Diffusion in monodisperse ferrofluids

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Abstract. The diffusion coefficients characterizing the translational and rotational Brownian motion of a particle in a concentrated suspension were determined in the long time diffusive regime for a ferrofluid suspension with the use of a Langevin equation approach. These dynamical properties depend on the equilibrium micro-structural information of the suspension and take into account the effect of direct anisotropic inter-particle's interactions on self-diffusion. The comparison of this theory with Brownian dynamic simulations results is made in terms of colloid density and dipole interaction strength.

1. Introduction

Nowadays, the effect of the direct anisotropic interactions among magnetic nanoparticles and external magnetic field gradients, on their collective diffusion is currently investigated with forced Rayleigh scattering techniques [1] and dynamic light scattering [2] in ferrofluid suspensions of up to 10% volume fractions. Yet, the non-direct long range hydrodynamic interaction (HI) in the system is experimentally measured by means of x-ray correlation spectroscopy [3] and with neutron spin-echo experiments [4,5,6]. Whereas, the description of the collective diffusion has been accomplished with gradient diffusion approach on concentrated suspensions [7,8], and through the mean field kinetic Smoluchowski equation for low and moderate volume fractions [9]. However, there is a clear absence of experimental studies of the rotational and translational self- and tracer diffusion coefficients in mono- and poli-disperse ferrofluids which remains to be performed in the already well characterized experimental systems. The above cited theories have been useful to describe the translational self-diffusion of Brownian dynamic simulations were dissipative HI was ignored for model systems of homogeneous moderately concentrated suspensions [9]. Thus, due to the lack of HI there are no cross correlation of distinct particle's velocities and therefore the collective gradient diffusion coefficient coincides with the self-diffusion expression [10,9]. The simulation studies of reference [9] confirmed good agreement with

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gradient diffusion theory. In the present paper we show that a Langevin equation description of the translational and rotational Brownian dynamics (BD) of a colloidal particle in concentrated ferrofluid suspensions without HI provides, in the long time diffusive regime the translational self-diffusion coefficient which yields good quantitative prediction as compared to BD results. We provide expressions both for the self- translational and rotational coefficients which depend in the equilibrium microstructural information of the fluid through the anisotropic pair correlation function. In ferrofluids the rotational diffusion of the particles can be measured with transient magnetic birefringence relaxation [11] and small-angle neutron-scattering [6].

2. Langevin equation of particle velocities and of their local concentration

The colloidal suspension contained in a volume $V$ consist of a carrier fluid plus the monodisperse system of $N$ particles of equal mass $M$ and moment of inertia $I$, where each particle can be either of spherical or rod-like shape having an embedded optical anisotropy or a permanent dipolar moment. The orientation of a particle's main axis of symmetry is defined with respect to tracer's body fixed frame. Thus, another particle's orientation will be denoted in this frame by the polar angles of its orientation $\Omega_i = (\theta_i, \phi_i)$ for $i = 1, \ldots, N$. Then the total potential energy of the system is $U = \sum_{ij} \psi_{ij} / 2$ where it is assumed that $\psi_{ij}$ is the direct pairwise interaction potential between particles. Notice that we will not consider in this paper the contribution of the non-additive HI among particles. The equation of motion governing the particle translational $v(t)$ and angular $\omega(t)$ velocity of its rotation can be written as

$$M \cdot \frac{dV(t)}{dt} = -\xi^0 \cdot V(t) + f(t) + \int d\Omega d\Omega' \psi(r, \Omega) \delta n(r, \Omega, t)$$  

(1)

where the dynamical fluctuation in concentration about its equilibrium value is

$$\delta n(r, \Omega, t) = n(r, \Omega, t) - n^eq(r, \Omega)$$

since the equilibrium concentration $n^{eq}$ does not contribute to the net force and torque component. The third term in the Langevin equation above represents the direct forces and torques on the diffusing particle by the host colloidal particles around it. We defined the generalized velocity $V(t) = (V, \omega)$, and mass $M_j = M \delta_{ij} \quad (i, j = 1, 2, 3)$, $\delta_{ij}I_{ij}$ with $I_{ij}$ the principal moments of inertia of the particle $(i, j = 4, 5, 6)$. The free particle's friction coefficient is diagonal with elements $\xi^0_{11} = \xi^0_{22} = \xi^0_{33}$, $\xi^0_{33} = \xi^0_{44}$, $\xi^0_{55} = \xi^0_{66}$, and $\xi^0_{66} = 0$, which are external inputs to the theory. The general random term $f(t)$ represents the force and torque imparted on the particle by its collision with the solvent molecules on its surface. The Langevin equation above is coupled to the fluctuation in concentration whose evolution equation can be written in its most general form as

