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Long-time self-diffusion in a model ferrofluid

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The long-time self-diffusion coefficients of a concentrated ferrofluid are determined theoretically with the use of the generalized Langevin equation approach. The dependences of the translational and rotational diffusions on the concentration and the dipolar strength are studied. These dependences are expressed through the static structural information of the ferrofluid suspension. It is found that the effect of the dipolar interaction leads to the strong suppression of both long-time coefficients compared to the free diffusion coefficients of the particles in the infinite dilute case. [S1063-651X(98)01601-8]

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I. INTRODUCTION

Transport phenomena in colloidal suspensions are a subject of long-standing interest. Among the most important diffusion properties in these systems are the mean-squared displacement $\langle[\Delta\mathbf{r}(t)]^2\rangle$ and the long-time tracer-diffusion coefficient D, which has been measured in monodisperse suspensions of polystyrene spheres using x-ray, neutron, and dynamic light-scattering techniques [1]. Presently, dynamical theories relating D to the microstructure of the suspension and therefore to the interparticle radially symmetric interactions are known to provide highly precise agreement with the experimental data [2,3]. However, there is a clear absence of the corresponding studies on suspensions constituted by nonspherical particles interacting through nonradially symmetric potentials [4]. In a recent paper some of us have given a general theoretical framework based on the generalized Langevin equation (GLE) to describe, in the absence of hydrodynamic interactions, the diffusion properties of a nonspherical Brownian tracer particle interacting, in general, through a nonradially symmetric potential with other nonspherical particles in a multicomponent colloidal suspension [5]. Ferrofluids, electrorheological fluids, suspensions of the tobacco mosaic virus (TMV), and dipolar fluids in general constitute important examples of the type of systems on which this theoretical scheme can be applied. In previous works, the GLE approach has been used to determine the rotational-translational electrolyte friction on a rodlike polyion of the TMV [6] and on a Brownian point electric dipole embedded in a hard sphere [7], where the supporting electrolyte solution was a one-component plasma.

In the case of ferrofluids the effect of magnetodipolar interactions on the transport properties in the presence of an applied external magnetic field has been studied recently [8]. In particular, the effect of the external field on the anisotropic collective diffusion in concentrated solutions has been investigated both experimentally and theoretically [9]. Also, the experimental measurements of viscosities in dilute systems has been compared with calculations based on the Smoluchowsky equation [10].

In the present work we study the transport properties in ferrofluids, which are stable colloidal dispersions of ferromagnetic particles coated with surfactants and dispersed in a host liquid such as water or paraffin [11]. The ferroparticles are usually considered to be hard spheres that carry a permanent magnetic dipole. In particular, we focus on the study of the effect of magnetodipolar interactions on single-particle dynamical properties in the simplest nonspherically symmetric generic case, namely, self-diffusion in a model ferrofluid (a Brownian dipolar liquid), in which case the particles around the tracer interact through a nonradially symmetric potential, and in the absence of an external magnetic field. Hydrodynamic interactions will be ignored in the present work since from the theoretical point of view it is important to understand first the effects of the dipolar interactions on the suspension dynamics, particularly on the long-time self-diffusion coefficients [2].

Thus we present here a simple theory, based on the GLE approach, to determine the long-time translational D and rotational D_R self-diffusion coefficients in this model ferrofluid. The dependences of these properties on the volume fraction concentration ϕ of the suspension and the dipolar strength μ of the particles, for a range of values representative of real ferrofluids, are studied using the resulting expressions.

The GLE provides us with general and exact expressions for the tracer friction contributions due to the translational friction in the directions parallel $\Delta\zeta_{\|}$ and perpendicular $\Delta\zeta_{\perp}$ to its symmetry axis and to the rotational friction around any axis perpendicular to the symmetry one $\Delta\zeta_R$. This friction leads to the departure of the long-time self-diffusion coefficient $D_\gamma(\gamma=\|,\perp,R)$ from its hydrodynamic free diffusion value D_γ^0 through the Einstein relation $D_\gamma=k_BT/(\zeta_\gamma^0+\Delta\zeta_\gamma)$, where k_B is Boltzmann's constant, T is the temperature, and $\zeta_\gamma^0=k_BT/D_\gamma^0$.

In order to compute the self-diffusion coefficients some approximations are introduced in the theory (homogeneity and Fick's diffusion approximations) that render our general expressions for the friction contributions with approximate but more useful and still general expressions for $\Delta\zeta_\gamma(t)$. This expressions are written in terms of the static microstructural properties of the suspension, i.e., the interaction potential between two particles $\psi(\mathbf{r},\Omega_1,\Omega_2)$ and the total correlation function $h(\mathbf{r},\Omega_1,\Omega_2)$, where $\mathbf{r}$ is the distance between the center of mass of two particles with the dipolar orientations $\Omega_i=(\phi_i,\theta_i)$ $(i=1,2)$, ϕ_i,θ_i being the polar angles. The required pair-correlation functions were calculated using the mean spherical approximation (MSA) for dipolar hard spheres [12]. The MSA should be quite reasonable for not too strongly interacting polar liquids and not too high concentrations [13]. Therefore, we expect only a qualitative accuracy of our predictions on the tracer diffusion properties when compared to real experiments and computer simulations.

