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Transport properties of ferrofluids

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Long-time self-diffusion coefficients of ferrofluid suspensions are derived from an effective Langevin equation approach. The dependences of these transport properties on the volume fraction of particles and the strength of interparticle interaction are investigated. Strong reduction of the rotational and the translational Brownian motion of the particles is manifested upon increase of particle-particle interaction or ferrofluid concentration.

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I. INTRODUCTION

This paper is concerned with the transport properties of magnetic fluids at thermodynamic equilibrium [1–4]. The long-time self-diffusion in ferrofluids is a subject of long standing interest [5]. The long-time self-diffusion manifests itself in standard x-ray, neutron, and depolarized light-scattering measurements which allow one to detect the translational and rotational diffusion of a particle in a concentrated suspension [6,7]. Ferrofluids are colloidal suspensions of magnetic particles dispersed in a host liquid. These complex fluids display important material properties that can be used as rheological probes to investigate local properties of a medium [8].

Here we provide an approach to derive general expressions of the rotational and translational diffusion coefficients D_R and D, respectively, in ferrofluids. Since these dynamical properties are dependent on the bulk microstructure of the suspension, we determined accurately the local structure of the magnetic liquid using both the mean spherical (MSA) and the linearized hypernetted chain (LHNC) liquid theory approximations. Explicit results are provided illustrating the behavior of the rotational diffusion coefficient in the experimentally accessible long-time limit as a function of the particle's strength of interaction and concentration. It is shown that an increase of interparticle interactions, or concentration, has the effect of suppressing substantially the rotational (translational) Brownian movement of the particles.

II. THEORY

The Langevin equations to describe the translational and the rotational Brownian motion of a tracer ferrocolloid particle that interacts through an axially symmetric pair potential with the surrounding particles are given as

$$\mathrm{M}\frac{d\mathbf{V}(t)}{dt}=-\zeta^0\cdot\mathbf{V}(t)-\zeta^0_{\mathrm{TR}}\cdot\mathbf{W}(t)+\mathbf{f}^0(t)+\mathbf{F}_{\mathrm{tot}}(t),$$

$$\mathbf{I}\cdot\frac{d\mathbf{W}(t)}{dt}=-\zeta^0_{\mathrm{RT}}\cdot\mathbf{W}(t)-\zeta^0\cdot\mathbf{V}(t)+\mathbf{t}^0(t)+\mathbf{T}_{\mathrm{tot}}(t). \quad (1)$$

$\mathbf{V}(t)$ and $\mathbf{W}(t)$ are the linear and angular velocities of the tracer whose components are referred to a space fixed frame with origin at the particle's center of mass, and frame axis following the orientation of the tracer's main axis of symmetry. M and $\mathbf{I}$ are the mass and particle's matrix of moment of inertia, respectively. We shall not treat the case with added hydrodynamic interactions among particles. The diagonal friction tensors of free particle, ζ^0, ζ^0_{TR}, ζ^0_{RT}, and ζ^0_{R}, produce hydrodynamic drag forces and torques linear on the velocities that couple to the thermally driven solvent random forces $\mathbf{f}^0$ and torques $\mathbf{t}^0$ on the tracer. They are related by fluctuation-dissipation theorems

$$\langle\mathbf{f}^0(t)\mathbf{f}^{0\dagger}(0)\rangle=k_BT\zeta^0 2\,\delta(t),\quad \langle\mathbf{f}^0(t)\mathbf{t}^{0\dagger}(0)\rangle=k_BT\zeta^0_{\mathrm{TR}}2\,\delta(t),$$

$$\langle\mathbf{t}^0(t)\mathbf{f}^{0\dagger}(0)\rangle=k_BT\zeta^0_{\mathrm{RT}}2\,\delta(t),\quad \langle\mathbf{t}^0(t)\mathbf{t}^{0\dagger}(0)\rangle=k_BT\zeta^0_{\mathrm{R}}2\,\delta(t). \quad (2)$$

For pairwise interaction energy, the total force $\mathbf{F}_{\mathrm{tot}}$ and torque $\mathbf{T}_{\mathrm{tot}}$ on the tracer exerted by the instantaneous local concentration $n(\mathbf{r},\Omega,t)=\Sigma_{i=1}^N\delta(\mathbf{r}-\mathbf{r}^i(t))\,\delta(\Omega-\Omega^i(t))$ of the host suspension of N particles are given by

$$\mathbf{F}_{\mathrm{tot}}(t)=\int d\mathbf{r}d\Omega[\boldsymbol{\nabla}\psi(\mathbf{r},\Omega)]n(\mathbf{r},\Omega,t),$$

$$\mathbf{T}_{\mathrm{tot}}(t)=\int d\mathbf{r}d\Omega[\mathbf{r}\times\boldsymbol{\nabla}\psi(\mathbf{r},\Omega)+\boldsymbol{\nabla}_\Omega\psi(\mathbf{r},\Omega)]n(\mathbf{r},\Omega,t), \quad (3)$$

with $\Omega=(\theta,\varphi)$ and θ,φ being the polar angles, $\psi(\mathbf{r},\Omega,\Omega')$ the pair potential, and $\boldsymbol{\nabla}_\Omega=\hat{\mathbf{n}}\times\partial/\partial\hat{\mathbf{n}}$ the angular gradient operator. It is to be noted that the tracer's dipole is located along the Z direction of the frame, that is, $\Omega'=(0,0)$. The unitary Cartesian vector $\hat{\mathbf{n}}$ is in the direction of the particle's axis of symmetry.

