t) - \mathbf{r}(0)|^2 = 4D_T t + v^2 t^2. \tag{2.26}
\]

This states that at very short times, the MSD will be diffusive as the term involving \( v^2 t^2 \) will be very small compared to \( 4D_T t \), however, at later times, the \( v^2 t^2 \) term will dominate which leads to a transition to ballistic MSD. Eqn. 2.25 also states that on timescales \( t >> \tau_\theta \), the translational MSD becomes diffusive with an effective higher diffusion coefficient \( D_{\text{eff}} = D_T + v^2 \tau_\theta \) which depends on the active propulsion \( v \). For a fix particle size, the short-time diffusion \( D_T \) remains constant as it is set by the bath temperature \( T \) while the long-time effective diffusion \( D_{\text{eff}} \) is caused by the randomization of the particle orientation and increases with \( v \). Fig. 2.8 (a) shows the trajectories of an active Janus particle half-coated with platinum moving with self-propulsion velocity \( v \) which is set by \( \text{H}_2\text{O}_2 \) concentration in its swimming medium which is subsequently increasing for the trajectories towards the right \[22\]. The MSDs corresponding to the trajectories in Fig. 2.8 (a) are plotted in Fig. 2.8 (b). As expected, with increase in \( v \) \( i.e., \) increase in \( \text{H}_2\text{O}_2 \) concentration, the long-time slope of the MSDs also increases which corresponds to the long-time effective diffusion coefficient \( D_{\text{eff}} \).

2.3.2 Rotational dynamics of an active colloid in a Newtonian fluid

Unlike the translational dynamics of an active particle in a Newtonian fluid which shows enhanced diffusion on long timescales, the orientational motion remains similar to that of a passive particle. Since there is no angular drift along the orientational degrees of freedom, therefore, the expression of the angular MSD remains the same as that of a passive particle \( i.e., \) similar to Eqn. 2.11 as

\[
\langle |\theta(t) - \theta(0)|^2 \rangle = 2D_\theta t \tag{2.27}
\]
Chapter 2  Fundamentals

**Figure 2.8:** (a) Trajectories of an active Brownian particle (diameter $2a = 1.62 \mu m$) at different self-propulsion velocities $v$ increasing towards the right in a Newtonian fluid. (b) Mean squared displacement of active particles as a function of time for different self-propulsion velocities $v$ (set by the H$_2$O$_2$ concentration). Reprinted with permission from the American Physical Society. Copyright 2007 [22].

2.3.3 Dynamics of an active colloid in a viscoelastic fluid

In comparison to the ample amount of research which has been conducted for comprehending the dynamics of active colloids in purely viscous fluids, their dynamics in viscoelastic fluids have remained largely unexplored despite the fact that they provide the natural habitat to the living microswimmers [45, 46, 48, 100]. The limited studies which have been done already demonstrate considerable qualitative differences compared to Newtonian fluids [26, 30, 34, 35, 41–44, 101]. The reason being, in contrast to the dynamics of an active particle in a Newtonian fluid where (apart from the thermal noise) the surrounding fluid only provides an opposing friction to the particle motion, its dynamics in a viscoelastic fluid gets coupled to the memory response of the surrounding fluid. In addition to this, non-linear effects such as shear thinning [36–38] and shear thickening [39] also greatly modifies the self-propulsion behavior. Even in the regime of small self-propulsion velocities, which do not instigate a non-linear fluid response, the dynamics show striking differences with respect to their Newtonian counterparts. For instance, an active particle exhibits a velocity-dependent enhancement of its translational and rotational diffusion coefficients [26]. Interestingly, the findings are not specific to the propulsion mechanism or the kind of viscoelastic fluid, they are rather general effects that originate from the elastic response in such fluids [34].

Translational dynamics

Typical trajectories of an active colloidal sphere (diameter $2a = 7.75 \mu m$) moving in a viscoelastic fluid at various velocities $v$ increasing towards the right are shown
2.3 Active Brownian motion

in Fig. 2.9. The trajectories are distinctly different not only in terms of distance travelled which would obviously be more for larger \( v \) but also in terms of orientational motion (shown by the arrows). Apparently, with increasing \( v \) the trajectories become more and more crooked as visible from the curvature of the path. This is in stark contrast to the behavior of an active particle in a Newtonian fluid where the rotational dynamics remains independent of the self-propulsion \( v \).

![Figure 2.9: Trajectories of an active particle (diameter \( 2a = 7.75 \, \mu m \)) in a viscoelastic fluid comprised of water and propylene glycol \( n\text{–propyl ether with added 0.05\% wt. polyacrylamide at various velocities \( v \) increasing from left to right as follow: } v = 0.032 \, \mu m \cdot s^{-1}, \quad v = 0.188 \, \mu m \cdot s^{-1}, \quad v = 0.227 \, \mu m \cdot s^{-1}, \quad v = 0.398 \, \mu m \cdot s^{-1} \quad \text{and, } \quad v = 0.534 \, \mu m \cdot s^{-1} \text{ measured over 1500 s. The arrows denote the instantaneous particle orientation } \mathbf{n} = (\cos \theta, \sin \theta). \) Reprinted with permission from the American Physical Society. Copyright 2016 [26].](image)

The translational MSDs of the particle are plotted in Fig. 2.10 for different self-propulsion \( v \). In contrast to the short-time behavior of the MSDs of an active particle in a purely viscous fluid which is independent of \( v \) and depends only of the temperature of the bath, here obviously this is not the case (see the log-log representation of the MSDs in Fig. 2.10 (b)). In this case, it is more complex as the caging effect of the surrounding polymer network leads to sub-diffusion while the coupling of translational fluctuations to the ones originate from the excited (non-equilibrium) viscoelastic fluid leads to enhanced diffusion. However, the long-time behavior of MSDs are very similar to that of an active particle in a Newtonian fluid.

**Rotational dynamics**

Opposite to the translational dynamics of an active particle where the differences (compared to a purely viscous) are not very dramatic, the orientational motion exhibits sharply distinct velocity-dependent behavior. For instance, the mean squared
angular displacements $\langle \Delta \theta(t)^2 \rangle$ of an active particle (diameter 7.75 $\mu$m) are shown in Fig. 2.11 (a) for increasing particle velocity $v$ from bottom to top. Vividly, the long-time slope of the curves increases with an increase in $v$, suggesting an enhancement of the rotational diffusion coefficient. The obtained diffusion coefficient as a function of Weissenberg number (related to $v$ as $Wi = v\tau_0/2a$) is shown in Fig. 2.11 (b) as squares. Notably, such a feature of the orientational dynamics is not specific to the particular size of a particle but occurs even for other sizes of the particles. For instance, the diamonds in Fig. 2.11 (b) correspond to diffusion coefficient of smaller particles with diameter $2a = 4.32$ $\mu$m. The parameter which sets the magnitude of the diffusion coefficient here is the Weissenberg number $Wi$ which quantifies the magnitude of deformation instigated by a particle in the viscoelastic medium. It should also be noted that the values of $Wi$ probed here are smaller than unity, meaning that the fluid behaved as a linear viscoelastic medium with its viscosity independent of $v$. In addition, the observed rotational enhancement effect is also not particular to the fact that whether the particles are self-propelled or driven. This is demonstrated by the open circles in Fig. 2.11 (b) which represents the rotational diffusion coefficient for a particle settling in gravity where the angle of inclination determines the $v$. As mentioned above, such an enhancement of the rotational diffusion is not specific to a particular kind of viscoelastic fluid but occurs for other kinds of fluids. For instance, a similar increase of the rotational diffusion is also observed for an active particle probing a viscoelastic glassy environment comprised of bi-disperse spheres as shown in Fig. 2.12. This proves the effect is a general one and is expected to occur for other complex environments offering memory effects. The present thesis aims at providing more sound knowledge of such orientational effects by not only demonstrating them through experiments but also through their theoretical modelling and simulations. The chapters following Chapter 3 deal with the detailed description of the dynamics of active particles under various complex
Figure 2.11: (a) Angular mean squared displacement $\langle \Delta \theta(t)^2 \rangle$ of an active Brownian particle ($2a = 7.75 \, \mu m$) for different self-propulsion velocities $v$. The dashed line corresponds to $\langle \Delta \theta(t)^2 \rangle$ of a particle of same size in a Newtonian fluid having same viscosity. Inset: Log-log representation of $\langle \Delta \theta(t)^2 \rangle$ as a function time. (b) The long time effective rotational diffusion coefficient normalized by the diffusion of the corresponding passive particle, for a particle of diameter $2a = 7.75 \, \mu m$ (squares), $2a = 4.32 \, \mu m$ (diamond) and, for passive particles $2a = 7.75 \, \mu m$ under gravity (circle) as a function of Weissenberg number $Wi$. The solid line is a guide to eye. Reprinted with permission from the American Physical Society. Copyright 2016 [26].

situations including a polymer solution, patterned substrates and even in dense rods suspension.
Figure 2.12: (a) Exemplary trajectory of an active Brownian sphere (diameter $2a = 6.3 \, \mu m$) moving with a free velocity $v = 1.0 \, \mu m \, s^{-1}$ in a suspension of bidisperse colloidal spheres at area fraction $\varphi = 0.784$. The arrows represent the instantaneous orientation of the particle. The scale bar is $5 \, \mu m$. (b) Normalized rotational diffusion coefficient of an active particle as a function of area fraction of the binary colloidal background for different self-propulsion $v$. The orange-shaded region corresponds to the glassy phase. Inset: Peak value of the rotational diffusion coefficient as a function of self-propulsion $v$ of the active particle. Reprinted with permission from the Nature Publishing Group. Copyright 2019 [34].
Chapter 3

Materials and Methods

The present experimental work investigates the dynamics of active colloidal particles on a flat as well as on a topographically structured substrate in both a Newtonian and a viscoelastic fluid. The experimental approach requires the following:

1. Creating asymmetric surface properties of spherical colloids i.e., making Janus particles.
2. Preparation of a critical Newtonian and a corresponding viscoelastic fluid.
3. Preparation of a sample cell.
4. Inducing self propulsion of the Janus particle in the critical fluid mixture.
5. Recording and tracking the motion of particles with a sub-micron resolution.

This chapter deals with a detailed description of each of the above-mentioned processes.

3.1 Carbon coating of particles

In this work, commercially available spherical silica particles from Microparticles GmbH of various sizes are used. For a batch of particles, they are quite monodisperse as the coefficient of variation (CV %) in their size is less than 5%. To cap them, a monolayer of these spheres is made on a glass substrate. For this purpose, a very dilute suspension of the particles is prepared by mixing 150 µL of the suspension provided by the Microparticles GmbH (5 wt.% of the particles) in 250 µL of milli-Q water having resistivity 18.2 MΩ cm⁻¹. This suspension is then poured on a glass slide which is cleaned first with isopropanol and then with plasma cleaner to render its surface hydrophilic. To obtain a perfect monolayer of the spheres, the prepared
suspension is poured on a glass slide drop by drop, by keeping a certain distance
between each subsequent drop, using a pipet, to avoid overlapping of the particles,
as sketched in Fig. 3.1 (a). The monolayer is then left out for drying for \( \approx 8 \) hours.
The dried monolayer of the spherical particles is then capped from the top using the
carbon sputtering machine (Leica MiKrosysteme GmbH), the situation is sketched
in Fig. 3.1 (b). The thickness of the cap can be precisely tuned as the evaporation
of the carbon thread in the process can be operated in two modes, namely, the flash
mode and the pulse mode. The flash mode follows the evaporation of the carbon
thread with the maximum power and thus, can be utilized for coarse adjustment of
the cap thickness. The pulse mode, on the other hand, uses short pulses of duration
150 ms and therefore, provides a fine-tuning of the cap thickness. The particles are
then extracted from the glass substrate in milli-Q water using ultrasonication, as
depicted in Fig. 3.1 (c). After which, they are allowed to sediment under gravity for
several hours (\( \approx 3 \) h) as shown in Fig. 3.1 (d). After sedimentation, the excess water
is removed from the top. The extracted particles are then transferred to smaller
tubes. Using centrifugation, the excess water is further removed. The prepared
Janus particles are finally transferred to micro-tubes which can then be used for
sample preparation. A typical optical image of a silica Janus particle of diameter
\( 2a = 7.75 \, \mu \text{m} \) with a cap thickness 50 nm (the darker half) is shown in Fig. 3.1 (e).

\[
\begin{align*}
(a) & \quad \text{(b)} \\
\text{(c)} & \quad \text{(d)} \\
\text{(e)} & \quad \text{10} \, \mu \text{m}
\end{align*}
\]

**Figure 3.1:** The process of carbon coating the spherical colloidal particles. (a) Preparation of a monolayer of the particles. (b) Carbon coating the dried monolayer
of the particles. (c) Process of removing the capped particles from the slide using an
ultrasonic bath. (d) Sedimentation of the capped particles. (e) Optical image (top
view) of a silica Janus particle of diameter \( 2a = 7.75 \, \mu \text{m} \) half capped with 50 nm
thick carbon layer which is visible as the darker half.
3.2 Preparation of a critical Newtonian and a viscoelastic fluid

3.2.1 Preparation of a critical Newtonian fluid

A Newtonian fluid is prepared by mixing propylene glycol \( n - \)propyl ether (PnP) and water in proportion 2:3. The mixture has lower critical temperature \( T_c = 305.05 \) K above which it exhibits phase separation via the spinodal decomposition [84, 102, 103]. Snapshots of the binary critical mixture, taken using video microscopy, at temperatures below and above \( T_c \) are shown in Fig. 3.2 (a) and (b), respectively. The phase diagram of this mixture is shown in Fig. 3.3, where the fluid remains homogeneously mixed below the dashed line for the corresponding mass fraction of PnP. The lower critical temperature of the mixture is at \( T_c = 305.05 \) K and 0.4 mass fraction as highlighted by the star in Fig. 3.3. In terms of rheological properties, this fluid behaves as Newtonian liquid with its viscosity \( \eta_f = 0.004 \text{ Pa s} \) at 298.15 K, obtained from the measured angular mean squared displacement\(^1\) (AMSD) of a Janus sphere (diameter \( 2a = 7.75 \) \( \mu \)m) suspended in it. The angular dynamics of the colloid, as confirmed experimentally (see Fig. 3.4), in such a medium is purely diffusive on all timescales i.e., \( \langle \Delta \theta(t)^2 \rangle = 2D_\theta t \) where \( \theta \) is the angular coordinate of the particle and \( D_\theta \) is the rotational diffusion coefficient. Using the Stokes-Einstein relation, the viscosity of the fluid can be computed directly as \( \eta_f = k_BT/8\pi a^3 D_\theta \).

\( \text{Figure 3.2:} \) Snapshots from the video microscopy of the critical fluid at 0.4 PnP mass fraction. (a) At temperature \( T = 298.15 \) K which is below the critical temperature \( T_c \) of the fluid, where the fluid remains homogeneously mixed. (b) At \( T = 308.15 \) K > \( T_c \), where the fluid undergoes phase separation.

\(^1\) Note that viscosity of the fluid can also be calculated using the translational mean squared displacement (MSD), however, because of vertical confining walls under our conditions, the probe particle in the medium experiences large viscous friction leading to a higher effective viscosity \( \eta_{f, \text{eff}} \approx 2.5\eta_f \).
Figure 3.3: Phase diagram of a critical binary mixture of propylene glycol \( n \)-propyl ether (40\% by mass) and water (60\% by mass). The area above the dashed curve represents the two-phase region, while the area below the dashed curve corresponds to the homogeneously mixed phase. The pentagram is the lower critical point (PnP mass fraction = 0.4 and \( T_c = 305.05 \text{ K} \)).

Figure 3.4: Angular mean squared displacement of a colloid (diameter \( 2a = 7.75 \text{ \mu m} \)) in a binary mixture of PnP and water at temperature \( T = 298.15 \text{ K} \). The colloid exhibits diffusive orientational dynamics with a diffusion coefficient \( D_\theta = 7.03 \times 10^{-4} \text{ rad}^2/\text{s} \) which gives the viscosity of the fluid \( \eta_f = 0.004 \text{ Pa s} \).

3.2.2 Preparation of a critical viscoelastic fluid

To impart viscoelastic properties to the critical binary mixture a small amount (0.05 \% wt. - 0.07\% wt.) of polyacrylamide (PAAM) from Polysciences, molecular weight \( M_w = 18 \times 10^6 \text{ g/mol} \) is added to the binary Newtonian mixture. PAAM renders the fluid to become viscoelastic. The concentration of the PAAM strongly dictates the viscoelastic properties of the solution. Again, the rheological properties of the fluid can be inferred from the dynamics of an embedded colloid in it i.e., passive microrheology [62, 104]. Unlike a Newtonian fluid, in this case, both viscous and elastic components are present which can be taken into account by considering the simplest three-parameter Jeffrey’s model for the relaxation modulus \( G(t) \) of the fluid [62]

\[
G(t) = 2\eta_\infty \delta(t) + \left( \frac{\eta_0 - \eta_\infty}{\tau_0} \right) \exp\left( -\frac{t}{\tau_0} \right) \tag{3.1}
\]

Adding PAAM also brings a very small shift in the critical demixing temperature of the fluid. The critical temperature of the ternary viscoelastic fluid reduces to \( T_c = 304.55 \text{ K} \).
3.3 Preparation of a micro-litre sample cell

The sample cell is prepared on a clean glass slide (dimensions 75 × 25 mm). The glass slide is first cleaned with isopropanol using a lens cleaning tissue and then again in a bath of isopropanol in an ultrasonic bath. The slide is then dried using nitrogen.
Table 3.1: Rheological parameters: $\eta_0$, $\eta_\infty$ and $\tau_0$ computed from the fit of the experimental translational mean-squared displacements of a passive colloid of mean diameter 7.75 $\mu$m as shown in Fig. 3.5 to Eqn. 3.3.

<table>
<thead>
<tr>
<th>PAAM conc. (% wt.)</th>
<th>$\eta_\infty$ (Pa s)</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\tau_0$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05%</td>
<td>0.13 ± 0.02</td>
<td>0.69 ± 0.05</td>
<td>17 ± 2</td>
</tr>
<tr>
<td>0.06%</td>
<td>0.14 ± 0.02</td>
<td>3.45 ± 0.08</td>
<td>40 ± 3</td>
</tr>
</tbody>
</table>

gas. On a cleaned slide, about 35 $\mu$L of the suspension which consists of suspended Janus particles, diameter $2a = 7.75$ $\mu$m ($\approx 1$ $\mu$L) and polystyrene spacers diameter 15 $\mu$m (0.1 $\mu$L) in the critical Newtonian or viscoelastic fluid, is poured with a pipet. The suspension is then sandwiched with a coverslip (dimensions 22 $\times$ 22 mm). To make the sample cell quasi-two-dimensional, the coverslip is gently pressed towards the bottom substrate by putting a small weight ($\approx 15$ g) on the coverslip. This reduces the height of the sample cell to the diameter of spacer particles i.e., 15 $\mu$m. A schematic of the sample cell is sketched in Fig. 3.6 (a). To avoid evaporation of the fluid from the sides, the sample cell is sealed with epoxy glue from the sides which then takes $\approx 5$ minutes to become fully dry. A typical image of a sample cell is shown in Fig. 3.6 (b).

Figure 3.6: (a) Schematic of a sample cell where the smaller spheres represent the carbon-coated Janus particles and the bigger spheres are the spacers particles. (b) Image of a prepared sample cell.

3.4 Inducing self-propulsion of the Janus particles

The sample cell described in the previous section (Sec. 3.3) is placed on the copper sample holder which is coupled to a heat bath kept at temperature $T = 298$ K. It should be noted that the temperature $T = 298$ K is sufficiently below the critical temperature of the fluid $T_c \approx 305$ K, so the fluid in the sample cell remains homogeneously mixed. To induce self-propulsion, a uniform laser illumination ($\lambda = 532$ nm),
3.4 Inducing self-propulsion of the Janus particles

Figure 3.7: (a) Experimental setup showing a guided laser beam ($\lambda = 532$ nm) illuminating the sample cell. The sample holder is connected to a thermal bath which maintains the sample cell at temperature $T = 298$ K < $T_c$. (b) An optical image of a heated Janus particle (radius $a = 8.02$ µm) where the carbon-coated half (darker half) of the particle creates a local demixing of the critical fluid [84].

whose intensity $I$ can be accurately adjusted, guided through a system of lenses, mirrors and, a beam splitter is perpendicularly applied onto the sample cell, as shown in Fig. 3.7 (a). A schematic of the experimental setup is sketched in Fig. 3.8. The selective absorption of the green light by the carbon cap side of the Janus spheres compared to the silica and the surrounding liquid results in a non-isotropic temperature distribution around the particle. Above certain intensity threshold $I_0$ of the laser light, the temperature of the capped side exceeds $T_c$, thus, creating a local demixing of the fluid (see Fig. 3.7 (b)), leading to a chemical potential gradient symmetry axis of the Janus particle. This results in inducing self-propulsion of the particle away from the capped side via thermo-diffusiophoresis [17,84,103,107]. The MSD of the translational motion of a self-propelled particle in 2D follows [17,22,23]

$$\langle |r(t) - r(0)|^2 \rangle = 4D_T t + v^2 t^2, \quad t << D_T^{-1}$$

which has a diffusive contribution $4D_T t$ because of collisions with the fluid molecules and a ballistic term $v^2 t^2$ because of active drift in the particle motion which becomes dominating at later times. A typical experimentally measured trajectory of an active particle ($2a = 7.75$ µm) in a critical binary mixture of water and PnP over 100 s is shown in Fig. 3.9 (a). The red arrows denote the instantaneous orientation of the particle. The computed MSD from the trajectory is plotted in Fig. 3.9 (b). As expected from Eqn. 3.4, the MSD is ballistic on long timescales. By fitting the measured MSD to Eqn. 3.4, the velocity $v$ of the particle can be obtained. The obtained velocities for different values of laser intensities $I$ are plotted in Figs. 3.9 (c). Clearly, below $I_0 \approx 0.5 \mu W \mu m^{-2}$, no self-propulsion is achieved as this intensity is
Figure 3.8: Schematic of the experimental setup where the alphabets represent the following components: $a$ is the laser ($\lambda = 532\, \text{nm}$) used for inducing self-propulsion of the Janus particles, $b$ represents the lenses to focus the light, $c$ is the microscope lamp, $d$ represents a beam splitter, $e$ is the sample holder which is coupled to a heat bath, $f$ corresponds to an objective for imaging and, $g$ a filter for blocking the green laser beam into the CCD chip. The image from the camera is transmitted to a computer.

not sufficient to heat the cap to the critical temperature $T_c$. While, for $I > I_0$, $v$ increases linearly with $I$ i.e., $v \propto I$. All the experiments reported in the present thesis work are performed in the regime where $v \propto I$. 

