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Translational and rotational dynamics of colloidal particles in suspension: Effect of shear

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We report a generalization of a nonequilibrium thermodynamic theory for the mesoscopic dynamics of radially symmetric interacting particles to anisotropic pairwise interactions and attain the one- and two-particle Fokker-Planck kinetics equations at a low-density limit that provides the translational-rotational coupling of their motion due to hydrodynamic interactions, from which we derived the balance equations of linear, angular momentum, and energy dissipation due to particle interactions and energy interchange with heat bath. In this low-density approximation, an already-known virial expression for the long-time translational collective diffusion coefficient of an orientational isotropic suspension in terms of the fluid equilibrium microstructure is recovered. An external shear flow induces, in the diffusive regime, vorticity effects into the rotational diffusion property of the colloidal particles. They manifest in the appearance of the particle's rotational viscosity due to vortex flow. The Smoluchowski equation that governs the dynamical relaxation of colloid microstructure due to particle's Brownian motion under stationary flow is provided.

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I. INTRODUCTION

The study of dynamical properties of colloidal suspensions is a problem of permanent interest [1–3]. These properties have important applications in industrial processes and material science. Experimental techniques based on x-ray correlations spectroscopy, dynamic light scattering, and small-angle quasielastic neutron scattering measure the long-time collective translational diffusion coefficient of the colloidal particles in suspension [4,5]. Most of the measurements on this coefficient are based on sedimentation experiments performed in systems made of particles that experience direct pair interaction potentials of spherical symmetry [6]. The experiments have reached a successful agreement with theory. Intense research has been conducted in the past few years in cases where colloidal particles interact through anisotropic potentials such as in ferrofluids or in suspensions of rod-like-shaped particles of fd virus. Due to birefringence measurements, it is known that even at low shear rates [7,8] there occurs phase separation in fd bacteriophage suspensions. Its rheological characterization is currently performed with diffusion wave spectroscopy [9] and optical tweezer microrheology experiments [10]. From the theoretical viewpoint, its rheological properties can be determined through evolution equations derived from the moments of the distribution function that satisfy the system's Fokker-Planck (FP) equation [11]. Recently, a mesoscopic approach to study colloid dynamics based on nonequilibrium thermodynamics (MNET) was developed and it permits us to attain the FP kinetic equation [12–15]. This theory has been successfully applied to describe anomalous diffusion in viscoelastic media [16] via the formation of patterns in liquid crystals [17], magnetization curves of ferrofluids under external magnetic fields [18], the diffusion in suspensions under oscillatory shear [19], and slow dynamics in colloids and supercooled liquids [20,21]. Using this approach Mayorga *et al.* [22] derived the above referred dynamical property for spherically symmetric interacting Brownian particles in the absence of applied shear. Santamaria-Holek *et al.* developed the theory to determine the single-particle dynamics under stationary conditions [23,24] and an oscillatory shear [19], including the many-body hydrodynamic interactions (HI) through the friction coefficients but neglecting direct interactions among particles. In this paper we extend these theoretical frameworks to encompass the particle's anisotropic interactions and coupling of their translational-rotational movements. In the first part of the paper we derive the one- and two-particle FP stochastic equations which allow us to obtain the hydrodynamic balance equations of linear, angular momentum and then for the energy interchange of particles with the heat bath. At the low-density limit and diffusion regime we recover from the balance of linear momentum a known expression for the diffusion coefficient of spherical colloidal particles in orientational isotropic suspensions with the particle's anisotropic interactions. This property is given in terms of the pair-correlation function of the bulk suspension without taking into account HI and shear. In the second part of the paper we present the derivation of the FP equation valid at arbitrary concentration and which couples the translational and rotational movement of the particles under flow conditions. The resulting rotational diffusion coefficient and its dependence on shear defines a rotational viscosity contribution due to vortex flow.

II. BROWNIAN SUSPENSION WITHOUT APPLIED SHEAR FLOW

Consider the system of volume V consisting of solvent with constant mass density ρ_s and colloid density ρ_B formed by N identical interacting particles of equal mass m with position $\mathbf{r}_i$ and orientation of its main axis of symmetry defined by the two polar angles of orientation $\Omega_i = (\theta_i, \phi_i)$. The total potential energy of the system is $U = \Sigma_{i,j}^{N} \phi_{ij}/2 + \Sigma_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i, \Omega_i, t)$, where it is assumed that ϕ_{ij} is the pairwise direct interaction and V_{ext} and external field acting on particle i at time t. The translational and angular velocities are, respectively, $\mathbf{v}_i$, ω_i, with $i = 1, \ldots, N$. Since particles are axial symmetric ω_i has only two components. Their components are referred to a

