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R. Peredo-Ortíz,  M. Hernández-Contreras, and R. Hernández-Gómez



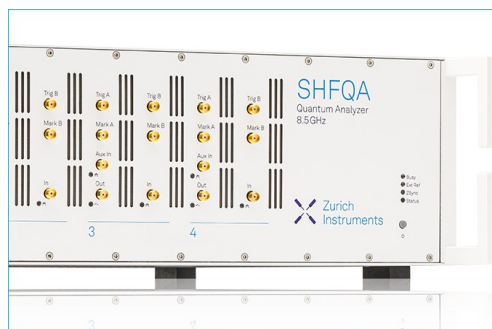
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R. Peredo-Ortíz,¹ M. Hernández-Contreras,^{1,a)}  and R. Hernández-Gómez²

AFFILIATIONS

¹Departamento de Física, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México Distrito Federal, Mexico

²Departamento de Computación, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México Distrito Federal, Mexico

^{a)}Author to whom correspondence should be addressed: marther@fis.cinvestav.mx

ABSTRACT

Based on the stochastic Langevin equation, we derived the total friction experienced by a tracer particle diffusing in thermally equilibrated colloidal magnetic fluids. This transport property leads to new expressions for its long-time diffusion coefficients, which satisfy an Einstein relation with the frictions of its translational and rotational Brownian motion. Further use of the nano-rheology theory allowed us to derive also the viscoelastic modulus of the colloid from such a property. The temporal relaxation of the viscoelasticity and transport coefficient turns out to be governed by the intermediate scattering function of the colloid. We derived an explicit formula for this evolution function within a hydrodynamic theory to include rotational degrees of freedom of the particles. In the limit of short frequencies, the viscous moduli render a new expression for the static viscosity. We found that its comparison with known experiments, at low and high concentration of ferroparticles in magnetite ferrofluids, is fair. However, comparing the predicted viscoelastic moduli with computer simulations as a function of frequency yields poor agreement.

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I. INTRODUCTION

Presently, there is a large body of research on the effect of magnetic fields on the viscosity of ferrofluids. Ferrofluids are colloidal suspensions of nanometer-sized particles with a constant magnetic anisotropy and dispersed in a solvent. The viscosity is an essential property of the rheology of complex fluids. For colloids with radially symmetric interactions among particles, it has been studied with linear response theories based on the Smoluchowski diffusion equation,¹ with statistical mechanics of charged suspensions,² including mode coupling theories of hard sphere-like dispersions,³ and experimentally with macroscopic techniques. Unlike these colloids, the interest to investigate magnetic fluids arises from the observation that magnetic fields produce dramatic changes in their rheology. Such effects prompted their use in diverse applications, including medicine and waste disposal. Comprehensive experiments in the absence of external fields allow us to understand the rheology of magnetic fluids. In most of these

experiments, use is made of mechanical shear stresses on the quiescent fluid to observe the liquid response. Moreover, to interpret these experiments, Rosensweig developed an electrodynamic theory of polar fluids to explain the viscosity in dilute ferrofluids.^{4,5} Meanwhile, Peshenichnikov *et al.*^{4,6} proposed using a known expression of the viscosity of polymeric fluids adapted adequately with the help of a free parameter for highly concentrated ferrofluids. They found good agreement with their experiments at low⁴ and high⁴ particles' volume fractions. At the same time, with the increased use of magnetic fluids controlled by external fields, there have emerged successful theories of their rheology. Such approaches are models of paramagnetic and ferromagnetic gas dynamics described by the kinetic Fokker-Planck theory.^{7,8} Moreover, use has been made of phenomenological extensions of the Debye mean-field theory⁹ of ferroelectric molecular liquids to include magnetic colloids. In these theories, the primary quantities of interest are the first and second moments of the probability density of a ferro-particle as a function of its dipole vector orientation while ignoring its

translational diffusion. These moments, in turn, are related to the magnetization. In contrast, the moments' dynamical evolution is related to the above-mentioned mechanical rheological properties of the fluid. An entirely different point of view is provided by the non-invasive nano- and micro-rheology experimental setup.¹⁰ In this technique, the most fundamental observable to describe the rheology is the measured mean squared displacement of a tracer particle that performs translational and rotational Brownian motion in the liquid. It has a significant advantage compared to invasive macroscopic experiments that allow for a higher time scale of resolution by several decades. Thanks to these methods, the comprehensive experiments by Roeben *et al.*,⁹ Mertelj *et al.*,¹¹ Yendeti *et al.*,¹² and Remmer *et al.*¹³ demonstrated that the use of such an observable of a probe particle senses the viscoelastic behavior in the thermally equilibrated liquid quite accurately. In this context, we notice an absence of a theoretical approach that uses this relationship between this observable and the liquid structure factor and its manifestation in the fluid rheology. Therefore, we propose in this manuscript a complementary yet alternative model that is appropriate for non-invasive nano-rheology. To our knowledge, a stochastic Langevin equation of nano-rheology in ferrofluids based on the translational diffusion coefficient of the probe particle has not been considered before. The diffusion constant of a tracer particle is directly related to the measured mean squared displacement through the general Stokes–Einstein relationship valid for Brownian motion.¹⁴ In Sec. II, we show that the time-dependent diffusion coefficient requires the knowledge of the intermediate scattering function whose form is derived in Appendix B. In this section, we present new expressions of the translational and rotational diffusion coefficients valid at the long-time regime. They take into account the effect of direct pairwise interaction among particles. In Sec. III, we also derive new explicit expressions of the viscosity from the time-dependent friction coefficients of Sec. II. Its quantitative comparison with the available experimental measurements of static viscosity on ferrofluids^{5,6} is in good agreement. Section IV provides the dynamical viscoelastic moduli of the ferrofluid and its relation to the friction function. We show here that the comparison of the viscoelastic moduli with its simulation counterpart agrees at short frequencies; however, they disagree at large frequencies. Nonetheless, both approaches show coincident slopes for this rheological property at these high frequency limits.

II. THE TOTAL FRICTION ON A LABELED FERROPARTICLE AND ITS LONG-TIME SELF-DIFFUSION

Because each magnetic particle during its diffusion experiences direct interactions with the others around it, the tracer's total friction also has to its free solvent friction, an additional contribution. The so-called interaction friction term is feasible to determine because the equations of translational and rotational motion of the tracer particle have the total force and torque terms expressed as a linear function of the local concentration of all particles $n(\vec{r}, \Omega; t)$. This variable represents the conservation number of particles with equilibrium ensemble average $n^{eq}(\vec{r}, \Omega) = \langle n(\vec{r}, \Omega; t) \rangle$. Its temporal evolution is governed by the continuity equation. The angle $\Omega = (\theta, \varphi)$ with θ and φ as the polar and azimuthal angles

determines the unit vector orientation $\hat{u}(\Omega)$ of a dipole. The current of particles implied by the continuity equation arises due to thermal fluctuations of the suspension's electrochemical potential at equilibrium. A critical property of the chemical potential is that, as a function of the local concentration variable, its spatial gradient is known from the liquid theory formalism to depend on the colloid's microscopic structure given by the static correlation function $\sigma(\vec{r}, \vec{r}', \Omega, \Omega')$. The static correlation property is an essential function related to the structure factor of the suspension $S(\vec{r}, \vec{r}', \Omega, \Omega')$. Furthermore, we solved this version of the continuity equation for the concentration variable, which allows us to re-write the force and torque terms of the dynamical Langevin equations of the tracer's motion. Consequently, we derive in Appendix A the exact form of the friction contribution due to interactions, and it is given by Eq. (A6). Consider a ferrofluid of N spherical particles of diameter d and mass m_0 , which occupies a volume V . The magnetic moment of a particle is $\mu_m \hat{u}$ with strength μ_m , and its number density in the colloid is $\rho = N/V$. In what follows, we outline the main steps leading to (A6) and its practical applications in this work. In (A6), we use the inverse Fourier transform properties and the notation of Appendix A to write the gradients $\nabla_{\vec{r}} n^{eq}(\vec{r}, \Omega) = \rho \nabla_{\vec{r}} h(\vec{r}, \Omega) = \frac{1}{(2\pi)^3} \int d\vec{k} e^{-i\vec{k} \cdot \vec{r}} (i\vec{k} h(\vec{r}, \Omega))$. Similarly, $[\vec{r} \times \nabla_{\vec{r}} + \vec{L}] n^{eq}(\vec{r}) = \rho [\vec{r} \times \nabla_{\vec{r}} + \vec{L}] h(\vec{r}, \Omega) = \frac{\rho}{(2\pi)^3} \int d\vec{k} e^{-i\vec{k} \cdot \vec{r}} [i\vec{k} \times \nabla_{\vec{k}} + i\vec{L}] h(\vec{k}, \Omega)$. We defined the six component vector $\vec{\nabla} = (\nabla_{\vec{r}}, \vec{r} \times \nabla_{\vec{r}} + \vec{L})$, whose Fourier transform $\vec{\nabla} h(\vec{r}, \Omega) = (\nabla_{\vec{r}}, \vec{r} \times \nabla_{\vec{r}} + \vec{L}) h(\vec{r}, \Omega)$ leads to terms of type $\rightarrow (i\vec{k}, i\vec{k} \times \nabla_{\vec{k}} + i\vec{L}) h(\vec{k}, \Omega)$. With these definitions, Eq. (A6) is

$$\Delta \vec{\zeta}(t) = \frac{k_B T \rho}{(2\pi)^3} \int d\vec{k} d\Omega d\Omega' d\Omega'' \left[(i\vec{k}, i\vec{k} \times \nabla_{\vec{k}} + i\vec{L}) h(\vec{k}, \Omega) \right] \times S^{-1}(\vec{k}, \Omega, \Omega') \chi(\vec{k}, \Omega', \Omega''; t) \times \left[(i\vec{k}, i\vec{k} \times \nabla_{\vec{k}} + i\vec{L}) h(\vec{k}, \Omega'') \right]^\dagger. \quad (1)$$

In the translational motion case, (1) corresponds to an order three submatrix that results from the vector component $i\vec{k}$ in the integrand of (1). The associated tracer's friction due to interactions is the average of the corresponding first three diagonal terms of Eq. (1) given as $\Delta \zeta(t) = (1/3) [\hat{e}_X \cdot \Delta \vec{\zeta}_{3 \times 3}(t) \cdot \hat{e}_X + \hat{e}_Y \cdot \Delta \vec{\zeta}_{3 \times 3}(t) \cdot \hat{e}_Y + \hat{e}_Z \cdot \Delta \vec{\zeta}_{3 \times 3}(t) \cdot \hat{e}_Z]$. \hat{e}_i is a Cartesian unit vector for the three axes $i = X, Y, Z$. Now, using polar coordinates, Eq. (1) is

$$\Delta \zeta(t) = \frac{k_B T \rho}{(2\pi)^3} \frac{1}{3} \int dk k^2 d\Omega_k d\Omega d\Omega' d\Omega'' \times \left[((\vec{k} \cdot \hat{e}_X)^2 + (\vec{k} \cdot \hat{e}_Y)^2 + (\vec{k} \cdot \hat{e}_Z)^2) h(\vec{k}, \Omega) \right] \times S^{-1}(\vec{k}, \Omega, \Omega') \chi(\vec{k}, \Omega', \Omega''; t) h^*(\vec{k}, \Omega''). \quad (2)$$

To evaluate the integral over the solid angle $\int d\Omega_k$, we use the intermolecular k -frame where $\vec{k} = (0, 0, k)$. Thus, $\vec{k} \cdot \hat{e}_X = k$,