Both Langevin equations can be written compactly as

$$\overleftrightarrow{\mathbf{M}}\cdot\frac{d\overleftrightarrow{\mathbf{V}}(t)}{dt}=-\overleftrightarrow{\zeta}^{0}\cdot\overleftrightarrow{\mathbf{V}}(t)+\overleftrightarrow{\mathbf{f}}^{0}(t)+\int d\mathbf{r}d\Omega[\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)]n(\mathbf{r},\Omega;t), \qquad (4)$$

where $\overleftrightarrow{\boldsymbol{\nabla}}=(\boldsymbol{\nabla},\boldsymbol{\nabla}_{\Omega})$, the generalized velocity $\overleftrightarrow{\mathbf{V}}=(\mathbf{V},\mathbf{W})$, $\overleftrightarrow{\mathbf{M}}_{ij}=M\delta_{ij}$ $(i,j=1,2,3)$, $\overleftrightarrow{\mathbf{M}}_{ij}=\delta_{ij}I_{i-3}$ $(i,j=4,5,6)$, with I_1,I_2, and I_3 being the principal moments of inertia of the tracer. The friction tensor $\overleftrightarrow{\zeta}^0$ has the nonzero components $\zeta^0_{11}=\zeta^0_{22}=\zeta^0_{\perp}$, $\zeta^0_{33}=\zeta^0_{\parallel}$, $\zeta^0_{44}=\zeta^0_{55}=\zeta^0_{\mathrm{R}}$, and $\zeta^0_{66}=0$. These short-time friction components are assumed to be provided by experiment or an external theory. Up to first order in concentration fluctuations $\delta n(\mathbf{r},\Omega;t)=n(\mathbf{r},\Omega;t)-n^{eq}(\mathbf{r},\Omega)$, with $n^{eq}(\mathbf{r},\Omega)=\langle n(\mathbf{r},\Omega,t)\rangle$ the equilibrium ensemble average, therefore the Langevin equation can be written as

$$\overleftrightarrow{\mathbf{M}}\cdot\frac{d\overleftrightarrow{\mathbf{V}}(t)}{dt}=-\overleftrightarrow{\zeta}^{0}\cdot\overleftrightarrow{\mathbf{V}}(t)+\overleftrightarrow{\mathbf{f}}^{0}(t)+\int d\mathbf{r}d\Omega[\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)]\delta n(\mathbf{r},\Omega;t), \qquad (5)$$

where $n^{eq}(\mathbf{r},\Omega)$ does not contribute to the total force and torque. A stochastic evolution equation for $\delta n(t)$ is obtained from general arguments of linear irreversible theory of fluctuations [9]

$$\begin{aligned}\frac{\partial\delta n(\mathbf{r},\Omega,t)}{\partial t}=&[\overleftrightarrow{\boldsymbol{\nabla}}n^{eq}(\mathbf{r},\Omega)]\cdot\overleftrightarrow{\mathbf{V}}(t)-\int_0^t dt'\int d\mathbf{r}'d\Omega'\\&\times\int d\mathbf{r}''d\Omega''L(\mathbf{r},\mathbf{r}',\Omega,\Omega';t-t')\\&\times\sigma^{-1}(\mathbf{r}',\mathbf{r}'',\Omega',\Omega'')\delta n(\mathbf{r}'',\Omega'';t')\\&+\overleftrightarrow{\boldsymbol{\nabla}}\cdot\mathbf{j}(\mathbf{r},\Omega;t),\end{aligned} \qquad (6)$$

with $\langle\overleftrightarrow{\boldsymbol{\nabla}}\cdot\mathbf{j}(\mathbf{r},\Omega;t)\overleftrightarrow{\boldsymbol{\nabla}}\cdot\mathbf{j}^{\dagger}(\mathbf{r}',\Omega';0)\rangle\equiv L(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)$ and $\overleftrightarrow{\boldsymbol{\nabla}}\cdot\mathbf{j}(t)$ a random diffusive flux. Its general solution is given by

$$\begin{aligned}\delta n(\mathbf{r},\Omega,t)=&\int d\mathbf{r}'d\Omega'\chi(\mathbf{r}',\Omega';t)\delta n(\mathbf{r},\Omega;0)\\&+\int_0^t dt'\int d\mathbf{r}'d\Omega'\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t-t')\\&\times[\overleftrightarrow{\boldsymbol{\nabla}}n^{eq}(\mathbf{r}',\Omega')]\cdot\overleftrightarrow{\mathbf{V}}(t')\\&+\int_0^t dt'\int d\mathbf{r}'d\Omega'\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t-t')\\&\times[-\overleftrightarrow{\boldsymbol{\nabla}}'\cdot\mathbf{j}(\mathbf{r}',\Omega';t')].\end{aligned} \qquad (7)$$

The collective diffusion propagator $\chi(t)$ satisfies

$$\begin{aligned}\frac{\partial\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)}{\partial t}=&-\int_0^t dt'\int d\mathbf{r}''d\Omega''d\mathbf{r}'''d\Omega'''\\&\times L(\mathbf{r},\mathbf{r}',\Omega,\Omega';t-t')\\&\times\sigma^{-1}(\mathbf{r}',\mathbf{r}'',\Omega',\Omega'')\\&\times\chi(\mathbf{r}'',\mathbf{r}''',\Omega'',\Omega''';t'),\end{aligned} \qquad (8)$$

with initial condition $\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t=0)=\delta(\mathbf{r}-\mathbf{r}')\delta(\Omega-\Omega')$. This equation can be converted into a dynamical equation for the Van Hove function of fluctuations in the concentration of particles with respect to the equilibrium value

$$\begin{aligned}n^{eq}(\mathbf{r},\Omega)&:C(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)\\&=\int d\mathbf{r}''d\Omega''\chi(\mathbf{r},\mathbf{r}'',\Omega,\Omega'';t)''\sigma(\mathbf{r}'',\mathbf{r}',\Omega'',\Omega')\\&\equiv\langle\delta n(\mathbf{r}',\Omega';0)\delta n(\mathbf{r}',\Omega';t)\rangle,\end{aligned}$$

which determines the relaxation modes of the tracer and of the cage of particles surrounding it. Its initial condition $\sigma=C(t=0)=\langle\delta n(0)\delta n(0)\rangle$ is the inhomogeneous static correlation function with inverse defined through

$$\begin{aligned}&\int d\mathbf{r}''d\Omega''\sigma(\mathbf{r},\mathbf{r}'',\Omega,\Omega'')''\sigma^{-1}(\mathbf{r}'',\mathbf{r}',\Omega'',\Omega')\\&\quad=\delta(\mathbf{r}-\mathbf{r}')\delta(\Omega-\Omega').\end{aligned} \qquad (9)$$