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space coordinate system. With respect to the polar axis of this frame are defined the angles of orientation Ω of the particle. According to the mesoscopic theory, we define a point in the phase space of the system by $\Gamma := (\mathbf{x}^N)$, where $\mathbf{x}^N = (\mathbf{r}_1,\Omega_1,\mathbf{v}_1,\omega_1,\ldots,\mathbf{r}_N,\Omega_N,\mathbf{v}_N,\omega_N)$. The probability density $P^{(N)}$ at any time t and state Γ satisfy the conservation of probability

$$\int P^{(N)}(\Gamma,t)d\Gamma = 1. \tag{1}$$

The time evolution of the colloidal system is characterized by three time scales. The hydrodynamic relaxation time for solvent molecules velocities is $\tau_H = \sigma^2/\nu = 10^{-8}$ s (average particle size $\sigma = 100$ nm, solvent shear viscosity $\nu = 10^{-5}$ m^2/s). The relaxation time of the Brownian (B) particle velocity $\tau_B = (2\tau_H/9)(\rho_p/\rho_s) = 2.2 \times 10^{-9}$ s (ρ_p, ρ_s densities of particle and fluid solvent). And the structural relaxation time on which particle configuration change $\tau_R = \sigma^2/D^0 = 4.7 \times 10^{-3}$ s ($D^0 = k_B T_{\mathrm{eq}}/6\pi\eta\sigma$, k_B Boltzmann constant, T_{eq} equilibrium temperature) [25]. We write the Liouville equation for colloids assuming that $\tau_R,\tau_B \gg \tau_H$ which implies that the dynamic of the solvent particles decouple from the dynamic of the colloids. It expresses the conservation of probability as a continuity equation [26],

$$\begin{aligned}
&\frac{\partial P^{(N)}}{\partial t} + \Sigma_{i=1}^N \mathbf{v}_i \cdot \frac{\partial P^{(N)}}{\partial \mathbf{r}_i} + \Sigma_{i=1}^N \omega_i \cdot \big(L_{\mathbf{u}_i} - \widehat{R}_i\big) P^{(N)} \\
&\quad - m^{-1} \Sigma_{i,j=1}^N \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial P^{(N)}}{\partial \mathbf{v}_i} \\
&\quad - I^{-1} \Sigma_{i,j=1}^N (L_{\mathbf{u}_i} - \widehat{R}_i)\phi_{ij} \frac{\partial P^{(N)}}{\partial \omega_i} \\
&\quad - m^{-1} \Sigma_{i=1}^N \frac{\partial V_{\mathrm{ext}}}{\partial \mathbf{r}_i} \cdot \frac{\partial P^{(N)}}{\partial \mathbf{v}_i} \\
&\quad - I^{-1} \Sigma_{i=1}^N \big(L_{\mathbf{u}_i} - \widehat{R}_i\big) V_{\mathrm{ext}} \cdot \frac{\partial P^{(N)}}{\partial \omega_i} \\
&\quad = -\Sigma_{i=1}^N \frac{\partial}{\partial \mathbf{v}_i} \cdot \mathbf{J}_{\mathbf{v}_i}^{(N)} - \Sigma_{i=1}^N \frac{\partial}{\partial \omega_i} \cdot \mathbf{J}_{\omega_i}^{(N)}.
\end{aligned} \tag{2}$$

In this version of the Liouville equation the fifth and seventh terms include the total torque on a particle due to pair interaction and external field as defined by Evans [27]. They are contributions to intrinsic angular momentum about the particle's center of mass given by the operator $L_{\mathbf{u}_i} = \mathbf{u}_i \times \frac{\partial}{\partial \mathbf{u}_i}$, where $\mathbf{u} = \mathbf{u}(\Omega(\theta,\phi))$ is a unitary vector in the direction of the main axis of symmetry of particle i. The orbital angular momentum is represented by $\widehat{R}_i = \mathbf{r}_{ij} \times \frac{\partial}{\partial \mathbf{r}_i}$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. In the fourth and sixth terms, however, there are the contributions of the total force of all pairs of particles due to their direct interactions and that from the external field, respectively [26]. $I = ml^2$ is the moment of inertia of a particle and l^2 its radius of gyration. We note that in the body-fixed frame the equation of motion of the angular momentum of a sphere with an embedded linear anisotropy or of a particle of rodlike shape in a solvent is [28]

$$\frac{d\omega_\gamma}{dt} = \frac{(I_k - I_l)}{I_\gamma}\omega_k\omega_l - \lambda_\gamma\omega_\gamma + A_\gamma(t), \tag{3}$$

where $\gamma,k,l = 1,2,3$, and I_l is the moment of inertia of the sphere about its center, or of the rod, about its principal axes. λ_γ is the viscous damping and $A(t)_\gamma$ the Gaussian random torque of the solvent on the particle. For the two particle's geometries considered it reduces to [28]