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3.5 Tracking of the particles

To characterize the dynamics of a self-propelled Janus particle in 2D, a precise knowledge of its centre of mass \( \mathbf{r} = (x, y) \) and its in-plane orientation \( \mathbf{n} = (\cos \theta, \sin \theta) \) (defined as a unit vector pointing from the capped side to the uncapped side) is required in each frame of a recorded video. The coordinates are sketched in Fig. 3.10. Unlike the conventional particle tracking routines [108, 109] (for non-capped spherical colloids), where the centre of a colloid is defined at the maximum intensity which coincides with the centre of its optical image, this is not the case for a Janus particle. Here, the cap causes an additional light gradient in the inner area of a particle which creates an asymmetric distribution of the intensity. This makes the standard particle tracking procedures ineffective. Therefore, a homemade particle tracking procedure is used. This is done in two steps, namely

1. Tracking of the center of a Janus particle \( i.e., \mathbf{r} = (x, y) \).
2. Tracking the polarity of a Janus particle \( i.e., \mathbf{n} = (\cos \theta, \sin \theta) \)

In the following detailed description of these steps is provided.

3.5.1 Tracking the barycenter of a Janus particle

Typically a microscopic image of a Janus colloidal sphere looks like a dark ring with its capped side appearing as the darker half and the uncapped side as the brighter half as shown in Fig. 3.12 (a)). The flow diagram of the algorithm to precisely locate

\[ I_0 \leq \mu W \mu m^{-2}, \]
Figure 3.10: An optical image of a Janus particle labeled with the relevant coordinates i.e., particle center of mass position \( \mathbf{r} \equiv (x, y) \) and its orientation \( \mathbf{n} \equiv (\cos \theta, \sin \theta) \) for describing its motion in two dimensions.

The barycenter of a particle is shown in Fig. 3.11. A description of the followed routine to track the barycenter with the snapshots at each stage of the tracking routine is displayed in Fig. 3.12. Irrespective of the distribution of the intensity of the pixel in the inner part of a particle, the darker ring (2D circumference of a colloid) is the feature of interest for locating its centroid. First, the image of a Janus particle is inverted, meaning that the darker pixels are transformed into the brighter ones and vice-versa. This is shown in Fig. 3.12(b). Inversion is followed by image sharpening, which can be performed by using an image sharpening filter function in MATLAB. A sharpened inverted image is shown in Fig. 3.12(c). This function enhances the contrast of the ring which defines the particle and uniformize the intensity gradient within the ring. The advantage of performing this operation...
3.5 Tracking of the particles

![Figure 3.12](image)

Figure 3.12: The sequence of tracking routine taken to locate the barycenter $\mathbf{r} = (x, y)$ and the diameter of the Janus particle. (a) An optical image of a Janus particle with a diameter 3.72 µm. (b) Image of the Janus particle with applied inversion operation. (c) Sharpened image of the particle. (d) Binary image obtained using a binary operation. (e) Image of the particle obtained after performing H-transformation to the binary image. (f) The optical image of the particle where inner and outer circle represent the tracked barycenter and the circumference, respectively. The scale bar corresponds to 5 µm.

is to provide a clean input to the H-transformation which locates the particle centre. Further, depending on a certain intensity threshold, the grayscale image is converted to a binary, using the binary function in MATLAB. Under this operation, the pixels of an image are assigned either as absolute black or white value depending on a certain intensity threshold. The binarized image is shown in Fig. 3.12 (d)). After this, an H-transformation is performed on the binary image. The H-transformation detects the white pixels of an image and defines a template circle of the radius of the white ring over a dark background. The H-transformed image of Fig. 3.12 (d) is shown in Fig. 3.12 (e) which then enables one to locate the centroid of a particle. An optical image of a particle with its tracked circumference (outer red ring) and centroid (inner red ring) is shown in Fig. 3.12 (f).

3.5.2 Tracking the orientation of a Janus particle

To define the orientation of a Janus particle, i.e., a vector pointing perpendicularly from its capped hemisphere to the uncapped one, the intensity distribution over the surface of a Janus particle is considered. The vector normal to the plane of intensity provides the orientation or the polarity of the particle. In principle, one can define the orientation vector from the position of the maximum and minimum intensity pixel, but this process is not robust to the noise. Therefore, a more robust approach is used which relies on the gradients of light intensity over the particle surface. As a first step, an inverted image of a Janus particle under consideration is cropped from its interior by a square. From this cropped image, an intensity-weighted centre of mass of the particle is determined. From the intensity-weighted centre, the nearest pixel of maximum intensity is searched. A disk of radius equal to the distance between the intensity-weighted centre and the pixel of maximum intensity constitutes the intensity gradient plane of interest. Using the covariance matrix, a vector nor-
Figure 3.13: (a) Image of a silica Janus particle where the darker half represents the carbon-coated side. (b) Image of the Janus particle with its center of mass and circumference tracked as the open inner and outer circle, respectively. The tracked orientation vector of the particle is shown by the arrow pointing from the capped side to the uncapped side.

3.6 Creating topographic structures on the glass substrate

In this section, the process of creating topographic features on a glass substrate are discussed. Such geometric features are required, for instance, to study the dynamics of an active particle in proximity to a flat and a curved wall. Using photolithography, the micro-structures of desired geometry are imprinted directly on the glass substrate using a photomask (Compugraphics Jena GmbH).

The standard procedures for making structures with photoresist SU-8 are well described in Ref. [110, 111]. Briefly, a thin layer ($\approx 10 \mu m$) of SU-8 2007 (Microresist technology) is prepared on the glass substrate using a spin coater at 3500 rpm for 30 s. The layer is then soft-baked at 95°C for 5 minutes. Through a photomask, the layer is then exposed to ultraviolet light for 80 s. The exposed slide is again soft baked at 95°C for 10 minutes. The structures are then developed using developer Mr 600 (micro-resist technology) for 90 s. The structures are then washed with isopropanol for 30 s and dried. Finally, the obtained structures are hard-baked for 90 minutes at 120°C. A microscopic image of prepared cylindrical confinement of radius 20 $\mu m$ and a square of side length 100 $\mu m$ using photolithography are shown in Figs. 3.14.
3.6  Creating topographic structures on the glass substrate

Figure 3.14: (a) Optical image of (a) cylindrical confinement of diameter 40 μm and height 10 μm and, (b) square confinement with side length 100 μm and height 10 μm, made using photoresist SU-8 2007 using photo-lithography.
Dynamics of an Active Brownian Particle in a Viscoelastic Fluid

There are immense examples in nature confirming that viscoelastic fluids constitute the natural environment for many motile bacteria and cells [48–50, 100]. Examples include, Helicobacter pylori moving inside the mucus which is a strongly viscoelastic liquid [45]; motion of sperms in the viscoelastic oviduct fluid [46] and, blood cells flowing in blood plasma which exhibits viscoelastic characteristics [47]. In comparison to purely viscous fluids i.e., Newtonian fluids which relax quasi instantaneously in response to the perturbation induced by a swimmer motion, viscoelastic fluids exhibit rather large relaxation times due to which the surrounding medium can not be considered in equilibrium [26]. Therefore, the induced transient stress by a swimmer couples back to its motion leading to highly non-trivial dynamics [26–30, 34, 35, 46, 101, 112, 113]. Thus, understanding the role of viscoelastic media on the swimming behavior of microorganisms is very crucial not only from the fundamental perspective [8, 95, 96, 114] but also for bio-medical applications [51, 52]. To address this, few experiments have been performed with active colloids i.e., Janus particles, in the viscoelastic surroundings such as semi-dilute polymers [26, 28] and colloidal glasses [34]. In contrast to the behavior of an active particle in a purely viscous solvent where the rotational dynamics are governed purely by the thermal noise and is independent of its velocity, here the rotational motion exhibits strikingly different features including, orders of magnitude enhancement of the translational and rotational dynamics [26]. In this chapter, the dynamics of active particles in a viscoelastic medium are further explored experimentally. Additionally, the experimental observations are rationalized using a phenomenological model via the generalized Langevin equations (GLE)
for active Brownian motion which takes into account the finite delayed response of the fluid with respect to self-propulsion of the particle.

4.1 Experimental parameters

As active particles, silica spheres with mean diameter $2a = 7.75 \mu m$ which are half coated with 50 nm thick carbon layer are suspended in the critical viscoelastic media with two different polymer concentrations—0.05% wt. and 0.06% wt. This suspension was filled in a sample cell of height $\approx 4a$ and placed on the sample holder which is coupled to a thermostat at 296 K. The illuminating laser intensity is varied from $I = 1 \mu W/\mu m^2$ to $I = 20 \mu W/\mu m^2$ which leads to active particle velocities $v$ ranging from 0.075 $\mu m/s$ to 1.200 $\mu m/s$. Using video microscopy, the videos of the particles are recorded at a frame rate of 17 frames/s. The videos are then analyzed by tracking the centre of mass of the particles and their in-plane orientation using home written MATLAB code.

4.2 Experimental results

4.2.1 Trajectories of active particles in a viscoelastic fluid

Typical trajectories of an active particle in the viscoelastic fluid (0.05% wt.) measured over 1500 s are shown in Fig. 4.1 for different velocities $v$ increasing from left to right. The arrows represent the instantaneous orientation $n(t)$ of the particle. Opposite to the rotational dynamics of an active particle in a Newtonian fluid, where the rotational motion of the particle remains independent of $v$ and is determined mainly by the thermal diffusion, in this case, the observed rotational motion depends strongly on $v$. Whereas for small $v$, the particle describes a rather straight trajectory, it becomes more and more crooked for increasing $v$. Surprisingly, above a certain critical velocity $v_c$, which depends on the polymer concentration, for instance, for 0.05% wt., $v_c \approx 0.240 \mu m/s$, the particle undergoes a persistent circular motion. Unlike the persistent circular motion of a chiral active particle where the direction of rotation remains fixed and is set by the shape of the particle [15,115–117], here, the direction of rotation can spontaneously reverse itself i.e., switch from clockwise sense to counter-clockwise and vice-versa. This is demonstrated by the middle trajectory in Fig. 4.1 where particle was moving with $v = 0.250 \mu m/s \approx v_c$. However, for $v$ values much higher than $v_c$ the direction of rotation becomes very consistent and such a reversal of rotation direction is not observed as shown by the two right-most trajectories in Fig 4.1.
4.3 Phenomenological model for the active Brownian motion in a viscoelastic fluid

Motivated by such non-trivial rotational dynamics of active particles in viscoelastic fluids, a phenomenological model using GLE is developed which takes into account the finite memory effects of a viscoelastic fluid [67]. The mechanical response of the viscoelastic fluid can be incorporated using Jeffrey’s model i.e., generalized Maxwell...
model with a single relaxation time [31,32,67,105,106]. The stress-relaxation modulus, in this case, takes the form [87,88]

\[ G(t) = 2\eta_\infty \delta(t) + \left( \frac{\eta_0 - \eta_\infty}{\tau_0} \right) \exp - \frac{t}{\tau_0} \] (4.1)

where \( \eta_\infty \) is the viscosity of the solvent in absence of polymer, \( \eta_0 \) is the zero-shear viscosity of the viscoelastic fluid i.e., with added polymer and, \( \delta(t) \) is the Dirac-delta function. Physically, the first term on the right-hand side in Eqn. 4.1 represents the instantaneous relaxation of the solvent and the second term corresponds to the time-delayed response of the polymer network. A schematic picture which is illustrating the mechanical response of a linear viscoelastic fluid on the translational motion of an active particle moving with self-propulsion force \( F_v \) which leads to self-propulsion velocity \( v \) is sketched in Fig. 4.3 (a). The dashpot labelled with \( \eta_\infty \) represents the viscous friction of the underlying solvent i.e., without adding polymer while the series combination of the dashpot \( (\eta_0 - \eta_\infty) \) and the spring \( g = (\eta_0 - \eta_\infty)/\tau_0 \) correspond to the polymer contribution to the viscosity and the stiffness, respectively. This mechanical response of the fluid can be coupled to the translational motion of an active particle through the memory friction kernel \( \Gamma(t) = 6\pi aG(t) \). Since for a colloid, the viscous dissipation dominates over the inertial forces, its translational motion in 2D can be expressed by the overdamped GLE as [120,121]

\[ \int_{-\infty}^{t} \Gamma_T(t - t') \dot{r}(t') dt' = \int_{-\infty}^{t} \Gamma_T(t - t') v n(t') dt' + \zeta_T(t). \] (4.2)
4.3 Phenomenological model for the active Brownian motion in a viscoelastic fluid

The left hand side (LHS) represents the drag force acting on the particle while the first term on the right hand side (RHS) corresponds to the self-propulsive force $F_v(t) = \int_{-\infty}^{t} \Gamma_T(t-t')vn(t')dt'$ and the second term mimics the thermal noise with zero mean i.e., $\langle \zeta_T(t) \rangle = 0$ and the correlation $\langle \zeta_T^j(t)\zeta_T^j(s) \rangle = k_B T \delta_{ij} \Gamma(|t-s|)$ [86]. Rewriting Eqn. 4.2 by rearranging the terms and taking average on both the sides give

$$\left\langle - \int_{-\infty}^{t} \Gamma_T(t-t')[\hat{r}(t') - vn(t')]dt' \right\rangle = -\langle \zeta_T(t) \rangle = 0. \quad (4.3)$$

Here, the LHS of the equation represents the total hydrodynamic force acting on the active particle which vanishes on average, therefore, fulfils the force-free condition as required for an active particle [98, 122]. Due to finite memory present, incorporated by the convolution over time from $-\infty$ to $t$, the propulsive force $F_v(t)$ at time $t$ is not parallel to the instantaneous particle orientation $n(t)$ but depends on the history $t' \leq t$. In general, $F_v(t)$ lags behind $n(t)$. Such a delayed $F_v(t)$ with respect to $n(t)$ leads to a torque $T_v(t) = T_v(t) \hat{z}$ acting on the active particle where $\hat{z}$ is orthogonal to $\hat{x}$ and $\hat{y}$ i.e., $\hat{z} = \hat{x} \times \hat{y}$. By using a spatial delay of $F_v(t)$ with respect to the particle center in the form of a lever arm $L(t)$, the torque can be expressed as a cross product as

$$T_v(t) = L(t) \times F_v(t) \quad (4.4)$$

where $L(t) = -\mu an(t)$ and $\mu$ is a fitting parameter of $O(1)$. Using, the expression of $F_v(t)$ from Eqn. 4.2, the torque can be expressed as

$$T_v(t) = -\mu av \int_{-\infty}^{t} \Gamma_T(t-t')n(t) \times n(t')dt'. \quad (4.5)$$

In consistent with the experimental observation, the torque vanishes for a passive particle ($v = 0$). The rotational motion of the particle is, therefore, subjected to this torque. In addition to this torque, the orientation of the particle is also affected by the surrounding viscoelastic fluid, as evident from the short-time subdiffusion of $\langle \Delta \theta(t)^2 \rangle$ in Fig. 4.2. Consequently, the orientational dynamics in 2D can be described by the following non-Markovian equation

$$\int_{-\infty}^{t} \Gamma_R(t-t')\dot{\theta}(t')dt' = T_v(t) + \zeta_R(t) \quad (4.6)$$

where $\zeta_R(t)$ is the thermal noise with zero mean and the autocorrelation $\langle \zeta_R(t)\zeta_R(s) \rangle = k_B TT\Gamma(|t-s|)$ [89].

A schematic illustration of the model describing the response of a Jeffrey’s fluid on the orientational motion of an active particle is sketched in Fig. 4.3 (b). In the case of vanishing noise, Eqn. 4.2 assumes two kinds of steady state solutions. One where the particle describes straight trajectories i.e., $\dot{\theta} = 0$ and $\theta = 0$ and, second where the particle exhibits periodic rotations i.e., $\theta(t) = \omega t + \text{constant}$, with
Figure 4.3: Schematic illustration of the mechanical response of Jeffrey’s fluid characterized by a single stress-relaxation time $\tau_0 = (\eta_0 - \eta_\infty)/g$ in combination with viscous contributions from the polymer network $(\eta_0 - \eta_\infty)$ and the underlying solvent $\eta_\infty$ for the (a) translational motion and, (b) orientational motion of an active Janus particle moving at propulsion velocity $vn$. The propulsive force and the velocity-dependent torque acting on the particle are represented by $F_v$ and $T_v$, respectively. Reprinted with permission from the American Physical Society. Copyright 2018 [35].

an angular velocity $\omega$. By substituting, $\theta(t) = \omega t + \text{constant}$, in Eqn. 4.6, and solving for $\omega$ gives

$$\omega = \frac{3\mu v}{4a\tau_0} \left( 1 - \frac{\eta_\infty}{\eta_0} \right),$$

(4.7)

Eqn. 4.7 is a cubic equation and, therefore, offers three solutions as

$$\omega = \begin{cases} 0 \\
\pm \frac{1}{\tau_0} \sqrt{\frac{3\mu v\tau_0}{4a} \left( 1 - \frac{\eta_\infty}{\eta_0} \right) \frac{\omega}{\omega^2 + \frac{1}{\tau_0^2}}} \end{cases}.$$  

(4.8)

Physically, $\omega = 0$ corresponds to straight trajectories while the two non-zero solutions correspond to the persistent rotation of the active particle. For real value of $\omega$ i.e., $\text{Im}(\omega) = 0$ Eqn. 4.8 straightforwardly provides the expression for the minimum propulsion velocity $v_c$ which is required to describe the persistent circular motion as

$$v_c = \frac{4a}{3\mu \tau_0 \left( 1 - \frac{\eta_\infty}{\eta_0} \right)}.$$

(4.9)

Substitution of Eqn. 4.9 in Eqn. 4.8 yields the two non-zero solutions of angular velocity as

$$\omega = \pm \frac{1}{\tau_0} \sqrt{\frac{v}{v_c} - 1}.$$  

(4.10)

As expected, due to axial symmetry of the system with respect to particle orientation $n$, $\omega$ assumes the same magnitude along both the directions of rotation i.e., clock-wise and counter clock-wise. Then the expression for the radius of curvature $R$ can
be related to the active particle velocity $v$

$$R = \frac{v\tau_0}{\sqrt{v_c - 1}} \quad (4.11)$$

As a matter of fact, the Eqns. 4.10 and 4.11, fits well to the experimental data for $\omega$ and $R$ as a function particle velocity $v$ as shown in Figs. 4.4 (a) and 4.4 (b), respectively. From the fit, the value of the critical propulsion velocity $v_c$ and the fitting parameter are determined to $0.240 \, \mu\text{m s}^{-1}$ and $= 1.3$, respectively.

**Figure 4.4:** (a) Experimentally measured angular velocity $\omega$ as a function of translational velocity $v$ of an active particle moving in a viscoelastic solution at 0.05% wt. PAAM concentration. The shaded region corresponds to the regime where only enhanced orientational diffusion is observed with no persistent rotation while the vertical dashed line corresponds to the critical propulsion velocity value $v_c$. The solid line is the fit according to Eqn. 4.10. (b) Dependence of the corresponding radius of curvature $R$ on $v$. The vertical dashed line corresponds to the critical velocity value $v_c$. The solid line is the fit to and Eqn. 4.11. The error bars in both (a) and (b) are the corresponding standard deviations computed over several cycles with the same sense of rotation.