$\vec{k} \cdot \hat{e}_Y = \vec{k} \cdot \hat{e}_Z = 0$. Consequently, $\int d\Omega_k [(\vec{k} \cdot \hat{e}_X)^2 + (\vec{k} \cdot \hat{e}_Y)^2 + (\vec{k} \cdot \hat{e}_Z)^2] h(k, \Omega) S^{-1}(k, \Omega, \Omega') \chi(\vec{k}, \Omega', \Omega''; t) h^*(\vec{k}, \Omega'')$
 $= \int d\Omega_k k^2 h(k, \Omega) S^{-1}(k, \Omega, \Omega') \chi(k, \Omega', \Omega''; t) h^*(k, \Omega'') = 4\pi k^2$
 $h(k, \Omega) S^{-1}(k, \Omega, \Omega') \chi(k, \Omega', \Omega''; t) h^*(k, \Omega'')$. Therefore, Eq. (2) becomes

$$\Delta\zeta(t) = \frac{k_B T \rho}{(2\pi)^3} \frac{4\pi}{3} \int dk k^4 d\Omega d\Omega' h(k, \Omega) S^{-1}(k, \Omega, \Omega') \times \chi(k, \Omega', \Omega''; t) h^*(k, \Omega''). \quad (3)$$

On the other hand, any function is expanded in spherical harmonics $S(k, \Omega, \Omega') = \sum_{l=0}^{\infty} \sum_{l'=0}^{\infty} \sum_{\chi=|l-l'|}^{|l+l'|} S_{\chi}^{ll'}(k) Y_{l\chi}(\Omega) Y_{l'\chi}^*(\Omega')$, where $*$ means complex conjugate. If we consider any pair of functions A and B as those appearing in the integrand of (3), they are integrated out first in one angle. With the help of the orthonormality condition $\int d\Omega Y_{lm}^*(\Omega) Y_{l'm'}(\Omega) = \delta_{ll'} \delta_{mm'}$, the integration on angle Ω' yields

$$\begin{aligned} & \int d\Omega' A(\Omega, \Omega') B(\Omega', \Omega'') \\ &= \int d\Omega' \left[\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{\chi=|m-n|}^{|m+n|} A_{\chi}^{mn}(k) Y_{m\chi}(\Omega) Y_{n\chi}^*(\Omega') \right] \\ & \times \left[\sum_{m'=0}^{\infty} \sum_{n'=0}^{\infty} \sum_{\chi'=|m'-n'|}^{|m'+n'|} B_{\chi'}^{m'n'}(k) Y_{m'\chi'}(\Omega') Y_{n'\chi'}^*(\Omega'') \right] \\ &= \sum_{mn\chi} A_{\chi}^{mn}(k) Y_{m\chi}(\Omega) \sum_{n'\chi'} B_{\chi'}^{nn'}(k) Y_{n'\chi'}^*(\Omega''). \end{aligned} \quad (4)$$

To perform the integral over Ω' in Eq. (3), we use in (4) the equalities $A \equiv S = \sum_{m_1 n_1 \chi_1} S_{\chi_1}^{m_1 n_1}(k) Y_{m_1 \chi_1}(\Omega) Y_{n_1 \chi_1}^*(\Omega)$ and $B \equiv \chi$, and the result is

$$\Delta\zeta(t) = \frac{k_B T \rho}{(2\pi)^3} \frac{4\pi}{3} \int dk k^4 d\Omega d\Omega'' h(k, \Omega) \left[\sum_{mn\chi} (S_{\chi}^{mn})^{-1}(k) \times \sum_{n'\chi'} \chi_{\chi'}^{nn'}(k; t) Y_{m\chi}(\Omega) Y_{n'\chi'}^*(\Omega'') \right] h^*(k, \Omega''). \quad (5)$$

Now, the integration over Ω is performed with the identification $A \equiv h$ and $B \equiv \left[\sum_{mn\chi} (S_{\chi}^{mn})^{-1}(k) \sum_{n'\chi'} \chi_{\chi'}^{nn'}(k; t) Y_{m\chi}(\Omega) Y_{n'\chi'}^*(\Omega'') \right]$, and the result is

$$\begin{aligned} & \int d\Omega h(k, \Omega) \left[\sum_{mn\chi} (S_{\chi}^{mn})^{-1}(k) \sum_{n'\chi'} \chi_{\chi'}^{nn'}(k; t) Y_{m\chi}(\Omega) Y_{n'\chi'}^*(\Omega'') \right] \\ &= \sum_{m_1 n_1 \chi_1} h_{\chi_1}^{m_1 n_1}(k) Y_{m_1 \chi_1}(0) \left[\sum_{mn\chi} (S_{\chi}^{mn})^{-1}(k) \sum_{n'\chi'} \chi_{\chi'}^{nn'}(k; t) Y_{n'\chi'}^*(\Omega'') \right]. \end{aligned} \quad (6)$$

Using this last equation (6) as the new definition for A in identity (4), and by defining now $B \equiv h^*(k, \Omega'') \equiv \sum_{m_2 n_2 \chi_2} h_{\chi_2}^{m_2 n_2}(k) Y_{m_2 \chi_2}^*(0) Y_{n_2 \chi_2}(\Omega'')$, finally, the last integral over Ω'' is

$$\begin{aligned} & \int d\Omega'' \sum_{m_1 n_1 \chi_1} h_{\chi_1}^{m_1 n_1}(k) Y_{m_1 \chi_1}(0) \left[\sum_{n'} (S_{\chi}^{nn'})^{-1}(k) \sum_{n'' \chi''} \chi_{\chi''}^{nn'}(k; t) Y_{n'' \chi''}^*(\Omega'') \right] \\ & \times \left[\sum_{m_2 n_2 \chi_2} h_{\chi_2}^{m_2 n_2}(k) Y_{m_2 \chi_2}^*(0) Y_{n_2 \chi_2}(\Omega'') \right] \\ &= \sum_{m_1 n_1 \chi_1} h_{\chi_1}^{m_1 n_1}(k) Y_{m_1 \chi_1}(0) \left[\sum_{n'} (S_{\chi}^{nn'})^{-1}(k) \sum_{n'' \chi''} \chi_{\chi''}^{nn'}(k; t) \right] \\ & \times \left[\sum_{m_2 n_2 \chi_2} h_{\chi_2}^{m_2 n_2}(k) Y_{m_2 \chi_2}^*(0) \right]. \end{aligned} \quad (7)$$

Substituting this result into Eq. (5) yields

$$\begin{aligned} \Delta\zeta(t) &= \frac{k_B T \rho}{(2\pi)^3} \frac{4\pi}{3} \int dk k^4 \sum_{m_1 n_1 \chi_1} h_{\chi_1}^{m_1 n_1}(k) Y_{m_1 \chi_1}(0) \\ & \times \left[\sum_{n'} (S_{\chi}^{nn'})^{-1}(k) \sum_{n'' \chi''} \chi_{\chi''}^{nn'}(k; t) \right] \left[\sum_{m_2 n_2 \chi_2} h_{\chi_2}^{m_2 n_2}(k) Y_{m_2 \chi_2}^*(0) \right]. \end{aligned} \quad (8)$$

Equation (8) considers the tracer dipole oriented along the Z axis. Relaxing this condition to allow the dipole to reach any angle orientation, and with Eq. (A7) projections $\chi_{\chi}^{nn'}(k; t) = \sum_l S_{\chi}^{nl}(k; t) (S_{\chi}^{ln'})^{-1}(k)$ and the identity $h = (S - 1)/\rho$, we get

$$\begin{aligned} \Delta\zeta(t) &= \frac{k_B T}{(2\pi)^3} \frac{4\pi}{3} \int dk k^4 \sum_{m_1 n_1 \chi_1} (S_{\chi_1}^{m_1 n_1} - 1) \\ & \times \left[\sum_{n'} (S_{\chi}^{nn'})^{-1}(k) \sum_{n'' \chi''} S_{\chi''}^{nl}(k; t) (S_{\chi''}^{ln'})^{-1}(k) \right] \\ & \times \left[\sum_{m_2 n_2 \chi_2} (S_{\chi_2}^{m_2 n_2} - 1) \right]. \end{aligned} \quad (9)$$

This procedure provides also the path to derive from (1) the rotational friction due to interacting particles. In what follows, we truncate the upper indices in Eq. (9) to two symmetric values $m_1 = m = l = n = n' \leq 0, 1$, which represent the minimal basis set of spherical harmonics of the hard sphere plus dipole interactions.¹⁵ The translational friction then becomes

$$\Delta\zeta(t) = \frac{k_B T}{6\pi^2 \rho} \int_0^\infty dk k^4 \sum_{l=0}^1 \sum_{m=-l}^l \left[\frac{S_{m,m}^l(k) - 1}{S_{m,m}^l(k)} \right]^2 S_{m,m}^l(k; t). \quad (10)$$

The case $l = 0$ recovers the known result derived in Refs. 16–18 for radially symmetric potentials. However, the coefficient of its rotational (rot) friction is

$$\begin{aligned} \Delta\zeta_{rot}(t) &= \frac{k_B T}{3\pi^2 \rho} \int_0^\infty dk k^2 \sum_{l=0}^1 \sum_{m=-l}^l [f_1 + f_2 + f_3] \left[\frac{S_{m,m}^l(k) - 1}{S_{m,m}^l(k)} \right] S_{m,m}^l(k; t), \\ f_1 &:= \frac{(m+l)(l+1-m)}{2} \left[\frac{S_{m-1,m}^l(k) - 1}{S_{m-1,m}^l(k)} \right], \\ f_2 &:= \frac{(l-m)(m+1+l)}{2} \left[\frac{S_{m+1,m}^l(k) - 1}{S_{m+1,m}^l(k)} \right], \\ f_3 &:= m^2 \left[\frac{S_{m,m}^l(k) - 1}{S_{m,m}^l(k)} \right]. \end{aligned} \quad (11)$$

A. Self-diffusion

In this section, we derive expressions for the diffusion coefficient of a tracer and its dynamical relaxation determined by the intermediate scattering function. For ferrofluids, the experiments of small-angle neutron scattering measure the correlation of density fluctuations, leading to the intermediate scattering function $S_m^l(k; t)$. Theoretically, $S_m^l(k; t)$ is calculated following a hydrodynamic level of description of the dynamical evolution equations of the density of particles and the currents produced by the thermal fluctuations. As a result, there is a coupling among the hydrodynamic equations of density and currents. One way to solve them is to assume that the force on a particle is given by a linear relationship with the current variable through a general dissipative friction function. Thus, one is led to a hydrodynamic current equation in terms of the friction. The solution of these equations is replaced in the continuity equation. Its thermal average with the density yields the two-time correlation function of density, that is to say, the dynamical structure factor in reciprocal space (see Appendix B). To study self-diffusion in ferrofluids using (10), we introduce the decoupling approximation for the intermediate scattering function $S_m^l(t) \approx S_m^{l, \text{self}}(t) S_m^{l, c}(t)$, where $S_m^{l, \text{self}}$ is the tracer's propagator and $S_m^{l, c}$ is similarly the collective (c) or host particles' propagator in the laboratory frame.^{17,19} We attained its specific form in Appendix B. The Laplace transform of the propagator $\int_0^\infty dt e^{-i\omega t} S_m^l(k; t)$ is

$$S_m^l(k; \omega) = \frac{S_m^l(k)}{i\omega + k^2 D^s \left[\frac{1}{S_m^l(k)} + \mu_T(\omega) \right] + l(l+1) D_r^s \left[\frac{1}{S_m^l(k)} + \mu_R(\omega) \right]}. \quad (12)$$