The final word on the accuracy of this approximation scheme can be obtained only by a comparison of our results with experiments or computer simulation calculations, presently unavailable. We consider that the simple theory introduced here may be useful in the study of transport properties in ferrofluids and that the measurements of these effects in real experimental systems is quite feasible with the present scattering techniques [8,10,11].

This paper is organized as follows. Our discussion starts in the following section with a brief review of the general results of the GLE theory for nonspherical colloidal particles. That is, the explicit expressions for the friction coefficients for the generic systems constituted of a *nonspherical* tracer immersed in a suspension of other *nonspherical* particles are given in Sec. II. In Sec. III we provide the definition of the model system and the most relevant structural information obtained by the MSA, which is also briefly discussed. The results for the long-time translational and rotational self-diffusion coefficients are presented and discussed in Sec. IV. Section V is a summary of our work.

II. LANGEVIN EQUATION THEORY

In this section we quote the main results of the GLE approach useful for the description the Brownian motion of a nonspherical but axisymmetric tracer particle interacting with other nonspherical axisymmetric particles of the suspension. The generalized Langevin equation for the tracer reads

$$\overleftrightarrow{M}\cdot\frac{d\vec{V}(t)}{dt}=-\overleftrightarrow{\zeta}^0\cdot\vec{\mathbf{V}}(t)+\vec{\mathbf{f}}^0(t)-\int_0^t dt'\Delta\overleftrightarrow{\zeta}(t-t')\cdot\vec{\mathbf{V}}(t')+\vec{\mathbf{F}}(t). \tag{1}$$

Here $\vec{\mathbf{V}}(t)=(\mathbf{V}(t),\mathbf{W}(t))$ embodies the linear $\mathbf{V}(t)$ and angular $\mathbf{W}(t)$ velocities of the tracer, whose components are defined with respect to a coordinate system with origin fixed to the laboratory frame, but whose orientation changes with time following the orientation of the main axis of symmetry of the tracer. $\overleftrightarrow{M}_{ij}=M\delta_{ij}(i,j=1,2,3);\overleftrightarrow{M}_{ij}=\delta_{ij}I_{i-3}(i,j=4,5,6)$, with M,I_1,I_2,I_3 being the mass and principal moments of inertia of the tracer; and $\overleftrightarrow{\zeta}_{ij}^0(i,j=1,2,\ldots,6)$, which turns out to be diagonal, are the friction coefficients coupling the random force $\mathbf{f}(t)$ and torque $\mathbf{T}(t)$, grouped in $\vec{\mathbf{f}}^0(t)$, with the generalized velocity $\vec{\mathbf{V}}(t)$. This friction tensor has the nonzero components $\zeta_{11}^0=\zeta_{22}^0=\zeta_{\perp}^0$, $\zeta_{33}^0=\zeta_{\|}^0,\zeta_{44}^0=\zeta_{55}^0=\zeta_R^0$, and $\zeta_{66}^0=0$. In Eq. (1), $\vec{\mathbf{F}}(t)$ is a fluctuating generalized force deriving from the spontaneous departures from zero of the net direct force exerted by the other particles on the tracer. It groups a random force and torque on the tracer with zero mean value and time-dependent correlation function given by $\langle\vec{\mathbf{F}}(t)\vec{\mathbf{F}}^\dagger(0)\rangle=k_BT\Delta\overleftrightarrow{\zeta}(t)$, where the time-dependent friction function is

$$\Delta\zeta_\gamma(t)=\beta\int d^3\mathbf{r}d^3\mathbf{r}'d\Omega d\Omega'[\nabla_\gamma\psi(\mathbf{r},\Omega)]C(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)\times[\nabla'_\gamma\psi(\mathbf{r}',\Omega')], \tag{2}$$

with $\beta=1/k_BT$.

The time-dependent memory function $\Delta\zeta_\gamma(t)$ contains the dissipative friction effects derived from the direct interactions of the tracer with the particles around it. This memory function defines the relaxation time $\tau_{\mathrm{I}}\gg\tau_B$ (τ_B is the relaxation time of the momenta of the particles) for the particles to diffuse a mean distance among them. Thus, in the diffusive regime $t\gg\tau_B$, long times mean $t\gg\tau_{\mathrm{I}}$. The generalized gradient operator is given by $\nabla_\gamma=(\nabla,\mathbf{r}\times\nabla+\nabla_\Omega)_\gamma$, where ∇_Ω is the angular gradient operator [14]. For axial symmetric potentials $\nabla_\Omega=\mathbf{n}\times d/d\mathbf{n}$, with $\mathbf{n}$ the unit Cartesian vector in the direction of the axis of symmetry of the particle. In Eq. (2), $C(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)\equiv\langle\delta n(\mathbf{r},\Omega;t)\delta n(\mathbf{r}',\Omega';0)\rangle$ is the Van Hove function of the fluctuations in the concentration of particles with respect to the equilibrium value $n(\mathbf{r},\Omega;t)$ and determines the relaxation modes of the tracer and of the cage of particles surrounding it. Its proper definition takes into account that it is referred to as the tracer position and orientation and has the initial condition value $C(t=0) = \langle \delta n(0)\delta n(0)\rangle \equiv \sigma$, i.e., the static correlation function, whose inverse σ^{-1} is defined by