### 4.3.1 Numerical solution of the non-Markovian Langevin equations

The equations of motion governing the translational particle dynamics (Eqn. 4.2) and the orientational particle dynamics (Eqn. 4.6) can be solved numerically by extending the number of variables which allows one to recast them in a Markovian form [123]. In order to do so, the auxiliary variables for the position $\mathbf{R} = (X, Y)$ and orientation $\Theta$ are introduced as

$$\mathbf{R}(t) = \frac{1}{\tau_0} \int_{-\infty}^{t} e^{-\frac{t-t'}{\tau_0}} [\mathbf{r}(t') + \tau_0\sqrt{2\Delta\gamma}\Xi(t')]dt' \quad (4.12)$$
\[ \Theta(t) = \frac{1}{\tau_0} \int_{-\infty}^{t} e^{-\frac{t-t'}{\tau_0}} \theta(t') + \tau_0 \sqrt{2\Delta_R} Z(t') \, dt' \]  

(4.13)

**Figure 4.5:** Examples of three independent numerical trajectories at different propulsion velocities: (a) 0.075 \( \mu m \) s\(^{-1}\), (b) 0.250 \( \mu m \) s\(^{-1}\) and, (c) 0.600 \( \mu m \) s\(^{-1}\), each obtained over 3000 s. The arrows denote the instantaneous particle orientation vector \( \mathbf{n} \).

\[ \Xi = (\Xi_1, \Xi_2) \] and \( Z \) are the Gaussian noises which satisfy \( \langle \Xi_i(t) \rangle = \langle Z(t) \rangle = 0 \) and \( \langle \Xi_i(t) \Xi_j(s) \rangle = \delta_{ij} \delta(t - s) \) and \( \langle Z(t)Z(s) \rangle = \delta(t - s) \). The variables \( \mathbf{R} \) and \( \Theta \) allow one to write Eqns. 4.2 and 4.6 as six Markovian Langevin equations

\[ \frac{d\mathbf{X}}{dt} = \frac{1}{\tau} M \mathbf{X} + \mathbf{v} \mathbf{N} + \Phi \]  

(4.15)

where \( \mathbf{X}^T = (x, y, \theta, X, Y, \Theta) \), \( M \) corresponds to a linear coupling between the real particle coordinates \((x, y, \theta)\) and the auxiliary particle coordinates \((X, Y, \Theta)\)

\[ M = \begin{pmatrix}
\frac{-\delta\eta}{\eta_\infty} & 0 & 0 & \frac{\delta\eta}{\eta_\infty} & 0 & 0 \\
0 & \frac{-\delta\eta}{\eta_\infty} & 0 & 0 & \frac{\delta\eta}{\eta_\infty} & 0 \\
0 & 0 & -\frac{\delta\eta}{\eta_\infty} & 0 & 0 & \frac{\delta\eta}{\eta_\infty} \\
1 & 0 & 0 & -1 & 0 & 0 \\
0 & 1 & 0 & 0 & -1 & 0 \\
0 & 0 & 1 & 0 & 0 & -1
\end{pmatrix} \]  

(4.16)
4.3 Phenomenological model for the active Brownian motion in a viscoelastic fluid

\( \mathbf{N} \) represents a non-linear coupling between the translation and rotational degrees of freedom as

\[
\mathbf{N} = \begin{pmatrix}
\cos \theta + \frac{\delta n}{\eta_{\infty} \tau_0} I_x \\
\sin \theta + \frac{\delta n}{\eta_{\infty} \tau_0} I_y \\
-\frac{3\mu}{4a \eta_{\infty} \tau_0} (I_y \cos \theta - I_x \sin \theta) \\
0 \\
0 \\
0
\end{pmatrix}
\] (4.17)

where \( I_x \) and \( I_y \) are the convolutions that represent the delayed response of the propulsive force with respect to the instantaneous orientation and are given by

\[
I_x = \int_{-\infty}^{t} e^{-\frac{t-t'}{\tau}} \cos \theta(t') dt',
\]

\[
I_y = \int_{-\infty}^{t} e^{-\frac{t-t'}{\tau}} \sin \theta(t') dt'
\] (4.18)

The last term \( \Phi \) in Eqn. 4.15 is the noise term

\[
\Phi = \begin{pmatrix}
\sqrt{2D_\infty^\mu} \xi \\
\sqrt{2D_\infty^\zeta} \\
\sqrt{\Delta \Xi} \\
\sqrt{\Delta \zeta}
\end{pmatrix}
\] (4.19)

where \( \xi = (\xi_1, \xi_2) \) and \( \zeta \) are the Gaussian white noises, which satisfy

\[
\langle \xi_i(t) \rangle = \langle \zeta(t) \rangle = 0,
\]

\[
\langle \xi_i(t) \xi_j(s) \rangle = \delta_{ij} \delta(t - s),
\]

\[
\langle \zeta(t) \zeta(s) \rangle = \delta(t - s)
\] (4.20)

The Eqn. 4.15 can be solved numerically by using the obtained rheological values of parameters for the model i.e., \( \eta_{\infty}, \eta_0 \) and \( \tau_0 \). The values are inferred using passive micro-rheology. A set of three independent numerical trajectories for different propulsion velocities \( v \), are plotted in Figs. 4.5 where \( v \) is consistently increasing from (a) to (c). Apparently, the crookedness of the trajectories increases with increasing \( v \) while for higher \( v \), trajectories along a circular path are also evident (see Fig. 4.5 (c)). Therefore, this minimal non-Markovian Langevin model reproduces all experimentally observed salient features of the active particle orientational motion in a viscoelastic fluid. Since the magnitude of the torque \( T_v \) depends strongly on the velocity \( v \) of the particle (see Eqn. 4.5), for smaller propulsion velocities \( v \lesssim 0.250 \ \mu \text{m s}^{-1} \), \( T_v \) is also small which leads to short-lived rotations as they
Figure 4.6: (a) Mean squared angular displacements $\langle \Delta \theta(t)^2 \rangle$ of the numerical trajectories for different propulsion velocities $v$ increasing from bottom to top. The bottom-most curve corresponds to the passive case $v = 0$, and the topmost curve corresponds to $v = 0.240 \, \mu m \, s^{-1}$. (b) The corresponding effective rotational diffusion coefficient $D_\theta$ normalized by the passive value $D_\theta^0$ as a function of $v$ labelled with the same color code as their corresponding $\langle \Delta \theta(t)^2 \rangle$. The vertical dashed line represents the critical propulsion velocity $v_c$ above which the particle starts to describe the persistent circular motion. Reprinted with permission from the American Physical Society. Copyright 2018 [35].

are randomized by the thermal fluctuations. These short-lived rotations on long timescales manifest as effectively enhanced angular diffusion. In order to quantify the diffusive angular dynamics for $v \lesssim 0.250 \, \mu m \, s^{-1}$, the corresponding angular mean squared displacements $\langle \Delta \theta(t)^2 \rangle$ are computed. The results are plotted in Fig. 4.6 (a). Since the equation of motion governing the orientational dynamics of the particle i.e., Eqn. 4.6) is also subjected to the surrounding viscoelastic drag, this results in the appearance of short time sub-diffusive $\langle \Delta \theta(t)^2 \rangle$ as evident from the initial deviation of curves from a linear increase Fig. 4.6 (a). However, on timescales larger than $t >> (\eta_\infty/\eta_0)\tau$, diffusive orientational dynamics are observed for all $v \lesssim v_c$ i.e., $\langle \Delta \theta(t)^2 \rangle = 2D_\theta t$ where the slope of $\langle \Delta \theta(t)^2 \rangle$ corresponds to an effective diffusion coefficient. The obtained diffusion coefficient $D_\theta$ as a function of $v$ is plotted in Fig. 4.6 (b). With increasing $v$, $D_\theta$ displays a continuous increase towards the critical velocity $v_c \approx 0.250 \, \mu m \, s^{-1}$ where it enhances by two orders of magnitude compared to the passive value i.e., $D_\theta^0$. A similar two orders of magnitude enhancement of the rotational diffusion coefficient for an active particle moving in a viscoelastic fluid has been reported in Ref. [26]. Therefore, the phenomenological model excellently describes the rotational diffusive behavior of an active particle in a viscoelastic fluid. For $v > v_c$, the torque term $T_v$ in Eqn. 4.6 dominates over the thermal noise $\zeta_R$, leading to a persistent rotation as shown in Fig. 4.5 (c). In addition, while describing a circular trajectory, an active particle can flip its direction of rotation between $+|\omega|$ and $-|\omega|$ on sufficiently long times (see Fig. 4.5 (c)). Such
4.4 Role of viscoelasticity

flips occur when a thermal fluctuation is comparable to the mean torque $8\pi \eta_0 \alpha^3 \omega$ which can destabilize the undergoing current orbit. Intuitively, this flipping behavior can be assessed by looking at the phase difference between the instantaneous particle orientation $n(t)$ and the propulsive force at time $t$ which is given by

$$F_v(t) = 6\pi |\eta^*(\omega)| v n\left( t - \frac{\phi}{\omega} \right)$$

(4.21)

where $|\eta^*(\omega)| = \eta'(\omega) - i\eta''(\omega)$ is the frequency dependent complex viscosity of the viscoelastic fluid whose real $\eta'(\omega)$ and imaginary $\eta''(\omega)$ parts are given by $\eta'(\omega) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{\omega^2 \tau_0^2 + \omega^2}$ and $\eta''(\omega) = \frac{\eta_0 - \eta_\infty}{\omega^2 \tau_0^2 + \omega^2} \omega \tau_0$ while the phase difference $\phi$ is given by

$$\phi = \arctan \left( \frac{\eta_0 - \eta_\infty}{\eta_0 + \eta_\infty \omega^2 \tau_0^2 + \omega^2} \right)$$

(4.22)

To show how the phase lag $\phi$ between $n(t)$ and $F_v(t)$ is influence by $v$ of an active particle, the trajectories of an active particle for two distinct $v$ values, namely, $v = 0.250 \, \mu\text{m s}^{-1} \approx v_c$ and $v = 0.600 \, \mu\text{m s}^{-1} > v_c$ are displayed in Figs. 4.7 (a) and (b), respectively. Here, the red arrows denote the instantaneous particle orientation $n(t)$ while the green ones represent the direction of instantaneous propulsive force $F_v(t)$. Apparently, $\phi$ corresponds to $v = 0.600 \, \mu\text{m s}^{-1}$ is larger than that of $v = 0.250 \, \mu\text{m s}^{-1}$. The corresponding time evolution of $\phi$ for both values of $v$ are shown in Fig. 4.8. It should be noted that depending of the direction of rotation, $\phi$ can assume both positive of negative values. Compared to $v = 0.250 \, \mu\text{m s}^{-1}$, $\phi$ is larger for $v = 0.600 \, \mu\text{m s}^{-1}$ and switches its sign less frequently. This suggests that the circular motion becomes more stable with increasing $v$, as also confirmed experimentally.

4.4 Role of viscoelasticity

The above observed non-trivial rotational dynamics for an active particle is a consequence of the surrounding viscoelastic fluid whose rheological properties are determined by the concentration of polymer (see subsection 3.2.2 of Chapter 3). In particular, the critical propulsion velocity $v_c$ where an active particle undergoes a transition from the enhanced rotational diffusion to the persistent circular motion depends strongly on the rheological parameters. According to Eqn. 4.9, the transition to persistent circular motion is expected to occur at smaller $v$ values for higher polymer concentrations. To verify that, experiments with a polymer concentration $0.06\% \, \text{wt.}$ are performed. Indeed, it is found that for the higher polymer concentration $i.e.,$ 0.06\% $\text{wt}$, $v_c$ decreases to $v_c = v = 0.105 \, \mu\text{m s}^{-1}$. The dependence of angular velocity $\omega$ and radius of orbits $R$ on the self-propelled velocity $v$ for 0.06\% $\text{wt.}$ PAAm are plotted in Figs. 4.9 (a) and 4.9 (b), respectively.
Chapter 4  Dynamics of an Active Brownian Particle in a Viscoelastic Fluid

Figure 4.7: Numerical trajectories of an active particle moving at self-propulsion velocity \( v \) (a) 0.250 \( \mu \text{m s}^{-1} \) and (b) 0.600 \( \mu \text{m s}^{-1} \). The red arrows show the instantaneous particle orientation vector \( \mathbf{n} \) whereas the green arrows show the direction of instantaneous propulsion force \( \mathbf{F}_v \). The phase difference between the two is denoted by \( \phi \). Reprinted with permission from the American Physical Society. Copyright 2018 [35].

Figure 4.8: Time evolution of the phase difference \( \phi \) between \( \mathbf{n} \) and \( \mathbf{F}_v \) moving at \( v = 0.250 \mu \text{m s}^{-1} \) (inner curve) and at \( v = 0.600 \mu \text{m s}^{-1} \) (outer curve). The horizontal lines represent the steady-state values of \( \phi \pm \). Reprinted with permission from the American Physical Society. Copyright 2018 [35].

4.5  Active motion in a Newtonian fluid

To demonstrate that the above-mentioned behavior of active particles is purely because of the viscoelasticity of the fluid, experiments under similar conditions with the corresponding Newtonian fluid \( \text{i.e., without adding polymer polyacrylamide} \) are performed. The measured trajectories are shown in Fig. 4.10 for different velocities...
4.5 Active motion in a Newtonian fluid

![Graph](image)

**Figure 4.9:** (a) Angular velocity $\omega$ as a function of the translational velocity $v$ for an active particle moving in a viscoelastic solution at 0.06% wt. concentration. (b) Dependence of the corresponding radius of curvature $R$ on $v$. The solid lines in (a) and (b) are the corresponding fits to Eqn. 4.10 and Eqn. 4.11, respectively.

$v$ increasing from left to right. Although the values of $v$ here are very similar to the ones mentioned for the viscoelastic case (see section 4.2.1), however, the rotational dynamics remained independent of $v$. For each trajectory, the coefficient of rotational diffusion $D_\theta$ follows well the Stokes-Einstein value i.e.,

$$D_\theta = \frac{k_B T}{8\pi a^3 \eta_f} = 0.0006 \text{ s}^{-1}$$

in agreement with previously reported experiments of active particles in the Newtonian liquid.

![Graph](image)

**Figure 4.10:** Typical trajectories $\mathbf{r} = (x, y)$ (solid lines) and the orientations $\mathbf{n} = (\cos \theta, \sin \theta)$ (red arrows) of a spherical self-propelled particle of radius $a = 3.88 \mu m$ moving in a Newtonian fluid at various $v$ increasing from left to right as: $v = 0.075 \mu m s^{-1}$, $v = 0.100 \mu m s^{-1}$, $v = 0.250 \mu m s^{-1}$ and, $v = 0.500 \mu m s^{-1}$. 

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Chapter 4 Dynamics of an Active Brownian Particle in a Viscoelastic Fluid

Summary

In summary, the dynamics of an active spherical particle is investigated for a broad range of their self-propulsion velocity $v$. With an increase in $v$, active particles exhibit a remarkable enhancement of their rotational diffusion coefficient by two orders of magnitude compared to a passive Brownian particle. Further increase in $v$ leads to the emergence of a persistent circular motion with stochastic orientational flips. Unlike the circular motion of chiral active particles, here, the emergence of such circular orbits is due to the delayed response of the surrounding fluid with respect to the orientation of the particle. Further, the angular velocity $\omega$ and radius of curvature $R$ of the described circular trajectories are characterized as a function of $v$. The experimental observations are explained using a minimal non-Markovian Langevin model which takes into account the delayed response of the fluid with respect to self-propulsion of the particle. Further, it is shown that such non-trivial orientational features for an active particle depend strongly on the rheological properties of the surrounding fluid. In particular, they enhance with increasing the viscoelastic properties of the fluid and vanish for a Newtonian liquid.
Most of our intuitive understanding of thermodynamics i.e., the flow of heat and the conversion of work into heat has been derived from the equilibrium states. The concepts of equilibrium thermodynamics have been further extended to linear irreversible systems which are very close to equilibrium [124,125]. Although they describe the state of a macroscopic system, however, their domain is limited. For example, they fall short in their application to mesoscopic systems which are driven arbitrarily far from thermal equilibrium. To overcome such limitations, in the last two decades, new forms of theorems called fluctuation theorems have been proposed [126–130]. They have extended our understanding of basic quantities such as work, entropy production and, heat for non-equilibrium mesoscopic systems. In this chapter, the discussion is limited to the concept of work for a microscopic system driven out of equilibrium. When dealing with microscopic systems e.g., suspended colloidal particles, such a thermodynamic quantity becomes fluctuating with its probability distribution exhibits finite width [131–134]. In such systems, the fluctuating work also exhibits negative values but they are restricted by the work fluctuation theorem [135–137]. The work fluctuation theorem quantifies the asymmetry distribution between the positive and negative values of work. From a fundamental point of view, the fluctuation theorem refines the second law of thermodynamics for microscopic systems. Mathematically, for a system in contact with a thermal bath at temperature $T$ driven in a non-equilibrium steady state by an external force, the fluctuation theorem states [130,138,139]

$$\ln \frac{P(+W_{\tau})}{P(-W_{\tau})} = \frac{W_{\tau}}{k_B T} \quad \text{for} \quad \tau >> \tau_c$$

(5.1)

where $P(+W_{\tau})$ and $P(-W_{\tau})$ are the probabilities of positive and corresponding negative work $W_{\tau}$ computed over time $\tau$, $k_B$ is the Boltzmann constant and $\tau_c$ represents the longest correlation time scale of the system. This relation has been
Chapter 5  Work Fluctuations of an Active Brownian Particle Moving in a Viscoelastic Fluid

tested and verified in numerous experiments including colloids in time-dependent potentials [139–143], charge transitions in electronic devices [144, 145], folding and unfolding of bio-molecules [146–149], mechanical torsion pendulums [150] and even in gravitational wave detectors [151]. Whereas in most of these experiments, the system is driven out of equilibrium by an external force and only very rare examples exist where the relation has been applied to internally driven systems e.g., active colloidal particles [152–154]. Moreover, it is also worth exploring how the fluctuation relation would get modified when the noise properties of the surrounding thermal bath couples non-linearly to the self-propulsion of the active particle e.g., a self-propelled particle in a viscoelastic fluid. An active particle moving in a persistent circular motion, as observed in Chapter 4, provides a rather elegant opportunity to explore the fluctuation theorem where the viscoelastic bath is non-linearly coupled to the particle orientational dynamics. In contrast to the translational motion of an active particle where the details of defining work can be complicated by the chemical potential and other effects required for the self-propulsion [153], the orientational dynamics can be regarded in purely mechanical terms. Under such conditions, the orientational motion can simply be considered to govern by an average constant torque. Further, it reduces the dimensionality of the problem as it occurs only in 1D (compared to the 2D translational motion). In that sense, the situation is reminiscent of a driven colloidal particle e.g., by an optical trap along one dimension [139]. To explain the sign convention for a positive and negative work fluctuation, a schematic of a particle in an optical trap is depicted in Fig. 5.1. In this case, the work can be considered positive if the particle undergoes displacement in the direction of applied force $F$ (Fig. 5.1 (a)) and negative if the displacement occurs direction opposite to $F$ (Fig. 5.1 (b)).

![Figure 5.1](image-url)

**Figure 5.1:** Schematic of a colloidal particle driven by an optical trap. In the left case, the colloid displaces $+\Delta x$ in the direction of applied driving force $F$ which leads to a positive work fluctuation while in the right case it undergoes displacement $-\Delta x$ opposite to the applied $F$ which corresponds to a negative work fluctuation. In both cases, the previous position of the colloid before the displacement is displayed by the dotted circle.

Similarly, for an active particle undergoing pronounced circular motion, one can
assign positive work if the change in orientation $\Delta \theta$ over a time $\tau$ w.r.t. the previous orientation occurs in the direction of rotation i.e., clockwise or counter-clockwise and negative otherwise. Thus, in this chapter, the orientational dynamics of an active particle undergoing persistent circular motion are studied in the context of the work fluctuation relation. Additionally, to show how distinct is the obtained fluctuation relation in a viscoelastic bath (non-Markovian) from that of a purely viscous bath (Markovian), experiments under similar situation are performed with an asymmetric L-shaped particle undergoing pronounced circular motion [115] in a Newtonian fluid.

5.1 Experimental parameters

In this work, spherical colloids with a mean diameter $2a = 7.75 \, \mu m$ half coated with 50 nm thick carbon layer are suspended in a critical viscoelastic media at polymer concentration 0.05% wt. This suspension is filled in a sample cell of height $\approx 4a$ and placed on the sample holder which is coupled to a thermostat at 296 K. The illuminating laser intensity was varied from $I = 10 \, \mu W/\mu m^2$ to $I = 20 \, \mu W/\mu m^2$ which leads to the self-propulsion velocities $v$ ranging from $0.250 \, \mu m \, s^{-1}$ to $1.200 \, \mu m \, s^{-1}$. Additionally, asymmetric L-shaped particles with long and short arm lengths 9 $\mu m$ and 6 $\mu m$, respectively are used as circular swimmers in the counter-part Newtonian fluid i.e., without adding polymer. They are prepared using photolithography technique (see section 3.6 of chapter 3) with their short arm edge capped by a carbon film of thickness 20 nm. Using video microscopy, the videos of the particles are recorded at a frequency 17 Hz. The videos are then analyzed by tracking the center of mass of the particles and their in plane orientation using home written MATLAB code.

5.2 Work fluctuation theorem applied to active particles in a Viscoelastic Fluid

As demonstrated in Chapter 4, that above a certain critical propulsion speed $v_c$ which depends on the polymer concentration, an active particle in a viscoelastic fluid undergoes persistent circular motion. A typical trajectory in which a particle performs persistent circular motion is shown in Fig. 5.2 (a). As explained in Chapter 4, this behavior originates from the time-delayed response of the surrounding viscoelastic fluid which leads to a misalignment between the self-propulsive force and the orientation of the particle which eventually generates a velocity-dependent torque. This torque can be assumed to be constant as the time evolution of accumulated particle angular coordinate $\theta$ follows a constant slope which corresponds to a linear angular drift $\omega t$ as plotted in Fig. 5.2 (b). For the application of the work fluctuation theorem (Eqn. 5.1) to the rotational motion of an active particle, one needs to compute the associated work. Under a constant torque $T_v = T_v \hat{z}$, exerted
by the fluid on an active particle, the orientational work $W$ normalized by $k_BT$ during time $\tau$ would be given by

$$W_\tau = \frac{1}{k_BT} \int_{t}^{t+\tau} \dot{\theta}(t')\langle T_v \rangle dt'.$$

(5.2)

Here $\langle T_v \rangle$ is the mean value of the torque which can be computed by equating it to the value of torque required to rotate a sphere of diameter $2a$ in a viscoelastic medium of viscosity $\eta_0(\omega)$ at angular velocity $\omega$ as

$$\langle T_v \rangle = \Gamma_\theta(\omega)\omega.$$  

(5.3)

where $\Gamma_\theta(\omega)$ is the rotational friction experienced by the spherical particle i.e., $\Gamma_\theta(\omega) = 8\pi a^3 \eta_0(\omega)$. Therefore, the Eqn. 5.3 becomes

$$\langle T_v \rangle = 8\pi a^3 \eta_0(\omega)\omega.$$  

(5.4)

Looking at Eqn. 5.2, the measurement of $\dot{\theta}(t)$ along with the value of $\langle T_v \rangle$ allows a straightforward computation of $W_\tau$. Following the sign-convention, the work done is considered to be positive when a change in angular coordinate after a time interval $\tau$ w.r.t. previous orientation i.e., $\Delta \theta(\tau) = \theta(t+\tau) - \theta(t)$ occurs towards the direction of rotation and is considered negative for the opposite case. The obtained probability distributions $P(W_\tau)$ of the computed $W_\tau$ for different integration times $\tau$ and for $\omega = 0.018$ rad s$^{-1}$ and $\omega = 0.095$ rad s$^{-1}$ are plotted in Fig. 5.3 (a) and Fig. 5.3 (b), respectively. Apparently, for the smallest integration time i.e., $\tau = 0.06$ s, the peak value of $P(W_\tau)$ corresponds to $W_\tau \approx 0$. This suggests that over such small integration time, the probability of observing negative and positive work fluctuations are likely equal. As pointed out in the introduction, this is a violation of the classical second law of thermodynamics. However, with increasing the integration time $\tau$, the peak value of $P(W_\tau)$ shifts away from the center. Consequently, the probability of observing negative work fluctuations decreases. Such a shift towards positive values of $W_\tau$ is a consequence of a persistent drift. Expectedly, for very large values of integration times $\tau$, the probability to observe the negative work fluctuations would eventually vanish leading to recovery of the second law of thermodynamics. Additionally, with increasing $\tau$, the work distribution also exhibits an asymmetry. This asymmetry results from the non-linear coupling of the active particle orientation to the surrounding viscoelastic bath. Similar asymmetric distributions have also been observed in other externally driven non-linear systems [151,155]. In order to check the validity of the work fluctuation theorem (Eqn. 5.1), the asymmetry function i.e., $\ln[P(+W_\tau)/P(-W_\tau)]$ is plotted as a function of $W_\tau$ for for different values of $\omega$ in Fig. 5.4 in a log-log representation. In comparison to the expectation of the fluctuation theorem (Eqn. 5.1) which is shown by the dashed line in Fig. 5.4, the obtained curves are deviated by more than a decade. Such deviations from Eqn. 5.1 can occur for large fluctuations, for instance, when the nature of force driving the
5.2 Work fluctuation theorem applied to active particles in a Viscoelastic Fluid

system is stochastic as demonstrated in a various experiments and simulations including a colloidal particle in a white [156] and colored noise bath [157], a chaotic vibrations in a metallic plate [158], in gravitational wave detector [151] and, in a electronic circuit [159]. Although in the situation considered here i.e., the orientational motion of the active particle in a viscoelastic bath, the driving is assumed deterministic (constant torque) but it shares similarity with the stochastic driving as the amplitude of the orientational fluctuations due to thermal noise can not be considered negligible due to orders of magnitude enhancement of the rotational diffusion coefficient by orders of magnitude. Therefore, a constant torque superposed over the large angular fluctuations can act as an effective stochastic driving. Hence, the diffusive angular dynamics holds the key for the observed deviations from the expectation of the work fluctuation theorem.

