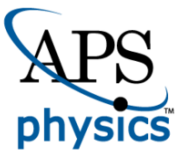

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Dynamics of a magnetic active Brownian particle under a uniform magnetic field

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The dynamics of a magnetic active Brownian particle undergoing three-dimensional Brownian motion, both translation and rotation, under the influence of a uniform magnetic field is investigated. The particle self-propels at a constant speed along its magnetic dipole moment that reorients due to the interplay between Brownian and magnetic torques, quantified by the Langevin parameter α. In this work, the time-dependent active diffusivity and the crossover time (τ^{cross})—from ballistic to diffusive regimes—are calculated through the time-dependent correlation function of the fluctuations of the propulsion direction. The results reveal that, for any value of α, the particle undergoes a directional (or ballistic) propulsive motion at very short times ($t \ll \tau^{\text{cross}}$). In this regime the correlation function decreases linearly with time and the active diffusivity increases with it. It the opposite time limit ($t \gg \tau^{\text{cross}}$), the particle moves in a purely diffusive regime with a correlation function that decays asymptotically to zero and an active diffusivity that reaches a constant value equal to the long-time active diffusivity of the particle. As expected in the absence of a magnetic field ($\alpha = 0$), the crossover time is equal to the characteristic timescale for rotational diffusion, τ_{rot}. In the presence of a magnetic field ($\alpha > 0$), the correlation function, the active diffusivity, and the crossover time decrease with increasing α. The magnetic field regulates the regimes of propulsion of the particle. Here, the field reduces the period of time at which the active particle undergoes a directional motion. Consequently, the active particle rapidly reaches a diffusive regime at $\tau^{\text{cross}} \ll \tau_{\text{rot}}$. In the limit of weak fields ($\alpha \ll 1$), the crossover time decreases quadratically with α, while in the limit of strong fields ($\alpha \gg 1$) it decays asymptotically as α^{-1}. The results are in excellent agreement with those obtained by Brownian dynamics simulations.

I. INTRODUCTION

Active colloids that move autonomously in environments dominated by viscous forces [1] and thermal fluctuations [2] are currently a subject of great interest. The intrinsic ability of these particles to transform the surrounding free energy into directed motion under non-equilibrium conditions makes them suitable for many practical applications (e.g. environmental remediation [3, 4], lab-on-a-chip [5], drug-delivery [6]). Examples of such colloidal particles are the widely investigated artificial catalytic motors driven autonomously through different mechanisms, such as diffusiophoresis, electrophoresis, surface-tension gradients, and bubble generation [7–9]. A large number of works have studied the propulsion mechanisms of these active systems. However, few studies have focused on their time-dependent dynamics behavior in the presence of an external field. In the present work we aim to shed some light in this area.

Regardless of the intricate propulsion mechanism, active colloids can be modeled as active Brownian particles (ABPs), a term which refers to colloidal particles moving at a constant speed, U_{act}, along a propulsion direction, $\boldsymbol{p}$, with reorientation time $\tau_{\text{rot}} = D_{\text{rot}}^{-1}$. In ABPs, the reorientation time is dictated by its rotational diffusivity, $D_{\text{rot}} = kT/\zeta_{\text{rot}}$, where kT is the thermal energy and ζ_{rot} is the rotational hydrodynamic resistance. However, in other self-propelled colloids (e.g. bacteria) the reorientation time could be a consequence of sudden complete randomization. A constant propulsion speed presumes that self-generated gradients (e.g. concentration, thermal) are established much faster than τ_{rot}. Another prominent behavior that characterizes the dynamics of ABPs is their transition from a ballistic (or directional) to a diffusive regime over τ_{rot} [10–12]. At short times ($t \ll \tau_{\text{rot}}$), the particle experiences an additional contribution to the mean squared displacement (MSD) that scales with time as $\sim U_{\text{act}}^2 t^2$. At longer times ($t \gg \tau_{\text{rot}}$) the propulsion direction, $\boldsymbol{p}$, is completely randomized by rotational diffusion, and the particle undergoes a persistent random walk with MSD $\sim D^{\text{act}} t$, resulting in an active contribution to the diffusivity, $D^{\text{act}} \sim U_{\text{act}}^2 \tau_{\text{rot}}$, hereafter called the active diffusivity. In a two-dimensional (2D) space, $D^{\text{act}} = U_{\text{act}}^2 \tau_{\text{rot}}/2$, and in 3D, $D^{\text{act}} = U_{\text{act}}^2 \tau_{\text{rot}}/6$ [13]. The sum of this active diffusivity and the Stokes-Einstein relation, $D = kT/\zeta$ with ζ denoting the translational hydrodynamic resistance, results in an effective translational diffusivity, D^{eff}.

The loss of directionality that ABPs exhibit at long times ($t \gg \tau_{\text{rot}}$) represents a serious problem in applications where precise motion control is required. Fortunately, recent experimental studies have shown different steering control strategies for artificial self-propelled motors [14]. The most commonly used strategy to control the orientation of self-propulsion is through external magnetic fields [15, 16]. In this case, the self-propelled particle is modified by incorporating a magnetic dipole, such that the particle is able to be remotely controlled [17, 18]. Due to the interaction of a magnetic field with the magnetic dipole of a particle, a torque is induced on the particle that competes against the randomization of its orientation due to rotational diffusion. Thus, for a strong magnetic field, the thermal fluctuations on the

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orientational motion of the particle are completely suppressed, and the magnetic dipole is fully aligned along the field direction. Consequently, a precise magnetic control (guidance and steering) of the propulsion of the particle is achieved by dynamically changing the direction of the applied field. (See [16] and references therein for more details on magnetic manipulation of active particles.)

Most of the experimental studies dealing with magnetic control of ABPs have been focused on monitoring (via particle tracking) their spatial trajectory in the presence of an externally applied magnetic field [19–26]. Even when these studies provide very useful information related to their movement (e.g. swimming paths, propulsion velocity, directionality) they are not sufficient to obtain a full understanding of the effect of a magnetic field on the dynamics of ABPs. There are only a few theoretical studies that, in one way or another, have made some important progress. For example, these studies have shown that at long times ($t \gg \tau_{\rm rot}$), the mean velocity of the particle parallel, $\parallel$, to the field direction increases with the field strength via the analytical formula $\langle U\rangle_{\parallel} = U_{\rm act}L(\alpha)$, where $L(\alpha) = \coth\alpha - \alpha^{-1}$ is the Langevin function, and α is the Langevin parameter that measures the relative importance between an applied external torque and fluctuations resulting from Brownian torques on the particle [27, 28]. Furthermore, the active diffusivity parallel $\parallel$ and perpendicular $\perp$ to the field in the limit of weak fields ($\alpha \ll 1$) decreases quadratically with the field strength via the asymptotic expression $D^{\rm act}_{\parallel,\perp} = U^2_{\rm act}\tau_{\rm rot}[1/6 - \lambda_{\parallel,\perp}\alpha^2 + O(\alpha^4)]$, where $\lambda_{\parallel} = 7/135$ and $\lambda_{\perp} = 1/40$, respectively; while under strong fields ($\alpha \gg 1$), $D^{\rm act}_{\parallel} \sim U^2_{\rm act}\tau_{\rm rot}/\alpha^3$ and $D^{\rm act}_{\perp} \sim U^2_{\rm act}\tau_{\rm rot}/\alpha^2$, respectively, which asymptotically tends to zero as α is increased [27–29].

The analytical predictions, both mean velocity and active diffusivity, presented above describe the dynamics of ABP motion only in the long-time limit ($t \gg \tau_{\rm rot}$). However, it is important to extend the analysis beyond this time limit in order to evaluate motion control mechanisms of particles moving in a system far from equilibrium or where transient effects are important. For instance, it is of interest to know how much time it takes for the active particle to change its direction in a magnetic field. Or asked differently, how does an external magnetic field affect the crossover behavior from a ballistic to a diffusive regime?

On this basis, a time-dependent theoretical framework that models a magnetic ABP sensitive to a uniform magnetic field is proposed. The particle self-propels at constant speed along a direction that coincides with the magnetic dipole orientation that undergoes three-dimensional (3D) rotational Brownian motion. Thus, the dynamics of the particle can be completely described by measuring the interplay between these fluctuations and the field strength. The present work investigates, for different field strength values (or Langevin parameter α), the correlation function of the fluctuations in the propulsion direction, $\boldsymbol{p}$, the time-dependent active diffusivity, and the crossover time from the ballistic (or directional) to the diffusive region. Finally, in the long-time limit ($t \to \infty$), closed-form analytic expressions for the active diffusivity and time correlations (or relaxation time) of the fluctuations in the propulsion direction with respect to the direction of the magnetic field are derived. It is important to point out that throughout the relaxation time the crossover time of the particle responding to the magnetic field is calculated.

The paper is organized as follows: In § II, the problem of interest is formulated, including a physical description of the model as well as the required theoretical framework to derive the analytical expressions for the time-dependent correlation function, the time-dependent active diffusivity, and the crossover time. The results are presented and discussed in § III. Finally, general conclusions of this work are presented in § IV.