This expression coincides with the one reported in Ref. 20, where a general stationary theorem of stochastic processes was used to derive it. It generalizes to anisotropic potentials the one attained by Bengtzelius *et al.*²¹ and Hess and Klein,²² valid for spherically symmetric potentials only.^{23,24} Here, $\mu_T(\omega) := D(\omega)/D^s$ and $D(\omega) = k_B T / \zeta(\omega)$, $\zeta(\omega) = \zeta^s + \Delta\zeta(\omega)$, and similarly for μ_R . The particle short-time diffusion coefficients satisfy the Stokes–Einstein relationships $D^s := k_B T / \zeta^s$ and $D_r^s := k_B T / \zeta_r^s$. These properties incorporate the hydrodynamic effects within the memory function $S_m^l(k; \omega)$ through ζ^s . The particle short-time friction coefficients ζ^s , ζ_r^s are experimentally known only for the hard sphere-like suspensions,^{25–27} and they are unknown for ferrofluids. However, in Sec. III, we propose the determination of $D(\omega = 0)$ with the dissipative modulus. At long time ($\omega = 0$), we attain from (10) the new result for the translational and rotational self-diffusion coefficients,

$$\begin{aligned} \frac{D}{D^s} &= \left[1 + \frac{1}{6\pi^2 \rho} \int_0^\infty dk \left(\frac{k^2 [S_0^{00}(k) - 1]^2}{(S_0^{00}(k) \mu_T + 1)} \right. \right. \\ &\quad \left. \left. + \sum_{l=0}^1 \sum_{m=-l}^l \frac{k^4 [S_m^l(k) - 1]^2}{\text{den}} \right) \right]^{-1}, \\ \text{den} &:= k^2 (S_m^l(k) \mu_T + 1) + l(l+1) \frac{D_r^s}{D^s} (S_m^l(k) \mu_R + 1), \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{D_r}{D_r^s} &= \left[1 + \frac{1}{6\pi^2 \rho} \int_0^\infty dk k^2 \sum_{l=0}^1 \sum_{m=-l}^l [f_1 + f_2 + f_3] \frac{S_m^l(k) - 1}{\text{denR}} \right]^{-1}, \\ \text{denR} &:= k^2 \frac{D^s}{D_r^s} (S_m^l(k) \mu_T + 1) + l(l+1) (S_m^l(k) \mu_R + 1), \end{aligned} \quad (14)$$

and $\mu_T := D/D^s$, $\mu_R := D_r/D_r^s$. The first two terms in the denominator of (13) reproduce the diffusion coefficient reported by other authors.^{16–18} To apply (13), we first approximate $D^s = D_0 = k_B T / \zeta^0$, the free diffusion (ζ^0 being the Stokes value), and $\mu_R = 0$. Then, (13) was solved self-consistently for $\mu_T = D/D_0$. As the starting input value $\mu_T = 1$ under the integrand in (13), the result of the integration yields a new value of $\mu_T = D/D_0$. We repeat this iteration scheme until its difference with the previous one is less than 0.001. If we take $\mu_R(\omega = 0) \neq 0$, then the calculated overdamped value of D/D_0 deviates dramatically from our simulations, which we consider as our reference data for the same system. Recently, Elizondo-Aguilera *et al.*^{28,29} found that a colloid with intrinsic particles' rotational diffusion $\mu_R(\omega = 0) \neq 0$ has an important role in slowing down the dynamics. Motivated by the research of Refs. 28 and 29, we included $\mu_R(\omega = 0) \neq 0$ in our study of the viscoelastic dynamics below. The self-diffusion coefficient $D := \mu_T D^s$ contains the effects of hydrodynamic interaction (HI) in concentrated colloids, through the use of measured D^s (not yet known for ferrofluids), for which there is also a known approximate analytical expression $D^s = D_0/g(\Phi)$.^{16,30} The ferrofluid is modeled by a potential energy $U_T = U_{LJ}(r) - U_{LJ}(r = 2^{1/6}d) + U_{dd}(r)$, which has a Lennard-Jones short range repulsive part

$$U_{LJ}(r) = 4\epsilon_0 \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right], \quad (15)$$

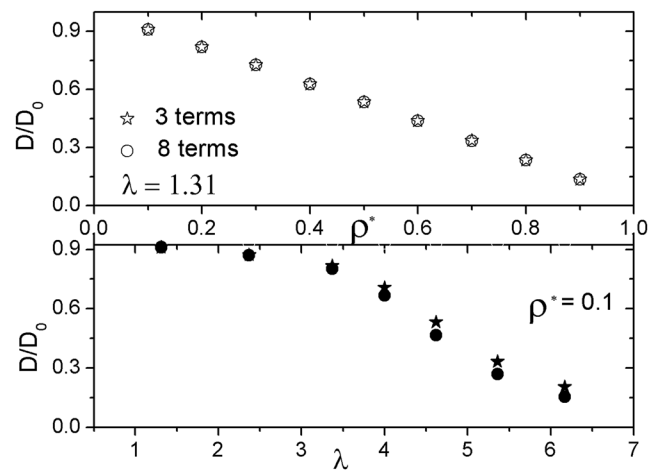


FIG. 1. Comparison of the predicted long-time ($t \rightarrow \infty$) self-diffusion coefficient D/D_0 vs density and dipole strength, respectively. Theory from Eq. (9) with spherical harmonic indices in the intermolecular frame $mn \leq 0, 2$ (corresponding to eight terms $mnl = 000, 110, 112, 022, 202, 220, 222, 224$, in the laboratory frame; symbol \circ) vs its first three terms (equivalently, $mm \leq 0, 1$) and use of Eq. (10) (symbol \star).

with strength ϵ_0 . This part represents the steric interaction that stabilizes the suspension. The truncated Lennard-Jones $U_{LJ}(r) - U_{LJ}(r = 2^{1/6}d) = 0$, $r > 2^{1/6}d$, yields the short range repulsion between the pair of particles at contact. The particles' long-range dipolar contribution is also included,

$$U_{dd}(r_{12}) = \frac{\mu_0 \mu_m^2}{4\pi} (\hat{\mathbf{u}}_1 \cdot \nabla_{\mathbf{r}_1})(\hat{\mathbf{u}}_2 \cdot \nabla_{\mathbf{r}_2}) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (16)$$

Due to the symmetries of the potential interaction, the projections $S_m^l(k)$ of the structure factor with $l = m = 0$ represents the radially symmetric potential. However, the dipole potential leads to $l = 1$, $m = -1, 0, 1$ of the static structure $S_m^l(k) = [1 - (-)^m c_m^l(k)]^{-1}$. We considered higher harmonics in Eq. (9) up to $m_1, l, m, n, n' \leq 0, 1, 2$ and found that the diffusion coefficient D/D_0 , as compared to that resulting from Eq. (13) for three terms, is indistinguishable. In

Fig. 1, we show that there are differences between Eqs. (9) and (10) for D/D_0 only at higher dipole strength and density. The first three harmonics in the Mean Spherical Approximation (MSA) are¹⁵

$$\begin{aligned} S_{0,0}^{00}(k) &= \frac{1}{1 - 8\Phi c(k)}, \\ S_{0,0}^{11}(k) &= \frac{1}{1 - 8\Phi [c_\Delta(k) + 2c_D(k)]}, \\ S_{\pm 1}^{11}(k) &= \frac{1}{1 - 8\Phi [c_\Delta(k) - 2c_D(k)]}, \end{aligned} \quad (17)$$

where c , c_Δ , and c_D are Wertheim's direct correlation function projections within the MSA.³¹ They depend on the particle volume fraction and dipole strength λ . We compared theory (13) with Langevin dynamic simulations at thermodynamic states given by

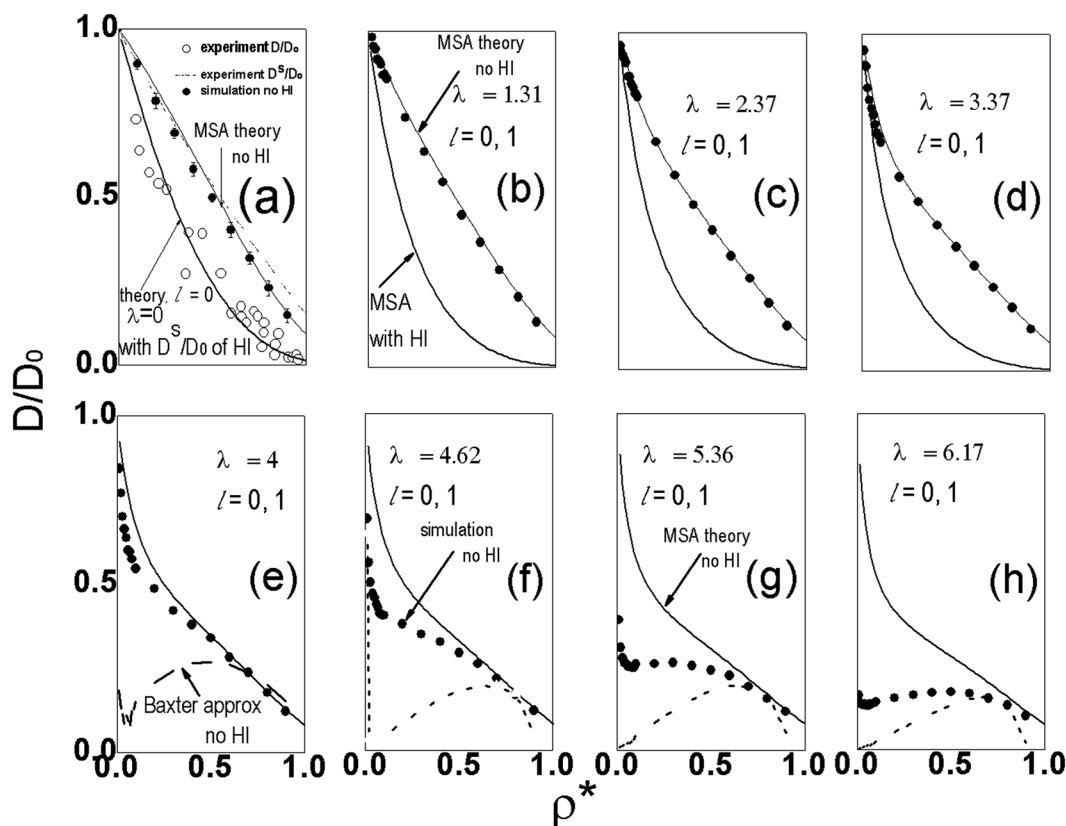


FIG. 2. Normalized long-time translational self-diffusion coefficient D/D_0 vs reduced density ρ^* at eight increasing values of the dipole moment per particle λ . (a) The measured D/D_0 ["Reprinted with permission from van Meegen *et al.*, Faraday Discuss. Chem. Soc. **83**, 47 (1987). Copyright 1987 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc."] (symbol \circ) was taken from Ref. 25 of a real HS suspension, and it is compared with theory (13) (for $l = 0$ HS interaction only, black thick line —), which includes hydrodynamic interactions (HI) through the measured²⁵ D^s/D_0 ["Reprinted with permission from van Meegen *et al.*, Faraday Discuss. Chem. Soc. **83**, 47 (1987). Copyright 1987 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.], given by the dashed line. The simulations do not include HI (symbol \bullet ; error bars are the same size as symbols). In (a), theory (13) (black thin line, under the MSA for the structure factor) is also given without HI ($D^s = D_0$). From low up to intermediate values of dipole moment $0 \leq \lambda \leq 3.37$, the agreement between simulation calculations (without using hydrodynamic interactions, symbol \bullet) and theory within the MSA (no HI, black continuous line) is good [(a)–(d)]. However, for higher values of the dipole moment $4.0 \leq \lambda \leq 6.17$ where there is a substantial amount of chain formation in the fluid, there is disagreement between theory and simulation [(e)–(h)]. In this last case, we approximated the micro-structure factors, $S_m^l(k)$, with a Baxter approximation (dashed line), which yields the qualitative non-monotonous behavior of D/D_0 as observed in the simulations.