$$\frac{d\omega_\gamma}{dt} = -\lambda_\gamma\omega_\gamma + A_\gamma(t), \tag{4}$$

where the z axis ($\gamma = 3$) is taken along the anisotropy, or of the rod, since $I_1 = I_2$. This demonstrates that for the two systems considered it is only necessary to know one component, $I_3 = I$. Nonetheless, in this paper we focus on spherical particles only. In order to derive the mesoscopic dynamic equation of $P^{(N)}$, it is assumed that $P^{(N)}$ fulfills the Gibbs entropy postulate [12,29]

$$S = -k_B \int P^{(N)}(\Gamma,t) \ln \frac{P^{(N)}(\Gamma,t)}{P_{\mathrm{LE}}^{(N)}(\Gamma)} d\Gamma + S_{\mathrm{LE}}, \tag{5}$$

$$\begin{aligned}
P_{\mathrm{LE}}^{(N)} = \exp\Bigg[&\frac{m}{k_B T}\left(\mu_B - \Sigma_{i=1}^N \frac{1}{2}\mathbf{v}_i^2\right) - \frac{ml^2}{k_B T}\Sigma_{i=1}^N \frac{1}{2}\omega_i^2 \\
&- \frac{1}{2k_B T}\Sigma_{i,j=1}^N \phi_{ij} - \frac{1}{k_B T}\Sigma_{i=1}^N V_{\mathrm{ext}}\Bigg],
\end{aligned} \tag{6}$$

with S_{LE} and μ_B the local equilibrium (LE) entropy and chemical potential. We will study colloid dynamic at the pair particle level. Thus, it is defined the n-particle probability density and flux given, respectively, by

$$P^{(n)}(\mathbf{x}_1,\ldots,\mathbf{x}_n,t) = \frac{N!}{(N-n)!}\int P^{(N)} d\mathbf{x}_{n+1}\ldots d\mathbf{x}_N,$$

$$\text{and} \quad \mathbf{J}_{\mathbf{v}_i}^{(n)} = \frac{N!}{(N-n)!}\int \mathbf{J}_{\mathbf{v}_i}^{(N)} d\mathbf{x}_{n+1}\ldots d\mathbf{x}_N,$$

and analogously for $\mathbf{J}_{\omega_i}^{(n)}$.

The time derivative of Eq. (5) together with Eq. (2) lead, after performing a partial integration, to the entropy production from which it results [22] (see Appendix A),

$$\begin{aligned}
\mathbf{J}_{\mathbf{v}_i}^{(N)} = &-\Sigma_{j=1}^N \overset{\leftrightarrow}{\beta}{}_{ij}^{tt} \cdot \left(P^{(N)}\mathbf{v}_j + \frac{k_B T}{m}\frac{\partial P^{(N)}}{\partial \mathbf{v}_j}\right) \\
&- \Sigma_{j=1}^N \overset{\leftrightarrow}{\beta}{}_{ij}^{tr} l^2 \left(P^{(N)}\omega_j + \frac{k_B T}{I}\frac{\partial P^{(N)}}{\partial \omega_j}\right),
\end{aligned} \tag{7}$$

$$\begin{aligned}
\mathbf{J}_{\omega_i}^{(N)} = &-\Sigma_{j=1}^N \frac{\overset{\leftrightarrow}{\beta}{}_{ij}^{rt}}{l^2} \cdot \left(P^{(N)}\mathbf{v}_j + \frac{k_B T}{m}\frac{\partial P^{(N)}}{\partial \mathbf{v}_j}\right) \\
&- \Sigma_{j=1}^N \overset{\leftrightarrow}{\beta}{}_{ij}^{rr} \left(P^{(N)}\omega_j + \frac{k_B T}{I}\frac{\partial P^{(N)}}{\partial \omega_j}\right).
\end{aligned} \tag{8}$$

In deriving the above expressions, a linear relationship between fluxes and thermodynamic forces was assumed [22,29]. Therefore, substituting these fluxes into the continuity equation (2) yields the Fokker-Planck equations of one- and two-particle distribution functions,