$$\frac{\partial \delta n(r, \Omega, t)}{\partial t} = [\nabla n^{eq}(r, \Omega)] \cdot V(t) - \int d\Omega' d\Omega'' d\Omega''' L(r, \Omega; r', \Omega', t - t') \times$$

$$\sigma^{-1}(r', \Omega'; r'', \Omega'') \delta n(r'', \Omega''; r', \Omega', t') + h(r, \Omega, t),$$  

(2)
where $\sigma^{-1}$ is the inverse of the static correlation function $\sigma(r, \Omega; r', \Omega') := \langle \delta n(r, \Omega; 0) \delta n(r', \Omega'; 0) \rangle$ [12] which will be denoted simply as $\sigma$ and similarly for the other quantities $\delta n(t), \chi(t), n^{\text{eq}}(t), \psi(t), L(t), h(t)$. Thus, it fulfills the identity

$$\int dr' \Omega'' \sigma(r, \Omega; r', \Omega') \sigma^{-1}(r', \Omega', r', \Omega') = \delta(r-r') \delta(\Omega-\Omega').$$

(3)

In equation (2) $L$ is an Onsager coefficient that satisfies the fluctuation-dissipation relation with the stationary random term of zero mean $\langle h(r, \Omega; t) h(r', \Omega'; t') \rangle = L(r, \Omega; r', \Omega'; t-t')$.

3. Effective friction function

The formal solution of equation (2) is known and given in references [13,14] as

$$\delta n(t) = \chi(t) \delta n(0) + \int_0^t dt' \chi(t') \left[ \nabla n^{\text{eq}} \cdot V(t') + \int_0^{t'} dt'' \chi(t''-t') - h(t') \right],$$

(4)

where $d\Omega = \int dr d\Omega$, and the propagator $\chi$ satisfies

$$\frac{\partial \chi(t)}{\partial t} = -\int_0^t dt' L(t-t') \sigma^{-1} \chi(t'),$$

(5)

with initial condition $\chi(t=0) = \delta(r-r') \delta(\Omega-\Omega')$. Substituting equation (4) in (1), we obtain the effective Langevin equation of the particle

$$M \frac{dV(t)}{dt} = -\sigma^{-1} \nabla n^{\text{eq}} \cdot \nabla \psi(t)$$

(6)

Where the dynamical friction function can be expressed in different equivalent forms with the use of the Wertheim-Lovett equation $\beta \nabla \psi = -\sigma^{-1} \nabla n^{\text{eq}}$ [15],

$$\Delta \zeta(t) = \frac{1}{\Omega^2} \beta [\nabla \psi] \chi(t) \sigma [\nabla \psi]^\dagger = \frac{1}{\Omega^2} \beta [\nabla \psi] C(t) [\nabla \psi]^\dagger = \frac{k_B T}{\Omega^2} [\nabla n^{\text{eq}}] \sigma^{-1} \chi(t) [\nabla n^{\text{eq}}]^\dagger.$$ (7)

Since the observable $\Delta \zeta(t)$ is related to the measured mean squared displacement, it’s average over the solid $\Omega = 4\pi$ is performed. Here $\beta = 1/ k_B T$ with $k_B$ the Boltzmann constant, $T$ the temperature, and $C(t)$ satisfying the fluctuation-dissipation relationship $\langle F(t) F^\dagger(0) \rangle = k_B T \Delta \zeta(t)$. The general expressions for the friction function in (7) can also be used to study tracer diffusion on rod-shaped particles suspensions [16]. Such as fd viruses on which the experimental techniques of birefringence, and forced Rayleigh scattering measure the diffusion properties. On the other hand, the propagator $C(t) = \chi(t) \sigma := \langle \delta n(t) \delta n(0) \rangle$ governs the collective relaxation of the particle’s configuration variables $(r, \Omega)$ due to thermal fluctuations, and it has initial condition $C(0) = \sigma := \langle \delta n(0) \delta n(0) \rangle$. The equation of $C(t)$ is obtained from (5) yielding
4. Monodisperse ferrofluid