II. PROBLEM FORMULATION

A. Model

Consider a single self-propelled colloidal spherical particle of radius a moving in a quiescent fluid. The particle translates autonomously with an instantaneous propulsion velocity $\boldsymbol{U}_{\rm act}(t) = U_{\rm act}\boldsymbol{p}(t)$, where the constant speed $U_{\rm act}$ is applied along an instantaneous unit vector $\boldsymbol{p}(t)$ that dictates the propulsion direction of the particle at time t (see Fig. 1). In this model, it is assumed that the constant speed results from a driving force $\boldsymbol{F}^{\rm act} = \zeta U_{\rm act}\boldsymbol{p}$ whose origin is left unspecified for the sake of generality. On account of its colloidal size, the particle is subjected to thermal fluctuations that affect its translational and rotational motion. As a result, the active particle undergoes Brownian motion (rotation and translation), here considered to take place in a 3D space. The particle is also assumed to be magnetically responsive via a permanent magnetic dipole, $\boldsymbol{m} = m\boldsymbol{u}$, of magnitude m, fixed (or embedded rigidly) at the geometric center of the sphere, and directed along a unit vector $\boldsymbol{u}$. This model consists of a large magnetic active colloid, where the reorientation of its magnetic dipole due to thermal agitation (or Néel relaxation) is neglected. Instead, the magnetic dipole undergoes rigid rotations (with the whole particle) only due to the rotational Brownian motion. In addition, a uniform magnetic field, $\boldsymbol{H} = H\hat{\boldsymbol{z}}$, of strength H is applied parallel to the z-axis of a space-fixed coordinate system (x, y, z), as illustrated in Fig. 1. On the other hand, it is assumed that the propulsion direction is parallel to the magnetic dipole orientation of the particle. Other orientation configurations between the propulsion direction and the magnetic dipole escape to the scope of the present work. Since the magnetic dipole is steered according to the magnetic field direction, $\boldsymbol{u}$ is regarded to be the "director" of the particle from this point onward.

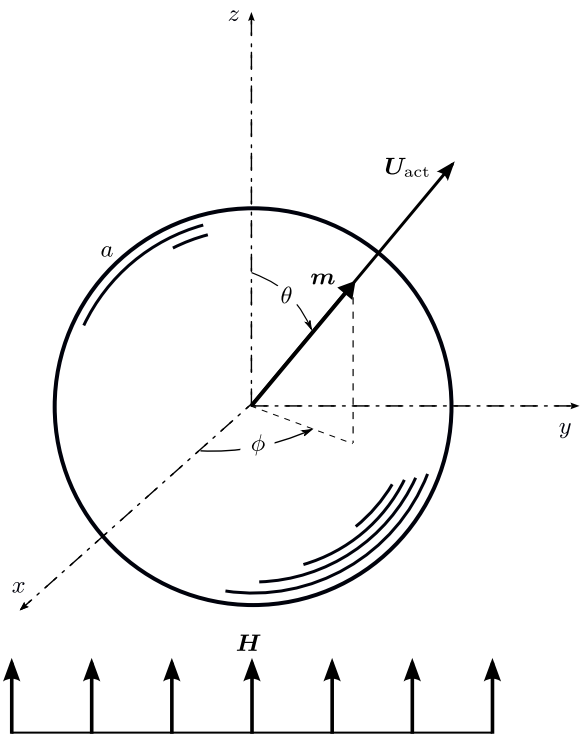

FIG. 1. The magnetic active Brownian particle model: a self-propelled colloidal particle of radius a that bears a magnetic dipole $\boldsymbol{m}$ oriented parallel to the self-propelled velocity $\boldsymbol{U}_{\rm act}$ undergoing 3D Brownian motion, both translation and rotation, under a uniform magnetic field $\boldsymbol{H}$ applied along the z-axis.

B. Theory

The objective of this section is to present the derivation of the general expression of the time-dependent active diffusivity of a magnetic ABP in terms of the time-dependent correlation function of the fluctuations of the propulsion direction. The starting point here is the Langevin equation for the translational motion of a magnetic ABP moving in an incompressible Newtonian fluid of density ρ and dynamic viscosity η. This equation in a coordinate system (x, y, z) fixed in space reads

$$0 = \boldsymbol{F}^{\rm hyd}(t) + \boldsymbol{F}^{\rm act}(t) + \boldsymbol{F}^{B}(t), \tag{1}$$

where $\boldsymbol{F}^{\rm hyd}(t) = \zeta \boldsymbol{U}(t)$ is the hydrodynamic Stokes force, and $\boldsymbol{F}^{\rm B}$ is the Brownian force due to thermal fluctuations in the fluid, which is characterized by a zero-mean force, $\langle \boldsymbol{F}^{\rm B}(t)\rangle = 0$, and a variance that is modeled via the fluctuation-dissipation theorem $\langle \boldsymbol{F}^{\rm B}(0)\boldsymbol{F}^{\rm B}(t)\rangle = 2kT\zeta \boldsymbol{I}\,\delta(t)$. The angular brackets denote a statistical ensemble average, $\delta(t)$ is the Dirac delta function, and $\boldsymbol{I}$ is the identity tensor.

The left-hand side of (1) is zero because the influence of inertia on the motion of a particle suspended in a viscous fluid is negligible in the colloidal regime. As a result, the particle moves at an instantaneous linear velocity, $\boldsymbol{U}(t)$, given by:

$$\boldsymbol{U} = \zeta^{-1}\left(\boldsymbol{F}^{\rm act} + \boldsymbol{F}^{\rm B}\right). \tag{2}$$

The ABP position and orientation are tracked over time to measure the diffusion properties in response to a magnetic field. For example, the long-time effective diffusivity tensor, $\boldsymbol{D}^{\rm eff}$, that also accounts for the effect of self-propulsion can be directly determined from the Green-Kubo relation [30, 31]

$$\boldsymbol{D}^{\rm eff} = \frac{1}{3}\lim_{t\to\infty}\int_0^t \Big[\langle \boldsymbol{U}(0)\boldsymbol{U}(t)\rangle - \langle \boldsymbol{U}(0)\rangle\langle \boldsymbol{U}(0)\rangle\Big]\,{\rm d}t, \tag{3}$$

where $\langle\cdots\rangle$ stands for the average over an equilibrium distribution function for the particle orientation

$$W_0(\boldsymbol{u}) = Z_0^{-1}\exp\left[-V(\boldsymbol{u})/kT\right], \tag{4a}$$

$$\text{with } Z_0 = \oint {\rm d}\boldsymbol{u}\,\exp\left[-V(\boldsymbol{u})/kT\right], \tag{4b}$$

which is proportional to the Boltzmann exponential of the magnetic potential, $V(\boldsymbol{u}) = -\mu_0 \boldsymbol{m}\cdot\boldsymbol{H}$, resulting from the interaction of the dipole with the magnetic field. Since the average velocity, $\langle \boldsymbol{U}\rangle$, of an ABP moving under an external field is different to zero [28], this contribution on the effective diffusivity has been included in (3) via the velocity autocorrelation function, which arises from the correlation of $\boldsymbol{U}(t) - \langle \boldsymbol{U}(0)\rangle$ at time 0 and at time t.

Substituting the instantaneous linear velocity given in (2) at times 0 and t, as well as the average velocity $\langle \boldsymbol{U}(0)\rangle = U_{\rm act}\langle \boldsymbol{p}(0)\rangle$ into the relation (3), the effective diffusivity reads as

$$\boldsymbol{D}^{\rm eff} = \frac{1}{3}\Big\{\boldsymbol{D} + U_{\rm act}^2\tau_{\rm rot}\lim_{t\to\infty}\int_0^t \Big[\langle \boldsymbol{p}(0)\boldsymbol{p}(t)\rangle - \langle \boldsymbol{p}(0)\rangle\langle \boldsymbol{p}(0)\rangle\Big]{\rm d}t\Big\}, \tag{5}$$

where $\boldsymbol{D} = D\boldsymbol{I}$ is the Stokes-Einstein diffusivity tensor, and time has been nondimensionalized by $\tau_{\rm rot}$.

For a single spherical particle moving in a Newtonian fluid the off-diagonal elements of the long-time effective diffusivity tensor are zero, while the diagonal elements can be expressed in the form

$$\boldsymbol{D}^{\rm eff} = D_{\parallel}^{\rm eff}\hat{\boldsymbol{z}}\hat{\boldsymbol{z}} + D_{\perp}^{\rm eff}\left(\boldsymbol{I} - \hat{\boldsymbol{z}}\hat{\boldsymbol{z}}\right), \tag{6}$$

where $D_{\parallel}^{\rm eff} = D_{zz}^{\rm eff}$ and $D_{\perp}^{\rm eff} = (D_{xx}^{\rm eff} + D_{yy}^{\rm eff})/2$ are the long-time effective diffusivities of the ABP in the direction parallel $\parallel$ and perpendicular $\perp$ to the magnetic field, respectively. Further, $D_{\perp}^{\rm eff} = D_{xx}^{\rm eff} = D_{yy}^{\rm eff}$ due to the spherical symmetry about the z-axis.

The parallel and perpendicular long-time effective diffusivities can be calculated by substituting $\boldsymbol{p}(t) = \boldsymbol{p}_{\parallel}(t) + \boldsymbol{p}_{\perp}(t)$ into (5) and by comparing the result with (6), thus

$$D_{\parallel}^{\rm eff} = D + U_{\rm act}^2\tau_{\rm rot}\lim_{t\to\infty}\int_0^t f_{\parallel}(t){\rm d}t, \tag{7a}$$

$$D_{\perp}^{\rm eff} = D + U_{\rm act}^2\tau_{\rm rot}\lim_{t\to\infty}\int_0^t f_{\perp}(t){\rm d}t, \tag{7b}$$

where $f_\parallel(t)$ and $f_\perp(t)$ are the correlation functions of the components of $\boldsymbol{p}(t)$ in the direction parallel and perpendicular to the magnetic field. They are defined as

$$f_\parallel(t) = \langle p_\parallel(0)p_\parallel(t)\rangle - \langle p_\parallel(0)\rangle\langle p_\parallel(0)\rangle, \tag{8a}$$
$$f_\perp(t) = \langle p_\perp(0)p_\perp(t)\rangle, \tag{8b}$$

where $\langle p_\perp(0)p_\perp(t)\rangle = \langle p_x(0)p_x(t)\rangle = \langle p_y(0)p_y(t)\rangle$ due to the symmetry about the z-axis.