$$\begin{aligned}
&\frac{\partial P^{(1)}}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial P^{(1)}}{\partial \mathbf{r}_1} + \omega_1 \cdot \big(L_{\mathbf{u}_1} - \widehat{R}_1\big)P^{(1)} - m^{-1}\int \frac{\partial \phi_{12}}{\partial \mathbf{r}_1} \cdot \frac{\partial P^{(2)}}{\partial \mathbf{v}_1} d\mathbf{x}_2 - I^{-1}\int \big(L_{\mathbf{u}_1} - \widehat{R}_1\big)\phi_{12} \cdot \frac{\partial P^{(2)}}{\partial \omega_1} d\mathbf{x}_2 \\
&\quad - m^{-1}\int \frac{\partial V_{\mathrm{ext}}}{\partial \mathbf{r}_1} \cdot \frac{\partial P^{(1)}}{\partial \mathbf{v}_1} d\mathbf{x}_1 - I^{-1}\int \big(L_{\mathbf{u}_1} - \widehat{R}_1\big)V_{\mathrm{ext}} \cdot \frac{\partial P^{(1)}}{\partial \omega_1} d\mathbf{x}_1
\end{aligned}$$

$$= \frac{\partial}{\partial \mathbf{v}_1}\cdot \overleftrightarrow{\beta}^{tt}_{11}\cdot\left(P^{(1)}\mathbf{v}_1+\frac{k_BT}{m}\frac{\partial P^{(1)}}{\partial \mathbf{v}_1}\right)+\frac{\partial}{\partial \omega_1}\cdot \overleftrightarrow{\beta}^{rr}_{11}\cdot\left(P^{(1)}\omega_1+\frac{k_BT}{I}\frac{\partial P^{(1)}}{\partial \omega_1}\right)$$
$$+\frac{\partial}{\partial \mathbf{v}_1}\cdot \overleftrightarrow{\beta}^{tr}_{11}l^2\left(P^{(1)}\omega_1+\frac{k_BT}{I}\frac{\partial P^{(1)}}{\partial \omega_1}\right)+\frac{\partial}{\partial \omega_1}\frac{\overleftrightarrow{\beta}^{rt}_{11}}{l^2}\left(P^{(1)}\mathbf{v}_1+\frac{k_BT}{m}\frac{\partial P^{(1)}}{\partial \mathbf{v}_1}\right), \tag{9}$$

$$\frac{\partial P^{(2)}}{\partial t}+\Sigma_{i=1}^2\mathbf{v}_i\cdot\frac{\partial P^{(2)}}{\partial \mathbf{r}_i}+\Sigma_{i=1}^2\omega_i\cdot\left(L_{\mathbf{u}_i}-\widehat{R}_i\right)P^{(2)}-m^{-1}\Sigma_{i,j=1}^2\frac{\partial\phi_{ij}}{\partial \mathbf{r}_i}\cdot\frac{\partial P^{(2)}}{\partial \mathbf{v}_i}-I^{-1}\Sigma_{i,j=1}^2(L_{\mathbf{u}_i}-\widehat{R}_i)\phi_{ij}\frac{\partial P^{(2)}}{\partial \omega_i}$$
$$-m^{-1}\Sigma_{i=1}^2\frac{\partial V_{\text{ext}}}{\partial \mathbf{r}_i}\cdot\frac{\partial P^{(2)}}{\partial \mathbf{v}_i}-I^{-1}\Sigma_{i=1}^2\left(L_{\mathbf{u}_i}-\widehat{R}_i\right)V_{\text{ext}}\frac{\partial P^{(2)}}{\partial \omega_i}$$
$$=\Sigma_{i,j=1}^2\frac{\partial}{\partial \mathbf{v}_i}\cdot \overleftrightarrow{\beta}^{tt}_{ij}\cdot\left(P^{(2)}\mathbf{v}_i+\frac{k_BT}{m}\frac{\partial P^{(2)}}{\partial \mathbf{v}_i}\right)+\Sigma_{i,j=1}^2\frac{\partial}{\partial \omega_i}\overleftrightarrow{\beta}^{rr}_{ij}\left(P^{(2)}\omega_i+\frac{k_BT}{I}\frac{\partial P^{(2)}}{\partial \omega_i}\right)$$
$$+\Sigma_{i,j=1}^2\frac{\partial}{\partial \mathbf{v}_i}\cdot \overleftrightarrow{\beta}^{tr}_{ij}l^2\left(P^{(2)}\omega_i+\frac{k_BT}{I}\frac{\partial P^{(2)}}{\partial \omega_i}\right)+\Sigma_{i,j=1}^2\frac{\partial}{\partial \omega_i}\frac{\overleftrightarrow{\beta}^{rt}_{ij}}{l^2}\cdot\left(P^{(2)}\mathbf{v}_i+\frac{k_BT}{m}\frac{\partial P^{(1)}}{\partial \mathbf{v}_i}\right), \tag{10}$$