Substituting the above solution for $\delta n(t)$ in the Langevin equation leads to

$$\begin{aligned}\overleftrightarrow{\mathbf{M}}\cdot\frac{d\overleftrightarrow{\mathbf{V}}(t)}{dt}=&-\overleftrightarrow{\zeta}^{0}\cdot\overleftrightarrow{\mathbf{V}}(t)+\overleftrightarrow{\mathbf{f}}^{0}(t)\\&-\int_0^t dt'\Delta\overleftrightarrow{\zeta}(t-t')\cdot\overleftrightarrow{\mathbf{V}}(t')+\overleftrightarrow{\mathbf{F}}(t),\end{aligned} \qquad (10)$$

where

$$\begin{aligned}\overleftrightarrow{\mathbf{F}}(t)=&+\int d\mathbf{r}d\Omega[\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)]\\&\times\int d\mathbf{r}'d\Omega'\chi(\mathbf{r}',\Omega';t)\delta n(\mathbf{r}',\Omega';0)\\&+\int d\mathbf{r}'d\Omega'\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t-t')\\&\times[-\overleftrightarrow{\boldsymbol{\nabla}}'\cdot\mathbf{j}(\mathbf{r}',\Omega';t')],\end{aligned} \qquad (11)$$

is a fluctuating generalized force arising from the spontaneous departures from zero of the net direct forces 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 $\langle\overleftrightarrow{\mathbf{F}}(t)\overleftrightarrow{\mathbf{F}}^{\dagger}(0)\rangle=k_{\mathrm{B}}T\Delta\overleftrightarrow{\zeta}(t)$, and the time-dependent friction function is

$$\Delta\overleftrightarrow{\zeta}(t)=-\int d\mathbf{r}d\mathbf{r}'d\Omega d\Omega'[\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)]\chi(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)\times[\overleftrightarrow{\boldsymbol{\nabla}}'n^{eq}(\mathbf{r}',\Omega')]. \tag{12}$$

Using Wertheim-Lovett's relation [10]

$$\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)=-k_BT\int d\mathbf{r}''d\Omega''\sigma^{-1}(\mathbf{r},\mathbf{r}'',\Omega,\Omega'')\times[\overleftrightarrow{\boldsymbol{\nabla}}''n^{eq}(\mathbf{r}'',\Omega'')], \tag{13}$$

still another expression for the dynamical friction function $\Delta\overleftrightarrow{\zeta}(t)$ is obtained,

$$\begin{aligned}\Delta\overleftrightarrow{\zeta}(t)&=k_BT\int d\mathbf{r}d\mathbf{r}'d\mathbf{r}''d\Omega d\Omega'd\Omega''[\overleftrightarrow{\boldsymbol{\nabla}}n^{eq}(\mathbf{r},\Omega)]\\&\quad\times\sigma^{-1}(\mathbf{r},\mathbf{r}',\Omega,\Omega')\chi(\mathbf{r}',\mathbf{r}'',\Omega',\Omega'';t)\\&\quad\times[\overleftrightarrow{\boldsymbol{\nabla}}''n^{eq}(\mathbf{r}'',\Omega'')]\\&=\beta\int d\mathbf{r}d\mathbf{r}'d\Omega d\Omega'[\overleftrightarrow{\boldsymbol{\nabla}}\psi(\mathbf{r},\Omega)]C(\mathbf{r},\mathbf{r}',\Omega,\Omega';t)\\&\quad\times[\overleftrightarrow{\boldsymbol{\nabla}}'\psi(\mathbf{r}',\Omega')],\end{aligned} \tag{14}$$

with $\beta=1/k_\mathrm{B}T$ and $C=\chi\bigcirc\sigma$, $\bigcirc\equiv\int d\mathbf{r}d\Omega$.

The time-dependent memory function $\Delta\overleftrightarrow{\zeta}(t)$ 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 $\tau_\mathrm{I}\gg\tau_\mathrm{B}$ (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 $t\gg\tau_\mathrm{B}$, long times mean $t\gg\tau_\mathrm{I}$.

This is a general expression for the friction contribution on the tracer due to direct interactions with the particles about it. It depends on the microstructural inhomogeneous total correlation function $h(\mathbf{r},\Omega)=n^{eq}(\mathbf{r},\Omega)/\rho-1$ of the host suspension of N particles at concentration ρ, and of the free friction constants $\overleftrightarrow{\zeta}^0$ through $\chi(t)$. We now introduce the homogeneity approximation which amounts to ignoring the tracer's field on the properties σ, $\chi(t)$, or equivalently on $C(t)$, which then can be determined in the bulk solution. Thus, $\sigma(\mathbf{r},\mathbf{r}',\Omega,\Omega')\approx\sigma(r=|\mathbf{r}-\mathbf{r}'|,\Omega,\Omega',\Omega_{|\mathbf{r}-\mathbf{r}'|})$. It as also adopted Fick's diffusion approximation for $\chi(t)=\exp(-tL\bigcirc\sigma^{-1})$, with $L(r-r',\Omega,\Omega',\Omega_{r-r'})=\rho[D^{*0}\boldsymbol{\nabla}^2+D_R^{*0}\boldsymbol{\nabla}_\Omega^2]\delta(\mathbf{r}-\mathbf{r}')\delta(\Omega-\Omega')$. In this approximation $D^{*0}=D^0+D^0_{other}$ and $D_R^{*0}=D_R^0+D^0_{R,other}$ (the case $D^0_{\gamma,other}\ll D^0_\gamma$, $\gamma=\parallel,\perp,R$ was made in Refs. [11,12]). The short-time diffusion coefficients $D^0_{other}=D^0$ and $D^0_{R,other}=D^0_R$ of the other particles are approximated by those of the tracer, and $D^0=k_BT/\zeta^0$ and $D^0_R=k_BT/\zeta^0_R$. For spherical solid particles, $\zeta^0=6\pi\eta d$, where η is the viscosity of the pure solvent, d is the diameter of the Brownian particle, and $\zeta^0_R=8\pi\eta d^3$.