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

Until now we have introduced no approximation in our theory. Therefore, Eq. (2) for $\Delta\zeta_\gamma(t)$ constitutes an exact result, and the most important one, of the GLE approach for the description of the effect on the translational and rotational diffusion of the tracer particle due to the direct interactions with the cloud of nonspherical particles that surround it. However, it is rather difficult to evaluate the precise description of the dynamical behavior of that surrounding cloud that is needed for this general expression of the friction coefficients. Thus, in order to apply the general results of Eqs. (1) and (2) we should introduce at this point the following approximations. First of all, we approximate the properties σ and $C(t)$ by their values far from the tracer particle, i.e., we introduce the homogeneity approximation. Then we also assume that $C(t)$ is given by the solution of the general linearized Fick diffusion equation

$$\frac{\partial C(\mathbf{r}-\mathbf{r}',\Omega,\Omega';t)}{\partial t} = -\rho[D^0\nabla^2+D_R^0\nabla_\Omega^2]\int dt'd^3\mathbf{r}''d\Omega'' \times\sigma^{-1}(\mathbf{r}-\mathbf{r}'',\Omega,\Omega'') \times C(\mathbf{r}''-\mathbf{r}',\Omega'',\Omega';t-t'), \tag{3}$$

where ρ is the bulk concentration of particles, whereas D^0 and D_R^0 are phenomenological parameters that should be provided by experiment or an external theory. Equation (3) governs the diffusive relaxation of $C(t)$, as described from the tracer's reference frame. In this manner, we have obtained a closed approximate expression for $\Delta\zeta_\gamma(t)$ in terms only of the static properties ψ,σ and of the phenomenological quantities D^0 and D_R^0.

Equation (3) can be solved for $C(t)$ with the use of the rotational invariant expansion useful for axialsymmetric particles [15]. In general, for any function $f(\mathbf{r},\Omega,\Omega')$, for example, $C(t)$ or σ, this expansion is given by

$$f(\mathbf{r},\Omega,\Omega') = (4\pi)^{3/2}\sum_{m,n,l}\frac{f^{mnl}(r)}{\sqrt{2l+1}}\sum_{\mu',\nu',\lambda'}\begin{pmatrix} m & n & l \\ \mu' & \nu' & \lambda' \end{pmatrix} \times Y_{m\mu'}(\Omega)Y_{n\nu'}(\Omega')Y_{l\lambda'}(\Omega_r), \tag{4}$$

where we have used the usual notation for the $3j$ symbols, the $Y_{l\lambda}$ are the spherical harmonics, and Ω_r is the angle of the orientation of the position vector $\mathbf{r}$. Using the Fourier and Laplace transforms, we can obtain an equivalent algebraic expression for Eq. (3), which reads

$$iwC_{,\chi}^{mn}(k,w)+C_{,\chi}^{mn}(k,0) = [D^0k^2+D_R^0m(m+1)]4\pi\rho(-1)^\chi\sum_{n_1}\ [\sigma^{-1}(k)]_{,\chi}^{mn_1} \times C_{,\chi}^{n_1n}(k,w), \tag{5}$$

where

$$f^{mnl}(k) = 4\pi i^l\int_0^\infty drr^2j_l(kr)f^{mnl}(r) \tag{6}$$

is the Fourier-Bessel transform, $j_l(x)$ being the spherical Bessel function of order l [16], and use was made of the definition

$$f_{,\chi}^{mn}(k) = \sum_{l=|m-n|}^{m+n}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} f^{mnl}(k) \tag{7}$$

plus the corresponding Laplace transformation

$$C_{,\chi}^{mn}(k,w) = \int_0^\infty dte^{iwt}C_{,\chi}^{mn}(k,t) \tag{8}$$

for the time dependence.

III. MODEL FERROFLUID AND STATIC STRUCTURE

In this section we describe the model ferrofluid system and the elementary parameters used to define it, i.e., the parameters that determine the static structural properties $\psi(\mathbf{r},\Omega,\Omega')$ and $h(\mathbf{r},\Omega,\Omega')$. Since

$$\sigma_{,\chi}^{mn}(k) = \rho S_{,\chi}^{mn}(k) = \rho[1+(-1)^\chi\rho h_{,\chi}^{mn}(k)],$$

those quantities provide all the information needed for the calculation of the dynamical friction functions $\Delta\zeta_\gamma(t)$.