the reduced density $\rho^* = \rho d^3$ and strength of dipole interaction $\lambda = \mu_0 \mu_m^2 / 4\pi k_B T d^3$. For this purpose, we considered typical material parameters of monodisperse ferrofluids.⁴ These states include the magnetic moment $\mu_m = 2.3352 \times 10^{-19}$ Am² at room temperature $T = 300$ K. The aqueous solvent viscosity is $\eta_{sol} = 0.852 \times 10^{-3}$ Kg/ms, $d = 10^{-8}$ m, and $m_0 = 2.707 \times 10^{-21}$ Kg, and we set the strength $\varepsilon_0 = 5.4531 \times 10^{-21}$ J, which are related by the time scale $t' = d\sqrt{(m_0/\varepsilon_0)}$ that measures the time step size in the Langevin dynamics simulations.³² For each simulation step of size $\Delta t = 0.001t'$, the dynamical Langevin equations (A1) were solved with the LAMMPS package.³² We used $N = 6750$ particles and 5×10^6 time steps to reach the thermal equilibrium. Since we investigated only equilibrated systems, the particles' momenta have entirely relaxed. The simulated system at this time scale does not display inertial effects in a particle's mean squared displacement. We found that with the use of the above material data, our system equilibrates quickly. After equilibrium, we additionally performed 5×10^6 simulation steps for statistical averages. Consequently, we restricted our study to the diffusive regime. In Fig. 2(a) the comparison of the normalized diffusion $D/D_0 = \mu_T D^s/D_0$ is shown against the experimental data of a hard sphere-like system. In the same plot, the measured^{25,26} value of the short-time diffusion coefficient D^s that accounts for hydrodynamic interactions in the colloid is provided. Figure 2(a) shows the already well-known high accuracy reached between the theory for the diffusion constant in the case $l = 0$ (hard-sphere suspension)¹⁸ when HI is introduced. Note that in Fig. 2, the MSA theory plots are given by the black thick continuous line and the corresponding simulation result (without HI) is given by symbol \bullet . We can observe that there is good agreement between the theory of Eq. (13) and the simulations for any density in the range $0 \leq \rho^* \leq 1.0$ and increasing dipole strength in the interval $0 \leq \lambda \leq 3.37$ [see Figs. 2(a)–2(d)]. Nevertheless, for higher dipole moments such as $\lambda \geq 4.0$, theory worsens vs simulations [see Figs. 2(e)–2(h)]. We point out that already at the high dipole moment $\lambda = 5.30$, we observed cluster formation of particles where the largest population of them (about 90%) corresponds to dimers of two particles stuck together, and there is formation of chain-like structures of three and more particles. In Fig. 2(h), for $\lambda = 6.17$, there are a large number of chain structures, and the simulation results of the long-time translational diffusion coefficient D/D_0 predict a non-monotonous behavior of this dynamical property. To our knowledge, we have not found in the literature a previous report on this phenomenon of self-diffusion in ferrofluids. In Figs. 2(f)–2(h), the theory prediction (black thick continuous line) using the MSA for $S_0^{00}(k)$ fails, which is an expected result since liquid theory intends MSA for low concentrated fluids and low dipole moments per particle. A better approximation that we found is the analytical extension of $g(r)$ of Baxter for higher dipole moments and particles' concentration³³ [dashed lines in Figs. 2(e)–2(h)]. Figure 2(h) shows the result of using this approximation for the highest dipole moment $\lambda = 6.17$. With this approximation, our calculations for D/D_0 display qualitatively the same trends as the simulation results. As already mentioned above, Fig. 2(a) shows the effect of hydrodynamic interactions on D/D_0 . There, the experiments of van Meegen *et al.*²⁵ on a hard sphere-like colloid and the theory of Eq. (13) for D/D_0 are compared, where we introduced hydrodynamic interactions through $S_m^l(k; t)$ by using the analytical expression of the short-time friction ζ^s , as prescribed in Ref. 18. We expect our results

for the diffusion coefficient to be reliable from low up to moderate values of particle volume fraction, and it would improve for higher densities if the experimental value (presently unknown for ferrofluids) of ζ^s (ζ_r^s) is used since, as shown in Fig. 2(a), Eq. (13) coincides with the theory of Ref. 18 for $l = 0$, for a radially symmetric pairwise potential case.

The diffusion property (13) is linked to the colloid rheology of concentrated magnetic fluids, and it is feasible to be determined experimentally.

III. VISCOSITY OF BROWNIAN MAGNETIC PARTICLES

Mason¹⁰ proposed a theory of micro-rheology. It resides on the assumption that the liquid bulk stress relaxation has the same frequency evolution as the microscopic stress relaxation of the total translational friction on a tracer particle. That is to say, $\zeta(\omega)$ is proportional to the bulk frequency-dependent viscosity of the colloid $\eta(\omega) = \zeta(\omega)/(3\pi d)$. For a dilute ($\Phi \ll 1$) monodisperse colloid of hard spheres, there are no direct interactions, and we can neglect the short-frequency limit of the friction $\Delta\zeta(\omega = 0) = 0$ [Eq. (10)]. Since $\zeta^s = \zeta^0 g(\Phi)$,^{16,30} therefore, the static viscosity becomes

$$\eta(\omega = 0) = \frac{\zeta^s + \Delta\zeta(\omega = 0)}{3\pi d} \approx \eta_{sol} g(\Phi). \quad (18)$$

Thus, our result is $\eta(\omega = 0)/\eta_{sol} \approx 1 + 2.5\Phi$, up to first order in Φ , which coincides with Einstein's viscosity. As mentioned above, for low concentrated ferrofluids, we found that the static viscosity is given by $\eta(\omega = 0) = \eta_{sol} g(\Phi)$. We depict in Fig. 3 the comparison of this expression (black thick line) with the experiments of

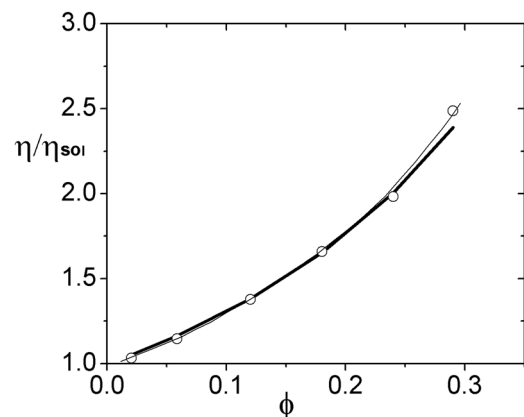


FIG. 3. Normalized static viscosity $\eta(\omega = 0)/\eta_{sol}$ as a function of volume fraction ϕ of particles. The Experimental data (symbol \circ) of a monodisperse kerosene-based ferrofluid of magnetite particles, are from Ref. 4 [“From Odenbach, *Magnetoviscous Effects in Ferrofluids*. Copyright 2002 Springer. Reprinted/adapted with permission from Springer Nature”]. The theory (18) is described in the main text (it is represented by thick black line —) $\eta(\omega = 0) = \eta_{sol} g(\phi)$ with $g(\phi) = (1 - 0.5\phi)/(1 - \phi)^3$ where $\phi = \Phi((d + 2s)/d)^3$, $d = 10$ nm, and $s = 2$ nm of surfactant layer on each particle. The gray continuous line [“From Odenbach, *Magnetoviscous Effects in Ferrofluids*. Copyright 2002 Springer. Reprinted/adapted with permission from Springer Nature”] is the theory of Rosensweig.⁴

Odenbach.⁴ The experimental data (symbol \circ) refer to a very diluted monodisperse magnetite ferrofluid in kerosene solvent. The gray continuous line is a theory proposed by Rosensweig.^{4,5} Figure 4 refers to the same monodisperse ferrofluid as in Fig. 3. The experimental data are from Pshenichnikov *et al.*^{4,6} (symbol \circ). Pshenichnikov *et al.* provided a theory based on polymer viscosity models that depend solely on the volume fraction of particles. The gray continuous line gives their prediction of viscosity. According to this model, they conclude that the viscosity arises from the steric interactions without the necessity to include the anisotropic dipole-dipole potential. Due to the high density of particles, in this case, we expect a non-negligible hard-core excluded volume interaction among particles, which makes the friction $\Delta\zeta(\omega = 0)$ a vital contribution to the viscosity of the ferrofluid. Thus, the total friction on the tracer can be approximated by $\zeta(\omega = 0) = \zeta^0 + \Delta\zeta(\omega = 0) = k_B T/D(\omega = 0)$. Then, the viscosity can be rewritten as

$$\eta(\omega = 0) = \frac{\zeta^0 + \Delta\zeta(\omega = 0)}{3\pi d} = \eta_{sol} \frac{D_0}{D(\omega = 0)} = \frac{\eta_{sol}}{\left[\left(\frac{D(\omega=0)}{D^s}\right)\left(\frac{D^s}{D_0}\right)\right]}. \quad (19)$$

In this equation, we used (13) for $D(\omega = 0)/D^s$ with the spherical harmonic term $l = 0$ and neglected all the values $l \geq 1$ for the reasons

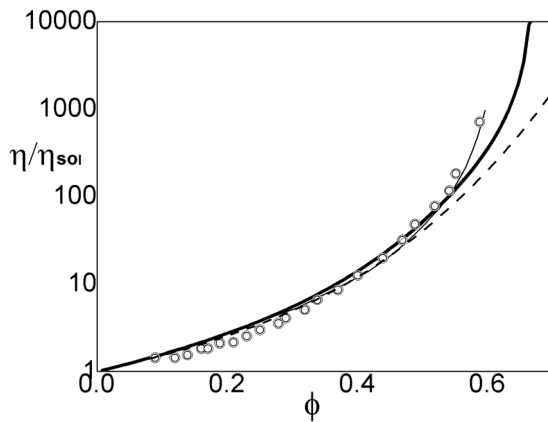


FIG. 4. Static viscosity $\eta(\omega = 0)/\eta_{sol}$ as a function of volume fraction ϕ of particles for a highly concentrated ferrofluid. Experimental data (symbol \circ) [“From Odenbach, *Magnetoviscous Effects in Ferrofluids*. Copyright 2002 Springer. Reprinted/adapted with permission from Springer Nature”] are from Ref. 4 of monodisperse suspension of magnetite in kerosene. Theory (19), $\eta(\omega = 0) = \eta_{sol} D_0/D$, for $l = 0$, $\lambda = 0$ (black thick line), with the incorporation of HI in the term $D/D_0 = \mu_T D^s/D_0$ through the experimental value of the volume fraction dependence of D^s/D_0 [“Reprinted with permission from van Megen *et al.*, *Faraday Discuss. Chem. Soc.* **83**, 47 (1987). Copyright 1987 Royal Society of Chemistry; permission conveyed through Copyright Clearance Center Inc.”] is depicted in Fig. 2(a). For comparison, we also included the prediction of theory (19) with the use of the analytical expression for $D^s/D_0 = 1/g(\phi)$ (dashed line). ϕ is defined as in Fig. 3. The gray continuous line [“From Odenbach, *Magnetoviscous Effects in Ferrofluids*. Copyright 2002 Springer. Reprinted/adapted with permission from Springer Nature”] represents the theory used by Pshenichnikov *et al.*⁴ for ferrofluids. The theory was proposed originally by Chow³⁹ for polymer solutions.

explained above. We included hydrodynamic interactions through the experimental knowledge of D^s/D_0 , as in Fig. 2(a). The black thick line represents the result of this model in Fig. 4. The dashed line is also our model where we used the analytical formula instead of $D^s/D_0 = 1/g(\phi)$ to include HI.