Using the above approximation for $\chi(t)$ and $C=\chi\bigcirc\sigma$, Eq. (8) can be written as

$$\begin{aligned}\frac{\partial C(r,\Omega,\Omega',\Omega_\mathbf{r};t)}{\partial t}&=-\rho[D^{*0}\boldsymbol{\nabla}^2+D^{*0}_\mathrm{R}\boldsymbol{\nabla}^2_\Omega]\\&\quad\times\int dt'd\mathbf{r}''d\Omega''\\&\quad\times\sigma^{-1}(r-r'',\Omega,\Omega'',\Omega_{\mathbf{r}-\mathbf{r}''})\\&\quad\times C(r''-r',\Omega'',\Omega',\Omega_{\mathbf{r}''-\mathbf{r}'};t-t').\end{aligned} \tag{15}$$

This last equation 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 $\Delta\overleftrightarrow{\zeta}(t)$ in terms of only the static properties ψ, σ, and of the phenomenological quantities D^0 and D^0_R. This expression will be used in Sec. IV for the calculation of the diffusion coefficients.

III. FERROFLUID MICROSTRUCTURE

We consider the ferrocolloid to be formed by a homogeneous and monodisperse suspension of same-size particles with magnetic moment of strength μ. The pair potential interaction is $\psi(\mathbf{r},\Omega_1,\Omega_2)=u_\mathrm{HS}-(\mu^2/r^3)D(\Omega_1,\Omega_2,\Omega_r)$. For $r<d$ there is a hard core repulsion interaction u_HS of hard sphere (HS) that is radially symmetric and $D(\Omega_1,\Omega_2,\Omega_r)=3(\hat{\mathbf{r}}\cdot\hat{\mathbf{n}}_1)(\hat{\mathbf{r}}\cdot\hat{\mathbf{n}}_2)-(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)$, where $r=|\mathbf{r}|$, $\hat{\mathbf{r}}=\mathbf{r}/r$ is the unitary vector with direction Ω_r and $\hat{\mathbf{n}}=\boldsymbol{\mu}/\mu$ is a unitary vector giving the dipolar orientation Ω of a particle.

Due to the symmetries of the dipole interaction we use Blum's expansion of functions $f=\sigma$, h, or $C(t)$ in rotational invariants with respect to a space fixed frame [13],

$$\begin{aligned}f(\mathbf{r},\Omega,\Omega')&=(4\pi)^{3/2}\sum_{mnl}\frac{f^{mnl}(r)}{\sqrt{2l+1}}\sum_{\mu\nu\lambda}\begin{pmatrix}m&n&l\\\mu&\nu&\lambda\end{pmatrix}\\&\quad\times Y_{m\mu}(\Omega)Y_{n\nu}(\Omega')Y_{l\lambda}(\Omega_r)\\&=\sum_{mnl}f^{mnl}(r)\Phi^{mnl},\end{aligned} \tag{16}$$

where we have used the $3j$ symbols, and $Y_{l\lambda}$ are the spherical harmonics. We note that in this representation the pair dipole interaction is given as $\psi=u_{HS}\Phi^{000}-(\mu^2/r^3)\sqrt{\frac{10}{3}}\Phi^{112}$, where

$$\psi^{mnl}(r)=\delta_{l,m+n}\left[\frac{(2l+1)!}{(2m+1)!(2n+1)!}\right]^{1/2}\mu^m\mu^n,$$

$$mnl=112, \tag{17}$$

with $D=\sqrt{\frac{10}{3}}\Phi^{112}$, $\Phi^{000}=1$. Also $(\mathbf{n}_1\cdot\mathbf{n}_2)=-\Phi^{110}/\sqrt{3}\equiv\Delta$. For a homogeneous monodisperse dipolar suspension, liquid theory allows one to obtain h within MSA, valid at low concentration or dipole strength [14],

$$h(r,\Omega_1,\Omega_2,\Omega_r)=-1, \quad r<d,$$

$$c(r,\Omega_1,\Omega_2,\Omega_r)=-\frac{\mu^2}{k_BTr^3}D, \quad r\geqq d. \tag{18}$$

For all r, the direct correlation function c is related to h through the Ornstein-Zernike (OZ) equation [10]

$$h(\mathbf{r},\Omega_1,\Omega_2)=c(\mathbf{r},\Omega_1,\Omega_2)+\rho\int d\mathbf{r}'d\Omega' \times c(\mathbf{r}-\mathbf{r}',\Omega_1,\Omega')h(\mathbf{r}-\mathbf{r}',\Omega',\Omega_2). \tag{19}$$