Let us consider a suspension, with bulk concentration ρ, of identical spheres of diameter d with a permanent magnetic-dipolar moment $\vec{\mu}$ located at their centers. In this monodisperse suspension the nonspherical tracer particle is then identical to the others. Thus the pair interaction potentials between any two particles in the suspension separated by a distance $\mathbf{r}$ is given by

$$\psi(\mathbf{r},\Omega_1,\Omega_2) = \begin{cases} -\mu_s\mu^2D(\Omega_r,\Omega_1,\Omega_2)/r^3, & r>d \\ \infty, \quad r<d, \end{cases} \tag{9}$$

where μ_s is the permeability of the solvent and μ is the size of the magnetic-dipolar moment of each particle. The function

$$D(\Omega_r,\Omega_1,\Omega_2) = 3(\hat{\mathbf{r}}\cdot\mathbf{n}_1)(\hat{\mathbf{r}}\cdot\mathbf{n}_2)-(\mathbf{n}_1\cdot\mathbf{n}_2)$$

gives the angular dependence of this pair potential, where $r = |\mathbf{r}|$, $\hat{\mathbf{r}} = \mathbf{r}/r$ is the unitary vector with direction Ω_r, and $\hat{\mathbf{n}}_i = \vec{\mu}_i/\mu$ are the unitary vectors giving the dipolar orientation Ω_i of each particle. For $r<d$ there is a hard-core repulsion contribution to the pairwise potential that is radially symmetric and produces a component ψ^{000}, whereas for $r>d$ the only nonvanishing component corresponds to ψ^{112}.

As mentioned in Sec. II, in all that follows we will consider that the origin of our coordinate system resides on the center of mass of the tracer particle, with the z axis along the axis of symmetry of the tracer. Therefore, in Eq. (9) the pair potential $\psi(\mathbf{r},\Omega_1,\Omega_2)$ reduces to $\psi(\mathbf{r},\Omega)$. We will assume that in the absence of interactions among the Brownian dipolar particles, their diffusion is characterized by the coefficients D^0 and D_R^0 of their translational and rotational free diffusions. In this fashion, we have given all the fundamental parameters that define our model system, namely, d, μ, D^0, D_R^0, and ρ.

The following step consists in the determination of $\sigma(\mathbf{r},\Omega,\Omega')$ or, equivalently, $h(\mathbf{r},\Omega,\Omega')$. The calculation of these quantities is not a straightforward task. We can resort, however, to the solution given by Wertheim for the the pair-correlation function of a monodisperse dipolar liquid that is obtained in an approximate manner using the MSA of the theory of molecular and simple liquids [12]. According to this theory, the function $h(\mathbf{r},\Omega,\Omega')$ of dipolar particles can be written in terms of the known total correlation function of hard spheres $h_{\mathrm{HS}}(r)$ with renormalized densities and for which both explicit analytical and numerical calculations exist in the literature [17]. In this regard, we follow closely the article by Wertheim to obtain numerically the total distribution function of the dipolar system.

Using the spherical invariant expansion as given in Eq. (4), we obtain the Fourier transformed components $h^{mnl}(k)$. In determining these components we considered only the values of $(mnl)=(000),(110),(112)$, which form a complete base by themselves, in the sense defined by Wertheim, and have been proved to be enough to determine with high accuracy the structural and dynamical properties of ferrofluids [9,18]. For the model system considered here these static properties are completely determined by the dimensionless parameters $\mu^{*2}=\beta\mu_r\mu^2/d^3$ and $\phi=\pi\rho d^3/6$.

Shown in Fig. 1 are the characteristic features of the components of the total correlation function $h_s(k)=h^{000}(k)$ (solid line), $h_\Delta(k)=-h^{110}(k)/\sqrt{3}$ (dotted line), and $h_D(k)=h^{112}(k)/\sqrt{30}$ (dashed line), when plotted versus kd, k being the magnitude of the wave vector $\mathbf{k}$. These components were obtained with values of the volume fraction $\phi=0.05$ and the reduced dipolar strength $\mu^{*2}=2.2$, which are typical values of real ferrofluids.

The behavior of the model suspension was studied in a wider range of values $0\leqslant\phi\leqslant0.5$ and $0\leqslant\mu^{*2}\leqslant4.4$. Higher values of ϕ and μ^{*2} are known to lead to a phase transition in the dipolar fluid and at these values it is to be expected that the MSA fails to predict correctly the structural properties h and σ [13]. At present, experimental techniques provide information on the structural and dynamical properties of ferrofluids far from these extreme values of ϕ and μ, as shown in Ref. [9]. Thus our numerical results for the structural properties using the Wertheim decomposition in terms of h^{000}, h^{110}, and h^{112} are reliable and should be useful in the determination of the diffusion properties $\Delta\zeta_\gamma$.

IV. LONG-TIME SELF-DIFFUSION

In this section the general scheme presented in Sec. II is specialized to the model ferrofluid discussed in Sec. III. We also provide a discussion of the behavior of the resulting diffusion coefficients D_γ as a function of the parameters of the system.