Figure 5.2: Representative trajectory (solid curve) of a spherical active particle of diameter $2a = 7.75 \, \mu m$ in a viscoelastic fluid displaying persistent circular motion with an angular velocity $\omega = 0.023 \, \text{rad s}^{-1}$. The red arrows denote the instantaneous particle orientation $n$. The scale bar corresponds to 10 $\mu m$ (b) Time evolution of the accumulated particle orientation $\theta$ exhibiting a linear angular drift $\omega t$.

5.2.1 Renormalization of the orientational work

In order to understand the origin of such a deviation from the expected work fluctuation theorem (Eqn. 5.1), the rotational diffusive dynamics of the active particle is considered while it is undergoing persistent circular motion. This can be done by subtracting the angular drift $\omega t$ from the time evolution of the particle angular coordinate $\theta(t)$ i.e., $\delta \theta(t) = \theta(t) - \omega t + \text{constant}$. This provides the angular fluctuations of particle around the mean circular path. The time dependence of the $\delta \theta(t)$ over 5000 s is plotted in Fig. 5.5 (a) where $\delta \theta(t)$ fluctuates around zero. Surprisingly, the mean squared displacement (as shown in Fig. 5.5 (b)) of $\delta \theta(t)$ displays diffusive dynamics for $t \gtrsim \tau_0$ i.e., $\langle \Delta \delta \theta(t)^2 \rangle = 2D_\theta t$ with $D_\theta$ is two orders of magnitude higher than the $D_\theta^0$ i.e., the diffusion coefficient of the passive particle. Qualitatively, this can be understood by considering the fact that as an active particle propel through
Chapter 5  Work Fluctuations of an Active Brownian Particle Moving in a Viscoelastic Fluid

Figure 5.3: Probability density function $P(W_\tau)$ of the computed work $W_\tau$ for an active particle undergoing persistent circular motion while moving in a viscoelastic fluid for different angular velocities (a) $\omega = 0.018$ rad s$^{-1}$ and, (b) $\omega = 0.095$ rad s$^{-1}$. The symbols correspond to different integration times $\tau$: $\tau = 0.06$ s (circles), $\tau = 0.59$ s (diamonds), $\tau = 2.94$ s (triangles), and, $\tau = 5.88$ s (squares).

Figure 5.4: The asymmetry function $\ln[P(+W_\tau)/P(-W_\tau)]$ as a function of $W_\tau$ computed for integration time $\tau = 5.88$ s for an active particles describing circular trajectory in the viscoelastic fluid at angular velocities $\omega = 0.018$ rad s$^{-1}$ (diamonds), $\omega = 0.025$ rad s$^{-1}$ (circles), and $\omega = 0.095$ rad s$^{-1}$ (squares). The dashed line corresponds to the work fluctuation theorem (Eqn. 5.1)

the viscoelastic polymer network, it instigates a local stress which then relaxes over $t \approx \tau_0$. Over this time, the excited fluid can couple to the orientational motion of the particle leading to enhanced amplitude of angular fluctuations which manifests as enhanced angular diffusion. Such an enhancement suggests that the orientational particle dynamics are governed by a higher effective temperature which can be expressed as $T^* = (D_\theta/D'_\theta)T$. For instance, for the case shown in Fig. 5.5 (b), $T^* = 7.4 \times 10^4$ K. This effective temperature then should be taken into account for the application of the work fluctuation theorem. This can be incorporated by normalizing the work as

$$W_\tau^* = W_\tau \frac{D_\theta^0}{D'_\theta}.$$  \hspace{1cm} (5.5)

The asymmetry function i.e., $\ln[P(W_\tau^*)/P(-W_\tau^*)]$ as a function of the normalized work is plotted in Fig. 5.6. In comparison to Fig. 5.4, $W_\tau^*$ in Fig. 5.6 provides much
5.3 Work fluctuation theorem applied to a L-shaped particle in a Newtonian liquid

Figure 5.5: (a) Time evolution of the angular fluctuations $\delta \theta$ around the mean circular path for an active particle, rotating at an angular velocity $\omega = 0.025 \, \text{rad} \, \text{s}^{-1}$, obtained by subtracting the angular drift $\omega t$ from the time evolution of the angular coordinate $\theta$ i.e., $\delta \theta(t) = \theta(t) - \omega t + \text{constant}$. (b) The angular mean squared displacement $\langle \delta \Delta \theta(t)^2 \rangle$ of the angular fluctuations for an active particle undergoing persistent circular motion with $\omega = 0.025 \, \text{rad} \, \text{s}^{-1}$ (solid curve) and the corresponding angular mean squared displacement of a passive particle in the same viscoelastic fluid (dotted curve) as a function of time.

better agreement to the work fluctuation relation, particularly for $W^*_\tau \lesssim 3$. For larger values of work, i.e., $W^*_\tau \gtrsim 3$, the deviations from the linear behavior appears. This occur mainly due to extreme but rare angular fluctuations because of non-linear coupling to the viscoelastic bath. Such deviations have also been reported for other systems when the variance of the fluctuating quantity becomes considerably larger than the thermal fluctuations [139,155].

5.3 Work fluctuation theorem applied to a L-shaped particle in a Newtonian liquid

In this section, the validity of the work fluctuation theorem is tested for an asymmetric L-shaped particle moving in purely viscous i.e., Newtonian fluid. Because of shape asymmetry, such a particle undergoes a velocity-dependent viscous torque which results in pronounced circular motion [15, 115]. However, here unlike the spherical particles in a viscoelastic fluid, the direction and radius of circular orbits are independent of their propulsion speed and depends only the particle shape [15, 115–117]. A typical trajectory of an asymmetric L-shaped particle moving at an angular velocity $\omega = 0.041 \, \text{rad} \, \text{s}^{-1}$ measured over 3200 s is shown in Fig. 5.7 (a) where the red arrows correspond to the particle orientation $\mathbf{n}(t) = (\cos \theta, \sin \theta)$ as defined in the inset Fig. 5.7(a). The time evolution of the particle orientation $\theta(t)$
Chapter 5  Work Fluctuations of an Active Brownian Particle Moving in a Viscoelastic Fluid

Figure 5.6: The asymmetry function of the normalized work \( W^*_\tau \ln[P(+W^*_\tau)/P(-W^*_\tau)] \) versus \( W^*_\tau \) of an active particle undergoing circular orbits at different angular velocities: \( \omega = 0.018 \text{ rad s}^{-1} \) (diamonds), \( \omega = 0.025 \text{ rad s}^{-1} \) (circles) and, \( \omega = 0.095 \text{ rad s}^{-1} \) (squares). The dashed line corresponds to the work fluctuation theorem.

is shown in Fig. 5.7 (b) where a constant angular drift \( \omega t \) is quite evident. From the time evolution of \( \theta(t) \), the associated orientational work can be obtained as

\[
W^*_\tau = \frac{1}{k_B T} \int_t^{t+\tau} \dot{\theta}(t') \langle T_v \rangle dt'.
\] (5.6)

The torque acting on the particle can be obtained as \( \langle T_v \rangle = \gamma_\theta \omega \), where \( \gamma_\theta \) is the rotational friction coefficient of the particle which is related to the rotational diffusion coefficient as \( \gamma_\theta = k_B T/D_\theta \). The computed probability distribution of the work \( P(W^*_\tau) \) for different integration times \( \tau \) of a particle moving at angular velocities \( \omega = 0.028 \text{ rad s}^{-1} \) and \( \omega = 0.041 \text{ rad s}^{-1} \) are shown in Fig. 5.8 (a) and Fig. 5.8 (b), respectively. In contrast to shape profile of \( P(W^*_\tau) \) observed in the viscoelastic case, here, the \( P(W^*_\tau) \) are rather symmetric and are well described by a Gaussian profile (as shown by the solid curve). The asymmetry function \( \ln[P(+W^*_\tau)/P(-W^*_\tau)] \) is plotted in Fig. 5.8 (c) for \( \tau = 2.00 \text{ s} \) for different values of \( \omega \). Evidently, the work fluctuation theorem represented by the dashed line in Fig. 5.8 (c), is obeyed well for all considered values of \( \omega \).

5.4 Application of the work fluctuation theorem

The work fluctuation theorem can be exploited to extract information about the active particles, in particular, it can be used to infer the acting propulsion forces and torques on them. Interestingly, it does not even require the prior knowledge of their friction coefficients and geometrical shape. In the following subsections the work fluctuation is applied to extract the torque acting on a spherical active particle undergoing circular orbits in a viscoelastic fluids and later it is exploited for computing torque on asymmetric L-shaped colloid moving the counter-part Newtonian fluid.
Figure 5.7: (a) Trajectory of an active L-shaped particle undergoing pronounced circular motion with an angular velocity $\omega = 0.033 \text{ rad s}^{-1}$ measured over 1500 s. The arrows denote the instantaneous particle orientation. The scale bar corresponds to the trajectory. Inset: An optical image of an L-shaped particle obtained from the video microscopy. The labeled arrow parallel to the long side of the particle represents the particle orientation vector $n$, which defines the angle $\theta$ with respect to $x$-axis (dashed line). (b) The time evolution of accumulated particle orientation $\theta$ shows a linear angular drift $\omega t$.

### 5.4.1 Torque acting on an active spherical particle moving in a viscoelastic fluid

The results obtained in Section 5.2, showed that because the rotational dynamics of the particle undergoing circular orbits are governed by a higher effective temperature $T^*$ which requires a renormalization of the work to satisfy the work fluctuation theorem. The renormalized work i.e., $W^*_\tau$ is related to the torque $T_v$ acting on the particle as

$$W^*_\tau = \frac{T_v \Delta \theta_\tau}{k_B T^*} \quad (5.7)$$

Therefore, according to the work fluctuation relation (Eqn. 5.1), the slope of the plot $\ln[P(\Delta \theta_\tau)/P(-\Delta \theta_\tau)]$ versus $\Delta \theta_\tau/k_B T^*$ (plotted in Fig. 5.9 (a) for different $\omega$) for $W^*_\tau \lesssim 3$ provides a direct measure of the torque acting on the particle. The obtained torque $T_v$ from the the slope is plotted in Fig. 5.9 (b) as a function of $\omega$. To compare the obtained torque $T_v$ to the average torque $\langle T_v \rangle$, they are plotted against each other in Fig. 5.9 (c). The obtained values of $T_v$ are in excellent agreement with $\langle T_v \rangle$ which proves the suitability of the work fluctuation theorem for computing forces and torques acting on self-propelled particles.
Figure 5.8: Probability density functions $P(W_\tau)$ of the work done $W_\tau$ by an asymmetric L-shaped particle moving with different angular velocities $\omega$ (a) $\omega = 0.012$ rad s$^{-1}$ and, (b) $\omega = 0.041$ rad s$^{-1}$. The symbols correspond to different integration times $\tau = 0.07$ s (circles), $\tau = 0.67$ s (diamonds), $\tau = 1.33$ s (triangles) and, $\tau = 2.00$ s (squares). The solid black lines in (a) and (b) are the respective Gaussian fits for $\tau = 2.00$ s. (c) The asymmetry function $\ln[P(+W_\tau)/P(-W_\tau)]$ of the distributions of $W_\tau$ calculated for the integration time $\tau = 2.00$ s for different angular velocities: $\omega = 0.012$ rad s$^{-1}$ (diamonds), $\omega = 0.028$ rad s$^{-1}$ (circles) and $\omega = 0.041$ rad s$^{-1}$ (squares). The dashed line corresponds to the work fluctuation theorem Eqn. 5.1.

Figure 5.9: (a) $\ln[P(\Delta \theta_\tau)/P(-\Delta \theta_\tau)]$ of the probability density functions of angular change $\Delta \theta_\tau/k_B T^*$ of an active particle undergoing persistent circular motion in a viscoelastic fluid, calculated for the integration time $\tau = 5.88$ s for various $\omega$: $\omega = 0.018$ rad s$^{-1}$ (diamonds), 0.025 rad s$^{-1}$ (circles) and 0.095 rad s$^{-1}$ (squares). The solid lines are the corresponding linear fits. (b) The torque $T_v$ obtained for a spherical Janus particle using the normalized fluctuation relation as a function of $\omega$. (c) Measured torque using fluctuation relation $T_v$ versus with the mean estimated values $\langle T_v \rangle$ computed using $\langle T_v \rangle = 8\pi \eta_0 a^3 \omega$. The dashed line represents $T_v = \langle T_v \rangle$.

5.4.2 Torque acting on an active particle moving in a Newtonian fluid

Similar to the viscoelastic case, using $W_\tau = T_\tau \Delta \theta_\tau/k_B T$ for an asymmetric L-shaped particle moving in circles in a purely viscous case, the torque $T_v$ can be measured.
5.4 Application of the work fluctuation theorem

The measured $T_v$ as a function of $\omega$ is plotted in Fig. 5.10 (a). Further, the comparison between the obtained value from the work fluctuation theorem and the estimated values $T_v = \gamma_0 \omega$ yields an excellent agreement as shown in Fig. 5.10 (b).

![Figure 5.10: (a) The obtained torque $T_v$ using the work fluctuation theorem i.e., 5.1 acting on an asymmetric L-shaped particle undergoing circular motion in a Newtonian fluid as a function of angular velocity $\omega$. (b) Comparison of the obtained torque $T_v$ with the estimated mean value $\langle T_v \rangle = \gamma_0 \omega$. The dashed-dotted line corresponds to the line with a slope unity.](image)

Summary

In this Chapter, the orientational motion of an active particle undergoing persistent circular motion in a viscoelastic fluid is studied in the context of the work fluctuation theorem. Because of the non-linear coupling of the active particle orientation to the surrounding viscoelastic bath, which leads to remarkably enhanced orientational diffusion of the particle, strong deviations from the work fluctuation theorem are observed. Taking the enhanced diffusion into account, in the form of an effective temperature, the fluctuation relation is recasted back to the work fluctuation theorem. Further, the proposed approach is verified by demonstrating that it provides a consistent measure of torque acting on the active particle. This suggests that the work fluctuation theorem can be used to obtain important information of active particles without knowing the precise details of their friction coefficients and geometrical shapes. In addition, to show the role of noise properties of the bath on the fluctuation relations, the work fluctuation theorem is applied to an asymmetric L-shaped particle undergoing pronounced circular motion in a Newtonian fluid. In this case, the usual fluctuation theorem is found to be obeyed for all the considered angular velocities.
Active Particles Moving Under Geometric Constraints

In chapter 4, it is shown that the rheology of the fluid can have a drastic impact on the dynamics of an embedded active particle \([26, 27, 29, 30, 34, 35, 101]\). Another factor that can greatly influence the behavior of an active particle is the presence of topographic features such as walls, confinements, corners and, patterned surfaces. Such spatial features can provide additional steric, phoretic and hydrodynamic interactions \([160–168]\) which can significantly alter the dynamics of an active particle. For instance, active particles get accumulated near walls when moving in a viscous fluid \([99, 162, 169, 170]\). Since their translational motion is halted by the wall, they stay at the wall surface over time scale set by the rotational diffusion coefficient \([99]\).

At other instances, an active particle is shown to be trapped by the spherical obstacles \([171–173]\). In situations, these geometric constraints can also be exploited to guide the active particles along topographic pathways \([174–178]\). Whereas much has been explored and understood about the motion of the active particles under such spatially imposed constraints when they are moving in a purely viscous fluid \(i.e.,\) Newtonian fluids. Experiments with active particles under such spatial conditions in viscoelastic fluids have not been realized. Therefore, as a natural step to extend our understanding under such conditions in this Chapter, the dynamics of active Janus particles moving under various geometrical constraints are studied in a viscoelastic fluid \([179, 180]\). For comparison, their behavior in a counter-part Newtonian fluid under the same spatial conditions is also discussed.

Firstly, in the simplest case \(i.e.,\) an active particle interacting with a flat wall is considered in a viscoelastic fluid. In contrast to the behavior of an active particle in a Newtonian fluid, where wall mere hinders its translational motion with no considerable influence on its rotation, in a viscoelastic fluid significant alteration of both translation and rotational motion of the particle is observed.

Secondly, the interaction of an active particle with a curved surface \(i.e.,\) a spherical obstacle is studied. Here also, unlike the Newtonian case, where depending on the
orientation of an active particle, it either gets halted or slides along the surface, the behavior in the corresponding viscoelastic fluid is much more complex where a particle can feel the presence of obstacle even at distances as large as several times the particle diameter.

Further, the behavior of an active particle confined in a cylindrical cavity is studied as a function of its propulsion speed $v$. Interestingly, for the considered $v$ values, the behavior in the Newtonian case remained independent of $v$, however, it displayed strong dependence on $v$ in the viscoelastic case.

Lastly, the dynamics of multi-active particles in the cylindrical cavity is probed. While in the Newtonian fluid, active particles undergo clustering, consistent with previous studies [5,17,181–185], in the viscoelastic fluid, it exhibited numerous novel features including self organization into crystalline-like patterns.

### 6.1 Experimental parameters

In this work, spherical colloids with mean diameter $2a = 7.82 \mu m$ half coated with 30 nm thick carbon layer are suspended in the critical Newtonian (mixture of water (60% by mass) and propylene glycol $n$-propyl ether (40% by mass)) and the viscoelastic fluid prepared by adding polymer polyacrylamide to the critical mixture at concentrations 0.03% wt. and 0.05% wt. in presence of various geometrical constraints such as flat walls, spherical obstacles and, cylindrical cavities. The geometric features are added directly on the glass substrate which is used as the bottom surface of the sample using photo-lithography [110]. The Janus particles suspended in the critical fluid mixture are poured on the patterned substrate and glued with the coverslip. The intensity of the illumination which induced self-propulsion of the particles is varied from $I = 0 \mu W \mu m^{-2}$ to $I = 15 \mu W \mu m^{-2}$ which leads to free active particle velocities $v$ ranging from 0 $\mu m s^{-1}$ to 1.200 $\mu m s^{-1}$. Using video microscopy, the videos of the particles were recorded at a frequency 10 Hz. The videos were then analyzed by tracking the centre of mass of the particles and their in-plane orientation using home written MATLAB script.

### 6.2 Interaction of an active particle with a flat wall

To understand how the behavior of a spherical active particle is altered on interacting with a solid surface, the simplest geometry i.e., a flat wall is considered in both the Newtonian and viscoelastic fluids. A snapshot of an active Janus particle close to a flat wall is shown in Fig. 6.1, where $d$ and $\theta$ denote the distance of the particle to the wall and the particle orientation, respectively. This section is divided into two subsections. In the former one, the behavior of an active particle interacting with a flat wall is discussed in the Newtonian medium. In the latter, its behavior in the corresponding viscoelastic fluid is discussed with a particular emphasis on the distinct features observed with respect to the Newtonian case.
6.2 Interaction of an active particle with a flat wall

6.2.1 Active particle interaction with a flat wall in a Newtonian fluid

A typical trajectory depicting the observed behavior of an active particle on interaction with a flat wall (grey-shaded region) in the Newtonian fluid is shown in Fig. 6.2 (a) as a solid black curve. The arrows represent the instantaneous orientation of the particle \( \mathbf{n} = (\cos \theta, \sin \theta) \). In agreement with the previously reported findings [99], when an active particle arrives at the wall surface, it stays there as long as it has a finite component of its orientation \( \mathbf{n} \) perpendicular to the wall surface tangent \( i.e., \cos \theta < 0 \). This is demonstrated in the lower part of the trajectory since the particle approached the wall with its orientation perpendicular to the wall tangent and got trapped at the wall surface (as depicted by the density of arrows). On the other hand when it has a finite component of its orientation \( \mathbf{n} \) parallel to the wall \( i.e., \sin \theta \neq 0 \), it undergoes lateral displacement along the wall. It remains at the wall until \( \mathbf{n} \) stochastically points away from the wall \( i.e., \cos \theta > 0 \). The reorientation process in the Newtonian case is governed purely by the thermal diffusion of the particle which for the present case occurs over \( 1/D_\theta \approx 25 \text{ min} \).