The solution to this integral equation for h and c, uses Eq. (18) and is given in Wertheim's Cartesian invariant expansion form with respect to a space fixed frame as

$$h(r,\Omega_1,\Omega_2,\Omega_r)=h_s(r)+h_\Delta(r)\Delta+h_D(r)D, \tag{20}$$

where h_s, h_Δ, and h_D are known functions given in Ref. [15]. This expansion is equivalent to Eq. (16) when the minimal basis set $mnl=000$, 110, 112 [13]. Their relationship is given by $h_s=h^{000}$, $h_\Delta=-\sqrt{3}h^{110}$ and $h_D=\sqrt{3/10}h^{112}$ [16]. At higher values of ρ and dipole moment μ, one needs to resort to a more precise solution of the Ornstein-Zernike equations as that given by the more accurate LHNC approximation defined as [14]

$$c_s(r)=h_s-\ln(h_s+1)-\frac{u_{HS}}{k_BT},$$

$$c_\Delta(r)=h_\Delta[1-1/(h_s+1)],$$

$$c_D(r)=\frac{\mu^2}{k_BTr^3}+b_D,$$

$$=\hat{c}_D(r)-\frac{3}{r^3}\int_0^r\hat{c}_D(s)s^2ds,$$

$$\hat{c}_D(r)=b_D(r)-3\int_r^\infty\frac{b_D(s)}{s}ds,$$

$$b_D(r)=h_D[1-1/(h_s+1)], \quad r\geqq d,$$

$$h_s(r)=-1, \quad r<d,$$

$$h_D(r)=h_\Delta(r)=0, \quad r<d,$$

$$\hat{c}_D(r)=-3\int_R^\infty\frac{h_D(s)}{s}ds, \quad r<d. \tag{21}$$

Using Blum's expansion and Fourier transform (Appendix A), the structure factor $S=\sigma/\rho$ and h are related by

$$\sigma^{mn}_{,\chi}(k)=\rho S^{mn}_{,\chi}(k)=\rho[1+(-1)^\chi h^{mn}_{,\chi}(k)], \tag{22}$$

where the definition that transforms quantities to an intermolecular frame was used, where the Z axis is along the vector $\mathbf{r}$ joining the centers of two particles,

$$f^{mn}_{,\chi}(k)=\sum_{l=|m-n|}^{m+n}\begin{pmatrix} m & n & l \\ \chi & -\chi & 0\end{pmatrix}f^{mnl}(k). \tag{23}$$

With the help of Eqs. (22), (23), and (B4) we obtain the structure factor of a hard sphere liquid, and the longitudinal $S^{11}_{,0}(k)$ and transverse $S^{11}_{,\pm1}(k)$ structure factors of the dipolar liquid,

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

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

$$S^{11}_{,\pm1}(k)=1-\frac{6\phi}{\pi}\left(\frac{1}{\sqrt{3}}h^{110}(k)+\frac{1}{\sqrt{30}}h^{112}(k)\right). \tag{24}$$

Units of $[h^{mnl}(k)]=1/d^3$ and $\varphi=\pi\rho d^3/6$ is the volume fraction of particles.

We determined with the Ornstein-Zernike equation the bulk microstructure of the ferrofluid suspension as induced by the pairwise dipole-dipole interaction for finite size particles. Figure 1 depicts our numerical solution of the OZ equation with MSA and LHNC approximations at volume fraction $\varphi=0.418$ and reduced dipole moment $\mu^{*2}=0.1$. Figure 1(a) is the total correlation function h_s of a hard sphere liquid ($\mu^{*2}=0$). Its value was determined with the Verlet-Weiss method that is known to provide good agreement with Monte Carlo simulations [10,14]. The contact value we obtained is $h_s(d)=5.018$.

Figure 1(b) gives the components $h^M_\triangle$ and h^M_D calculated with the MSA approximation, and in Fig. 1(c) the corresponding functions $h^L_\triangle$ and h^L_D obtained using LHNC are shown. It is apparent from these plots that components of h, as obtained from MSA, do not display any oscillation associated with a locally structured liquid. However, such oscillations do appear when LHNC was used at the same parameter values of μ^{*2} and φ. In this case the latter approximation provides more accurate components for $h^L_\triangle$ and h^L_D [14]. The properties h_s, $h_\triangle$, and h_D provide all the static information of the dipolar liquid needed for the calculation of the dynamical friction functions $\Delta\zeta_\gamma(t)$, $\gamma=\perp,\parallel,R$.

IV. DIFFUSION COEFFICIENTS

The long-time friction coefficient on the tracer particle is obtained from

$$\Delta\overleftrightarrow{\zeta}=\int_0^\infty dt\Delta\overleftrightarrow{\zeta}(t), \tag{25}$$

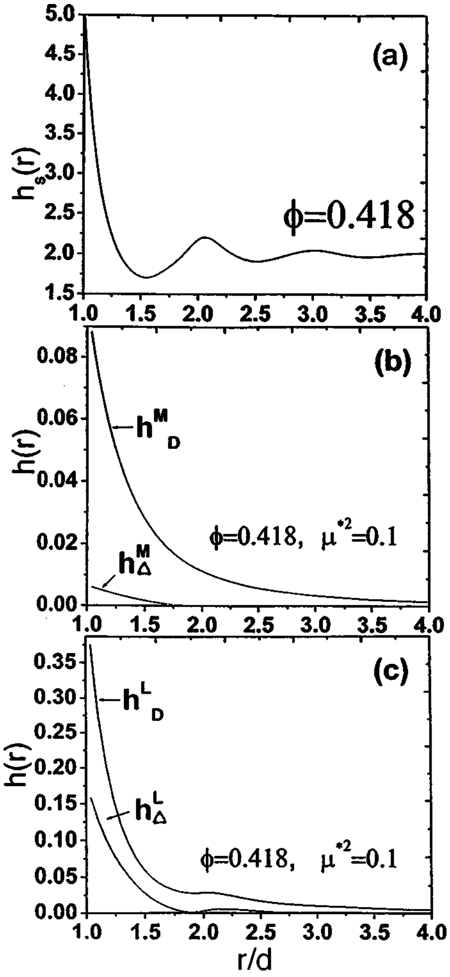

FIG. 1. Total correlation functions for (a) hard spheres. The same functions as (a) for dipolar liquids in the MSA (b) and (c) LHNC approximations.