Using the invariant expansion of Eq. (4) and the basis set $[mnl=(000),(110),(112)]$ that was used in the determination of the structural quantities, we obtain from Eq. (5) a closed expression for the $(11,\chi)$ components of the frequency-dependent collective diffusion propagator, which reads

$$C^{11}_{,\chi}(k,w)=\frac{C^{11}_{,\chi}(k,t=0)}{-iw+\rho4\pi(-)^{\chi}(D^0k^2+2D_R^0)[\sigma^{-1}(k)]^{11}_{,\chi}}, \tag{10}$$

with $\chi=0,\pm1$ and $i=\sqrt{-1}$. Rewriting the expression of $\Delta\zeta_\gamma$ in Eq. (2) in its Fourier transformed form and then using the Laplace transform of $C(t)$ in that expression, in combination with Eq. (10) and the definition given in Eq. (4), it is straightforward to obtain the corresponding expressions of $\Delta\zeta_\gamma(w)$. Thus the procedure explained just above allows us to determine the full frequency dependence of the dynamical friction functions $\Delta\zeta_\gamma(w)$. However, here we are interested in the static properties

$$\Delta\overleftrightarrow{\zeta}=\int_0^\infty dt\,\Delta\overleftrightarrow{\zeta}(t),$$

derived from the dynamical friction functions and obtained in the diffusive regime $t\gg\tau_{\mathrm{I}}$ or, equivalently, in the limit $w=0$. Thus the long-time translational friction reads

$$\Delta\zeta_\gamma(w=0)=\Delta\zeta^{\mathrm{HS}}+\Delta\zeta^p_\gamma \tag{11}$$

for $\gamma=\perp,\|$, where

$$\Delta\zeta^{\mathrm{HS}}=\frac{\zeta^0}{288\pi^2\phi}\int_0^\infty dx\,x^2[S^{00}_{,0}(x)-1]^2 \tag{12}$$

is the contribution from the hard-sphere core [2], whereas

$$\Delta\zeta^p_\perp=\frac{576}{5}\zeta^0\phi\mu^{*4}\int_0^\infty dx\,\frac{j_2(x)^2}{x^2+3/2}[2S^{11}_{,1}(x)^2+3S^{11}_{,0}(x)^2] \tag{13}$$

and

$$\Delta\zeta^p_\|=\frac{4}{3}\Delta\zeta^p_\perp \tag{14}$$

are the corresponding contributions from the dipole-dipole interactions. The parameter ζ^0 is the translational friction coefficient for a solid sphere in a fluid of viscosity η and is given by the Stokes formula $\zeta^0=6\pi\eta d$ [19]. In the same fashion, the long-time rotational friction gives

$$\Delta\zeta_R=\frac{48}{135}\zeta_R^0\phi\mu^{*4}\int_0^\infty dx\,\frac{j_1(x)^2}{x^2+3/2}[133S^{11}_{,1}(x)^2+164S^{11}_{,0}(x)^2], \tag{15}$$

where ζ_R^0 is the rotational friction coefficient for a spherical particle and is given by $\zeta_R^0=8\pi\eta d^3$ [19]. Details of the derivations of Eqs. (10), (13), and (15) will be given elsewhere.

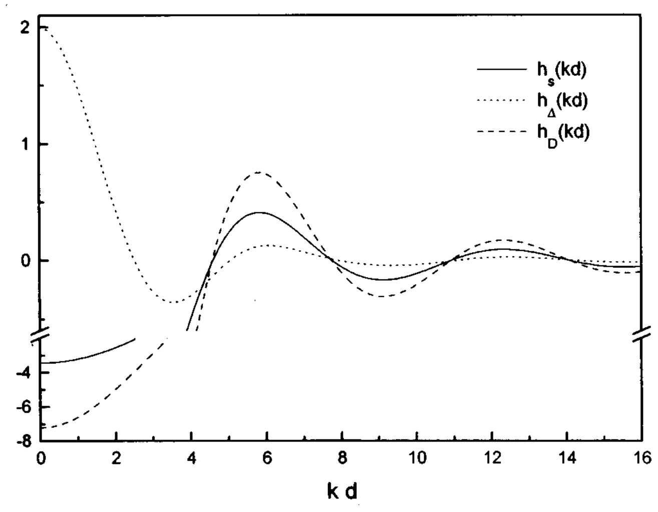

FIG. 1. Three components of the Fourier transform of the total correlation function h_s, h_Δ, and h_D plotted versus kd, for the volume fraction $\phi=0.05$, and reduced dipolar strength of $\mu^{*2}=2.2$, as given by the MSA.

Thus all the static structural information needed for the determination of these dynamical properties is contained in the components

$$S^{00}_{,0}(x)=1+\frac{6\phi}{\pi}h^{000}(x),$$

$$S^{11}_{,0}(x)=1-\frac{6\phi}{\pi}\left(\frac{1}{\sqrt{3}}h^{110}(x)-\frac{2}{\sqrt{30}}h^{112}(x)\right),$$

$$S^{11}_{,\pm 1}(x)=1-\frac{6\phi}{\pi}\left(\frac{1}{\sqrt{3}}h^{110}(x)+\frac{1}{\sqrt{30}}h^{112}(x)\right). \qquad (16)$$

In order to get a precise understanding of the behavior of the diffusion coefficients $D_\gamma/D^0_\gamma=(1+\Delta\zeta_\gamma/\zeta^0_\gamma)^{-1}$ ($\gamma=\|,\perp,R$, where $\zeta^0_\|=\zeta^0_\perp=\zeta^0$) predicted by the present theory, we will discuss their dependence on the parameters ϕ and μ^{*2}. In particular, let us focus on the average long-time translational $D=(2D_\perp+D_\|)/3$ and rotational D_R diffusion coefficients, which are the properties that can be experimentally observed.