The effective diffusivity, either the parallel (7a) or perpendicular (7b) components, can be physically interpreted as the sum of two diffusivities. The first term on the right-hand side of (7a) and (7b) is the Stokes-Eintein diffusion coefficient, $D = kT/\zeta$, which arises from the translational Brownian motion of the particle. Note that this "passive" diffusivity is the same in any direction due to its isotropic nature. On the other hand, the second term on the right-hand side of (7a) and (7b) can be defined as an active contribution to the diffusivity of the particle. In the absence of a magnetic field, this active diffusivity measures the level of randomization to the direction of self-propulsion by the rotary Brownian motion of the particle. When a magnetic field is applied, the direction of self-propulsion is aligned with the field and changes to the active diffusivity are expected. Because the applied magnetic field in this model is unidirectional, the response to the diffusivity is anisotropic, resulting in different values based on the relative motion of the particle parallel and perpendicular to the field.

The expressions (7a) and (7b) can then be rewritten in the following form

$$D^{\mathrm{act}}_{\infty,\parallel} = U^2_{\mathrm{act}}\tau_{\mathrm{rot}} \lim_{t\to\infty}\int_0^t f_\parallel(t)\mathrm{d}t, \tag{9a}$$
$$D^{\mathrm{act}}_{\infty,\perp} = U^2_{\mathrm{act}}\tau_{\mathrm{rot}} \lim_{t\to\infty}\int_0^t f_\perp(t)\mathrm{d}t, \tag{9b}$$

where $D^{\mathrm{act}}_{\infty,\parallel} = D^{\mathrm{eff}}_\parallel - D$ and $D^{\mathrm{act}}_{\infty,\perp} = D^{\mathrm{eff}}_\perp - D$ are the active diffusivities along and perpendicular to the magnetic field at long times.

The fluctuation of any stochastic property is defined as the deviation of that property from its mean value. This definition can then be applied to the parallel and perpendicular components of the propulsion direction. Thus, $\delta p_\parallel(t) = p_\parallel(t) - \langle p_\parallel(0)\rangle$ and $\delta p_\perp(t) = p_\perp(t) - \langle p_\perp(0)\rangle = p_\perp(t)$ are the fluctuations of the propulsion direction parallel and perpendicular to the magnetic field. Consequently, the parallel and perpendicular correlation functions in (8a) and (8b) can be rewritten as $f_\parallel(t) = \langle \delta p_\parallel(0)\delta p_\parallel(t)\rangle$ and $f_\perp(t) = \langle \delta p_\perp(0)\delta p_\perp(t)\rangle$. Substituting these expressions into (9a) and (9b), one concludes that the active diffusivity is a direct consequence of the fluctuations taking place in the direction of propulsion of the particle. Note that, for ABPs, whose orientation is affected by its own rotary Brownian diffusion, these fluctuations are of the Brownian (or passive) type.

At this point, it is straightforward to define the general expression for the time-dependent active diffusivity. The parallel and perpendicular components read as

$$D^{\mathrm{act}}_\parallel(t) = U^2_{\mathrm{act}}\tau_{\mathrm{rot}}\int_0^t \langle \delta p_\parallel(0)\delta p_\parallel(t)\rangle \mathrm{d}t, \tag{10a}$$
$$D^{\mathrm{act}}_\perp(t) = U^2_{\mathrm{act}}\tau_{\mathrm{rot}}\int_0^t \langle \delta p_\perp(0)\delta p_\perp(t)\rangle \mathrm{d}t. \tag{10b}$$

Note that in the long-time limit, these expressions reduce to (9a) and (9b), respectively. In the present work, the active diffusivities, both the time-dependent and long-time behavior, are studied first by evaluating the time-dependent correlation function of the fluctuations of the propulsion direction.

For a magnetic ABP whose propulsion direction coincides with the magnetic dipole orientation, the orientation dynamics of the particle can be described through the dipole orientation. Thus, the time-dependent correlation functions $f_\parallel(t)$ and $f_\perp(t)$ can be expressed in terms of $\boldsymbol{u}$ components. Introducing the spherical polar coordinates fixed in the coordinate system (x, y, z), the unit vector $\boldsymbol{u}$ can be described by the polar θ angle and the azimuthal ϕ angle, as illustrated in Fig. 1, in terms of which their Cartesian components can be expressed as $u_x = \sin\theta\cos\phi$, $u_y = \sin\theta\sin\phi$ and $u_z = \cos\theta$. Thus, the time-dependent correlation functions (8a, 8b) read as

$$f_\parallel(t) = \langle \cos\theta(0)\cos\theta(t)\rangle - \langle\cos\theta(0)\rangle\langle\cos\theta(0)\rangle, \tag{11a}$$
$$f_\perp(t) = \langle \cos\phi(0)\sin\theta(0)\cos\phi(t)\sin\theta(t)\rangle, \tag{11b}$$

Here, the above correlation functions are calculated by solving numerically two hierarchies of differential-recurrence relations for $f_\parallel(t)$ and $f_\perp(t)$; see (23a) and (23b) in next section. Two systems of equivalent equations were previously derived by Coffey *et al.* [32, 33] on the basis of the Langevin equation approach for the rotational Brownian motion of polar linear molecules in the presence of a uniform electric field. The mathematical formulation of the Langevin equation approach in the context of a magnetic active Brownian particle under a uniform magnetic field is addressed below.

C. The Langevin equation approach

The equation of motion that governs the three-dimensional rotational Brownian motion of a spherical colloidal particle in the presence of an external potential $V[\boldsymbol{u}(t), t]$ can be described on the basis of the Euler-Langevin equation [34] for the instantaneous angular velocity written in the coordinate system (x, y, z) as

$$0 = \boldsymbol{T}^{\mathrm{hyd}}(t) + \boldsymbol{T}^{\mathrm{ext}}(t) + \boldsymbol{T}^{\mathrm{B}}(t), \tag{12}$$

where $\boldsymbol{T}^{\mathrm{hyd}}(t) = -\zeta_{\mathrm{rot}}\boldsymbol{\Omega}(t)$ is the hydrodynamic torque exerted on the particle due to its angular velocity $\boldsymbol{\Omega}$ relative to the fluid with $\zeta_{\mathrm{rot}} = 8\pi\eta a^3$; $\boldsymbol{T}^{\mathrm{B}}$ is the Brownian torque characterized by $\langle \boldsymbol{T}^{\mathrm{B}}(t)\rangle = 0$ and $\langle \boldsymbol{T}^{\mathrm{B}}(0)\boldsymbol{T}^{\mathrm{B}}(t)\rangle =$

$2kT\zeta_{\rm rot}\boldsymbol{I}\,\delta(t)$; and $\boldsymbol{T}^{\rm ext}(t)$ is the non-hydrodynamic external torque (e.g., magnetic) acting on the particle. Here, this torque can be expressed in terms of an external potential on the particle as $\boldsymbol{T}^{\rm ext}(t) = -\boldsymbol{\mathcal{R}}V\left[\boldsymbol{u}(t),t\right]$, where $\boldsymbol{\mathcal{R}} = \boldsymbol{u}\times\partial/\partial\boldsymbol{u}$ is the gradient operator in orientation space.

The angular velocity resulting from this torque balance reads

$$\boldsymbol{\Omega}(t) = \zeta_{\rm rot}^{-1}\left[\boldsymbol{T}^{\rm B}(t) - \boldsymbol{u}(t)\times\frac{\partial}{\partial\boldsymbol{u}}V\left[\boldsymbol{u}(t),t\right]\right]. \tag{13}$$

The rotational motion of the unit vector $\boldsymbol{u}(t)$ is described by the angular velocity. Thus, the instantaneous direction of $\boldsymbol{u}(t)$ satisfies the equation

$$\frac{{\rm d}\boldsymbol{u}(t)}{{\rm d}t} = \boldsymbol{\Omega}(t)\times\boldsymbol{u}(t), \tag{14}$$

this being a purely kinematical relation which holds for any vector fixed in the particle, and with no particular reference either to the Brownian motion or to the shape of the particle.

Substituting (13) into (14), and using the properties of the triple vector product $(\boldsymbol{u}\times\partial V/\partial\boldsymbol{u})\times\boldsymbol{u}$, it yields the Langevin equation for the motion of $\boldsymbol{u}(t)$

$$\begin{aligned}\frac{\rm d}{{\rm d}t}\boldsymbol{u}(t) = -\zeta_{\rm rot}^{-1}\;&\left[\frac{\partial}{\partial\boldsymbol{u}}V\left[\boldsymbol{u}(t),t\right] - \right.\\ &\left.\boldsymbol{u}(t)\left(\boldsymbol{u}(t)\cdot\frac{\partial}{\partial\boldsymbol{u}}V\left[\boldsymbol{u}(t),t\right]\right)\right] + \\ &\zeta_{\rm rot}^{-1}\boldsymbol{T}^{\rm B}(t)\times\boldsymbol{u}(t),\end{aligned} \tag{15}$$

which is a stochastic, non-linear differential equation with multiplicative random terms given by the components of the vector product $\boldsymbol{T}^{\rm B}(t)\times\boldsymbol{u}(t)$. This equation can be interpreted either as an Itô or Stratonovich equation as has been discussed by Risken [35] and Coffey *et al.* [32]. Since the physical stochastic processes within the dynamics of orientation of a colloidal particle are best modeled within the framework of the Stratonovich definition [36], this definition will be used here to average stochastic differential equations by involving the average of multiplicative random terms.