For a hard ferrofluid suspension made of spherical particles with permanent magnetic moment of magnitude, \( \mu \), we obtain a hard sphere (HS) diameter \( d \) with a Lennard-Jones short range (sr) repulsive interaction. Thus, the total pair direct interaction is \( \psi_{12} = u_{sr} + \phi_{dd} \)

\[
u_{dr} = 4 \varepsilon_0 \left( \frac{d}{r} \right)^{12} - \left( \frac{d}{r} \right)^{6}, r \geq 2.5d \tag{9} \]

\( 1/\beta\varepsilon_0 = 1.35 \). Plus the dipolar interaction \( \phi_{dd} = -\mu_0 \mu^2 D(\Omega, \Omega, \Omega) / 4 \ r^3 \). \( \mu_0 \) is the magnetic permeability of vacuum. \( D(\Omega, \Omega, \Omega) := 3(\mathbf{r}_{12} \cdot \mathbf{u}_1)(\mathbf{r}_{12} \cdot \mathbf{u}_2) - (\mathbf{u}_1 \cdot \mathbf{u}_2), \) Where \( \mathbf{r} = \mathbf{r} / r \) is a unitary vector along vector \( \mathbf{r} \) and with orientation \( \Omega, \mathbf{u} = \mathbf{u}(\theta, \phi) \) is a unitary vector of dipole orientation.

At equilibrium, the bulk profile concentration of particles around the tracer \( g(r, \Omega_1, \Omega_2) \) is proportional to the pair correlation function which for a dipolar fluid is provided by its first three terms in a series expansion of spherical harmonics. Here \( \rho = N/V \) is the number density of particles and \( g(r, \Omega_1, \Omega_2) \) has the fixed space rotational invariant expansion of Wertheim [17,18]

\[
g(r, \Omega_1, \Omega_2) = g(r) + h_{10}(r) \Delta + h_{01}(r)D, \tag{10} \]

with \( \Delta := \mathbf{u}_1 \cdot \mathbf{u}_2 \). There is an equivalent rotational invariant expansion of (10) given in [19]

\[
f(r, \Omega, \Omega') = (4\pi)^{3/2} \sum_{mnl} \left( \frac{r_{mnl}(r)}{(2l + 1)^{1/2}} \right) \sum_{\mu \nu \lambda} Y_{n\mu}(\Omega)Y_{m\nu}(\Omega')Y_{l\lambda}(\Omega'), \tag{11} \]

With the identification \( g^{00} = g(r), h^{10} = h_{10}(r) / \sqrt{3}, h^{11} = h_{01}(r) / \sqrt{10} / 3 \) [20]. We determined these micro-structural properties using the reaction field method as boundary condition [21, 22] in the Brownian dynamic simulation [16]. The vector positions were decomposed into its parallel (\( \parallel \)) and perpendicular (\( \perp \)) projections along the particle’s axis of symmetry (in this case \( \mathbf{u}_i \), \( \mathbf{r} = \mathbf{r} + \mathbf{r}_i \) where for particle \( i \) is \( \mathbf{r}_i = [\mathbf{u}_i \cdot \mathbf{r}_i] \mathbf{u}_i \), therefore [16]

\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{\Delta t}{\zeta_0} \mathbf{F}_i(t) + \Delta t \mathbf{u}_i(t) \\
\mathbf{r}_i^\perp(t + \Delta t) = \mathbf{r}_i^\perp(t) + \frac{\Delta t}{\zeta_0} \mathbf{F}_i^\perp(t) + \Delta \mathbf{r}_i^\perp(t) + \mathbf{r}_i^\perp \mathbf{e}_{i_1}(t) + \mathbf{r}_i^\perp \mathbf{e}_{i_2}(t). \tag{12} \]

Here \( \mathbf{F}_i = -\nabla U, r, r_i^\parallel, r_i^\perp \) are three uncorrelated Gaussian random numbers of variance \( 2\Delta t / \zeta_0 \) and \( \mathbf{e}_{i_1}(t), \mathbf{e}_{i_2}(t) \) two orthogonal unit vectors which are perpendicular to \( \mathbf{u}_i(t) \),
\[ \mathbf{u}_i(t + \Delta t) = \mathbf{u}_i(t) + \frac{\Delta t}{\zeta_R} \mathbf{T}_i(t) \mathbf{u}_i(t) + \mathbf{x}_1 \mathbf{e}_i(t) + \mathbf{x}_2 \mathbf{e}_j(t). \]  