Equations (9) and (10) constitute extensions of the corresponding FP equations derived by Mayorga *et al.* [22] and Refs. [34,35] for the purely translational motion case of Brownian spheres. These equations were cut up to pair distribution functions and neglect the triplet $P^{(3)}$ distribution function, and, therefore, they are expected to be valid at low colloid concentration. The above FP Eqs. (9) and (10) depend on the time-independent friction tensors $\zeta_{ij}(\mathbf{x}^N)$ and refer to the temporal evolution of the probability density in the internal phase space of configurations and velocities. These FP were derived under the assumption of $\tau_B \gg \tau_H$, which means that hydrodynamic interactions (HI) are instantaneous on time scale τ_B since solvent dynamics is completely decoupled from colloids variables. However, it is known that for bouyant colloids where $\rho_p \approx \rho_s$, then $\tau_B \approx \tau_H$ and, therefore, ζ_{ij} can no longer be time independent. In this case, for the FP equations above to describe correctly the dynamics on this time scale we must use the time-dependent friction tensors. These time-dependent properties have been calculated approximately by Van Saarlos and Mazur [36] and by Pusey *et al.* [37] at the two-particle level, which, consequently, ignores many-particle interactions for concentrated suspensions. Nonetheless, such time-dependent hydrodynamic friction coefficients also can be determined experimentally with diffusing wave spectroscopy [38] and through lattice Boltzmann simulations [39]. When the time relaxation of the colloids velocities are faster than their structural relaxation time $\tau_R \gg \tau_B \gg \tau_H$, we enter the overdamped (difussion) regime described by the Smoluchowski equation (SE) that will be derived in this paper in the second section below from the first moments of FP. SE governs the temporal evolution of the particle's distribution function in configuration space $(\mathbf{r}(t),\Omega(t))$. In deriving the SE equation from FP we will obtain the known relation in the long-time limit $t \gg \tau_B$ of the diffusion coefficient $D_{ij} = kT\zeta_{ij}^{-1}$ for the relative motion of particles i and j, as has been done for colloids of hard spheres [40]. We note that time-dependent D_{ij} (equivalently of ζ_{ij}) can also be derived from a linear response treatment of FP [25,41]. We can see that FPs (9) and (10) are dimensionally correct if we just use the lowest-order multipole expansion of the static friction coefficients for two-body HI as given in Ref. [42]. These properties have units $[\beta^{tt}_{ij}] \sim [6\pi\eta\sigma/m] = 1/\text{time}$, $[\beta^{rr}_{ij}] = [8\pi\eta\sigma^3/I] = 1/\text{time}$ for every i,j, and $[\beta^{tr}_{11}] = 0 = [\beta^{rt}_{11}]$, $[\beta^{tr}_{ij}] = [8\pi\eta r_{ij}^2/I] = 1/(\text{length} \times \text{time})$, and $[\beta^{rt}_{ij}] = [8\pi\eta r_{ij}^2/m] = \text{length}/\text{time}$ for $i \neq j$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. η is the solvent shear viscosity.

III. MACROSCOPIC DYNAMICS

The hydrodynamical evolution of the system is determined by the conserved laws associated to the hydrodynamics fields. These laws are given by the moments of the probability density $P^{(1)}$; the density of Brownian particles in real space,

$$\rho_B(\mathbf{r},t) = m\int P^{(1)}d\mathbf{v}_1 d\omega_1 d\Omega_1, \tag{11}$$

the linear momentum density,

$$\rho_B\mathbf{v}_B(\mathbf{r},t) = m\int P^{(1)}\mathbf{v}_1 d\mathbf{v}_1 d\omega_1 d\Omega_1, \tag{12}$$

by the intrinsic angular-momentum density,

$$\rho_B l^2\omega_B = \rho_B\mathbf{s}_B = ml^2\int P^{(1)}\omega_1 d\mathbf{v}_1 d\omega_1 d\Omega_1, \tag{13}$$

and energy density. Here $I\omega = m\mathbf{s}$, with $\mathbf{s} = l^2\omega$. Following the methods of Refs. [12,22] we obtain the mass conservation equation $\partial\rho_B/\partial t = -\nabla\cdot(\rho_B\mathbf{v}_B)$, whereas the balance equation for the linear momentum is derived by using (12) and the kinetic equation (9) [43] (see Appendix B),

$$\rho_B\frac{d\mathbf{v}_B}{dt} = -\frac{\partial}{\partial \mathbf{r}_1}\cdot \overleftrightarrow{P}^{K,\mathbf{vv}}_{B} + \mathbf{F}^d(t) - \frac{\rho_B}{m}\frac{\partial V_{\text{ext}}}{\partial \mathbf{r}_1}$$
$$-\rho_B\overleftrightarrow{\beta}^{tt}_{11}\cdot\mathbf{v}_B - \rho_B\overleftrightarrow{\beta}^{tr}_{11}\cdot\mathbf{s}_B. \tag{14}$$