The velocity \( v \) of the active particle, obtained from its trajectory, as a function of its distance to the wall while approaching the wall (squares) and while departing from it (circles), is plotted in Fig. 6.2 (b). Apparently, \( v \) of the particle remains rather constant irrespective of the active particle distance to the wall. A small decrease in \( v \) is observed during its departure away from the wall surface which occurs because of phoretic interactions induced by the concentration gradient adjacent to the capped hemisphere when the particle cap faces the wall surface [103,186]. Therefore, in a Newtonian fluid, the interaction between an active particle and the wall surface is mainly mediated by steric forces and the hydrodynamic interactions are...
Figure 6.2: (a) Representative trajectory of a spherical active particle interacting with a rigid flat wall in a Newtonian fluid. The arrows denote the instantaneous particle orientation \( \mathbf{n} \). (b) The velocity of the active particle \( v \) as a function of its distance to the wall while approaching towards the wall (squares) and while departing away from the wall (circles). The shaded regions are the corresponding standard deviations, computed over 20 independent trajectories.

negligible.

6.2.2 Active particle interacting with a flat wall in a viscoelastic fluid

On contrary to the behavior of an active particle interacting with a flat wall in a Newtonian fluid, striking differences are observed in the viscoelastic fluid. Specifically, an active particle shows a pronounced systematic rotation on interaction with a wall as shown in Fig. 6.3 (a). This is strictly opposite to the rotational behavior observed in a Newtonian fluid, where the particle orientation remained affected on interaction with a solid surface and only determined by the thermal diffusion. In addition, when it approaches the wall, it exhibits a significant decrease in velocity \( v \) even at distances as large as \( d \approx 6a \) from the wall as plotted in Fig. 6.3 (b) as solid circles. What is even more notable is the fact that an active particle stays on the wall surface only for \( \sim 1 \text{ min} \), which is orders of magnitude below the rotational diffusion time \( (1/D_\theta) \approx 21 \text{ h} \) of a passive particle in the same fluid. Thereafter, it rotates and departs from the wall surface. While departing from the wall its velocity \( v \) is highly increased (approximately two times its value far from the wall) which then takes \( (d \approx 6a) \) to recover its free velocity \( v \) \( i.e., \) far from the wall.

The observed behavior can be understood by considering the accumulation and relaxation processes of the mechanical stress in the microstructure of the viscoelastic fluid. While an active particle moves towards the wall surface it compresses the enclosed viscoelastic fluid between the wall surface and the active particle. Moving against the strained fluid dramatically hinders the motion of the particle which leads to the observed decrease in particle velocity. Because of spatial fluctuations,
6.2 Interaction of an active particle with a flat wall

Figure 6.3: (a) Representative trajectory of a spherical particle interacting with a rigid flat wall in the viscoelastic fluid. The arrows denote the instantaneous particle orientation \( \mathbf{n} \). (b) The velocity of the active particle \( v \) as a function of its distance to the wall while approaching towards the wall (circles) and while departing away from the wall (squares). The shaded regions represent the corresponding errors bars which are computed over 20 independent trajectories.

The strained fluid not only affects the translational motion of the active particle but also couples to the rotational motion of the particle leading to a viscoelastic torque. This results in faster reorientation close to a wall surface. The reorientation away from the wall surface also allows a sudden release of the accumulated stress which adds to the active particle velocity away from the wall surface leading to a strong increase in its velocity while departing away from the wall surface.

To prove that the effect solely arises due to the viscoelastic nature of the surrounding fluid, the concentration of the polymer is decreased from 0.05\% wt. to 0.03\% wt.. As a matter of fact, decreasing polymer concentration leads to a less pronounced effect. The resulting \( v \) as a function of \( d \) for 0.03\% wt. is shown in Fig. 6.4. In comparison to higher polymer concentration, when a particle approaches the wall, its speed begins to decrease only at \( d \approx 5a \) with respect to the value far away from the wall. Even the decrease is less pronounced (compared to 0.05\% wt.). Moreover, the particle resides at the wall for about \( \approx 9 \) min, which is significantly larger than the higher polymer concentration (\( \approx 1 \) min) but still orders of magnitude shorter than the \( 1/D_\theta \) of the passive particle. After detaching from the wall, the velocity of the particle increases due to the sudden release of the accumulated stress of the viscoelastic fluid, compared to its value far away from the wall which then takes \( d \approx 3a \) to recover to its value away from the wall.
Chapter 6  Active Particles Moving Under Geometric Constraints

Figure 6.4: The velocity of an active particle $v$ measured at polymer concentration 0.03% wt. as a function of its distance to the wall while approaching towards the wall (circles) and, while departing away from the wall (squares). The shaded regions represent the corresponding particle velocity measured at polymer concentration 0.05% wt. (see Fig. 6.3 (b)) [179].

6.3 Interaction of an active particle with a rigid spherical obstacle

In this section, the interaction of an active particle with a curved wall is investigated. For this, immobile spherical obstacles (radius $2a$) are deployed in the surrounding environment and the interaction of an active particle with them is explored. For convenience, the 2D motion of the active particle is characterized in polar coordinates $(r, \phi)$ system which is sketch in Fig. 6.5. The centre of the obstacle is taken as the origin O of the coordinate system. The initial active particle position $r_0$ and orientation $\theta_0$ which defines the polar axis $P$, the initial polar angle $\phi_0$ and the impact parameter $b$. The polar angle $\phi_0$ is related to the initial position $r_0$ and the particle orientation $n$ as $\cos \phi_0 = r_0 \cdot n / |r_0|$ and the impact parameter $b$ is related to the initial coordinates of the particle as $b = r_0 \sin \phi_0$. To understand the distinct behavior which results from the interaction of an active particle with the obstacle, $r_0$ is chosen to be $\approx 15a$ and, $b$ is varied from 0 to several times the particle radius $a$. 
6.3 Interaction of an active particle with a rigid spherical obstacle

Figure 6.5: Sketch of the encounter of an active particle of radius $a$, orientation $\mathbf{n}$ with an immobile spherical obstacle of radius $2a$. The origin $O$ of the coordinate system is located at the center of the obstacle, whereas $P$ represents the polar axis. Here, $\mathbf{r} = (r, \phi)$ denotes the position of the active particle relative to $O$, where $r = |\mathbf{r}|$ and $\phi$ is the polar angle between $\mathbf{r}$ and $P$. The initial position of the active particle ($\times$) is $\mathbf{r}_0 = (r_0, \phi_0)$. The impact parameter, i.e. the distance of closest approach to $O$ in absence of the obstacle, is denoted as $b$ [179].

6.3.1 Active particle interacting with an immobile spherical obstacle in a Newtonian fluid

The typical behavior of an active particle interacting with a spherical obstacle approaching at two different values impact parameters $b$ in the Newtonian fluid is shown in Fig. 6.6 (a) and (b). Under the considered experimental conditions, the active particle propels with a velocity $v = 0.460 \, \mu\text{m} \, \text{s}^{-1}$, which enables it to transverse the distance to the obstacle much faster ($r_0/v \approx 2 \, \text{min}$) compared to the rotational diffusion time i.e., $1/D_\theta \approx 25 \, \text{min}$. Therefore, the particle reaches the obstacle surface following a rather straight trajectory without displaying any significant orientational change. For $b << a$, the particle arrives at the obstacle surface almost perpendicularly as demonstrated for $b \approx 0$, in Fig. 6.6 (a). On its arrival at the obstacle surface, its translational motion is completely halted, however, the orientational dynamics is governed purely by the thermal diffusion. It escapes the obstacle via sliding when it has a component of the orientation vector $\mathbf{n}$ tangential to the obstacle surface. Increasing $b$ would result in reducing the residence times of the active particle at the obstacle surface since now only a smaller orientation change is needed to escape the obstacle surface. This is illustrated in Fig. 6.6 (b), where an active particle arrives at the obstacle surface with its orientation vector $\mathbf{n}$ at $0.84 \, \text{rad}$ relative to the tangent of the obstacle surface where it only takes $\approx 4a/v \approx 1 \, \text{min}$ to slide along the obstacle surface and leaves it. For $b > 3a$, an active particle motion remains unaltered by the presence of an obstacle.

In order to show that the orientational motion of an active particle in a Newtonian fluid remains unaffected by the presence of an obstacle, the mean squared angular displacement $\langle \Delta \theta(t)^2 \rangle$ of an active particle is plotted in Fig. 6.7 for the...
three distinctly different situations, namely, when the particle is very far away from the obstacle *i.e.*, a free active particle (plotted as squares in Fig. 6.7), when it is trapped at the obstacle which corresponds to the case shown in Fig. 6.6 (a) (plotted as triangles in Fig. 6.7) and, when it slides along the obstacle which corresponds to the case depicted in Fig. 6.6 (b) (plotted as circles in Fig. 6.7). In all the cases, \( \langle \Delta \theta(t)^2 \rangle = 2D_\theta t \) exhibits diffusive angular dynamics with a situation independent diffusion coefficient \( D_\theta \) and is given by the Stokes-Einstein relation *i.e.*, \( D_\theta = k_B T / \pi \eta f a^3 = 6.8 \times 10^{-4} \, \text{rad}^2 \text{s}^{-1} \), shown by the solid line in Fig. 6.7. These observations suggest that the hydrodynamic and phoretic effects in the present system are negligible along the orientational degrees of freedom as the orientational dynamics of an active particle remained uninfluenced even in presence of boundaries when moving in the Newtonian fluid.

### 6.3.2 Active particle interacting with an immobile spherical obstacle in a viscoelastic fluid

Here, similar to subsection 6.3.1 where the interaction of an active particle with a spherical obstacle is explored in the Newtonian fluid, the corresponding behavior of an active particle interacting with a spherical obstacle is investigated in the viscoelastic fluid at 0.05 % *wt.* polymer concentration. Representative trajectories of an active particle interacting with an immobile spherical obstacle is shown in Fig. 6.8 (a) and (b) for different values of the impact parameter \( b \). In Fig. 6.8 (a), the impact parameter \( b << a \) *i.e.*, the active particle approached the obstacle surface perpendicularly, it is observed that its motion is halted at a distance \( r - 2a \approx 4a \) from the obstacle by the strong viscoelastic repulsions. The halt is followed by a
sudden deflection of its orientation by an angle $\Delta \theta \approx \pi/3$ which is apparent from the time evolution of its orientation at time $t \approx 200$ s plotted in Fig. 6.9 (a). What is even more surprising is the fact that while deflecting the orientation vector $\mathbf{n}$ of the particle does not coincide with translational motion. This indicates the presence of an effective repulsive interaction induced by the strained viscoelastic fluid, which not only opposes its active motion but also couples to its orientation. Quantifying the observation shows that the orientational change during deflection occurred over $\sim 1$ min, which is orders of magnitude shorter than the rotational diffusion time $1/D_\theta \approx 21$ h of a passive particle of the same size embedded in the same viscoelastic fluid. This implies the strained viscoelastic fluid also imparts a random torque to the active particle because of a strong asymmetry created by the solid surface of the obstacle.

For the other extreme case of the impact parameter i.e., $b = 5a$ which is shown in Fig. 6.8 (b) the observed behavior is even more intricate. As expected, for such a large value of $b$, the particle motion would have remained unaffected by the presence of the obstacle in the Newtonian fluid. Surprisingly, that is not the case here, rather the obstacle strongly affects the motion of the active particle even at distance $r - 2a \approx 3a$ from the obstacle surface. Even at such large distances, the active particle experiences the torque imparted by the viscoelastic fluid, which reorients the active particle towards the obstacle. Thereafter, the particle performs hovering around the obstacle surface $r - 2a > a$. During hovering the orientational motion of the particle exhibit strong fluctuations due to the interplay of its active motion, rotational diffusion and viscoelastic torque. Eventually, when $\mathbf{n}$ points away from the obstacle surface leading to an escape from the obstacle.

Again to quantify the rotational dynamics of the active particle undergoing interaction with a spherical obstacle its mean squared angular displacement $\langle \Delta \theta(t)^2 \rangle$ is computed for various distinct situations encountered by the particle. The obtained results are plotted in Fig. 6.9 (b). The distinct cases include, when the particle is...
significantly far away from the obstacle ($r \approx 10a$) i.e., a free active particle (dotted curve), during deflection away from the obstacle which occurred for $b << a$ (solid curve) and, during hovering around the obstacle which is observed for $b = 5a$ (dashed curve)). In all the cases, the long time $\langle \Delta \theta(t)^2 \rangle$ displays diffusive orientational dynamics with a diffusion coefficient that strongly depends on the situation. For instance, when the particle is moving at a self-propelled velocity $v = 0.100 \, \mu\text{ms}^{-1}$ far away from the obstacle, its diffusion coefficient is enhanced by 50 times compared to $D_\theta$ of a passive particle suspended in the same fluid (shown by the dashed-dotted curve in Fig. 6.9 (b)), consistent with previously reported results [26,35]. When the particle is deflected from the obstacle, its diffusion coefficient becomes 200 times $D_\theta$ and when it hovers close to the obstacle it gets enhanced by 450 times.

Figure 6.8: Exemplary trajectories of an active particle interacting with a spherical obstacle of radius $2a$ in the viscoelastic fluid for different values of the impact parameter $b$: (a) $b = 0$ where the active particle is deflected by the obstacle and, (b) $b = 5a$ where the active particle performs hovering motion around the obstacle. The symbol × represents the initial position of the particle which defines the impact parameter $b$ [179].

Such an effective repulsive force and torque imparted by a curved surface on an active particle moving in a viscoelastic fluid can be exploited, for instance, for local trapping and guidance of an active particle. As an example, which is shown in Fig. 6.10 (a) when an active particle comes near the gap between two immobile obstacles, its angular fluctuations increases while its velocity decreases when it approaches the gap, as depicted by the time evolution of the active particle orientation $\theta$ and its velocity $v$ in Fig. 6.10 (b) and (c), respectively. This leads to local trapping of the active particle. The effective repulsive forces and torques induced by the two curved surfaces of the obstacles reorient the particle which results in a guided motion within the gap. During guiding, the angular fluctuations of the particle decrease while $v$ increases which occurred during $600 \, s < t < 900 \, s$. Eventually, the
6.3 Interaction of an active particle with a rigid spherical obstacle

Figure 6.9: (a) Time evolution of the angular coordinate $\theta$ of an active particle during deflection from the obstacle which occurs when the active particle approaches the obstacle with the impact parameter $b = 0$ i.e., perpendicular to the obstacle surface in the viscoelastic fluid (shown in Fig 6.8(a)). (b) Mean squared angular displacement $\langle \Delta \theta(t)^2 \rangle$ of an active particle undergoing interaction with a spherical obstacle under different situations— when the active particle is far away from the obstacle (dotted line), when the active particle undergoes deflection from the obstacle surface which occurs when it approaches the obstacle with an impact parameter $b = 0$ (solid line), during hovering around the obstacle which occurs when the active particle approaches the obstacle with a large impact parameter $b = 5a$ (dashed line). The dashed-dotted line corresponds to the $\langle \Delta \theta(t)^2 \rangle$ of a passive particle suspended in the same viscoelastic fluid.

6.3.3 Interaction of two active particles in both Newtonian and viscoelastic fluids

In subsections 6.3.1 and 6.3.2, the interaction of an active particle with an immobile spherical obstacle is discussed both in the Newtonian as well as in the viscoelastic fluid. It is natural to think what how the interaction will get influenced when both an interacting particle and the obstacle are mobile. This can be realized e.g., considering the interactions between two active particles. Exemplary trajectories which resulted from the interactions of two active particles in a Newtonian and in a viscoelastic fluid are shown in Figs. 6.11 (a) and (b), respectively. In the Newtonian case, the active particles get in contact with each other, slide and move forward. The orientation of the particles in this case remains unaltered by their interaction. Contrary to this, in the viscoelastic fluid, they undergo a mutual repulsion, which

particle escapes the gap after 900 s where its angular motion and velocity become very similar to those before the local trapping.
Figure 6.10: (a) Trajectory (black solid line) and orientation (red arrows) of an active particle interacting with two spherical obstacles (radius 2\(a\)) in a viscoelastic fluid. The symbol \(\times\) corresponds to the initial position of the particle. (b) Time evolution of the angular coordinate \(\theta\) of the active particle during the entire process of trapping, guided motion and, eventually its escape between the two obstacles in the viscoelastic fluid. (c) Self-propelled velocity \(v\) of the active particle as a function of time for the trajectory described in (a) [179].

prevents them from touching each other, thus resulting in deflection of their initial trajectories. In addition, the fluid also exerts a torque on both particles, which leads to a significant change in their orientation. Although their behaviors while interacting are qualitatively similar to the case of an immobile spherical obstacle, the resulting trajectories are more complex here because of the mobility of both the particles.

6.4 Active particle in a cylindrical confinement

In the previous sections, the behaviors of an active particle emerging from its interaction with a flat surface (flat wall) and a convex surface (spherical obstacle) are explored in great detail. To extend further the understanding of how the curvature influences the behavior, concave walls, in the form of cylindrical pores of radius \(R = 20 \mu m\) are employed in the landscape of active particles. The resulting behavior is investigated in both a Newtonian and a viscoelastic fluid environment. The cylindrical cavity confines the 2D motion of a particle in a circular region \(0 \leq r \leq R - a\). To characterize the active particle motion, the polar coordinate system \((r, \phi)\) is chosen with the pore centre as the origin \(O\) of the coordinate system. A snapshot from
6.4 Active particle in a cylindrical confinement

Figure 6.11: Interaction of two self-propelled particles in a (a) Newtonian fluid and, (b) viscoelastic fluid. The solid lines are the trajectories while the arrows represent the instantaneous particle orientation vector [179].

Figure 6.12: Snapshot of an active particle confined in a cylindrical cavity of radius $R = 20 \mu m$. The motion of the particle is described by the polar coordinates $(r, \phi)$ where the origin O of the coordinate system coincides with the center of the confinement. The scale bar is 10 $\mu m$ [179].

the video microscopy of a Janus particle confined in a cylindrical pore is which is shown in Fig. 6.12.

6.4.1 Active particle moving inside a pore in a Newtonian fluid

In this subsection, the 2D motion of an active particle in cylindrical confinement of radius $R = 20 \mu m$ is characterized when moving in a Newtonian fluid. The resulting trajectories of an active particle under such a confinement measured at the illumination intensities $I = 10 \mu W\mu m^{-2}$ and $I = 15 \mu W\mu m^{-2}$, respectively, are plotted in Fig 6.13. For the described trajectory in Fig. 6.13 (a), the illumination intensity leads to a free particle self-propulsion velocity $v \approx 0.800 \mu ms^{-1}$. This velocity for the considered active particle size ($2a = 7.75 \mu m$) corresponds to a
persistent length $l_p = v/D_\theta \approx 1200 \mu m$, which is much larger compared to the pore size i.e., $l_p > 2R = 40 \mu m$. Such a large $l_p$ enables the active particle to approach the pore wall without undergoing any significant change in its orientation. Once the active particle arrives at the wall, it stays there as its radially outwards motion, with respect to the confinement centre, is ceased by the confinement wall. It slides along the confinement wall when it has a non-zero component of the orientation parallel to the wall surface tangent. A complete detachment from the wall can only occur when it has a non-zero radial component pointing toward the pore centre. Since the orientational motion is dominated by rotational diffusion, the probability to observe such events is very small under the present experimental conditions. Moreover, increasing the velocity of the particle further does not modify the behavior of an active particle (see Fig. 6.13 (b)). Even when the particle detaches from the wall, as observed on the left side of Fig. 6.13 (b), it again quickly encounters the wall because of its large persistent length. This leads to a persistent radial trapping of the active particle. To investigate the radial positional fluctuations while it is moving close to the confinement wall, normalized time evolution of its radial coordinate $r/R$ is plotted in Fig. 6.14 (a). Apparently, for both $I$ values, the radial trajectory of the particle remains tightly confined around the pore wall i.e., $r/R \approx 0.78$. This value is very close to the value when it is in contact with the pore wall i.e., $r/R = 0.80$. The observation is further supported by the probability density function of the radial position $P(r/R)$ as shown in Fig. 6.14 (b) where it peaks sharply at $r/R = 0.78$ for both the intensities $I$ of the illumination.

**Figure 6.13:** Representative trajectories of an active Brownian particle moving in a Newtonian fluid under cylindrical confinement of radius $R = 20 \mu m$ at two different illumination intensities (a) $I = 10 \mu W \mu m^{-2}$ and (b) $I = 15 \mu W \mu m^{-2}$. In both (a) and (b), the cyan $\times$ represents the initial position of the particle while the black $\times$ marks the final position of the particle.
6.4 Active particle in a cylindrical confinement

Figure 6.14: (a) Time evolution of the radial position of an active particle normalized by the confinement radius \( r/R \) moving in a Newtonian fluid under a cylindrical confinement of radius \( R = 20 \, \mu m \) for the trajectories depicted in Fig 6.13 labelled with the same color code of their corresponding trajectories. Inset: An enlarged view of the main figure showing no significant variation of the radial particle position \( r/R \). (b) The probability density function \( P(r/R) \) of the radial particle position as a function of the normalized radial position \( r/R \) for the described radial trajectory in (a) labelled with the same color scheme [179].

6.4.2 Active particle moving under a cylindrical confinement in a viscoelastic fluid

In this subsection, the dynamics of an active particle under a cylindrical pore is explored inside the viscoelastic fluid. Here, it offers a sharp contrast to the behavior observed in the Newtonian fluid. Unlike in the Newtonian case, the resultant behavior, in this case, depends strongly on the active particle velocity \( v \) or intensity of the illumination \( I \). This is demonstrated in Figs. 6.15, which show the trajectories of an active particle measured over 3500 s moving in the viscoelastic fluid at different \( I \) increasing from (a) to (c). Clearly, with increasing \( I \), the particle undergoes more events of departing away from the confinement walls. Such observations indicate that the viscoelastic response of the fluid in the form of repulsive forces and torques experienced by an active particle increases with its \( v \). To assess how the active motion of an active particle is influenced by the pore wall, the normalized radial position of the particle is investigated which is plotted in Fig. 6.16 (a). opposite to the behavior of an active particle in a Newtonian fluid where the radial position remained tightly close to the wall, here, it undergoes very strong positional variations. Moreover, the amplitude of such positional fluctuations increases with \( v \). This can be explained by considering the coupling of an active particle motion with the process of accumulation and relaxation of the mechanical stresses in the viscoelastic network close to a wall. Intuitively, the viscoelastic response of the fluid would depend on the amount of deformation caused by the particle and therefore, it increases with \( v \). In order to highlight vividly the observed dependence of radial position variation of the active particle on \( v \), a magnified view of the Fig. 6.16 (a) is
shown in Fig. 6.17. The probability density function $P(r/R)$ of the active particle for different $v$ is plotted in Fig 6.16 (b) shows a shift towards the centre of the confinement with increasing $v$ which is directly opposite to that expected for an active particle in a Newtonian fluid [99].