which is the expression for the friction contribution due to direct particle interactions given in the diffusive regime $t \gg \tau_I$, or equivalently in the limit $w=0$ where we use the Laplace transformed $\Delta\overset{\leftrightarrow}{\zeta}(w=0)$ [16]. Thus, the long-time translational friction reads (Appendix B)

$$\Delta\zeta_\gamma(w=0)=\Delta\zeta^{\mathrm{HS}}+\Delta\zeta_\gamma \tag{26}$$

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

$$\Delta\zeta^{\mathrm{HS}}=\frac{\zeta^0}{36\pi\phi}\int_0^\infty dx\,x^2\frac{[S^{00}_{,0}(x)-1]^2}{1+S^{00}_{,0}(x)} \tag{27}$$

is the contribution from the hard sphere core, whereas

$$\Delta\zeta_\perp=\frac{96}{5}\zeta^0\phi(\mu^{*2})^2\int_0^\infty dx\frac{j_2(x)^2}{x^2+3/2}[6S^{11}_{,1}(x)^2+9S^{11}_{,0}(x)^2]. \tag{28}$$

In the case of pure translational Brownian motion ($D^{*0}_R=0$) the factor in the integrand $1/(x^2+3/2)$ is replaced by $1/x^2$. In any case

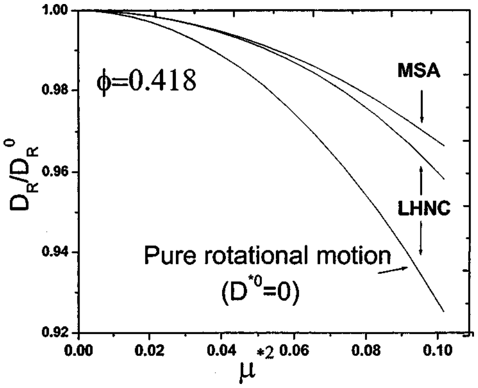

FIG. 2. Long-time rotational self-diffusion coefficient normalized to its free rotational value vs reduced dipole moment: in MSA approximation (upper curve, $D^{*0}\neq 0$); LHNC (middle curve, $D^{*0}\neq 0$), and pure rotational motion (bottom curve, $D^{*0}=0$).

$$\Delta\zeta_\parallel=\tfrac{4}{3}\Delta\zeta_\perp \tag{29}$$

are the corresponding contributions from the dipole-dipole interactions. They hold also for dipole-monopole charge pairwise interactions. However, they are not valid for quadrupolar liquids, in that case one should use the rotational invariant expansion with $mnl=000,220,222,224$ [14].

In the same manner the long-time rotational friction gives

$$\Delta\zeta_R=\frac{48}{105}\zeta^0_R\phi(\mu^{*2})^2\int_0^\infty dx\frac{j_1(x)^2}{x^2+3/2}\times[134S^{11}_{,1}(x)^2+76S^{11}_{,0}(x)^2]. \tag{30}$$

For pure rotational Brownian motion ($D^{*0}=0$), the above equation is modified to

$$\Delta\zeta_R=\frac{96}{315}\zeta^0_R\phi(\mu^{*2})^2\int_0^\infty dx\,j_1(x)^2[67S^{11}_{,1}(x)^2+38S^{11}_{,0}(x)^2]. \tag{31}$$

We may now obtain the long-time self-diffusion coefficients $D_\gamma/D^0_\gamma=(1+\Delta\zeta_\gamma/\zeta^0_\gamma)^{-1}$, ($\gamma=\parallel$, $\perp$, R, $\zeta^0_\parallel=\zeta^0_\perp=\zeta^0$) and the experimentally observable center of mass diffusion $D=(2D_\perp+D_\parallel)/3$ and rotational diffusion coefficient D_R/D^0_R.

To illustrate the theoretical results presented in this paper to study long-time diffusion in a Brownian dipolar liquid, we apply this approach to the generic case of rotational Brownian movement. In Fig. 2 the calculated D_R/D^0_R is shown as a function of dipolar strength at constant volume fraction of particles using MSA and LHNC approximations. The observed differences between the components of h in both approximations are again manifested in the plot of D_R/D^0_R. The middle curve of Fig. 2 corresponds to the long-time rotational diffusion of the tracer normalized to its free short-time rotational value D^0_R, Eq. (30); here the free short-time center of mass translational diffusion of each particle is finite ($D^{*0}=2D^0\neq 0$). However, when $D^{*0}=0$ [particle translational motion is neglected, Eq. (31)], case of pure rotational movement, its effect on D_R/D^0_R is to produce a strong reduc-

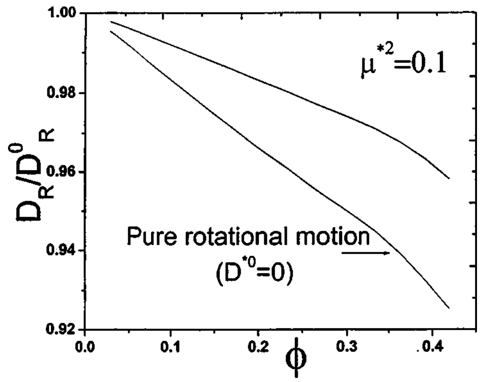

FIG. 3. D_R/D_R^0 as a function of ferrofluid concentration in LHNC approximation only (see Sec. IV). Upper curve with $D^{*0} \neq 0$.

tion of the rotational diffusion, and this effect becomes more important at higher dipole-dipole interactions among particles, as it is observed in the bottom curve of Fig. 2.

In Fig. 3 D_R/D_R^0 is plotted in the LHNC approximation for constant dipole moment as a function of particle volume fraction φ. Here again we observe that for pure rotational diffusion (bottom curve) the ratio D_R/D_R^0 is more suppressed than when short-time translational diffusion is included, $D^{*0} \neq 0$ (upper curve). Similar conclusions are obtained for the translational self-diffusion coefficient D/D^0 (not depicted). From these plots it is concluded that an increase of interparticle strength of interaction among particles, or their concentration, reduces substantially both the rotational and the translational Brownian movement of the ferroparticles.