(13)

\[ \mathbf{T}_i = -L_u U. \]  

The angular operator \( L_u = \mathbf{u} \times \partial / \partial \mathbf{u} \). \( x_1, x_2 \) are two uncorrelated Gaussian random numbers of variance \( 2\Delta t / \zeta_R^0 \). We used for \( \zeta^0 = 3\pi \eta d \), \( \zeta_R^0 = \pi \eta d^3 \) and \( N = 125 \) particles. To equilibrate the system 400000 time steps of size \( \Delta t^* = \Delta t / t_0 = 5 \times 10^{-4} \), \( t_0 = 3\pi \eta d^3 / k_B T \) are performed. After this, 3 million more new particle's configurations were generated and used 30000 configurations for statistics to get the micro-structural functions of figure 1(a), and dynamical properties such as the long time and time-dependent translational and rotational self-diffusion. Using the definitions [23]

\[ g(r) = \frac{\sum \delta(r - |r_j|)}{N 4\pi \rho^* r^2}, \]

\[ h(r) = 3 \frac{\sum \delta(r - |r_j|)\mathbf{u}_i \cdot \mathbf{u}_j}{N 4\pi \rho^* r^2}, \]

\[ h_D(r) = \frac{3}{2} \frac{\sum \delta(r - |r_j|)[3\mathbf{u}_i \cdot \mathbf{r}_j \mathbf{u}_j \cdot \mathbf{r}_j - \mathbf{u}_i \cdot \mathbf{u}_j]}{N 4\pi \rho^* r^2}. \]

(14)

We determined typical correlation functions as displayed in figure 1(a) for a dimensionless number density \( \rho^* = n d^3 = 0.02 \) and reduced dipolar strength \( \mu^* = \mu / 4 \pi k_B T d^3 = 2.75 \). The term \( g(r) \) is calculated as the usual isotropic pair correlation function [21]. By taking the Fourier-Bessel transform \( f^{\text{mnl}}(k) = 4\pi i \int_0^\infty r^2 j_i(kr) f^{\text{mnl}}(r) dr \) [22] with \( j_i \) being the spherical Bessel function, and Laplace transform \( C_{\alpha\alpha}^{\text{mnl}}(k, w) = \int_0^\infty dt e^{-\lambda t} C_{\alpha\alpha}^{\text{mnl}}(k, t) \) of (8) we find

\[ [-iwC_{\alpha\alpha}^{\text{mnl}}(k, w) - C_{\alpha\alpha}^{\text{mnl}}(k, w = 0)] = -\rho 4\pi (2l + 1) [D_0^m k^2 + D_R^m m(m + 1)] \times \sum_{n_i} (-1)^n C^{n_i\alpha}_\alpha(k, w)[\sigma^{-1}]_{\alpha\alpha}, \]

(15)
Figure 1. Figure (a) gives \( g(r) \) (black dots •) \( h_D(r) \) (open circles °) and bottom curve for \( h_\lambda(r) \) (continuous line) from BD simulations of equations (12-13) for the model ferrofluid of soft Lennard-Jones short range repulsion and dipolar interaction with \( \rho^* = 0.02 \) and \( \mu_2^2 = 2.75 \). Notice that all functions are different from zero for \( r/d \approx 1 \), which fixes the lower limit in the radial dependence of equations (20-23). Figure (b) depicts the translational \( D/D^0 \) (symbol •) and rotational \( D_R/D_R^0 \) (symbol °) self-diffusion coefficients calculated from theory (20-23) for \( \mu_2^2 = 2.75 \) and as a function of reduced density \( \rho^* \). No HI’s are included in the calculation on the properties of (b).

Where \( i = \sqrt{-1} \) and \( C_{\alpha l}^{m,n}(k,w) = \sum_{\alpha = 0,\pm 1}^{m+n} \binom{m}{\alpha} \binom{n}{-\alpha} \binom{l}{0} C_{\alpha l}^{m,n}(k,w) \) [22]. Using the above values of \( mnl = 000,110,112, \) then for dipolar liquids \( \alpha = 0, \pm 1 \) [19], and using the approximation \( D^{\alpha 0} = 2D^0, D_R^{\alpha 0} = 2D_R^0 \) [14], we get for equation (15)

\[
C_{\alpha l}^{11}(k,w) = \frac{[\sigma(k)]_{\alpha l}^{11}}{-iw + \rho \pi (1)^{2} 4D^{\alpha 0} k^2 2D_R^{\alpha 0} \left[ \sigma^{-1}(k) \right]_{\alpha l}^{11}}. \tag{16}
\]