IV. MAGNETIC VISCOELASTICITY OF FERROFLUIDS

Now, using (10) in $\zeta(t) = \zeta^s + \Delta\zeta(t)$ and $i\omega\eta(\omega) = i\omega\zeta(\omega)/(3\pi d) = G(\omega) = G' + iG''$, we derived a new expression for the viscoelastic modulus of ferrofluids at thermal equilibrium, which is given by

$$G(\omega) = \frac{i\omega\zeta^s}{3\pi d} + \int_0^\infty dx x^4 \sum_{l=0}^\infty \sum_{m=-l}^l G_{m,l}^{\parallel}(x) \frac{i\omega\tau_{m,l}^{\parallel}(x)}{1 + i\omega\tau_{m,l}^{\parallel}(x)}, \quad (20)$$

$$G_{m,l}^{\parallel}(x) := \frac{\eta_{sol}(S_{m,l}^{\parallel}(x) - 1)^2}{6t_B^s \pi^2 \rho^* S_{m,l}^{\parallel}(x)}, \quad \tau_{m,l}^{\parallel}(x) := \frac{t_B^s}{A_0},$$

$$A_0 := x^2 \left[\mu_T(\omega = 0) + \frac{1}{S_{m,l}^{\parallel}(x)} \right] + l(l+1) \left[\mu_R(\omega = 0) + \frac{1}{S_{m,l}^{\parallel}(x)} \right],$$

where $x := kd$, $\rho^* = \rho d^3$, and $t_B^s = d^2/D^s$ is the time that a particle takes to diffuse its diameter. With numerical methods, we will now analyze the viscoelastic moduli (20). For this purpose, we use a self-consistent scheme as in Sec. II where $\mu_t \neq 0$ and $\mu_R \neq 0$ are calculated through the use of Eqs. (13) and (14). In Figs. (5) and (6), we can see that, from low (10^{-1} Hz) up to intermediate (10^6 Hz) frequencies ω , the dissipative modulus G'' is always larger than the

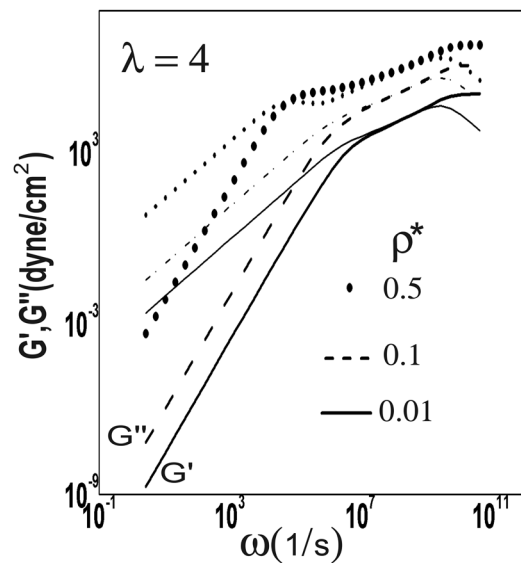


FIG. 5. Logarithmic plot of viscoelastic modulus vs frequency ω at fixed dipole coupling $\lambda = 4$ and three densities $\rho^* = 0.01, 0.1$, and 0.5 without HI ($D^s = D_0$) in Eq. (20). Theory for $G'(\omega)$ is represented with black thick symbols (continuous line, dotted line, and dashed line). The approach for $G''(\omega)$ is represented with gray symbols.

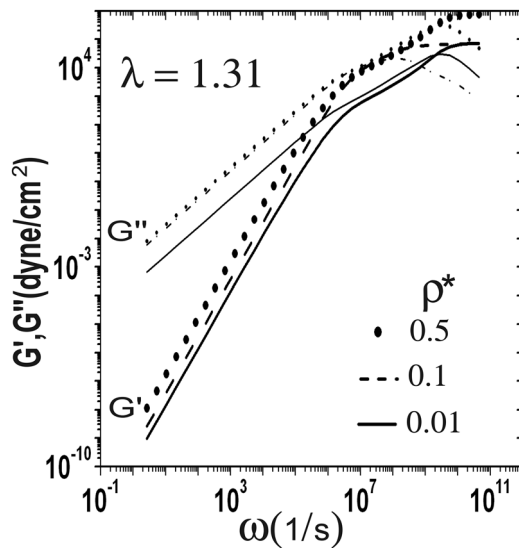


FIG. 6. Same legends and equilibrium properties as in Fig. 5 at a lower dipole strength $\lambda = 1.31$.

storage modulus G' . Such behavior is in qualitative agreement with similar experimental observations made by Yendeti *et al.*,¹² using a ferrite ferrofluid at low ω of a few Hertz (10 Hz). In contrast, it appears that our calculated G'' for magnetite in kerosene solvent ferrofluid can be of a smaller magnitude than those observed by Roeben *et al.*⁹ in cobalt based particles in polymer solutions at low frequencies. However, in all our theoretical cases, G'' and G' are on the scale of their measured magnitudes^{9,12} over the probed experimental range of fluid frequencies. The G moduli are compared in Fig. 5 as well as in Fig. 6 at three reduced densities $\rho^* = 0.01, 0.1$, and 0.5 . Figure 5 depicts the case with the high dipole coupling $\lambda = 4$ and exhibits a smooth transition where $G'' \approx G'$ with their increasing values in the range $10^4 \text{ Hz} < \omega < 10^9 \text{ Hz}$ until the appearance of their crossover to $G'' > G'$ for $\omega < 10^9 \text{ Hz}$. We also note that the values of G'', G' enhance by three orders of magnitude when the reduced density ρ^* increases by one order from 0.01 up to 0.5 and for weaker couplings of $\lambda = 1.31$ than with $\lambda = 4$. Additionally, at $\lambda = 1.31$, the crossover of G'' to G' vs ω becomes sharper at the highest density $\rho^* = 0.5$ than in the case of $\lambda = 4$. The general behavior of the viscoelastic moduli can be deduced from Eq. (20), with their asymptotic behavior at the overdamped $\omega = 0$ and the short-time limits, equivalently $\omega \rightarrow \infty$. In the first limit, the storage G' and loss G'' moduli are

$$\begin{aligned} G'(\omega) &\approx \frac{\eta_{sol}}{t_B} (\omega^*)^2 A_1, \quad \omega^* := \omega t_B \rightarrow 0, \\ G''(\omega) &\approx \frac{\eta_{sol}}{t_B} \frac{D^s}{D} \omega^*. \end{aligned} \quad (21)$$

Here,

$$A_1 := \frac{1}{6\pi^2 \rho^*} \int_0^\infty dx x^4 \sum_{l=0}^1 \sum_{m=-l}^l \frac{[S_{m,l}^l(x) - 1]^2}{S_{m,l}^l(x) A_0^2}. \quad (22)$$

We note that the second expression in (21) yields an important relationship of the loss modulus G'' with the long-time self-diffusion coefficient D in (13) of the tracer particle. Therefore, we propose that the experimental measurement of this modulus, at the short-frequency limit, will give access to the determination of this diffusion property. Its practical measurement has not been reported in the literature up to now. We suggest a fit to the measured G'' with expression (21). The long-frequency limits for these moduli have the forms

$$\begin{aligned} G'(\omega) &\approx \frac{\eta_{sol}}{t_B} A_2(\omega), \quad \omega^* \rightarrow \infty, \\ G''(\omega) &\approx \frac{\eta_{sol}}{t_B} \frac{A_3}{\omega^*}. \end{aligned} \quad (23)$$

$$\begin{aligned} A_2(\omega) &:= \frac{1}{6\pi^2 \rho^*} \int_0^\infty dx x^4 \sum_{l=0}^1 \sum_{m=-l}^l \frac{[S_{m,l}^l(x) - 1]^2}{S_{m,l}^l(x)} \left[1 - \frac{A_0^2}{(\omega^*)^2} \right], \\ A_3 &:= \frac{1}{6\pi^2 \rho^*} \int_0^\infty dx x^4 \sum_{l=0}^1 \sum_{m=-l}^l \frac{[S_{m,l}^l(x) - 1]^2}{S_{m,l}^l(x)} A_0. \end{aligned} \quad (24)$$

These asymptotic limits are compared with the full numerical solution of (20), and they are depicted in Fig. 7 with dashed lines for a ferrofluid state with $\lambda = 0.292$ and $\rho^* = 0.086$. We note that in all systems studied, the asymptotic limits of G'' and G' have the initial ω and ω^2 dependencies, respectively, at short frequencies. In summary, we may conclude that Eq. (20) predicts a quadratic growth of $G'(\omega)$ and a linear dependency of G'' on the frequency at short and intermediate values in the range $1 \text{ Hz} \leq \omega \leq 10^5 \text{ Hz}$ where there are predominantly dissipative effects ($G'' > G'$) (see Fig. 7). In Fig. 8 is provided the comparison of the simulation results for the viscoelastic moduli $G(\omega)$ with its theoretical counterpart (20). From this figure, we observe that theory (20) predicts the short frequency behavior of

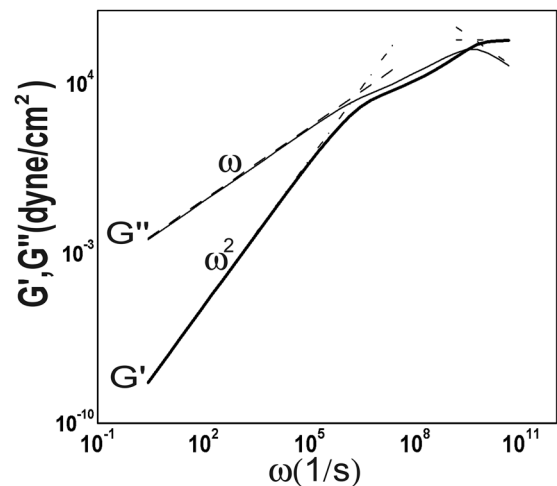


FIG. 7. Storage G' (gray line) and dissipative moduli G'' (black line) vs frequency for low density $\rho^* = 0.086$ and dipole coupling strength $\lambda = 0.292$. Dashed lines described in the main text are their asymptotic limits at short and long frequencies.

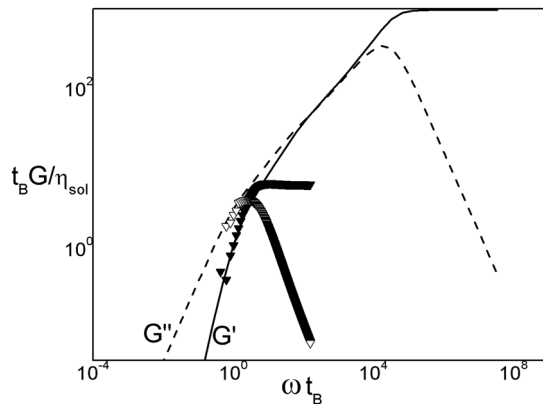


FIG. 8. Comparison of model viscoelastic moduli G' , G'' (continuous line) with simulations (triangles) as a function of reduced frequency. Case of reduced density $\rho^* = 0.086$ and dipole coupling strength $\lambda = 0.292$.

both components of G correctly as compared to simulations. Simulation data used the mean squared displacement from the simulated particles' trajectories in the expression $\eta(\omega) = \zeta(\omega)/(3\pi d)$, as given in Ref. 10. This finding is also a confirmation that at $\omega = 0$, the static viscosity in Eq. (19), which results from the component G'' , yields a correct prediction as we already confirmed in Fig. 5 in Sec. II. However, theory (20) for the rheology worsens at larger frequencies $\omega t_b > 10^2$ where it deviates from simulations.