Here we have introduced the symmetric kinetic (K) pressure tensor for the particles,

$$\overleftrightarrow{P}^{K,\mathbf{vv}}_{B} = m\int P^{(1)}(\mathbf{v}_1-\mathbf{v}_B)(\mathbf{v}_1-\mathbf{v}_B)d\mathbf{v}_1 d\omega_1\Omega_1, \tag{15}$$

and the density of pair direct force,

$$\mathbf{F}^d(t) = -\int \left[\frac{\partial \phi_{12}}{\partial \mathbf{r}_1}(\mathbf{r}_1,\mathbf{r}_2,\Omega_1,\Omega_2)\right] P^{(2)} d\mathbf{r}_1 d\mathbf{r}_2 \times d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\omega_1 d\mathbf{v}_2 d\omega_2 \approx -\frac{\partial}{\partial \mathbf{r}} \cdot \overleftrightarrow{P}^{\phi}_{B}. \tag{16}$$

This force contributes a potential component to the pressure tensor [22,32],

$$\begin{aligned}\overleftrightarrow{P}^{\phi}_{B} = -\frac{1}{2}\int \mathbf{r}_{12}\mathbf{r}_{12}\frac{\phi^{'}(r_{12},\Omega_1,\Omega_2)}{r_{12}}\int_0^1 P^{(2)} \\ \times (\mathbf{r}_1-(1-\alpha)\mathbf{r}_{12},\mathbf{r}_1+\alpha\mathbf{r}_{12},\mathbf{v}_1,\mathbf{v}_2,\omega_1,\omega_2,\Omega_1,\Omega_2,t) \\ \times d\alpha d\mathbf{r}_{12} d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\omega_1 d\mathbf{v}_2 d\omega_2,\end{aligned} \tag{17}$$

$\phi' := \partial\phi_{12}/\partial r_{12}$.

Equation (14) therefore can be rewritten into its equivalent form,

$$\begin{aligned}\rho_B \frac{d\mathbf{v}_B}{dt} = -\frac{\partial}{\partial \mathbf{r}_1} \cdot \overleftrightarrow{P}_{B} - \frac{\rho_B}{m}\frac{\partial V_{\text{ext}}}{\partial \mathbf{r}_1} \\ -\rho_B \overleftrightarrow{\beta}^{tt}_{11} \cdot \mathbf{v}_B - \rho_B \overleftrightarrow{\beta}^{tr}_{11} \cdot \mathbf{s}_B,\end{aligned} \tag{18}$$

where $\overleftrightarrow{P}_{B} = \overleftrightarrow{P}^{K,\mathbf{vv}}_{B} + \overleftrightarrow{P}^{\phi}_{B}$.

The density of total angular momentum $\mathbf{L}(t)$ contains two parts, the orbital $\rho_B \mathbf{r} \times \mathbf{v}_B$ and intrinsic $\mathbf{s}_B$ angular-momentum components. Starting from the evolution equation for $d\mathbf{L}/dt$, one can derive from Eq. (18) the orbital angular-momentum equation $d(\rho_B \mathbf{r} \times \mathbf{v}_B)/dt$ which, when subtracted from $d\mathbf{L}(t)/dt$, yields the corresponding balance of intrinsic angular momentum (see Appendix B),

$$\begin{aligned}\rho_B \frac{d\mathbf{s}_B}{dt} = -\frac{\partial}{\partial \mathbf{r}_1} \cdot \overleftrightarrow{Q}_{B} - \frac{l^2 \rho_B}{I}(L_{\mathbf{u}_1} - \widehat{R}_1)V_{\text{ext}} - 2P^a \\ -\rho_B \overleftrightarrow{\beta}^{rr}_{11} \cdot \mathbf{s}_B - \rho_B \overleftrightarrow{\beta}^{rt}_{11} \cdot \mathbf{v}_B,\end{aligned} \tag{19}$$

where $\overleftrightarrow{Q}_{B} = l^2 \overleftrightarrow{P}^{K,\mathbf{v}\omega}_{B} + \overleftrightarrow{Q}^{\phi}_{B}$. P^a is the antisymmetric part of the pressure tensor [46,47] of Eq. (17) [27].