Moreover, the inverse relation holds

\[
C_{\alpha l}^{m,n}(k,w) = (2l + 1) \sum_{\alpha = 0,\pm 1}^{m+n} \binom{m}{\alpha} \binom{n}{-\alpha} \binom{l}{0} C_{\alpha l}^{m,n}(k,w) \tag{17}
\]

Thus

\[
C^{000}(k,w) = C_{00}^{00}(k,w)
\]

\[
C^{110}(k,w) = \frac{1}{\sqrt{3}} \left[ 2C_{11}^{11}(k,w) - C_{00}^{11}(k,w) \right]
\]
The structure factor \( S = \sigma / \rho \) and total correlation function \( h \) are related by
\[
\sigma_{\mu\nu}^{\text{mm}}(k) = \rho S_{\mu\nu}^{\text{mm}}(k) = \rho [1 + (1)^{\nu} h_{\mu\nu}^{\text{mm}}(k)],
\]
\[
S_{00}^{00}(k) = 1 + \frac{\rho_{*}}{d^{3}} h_{000}^{000}(k),
\]
\[
S_{01}^{11}(k) = 1 - \frac{\rho_{*}}{d^{3}} \left( \frac{1}{\sqrt{(3)}} h_{110}^{110}(k) - \frac{2}{\sqrt{(30)}} h_{112}^{112}(k) \right),
\]
\[
S_{13}^{11}(k) = 1 - \frac{\rho_{*}}{d^{3}} \left( \frac{1}{\sqrt{(3)}} h_{110}^{110}(k) + \frac{1}{\sqrt{(30)}} h_{112}^{112}(k) \right),
\]
with \( h_{000}^{000} = g^{000} - 1 \). Therefore from the Laplace transform of the second identity of (7) we attain in the long time limit \( w = 0 \) [14]
\[
\Delta \zeta_{\nu}(w = 0) = \Delta \zeta_{\nu}^{\text{HS}} + \zeta_{\nu},
\]
for \( \gamma = \perp \), where [24]
\[
\Delta \zeta^{\text{HS}} = \frac{\zeta_{0}}{36 \pi \phi} \int_{0}^{\infty} dx \frac{dx^{2} \left[ S_{00}^{00}(x) - 1 \right]^{2}}{1 + S_{00}^{00}(x)}.
\]
Notice that in the above equation (23) the first term is the hard sphere contribution [24] that results from the third form of \( \Delta \zeta \) in equation (7) which depends on the gradient of particle concentration \( \nabla n^{\eta} \). This first contribution was used here instead of the Lennard-Jones short range contribution to the friction that would be attained from the second identity of (7) that depends on \( \nabla u_{\nu} \). The second part \( \Delta \zeta_{\nu} \) results from the last identity of (7). Here \( x = k \sigma \). Whereas the contribution to the translational friction, in the direction perpendicular to the main axis of symmetry of the particle, due to direct interactions is [14]
\[
\Delta \zeta_{\perp} = \frac{204 \phi(\mu^{2})^{2}}{5 \Omega^{2}} \int_{0}^{\infty} dx \frac{j_{2}(x)^{2}}{x^{2} + 2 \frac{D_{\theta}^{0}}{D_{\sigma}^{0}} d^{2}} \times \left[ 6 \left( S_{0}^{11}(x) \right)^{2} - 9 \left( S_{0}^{11}(x) \right)^{2} \right].
\]
On the other hand, the component of the friction parallel to the main body axis is \( \Delta \zeta_{\nu} = \frac{4}{3} \Delta \zeta_{\perp} \).