Figure 6.15: Typical trajectories of an active particle moving in a viscoelastic fluid under the cylindrical confinement of radius $R = 20 \mu m$ at various intensity of the illumination $I$: (a) $I = 8 \mu W \mu m^{-2}$, (b) $I = 10 \mu W \mu m^{-2}$ and, (c) $I = 12 \mu W \mu m^{-2}$. The cyan and black $\times$ symbols represent the initial and the final position of the particle, respectively.

Figure 6.16: (a) Normalized radial position of the active particle as a function of time corresponding to the trajectories shown in Figs. 6.15 with the same color code. (b) The corresponding normalized radial probability density function $P(r/R)$ of the radial positions shown in (a), labelled with same color code. Inset: Magnified view of the main figure around the peak values of $P(r/R)$. 
6.5 Circularly confined multi-active particle system

In this section, extending the developed understanding further, the system is made more complex by confining several active particles in cylindrical confinement of radius \( R = 20 \, \mu m \) in both the Newtonian and viscoelastic fluids. Depending on the activity of the particles such strong confinement of the active particles can have striking consequences on their collective motion as their behaviour would now originate from the combined effects of interactions among the active particles and the active particles and the walls. To draw a distinction, this section is divided into two subsections in the first the dynamics of confined (in cylindrical confinements) multi-active particles is explored in the Newtonian fluid. In the second the emergent dynamics of multi-active particles under similar experimental conditions in the viscoelastic fluid are studied.

6.5.1 Circularly confined multi-active particle system in a Newtonian fluid

A snapshot from the video microscopy of five active particles confined in circular confinement \( R = 20 \, \mu m \) in the Newtonian case is shown in Fig. 6.18 (a). Because the rotational dynamics of the active particles in a Newtonian fluid is completely decoupled from their interactions either with the walls or with the other active particles and is determined mainly by the thermal diffusion, this leads to well-known clustering behavior [5, 17, 181–185]. Once an active particle encounters a surface which is either of the wall or of another active particle it stays there until its orientation has a component pointing away from the surface which occurs over timescales \( \sim 1/D_{\theta} \) set by the rotational diffusion \( D_{\theta} \) of the particle. Therefore, under the condition for the considered persistent lengths \( l_p >> 2R \) of the active particles, they either exhibit clustering or remain at the confinement walls as shown in Fig. 6.18 (b) and (c) for two different values of laser intensities \( I \). Here, in contrast to a single active particle, the trajectories are more complex due to the mobility of other particles as well. This, for instance, can give finite probability density in the middle of the pore due to crowding effects as apparent from the trajectories. The
activity under the condition for the persistent length $l_p >> 2R$ does not lead to any significant influence on the dynamics of the active particles in a Newtonian fluid as evident from Fig. 6.18 (c) which is not distinctly different from Fig. 6.18 (b).

![Figure 6.18:](image)

**Figure 6.18:** (a) A video microscopy image of five Janus particles confined in a circular confinement of radius $R = 20 \mu m$. The scale bar is 10 $\mu m$. Trajectories of five active particles confined in the circular confinement at different intensities of the illumination $I$: (b) $I = 5 \mu W \mu m^{-2}$ and, (c) $I = 10 \mu W \mu m^{-2}$.

### 6.5.2 Circularly confined multi-active particle system in the viscoelastic fluid

This section describes the behavior of multi-active particles confined in a cylindrical pore in the corresponding viscoelastic fluid. In this case, the resulting behavior would be quite intriguing due to the following reasons: First, unlike the interaction of two active particles in a Newtonian fluid, here they would interact repulsively with each other due to the elastic response of the enclosed viscoelastic fluid between them. As discussed in subsection 6.3.3, the repulsive viscoelastic interaction not only deflects their initial trajectories but also imparts a viscoelastic torque which reorients them away from each other. Moreover, the strength of viscoelastic fluid mediated interactions depends strongly on the activity of the particles. In addition to interactions among the active particles, there would be repulsions from the confinement walls which acts on a length-scale of confinement radius $R$. The repulsion from the walls will act as an effective attraction towards the pore centre. Owing to such richness in terms of activity-dependent interactions, in this system, the active particles exhibit fascinating activity-dependent collective motion. A snapshot of five active particles confined in a pore of radius $R = 20 \mu m$ for different intensities of the illumination $I$ (increasing towards right) which is directly proportional to the active particle velocity $v$ is shown in Figs. 6.19. The corresponding trajectories measured for each case over 3600 s are plotted in Figs. 6.20.

Opposite to the Newtonian case, here, because of inter-particle repulsive interactions, no clustering is observed. At low activity (i.e., low value of $I$), the active
6.5 Circularly confined multi-active particle system

**Figure 6.19:** Snapshots from the video microscopy of five active particles confined in a cylindrical cavity of radius $R = 20 \mu m$ in a viscoelastic fluid at different intensities of the illumination $I$: (a) $I = 5 \mu W \mu m^{-2}$, (b) $I = 6 \mu W \mu m^{-2}$, (c) $I = 8 \mu W \mu m^{-2}$, (d) $I = 10 \mu W \mu m^{-2}$. The scale bar corresponds to 10 $\mu m$ [179].

**Figure 6.20:** Trajectories of five self-propelled colloids in the circular confinement of radius $R = 20 \mu m$ in the viscoelastic fluid at different intensities of the illumination $I$: (a) $I = 5 \mu W \mu m^{-2}$, (b) $I = 6 \mu W \mu m^{-2}$, (c) $I = 8 \mu W \mu m^{-2}$ and, (d) $I = 10 \mu W \mu m^{-2}$.

particles do not excite the fluid strongly and therefore the corresponding response of the fluid in the form of forces and torques are smaller which can hamper their clustering due to which they explore the available rather evenly. For instance, as shown in Fig. 6.20 (a), the trajectories of five active particles moving in a cylindrical cavity ($R = 20 \mu m$) at $I = 5 \mu W \mu m^{-2}$. Their uniform exploration of the available space is also evident from the time evolution of their polar angles $\phi$ which is plotted in Fig. 6.21 (a). Although the motion along the polar angular coordinate is correlated, due to the weaker repulsions amongst active particles, they can still touch each other which is mirrored in $\phi(t)$ at instances whenever the polar angle of one particle interacts $\phi$ of the other particles. Counter-intuitively, increasing $I$ results in slower dynamics of the active particles, for example, increasing $I$ to $6 \mu W \mu m^{-2}$ (Fig. 6.20 (b)) leads to a highly localized motion of the active particles along both the radial $r$ and polar $\phi$ (Fig. 6.21(b)) coordinates. Clearly, $\phi(t)$ of the active particles do not show any interacting events over 3600 s which reveals stronger inter-particle repulsive interactions. In this highly localized state, the particles organize themselves in an ordered fashion which obeys a rotational symmetry of order
five. Interestingly, the order remains highly stable over the entire measurement time \( \text{i.e.,} \approx 3600 \text{ s} \). Such an observation can be explained by the fact that with increasing \( I \), the viscoelastic response of the fluid also increases. The inter-particle repulsions become stronger which tend to shift them away from the pore centre. On the other hand, repulsions from the confinement walls also increase which tend to push them towards the pore centre. Therefore, at this intensity, the active forces of the particles and the fluid mediated forces balance out each other which leads to a quasi-steady arrest that localizes their motion. Notably, such an ordering behavior is reminiscent of the formation of crystalline clusters in paramagnetic colloids under confinements \([187–189]\). In that case, the dipole-dipole interactions due to the applied magnetic field assist the formation of classical 2D atomic-like structures composed of concentric shells. In contrast, here, the repulsive interactions are an intrinsic property of the surrounding viscoelastic fluid where the activity of the particles plays the role of the applied magnetic field. While the stability of the paramagnetic colloidal crystals increases with the strength of the applied magnetic field, the same is not observed here. Since increasing activity increases the strength of repulsive forces but it also increases the viscoelastic torques which can destabilize the force balance. This is demonstrated in Figs. 6.20 (c) and (d) and the time evolution of their corresponding polar angles Figs. 6.21 (c) and (d) whence further increasing the activity, the ordering of the particles is smeared out.

Figure 6.21: Time evolution of the polar angle \( \phi \) of five self-propelled colloids confined in a cylindrical confinement of radius \( R = 20 \mu m \) in a viscoelastic fluid (corresponding to the trajectories shown in Fig. 6.20) at different intensities of the illumination \( I \): (a) \( I = 5 \mu W \mu m^{-2} \), (b) \( I = 6 \mu W \mu m^{-2} \), (c) \( I = 8 \mu W \mu m^{-2} \), (d) \( I = 10 \mu W \mu m^{-2} \).

To quantify the non-monotonic collective behavior of active particles as a function of their activity (determined by intensity of the illumination \( I \)), the corresponding mean squared displacements of radial position \( r \), \( \langle \Delta r(t)^2 \rangle = \langle [r(t + t_0) - r(t_0)]^2 \rangle \) and polar angle \( \phi \), \( \langle \Delta \phi(t)^2 \rangle = \langle [\phi(t + t_0) - \phi(t_0)]^2 \rangle - \langle \phi(t + t_0) - \phi(t_0) \rangle^2 \) and the probability distribution \( P(r/R) \) for each case displayed in Figs. 6.20 are computed. The results are plotted in Figs. 6.22. Clearly, for \( I = 5 \mu W \mu m^{-2} \) at sufficiently long times, both \( \langle \Delta r(t)^2 \rangle \) and \( \langle \Delta \phi(t)^2 \rangle \) exhibit diffusive dynamics shown by the solid violet line in Figs. 6.22 (a) and (b), respectively, which confirms their observed liquid-like behavior. In addition, as expected from liquid-like behavior, their corre-
Circularly confined multi-active particle system

The corresponding radial probability density function \( P(r/R) \) spans over a large range of radial position \( r \) (Fig. 6.22 (c)). As shown previously, with increasing \( I \) to 6 \( \mu \text{W} \mu\text{m}^{-2} \), the system undergoes a dynamical arrest. In such a case, \( \langle \Delta r(t)^2 \rangle \) becomes sub-diffusive due to the strong radial localization, while \( \langle \Delta \phi(t)^2 \rangle \) remains diffusive but with a largely reduced slope as plotted in Figs. 6.22 (a) and (b) by the dotted turquoise line). Consequently, the spread of \( P(r/R) \) over \( r \) decreases appreciably (Fig. 6.22 (c)). For even higher intensities \( I \), \( \langle \Delta r(t)^2 \rangle \) exhibits a swift increase at short times due to breakdown of viscoelastic fluid mediated structural order and followed by a sub-diffusion at long time because of confinement by the cavity walls as shown in Fig. 6.22 (a) for \( I = 10 \mu \text{W} \mu\text{m}^{-2} \) by the dashed-dotted orange line. The appearance of the re-entrant liquid-like phase is also reflected in the broadening of the radial probability distribution \( P(r/R) \) of the particles (dashed-dotted line in Fig. 6.22 (c)). Since for all \( I \), the polar-angular mean squared displacement \( \langle \Delta \phi(t)^2 \rangle \) shows diffusive dynamics with remarkably enhanced slope. This reflects the emergence of re-entrant liquid like behavior. The diffusion coefficient \( D_\phi \) can be used to characterize the order within the confinement. It should be noted that \( D_\phi \) results from the combined effect of the viscoelasticity-mediated interactions and thermal fluctuations in the fluid.

In Fig. 6.23 (a), \( D_\phi \) for five active particles confined in a circular pore of \( R = 20 \mu\text{m} \) is plotted as pentagrams as a function of \( I \), which clearly shows a strong non-monotonic dependence on \( I \). Markedly, \( D_\phi \) exhibits a pronounced drop by one order of magnitude at \( I = 6 \mu \text{W} \mu\text{m}^{-2} \) at which the particles show structural ordering. For \( I > 6 \mu \text{W} \mu\text{m}^{-2} \), \( D_\phi \) sharply grows 2 orders of magnitude with respect to the minimum, thereby disclosing the appearance of the re-entrant liquid-like behavior of the active suspension. Apart from the polar-angular diffusive behavior, the orientational order can also be quantified by the order parameter \( \psi_N \) defined as

\[
\psi_N = \left\langle \frac{1}{N^2} \left| \sum_{j=1}^{N} e^{iN\phi_j} \right|^2 \right\rangle
\]  

(6.2)

where \( N \) is the total number of particles in the confinement and \( \phi_j \) is the polar angle of the \( j^{th} \) particle \((j = 1, ..., N) \) as defined in Fig. 6.12, and the brackets denote the average over all frames. The order parameter is \( \psi_N = 1 \) for a perfect polygon shape for the corresponding \( N \), while \( \psi_N = 0 \) for a fully disordered system. Fig. 6.23 (b) shows the dependence of \( \psi_N \) on \( I \). Clearly, \( \psi_N \) attains a maximum value \( \approx 0.7 \) at \( I = 6 \mu \text{W} \mu\text{m}^{-2} \), which confirms the emergence of high orientational order of the particles in the string-like structure. Such an orientational order is curtailed for \( I < 6 \mu \text{W} \mu\text{m}^{-2} \) due to weak repulsive interactions in the liquid-like phase, while for \( I > 6 \mu \text{W} \mu\text{m}^{-2} \) it also drops due to the increasing strength of the destabilizing torques. The explanation for such a strong non-monotonic behavior
of active particles moving in the viscoelastic fluid under cylindrical confinement is consistent as also confirmed by varying the total number of particles in the confinement i.e., $N$. For instance, a slight increase (or decrease) of the number of particles $N$ within the confinement of same size ($R = 20 \, \mu\text{m}$) would decrease (or increase) the space available for them to explore. For a fixed value of $I$, this would influence the strength of the forces and torques acting on each particle and the resulting correlations. Accordingly, it is expected that the values $D_\phi$, $\psi_N$ and, $I$ at which the structural order persists will depend on $N$. As a matter of fact, the polar-angular diffusion coefficient $D_\phi$ assumes comparatively lower values for $N = 6$ as plotted in the inset Fig. 6.23 (a) as circles. Since for a given activity, which is determined by $I$, the particles have less accessible space, thus resulting in closer inter-particle interactions. As a consequence, smaller particle activity is required to attain the ordered arrested state, leading to a minimum of $D_\phi$ at lower $I$ (Fig. 6.23 (a)). Additionally, in comparison to $N = 5$, a higher orientational order is expected for larger values of $I$. Infact, this is in agreement with the results shown in Fig. 6.23 (b) for which the values of $\psi_{N=6}$ are larger than those of $\psi_{N=5}$ at $I > 6 \mu\text{W} \mu\text{m}^{-2}$. On the other hand, one expects an opposite trend for decreasing the number of particles to $N = 4$. For instance, a higher value of the intensity $I$ is required to achieve maximum ordering (in comparison to $N = 5$), as a larger particle activity is needed to induce collective order of the system at larger inter-particle distances, as seen in Fig. 6.23 (b). Additionally, the order of the resulting structure for $N = 4$ is less pronounced compared to higher values of $N$.

**Summary**

In summary, the behavior of the active particles in both the Newtonian and viscoelastic fluids is investigated in presence of various geometrical constraints. Unlike in a Newtonian fluid where such constrains only provides steric interactions, in viscoelastic fluid active particle interact repulsively with the walls. The repulsive interaction stems from the accumulated strain of the viscoelastic fluid confined between an active particle and the wall and therefore strongly depends on its activity and the local curvature of the wall surface. Moreover, the spatial asymmetry imposed by the confinement imparts a viscoelastic torque to an active particle, which would otherwise be governed by rotational diffusion. Various examples are discussed where active particles exhibited viscoelasticity-mediated novel effects. For example, a single active particle exhibits very short residence times on planar wall surfaces, pronounced deflections by stationary obstacles, steering by arrays of obstacles and localization within circular pores. These effects resulted in the emergence of intriguing collective behavior for several active particles confined in circular confinements. Particularly, a transition from liquid-like behavior to a self-organized ordered state upon increasing their activity is observed. Thus, such findings are expected to be of great importance for the understanding of self-organization of concentrated sus-
Figure 6.22: (a) Mean-squared displacement of the radial position of five active particles, $\langle \Delta r(t)^2 \rangle$, for different intensities $I$: $I = 5 \, \mu W\mu m^{-2}$ (solid violet line), $I = 6 \, \mu W\mu m^{-2}$ (dotted turquoise line), $I = 8 \, \mu W\mu m^{-2}$ (dashed green line), and $I = 10 \, \mu W\mu m^{-2}$ (dotted-dashed orange line) confined in a cylindrical confinement of radius $R = 20 \, \mu m$ in a viscoelastic fluid. Inset: enlarged view around the order state at $I = 6 \, \mu W\mu m^{-2}$. (b) Mean-squared displacement of the corresponding polar angle $\langle \Delta \phi(t)^2 \rangle$ labelled with same line style and color code as in (a). Inset: Magnified view around the ordered state. (c) The corresponding probability distribution function $P(r/R)$ of the radial positions $r$ of the active particles labelled with same line style and color code as in (a) [179].

Figure 6.23: (a) Angular diffusion coefficient $D_\phi$ of active particles confined in a cylindrical cavity of radius $R = 20 \, \mu m$ in a viscoelastic fluid as a function of intensity of the illumination for $N = 5$. Inset: semilog-representation dependence of $D_\phi$ on the intensity of illumination $I$ for $N = 4$ (squares), $N = 5$ (pentagrams), $N = 6$ (circles). (b) Angular order parameter $\psi_N$ as a function of illuminating laser intensity $I$ for different $N$ labelled with the same symbols as in (a) [179].

Solutions of microswimmers under confined conditions [191–193].
Artificially developed active colloidal particles have recently caught immense attention from the diverse scientific community [1–3]. Besides their behavior showing remarkable resemblance to living active matter, they can also be employed in biomedical applications [53,194,195]. More recently, they have even proved themselves very potential candidates for probing the micro-mechanical properties of their surroundings [34,101]. The underlying principle is that when an active particle propels through a medium its dynamics, due to coupling with the surrounding medium, undergoes distinct modifications. Thus, its motion can be inferred to gather information about the properties of the surrounding medium. For instance, an active colloid moving in a suspension of bi-disperse spheres has been shown to exhibit a continuous enhancement of its rotational diffusion towards the glass transition. The enhancement peaks right at the density which characterizes the glass transition of the colloidal system [34]. Such observations are explained using phenomenological model following the generalized Langevin approach which takes into account the bulk relaxation time of the surrounding dense suspension [34,35]. In this model, the salient features of the rotational motion exhibited by the active particle are reproduced by assuming a velocity-dependent torque with a fitting parameter. The origin of such a velocity-dependent torque is rationalized by considering a delayed response of fluid which leads to misalignment of the drag force with the instantaneous particle orientation. Apart from this phenomenological explanation, yet another approach has also been developed using numerical simulations which assumes frictional coupling of an active particle to the disordered viscoelastic surroundings [101]. Such frictional contacts can transform the translational motion of an active particle into rotation which results in the enhancement of rotational dynamics. Till this point, direct mechanical coupling of an active particle with the surrounding disordered medium has not been resolved in experiments. This can confirm whether the rotational enhancement of an active particle under such crowded surroundings is due
to the bulk stress relaxation processes or it is stochastic mechanical interaction between an active particle and the disordered medium.

To confirm that, in this chapter, the dynamics of an active particle are investigated in a quasi 2D suspension of colloidal rods. Similar to bi-disperse spherical surroundings, enhancement of rotational diffusion is observed towards approaching the glass transition. The advantage of using rods instead of spheres is that the rods enable one to track not only the translational motion of the background but also its orientational motion. Additionally, such elongated particles provide very large relaxation times [196–198]. Consequently, this leads to a large separation of different times scales present in the system when considering the dynamics of an active particle. Therefore, such an experiment allow us to focus specifically on whether the enhancement of the rotational dynamics originates from the local micro-structure fluctuations (which is a short time feature) or is it due to the bulk relaxation which play an important role (which is a long-time feature).

7.1 Experimental parameters

In these experiments, silica rods (purchased from Nippon Electric Glass Co. Ltd.) are suspended in a critical mixture of water (60% by mass) and propylene glycol n−propyl ether (40% by mass). The rods are highly polydisperse along their long axis with a 42% coefficient of variation and are rather monodisperse along their short axis with 2.5% variance as measured from their dense suspension using video microscopy. The mean length $l$ and width $w$ of the rods are determined to be $9.8\,\mu m$ and $1.5\,\mu m$. To characterize the suspension of rods, they were confined in a thin sample cell kept in contact with a thermal bath at $T = 298$ K in the critical fluid mixture. In the fluid, their gravitational height is as small as $\approx 15$ nm, therefore they sediment towards the bottom of the sample cell. This limits their dynamics to two dimensions (2D). Using video microscopy, their dynamics are recorded for about 4-10 hours and analyzed by varying their area fractions $\varphi$ which spans from 0.40 to 0.94. Owing to large polydispersity in their length, no crystallization is observed. Rather they undergo a two-fold glass transition similar to other anisotropic colloidal particles [196, 197, 199]. With increasing $\varphi$, first, their reorientation motion slows down and eventually freezes out at $\varphi_g^r \approx 0.88$, leading to an orientational glassy state. Further increasing $\varphi$ causes an additional slowing down and freezing ($\varphi_g^T \approx 0.92$) of their translational displacements marking the translational glass transition. The characterization of the rods suspension is discussed in detail in Section 7.2.