A stochastic differential equation for an arbitrary differentiable function $f[\boldsymbol{u}(t)]$ may be obtained by multiplying (15) by $\partial f\left[\boldsymbol{u}(t)\right]/\partial\boldsymbol{u}$, respectively:

$$\begin{aligned}\frac{\rm d}{{\rm d}t}f\left[\boldsymbol{u}(t)\right] = \zeta_{\rm rot}^{-1}&\left[\boldsymbol{T}^{\rm B}(t)\times\boldsymbol{u}(t)\right]\cdot\frac{\partial}{\partial\boldsymbol{u}}f\left[\boldsymbol{u}(t)\right] - \\ &\zeta_{\rm rot}^{-1}\left[\frac{\partial}{\partial\boldsymbol{u}}V - \boldsymbol{u}(t)\left(\boldsymbol{u}(t)\cdot\frac{\partial}{\partial\boldsymbol{u}}V\right)\right]\cdot \\ &\frac{\partial}{\partial\boldsymbol{u}}f\left[\boldsymbol{u}(t)\right],\end{aligned} \tag{16}$$

where the first term on the right-hand side of (16) is a multiplicative random term. Thus, by using Stratonovich's rule the average of this equation over an ensemble of colloidal particles that all start at time t with the same dipole moment orientation becomes

$$\begin{aligned}D_{\rm rot}^{-1}\frac{\rm d}{{\rm d}t}f(\boldsymbol{u}) = \frac{1}{2kT}\;&\left[V(\boldsymbol{u},t)\mathcal{R}^2 f(\boldsymbol{u}) + f(\boldsymbol{u})\mathcal{R}^2 V(\boldsymbol{u},t) - \right.\\ &\left.\mathcal{R}^2\left(V(\boldsymbol{u},t)f(\boldsymbol{u})\right)\right] + \;\mathcal{R}^2 f(\boldsymbol{u}),\end{aligned} \tag{17}$$

which is an averaged stochastic differential equation valid for any function $f(\boldsymbol{u})$. Here, $\boldsymbol{u}$ represents the average of the orientations which all particles adopt at the instant t. Further, this vector is a random variable with a probability density function $W(\boldsymbol{u},t)$ such that $W(\boldsymbol{u},t){\rm d}\boldsymbol{u}$ is the probability of finding a particle with the dipole axis $\boldsymbol{u}$ pointing in the interval $(\boldsymbol{u},\boldsymbol{u}+{\rm d}\boldsymbol{u})$. In (17), the squared rotation operator $\mathcal{R}^2$ is defined as $\boldsymbol{\mathcal{R}}\cdot\boldsymbol{\mathcal{R}} = (\boldsymbol{u}\times\partial/\partial\boldsymbol{u})\cdot(\boldsymbol{u}\times\partial/\partial\boldsymbol{u})$, in analogy with the Laplace operator $\nabla^2 = \boldsymbol{\nabla}\cdot\boldsymbol{\nabla}$. In spherical polar coordinates the $\boldsymbol{\mathcal{R}}$ and $\mathcal{R}^2$ operators read

$$\boldsymbol{\mathcal{R}} = \boldsymbol{e}_\phi\frac{\partial}{\partial\theta} - \boldsymbol{e}_\theta\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}, \tag{18}$$

$$\mathcal{R}^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}, \tag{19}$$

where $\boldsymbol{e}_\theta$, $\boldsymbol{e}_\phi$ are the unit vectors in the θ, ϕ directions respectively.

The functions more appropriate to model the orientational dynamics of a colloidal particle involving three-dimensional rotations of a unit vector $\boldsymbol{u}$ are the normalized spherical harmonics (see, for example, the explicit form (7.2.9) in [32], and Chapter 5 of [37] for more details) denoted as $Y_{n,m}(\boldsymbol{u})$ or equivalently $Y_{n,m}(\theta,\phi)$, where θ and ϕ are the definite values of the random variables $\theta(t)$ and $\phi(t)$ at the averaging instant t. Thus, equation (17) written in dimensionless form is

$$\begin{aligned}\frac{\rm d}{{\rm d}t}Y_{n,m} = \frac{1}{2}&\left[V\mathcal{R}^2 Y_{n,m} + Y_{n,m}\mathcal{R}^2 V - \mathcal{R}^2\left(VY_{n,m}\right)\right] + \\ &\mathcal{R}^2 Y_{n,m},\end{aligned} \tag{20}$$

where time t has been nondimensionalized by $\tau_{\rm rot}$, and the potential V by the thermal energy kT, respectively.

Substituting the dimensionless potential V expanded in terms of the spherical harmonics

$$V = \sum_{R=0}^{\infty}\sum_{S=-R}^{R}\nu_{R,S}Y_{R,S} \tag{21}$$

into (20), and using the known property $\mathcal{R}^2 Y_{n,m} = -n(n+1)Y_{n,m}$ as well as the product of two spherical harmonics expanded in the so-called Clebcsh-Gordan series (see, for example, subsection (5.6.2) of [37]), the system of equations for $Y_{n.m}$ can be transformed to

$$\begin{aligned}\frac{\rm d}{{\rm d}t}Y_{n,m} = &-n(n+1)Y_{n,m} + \\ &\frac{1}{4}\sum_{R=0}^{\infty}\sum_{S=-R}^{R}\sum_{J=|n-R|}^{n+R}\nu_{R,S}\sqrt{\frac{(2R+1)(2n+1)}{\pi(2J+1)}} \\ &\left[J(J+1) - n(n+1) - R(R+1)\right] \\ &C_{n,0,R,0}^{J,0}C_{n,m,R,S}^{J,m+S}Y_{J,m+S},\end{aligned} \tag{22}$$

where $\nu_{R,S}$ is a coefficient dependent on the nature of the external potential, and $C^{c,\lambda}_{a,\kappa,b,\beta}$ are the Clebsch-Gordan coefficients (see, for example, Chapter 8 of [37] for various definitions).

We have thus obtained from the Langevin equation an important and general set of moment equations (22) for $Y_{n,m}$ at time t, valid for any external potential. For an ABP subjected to an external potential of the magnetic type, $V = -\mu_0 \boldsymbol{m}\cdot\boldsymbol{H}/kT = -\alpha\cos\theta = -\alpha\sqrt{4\pi/3}Y_{1,0}$, where $\alpha = \mu_0 mH/kT$ is the Langevin parameter that measures the competition between the magnetic and thermal torque. Comparing the explicit expression for V with (21) one can easily find that $\nu_{1,0} = -\alpha\sqrt{4\pi/3}$ and the all remaining terms $\nu_{R\neq1,S\neq0}$ are equal to zero.

Substituting the proper values of $\nu_{R,S}$ into (22), a system of equations for $Y_{n,m}(t)$ in terms of α is obtained. This equation will be used to derive two systems of differential-recurrence relations for the time-dependent correlation functions (11a) and (11b), respectively. This can be accomplished by following the same procedure as the one employed by Coffey *et al.* [32] for a polar linear molecule in the presence of a uniform electric field applied along the z-axis. The end results are

$$\frac{\mathrm{d}}{\mathrm{d}t}f_n(t) = -n(n+1)f_n(t) + \frac{\alpha n(n+1)}{2n+1}\Big[f_{n-1}(t) - f_{n+1}(t)\Big], \tag{23a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}g_n(t) = -n(n+1)g_n(t) + \frac{\alpha}{2n+1}\Big[(n+1)^2 g_{n-1}(t) - n^2 g_{n+1}(t)\Big]. \tag{23b}$$

These are dynamic equations governing the parallel, $f_n(t)$, and perpendicular, $g_n(t)$, time-dependent correlations functions defined as

$$f_n(t) = \langle P_1[\cos\theta(0)]P_n[\cos\theta(t)]\rangle - \langle P_1[\cos\theta(0)]\rangle\langle P_n[\cos\theta(0)]\rangle, \tag{24a}$$

$$g_n(t) = \langle \cos\phi(0)P_1^1[\cos\theta(0)]\cos\phi(t)P_n^1[\cos\theta(t)]\rangle, \tag{24b}$$

where the quantities $P_n(\cos\theta)$ and $P_n^m(\cos\theta)$ are the Legendre polynomials of order n and the associated Legendre functions of the first kind of order n and rank m, respectively [38]. It is easy to show that for $n = 1$, $f_1(t) = f_\parallel(t)$ and $g_1(t) = f_\perp(t)$, respectively.

Using the recurrence formulas of the Legendre polynomials and the associated Legendre functions, the relation $\exp(\alpha\cos\theta) = \sqrt{\pi/(2\alpha)}\sum_{n=0}^{\infty}(2n+1)I_{n+1/2}(\alpha)P_n(\cos\theta)$ (obtained from (10.2.36) of [38]), and the orthogonality property of Legendre polynomials, the initial conditions $f_n(0)$ and $g_n(0)$ may be expressed in terms of the modified Bessel functions as

$$f_n(0) = \frac{n+1}{2n+1}\frac{I_{n+3/2}(\alpha)}{I_{1/2}(\alpha)} + \frac{n}{2n+1}\frac{I_{n-1/2}(\alpha)}{I_{1/2}(\alpha)} - \frac{I_{3/2}(\alpha)}{I_{1/2}(\alpha)}\frac{I_{n+1/2}(\alpha)}{I_{1/2}(\alpha)}, \tag{25a}$$

$$g_n(0) = \frac{n(n+1)}{2\alpha}\frac{I_{n+1/2}(\alpha)}{I_{1/2}(\alpha)}, \tag{25b}$$

where $I_\nu(\alpha)$ is the modified Bessel function of the first kind [38].

Thus, the initial conditions $f_\parallel(0)$ and $f_\perp(0)$ can then be readily determined by setting $n = 1$ into (25a) and (25b), respectively. Substituting the appropriate expressions of the Bessel functions $I_{1/2}(\alpha)$, $I_{3/2}(\alpha)$ and $I_{5/2}(\alpha)$ (see e.g., (10.2.13) Ref. [38]) into (25a) and (25b), one finds that

$$f_\parallel(0) = 1 + \frac{1}{\alpha^2} - \coth^2\alpha, \tag{26a}$$

$$f_\perp(0) = -\frac{1}{\alpha^2} + \frac{1}{\alpha}\coth\alpha. \tag{26b}$$

In the limit of weak fields ($\alpha \ll 1$), $f_\parallel(0)$ and $f_\perp(0)$ are calculated using the Taylor expansion of the modified Bessel functions (see e.g., (9.6.10) of Ref. [38]) here rewritten as

$$I_\nu(\alpha) = \Big(\frac{\alpha}{2}\Big)^\nu \sum_{k=0}^{\infty}\frac{(\alpha/2)^{2k}}{k!\Gamma(\nu+k+1)}, \tag{27}$$

where $\nu = (2n-1)/2$ for $n \geq 1$. Thus, the asymptotic analytical expressions for both correlation functions yield

$$f_\parallel(0) = \frac{1}{3} - \frac{\alpha^2}{15} + \frac{2}{189}\alpha^4 - O(\alpha^6), \tag{28a}$$

$$f_\perp(0) = \frac{1}{3} - \frac{\alpha^2}{45} + \frac{2}{945}\alpha^4 - O(\alpha^6). \tag{28b}$$

Note that for $\alpha = 0$, the above formulas reduce to $f_\parallel(0) = f_\perp(0) = 1/3$.