Moreover, for the rotational friction we get
\[
\Delta \zeta_{R} = \frac{204 \phi(\mu^{2})^{2}}{105 \Omega} \int_{0}^{\infty} dx \frac{j_{1}(x)^{2}}{x^{2} + 2 \frac{D_{\theta}^{0}}{D_{\sigma}^{0}} d^{2}} \times \left[ 6 \left( S_{0}^{11}(x) \right)^{2} - 9 \left( S_{0}^{11}(x) \right)^{2} \right].
\]
Thus, the components of the self-diffusion properties are $D_{\gamma} / D^0 = (1 + \Delta \zeta / \zeta^0)^{-1}$, $\gamma = \perp, R, \varsigma^0 = \varsigma^0$, and the average total translational and rotational diffusion coefficient are, respectively, $D = (2D_\perp + D_R) / 3$, $D_R / D^0$ and $D^0 = k_B T / \zeta^0$. Figure 1(b) is the plot of the average translational property $D / D^0$ (black dots), and rotational self-diffusion $D_R / D^0$ (open circles) obtained from the theory, equations (20-23), as a function of $\rho^*$ for $\mu^* = 2.75$. In general, both translational and rotational diffusion of the particle diminish by an increase in ferrofluid density. In figure 2(a) we compared theory (20-22) for $D / D^0$ (symbol •) versus the Brownian dynamics results of reference [9] denoted with A, as function of volume fraction and fixed dipolar strength $\mu^{*2} = 0.58$. Notice that in reference [9] the reduced dipolar strength is denoted as $\lambda = \mu_0 \mu^2 / k_B T d_0$, with $d_0 = 1.2 d$, and its value is related to ours $\mu^{*2} = \lambda \times 0.58$. Thus, they used the value $\lambda = 1$. The fraction volume definition
used in reference [9] is \( \rho d_0^3 \pi / 6 \) which is related to our expression for this quantity as \( \phi = (\rho d_0^3 \pi / 6) / 0.58 \). Figure 2 is the theoretical prediction of (23) for the rotational diffusion. Figure 3(a) provides the comparison of theory (20-22) (symbol •) and Brownian dynamic simulation (symbol A) of reference [9] for translational diffusion at volume fraction \( \phi = 0.05 / 0.58 \) where the value of 0.05 was used by authors of reference [9]. We plotted this property as function of dipolar strength \( \mu^2 = \lambda \times 0.58 \). Whereas figure 3(b) is the corresponding theory, results for \( D_R / D_R^0 \). We consider now a ferrofluid under the influence of a constant external magnetic field \( H \). Therefore, the energy of the system is. Figure 4 depicts the time-dependent self-diffusion coefficients results from Brownian dynamic simulation only at volume fraction \( \phi = 0.05 / 0.58 \) versus reduced time \( t / \tau_0 \) and three magnitudes of particle's dipole moment \( \mu^2 \), and under applied magnetic field in dimensionless units of \( H^\star = (\mu_0 \mu H / k_B T) = 4 \), where \( H = |H| \). The field orientation is along the \( Z \) axis. For translational diffusion, we determined the coefficient as \( D(t) = (1 / N)^{\sum_{i=1}^{N} (\mathbf{r}_i(t) - \mathbf{r}_i(0))^2 / 6t} \), where the component \( D(t)_{\perp} = D(t)_{xx}, D(t)_{yy} [25] \) refers to diffusion parallel to axis \( X \) and \( Y \) but perpendicular to the diffusion along the main particle symmetry axis which is along \( Z \) [9], direction about which we defined the component \( D = D_{zz} \). For the rotational motion, we used \( D(t) = -\ln[(\mathbf{u}_n(t) \cdot \mathbf{u}_n(0))] / 2t \) [16]. Figure 4(a) shows that at the lowest dipole strength \( \mu^2 = 0.14 \), and \( H^\star = 0 \) the short time diffusion limit presents a plateau in the diffusion coefficient (upper continuous line) where it remains constant and then drops continuously due to direct inter-particle's interactions that restrain its movement. For \( H^\star = 4 \) the short time section of the diffusion, curve lowers (dotted curve) and then converges for longer times to the zero field case above. For a slightly larger dipole, strength of \( \mu^2 = 0.59 \) either with field (dot-dash line) or not (dash line) both curves almost coincide in general. For the highest dipolar case of \( \mu^2 = 4.64 \), in contrast to the lowest dipole moment case before, the field now increases, in general, the average translational diffusion \( D(t) / D^0 \) at all times (second curve from bottom continuous line curve) as compared to the case of the zero field homogeneous suspension (bottom curve thick black line). Figure 4(b) depicts the rotational diffusion without magnetic field at the three dipole moments discussed before. In this plot and for the two curves with corresponding \( \mu^2 = 0.14, 0.59 \) values the diffusion coefficient \( D_R(t) \) is given correctly only in the small time interval \( 0 \leq t / \tau_0 \leq 20 \) where the mean square displacement is well defined whereas for larger times is incorrectly provided by the remaining part of those two curves. At the highest dipole moment (bottom line) the rotational diffusion lowers as
Figure 4. Figure (a) is the BD simulation results from equations (12-13) for the time-dependent translational self-diffusion coefficient versus reduced time $t/t_0$ at volume fraction $\phi = 0.05/0.58$ for five values of reduced dipole moment $\mu^r$ with and without magnetic field $H^r$. Figure (b) yields the corresponding time-dependent rotational diffusion of the particle.