To order to probe the suspension of rods, silica Janus spherical particles with mean diameter $2a = 13.72\,\mu m$ coated with carbon film of thickness 80 nm are added to the suspension of rods with their area fraction contribution $\varphi \lesssim 0.01$. The choice of rather large size of the Janus particle is made, in comparison to experiments reported in previous chapters, as it allows tracking of its orientation with great precision even under dense surrounding conditions. Because of the difference in the gravitational
7.2 Characterization of rods suspension

heights of the Janus sphere and the rods, the rods interact with an effective diameter of 8 µm of the sphere. Because of gravity and hydrodynamic interactions with the bottom surface of the sample cell, the translational and rotational motion of the Janus sphere is also confined to 2D [84,177]. The intensity of the illumination \( I \) was varied from 2 µW/µm\(^2\) to 8 µW/µm\(^2\) which leads to propulsion velocity of a free active particle ranging from 0.100 µm s\(^{-1}\) to 0.700 µm s\(^{-1}\). The videos are recorded using video microscopy at a frame rate of 1-2 frames/s and tracked using home written MATLAB script by following standard routines of particle tracking [108].

7.2 Characterization of rods suspension

In this section, a detailed description of the characterization of the suspension of rods is provided. To characterize the suspension, a mono-layer of the rods is confined in a sample cell where their dynamics are confined in 2D. The density of the rods is varied which determines the area fraction \( \phi = \sum_{i=1}^{N} l_i \cdot w_i / A \); where \( l_i \) and \( w_i \) correspond to the length and width of the \( i \)th rod and, \( N \) and \( A \) being the total number of rods in focus and the total area of the field of view, respectively. Typical snapshots of the suspension of rods at different area fractions \( \phi \) are shown in Fig. 7.1. For area fractions \( (\phi \gtrsim 0.80) \), the rods form rafts, where several rods align parallel to each other. This is quite apparent, for instance, in Fig. 7.1 (c) and Fig. 7.1 (d).

![Figure 7.1](image)

**Figure 7.1:** Snapshots from video microscopy of a quasi-two-dimensional system of rods with mean length and width equal to 9.8 µm and 1.5 µm, respectively, with their corresponding coefficients of variation (CV%) of 40% and 2.5%, respectively. The frames show various area fractions \( \phi \) increasing towards right — (a) \( \phi = 0.40 \), (b) \( \phi = 0.55 \), (c) \( \phi = 0.85 \) and, (d) \( \phi = 0.94 \). The scale bar corresponds to 10 µm.

The translational relaxation process of the rods is characterized by the self-intermediate scattering function \( F_s(\mathbf{q}_m, t) \). Mathematically,

\[
F_s(\mathbf{q}_m, t) = \left\langle \sum_{j=1}^{N} e^{i\mathbf{q}_m \cdot [r_j(t) - r_j(0)]} \right\rangle / N, \tag{7.1}
\]

where \( \mathbf{q}_m \) is the scattering vector and \( r_j(t) \) is the particle position at time \( t \). The sample is isotropic and hence the vector \( \mathbf{q}_m \) can be replaced by its length \( q_m = |\mathbf{q}_m| \).
For the computation of $F_s(q_m, t)$, $q_m = 1.12 \mu m^{-1}$ is chosen. The computed $F_s(q_m, t)$ is plotted in Fig. 7.2 (a) for various values of area fractions $\varphi$ of the rods. At high $\varphi \gtrsim 0.73$, $F_s(q_m, t)$ develops a two-step relaxation which is a typical signature of dense colloidal suspensions. Whereas the short-time relaxation corresponds to the motion within cages formed by the neighboring particles, the long-time relaxation mirrors the bulk structural rearrangements [200–202]. The translational relaxation time $\tau_T$ is defined as the time after which $F_s(q_m, t)$ is reduced by a factor $1/e$, is plotted in Fig. 7.2 (b). The area fraction which characterizes the translational glass transition $\varphi_g^T$ is obtained by fitting the data with the following function [196],

$$\tau_T = (\varphi_g^T - \varphi)^{-\gamma_T},$$

(7.2)
as shown by the solid line Fig. 7.2 (b). From the fit, the $\varphi_g^T$ and $\gamma_T$ are determined to 0.922 and 2.56, respectively.

![Figure 7.2:](image)

Figure 7.2: (a) The self-intermediate scattering function $F_s(q_m, t)$ as a function of time $t$ at wave number $|q_m| = 1.12 \mu m^{-1}$ for different area fractions $\varphi$ of the rods suspension. (b) The translational relaxation time $\tau_T$, obtained from $F_s(q_m, t)$ when it reduces to $1/e$. The solid line is a fit according to $\tau_T = (\varphi_g^T - \varphi)^{-\gamma_T}$ which determines the translational glass transition at $\varphi_g^T = 0.922$. The shaded area represents the translational glassy phase.

Similarly, orientational relaxation can be characterized by the orientational correlation function as

$$L_n(t) = \left\langle \sum_{j=1}^{N} \cos n[\theta_j(t) - \theta_j(0)] \right\rangle / N$$

(7.3)

where $n$ is an integer and $\theta_j(t)$ is the angle of the rod with respect to the $x-$axis. The orientational correlation function $L_n(t)$ for $n = 4$ is plotted in Fig 7.3 (a) and the corresponding relaxation time which is also defined as $1/e$ reduction of the
7.3 Dynamics of a Janus particle embedded in the suspension of rods

correlation function is shown in Fig. 7.3 (b). The orientational relaxation time \( \tau_\theta \) fits well to the function

\[
\tau_\theta = (\varphi_\theta^g - \varphi)^{-\gamma_\theta}.
\]  (7.4)

Fitting \( \tau_\theta \) versus \( \varphi \) to Eqn. 7.4 gives \( \gamma_\theta = 2.40 \) and, the divergence of the relaxation time \( \tau_\theta \) at \( \varphi = 0.883 = \varphi_\theta^g \), which marks the orientational glass transition.

**Figure 7.3:** (a) The orientational correlation function \( L_4(t) \) as a function of time for various area fractions \( \varphi \). (b) The orientational relaxation time \( \tau_\theta \), defined as time at which \( L_4(t) \) drops to \( 1/e \), as a function of \( \varphi \). The solid line corresponds to the fitting function \( \tau_\theta = (\varphi_\theta^g - \varphi)^{-\gamma_\theta} \). The shaded region represents the orientational glassy state.

7.3 Dynamics of a Janus particle embedded in the suspension of rods

Having characterized the suspension of rods, now the Janus particles (mean diameter 13.72 \( \mu \)m) are employed to probe the rods’ environment. As mentioned previously the section 7.1, the density of Janus particles is kept so small (\( \varphi \lesssim 0.01 \)) that only one Janus particle is observed in the entire field of view. In the following subsection 7.3.1, the dynamics of an embedded passive Janus particle is discussed by varying the area fraction of the rods. Further, in subsection 7.3.2, the Janus particle is turned active by illuminating it with a green laser and its 2D translational and rotational dynamics are explored in great depth for different packing fractions of rods.

7.3.1 Dynamics of a passive Janus particle in the rods suspension

Passive translational dynamics

A typical trajectory in 2D of a passive Janus particle measured over 1500 s in the rods suspension with area fraction \( \varphi = 0.55 \) is shown in Fig 7.4 (a). The arrows cor-
respond to the instantaneous orientation of the particle defined by the unit vector $\mathbf{n} = (\cos \theta, \sin \theta)$ pointing from the capped side of the Janus particle to the uncapped side. In order to characterize its translational dynamics, from its trajectory, the translational mean squared displacements $\langle \Delta r(t)^2 \rangle = \langle |r(t + t_0) - r(t_0)|^2 \rangle$ are computed for different values of $\varphi$. The obtained $\langle \Delta r(t)^2 \rangle$ are plotted in Fig. 7.4 (b). As expected, $\langle \Delta r(t)^2 \rangle$ of the Janus particle decreases monotonically with increase of $\varphi$. In addition to this, independent of $\varphi$, at short timescales $t \lesssim 10$ s, $\langle \Delta r(t)^2 \rangle$ displays diffusive translational dynamics. However, for $\varphi \gtrsim 0.73$ and for intermediate timescales it develops a plateau, reflecting the caging effect of the surrounding rods, a typical signature of particle dynamics in dense environments [89, 118, 119]. The time span for which it remains within the cage depends strongly on $\varphi$. For instance, for $\varphi \gtrsim 0.85$, it remained trapped in the cage for 1000 s and consequently exhibits sub-diffusive dynamics.

Passive orientational dynamics

In contrast to the translational dynamics, the rotational dynamics characterized by mean squared angular displacement $\langle \Delta \theta(t)^2 \rangle = \langle |\theta(t + t_0) - \theta(t_0)|^2 \rangle$ shows diffusive behavior on all time-scales, with a slope which is independent of $\varphi$ as plotted in Fig. 7.4 (c). The value of diffusion coefficient agrees well with the Stokes Einstein relation, i.e., $D_\theta = k_B T / 8 \pi \eta a^3 = 1.27 \times 10^{-4}$ rad$^2$/s. Here, $\eta$ represent the viscosity of the critical mixture of water and propylene glycol $n$-propyl ether. The fact that $\langle \Delta \theta(t)^2 \rangle$ is diffusive even on short timescales suggests, unlike the translational motion of the embedded particle, the orientational motion of the embedded passive particle is not subjected to coupling with the surrounding rods.

7.3.2 Dynamics of an active Janus particle in the rods suspension

Active translation dynamics

Now the Janus particle is made active, by shining laser light on it due to which it undergoes thermo-diffusiophoresis leading to its self-propelled motion in 2D with unconstrained orientational degrees of freedom [17, 103]. Typical trajectories of an active particle with mean velocity $v = 0.700$ $\mu$m s$^{-1}$, which is measured in rods free environment $\varphi = 0$, are shown in Fig. 7.5 for different area fractions $\varphi$ of the rods. Opposite to the passive case for the same $\varphi$ (Fig. 7.4 (a); $\varphi = 0.55$) where the particle undergo minimal positional change, here Fig. 7.5 (a), obviously it translated over much larger distances. The orientational dynamics for $\varphi = 0.55$, however, did not show any significant changes compared to the passive case. As expected, with increasing $\varphi$, the translational motion decreases as shown for $\varphi = 0.85$ in Fig. 7.5 (b). This is because of effective increase in viscosity of the medium with increasing $\varphi$. Surprisingly, the orientation of the particle began to display large orientational changes (Fig. 7.5 (b)) over the same measurement time. Increasing
7.3 Dynamics of a Janus particle embedded in the suspension of rods

Figure 7.4: (a) Representative trajectory of a passive Janus colloid (mean diameter \(2a = 13.72 \mu m\)) measured over 1500 s embedded in a suspension of rods at an area fraction \(\varphi = 0.55\). The arrows represent instantaneous particle orientation vector \(\mathbf{n}\). The scale bar is 10 \(\mu m\). (b) Mean squared translational displacements \(\langle \Delta r(t,t)^2 \rangle\) of a passive Janus particle inserted inside the suspension of rods at various area fractions \(\varphi\) of the rods. (c) Mean squared angular displacement \(\langle \Delta \theta(t)^2 \rangle\) of the passive particle in the suspension of rods for various \(\varphi\) labelled with the same color code as in (b).

\[ \varphi \geq \varphi^g, \] the translational motion of the particle freezes while its orientation undergo minimal fluctuations as shown in Fig. 7.5 (c) for \(\varphi = 0.92\).

In order to quantify the above mentioned observations, the mean squared translational \(\langle \Delta r(t)^2 \rangle\) and angular \(\langle \Delta \theta(t)^2 \rangle\) displacements of the active particle are computed. The results are plotted in Fig. 7.6. As expected, for an active particle at lower \(\varphi\), \(\langle \Delta r(t)^2 \rangle\) displays transition from the short-time diffusion to a ballistic behavior \(v^2 t^2\) at later times [22–24]. The ballistic part decreases monotonically with increasing \(\varphi\), towards \(\varphi = \varphi^g\) and vanishes for \(\varphi > \varphi^g\), reflecting an effective increase of the viscous friction of the surroundings. In contrast to this, the short-time behavior is non-monotonic, in particular, close to \(\varphi^g\) where it enhances because of collision with the surrounding rods. Depending on the system, such collisions usually result in either enhanced diffusion or super-diffusive dynamics [179,203,204].

Active orientational dynamics

Focusing now on the orientational mean squared displacements \(\langle \Delta \theta(t)^2 \rangle\) of an active particle which are plotted for \(v = 0.700 \mu m s^{-1}\) in Fig. 7.6 (b). In comparison to \(\langle \Delta \theta(t)^2 \rangle\) of a passive particle (shown in Fig. 7.4 (c)) which exhibits linear behavior on all timescales with a constant slope, for an active particle, the behavior of \(\langle \Delta \theta(t)^2 \rangle\) is highly non-monotonic and depends strongly on \(\varphi\). Particularly, close to the orientational glass transition \(\varphi = 0.85 \approx \varphi^g\), \(\langle \Delta \theta(t)^2 \rangle\) displays a plateau at intermediate time scales, similar to \(\langle \Delta r(t)^2 \rangle\) of an embedded particle in a viscoelastic fluid [89,118,119]. Such an observation suggests that unlike the orientational dynamics of the passive particle which remained decoupled from the surrounding rods
Figure 7.5: Typical trajectories of an active Janus particle mean diameter $2a = 13.72 \, \mu m$ moving with $v = 0.700 \, \mu m \, s^{-1}$ (in the rod free system $\varphi = 0$) in the suspension of rods at various area fractions $\varphi$—(a) $\varphi = 0.55$, (b) $\varphi = 0.85$ and, (c) $\varphi = 0.92$. The scale bar corresponds to $10 \, \mu m$.

Figure 7.6: (a) Mean squared translational displacement $\langle (\Delta r(t))^2 \rangle$ of an active Janus particle mean diameter $2a = 13.72 \, \mu m$ moving inside the suspension of rods with velocity $v = 0.700 \, \mu m \, s^{-1}$ (measured in a rod free environment) at various area fractions $\varphi$. (b) Corresponding mean squared orientational displacement $\langle (\Delta \theta(t))^2 \rangle$ of the active particle moving inside the suspension of rods for various area fractions $\varphi$ labelled with the same color code as $\langle (\Delta r(t))^2 \rangle$ in (a). The dashed line corresponds to $\langle (\Delta \theta(t))^2 \rangle$ for the passive case at $\varphi = 0.85$.

environment (Fig. 7.4 (c)), the orientation of an active particle undergoes coupling with the surrounding rods. On long timescales $t \gtrsim 200 \, s$, $\langle (\Delta \theta(t))^2 \rangle$ shows linear behavior for all $\varphi$ with its slope that depends strongly on $\varphi$. The long-time slope of $\langle (\Delta \theta(t))^2 \rangle$ corresponds to an effective diffusion coefficient i.e., $\langle (\Delta \theta(t))^2 \rangle = 2D_\theta^{AP} t$, which is plotted in Fig. 7.7 (a) as a function of $\varphi$. Clearly, $D_\theta^{AP}$ increases towards approaching the orientational glass transition $\varphi^\theta_g$ close to which it peaks with its
7.3 Dynamics of a Janus particle embedded in the suspension of rods

Figure 7.7: (a) The long-time rotational diffusion coefficient normalized by the diffusion coefficient of an active particle $D_{\theta}^{AP}$ normalized by diffusion coefficient of a passive particle $D_\theta$ (at $\phi = 0$) obtained from linear fitting of the long-time slope of angular mean squared displacement as a function of area fraction $\phi$ for different velocities $v$ of an active particle measured in a rod-free environment. (b) Angular mean squared displacement $\langle \Delta \theta(t)^2 \rangle$ of an active particle moving with $v = 0.700 \mu m s^{-1}$ normalized by the $\phi = 0$ passive value $v = 0$ i.e., $D_\theta$ at different short timescales— $t = 1$ s (diamonds), $t = 5$ s (squares) and, $t = 10$ s (circles).

magnitude an order higher than the diffusion coefficient of the passive case $D_\theta$. Whereas the maximum value of $D_{\theta}^{AP}$ depends strongly on propulsion velocity $v$ of an active particle, its position depends weakly on $v$. For instance, as shown in Fig. 7.7 (a), where with decreasing $v$, the peak value decreases significantly, however, its position shows a minor shift. This is due to the fact that for higher $v$, an active particle perturbs the system by pushing the rods considerably in its front leading to a local higher area fraction $\phi$. For $\phi > \phi_\theta^g$, it drops down to the passive value $i.e., D_\theta = 1.27 \times 10^{-4}$ rad$^2$/s. Interestingly, the long-time enhancement feature of $\langle \Delta \theta(t)^2 \rangle$ is already observed in the short-time $\langle \Delta \theta(t)^2 \rangle$. This is shown in Fig. 7.7 (b), where $\langle \Delta \theta(t)^2 \rangle$ (normalized by the diffusion of the passive particle value $D_\theta$) for an active particle with free particle velocity $v = 0.700 \mu m s^{-1}$ is plotted $^1$ at different values of short times $t$ which qualitatively show the same dependence on $\phi$ as $D_{\theta}^{AP}$. Appearance of the long-time features at such short times suggest the observed enhancement of the rotational diffusion coefficient $D_{\theta}^{AP}$ is a consequence of local structural fluctuations around the active particle. Had it been originated from the bulk relaxation processes of the environment, it would have taken timescales which are orders of magnitude higher $\sim 10^4$ s for the active particles dynamics to become diffusive. Whereas as observed $\langle \Delta \theta(t)^2 \rangle$ becomes diffusive on rather short times scales i.e., $t \approx 200$ s.

$^1$ Note that the dynamics at short times are not diffusive which does not allow to compute the diffusion coefficient. Therefore, the short-time dynamics are compared by directly using the $\langle \Delta \theta(t)^2 \rangle$ values for the considered $t$ value.
7.4 Link between the active rotational motion and the rods background

In order to understand how an active particle orientation mechanically couples to the surrounding bath of passive rods which can impart its diffusive character on time scales as short as $t \approx 200$ s. Intuitively, amongst the various time scale present in the passive rods system, which can not only potentially be of the same order $\sim 100$ s but can also provide effective coupling to an embedded spherical particle through mechanical contacts, is the motion of the rod along the long axis. The other time scales present in the rods suspension e.g., the translational and rotational motion of the rods are orders of magnitude higher as characterized by the self-intermediate scattering function and the orientational correlation function in section 7.2. In order to calculate the time scale associated with the longitudinal rods motion, the translational rod motion $\mathbf{r}(t) = (x(t), y(t))$ in the laboratory frame of reference is transformed into body frame of reference $\tilde{\mathbf{r}}(t) = (\tilde{\mathbf{r}}_\parallel(t), \tilde{\mathbf{r}}_\perp(t))$ where $\tilde{\mathbf{r}}_\parallel$ and $\tilde{\mathbf{r}}_\perp$ are the displacement of the rod in the body frame of reference. A schematic describing the coordinates of a rod is shown in Fig. 7.8. The two frames of references i.e., the body and the laboratory frames are related to each other through the rotation matrix as

$$
\mathbf{r}(t) = \begin{pmatrix}
\cos \theta(t) & \sin \theta(t) \\
-\sin \theta(t) & \cos \theta(t)
\end{pmatrix}
\tilde{\mathbf{r}}(t)
$$

(7.5)

The trajectory along the long rod axis $r_\parallel(t)$ then can be constructed summing the body frame displacements in all frames as $r_\parallel(t) = \Sigma \tilde{r}_\parallel$. The associated time scale $\tau_\parallel$ with the longitudinal rod motion is then calculated from the mean squared displacement $\langle \Delta r_\parallel(t)^2 \rangle$ of $r_\parallel(t)$. The computed $\langle \Delta r_\parallel(t)^2 \rangle$ is plotted in Fig. 7.9 (a). Irrespective of $\varphi$, $\langle \Delta r_\parallel(t)^2 \rangle$ exhibits diffusive dynamics on short time scales ($t \lesssim 10$ s). On long time scales, the behavior of $\langle \Delta r_\parallel(t)^2 \rangle$ depends strongly on $\varphi$. For instance, for $\varphi \lesssim 0.85$, $\langle \Delta r_\parallel(t)^2 \rangle$ display linear behavior on all time scales whereas for $\varphi > 0.85$, the long time behavior is sub-diffusive. Since for $\varphi \lesssim 0.85$, the dynamics remains diffusive on long time scales, enables one to compute the diffusion coefficient $D_\parallel$ and thereby the associated time scale $\tau_\parallel$ as $\tau_\parallel = 1/D_\parallel$. The obtained $\tau_\parallel$ as a function of $\varphi$ is plotted in Fig. 7.9 (b). Interestingly, the obtained time scale is similar to the time where the rotational dynamics of the active particle becomes diffusive (see Fig. 7.6 (b)).

It is noteworthy to look at how large are the longitudinal rod fluctuations under rather dense surroundings. As mentioned previously, at rather large area fractions $\varphi \gtrsim 0.80$, the rods form rafts where several rods align parallel to each other. A typical raft at $\varphi = 0.88$ is shown in Fig. 7.10) (a). The associated length scale for the motion of the longitudinal rod is quantified by $d$ which is defined as the distance from the centre of mass of rod from the mid of the line joining the centre of mass of two rods adjacent to it which is sketched in Fig. 7.10 (a) (right). The probability distribution $\rho(d)$ of $d$ is plotted for $\varphi \geq 0.80$ in Fig. 7.10 (b). As expected, the width of $\rho(d)$ decreases with increasing $\varphi$. The profile of the $\rho(d)$ is not Gaussian which
7.4 Link between the active rotational motion and the rods background

![Image](Image)

**Figure 7.8:** Relevant coordinates to characterize the motion a rod in 2D. The coordinate \( r \) describes the rods position in the laboratory frame while the \( \tilde{r}_\perp \) and \( \tilde{r}_\parallel \) describe the displacement of a rod perpendicular and parallel to its long axis in the body frame of reference.