V. CONCLUSION

Utilizing the stochastic Langevin equation that describes the Brownian dynamics of a tracer particle, we derived the equation of its friction function [Eq. (10)] due to its many particle anisotropic interactions in colloids such as ferrofluids. From this friction, we obtained at the long-time limit the diffusion coefficient [Eq. (13)] of the probe particle in terms of the equilibrium structure factor of the magnetic fluid. Our expression of the diffusion coefficient can include the many-body HI that is provided by an external theory or from its experimental measurement on ferrofluids. Based on the friction (10), we presented, in Sec. III, a model of static viscosity η given by Eqs. (18) and (19) for low and high volume fractions in monodisperse ferrofluids. We have shown in Figs. (3) and (4) the comparison of the viscosity η with the available experimental data for magnetite based monodisperse ferrofluids in kerosene. The theory of Eqs. (18) and (19) fits the experiments well as other approaches proposed by Rosensweig, Pshenichnikov, and Chow. Furthermore, in Sec. IV, by using the friction $\Delta\zeta(t)$ [Eq. (10)], together with the nano-rheology theory of Mason, we derived the viscoelastic modulus $G(t)$ of the ferrofluid. An essential portion of our work was also dedicated to the derivation of the intermediate scattering function [Eq. (12)] from the hydrodynamic theory presented in Appendix B. The resulting picture was the setup of the link through $G(\omega) = i\omega\zeta(\omega)/(3\pi d)$ between the friction $\Delta\zeta(t)$ and the viscoelastic modulus $G(t)$ in thermally equilibrated ferrofluids. We made a numerical analysis of the

viscoelasticity at various thermodynamic states typical of real ferrofluids, shown in Figs. (5) and (6). Our numerical study of $G(\omega)$ [Eq. (20)] was restricted to using the MSA for the structure factor, which is valid for low dipole coupling and volume fractions. However, in the case of a real ferrofluid, the measured structure factor can be used, avoiding such limitations on the microstructural information of the ferrofluid. Additionally, we derived the asymptotic limits of $G(\omega)$ at low and high frequency limits.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to this work.

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APPENDIX A: BROWNIAN MOTION OF A TRACER PARTICLE

In this appendix, we outline the main steps to derive the friction functions of a tracer given in Sec. II (see Refs. 34–36 for details). The rotational motion of the tracer uses a body frame with the origin at its center of mass and follows the orientation of its principal axis of symmetries. In this frame, the tracer's dipole orientation is $\hat{\mathbf{u}}(\Omega_t) = (0, 0, 1)$, $\Omega_t = (\theta_t = 0, \varphi_t = 0)$,^{19,35,36} and the dynamics is given by the stochastic equations

$$\begin{aligned} m_0 \frac{d\vec{\mathbf{v}}_t(t)}{dt} &= -\zeta^s \vec{\mathbf{v}}_t(t) + \vec{\mathbf{F}}^s(t) \\ &+ \int d\vec{\mathbf{r}} d\Omega [\nabla_{\vec{\mathbf{r}}} U_T(\vec{\mathbf{r}}, \Omega)] n(\vec{\mathbf{r}}, \Omega; t), \\ \mathbf{I} \cdot \frac{d\vec{\omega}_t(t)}{dt} &= -\zeta_r^s \vec{\omega}_t(t) + \vec{\tau}^s(t) \\ &+ \int d\vec{\mathbf{r}} d\Omega [(\vec{\mathbf{r}} \times \nabla_{\vec{\mathbf{r}}} + \vec{\mathbf{L}}) U_T(\vec{\mathbf{r}}, \Omega)] n(\vec{\mathbf{r}}, \Omega; t), \end{aligned} \quad (\text{A1})$$

where $\nabla_{\vec{\mathbf{r}}} = (\partial_x, \partial_y, \partial_z)$ is the translational gradient operator, $d\Omega = \sin\theta d\theta d\varphi$, $\vec{\mathbf{L}} = \hat{\mathbf{u}} \times \partial/\partial\hat{\mathbf{u}}$, $U_T(\vec{\mathbf{r}}, \Omega)$ is the potential energy of the tracer and another particle, and $n(\vec{\mathbf{r}}, \Omega; t) = \sum_{i=1}^N \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}'_i) \delta(\Omega - \Omega'_i)$ is the local concentration of particles. The order three diagonal matrix of tracer's principal moments of inertia \mathbf{I} has components I_{11} , I_{22} , $I_{32} := I = m_0 d^2/10$. The first two terms on the right-hand side of Eq. (A1) arise from the molecular nature of the solvent and produce friction and random forces and torques on the tracer, where the short-time frictions ζ^s , ζ_r^s represent hydrodynamic drag. These frictions and random forces (torques) ignore the molecular degree of freedom of position and momenta. The frictions are coupled to the random forces $\vec{\mathbf{F}}^s$ and torques $\vec{\tau}^s$ by fluctuation-dissipation theorems of thermally equilibrated suspensions, and the

Langevin equations are Markovian stochastic processes. However, the third terms convert them into non-Markovian stationary processes. The frictions are free parameters to this theory; nonetheless, they can be provided by experiment on hard sphere-like suspensions^{25–27} or an external theory.^{16,30} In the limit of infinite dilution of spherical particles $\zeta^s = \zeta^0 = 3\pi\eta_{sol}d^2$, $\zeta_r^s = \zeta_r^0 = \pi\eta_{sol}d^3$ with η_{sol} as the viscosity of the solvent. We now write (A1) up to first order in concentration fluctuations $\delta n(\vec{r}, \Omega; t) = n(\vec{r}, \Omega; t) - n^{eq}(\vec{r}, \Omega)$, with the profile distribution of host particles in the probe's field given as $n^{eq}(\vec{r}, \Omega) = \langle n(\vec{r}, \Omega, t) \rangle$ being an equilibrium ensemble average. At thermal equilibrium, the term n^{eq} does not contribute to a force. However, the inhomogeneous concentration of particles δn does produce a local force on the tracer. For this reason, we need to find the stochastic evolution equation for $\delta n(t)$. This can be derived with the help of linear irreversible theory of fluctuations.^{35–37} The starting point is the equation of conservation of particles $\partial\delta n/\partial t = -\vec{\nabla} \cdot \vec{J}$, where the current of particles is $\vec{J} = \vec{V}n(\vec{r}, \Omega; t)$. \vec{V} is an average velocity of the particles, and its definition encompasses six components,

$$\vec{V} := \begin{pmatrix} \vec{v}_t \\ \vec{\omega}_t \end{pmatrix}. \quad (A2)$$

One representative particle experiences a force $-\vec{\nabla}\mu$, which is counterbalanced by the particle friction $\vec{\zeta}^s$ with the solvent (μ is the electrochemical potential of the suspension), that is to say, $-\vec{\nabla}\mu = \vec{\zeta}^s \cdot \vec{V}$, where the general gradient operator

$$\vec{\nabla} := \begin{pmatrix} \vec{\nabla}_{\vec{r}} \\ \vec{r} \times \vec{\nabla}_{\vec{r}} + \vec{L} \end{pmatrix}, \quad (A3)$$

with \vec{r} denoting the vector joining the centers of the probe and another particle. Finally, we find for the current $\vec{J} = -n(\vec{r}, \Omega; t)k_B T \vec{\zeta}^s \cdot \vec{\nabla}\beta\mu(\vec{r}, \Omega; n(t))$, with $\beta = 1/k_B T$. Replacing this form of the generalized current in the above diffusion equation and linearizing it in the right-hand side to first order in the concentration and chemical potential fluctuations leads to $\partial\delta n(t)/\partial t = \vec{\nabla} \cdot [n^{eq}(\vec{r}, \Omega) \vec{D}^s \cdot \vec{\nabla}\delta\beta\mu(\vec{r}, \Omega; n(t))] + g(\vec{r}, \Omega; t)$. Here, the Stokes–Einstein relation holds, $\vec{D}^s = k_B T \vec{\zeta}^s$ ($\zeta_{ij}^s = 1/\zeta^s$ for $i = j = 1, 2, 3$; $1/\zeta_r^s$ for $i = j = 4, 5$; and 0 for $i = j = 6$), and we added the term $g(\vec{r}, \Omega; t)$ to represent random diffusive fluxes. The statistical thermodynamic theory of liquids provides the derivative $\vec{\nabla}\delta\beta\mu(\vec{r}, \Omega; t) = \int d\vec{r}' d\Omega' \sigma^{-1}(\vec{r}, \vec{r}', \Omega, \Omega') \delta n(\vec{r}', \Omega'; t)$. Here, σ^{-1} is the inverse of the inhomogeneous static correlation function $\sigma = \langle \delta n(0) \delta n(0) \rangle$ of liquid theory. We note that the rate of change of $\delta n(t)$ is due to two mechanisms. One is the diffusive process of translational and rotational diffusion of particles around the tracer that we have just discussed. The other is a kinematic process that appears because of the position and orientation variable (\vec{r}, Ω) dependency of $n(t)$, which are defined with respect to a reference frame attached to the tracer. Since the tracer moves with instantaneous velocities $(\vec{v}_t, \vec{\omega}_t)$, $\delta n(t)$ will change by the amount $[\vec{\nabla}n(t)] \cdot \vec{V}(t)$ due to

the movement of the tracer.^{35,36} Thus, the final form of the diffusion equation has in addition this last contribution. The solution of this diffusion equation for $\delta n(t)$ is replaced in Eq. (A1), yielding the stochastic equation for the labeled tracer

$$\begin{aligned} \vec{M} \cdot \frac{d\vec{V}(t)}{dt} = & -\vec{\zeta}^s \cdot \vec{V}(t) + \vec{F}(t) \\ & - \int_0^t dt' \Delta \vec{\zeta}(t-t') \cdot \vec{V}(t') + \vec{F}(t), \end{aligned} \quad (A4)$$

where $\vec{F}(t)$ is a generalized random force and torque with zero mean and second moment $\langle \vec{F}(t) \vec{F}^\dagger(0) \rangle = k_B T \Delta \vec{\zeta}(t)$ ^{34–36} and \dagger means transpose and complex conjugate. We defined the 6×6 diagonal matrix of effective mass $\vec{M}_{ij} = m_0 \delta_{ij}$ ($i, j = 1, 2, 3$), $\vec{M}_{ij} = \delta_{ij} I_{i-3, i-3}$ ($i, j = 4, 5, 6$).

Similarly, the generalized random friction force is

$$\vec{F}(t) = \begin{pmatrix} \vec{f}(t) \\ \vec{\tau}(t) \end{pmatrix}. \quad (A5)$$

The components of the six order diagonal friction matrix $\vec{\zeta}^s$ are $\zeta_{ij}^s = \zeta^s \delta_{ij}$ ($i, j = 1, 2, 3$), with $\zeta_{ij}^s = \zeta_r^s \delta_{ij}$ for $i, j = 4, 5$ and 0 for $i, j = 6$. The exact expression of the time-dependent friction of the tracer is the order six matrix

$$\begin{aligned} \Delta \vec{\zeta}(t) = & k_B T \int d\vec{r} d\vec{r}' d\Omega' d\Omega'' [\vec{\nabla} n^{eq}(\vec{r}, \Omega)] \\ & \times \sigma^{-1}(\vec{r}, \vec{r}', \Omega, \Omega') \chi(\vec{r}', \vec{r}'', \Omega', \Omega''; t) \\ & \times \left[\vec{\nabla} n^{eq}(\vec{r}'', \Omega'') \right]^\dagger, \end{aligned} \quad (A6)$$

where $\chi(t)$ describes the temporal evolution of other particles in space and up to the time t when they diffuse in the field of the tracer, the center of mass of which locates the origin of its body frame. $\chi(t)$ fulfills the identity with the intermediate scattering function

$$\begin{aligned} S(\vec{k}, \Omega, \Omega'; t) = & \frac{1}{N} \langle \delta n(\vec{k}, \Omega, t) \delta n(\vec{k}, \Omega', 0) \rangle \\ = & \frac{1}{\rho} \int d\Omega''' \chi(\vec{k}, \Omega, \Omega'''; t) \sigma(\vec{k}, \Omega''', \Omega'), \end{aligned} \quad (A7)$$

the initial value of which at $t = 0$ is $S(\vec{k}, \Omega, \Omega')$. The correlation function $S(\vec{k}, \Omega, \Omega'; t)$ was originally derived within mode coupling theory for radially symmetric potentials by Bengtzelius *et al.*²¹ and Hess and Klein,²² and in Appendix B, we show its derivation for anisotropic potentials. From Eq. (A6), a new expression of the friction is derived by using the reference frame with the selection $\vec{k} = (0, 0, k = |\vec{k}|)$. In this case, any function in the integrand is expanded in spherical harmonics Y_{lm} as $S(k, \Omega, \Omega') = \sum_{l'm'} (-)^m S_{l'm}^{ll'}(k) Y_{lm}(\Omega) Y_{l'm'}^*(\Omega')$, where $S_{l'm}^{ll'}(k)$ are structure factor projections and $*$ means complex conjugate.¹⁵ Equation (A6) yields the dynamical frictions in Sec. II.