In the limit of strong fields ($\alpha \gg 1$), using the asymptotic expansion of the modified Bessel functions (see e.g., (9.7.1) Ref. [38]) here rewritten as

$$I_\nu(\alpha) \sim \frac{e^\alpha}{\sqrt{2\pi\alpha}}\left[1 - \frac{\mu-1}{8\alpha} + \frac{(\mu-1)(\mu-9)}{2!(8\alpha)^2} - \frac{(\mu-1)(\mu-9)(\mu-25)}{3!(8\alpha)^3} + \cdots\right], \tag{29}$$

where $\mu = 4\nu^2$, the asymptotic expressions for the initial condition correlation functions read $f_\parallel(0) \sim \alpha^{-2} + O(\alpha^{-3})$ and $f_\perp(0) \sim \alpha^{-1} + O(\alpha^{-2})$, respectively.

D. Solution via Brownian dynamics (BD) simulations

The dynamics of a magnetic active particle undergoing 3D Browniain motion, in translation and rotation,

in the presence of a uniform magnetic field can also be examinted *via* BD simulations. The starting point of this method are the equations in (1) and (12), which are solved to find the evolution equations for transitional ($\Delta\boldsymbol{x}$) and rotational ($\Delta\boldsymbol{\theta}$) steps during a time step Δt, given by

$$\Delta\boldsymbol{x}(t) = \frac{4}{3}Pe\Delta t\,\boldsymbol{p}(t) + \sqrt{\frac{8}{3}\Delta t}\,\boldsymbol{\xi}(t), \tag{30}$$

$$\Delta\boldsymbol{\theta}(t) = \alpha\Delta t\Big[\boldsymbol{u}(t)\times\hat{\boldsymbol{z}}\Big] + \sqrt{2\Delta t}\,\boldsymbol{\xi}(t). \tag{31}$$

Here $\boldsymbol{x}$ has been nondimensionalized by the active particle size a, and time by the time scale for rotational diffusion $\tau_{\rm rot}$.

The second terms on the right-hand sides of (30) and (31) are the linear and angular random displacements, respectively, due to Brownian motion, where $\boldsymbol{\xi}(t)$ is a unit random normal deviate characterized by $\langle\boldsymbol{\xi}(t)\rangle = 0$ and $\langle\boldsymbol{\xi}(t)\boldsymbol{\xi}(0)\rangle = \delta(t)\boldsymbol{I}$. The contribution to the change in position of the particle due to propulsive (or active) forces is given by the first term on the right-hand side of (30), where $Pe = F^{\rm act}/(kT/a) = U_{\rm act}a/D$ is the Péclet number that measures the interplay between the active, $F^{\rm act}$, and Brownian forces. The contribution of the magnetic field to the angular displacement is given by the first term on the right-hand side of (31).

The change in the orientation of the particle at each time step Δt is calculated by using the kinematical relation, $\Delta\boldsymbol{u} = \Delta\boldsymbol{\theta}\times\boldsymbol{u}$, derived from (14). Substituting (31) into this relation, one finds that

$$\Delta\boldsymbol{u} = \alpha\Delta t\Big[\,(\boldsymbol{u}\times\hat{\boldsymbol{z}})\times\boldsymbol{u}\Big] + \sqrt{2\Delta t}\,(\boldsymbol{\xi}\times\boldsymbol{u})\,. \tag{32}$$

At each time step in the simulation the ABP position is updated with a Brownian step and an active step. The latter step depends on the propulsion orientation, see (30), that is obtained from (32). This is because the propulsion direction coincides with the orientation of the particle, i.e. $\boldsymbol{p}(t) = \boldsymbol{u}(t)$. Here, at each time step the particle orientation is updated with a Brownian step and a magnetic step.

The time-dependent effective diffusivity of the active particle, $\boldsymbol{D}^{\rm eff}(t)$, is obtained from MSD, $\langle\boldsymbol{x}'(t)\boldsymbol{x}'(t)\rangle$, according to $\boldsymbol{D}^{\rm eff}(t) = {\rm d}\langle\boldsymbol{x}'(t)\boldsymbol{x}'(t)\rangle/(2{\rm d}t)$, where $\boldsymbol{x}'(t) = \boldsymbol{x} - \langle\boldsymbol{x}(t)\rangle$ and the angular brackets $\langle\,\rangle$ denote an ensemble average over time and over all simulations. Therefore, the computation of the active diffusivity, $\boldsymbol{D}^{\rm act}(t)$, can be readily carried out by substracting from the effective diffusivity its passive contribution. This latter diffusivity is easily calculated from the mean-square displacement of the particle in the absece of self-propulsion (or $Pe = 0$).

The time-dependent correlation functions $f_{\parallel}(t)$ and $f_{\perp}(t)$ are obtained from

$$f_{\lambda}(t) = \langle\delta u_{\lambda}(0)\delta u_{\lambda}(t)\rangle, \tag{33}$$

where $\delta u_{\lambda}(t) = u_{\lambda}(t) - \langle u_{\lambda}\rangle$ is the fluctuation of the orientation of the particle, $u_{\lambda}(t)$ is the instantaneous particle orientation obtained from (32), and $\langle u_{\lambda}\rangle$ its mean value. Here, λ is a dummy index to represent the relative orientation parallel $\parallel$ or perpendicular $\perp$ to the field.

The crossover time of the active particle is obtained from (33) by dividing it by $f_{\lambda}(0) = \langle\delta u_{\lambda}^2(0)\rangle$ and integrating over time to yield

$$\tau_{\lambda}^{\rm cross} = \frac{2}{\langle\delta u_{\lambda}^2(0)\rangle}\int_0^{\infty} f_{\lambda}(t){\rm d}t. \tag{34}$$

The active diffusivity and the crossover time have been calculated for each value of the Langevin parameter α ranging from 0.02 to 50 and for $Pe = 1$. For each value of α, 550 repetitions have been performed to achieve good statistics. The time of simulation was $5000\tau_{\rm rot}$ with a time step of $\Delta t = 0.001$.

III. RESULTS AND DISCUSSIONS

Figures 2(a) and 2(b) show the parallel and perpendicular time-dependent correlation functions $f_{\parallel}(t)$ and $f_{\perp}(t)$, respectively, for different values of α. These results have been obtained by solving numerically two systems of differential-recurrence relations (23a, 23b) with their proper initial conditions (25a, 25b). The number of equations is increased systematically until convergence is attained over the range of α studied. For example, in the evaluation of (23a, 23b), for values of $\alpha \leq 50$, convergence is obtained by solving a system of 50 equations.

For any α, $f_{\parallel}(t)$ and $f_{\perp}(t)$ follow the typical behavior of a time-dependent correlation function of any physical quantity that is involved in a stochastic process [39]. That is, at $t = 0$, the parallel and perpendicular correlation functions are equal to the mean squares of $\delta p_{\parallel}(0) = p_{\parallel}(0) - \langle p_{\parallel}(0)\rangle$ and $\delta p_{\perp}(0) = p_{\perp}(0)$, respectively, i.e. $f_{\parallel}(0) = \langle p_{\parallel}^2(0)\rangle - \langle p_{\parallel}(0)\rangle^2$ and $f_{\perp}(0) = \langle p_{\perp}^2(0)\rangle$, which represent the variances of the propulsion direction of the particle. The behavior of $f_{\parallel}(0)$ and $f_{\perp}(0)$ as a function of α is shown in Fig. 2(c). As time increases, the correlation between $p_{\perp,\parallel}(t)$ and $p_{\perp,\parallel}(0)$ decreases, and therefore $f_{\parallel}(t)$ and $f_{\perp}(t)$ decrease as well. For times sufficiently large compared to the characteristic time for fluctuations of $p_{\perp,\parallel}(t)$, the correlations between $p_{\perp,\parallel}(t)$ and $p_{\perp,\parallel}(0)$ vanish completely. Therefore, $\lim_{t\to\infty} f_{\parallel}(t) \to 0$ and $\lim_{t\to\infty} f_{\perp}(t) \to 0$, respectively.

In the absence of a magnetic field ($\alpha = 0$), the correlation function, in both the parallel and perpendicular cases, follows the classical exponential decay of a Brownian (passive) particle: $f_{\parallel}(t) = f_{\perp}(t) = \exp(-2D_{\rm rot}t)/3$ [39]. This equation in dimensionless form can be readily obtained by setting $n = 1$ and $\alpha = 0$ into (23a, 23b) and solving the system analytically together with the initial condition $f_{\parallel}(0) = f_{\perp}(0) = 1/3$ obtained from (28a, 28b) for $\alpha = 0$.