V. CONCLUSION

We have presented the derivation of an effective Langevin equation for the description of the long-time self-diffusion coefficients of a tracer particle diffusing in a concentrated colloidal suspension of ferromagnetic particles. The main result contained in the Langevin equation is the general expression for the long-time rotational and translational diffusion coefficients D_R and D, respectively, which describe the Brownian motion of a particle interacting with the particles of the host suspension through an axial-symmetric pair potential. We proved these expressions for D_R, using two approximate liquid state theories, MSA and LHNC, to take into account the microstructural order present in the bulk suspension, as induced by the direct interparticle interactions. Important qualitative differences in D_R (D) are found when bulk microstructure is calculated using both approximations. These differences are especially relevant at high strength of interparticle interaction and concentration, in which case we also observe that rotational and translational Brownian movements are restrained.

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APPENDIX A

Using the Fourier $f^{mnl}(k)=4\pi i^l \int_0^\infty dr\, r^2 j_l(kr) f^{mnl}(r)$ and Laplace $f^{mn}(k,w)=\int_0^\infty dt\, e^{iwt} f^{mn}(k,t)$ transforms and expansion of Eq. (16) in Eq. (15) yield

$$\begin{aligned}
&[-iwC^{mnl}(k,w)-C^{mnl}(k,0)]\begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \\
&\quad = 4\pi(2l+1)\rho \sum_{n_1 l_1} \sum_{\nu_1 \lambda_1} \sum_{l_2 \lambda_2} (-1)^{1+\nu_1+\lambda_1+\lambda_2} \\
&\qquad \times [D^{*0}k^2 + D_R^{*0} m(m+1)] \begin{pmatrix} l_1 & l_2 & l \\ \lambda_1 & \lambda_2 & -\lambda \end{pmatrix} \\
&\qquad \times \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} n_1 & n_2 & l_2 \\ -\nu_1 & \nu & \lambda_2 \end{pmatrix} \begin{pmatrix} m & n_1 & l_1 \\ \mu & \nu_1 & \lambda_1 \end{pmatrix} \\
&\qquad \times [\sigma^{-1}(k)]^{mn_1 l_1} C^{n_1 n l_2}(k,w),
\end{aligned} \tag{A1}$$

$j_l(x)$ being the spherical Bessel function of order l. Using now

$$\begin{aligned}
&(-1)^{m+n+n_1} \begin{Bmatrix} l_2 & l_1 & l \\ m & n & n_1 \end{Bmatrix} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \\
&\quad = \sum_{\nu_1 \lambda_1 \lambda_2} (-1)^{\lambda_1+\lambda_2+\nu_1} \begin{pmatrix} m & n_1 & l_1 \\ \mu & \nu_1 & \lambda_1 \end{pmatrix} \begin{pmatrix} n_1 & n & l_2 \\ -\nu_1 & \nu & \lambda_2 \end{pmatrix} \\
&\qquad \times \begin{pmatrix} l_1 & l_2 & l \\ \lambda_1 & \lambda_2 & -\lambda \end{pmatrix}
\end{aligned} \tag{A2}$$

and

$$\sum_{\mu\nu} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \begin{pmatrix} m & n & l' \\ \mu & \nu & \lambda' \end{pmatrix} = (2l+1)^{-1} \delta_{ll'} \delta_{\lambda\lambda'} \tag{A3}$$

in Eq. (A1) yields

$$\begin{aligned}
&[-iwC^{mnl}(k,w)-C^{mnl}(k,0)] \\
&\quad = -\rho 4\pi(2l+1)[D^{*0}k^2 + D_R^{*0} m(m+1)] \\
&\qquad \times \sum_{n_1 l_1 l_2} (-1)^{m+n+n_1} \begin{Bmatrix} l_2 & l_1 & l \\ m & n & n_1 \end{Bmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \\
&\qquad \times [\sigma^{-1}(k)]^{mn_1 l_1} C^{n_1 n l_2}(k,w).
\end{aligned} \tag{A4}$$

Using Eq. (A2) with $\mu=\chi$, $\nu=-\chi$, $\lambda=\lambda'=0$, and the χ representation [13,17]

$$\begin{aligned}
&\sum_\chi (-)^\chi \begin{pmatrix} n_1 & n & l_2 \\ \chi & -\chi & 0 \end{pmatrix} \begin{pmatrix} m & n_1 & l_1 \\ \chi & -\chi & 0 \end{pmatrix} \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \\
&\quad = (-1)^{m+n+n_1} \begin{Bmatrix} l_2 & l_1 & l \\ m & n & n_1 \end{Bmatrix} \begin{pmatrix} l_2 & l_1 & l \\ 0 & 0 & 0 \end{pmatrix},
\end{aligned} \tag{A5}$$

we get for the equation of the propagator

$$[-iwC^{mnl}_{,\chi}(k,w)-C^{mnl}_{,\chi}(k,0)] \\ =-\rho 4\pi(2l+1)[D^{*0}k^2+D^{*0}_R m(m+1)] \\ \times\sum_{n_1}(-1)^{\chi}C^{n_1 n}_{,\chi}(k,w)[\sigma^{-1}(k)]^{mn_1}_{,\chi}. \quad \text{(A6)}$$

For dipolar liquids, correlations $[\sigma^{-1}]^{01}_{,\chi}$ and $[\sigma^{-1}]^{-11}_{,\chi}$ with $\chi=0,\pm 1$ are forbidden [13]. Therefore, one gets

$$C^{11}_{,\chi}(k,w)=\frac{C^{11}_{,\chi}(k,t=0)}{-iw+\rho 4\pi(-)^{\chi}(D^{*0}k^2+2D^{*0}_R)[\sigma^{-1}(k)]^{11}_{,\chi}}, \quad \text{(A7)}$$

with $\chi=0,\pm 1$, $i=\sqrt{-1}$, $D^{*0}=2D^0$, and $D^{*0}_R=2D^0_R$. We use this expression for C in Appendix B.