Aside from the dissipative processes embodied in the currents appearing in the balance equations of linear and angular momentum, the balance equation of energy density also takes into account the dissipation of energy due to the relative movement of all particles in the fluid. In order to account for this process we can follow the same method as used before to derive (14) and attain the balance equation for the total internal energy density of the colloids in the solvent $\rho_B u_B := u^{\phi}_B + u^{K,\mathbf{v}}_B + u^{K,\omega}_B$, where

$$\begin{aligned}\rho_B u^{\phi}_B &= \frac{m}{2}\int P^{(1)}\phi_{12} d\mathbf{v}_1 d\mathbf{v}_2 d\omega_1 d\omega_2 d\mathbf{r}_2 \Omega_1 d\Omega_2, \\ \rho_B u^{K,\mathbf{v}}_B &= \frac{m}{2}\int P^{(1)}(\mathbf{v}_1 - \mathbf{v}_B)^2 d\mathbf{v}_1 d\omega_1 d\Omega_1, \\ \rho_B u^{K,\omega}_B &= \frac{I}{2}\int P^{(1)}(\omega_1 - \omega_B)^2 d\mathbf{v}_1 d\omega_1 d\Omega_1.\end{aligned} \tag{20}$$

The result is

$$\begin{aligned}&\frac{\partial \rho_B u_B}{\partial t} + \frac{\partial}{\partial \mathbf{r}_1}\cdot(\mathbf{J}^B_q + \rho_B u_B \mathbf{v}_B) \\ &= +m\int P^{(2)}\frac{\partial \phi_{12}}{\partial \mathbf{r}_1}\mathbf{u}_1 d\mathbf{u}_1 d\mathbf{u}_2 d\omega_1 d\omega_2 d\mathbf{r}_2 d\Omega_1 d\Omega_2 \\ &\quad + m\int P^{(2)}\big[(L_{\mathbf{u}_1} - \widehat{R}_1)\phi_{12}\big]\mathbf{u}_1 d\mathbf{u}_1 d\mathbf{u}_2 d\omega_1 d\omega_2 d\mathbf{r}_2 d\Omega_1 d\Omega_2 \\ &\quad - \overleftrightarrow{P}^{\dagger}_{B} : \frac{\partial \mathbf{v}_B}{\partial \mathbf{r}_1} - \overleftrightarrow{Q}^{\dagger}_{B} : \frac{\partial \omega_B}{\partial \mathbf{r}_1} - l^2(\overleftrightarrow{\beta}^{tr}_{11})^{\dagger} : \overleftrightarrow{P}^{K,\omega\mathbf{v}}_{B} \\ &\quad - (\overleftrightarrow{\beta}^{rt}_{11})^{\dagger} : \overleftrightarrow{P}^{K,\mathbf{v}\omega}_{B} - 2\beta^{tt}_{11}\big(\rho_B u^{K,\mathbf{v}}_B - \rho_{B\text{eq}} u^{K,\mathbf{v}_B}_{B\text{eq}}\big) \\ &\quad - 2\beta^{rr}_{11}\big(\rho_B u^{K,\omega}_B - \rho_{B\text{eq}} u^{K,\omega_B}_{B\text{eq}}\big),\end{aligned} \tag{21}$$

where the superscript index † means the transpose of a matrix. The terms containing the friction tensors are dissipative contributions due to the interchange of energy between colloids and solvent [22].

We defined the fluxes and energy contributions

$$\begin{aligned}\mathbf{J}^B_q &= \mathbf{J}^{K,\mathbf{vv}}_q + \mathbf{J}^{K,\omega\mathbf{v}}_q + \mathbf{J}^{(1)}_{q\phi} + \mathbf{J}^{(2)}_{q\phi} + Q^{(2)}_{q\phi} \\ \mathbf{J}^{(1)}_{q\phi} &= \frac{m}{2}\int(\mathbf{v}_1 - \mathbf{v}_B)P^{(2)}\frac{\phi_{12}}{2} d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_2 d\omega_1 d\omega_2 \Omega_1 d\Omega_2 \\ \mathbf{J}^{(2)}_{q\phi} &= -\frac{m}{4}\int \mathbf{r}_{12}\mathbf{r}_{12}\frac{\phi'}{r_{12}}\int_0^1(\mathbf{v}_1 + \mathbf{v}_2 - 2\mathbf{v}_B)P^{(2)} d\alpha dr_{12} d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\mathbf{v}_2 d\omega_1 d\omega_2 \\ \mathbf{Q}^{(2)}_{q\phi} &= -\frac{m}{4}\int \mathbf{r}_{12}\big[(L_{\mathbf{u}_1} - \widehat{R}_1)\phi_{12}\big]\int_0^1(\omega_1 + \omega_2 - 2\omega_B)P^{(2)} d\alpha dr_{12} d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\mathbf{v}_2 d\omega_1 d\omega_2 \\ \mathbf{J}^{K,\mathbf{vv}}_q &= \frac{m}{2}\int(\mathbf{v}_1 - \mathbf{v}_B)^2(\mathbf{v}_1 - \mathbf{v}_B)P^{(1)} d\mathbf{v}_1 d\omega_1 \Omega_1 \\ \mathbf{J}^{K,w\mathbf{v}}_q &= \frac{I}{2}\int(\omega_1 - \omega_B)^2(\mathbf{v}_1 - \mathbf{v}_B)P^{(1)} d\mathbf{v}_1 d\omega_1 \Omega_1 \\ \rho_{B\text{eq}} u^{K,\omega_B}_{B\text{eq}} &= \frac{2\rho_{B\text{eq}} k_B T}{2} = \frac{I}{2}\int(\omega_1 - \omega_B)^2 P^{(1)}_{\text{eq}} d\mathbf{v}_1 d\omega_1 d\Omega_1 \\ \rho_{B\text{eq}} u^{K,\mathbf{v}_B}_{B\text{eq}} &= \frac{3\rho_{B\text{eq}} k_B T}{2} = \frac{m}{2}\int(\mathbf{v}_1 - \mathbf{v}_B)^2 P^{(1)}_{\text{eq}} d\mathbf{v}_1 d\omega_1 d\Omega_1.\end{aligned} \tag{22}$$