A function of time due to the accumulative effect of inter-particle's interactions that lowers the rotational movement of the particle. It should be noticed that similar time-dependent translational diffusion properties have been measured in a super-paramagnetic colloid confined to a surface [26], and through BD simulations in suspensions of hard spherocylinders [25].

5. Conclusions

A Langevin equation theory allowed us the determination of the friction contribution due to direct inter-particle's interactions that experience a colloid particle during its diffusion in a concentrated mono-disperse suspension. In the long time diffusive limit the resulting expressions of the particle self-diffusion coefficient of its translation and rotational movement shows a good comparison with Brownian dynamic results of reference [9] as a function of colloid concentration and dipole strength of interaction. The expression we derived for the friction function apply to colloidal systems made of rod-shaped particles with anisotropic pairwise inter-particle's interactions. Its generalization for colloidal mixtures is straightforward. Future work incorporates the effect of external gradient magnetic field and the dissipative HI. These dynamical properties are feasible to be measured experimentally [1].
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References

[1] Bacri C, Cebers A, Bourdon A, Demouchy G, Heegaard B M, Kashevsky B and Perzynski R 1995 Phys. Rev. E 52 3936
[2] Mertelj A, Cmok L and Copie M 2009 Phys. Rev. E 79 041402
[3] Wagner J, Fischer B, Autenrieth T and Hempelmann R 2006 J. Phys.: Condens. Matter 18 S2697
[4] Gazeau F, Boué F, Dubois E and Perzynski R 2003 J. Phys.: Condens. Matter 15 S1305
[5] Gazeau F, Dubois E, Bacri J C, Boué F, Cebers A and Perzynski R 2002 Phys. Rev. E 65 031403
[6] Mériguet G, Dubois E, Jardat M, Bourdon A, Demouchy G, Dupois V, Farago B, Perzynski R and Turq P 2006 J. Phys. Condens. Matter 18 S2685
[7] Morozov K I 1996 Phys. Rev. E 53 3841
[8] Pshenichnikov A F, Elfimova E A and Ivanov A O 2011 J. Chem. Phys. 134 184508
[9] Ilg P and Kroger M 2005 Phys. Rev. E 72 031504
[10] Gomer R 1990 Rep. Prog. Phys. 53 917
[11] Bacri J C, Perzynski R, Salin D and Servais J 1987 J. Phys. (Paris) 48 1385
[12] Hansen J P and McDonald I R 1980 The Theory of Simple Liquids (London: Academic Press)
[13] Hernández-Contreras M, Medina-Noyola M and Vizcarra-Rendón A 1996 Physica A 234 271
[14] Hernández-Contreras M and Ruíz-Estrada H 2003 Phys. Rev. E 68 031202
[15] Gubbins K E 1980 Chem. Phys. Lett. 76 329
[16] Löwen H 1994 Phys. Rev. E 50 1232
[17] Wertheim M S 1971 J. Chem. Phys. 55 4291
[18] Levesque D, Patey G N and Weis J J 1977 Mol. Phys. 34 1077
[19] Blum L 1972 J. Chem. Phys. 75 1862
[20] Gray C G, Gubbins K E and Joslin C G 2011 Theory of Molecular Fluids (USA: Oxford University Press)
[21] Allen M P and Tildesley D J 1989 Computer Simulation of Liquids (Clarendon Press)
[22] Fries P H and Patey G N 1985 J. Chem. Phys. 82 429
[23] Weis J J and Levesque D 1993 Phys. Rev. E 48 3728
[24] Nägele G, Medina-Noyola M, Klein R and Arauz-Lara J L 1988 Physica A 149 123
[25] Kirchhoff T, Löwen H and Klein R 1996 Phys. Rev. E 53 5011
[26] Kollmann M, Hund R, Rinn B, Nägele G, Zahn K, Krönig H, Maret G, Klein R and Dhont J K G 2002 Europhys. Lett. 58 919