Interestingly, Figs. 2(a) and 2(b) suggest that this exponential behavior for $f_{\parallel}(t)$ and $f_{\perp}(t)$ is maintained even for $\alpha > 0$. As stated before, the orientation of the particle undergoes fluctuations of the Brownian type, which

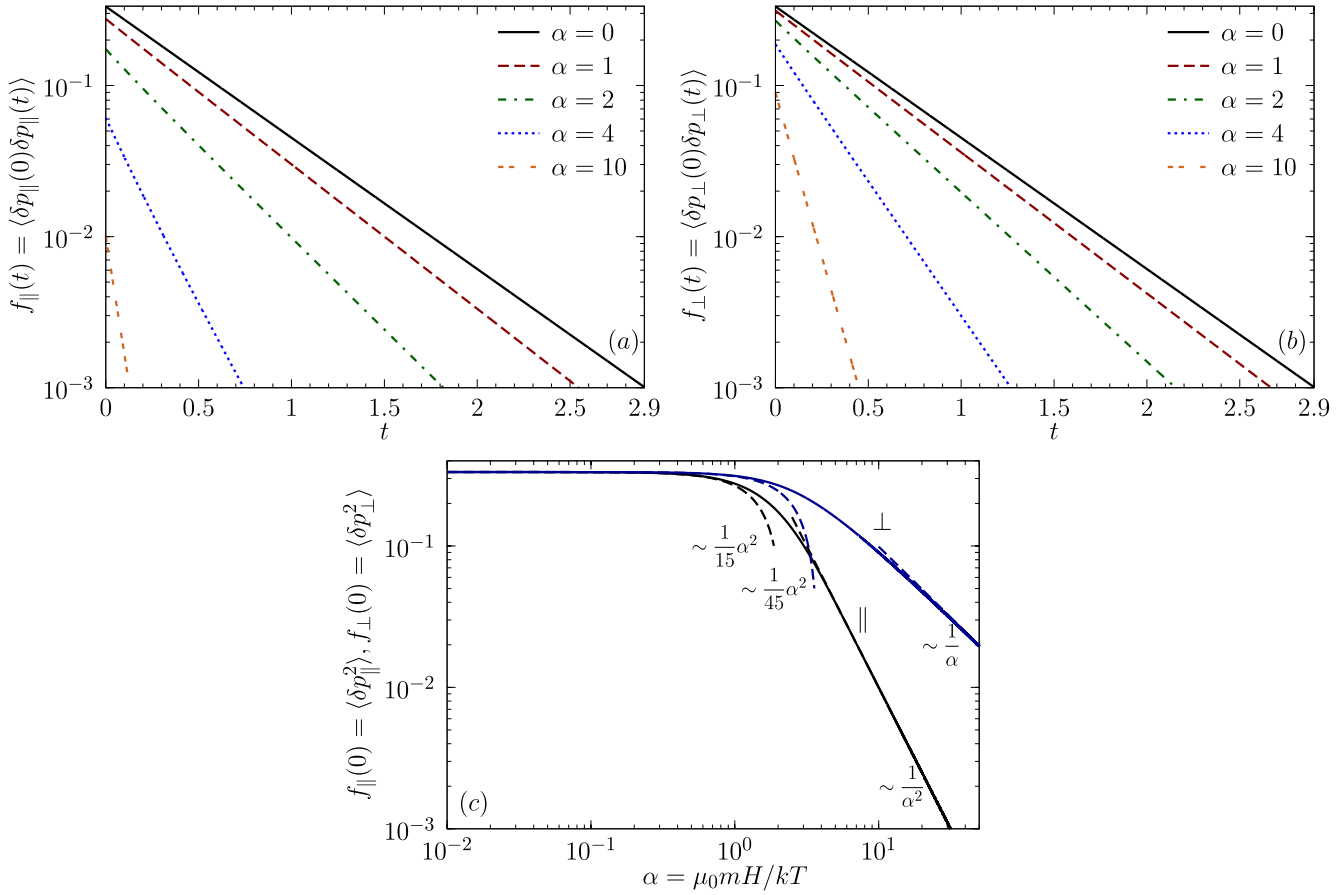

FIG. 2. Parallel (a) and perpendicular (b) time-dependent correlation functions as a function of the time t for different values of α. Lines represent the numerical solutions of the systems of differential-recurrence relations (23a) and (23b) for $f_\parallel(t)$ and $f_\perp(t)$, respectively. (c) Variances ($\parallel$ and $\perp$) of the propulsion direction as a function of α. Solid and dashed curves represent the exact and asymptotic analytical solutions.

clearly are induced by the rotary Brownian diffusion. In the presence of a magnetic field, the field does not transform this type of fluctuation into something non-Brownian, in fact, it only reduces the intensity of these fluctuations. As a consequence, the magnetic field affects quantitatively the exponential decay of $f_\parallel(t)$ and $f_\perp(t)$ as well as its decay rate. Thus, for example, the results in Figs. 2(a) and 2(b) show that, for any instant of time t, the correlation functions decrease with increasing α. Here, the magnetic field hinders the rotational Brownian motion of the particle, and therefore, the fluctuations in the orientation of the particle.

Figures 2(a) and 2(b) also show that, for $\alpha > 0$, the time-dependent correlation function parallel to the field direction decays faster than the perpendicular one. This happens because the magnetic torque restricts the rotational Brownian motion of $p_\parallel(t)$ around the x- and y-axes; whereas it only restricts the Brownian rotation of $p_\perp(t)$ around the y-axis. Note that the torque along the field direction is zero, therefore, $p_\perp(t)$ can freely rotate around the z-axis. This quantitative difference between $f_\parallel(t)$ and $f_\perp(t)$ is more evident for moderate and high values of α than for small values. The differences of decay rate between $f_\parallel(t)$ and $f_\perp(t)$, for $\alpha > 0$, evidences the anisotropic effect of the magnetic field on the dynamics of an ABP. Note that the magnetic field also induces an anisotropic behavior on the variance of the particle, as illustrated in Fig. 2(c).

Since the numerical results found for $f_\parallel(t)$ and $f_\perp(t)$ show an exponential decay with time, we propose that this decay follows the relations

$$f_\parallel(t) = f_\parallel(0)\exp(-t/\tau_\parallel^{\rm mag}), \tag{35a}$$

$$f_\perp(t) = f_\perp(0)\exp(-t/\tau_\perp^{\rm mag}), \tag{35b}$$

where $\tau_\parallel^{\rm mag}$ and $\tau_\perp^{\rm mag}$ are the parallel and perpendicular correlation (or magnetic relaxation) timescales of the propulsion direction of the particle, respectively. At $\alpha = 0$, $\tau_{\parallel,\perp}^{\rm mag} = 1/2$, such that (35a) and (35b) agree with the classical exponential formula, $\exp(-2D_{\rm rot}t)/3$, for the orientational correlation function of a Brownian particle [39].

In order to obtain the explicit expressions for (35a) and (35b), it is necessary first to find the exact formulas for $\tau_\parallel^{\rm mag}$ and $\tau_\perp^{\rm mag}$ for any value of α. The magnetic

relaxation timescales can be defined as the area under the curves of $f_\parallel(t)$ and $f_\perp(t)$, respectively, resulting in

$$\tau_\parallel^{\mathrm{mag}} = \frac{1}{f_\parallel(0)} \int_0^\infty f_\parallel(t)\mathrm{d}t, \tag{36a}$$

$$\tau_\perp^{\mathrm{mag}} = \frac{1}{f_\perp(0)} \int_0^\infty f_\perp(t)\mathrm{d}t. \tag{36b}$$

Even though the general formulas (36a) and (36b) allow one to directly calculate the magnetic relaxation time, it is instructive to do this via the long-time active diffusivity. Combining (36a, 36b) with (9a, 9b) one obtains

$$\frac{D_{\infty,\parallel}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \tau_\parallel^{\mathrm{mag}} f_\parallel(0), \tag{37a}$$

$$\frac{D_{\infty,\perp}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \tau_\perp^{\mathrm{mag}} f_\perp(0), \tag{37b}$$

which shows that the long-time active diffusivity is directly related to the variance and the correlation time of the propulsion direction of the particle. This implies that the active diffusivity can be obtained from the magnetic relaxation time and vice versa.

The calculation of the analytical expressions for the long-time active diffusivity and correlation time proceeds as follows. Equations (9a) and (9b) can be rewritten as shown below:

$$\begin{aligned}\frac{D_{\infty,\parallel}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} &= \lim_{s\to 0} \int_0^\infty f_1(t) e^{-st}\mathrm{d}t \\ &= \lim_{s\to 0} \tilde{f}_1(s) = \tilde{f}_1(0),\end{aligned} \tag{38a}$$

$$\begin{aligned}\frac{D_{\infty,\perp}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} &= \lim_{s\to 0} \int_0^\infty g_1(t) e^{-st}\mathrm{d}t \\ &= \lim_{s\to 0} \tilde{g}_1(s) = \tilde{g}_1(0),\end{aligned} \tag{38b}$$

where $\tilde{f}_1(0)$ and $\tilde{g}_1(0)$ are the Laplace transforms of $f_1(t)$ and $g_1(t)$, respectively, denoted by $\tilde{f}_1(s)$ and $\tilde{g}_1(s)$, in the $s = 0$ limit.