APPENDIX B: INTERMEDIATE SCATTERING FUNCTION

The intermediate scattering function was derived from an extension of Hess and Klein hydrodynamic theory²² to include anisotropic potentials. The use of (A7) leads to

$$\begin{aligned} S(k, \Omega, \Omega'; t) &= \frac{1}{N} \langle \delta n(\vec{k}, \Omega, t) \delta n(\vec{k}, \Omega', 0) \rangle \\ &= \frac{1}{N} \left\langle \sum_{i,j=1}^N e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(t))} \hat{\mathbf{u}}_i(t) \hat{\mathbf{u}}_j^\dagger(t) \right\rangle, \end{aligned} \quad (\text{B1})$$

where \dagger means transpose and conjugate. Use was also made of the Fourier transform definition $f(\vec{k}) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} f(\vec{r})$ of a function f . The spherical harmonic representation of $\hat{\mathbf{u}}_i$ yields the components of the correlator (B1) as

$$S_{lm;l'm'}(k; t) = \frac{4\pi}{N} i^{l-l'} \left\langle \sum_{i,j=1}^N e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(t))} Y_{lm}^*(\hat{\mathbf{u}}_i(t)) Y_{l'm'}(\hat{\mathbf{u}}_j(t)) \right\rangle, \quad (\text{B2})$$

which defines the coherent intermediate scattering function $S_{lm;l'm'}(k; t)$,¹⁵ where $l, l' = 0, 1, 2, \dots, \infty$ and $-l, l' \leq m \leq l, l'$. Note that the initial time value of this dynamical function is the static structure factor, which according to Eq. (B2) has the definition $S_{lm;l'm'}(\vec{k}; 0) = \langle \delta n_{klm}^* \delta n_{kl'm'} \rangle / N$; thus, $S_{lm;l'm'}(k; t)$ is also the dynamical structure factor. From (B2), the definition of the k th Fourier component of the microscopic density, $n_{klm}(t) := \sum_{i=1}^N e^{-i\vec{k} \cdot \vec{r}_i} Y_{lm}(\hat{\mathbf{u}}_i(t))$, results.²² The temporal evolution of this quantity is the continuity equation of the conservation of the number of particles. It can be obtained in two ways up to first order in the fluctuation in concentration $\delta n(t)$. One uses the Fokker–Planck operator and follows similar methods in Ref. 22, and the second one uses the definition of n_{klm} and successive applications of the chain rule for the time derivatives of the position and orientation variables; thus, we are led to

$$\frac{\partial \delta n_{klm}}{\partial t} = i\vec{k} \cdot \mathbf{J}_{klm}^t + i\mathbf{L} \cdot \mathbf{J}_{klm}^r, \quad (\text{B3})$$

where $\mathbf{L} = \hat{\mathbf{u}} \times \partial / \partial \hat{\mathbf{u}}$ is the angular gradient operator with property $\mathbf{L}^2 Y_{lm} = l(l+1) Y_{lm}$. We have defined as in Ref. 22 the translational and rotational currents

$$\begin{aligned} \mathbf{J}_{klm}^t(t) &= \sum_{i=1}^N \vec{v}_i e^{-i\vec{k} \cdot \vec{r}_i} Y_{lm}(\hat{\mathbf{u}}_i), \\ \mathbf{J}_{klm}^r(t) &= \sum_{i=1}^N \vec{\omega}_i e^{-i\vec{k} \cdot \vec{r}_i} Y_{lm}(\hat{\mathbf{u}}_i). \end{aligned} \quad (\text{B4})$$

Here, \vec{v}_i and $\vec{\omega}_i$ are the instantaneous translational and angular velocities of colloidal particle i , respectively.

1. Intermediate scattering function

We shall derive an expression for $S_{lm;l'm'}(k; t)$. The structure factor is a static property; thus, its time derivative leads to the equal

time correlations $\langle \mathbf{J}_{klm}^t(t) \delta n_{lm}(t) \rangle = \langle \mathbf{J}_{klm}^r(t) \delta n_{lm}(t) \rangle = 0$ due to the fact that the average of the velocity is zero. Moreover, a second derivative of these identities with use of Eq. (B3) results in

$$\left\langle \frac{\partial \mathbf{J}_{klm}^t}{\partial t} \delta n_{klm} \right\rangle = -i \sum_{\gamma} \mathbf{k}^\gamma \cdot \langle \mathbf{J}_{klm}^t \mathbf{J}_{klm}^\gamma \rangle, \quad (\text{B5})$$

where $\mathbf{k}^\gamma = \vec{k}$ and \mathbf{L} for $\alpha, \gamma = t$ and r , respectively. Equations (B1)–(B5) were expressed in the laboratory frame of coordinates. From now on, it is more convenient to use the k -frame where $\vec{k} = (0, 0, k)$ with $k = |\vec{k}|$. Thus, $S_{lm;l'm'}(\vec{k}) = S_{lm;l'm'}^{ll'}$ with $\delta_{ll'}$ being the Kronecker delta. Then, the structure factor is $S(\vec{k}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \sum_{lm} \sum_{l'm'} Y_{lm}(\hat{\mathbf{u}}_1) Y_{l'm'}(\hat{\mathbf{u}}_2) S_{lm;l'm'}^{ll'}(k) \delta_{mm'}$ in the intermolecular reference frame. According to Ref. 22, the concentration of particles δn is the only conserved quantity, and it can be used for the definition of local equilibrium. Linear and angular momentum and energy are not conserved quantities due to the dissipation of energy by the particle friction with the solvent. Thus, any other dynamical variable $\mathbf{A}(\vec{k})$ can be decomposed into two parts with respect to δn_{klm} : a parallel equilibrium and a perpendicular out of equilibrium $\mathbf{A}'(\vec{k})$ component. This decomposition is an instance of the mode coupling theory of density fluctuations where one can define δn as a slow variable and construct the projection operator $P = \langle \delta n, \mathbf{A}(t) \rangle \langle \delta n \delta n \rangle^{-1} \delta n$ that projects onto δn the slow dependent part. The inner product $\langle \mathbf{A}^* \delta n \rangle$ is the equilibrium ensemble average of the complex conjugate $*$ of the dynamical variable $\mathbf{A}(t)$ by δn . Using the complementary operator $Q = 1 - P$, the fast component of $\mathbf{A}(t)$ can be obtained. From Hamilton's equations of motion, the time rate of change of $d\mathbf{A}/dt$ can be computed, and with the help of the above operators, the resulting equation has the form

$$\mathbf{A}(\vec{k}) = \frac{\langle \mathbf{A}(\vec{k}) \delta n_{klm} \rangle}{\langle \delta n_{klm} \delta n_{kl'm'} \rangle} \delta n_{kl'm'} + \mathbf{A}'(\vec{k}). \quad (\text{B6})$$

In the above equation, if we define $\mathbf{A} := \partial \mathbf{J}_{klm}^\alpha / \partial t$ and with the use of (B5), we obtain for the equilibrium part

$$\begin{aligned} \frac{\langle \frac{\partial \mathbf{J}_{klm}^t}{\partial t} \delta n_{klm} \rangle}{S_{lm}^{ll'}(k)} \delta n_{kl'm'} &= -i \frac{\langle \mathbf{J}_{klm}^t \mathbf{J}_{klm}^t \rangle}{S_{lm}^{ll'}(k)} \cdot \vec{k} \delta n_{klm} \\ &\quad - i \frac{\langle \mathbf{J}_{klm}^t \mathbf{J}_{klm}^r \rangle}{S_{lm}^{ll'}(k)} \cdot \mathbf{L} \delta n_{klm}, \end{aligned} \quad (\text{B7})$$

$$\begin{aligned} \frac{\langle \frac{\partial \mathbf{J}_{klm}^r}{\partial t} \delta n_{klm} \rangle}{S_{lm}^{ll'}(k)} \delta n_{kl'm'} &= -i \frac{\langle \mathbf{J}_{klm}^r \mathbf{J}_{klm}^t \rangle}{S_{lm}^{ll'}(k)} \cdot \vec{k} \cdot \delta n_{klm} \\ &\quad - i \frac{\langle \mathbf{J}_{klm}^r \mathbf{J}_{klm}^r \rangle}{S_{lm}^{ll'}(k)} \cdot \mathbf{L} \delta n_{klm}. \end{aligned} \quad (\text{B8})$$

The initial values of the diagonal components of the correlation matrix $\langle \mathbf{J}_{klm}^\alpha(t=0) \mathbf{J}_{klm}^\gamma(t=0) \rangle$ are $k_B T / m_0$ and $k_B T / I$ for $\alpha = \gamma = t, r$, respectively, whereas m_0 and I are the mass and moment of inertia of a spherical particle. k_B is Boltzmann's constant, and T is room temperature. The currents on the right-hand side of Eq. (B3)

satisfy equations of motion, which can be derived at the hydrodynamic level of description of low wave vectors and frequencies.²² The stress fluctuations produce current fluctuations that are the origin of the force \vec{F} and torque $\vec{\tau}$ on a particle. They can be given by velocity gradients where the constants of proportionality are the tensors of viscosities with couple translational and rotational motion components $\zeta^{\text{tt}}(t)$, $\zeta^{\text{tr}}(t)$, $\zeta^{\text{rt}}(t)$, $\zeta^{\text{rr}}(t)$,

$$\vec{F}(t) = - \int_0^t dt' \zeta^{\text{tt}}(t-t') \mathbf{J}^{\text{t}}(t') - \int_0^t dt' \zeta^{\text{tr}}(t-t') \mathbf{J}^{\text{r}}(t'), \quad (\text{B9})$$

$$\vec{\tau}(t) = - \int_0^t dt' \zeta^{\text{tr}}(t-t') \mathbf{J}^{\text{t}}(t') - \int_0^t dt' \zeta^{\text{rr}}(t-t') \mathbf{J}^{\text{r}}(t'), \quad t \geq 0. \quad (\text{B10})$$

The rank three diagonal friction matrices are defined by $\zeta^{\text{tr}}(t-t') = -\delta \vec{F}(t)/\delta \mathbf{J}^{\text{t}}(t')$ and similarly for the other components tr, rt, rr. The fluctuating force and torque satisfy equations of motion of type (B6) for the current fluctuations

$$\vec{F}_{klm}(t) = \left[m_0 \frac{\partial \mathbf{J}_{klm}^{\text{t}}}{\partial t} \right]^{eq} + m_0 \frac{\partial \mathbf{J}_{klm}^{\text{t}}}{\partial t}, \quad (\text{B11})$$

$$\vec{\tau}_{klm}(t) = \left[\mathbf{I} \cdot \frac{\partial \mathbf{J}_{klm}^{\text{r}}}{\partial t} \right]^{eq} + \mathbf{I} \cdot \frac{\partial \mathbf{J}_{klm}^{\text{r}}}{\partial t}. \quad (\text{B12})$$