APPENDIX B

Taking Laplace transform of Eq. (14) and Fourier transform of ψ and C (A7) we get for the rotational friction tensor ($\Delta\overleftrightarrow{\zeta}_{11}=\Delta\overleftrightarrow{\zeta}_{22}=\Delta\overleftrightarrow{\zeta}_{\perp}$, $\Delta\overleftrightarrow{\zeta}_{33}=\Delta\overleftrightarrow{\zeta}_{\parallel}$, $\Delta\overleftrightarrow{\zeta}_{44}=\Delta\overleftrightarrow{\zeta}_{55}$, and $\Delta\overleftrightarrow{\zeta}_{66}=0$)

$$\Delta\overleftrightarrow{\zeta}_{44}(w)=\frac{\beta}{(2\pi)^3}\int d\mathbf{k}d\Omega_1 d\Omega_2[\mathbf{k}\times\boldsymbol{\nabla}_{\mathbf{k}}+\boldsymbol{\nabla}_{\Omega_1}] \\ \times\psi(\mathbf{k},\Omega_1)C(\mathbf{k},\Omega_1,\Omega_2;w)[\mathbf{k}\times\boldsymbol{\nabla}_{\mathbf{k}}+\boldsymbol{\nabla}_{\Omega_2}]^* \\ \times\psi^*(\mathbf{k},\Omega_2). \quad \text{(B1)}$$

The observable $\Delta\zeta_R=\hat{\mathbf{i}}\cdot\Delta\overleftrightarrow{\zeta}_{44}\cdot\hat{\mathbf{i}}=\hat{\mathbf{j}}\cdot\Delta\overleftrightarrow{\zeta}_{55}\cdot\hat{\mathbf{j}}$, where $\boldsymbol{\nabla}_{\Omega}\cdot\hat{\mathbf{i}}=(i/2)(L_+-L_-)$. Similarly $\underline{\mathbf{k}\times\boldsymbol{\nabla}_{\mathbf{k}}\cdot\hat{\mathbf{i}}}=(i/2)(L^k_+-L^k_-)$ and $L_{\pm}Y^m_l(\theta,\phi)=+\sqrt{(l\mp m)(l\pm m+1)}Y^{m\pm 1}_l(\theta,\phi)$ are ladder operators. For the dipole potential

$$\psi(\mathbf{k},\Omega_1)=\sqrt{\pi}(4\pi)^2\frac{\mu^2}{(kd)^{3/2}}J_{3/2}(kd)\sum_{\mu'\nu'}\begin{pmatrix}1 & 1 & 2\\ \mu' & 0 & \lambda'\end{pmatrix} \\ \times(-1)^{\mu'+\lambda'}Y'_{1\mu}(\Omega_1)Y'_{2\lambda'}(\Omega_k), \quad \text{(B2)}$$

where $J_{3/2}$ is the half integer Bessel function.

An analogous expansion holds for $C(k,\Omega_{1,}\Omega_2,\Omega_k;w)$ in terms of $C^{mnl}(k,w=0)$, result which is replaced in Eq. (B1), and use of Eq. (B2), yields after integration on Ω_1, Ω_2, and Ω_k,

$$\Delta\zeta_R=\frac{64\pi^3\mu^4\beta}{d^3}\int_0^{\infty}dk\frac{J^2_{3/2}(k)}{k} \\ \times\left(-\frac{2}{3\sqrt{3}}C^{110}(k,0)+\frac{1}{35}\sqrt{\frac{2}{15}}C^{112}(k,0)\right). \quad \text{(B3)}$$

Then using the relationship between C^{110} and C^{112} with S^{11}_0 and S^{11}_1, and using $D^0/D^0_R=4d^2/3$, $\mu^{*2}=\beta\mu^2/d^3,\rho^*=\rho d^3$, and $C^{11}_{,\chi}=\sigma^{11}_{,\chi}=\rho S^{11}_{,\chi}$,

$$C^{mnl}(k)=(2l+1)\sum_{\chi=-\mathrm{inf}(m,n)}^{\mathrm{inf}(m,n)}C^{mn}_{,\chi}(k)\begin{pmatrix}m & n & l\\ \chi & -\chi & 0\end{pmatrix}, \quad \text{(B4)}$$

in Eq. (B3) yield

$$\Delta\zeta_R=\zeta^0_R(\mu^{*2})^2\rho^*\int_0^{\infty}dx\frac{J^2_{3/2}(x)}{x\left(x^2+\frac{3}{2}\right)}\left(\frac{12\pi^2}{9}\{2[S^{11}_{,1}(x)]^2\right. \\ \left.+[S^{11}_{,0}(x)]^2\},-\frac{12\pi^2}{105}\{[S^{11}_{,1}(x)]^2-[S^{11}_{,0}(x)]^2\}\right), \quad \text{(B5)}$$

where $x=kd$. Finally using $j_n(x)=\sqrt{\pi/2x}J_{n+1/2}(x)$ yields Eq. (30). With the same methods $\Delta\zeta_{\gamma}$, $\gamma=\parallel,\perp$ can be obtained. Thus

$$\Delta\zeta_{\perp}=\zeta^0(\mu^{*2})^2\rho^*\int_0^{\infty}dx\frac{J^2_{5/2}(x)}{x\left(x^2+\frac{3}{2}\right)}\left(8\pi^2\{2[S^{11}_{,1}(x)]^2\right. \\ \left.+[S^{11}_{,0}(x)]^2\}-\frac{32\pi^2}{5}\{[S^{11}_{,1}(x)]^2-[S^{11}_{,0}(x)]^2\}\right). \quad \text{(B6)}$$

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