Since each of the infinite hierarchies of moment equations (23a) and (23b) takes the form of a scalar three-term differential-recurrence relation, it is possible to obtain an exact solution for $\tilde{f}_1(s)$ and $\tilde{g}_1(s)$ in terms of ordinary infinite continued fractions [32, 35]. Using the continued fraction method (see Section 2.7.3 of [32] for details), one obtains

$$\tilde{f}_1(s) = \frac{1}{\alpha} \sum_{n=1}^\infty (-1)^{n+1} f_n(0) \frac{2n+1}{n(n+1)} \prod_{k=1}^n S_k^\parallel(s), \tag{39a}$$

$$\tilde{g}_1(s) = \frac{1}{\alpha} \sum_{n=1}^\infty (-1)^{n+1} g_n(0) \frac{2n+1}{n^2(n+1)^2} \prod_{k=1}^n S_k^\perp(s), \tag{39b}$$

where $S_n^\parallel(s)$ and $S_n^\perp(s)$ are the infinite continued fractions defined by the recurrence equations

$$S_n^\parallel(s) = \cfrac{\alpha/(2n+1)}{\cfrac{s}{n(n+1)} + 1 + \cfrac{\alpha S_{n+1}^\parallel(s)}{2n+1}}, \tag{40a}$$

$$S_n^\perp(s) = \cfrac{\alpha(n+1)/[n(2n+1)]}{\cfrac{s}{n(n+1)} + 1 + \cfrac{n}{n+1}\cfrac{\alpha S_{n+1}^\perp(s)}{2n+1}}. \tag{40b}$$

Therefore, the closed-form expressions for the parallel and perpendicular active diffusivities are easily calculated from (38a) and (38b) using the closed formulas for $\tilde{f}_1(0)$ and $\tilde{g}_1(0)$ obtained from (39a) and (39b) at $s = 0$. After some algebra, the exact analytical solutions for both diffusivities, valid for any α value, read

$$\begin{aligned}\frac{D_{\infty,\parallel}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{\alpha} \sum_{n=1}^\infty (-1)^{n+1} \frac{I_{n+1/2}^2(\alpha)}{n I_{1/2}^2(\alpha)} \\ \left[\frac{I_{n+3/2}(\alpha)}{I_{n+1/2}(\alpha)} + \frac{n}{n+1}\frac{I_{n-1/2}(\alpha)}{I_{n+1/2}(\alpha)} - \right. \\ \left. \frac{2n+1}{n+1}\frac{I_{3/2}(\alpha)}{I_{1/2}(\alpha)}\right],\end{aligned} \tag{41a}$$

$$\frac{D_{\infty,\perp}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{2\alpha^2} \sum_{n=1}^\infty (-1)^{n+1} \frac{2n+1}{n(n+1)} \frac{I_{n+1/2}(\alpha)}{I_{1/2}(\alpha)} \prod_{k=1}^n S_k^\perp(0), \tag{41b}$$

where the continued fraction $S_n^\perp(0)$ is obtained from (40b) for $s = 0$. Besides, using (27) and (29), one can find from (41a) and (41b) the asymptotic analytical expressions for the parallel and perpendicular active diffusivities in the limits of weak and strong magnetic fields. Thus, for $\alpha \ll 1$,

$$\frac{D_{\infty,\parallel}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{6} - \frac{7}{135}\alpha^2 + \frac{41}{3780}\alpha^4 - O(\alpha^6), \tag{42a}$$

$$\frac{D_{\infty,\perp}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{6} - \frac{1}{40}\alpha^2 + \frac{299}{90720}\alpha^4 - O(\alpha^6), \tag{42b}$$

while in the opposite limit ($\alpha \gg 1$),

$$\frac{D_{\infty,\parallel}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{2\alpha^3} + O(\alpha^{-4}), \tag{43a}$$

$$\frac{D_{\infty,\perp}^{\mathrm{act}}}{U_{\mathrm{act}}^2 \tau_{\mathrm{rot}}} = \frac{1}{\alpha^2} + O(\alpha^{-3}), \tag{43b}$$

respectively, which are in full agreement with the asymptotic formulas derived by Takori and Brady [28] for a dilute suspension of active colloidal particles moving in the presence of an external torque of any type. The exact (41a, 41b) and asymptotic (42a – 43b) expressions of the long-time active diffusivity, both the parallel and perpendicular components, are plotted against α in Fig. 3(a).

The closed-form exact expressions for the parallel and perpendicular magnetic relaxation times are calculated by dividing (41a) and (41b) by $f_\parallel(0)$ (26a) and $f_\perp(0)$

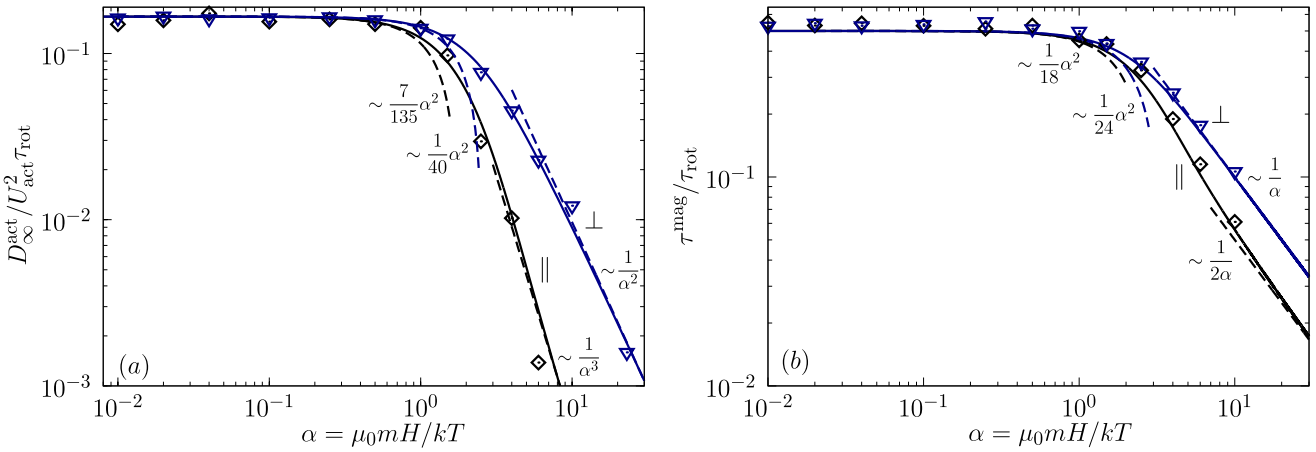

FIG. 3. Parallel (black) and perpendicular (blue) long-time active diffusivities (a) and magnetic relaxation times (b) as a function of α. The exact and asymptotic solutions are shown by solid and dashed curves, which are compared with BD simulations (symbols). Each marker open symbol is an ensemble average over 550 simulations.

(26b), respectively, as stated by the relations (37a) and (37b). Thus, the magnetic relaxation time formulas, valid for any α, read

$$\tau_{\parallel}^{\rm mag} = \frac{1}{\alpha(1+\alpha^{-2}-\coth^2\alpha)}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{I_{n+1/2}^2(\alpha)}{nI_{1/2}^2(\alpha)} \left[\frac{I_{n+3/2}(\alpha)}{I_{n+1/2}(\alpha)}+\frac{n}{n+1}\frac{I_{n-1/2}(\alpha)}{I_{n+1/2}(\alpha)}- \frac{2n+1}{n+1}\frac{I_{3/2}(\alpha)}{I_{1/2}(\alpha)}\right], \tag{44a}$$

$$\tau_{\perp}^{\rm mag} = \frac{1}{2\alpha}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{2n+1}{n(n+1)}\frac{I_{n+1/2}(\alpha)}{I_{3/2}(\alpha)}\prod_{k=1}^{n}S_k^{\perp}(0). \tag{44b}$$

Using (27) and (29) in the above equations, it is found that for weak magnetic fields ($\alpha \ll 1$), the magnetic relaxation times are

$$\tau_{\parallel}^{\rm mag} = \frac{1}{2}-\frac{\alpha^2}{18}+\frac{\alpha^4}{180}-O(\alpha^6), \tag{45a}$$

$$\tau_{\perp}^{\rm mag} = \frac{1}{2}-\frac{\alpha^2}{24}+\frac{17\alpha^4}{4320}-O(\alpha^6), \tag{45b}$$

whereas for strong magnetic fields ($\alpha \gg 1$),

$$\tau_{\parallel}^{\rm mag} \sim \frac{1}{2\alpha}, \tag{46a}$$

$$\tau_{\perp}^{\rm mag} \sim \frac{1}{\alpha}. \tag{46b}$$

These magnetic relaxation time formulas are mathematically equivalent to the dielectric relaxation time expressions presented in Ref. [33] for a system of noninteracting polar molecules subjected to an external electric field.

The exact analytical (44a, 44b) and asymptotic expressions for weak (45a, 45b) and strong (46a, 46b) magnetic fields of the magnetic relaxation times (as illustrated in Fig. 3(b)) allow one to complete from a quantitative point of view (via the relations (35a, 35b)) the description of the time-dependent correlation functions presented at the beginning of this section. One can measure the effect of a magnetic field on the correlation functions, for example, by evaluating the exponential formulas (35a) and (35b) in the limits of weak ($\alpha \ll 1$) and strong ($\alpha \gg 1$) magnetic fields. Substituting the asymptotic analytical expressions, for $\alpha \ll 1$ and $\alpha \gg 1$, of $f_{\parallel}(0)$, $f_{\perp}(0)$, $\tau_{\parallel}^{\rm mag}$, and $\tau_{\perp}^{\rm mag}$, into (35a) and (35b), one finds that for weak magnetic fields,

$$f_{\parallel}(t) = \left(\frac{1}{3}-\frac{\alpha^2}{15}\right)\exp\left(\frac{-2t}{1-\alpha^2/9}\right), \tag{47a}$$

$$f_{\perp}(t) = \left(\frac{1}{3}-\frac{\alpha^2}{45}\right)\exp\left(\frac{-2t}{1-\alpha^2/12}\right), \tag{47b}$$

while in the opposite limit

$$f_{\parallel}(t) = \frac{1}{\alpha^2}\exp(-2\alpha t), \tag{48a}$$

$$f_{\perp}(t) = \frac{1}{\alpha}\exp(-\alpha t). \tag{48b}$$

On the basis of the results obtained for the time-dependent correlation function of the fluctuations of the propulsion direction, the time-dependent active diffusivity is calculated following two procedures. The first consists of using the numerical solutions of $f_{\parallel}(t)$ and $f_{\perp}(t)$, and then calculating the diffusivity by computing numerically the integrals defined in (10a) and (10b). In addition to this numerical procedure, the exact analytical expressions are found after substituting the exact formulas (35a, 35b) into (10a, 10b), respectively, to give

$$\frac{D_{\parallel}^{\rm act}(t)}{U_{\rm act}^2\tau_{\rm rot}} = \tau_{\parallel}^{\rm mag}f_{\parallel}(0)\left[1-\exp(-t/\tau_{\parallel}^{\rm mag})\right], \tag{49a}$$

$$\frac{D_{\perp}^{\rm act}(t)}{U_{\rm act}^2\tau_{\rm rot}} = \tau_{\perp}^{\rm mag}f_{\perp}(0)\left[1-\exp(-t/\tau_{\perp}^{\rm mag})\right]. \tag{49b}$$