In Figs. 2 and 3 we present the graphics of D/D^0 and D_R/D^0_R, respectively, as functions of dipolar strength μ^{*2}, for fixed concentrations $\phi=0.0005$ (dash-dotted line), $\phi=0.01$ (dotted line), $\phi=0.3$ (dashed line), and $\phi=0.5$ (solid line). As can be observed in these figures, the most noticeable effect of the dipolar interactions is the strong suppression of both the long-time translational and rotational diffusion processes, with respect to their corresponding hydrodynamic free-diffusion values $D^0=k_BT/\zeta^0$ and $D^0_R=k_BT/\zeta^0_R$.

It can also be observed in Fig. 2 that for $\mu^{*2}=0$ the values of the translational diffusion coefficient for sufficiently large concentrations are clearly lower than the free-diffusion value, which is to be expected since they correspond to the translational diffusion on a suspension of pure hard spheres at those concentrations, $D^{\rm HS}/D^0=1/(1+\Delta\zeta^{\rm HS}/\zeta^0)$. This illustrates the effect of the hard-sphere contribution $\Delta\zeta^{\rm HS}$ to the total friction on the tracer $\Delta\zeta_\gamma$ (for $\gamma=\|,\perp$) and signals that this term turns out to be more important at higher concentrations.

As the dipolar strength μ^{*2} is increased at a constant concentration ϕ both diffusion coefficients decrease monotonically, which is even more evident for concentrated suspensions. This last statement is more clearly illustrated in Figs. 4 and 5, where the same quantities D/D^0 and D_R/D^0_R, respectively, are presented as a function of the volume fraction ϕ for fixed dipolar strengths $\mu^{*2}=0.0$ (dash-dotted line), $\mu^{*2}=0.2$ (dotted line), $\mu^{*2}=1.0$ (dashed line), and $\mu^{*2}=2.2$ (solid line) and monotonically decreasing behavior is also exhibited.

In the absence of dipolar interactions [the dash-dotted lines at the top of Figs. 4 and 5], the only interaction among the particles, in particular between the tracer and the others, is due to the hard-sphere core. In this case, the translational friction is just the pure hard-sphere friction, i.e., $\Delta\zeta_\perp=\Delta\zeta_\|=\Delta\zeta^{\rm HS}$, and the rotational friction is just, as expected, $\Delta\zeta_R=0$. Therefore, those dotted lines in the last two figures represent the dependence on the concentration of the translational and rotational diffusion coefficients of a suspension of hard spheres, $D^{\rm HS}$ and $D^{\rm HS}_R=D^0_R$, respectively. Thus the dipolar interactions among the colloidal particles of a ferrofluid have the effect of strongly restraining the translational and rotational Brownian movement of the particles even in comparison to the hard-core interaction. As a consequence, the experimental measurement of this effect should be quite feasible and the coefficients D and D_R are sensible properties to be observed in order to characterize the ferrofluids in terms of their magnetic-dipolar interactions and concentrations.

Some general comments are in order concerning Eqs. (10) and (13)–(15), which are the main results of our theory. It is clear that the main advantage of using the MSA in the determination of the structural quantities h^{mnl} was the convenience of allowing us to truncate the infinite invariant expansions of Eqs. (4) and (5) by taking only three terms that embody all the thermodynamic information of the system. With the help of this approximation in the structural quantities, it was then possible to obtain simple quadratures for the collective diffusion propagator [Eq. (10)] and of the long-time diffusion coefficients [Eqs. (13)–(15)]. The theoretical scheme exposed here is then the simplest nontrivial approach to the determination of these self-diffusion properties in ferrocolloids.

V. SUMMARY

In this work we have applied of the generalized Langevin equation approach to the description of the tracer diffusion of a nonspherical axial symmetric tracer in a suspension of other *nonspherical* but axial symmetric particles. For this generic system we considered a model ferrofluid of identical spherical particles with a point magnetic dipole at their centers. The long-time translational D and rotational D_R diffusion coefficients of the tracer were determined, taking into account its direct dipolar interactions with the other particles in the suspension.