[Equation (B11) is an extension of the known current fluctuation equation $[m_0 \partial \mathbf{J}^{\text{t}} / \partial t]^{eq} = -\nabla \delta p(\mathbf{k}, t) + \vec{F}(t)$, when angular degrees of freedom are neglected,²² and δp is the pressure fluctuation at equilibrium, $\langle (\partial \mathbf{J}^{\text{t}} / \partial t) \delta n \rangle / \langle \delta n \delta n \rangle := -(\nabla p / m_0)$.] \mathbf{I} is the rank three matrix of moment of inertia of a particle. The upperscript *eq* denotes the equilibrium part. We attain the second terms on the right-hand side of the above equations with the help of Eqs. (B7) and (B8), together with (B11) and (B12),

$$\begin{aligned} \frac{\partial}{\partial t} [m_0 \mathbf{J}_{klm}^{\text{t}}] &= - \left(m_0 \mathbf{1} \quad \mathbf{0} \right) \frac{\partial}{\partial t} [m_0 \mathbf{J}_{klm}^{\text{t}}]^{eq} \\ &\quad - \int_0^t dt' \begin{pmatrix} \zeta^{\text{tt}} & \zeta^{\text{tr}} \\ \zeta^{\text{rt}} & \zeta^{\text{rr}} \end{pmatrix} (t-t') \begin{bmatrix} \mathbf{J}_{klm}^{\text{t}} \\ \mathbf{J}_{klm}^{\text{r}} \end{bmatrix} (t'). \end{aligned} \quad (\text{B13})$$

Using the Laplace transform $f(z) = \int_0^\infty f(t) e^{-zt} dt$ of the above equation and using Eqs. (B7) and (B8) yields

$$\begin{aligned} z \begin{bmatrix} m_0 \mathbf{J}_{klm}^{\text{t}}(z) \\ \mathbf{I} \cdot \mathbf{J}_{klm}^{\text{r}}(z) \end{bmatrix} &- \begin{bmatrix} m_0 \mathbf{J}_{klm}^{\text{t}}(t=0) \\ \mathbf{I} \cdot \mathbf{J}_{klm}^{\text{r}}(t=0) \end{bmatrix} \\ &= \begin{pmatrix} m_0 \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \frac{1}{S_{,m}^{\text{ll}}(k)} (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{C}^{\text{tt}}(0) & \mathbf{C}^{\text{tr}}(0) \\ \mathbf{C}^{\text{rt}}(0) & \mathbf{C}^{\text{rr}}(0) \end{pmatrix} \delta n_{klm}(z) \\ &\quad - \begin{pmatrix} \zeta^{\text{tt}}(z) & \zeta^{\text{tr}}(z) \\ \zeta^{\text{rt}}(z) & \zeta^{\text{rr}}(z) \end{pmatrix} \begin{bmatrix} \mathbf{J}_{klm}^{\text{t}}(z) \\ \mathbf{J}_{klm}^{\text{r}}(z) \end{bmatrix}, \end{aligned} \quad (\text{B14})$$

where $\mathbf{C}^{\alpha\gamma}(t=0) = \langle \mathbf{J}_{klm}^{\alpha}(0) \mathbf{J}_{klm}^{\gamma\dagger}(0) \rangle^{eq}$. Here the upper indices $\alpha, \gamma = \text{t, r}$, mean translation and rotation components, respectively, and the identity matrix $\mathbf{1}$ is of rank three. The Laplace transform of Eq. (B3) is

$$z \delta n_{klm}(z) - \delta n_{klm}(0) = i \vec{\mathbf{k}} \cdot \mathbf{J}_{klm}^{\text{t}}(z) + i \mathbf{L} \cdot \mathbf{J}_{klm}^{\text{r}}(z). \quad (\text{B15})$$

Substituting now $\delta n_{klm}(z)$ from this equation into (B14) yields

$$\begin{aligned} &\left\{ z \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} - \frac{1}{z S_{,m}^{\text{ll}}(k)} (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{C}^{\text{tt}}(0) & \mathbf{C}^{\text{tr}}(0) \\ \mathbf{C}^{\text{rt}}(0) & \mathbf{C}^{\text{rr}}(0) \end{pmatrix} \right\} \\ &\quad \times \begin{bmatrix} \mathbf{J}_{klm}^{\text{t}}(z) \\ \mathbf{J}_{klm}^{\text{r}}(z) \end{bmatrix} + \begin{pmatrix} m_0 \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}^{-1} \begin{pmatrix} \zeta^{\text{tt}}(z) & \zeta^{\text{tr}}(z) \\ \zeta^{\text{rt}}(z) & \zeta^{\text{rr}}(z) \end{pmatrix} \begin{bmatrix} \mathbf{J}_{klm}^{\text{t}}(z) \\ \mathbf{J}_{klm}^{\text{r}}(z) \end{bmatrix} \\ &= \begin{bmatrix} \mathbf{J}_{klm}^{\text{t}}(0) \\ \mathbf{J}_{klm}^{\text{r}}(0) \end{bmatrix} + \frac{1}{z S_{,m}^{\text{ll}}(k)} (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{C}^{\text{tt}}(0) & \mathbf{C}^{\text{tr}}(0) \\ \mathbf{C}^{\text{rt}}(0) & \mathbf{C}^{\text{rr}}(0) \end{pmatrix} \delta n_{klm}(0). \end{aligned} \quad (\text{B16})$$

Taking an ensemble average of the above equation with the translational and rotational currents at $z=0$ and using the fact that $\langle \delta n_{klm}(0) \mathbf{J}_{klm}^{\alpha}(0) \rangle^{eq} = 0$ with $\alpha = \text{t, r}$, we obtain

$$\begin{aligned} &\begin{pmatrix} \mathbf{C}^{\text{tt}}(z) & \mathbf{C}^{\text{tr}}(z) \\ \mathbf{C}^{\text{rt}}(z) & \mathbf{C}^{\text{rr}}(z) \end{pmatrix} = \left\{ z \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} + \begin{pmatrix} m_0 \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{I} \end{pmatrix}^{-1} \begin{pmatrix} \zeta^{\text{tt}}(z) & \zeta^{\text{tr}}(z) \\ \zeta^{\text{rt}}(z) & \zeta^{\text{rr}}(z) \end{pmatrix} \right. \\ &\quad \left. - \frac{1}{z S_{,m}^{\text{ll}}(k)} (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{C}^{\text{tt}}(0) & \mathbf{C}^{\text{tr}}(0) \\ \mathbf{C}^{\text{rt}}(0) & \mathbf{C}^{\text{rr}}(0) \end{pmatrix} \right\}^{-1} \\ &\quad \times \begin{pmatrix} \mathbf{C}^{\text{tt}}(0) & \mathbf{C}^{\text{tr}}(0) \\ \mathbf{C}^{\text{rt}}(0) & \mathbf{C}^{\text{rr}}(0) \end{pmatrix}. \end{aligned} \quad (\text{B17})$$

Now, taking into account the ensemble average of Eq. (B15) with the complex conjugate of the concentration fluctuation $\delta n_{klm}^*(0)$ leads to

$$\begin{aligned} z S_{,m}^{\text{ll}}(k; z) - S_{,m}^{\text{ll}}(k) &= i \vec{\mathbf{k}} \cdot \langle \delta n_{klm}(0) \mathbf{J}_{klm}^{\text{t}}(z) \rangle^{eq} \\ &\quad + i \mathbf{L} \cdot \langle \delta n_{klm}(0) \mathbf{J}_{klm}^{\text{r}}(z) \rangle^{eq}. \end{aligned} \quad (\text{B18})$$

Since $\partial \langle \delta n_{klm}^*(t) n_{klm}(t) \rangle^{eq} / \partial t = 0$, and in addition, with the Laplace transform of Eq. (B5) and together with (B18), we get

$$S_{,m}^{\text{ll}}(k; z) = \frac{1}{z} S_{,m}^{\text{ll}}(k) - \frac{1}{z^2} (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{C}^{\text{tt}}(z) & \mathbf{C}^{\text{tr}}(z) \\ \mathbf{C}^{\text{rt}}(z) & \mathbf{C}^{\text{rr}}(z) \end{pmatrix}. \quad (\text{B19})$$

We can now replace Eq. (B17) into (B19) and after some algebra, the expression of the intermediate scattering function or dynamical structure factor results as

$$S_{,m}^{\text{ll}}(k; z) = \left[z + (\vec{\mathbf{k}}, \mathbf{L}) \begin{pmatrix} \mathbf{D}^{\text{tt}}(z) & \mathbf{D}^{\text{tr}}(z) \\ \mathbf{D}^{\text{rt}}(z) & \mathbf{D}^{\text{rr}}(z) \end{pmatrix} \right]^{-1} S_{,m}^{\text{ll}}(k), \quad (\text{B20})$$

where the dynamical matrix of tracer diffusion coefficients in Laplace space is defined by

$$\begin{pmatrix} \mathbf{D}^{tt}(z) & \mathbf{D}^{tr}(z) \\ \mathbf{D}^{rt}(z) & \mathbf{D}^{rr}(z) \end{pmatrix} := \frac{1}{S_{,m}^{\text{ll}}(k)} \left\{ z \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} + \begin{pmatrix} m_0 \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix} \right. \\ \left. \times \begin{pmatrix} \vec{\zeta}^{\text{tr}}(z) & \vec{\zeta}^{\text{tr}}(z) \\ \vec{\zeta}^{\text{tr}}(z) & \vec{\zeta}^{\text{tr}}(z) \end{pmatrix} \right\}^{-1} \begin{pmatrix} \mathbf{C}^{tt}(0) & \mathbf{C}^{tr}(0) \\ \mathbf{C}^{rt}(0) & \mathbf{C}^{rr}(0) \end{pmatrix}. \quad (\text{B21})$$

Equation (B20) is our generalization to include rotational dynamics into the translational diffusion formalism in colloids, as given by Hess and Klein.²² Similar results to Eq. (B20) were derived by Schilling and Scheidsteger³⁸ using mode coupling theory for a molecular fluid of hard linear molecules. However, Eq. (B20) coincides at the overdamped limit with the one derived by Elizondo-Aguilera *et al.*²⁰ who used a general theorem of stationary stochastic processes. Using (B20), we can now attain explicit expressions for each spherical harmonic projection of the intermediate scattering function of Eq. (B20). At the overdamped limit (for spherical particles) $l z / \zeta_r^s, m_0 z / \zeta^s \ll 1$, they are

$$S_{,m}^{\text{ll}}(k; z) = \frac{S_{,m}^{\text{ll}}(k)}{z + \frac{1}{S_{,m}^{\text{ll}}(k)} \left(\frac{k^2 D^s \zeta^s}{\zeta_{\text{tr}}(z)} + \frac{l(l+1) D_r^s \zeta_r^s}{\zeta_{\text{rot}}(z)} \right)} \\ := \frac{S_{,m}^{\text{ll}}(k)}{z + \frac{1}{S_{,m}^{\text{ll}}(k)} [k^2 D^s \mu_T(z) + l(l+1) D_r^s \mu_R(z)]}, \quad (\text{B22})$$

and the same formula holds for the tracer (self, s) scattering function $S_{,m}^{\text{ll},s}(k; z)$ by applying the dilute limit of $S_{,m}^{\text{ll}}(k) \rightarrow 1$. That is, when using Eq. (B22), we further made the approximation, as in Ref. 22, that $(\zeta^s / \zeta_{\text{tr}}(z)) = (\zeta_r^s / \zeta_r(z)) = 1$ in the collective (c) propagator $S_{,m}^{\text{ll},c}(k; z) = S_{,m}^{\text{ll}}(k) / [z + (k^2 D^s + l(l+1) D_r^s) / S_{,m}^{\text{ll}}(k)]$, but for the tracer propagator, $S_{,m}^{\text{ll},s}(k; z) = 1 / [z + (k^2 D^s \zeta^s / \zeta_{\text{tr}}(z) + l(l+1) D_r^s \zeta_r^s / \zeta_{\text{rot}}(z))]$. Thus, with $z = i\omega$, we recover Eq. (3). Hydrodynamic effects on the memory functions $S^{\text{ll},c}$, $S^{\text{ll},s}$ are included by replacing ζ^s and ζ_r^s with their short time values that depend on volume fraction.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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