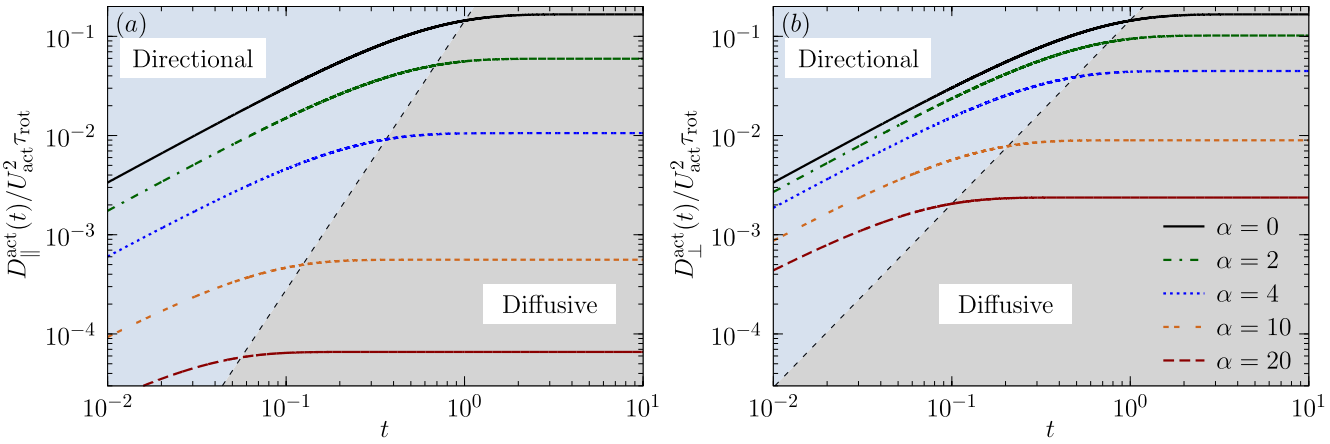

FIG. 4. Parallel (a) and perpendicular (b) time-dependent active diffusivities as a function of dimensionless time t for different α values. The diagonal dashed line, in both (a) and (b), defines two well differentiated propulsion regions: one directional or ballistic (colored in light steel blue) and another diffusive (colored in dark grey).

In the limit of $t \to \infty$, the long-time active diffusivity relations (37a, 37b) are recovered. The numerical solutions of the time-dependent active diffusivity for different values of α are shown in Figs. 4(a) and 4(b). The numerical results are in good agreement with the exact solutions.

In the absence of a magnetic field ($\alpha = 0$), the particle self-propels with an isotropic active diffusivity that grows exponentially with time via $D_{\parallel,\perp}^{\rm act}(t)/U_{\rm act}^2\tau_{\rm rot} = [1-\exp(-2t)]/6$. At short times ($t \ll \tau_{\rm rot}$), the particle moves without undergoing changes in its propulsion direction (or ballistically) characterized by an active diffusivity $D^{\rm act}(t) = U_{\rm act}^2 t/3$ that increases linearly with time. At long times ($t \gg \tau_{\rm rot}$), the propulsion direction of the particle is completely randomized by its own rotary Brownian diffusion, which leads to a plateau region where the active diffusivity of the particle reaches a constant value, $D_{\infty}^{\rm act} = U_{\rm act}^2\tau_{\rm rot}/6$ [13], see Fig. 4. The crossover behavior between ballistic (directional) to diffusive (random) regimes in the dynamics of ABPs has been verified experimentally in [40], where the 2D motion of self-propelled catalytic particles immersed in hydrogen peroxide solutions was analyzed. For self-propelled colloidal particles undergoing 2D active Brownian motion, this crossover behavior was demonstrated analytically in [10–12] via measurement of the mean squared displacement.

As α is increased, the transition from directional to diffusive regimes occurs much faster, as illustrated in Fig. 4. This is better understood by examining the characteristic timescale that regulates the crossover behavior, here denoted as $\tau^{\rm cross}$. When no magnetic field is applied, the transition from one region to another occurs at $\tau^{\rm cross}(\alpha = 0) = \tau_{\rm rot}$. In general, for any value of α, the crossover time is twice the magnetic relaxation time of the particle:

$$\tau^{\rm cross} = 2\tau^{\rm mag} \tag{50}$$

which are directly obtained by multiplying (44a, 46b) by a factor of two. On the other hand, even when both the time scales are mathematically equivalent, they do not represent physically the same thing. However, the correlation time helps to explain why the crossover time decreases as the field strength increases, and as a consequence to understand why the crossover region in the active diffusivity of the particle moves to the left upon increasing the magnetic field, as illustrated in Fig. 4.

Combining (50) with (49a, 49b) and by evaluating the results at the short ($t \ll \tau_{\parallel,\perp}^{\rm cross}$) and long ($t \gg \tau_{\parallel,\perp}^{\rm cross}$) time limits, the active diffusion crossover behavior, both parallel $\parallel$ and perpendicular $\perp$, for any value of field can be described by

$$\frac{D_{\parallel,\perp}^{\rm act}}{U_{\rm act}^2\tau_{\rm rot}} = \begin{cases} f_{\parallel,\perp}(0)t & t \ll \tau_{\parallel,\perp}^{\rm cross}, \\ f_{\parallel,\perp}(0)\tau_{\parallel,\perp}^{\rm mag} & t \gg \tau_{\parallel,\perp}^{\rm cross}. \end{cases} \tag{51}$$

This states that for short times, the active diffusion of the particle increases linearly with the time with a slope that decreases as the field strength increases. As the time increases, the particle loses its directed propulsion until it reaches a diffusive motion in the limit of long times with a constant active diffusion coefficient given by $D_{\infty,\parallel,\perp}^{\rm act} = U_{\rm act}^2\tau_{\rm rot}f_{\parallel,\perp}(0)\tau_{\parallel,\perp}^{\rm mag}$ that decreases with the field strength, as illustrated in Fig. 3(a).

IV. CONCLUDING REMARKS

The time-dependent dynamics of a magnetic active Brownian particle (ABP) undergoing three-dimensional Brownian motion, both translation and rotation, in the presence of a uniform magnetic field was studied. In order to achieve that goal, properties such as the time-dependent correlation function $f_\lambda(t)$, time-dependent active diffusivity $D_\lambda^{\rm act}(t)$, and the characteristic crossover time $\tau_\lambda^{\rm cross}$ have been examined for different values of the

Langevin parameter α and relative to the direction of the applied field. The results obtained from theory have been verified with Brownian dynamics (BD) simulations, and they are in good agreement.

The results reveal that a uniform magnetic field affects the dynamics behavior of a magnetic active particle. It was found that the correlation function, the active diffusivity, and the crossover time decrease upon increasing the magnetic field strength. In addition to this hindered effect, the field also induces anisotropy in the particle dynamics. For instance, the correlation function parallel to the field decays with time much faster than the perpendicular one. The parallel active diffusivity grows with time much slower than the perpendicular one. For moderate values of the field, the parallel components of the active diffusivity and crossover time are greater than their perpendicular ones.

This study has shown that the transition from a ballistic (or directional) to a diffusive regime characteristic of the ABP dynamics is regulated by the magnetic field. In the presence of a magnetic field, the particle undergoes a directional propulsion during a period of time that decreases with an increase in the field. As a result, the particle rapidly reaches a diffusive regime characterized by a constant value of the active diffusivity. This latter is called the long-time active diffusivity which decreases with α.

The characteristic time that measures the transition (or crossover) from one region to another is the crossover time. This work has found that at short times ($t \ll \tau_\lambda^{\text{cross}}$), the particle performs a directional propulsion with an active diffusivity that increases linearly with the time via $D_\lambda^{\text{act}}(t) \sim f_\lambda(0)t$, while, at long times ($t \gg \tau_\lambda^{\text{cross}}$), the particle undergoes a diffusive propulsion with a diffusivity equal to the long-time active diffusivity, i.e. $D_\lambda^{\text{act}}(t \to \infty) = D_{\lambda,\infty}^{\text{act}}$. Finally, it was found that for weak fields ($\alpha \ll 1$), the crossover time decreases quadratically with α as $\tau_\lambda^{\text{cross}} \sim 1/2 - \alpha^2$, while in the opposite field limit ($\alpha \gg 1$), it asymptotically decays to zero as $\tau^{\text{cross}} \sim \alpha^{-1}$.

We provide relevant theoretical predictions of the active diffusivity of the particle in all time regimes for different strengths of the external magnetic field. One of the most important results is the characteristic time for crossover from a ballistic to a diffusive regime. This result shows how in the presence of a magnetic field this crossover time is regulated according to the magnetic field strength. This characteristic time could be used by experimentalists as an estimation of the time to wait before reaching enhanced diffusion in a colloidal system with more degrees of freedom than our simple model.

Future work in this area should address several generalizations of the magnetic ABP model. First of all, in the present model, the particle self-propels along a direction that coincides with the magnetic dipole orientation. This can be generalized to arbitrary relative orientations. In experimental studies with magnetic ABPs, two types of alignment between the propulsion direction and the dipole orientation have been commonly observed: one parallel [21–23] and the other perpendicular [19]. Another feature is to consider the spin motion of Brownian type around an axis of revolution that, for example, lies parallel to the dipole moment. A fundamental understanding of the time-dependent dynamics of an ABP under a magnetic field is essential to extend the study to more complex scenarios, such as their collective dynamics when many of these particles are manipulated by external fields [41, 42].

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