We started in Sec. II by reviewing the results of the GLE

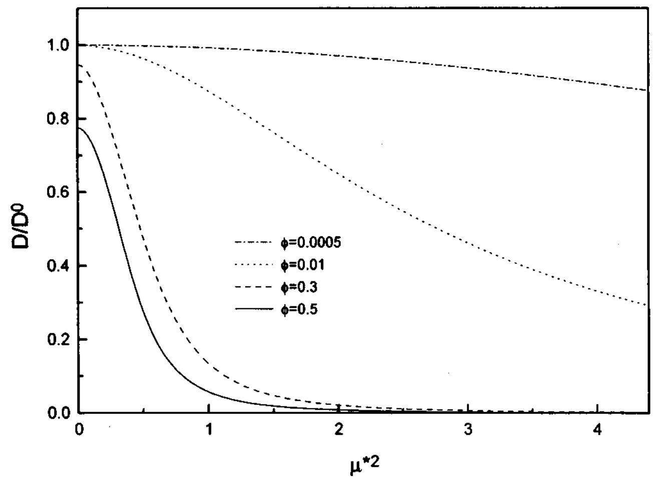

FIG. 2. Ratio D/D^0 of the translational self-diffusion coefficient of the center of mass to its hydrodynamic value, as a function of the dimensionless dipolar strengh μ^{*2}, for fixed volume fractions $\phi=0.0005$ (dash-dotted line), $\phi=0.01$ (dotted line), $\phi=0.3$ (dashed line), and $\phi=0.5$ (solid line).

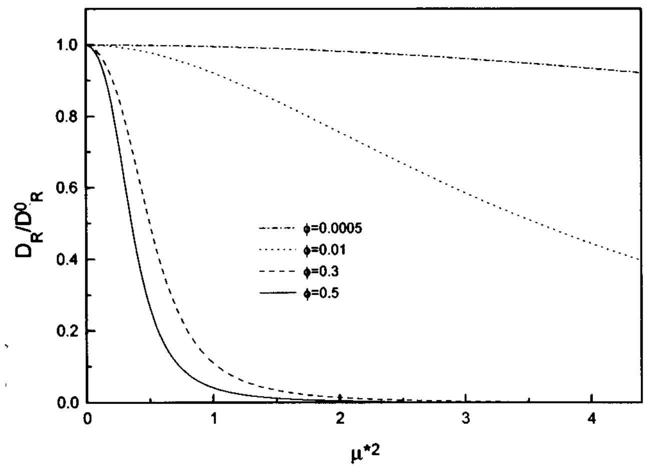

FIG. 3. Ratio D_R/D_R^0 of the rotational self-diffusion coefficient of the tracer to its hydrodynamic value, as a function of μ^{*2}, for the same values of ϕ of Fig. 2.

theory as concerned the general and exact expressions of the time-dependent friction contributions on the tracer $\Delta\zeta_\gamma(t)(\gamma=\|,\perp,R)$ due to its direct interactions with the other particles diffusing around it [Eq. (2)]. These dynamical properties were written in terms of the pairwise interaction potential $\psi(\mathbf{r},\Omega,\Omega')$ and the time-dependent collective diffusion propagator $C(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)$.

In order to be able to use those results in a specific application we needed first to determine the precise form of the, until then unknown, relaxation process $C(t)$. For this purpose, we introduced, as in previous work [5], the most simple approximation, namely, the Fick diffusion equation (3) that governs the time dependence of $C(t)$. Then the homogeneity approximation was employed to reduce the three-body static correlation function $\sigma(\mathbf{r},\mathbf{r}',\Omega,\Omega')$ that appears in the diffusion equation to a two-body property $\sigma(\mathbf{r}-\mathbf{r}',\Omega,\Omega')$, which could be calculated approximately for the specified model system by means of the statistical mechanics theory of molecular and simple liquids. Thereafter, due to the axial symmetry of the interaction, we used an auxiliary technique given by an invariant expansion of all functions of the form $f(\mathbf{r},\Omega,\Omega')$, in terms of the spherical harmonics. This infinite but otherwise convergent expansion allowed us to rewrite in an equivalent manner the dynamical equation of $C(t)$, i.e., Eq. (5). Thus our problem was reduced to the calculation of the components $C^{mn}_{,\chi}(k,w)$ of the propagator in terms of the components $[\sigma^{-1}(k)]^{mn}_{,\chi}$, as given by that equation.

In Sec. IV even simpler expressions were derived for the components $C^{11}_{,\chi}(k,w)$, using the minimal basis set $(mnl)=(000)$, (110), and (112) [Eq. (10)]. It was then a simple procedure to introduce those components into the Fourier-transformed version of Eq. (2) in order to get the final expressions of the friction contributions $\Delta\zeta_\gamma(w)$. These results are then ready to be used in any application of the generic system referred to above, namely, a monodisperse Brownian liquid of nonspherical but axial symmetric particles. The specific forms of those expressions in the diffusive regime $w=0$ are given in Eqs. (13)–(15).

In Sec. III we defined our model ferrofluid suspension, which is completely characterized by the dimensionless volume fraction $\phi=\pi\rho d^3/6$ and magnetic-dipolar strength $\mu^{*2}=\beta\mu_r\mu^2/d^3$. We used the mean spherical approximation for the description of the structural properties of this model system. The MSA allows the determination of the components of the total correlation function $h^{mnl}(k)$ precisely for the minimal basis set (000),(110),(112). In this section we showed typical plots of the components $h^{mnl}(k)$. At the different ranges of parameter values studied here we found that there is no anomalous behavior on these static quantities that could imply a serious failure of the MSA. These ranges of values of ϕ and μ^{*2} were in fact selected in correspondence with the values measured for these parameters in most of the experimental studies on ferrofluids [8] and also correspond to the typical values considered in the theoretical counterparts [9,18].