![Image](Image)

**Figure 7.9:** (a) Mean squared displacement of the rods motion parallel to their orientation \( \langle \Delta r_\parallel(t)^2 \rangle \) as a function of time for different area fractions \( \varphi \) of the rods. (b) The time scale associated with the longitudinal rods motion \( i.e., \) along their orientation, obtained from the linear fitting of long-time \( \langle \Delta r_\parallel(t)^2 \rangle \), as a function of \( \varphi \).

is not surprising as the dynamics close to glass transitions usually deviate from Gaussian behavior \([34, 196, 205]\). Therefore, the width \( h \) of the \( \rho(d) \) distribution is computed using a general function as

\[
\rho(d) = \frac{\exp \left[ \left( \frac{\|d\|}{c} \right)^2 \right]}{2h \Gamma(1 + 1/c)}
\]

where the Gamma function is defined as \( \Gamma(x) = 1 + \text{Erf}(x/\sqrt{2})/2 \). The Gaussian distribution is a special case of this function for \( c = 2 \). The calculated width of \( \rho(d) \) is plotted in Fig. 7.10 (c). What is important to note here is that whereas other modes of motion freeze at such large area fraction as demonstrated by the self-intermediate scattering and the orientational correlation functions in section 7.2, the
longitudinal mode survives even for $\phi$ values as large as 0.92. Since the amplitude of such longitudinal fluctuations is of the order $\sim 1 \mu m$, this rationalizes the relevance of the associated time scale as $\tau_\parallel = 1/D_\parallel$ used in Fig. 7.9. Such a commensuration of the time scale of the longitudinal rod motion of the passive rod background with the time scale for an active particle to show diffusive dynamics provide a direct link of rods longitudinal fluctuations to be responsible for the modification of angular dynamics of an embedded active particle. In order to see how exactly these longitudinal rod fluctuations couple to an active particle, one has to look directly at the mechanical contacts which allow visualization of the interaction between rods and an active particle. In experiments, direct contact of the surrounding rods with an active particle can not be resolved with precision due to the size difference between an active particle and the rods. To overcome that, numerical simulations are performed where precise knowledge of such contacts can be gathered. The details of the numerical simulations of the experimental system (qualitatively) are discussed in the following section.
7.5 Modelling details of the numerical simulations

In this section, the details of modelling of the passive rods background which includes the details of the rods interaction with each other and their equation of motion are provided. In addition, the modelling details of an active particle probing the suspension of rods are also provided.

7.5.1 Modelling passive dynamics of the suspension of rods

The rods are chosen in simulations as a stadium-like shape which consists of a rectangle with two disk-shaped caps on either side as shown in Fig. 7.11 (a). The width of the rod is given by $\sigma$ which is kept constant for all rods, which is also the diameter of the disk-shaped caps. The rods are assumed polydisperse along the long axis where the distribution is chosen from a Gaussian distribution with mean $\langle L \rangle = 3\sigma$ and standard deviation $\Delta_L = 0.3\sigma$. The centre of mass position and orientation of a rod are denoted by $r = (x, y)$ and $\theta$, respectively. In order to impart a short-range repulsion between the rods a repulsive Week, Chandler and Anderson (WCA) potential between the rods $i$ and $j$ is used as

$$u_{WCA}(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \epsilon & \text{if } r_{ij} \leq 2^{1/6}\sigma_{ij}, \\ 0 & \text{if } r_{ij} > 2^{1/6}\sigma_{ij}, \end{cases}$$

(7.7)

where $\sigma_{ij} = \frac{\sigma_{i} + \sigma_{j}}{2}$ is the particle width which in a general system can vary for particle $i$ and $j$. The distance between the center of mass of two rods is given by $r_{ij} = |r_i - r_j|$. The interaction strength between the rods is set to $\epsilon = 10 k_B T$. In the present model, due to anisotropic shape of the rods, they not only exert a force but also exert a torque on interaction with each other. The torque experienced by the rod $i$ due to the interaction between rod $i$ and rod $j$ is given by

$$\tau_{ij} = r_{ij}' \times F_{ij},$$

(7.8)

where $r_{ij}'$ is the arm of rod $i$ as shown in Fig. 7.11 (b). It is given by the vector connecting the center of mass of rod $i$ and the interaction point on its center line.

The translational motion of the rod is decomposed into components parallel and perpendicular to the orientation of the rod as: $v_{i,rod} = v_{i,rod}^\parallel + v_{i,rod}^\perp$. The equation of motion of the rod parallel to $\hat{e}_{i,rod}$ and perpendicular to $\hat{e}_{i,rod}$ the rod orientation can then be written as

$$v_{i,rod}^\parallel = \frac{D^\parallel}{k_B T} \sum_j F_{ij}^\parallel + \sqrt{2D^\parallel} \xi^\parallel (t) \hat{e}_{i,rod}^\parallel,$$

(7.9)

$$v_{i,rod}^\perp = \frac{D^\perp}{k_B T} \sum_j F_{ij}^\perp + \sqrt{2D^\perp} \xi^\perp (t) \hat{e}_{i,rod}^\perp,$$

(7.10)

(7.11)
where the rods interact with each other with a force $F_{ij}$ given by $F_{ij} = -\nabla u_{ij}$, where $u_{ij}$ is given by Eq. 7.7. The equation of motion governing the orientational dynamics of the rods is then given by

$$\mathbf{\omega}_{i,\text{rod}} = \sum_j \tau_{ij} + \sqrt{2D_{\theta,\text{rod}}} \xi_{\theta} \times \mathbf{\dot{e}}_{i,\text{rod}}(t) \quad (7.12)$$

The total angular velocity of the rod is the sum of the torques exerted by all neighboring particles $\sum_j \tau_{ij}$ and random Brownian fluctuations. In the equations of motion, $T$ denotes the temperature of the system and $k_B$ the Boltzmann constant. $\xi(\theta)$ is a Gaussian white-noise that account for the thermal fluctuations of the fluid with zero mean i.e., $\langle \xi \rangle = 0$ and $\langle \xi(t) \otimes \xi(t') \rangle = I \delta_{ij} \delta(t - t')$, with $\otimes$ the dyadic product, $I$ the 2D identity matrix, $\delta_{ij}$ the Kronecker delta function and $\delta(t - t')$ the Dirac delta function. The diffusion coefficient of the rod differs along its long and short axis. The diffusion coefficient of a rod along its long axis is given by $D^\parallel = k_B T (\log(l/\sigma) + \nu_\parallel) / 2\pi \eta l$, the diffusion coefficient along it shorts axis is given by $D^\perp = k_B T (\log(l/\sigma) + \nu_\perp) / 2\pi \eta l$ where $\eta$ denotes the viscosity of the fluid. The values of $\nu_\perp$ and $\nu_\parallel$ are determined numerically [206]. The rotational diffusion of the rod is given by $D^\theta_{\text{rod}} = 3k_B T (\log(l/\sigma) + \delta_\perp / \pi \eta l^3)$, where $\delta_\perp$ is a number determined numerically using Ref. [206].

The simulations are performed in 2D square simulation box with 1000 rods using periodic boundary conditions. The area fraction $\varphi$ is varied by varying the size of the simulation box. The system is first initialized by placing all rods randomly in the box and then increasing the interaction strength from $\epsilon = 0$ to $\epsilon = 10$ in approximately $10^5 t_{\text{sim}}$, where $t_{\text{sim}} \approx 2.5 \cdot 10^{-7} D^{-1}_\theta$. After this initialization the system is allowed to equilibrate for $1.079 \times 10^7 t_{\text{sim}}$. Thereafter the measurements we performed over $1.07 \times 10^8 t_{\text{sim}}$. Typical snapshots of the system at various area fractions are shown in Fig. 7.1 (a)-(c). Similar to experiments at large values of $\varphi \gtrsim 0.75$ the rods organise themselves in rafts where several rods angularly align.
7.5 Modelling details of the numerical simulations

Figure 7.12: (a)-(c) Typical snapshots of a simulation box of passive rods at different area fractions $\varphi$. The color bar represents orientation of rods in the interval $[0, \pi]$. (d) Self-intermediate scattering function $F_s(q_m, t)$ of rods for various $\varphi$ values which is used for characterizing the translational relaxation process of the suspension of rods. (e) The translational relaxation time $\tau_T$ obtained by fitting the tail of $F_s(q_m, t)$ by a stretched exponential function (Eqn. 7.13). (f) The orientational correlation function $L_4(t)$ for various area fractions labeled with the same color code as $F_s(q_m, t)$. (g) The orientational relaxation time $\tau_\theta$ obtained by fitting the tail of $L_4(t)$ by a stretched exponential function (Eqn. 7.13).

with their neighbours, however, no long range order is observed. Here, again in line with the experiments, the systems is characterized by the self-intermediate scattering function $F_s(q_m, t)$ (Eqn. (7.1)) and the orientational scattering function $L_4(t)$ (Eqn. (7.3)) as shown in Fig. 7.12 (d) and (f), respectively. The value of $q_m = 0.5\sigma^{-1}$, is chosen for computing $F_s(q_m, t)$ which is taken from the first peak in the structure factor. The tail of both $F_s(q_m, t)$ and $L_4(t)$ follow a stretched exponential
which gives a measure of the associated translational $\tau_T$ and orientational $\tau_\theta$ relaxation times. The obtained $\tau_T$ and $\tau_\theta$ are plotted in Fig. 7.12 (e) and (g), respectively. The occurrence of translational $\phi_T^g$ and orientational $\phi_\theta^g$ glass transitions, using fits to Eqn. (7.2) and Eqn. (7.4), respectively are found at $\phi_T^g = 0.775$ and $\phi_\theta^g = 0.767$.

### 7.5.2 Modelling an active particle moving in the suspension of rods

The active particle is modelled as a disk having diameter $\sigma_{AP} = 8\sigma$, the schematic of which is shown in Fig. 7.13 (a). The propulsion velocity of the active particle is set to $v_0 = 100\sigma_{AP}D_\theta$. The active particle interacts with the surrounding rods via the WCA potential (Eq. 7.7). The translational and orientational dynamics of the active particle are modelled by the overdamped Langevin equations as

$$v_{AP} = \frac{D_{AP}}{k_BT} \sum_j F_{APj} + v_0 \hat{e}_{AP}(t) + \sqrt{2D_{AP}\xi(t)},$$

$$\omega_{AP} = \sum_j \tau_{APj} + \sqrt{2D_\theta\phi_{AP}\hat{\epsilon}\times\hat{e}_{AP}(t)},$$

where $D_{AP} = k_BT/3\pi\eta\sigma_{AP}$ is the translational diffusion coefficient of the active particle, and $D_\theta = k_BT/\pi\eta\sigma_{AP}^3$ is the rotational diffusion coefficient of the probe. An active particle is subjected to a torque on interaction with a rod which is modelled by

$$\tau_{APj} = \frac{2\beta_c D_\theta}{k_BT} (\hat{r}_{APj} \times (\hat{r}_{APj} \cdot \hat{n}(t)) \hat{r}_{APj}),$$

where $\hat{r}_i$ is the unit vector pointing along the direction connecting the center of mass of the active particle with the closest point of the rod, the schematic of which is shown in Fig. 7.13 (b) and $\hat{n}$ is the unit vector perpendicular to this direction. $\beta_c$ is the coupling parameter. The value of $\beta_c$ depends on the magnitude of the interaction force between rod $i$ and the probe. When the interaction force is larger than a set cutoff force $F_c$ the coupling constant has a constant value of 0.5, below this force threshold $\beta_c$ scales linearly with the magnitude of the interaction force as

$$\beta_c = \begin{cases} 0.5 \frac{F_i}{F_c} & \text{if } F_i < F_c, \\ 0.5 & \text{if } F_i \geq F_c. \end{cases}$$

Because of the force threshold $F_c$, an active particle would only experience a minor torque if it interacts with a single isolated rod. However, at a high area fraction, when interacting many rods at once, it would undergo significant torque and consequently would reorient. In this case, the AP cannot push away the rod and will reorient. In order to find a suitable choice of $F_c$, simulations under very dilute conditions such as $\varphi = 0.24$ with various choices of $F_c$ are performed. At this
7.5 Modelling details of the numerical simulations

Figure 7.13: (a) Sketch of an active particle with diameter $\sigma_{AP}$. (b) Schematic of an active particle interaction with a rod.

Figure 7.14: Mean squared angular displacement $\langle \Delta \theta^2(t) \rangle$ of an active particle for different force threshold which sets the angular change in an active particle orientation on its interaction with the surrounding rods.

$\varphi$, any change in the long-time rotational diffusion coefficient of an active particle (compared to a passive particle) is not expected to occur as confirmed in experiments. The obtained $\langle \Delta \theta(t)^2 \rangle$ for various choices of $F_c$ values are plotted in Fig. 7.14. Clearly, in comparison to other $F_c$ values, $F_c = 20k_B T/\sigma$ recovers long time $\langle \Delta \theta(t)^2 \rangle$ equal to that of a passive case (dashed line). Thus, this validates $F_c = 20k_B T/\sigma$ as a suitable choice to use in simulations.

A single disc-shaped active particle is positioned in the simulation box followed
Chapter 7 Probing the Suspension of Rods with an Active Particle

Figure 7.15: (a) Typical snapshots of simulation where an active particle probing the suspension of rods at $\varphi = 0.75$ at subsequent time-step of $0.6 \times 10^{-2} D_\theta^{-1}$ where the active particle does not show any significant change in its position over subsequent time-steps. The arrow represents the orientation of the active particle. The rods are labelled with color code projected on the interval $[0, \pi]$ which corresponds to their orientation. (b) Snapshots of active particle probing the suspension of rods at $\varphi = 0.75$ at subsequent time-step of $0.6 D_\theta^{-1}$.

by the same set of conditions for the initialization and equilibration as used for the passive rod system. During this phase, the propulsion speed of the probe is set to zero. Only in the measurement phase, the self-propulsion speed of the active particle was turned on. Typical snapshots of the active particle at $\varphi = 0.75$ are shown in Fig. 7.15 (a) with a subsequent time-steps of $10^{-2} D_\theta^{-1}$. On such small time scales, the active particle exhibits minimal position change but the orientation fluctuates in response to torques from the surrounding rods. On relatively larger time-steps the active particle undergoes substantial positional and orientational changes, as shown in Fig. 7.15 (b) subsequent snapshots for time-steps $10^{-1} D_\theta^{-1}$ where the surroundings of the active particle change completely over time.

The translational motion of the active particle is characterized by the mean squared displacement $\langle \Delta r^2(t) \rangle$ which is plotted for various area fractions $\varphi$ in Fig. 7.16 (a). Similar to experiments, they undergo transition from diffusive dynamics at short times to ballistic motion at later times. On even long time scales, because of orientational changes $\langle \Delta r^2(t) \rangle$ shows diffusive behavior with the diffusion coefficient depends strongly on $\varphi$. The measured translational diffusion coefficient $D_{AP}^T$ normalized by the diffusion $D_0^T$ of an active particle in rod-free system as a function of $\varphi$ is plotted in Fig. 7.16 (b). As expected, $D_0^T$ decreases monotonically with increasing $\varphi$ due to increasing effective viscous friction with increase in $\varphi$. Similarly, the orientational dynamics are quantified by the mean squared angular displacement $\langle \Delta \theta^2(t) \rangle$ as shown in Fig. 7.17 (a).

In contrast to the $\langle \Delta r^2(t) \rangle, \langle \Delta \theta^2(t) \rangle$ displays non-monotonic behavior as a func-
7.5 Modelling details of the numerical simulations

Figure 7.16: (a) Translational mean squared displacement $\langle \Delta r^2(t) \rangle$ of an active particle moving in the suspension of rods at various area fractions $\varphi$. (b) The long-time effective translational diffusion coefficient $D_{\text{AP}}^T$ normalized by the value $D_T^T$ in a rod-free condition, obtained from $\langle \Delta r^2(t) \rangle$ as a function of $\varphi$.

Figure 7.17: (a) Rotational mean squared displacement $\langle \Delta \theta^2(t) \rangle$ of an active particle moving in suspension of rods at various area fractions $\varphi$. (b) The long-time effective angular diffusion coefficient $D_{\theta}^{\text{AP}}$ normalized by the passive value $D_{\theta}$ obtained from $\langle \Delta \theta^2(t) \rangle$ as a function of $\varphi$.

The long time slope of $\langle \Delta \theta^2(t) \rangle$ exhibits linear behavior i.e., $\langle \Delta \theta^2(t) \rangle = 2D_{\theta}^{\text{AP}} t$ from which the diffusion coefficient can be deduced. The obtained $D_{\theta}^{\text{AP}}$ normalized by the diffusion coefficient of a free particle is plotted in Fig. 7.17 (b). In agreement with the experiments, $D_{\theta}^{\text{AP}}$ peaks close to the orientational glass transition i.e., $\varphi\theta^g$. Interestingly, similar to experiments, the long time behavior of $\langle \Delta \theta^2(t) \rangle$ is reflected already at short time $\langle \Delta \theta^2(t) \rangle$ (see Inset Fig. 7.17 (b)). This again confirms that the enhancement effect originates from local fluctuations rather than the bulk relaxation of the surroundings which modifies the angular fluctuations of an active particle at such short times.
Now coming back to the narrative developed from experimental observations that the rod’s longitudinal motion is responsible for the enhanced alteration of the active particle dynamics, direct mechanical contacts are explored in simulations. A snapshot of the situation is shown in the inset of Fig. 7.18. Surprisingly, wherewith increase in $\varphi$, all modes of rods fluctuations tend to decrease, it is found that the variance of rods in contact with an active particle increases towards $\varphi^g$ and decreases for $\varphi > \varphi^g$ in a very similar manner as $D^{\text{AP}}$. The dependence of variance of number of rods in contact with the active particle $s_N$ on $\varphi$, normalized by the circumference $C$ of the active particle, is plotted in Fig. 7.18. To check whether such qualitative resemblance of $s_N$ with $D^{\text{AP}}$ is caused by the active particle itself or is it an intrinsic feature of the suspension of rods, $s_N$ around a passive particle of the same size is also computed. Interestingly, it remained invariant irrespective of a particle being active or passive (see Fig. 7.18). This observation completes the proposed narrative for the observed enhanced rotational dynamics of an active particle. The explanation of which is as follows—although a variance of such contacts is already present in the passive rod background it couples to an embedded particle when it is active. This is supported by the experimentally measured short time feature in $\langle \Delta \theta^2(t) \rangle$ of an active particle (Fig. 7.4 (b)) which is a manifestation of particle orientational coupling with the rods surroundings. Since for a passive embedded particle, such a feature is found completely absent verifies the fact that coupling on particle orientation to the longitudinal fluctuations of the rods is mediated by the activity. Thus the combination of experimental observations corroborated with numerical simulations confirmed short-time local structural fluctuations to be responsible for the observed enhanced rotational dynamics in the present system.

**Summary**

In summary, the dynamics of an active particle is explored experimentally in a highly polydisperse suspension of colloidal rods which exhibits a two-fold glass transition.
Modelling details of the numerical simulations

(along both orientational and rotational degrees of freedom) with increasing area fraction \( \varphi \) of rods. On increasing \( \varphi \), while the translational motion of the active particle decreases, its orientational motion increases and peaks at the orientational glass transition \( \varphi = \varphi_g^\theta \). Increasing \( \varphi \) further \( i.e., \varphi > \varphi_g^\theta \), it drops down to that of a passive Brownian particle of same size in a rod-free environment. Experimentally, an explicit connection is shown between the fluctuations of rods parallel to their long axis and the active particle orientational dynamics via the time-scales matching of the corresponding motion. In addition, numerical simulations are performed to visualize direct micro-mechanical contacts of rods with the active particle. Interestingly, the variance of number of rods \( s_N \) in contact with the probe particle displays the same dependence on \( \varphi \) as that of rotational diffusion of the active particle. Although the trend of \( s_N \) as a function \( \varphi \) remains unaffected by the fact whether the probe particle is passive or active, the coupling to the longitudinal fluctuations occurs only for an active particle. This is supported by the experimentally measured mean squared angular displacements at short times which clearly show signatures of coupling with the rod’s background which are completely absent for a passive probe particle. Such findings highlight the significance of using active particles as probes to pick up certain structural dynamics modes that can remain hidden in conventional microrheological techniques.
Conclusion and Outlook

In this work, the dynamics of a self-propelled particle are experimentally investigated under several complex environmental conditions. These encompass a free active particle in a viscoelastic polymer solution, with additionally imposed spatial constraints e.g., flat walls, spherical obstacles, and circular confinements. Besides, its dynamics are also explored in a dense colloidal suspension of polydisperse rods. Unlike a purely viscous fluid, where the rotational motion of an active particle is predominantly determined by thermal diffusion, in a viscoelastic fluid, it gets strongly coupled to the slow microstructural response of the surroundings. Such a coupling is found to depend strongly on its self-propelled velocity \( v \). For instance, with increasing \( v \), an active particle undergoes orders of magnitude enhancement of its rotational diffusion coefficient. A further increase of \( v \) leads to a transition to an unexpected persistent circular motion, despite owing spherical shape. The observed orientational features are reproduced numerically using a minimal non-Markovian Langevin model for the active Brownian motion which takes into account the delayed response of the fluid with respect to self-propulsion of the particle.

In addition, the presence of spatial constraints in a viscoelastic fluid induces long-range repulsive forces and torques on an active particle interacting with the boundary wall. In contrast to entirely viscous conditions, such interactions remarkably modify the behavior of an active particle. For instance, they drastically reduce the residence time of an active particle on the wall surface. Moreover, such interactions have distinctive consequences on the behavior of several active particles confined in circular confinement. As observed, with increasing the activity of the particles, they exhibit a transition from liquid-like behavior to a crystal-like order. Further, increasing the activity leads to re-entrant liquid-like behavior.

Furthermore, the dynamics of an active particle are studied in a dense suspension of colloidal rods which are of similar size as that of the active particle i.e., an effective homogeneous fluid medium picture is no more valid. Despite that, the active particle displayed an order of magnitude enhancement of the rotational diffusion coefficient. To understand the origin of such an enhancement, the micro-mechanical contacts of
the active particle with the surrounding rods are resolved using Brownian dynamics numerical simulations. They reveal that the active particle picks up the fastest timescale of the background i.e., rods motion along their long axis. Although the mechanism governing the rotational dynamics of an active particle is quite different in molecular liquids and dense colloidal surroundings, the increased rotational motion remained a common feature. This suggests that such an enhancement is not particular to a kind of viscoelastic background, but is expected to occur for other types of viscoelastic media. Being able to respond to the background fluctuations, an active particle can be reliably used to probe micro-mechanical properties of crowded surroundings [34, 101]. Moreover, it is worth understanding such effects of viscoelastic fluids on active particles in other complex situations such as optical [207–210] and chemical gradients [211–215], moving potentials [32], time-dependent motility [28] and corrugated substrates [216] which are commonly found in nature.
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