The approximate expressions of the components of the

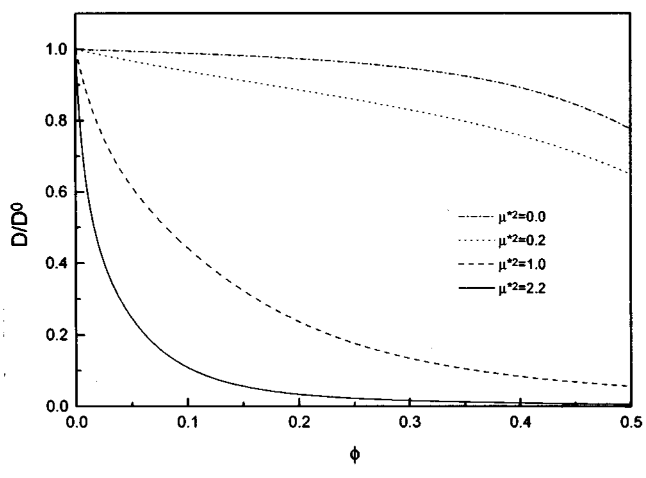

FIG. 4. Ratio D/D^0 as a function of ϕ, for fixed dipolar strengths $\mu^{*2}=0.0$ (dash-dotted line), $\mu^{*2}=0.2$ (dotted line), $\mu^{*2}=1.0$ (dashed line), and $\mu^{*2}=2.2$ (solid line).

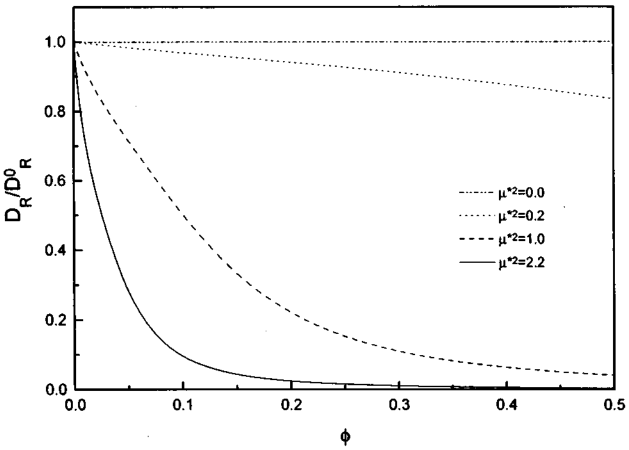

FIG. 5. Ratio D_R/D_R^0 as a function of ϕ, for the same values of μ^{*2} as in Fig. 4.

translational static friction of the tracer $\Delta\zeta_{\parallel}$ and $\Delta\zeta_{\perp}$ and of the rotational static friction $\Delta\zeta_R$ valid for this model system, are given by Eqs. (11)–(15). These equations constitute our most important results since they provide the friction contribution, in the diffusive regime, to the diffusion coefficient $D_\gamma = k_B T/(\zeta_\gamma^0 + \Delta\zeta_\gamma)(\gamma = \parallel, \perp, R)$ of a nonspherical tracer in a monodisperse Brownian suspension of nonspherical particles.

In Sec. IV we also presented the results obtained from the theoretical scheme presented here. The main conclusion derived from this study is that both the long-time translational and rotational diffusion coefficients D and D_R, respectively, are strongly suppressed with respect to the corresponding hydrodynamic free-diffusion values D^0 and D_R^0 when the dipolar strength is increased at a constant concentration. This effect is even more evident when the suspension becomes more concentrated.

Concerning the accuracy of our method in calculating these properties, let us note that in the present work we used the same general approximations as has been done in the previous version of this theory when applied to describe the same properties for spherically symmetric interactions. In that case the theory has been shown to give a precise prediction for these diffusion properties compared to experiments on real suspensions of polystyrene particles and where hydrodynamic interactions where included by renormalizing the short-time coefficient of the tracer in the suspension, such that its value departs from that corresponding to the infinitely dilute case [2]. Reliable structural properties where included for the short-range pairwise interaction as provided by the Percus-Yevick theory. Let us point out the differences of the present work from the case explained just above. In this respect we would like to say that here we have not included the renormalized value of the short-time diffusion coefficient of the dipolar tracer. Its precise value should be provided by an external theory or experiment. Instead, use has been made of the analytical short-time coefficient of a neutral spherical tracer [19]. The other concern in our approximations is related to the determination of the microstructural properties. This was assessed with the MSA theory for the long-range dipolar interaction, which should be useful for low-concentration suspensions. Therefore, we expect only a qualitative accuracy of our predictions for the tracer diffusion properties when compared to real experiments and computer simulations.

However, we believe that the insights provided by these results might be useful in the understanding of the long-time self-diffusion in real ferrofluids. Our results can also be applied to the study of the same diffusion properties on electrorheological fluids. These results are also easy to generalize to the important situation in which several species of ferroparticles are present.

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