The last two energy identities are the equipartition theorems of translational and rotational movement of a particle and we introduced the symmetric pressure tensor,

$$\overleftrightarrow{P}_B^{K,\omega\mathbf{v}} = m \int P^{(1)}(\omega_1 - \omega_B)(\mathbf{v}_1 - \mathbf{v}_B)d\mathbf{v}_1 d\omega_1 d\Omega_1. \tag{23}$$

Equations (18), (19), and (21) are similar to those derived by Evans *et al.* [45] for a dense homogeneous homonuclear diatomic fluid. In the diffusion regime, limit $\rho_B \frac{d\mathbf{v}_B}{dt} = \mathbf{0}$, $\rho_B \frac{d\mathbf{s}_B}{dt} = \mathbf{0}$, and no hydrodynamic interaction among particles $\overleftrightarrow{\beta}_{11}^{rt} = \overleftrightarrow{\beta}_{11}^{tr} = \mathbf{0}$. Consider $V_{\text{ext}} = 0$. For *orientational isotropic fluids* $P^{(1)}(\mathbf{r},\Omega,t) = P^{(1)}(\mathbf{r},t)$, and both the pair potential $\phi_{12}(\mathbf{r}_{12},\Omega_{12})$ and $P^{(2)}(\mathbf{r}_1,\mathbf{r}_1 + \mathbf{r}_{12},\Omega_{12})$ depend only on the relative orientation of two particles but not on each of the two particle's angles separately [27]. An important example of this is the pair dipolar interaction potential to model ferrofluids. The pressure tensor Eq. (17) and $\overleftrightarrow{P}_B$ then are symmetric [27]. Since there is no external flow $\overleftrightarrow{P}_B = p_B\mathbf{1}$ is the osmotic pressure, with $\mathbf{1}$ the third-order unit tensor. Using the fact that the pair-correlation function and the two-particle reduced distribution function $\rho^{(2)}$ are related by [26]

$$\begin{aligned} g^{(2)}(r_{12},\Omega_1,\Omega_2) &= \left(\frac{m\Omega}{\rho_{B\text{eq}}}\right)^2 \rho^{(2)}(r_{12},\Omega_1,\Omega_2), \\ \rho^{(2)} &:= \int P^{(N)} d\mathbf{v}_1 d\omega_1 d\mathbf{v}_2 d\omega_2 d\mathbf{r}_3 d\Omega_3 \\ &\quad \times d\mathbf{v}_3 d\omega_3 \dots d\mathbf{r}_N d\Omega_N d\mathbf{v}_N d\omega_N, \end{aligned} \tag{24}$$

where $\Omega = 4\pi$. At thermal equilibrium, $T = T_{\text{eq}}$, $\rho_{B\text{eq}} = mN/V = mn$. We may obtain the osmotic pressure of the solution using the method of Irving *et al.* [32],

$$\begin{aligned} p_B = k_B T_{\text{eq}} \frac{\rho_{B\text{eq}}}{m} - \frac{2\pi}{3}\left(\frac{\rho_{B\text{eq}}}{m\Omega}\right)^2 \int_0^\infty \int_0^\pi \int_0^{2\pi} g^{(2)}(r_{12},\Omega_1,\Omega_2) \\ \times \phi' r_{12}^3 dr_{12} d\Omega_1 d\Omega_2, \end{aligned} \tag{25}$$

where $d\Omega = \sin\theta d\theta d\phi$. This coincides with the well-known expression given in Ref. [26]. Under the same *orientational isotropic fluid* assumption, in equilibrium, diffusive regime, and ignoring translation-rotation coupling, Eq. (18), leads to

$$-\frac{\partial}{\partial \mathbf{r}_1} \cdot p_B \mathbf{1} = \rho_B \beta_{11}^{tt} \mathbf{1} \cdot \mathbf{v}_B. \tag{26}$$

From the chain rule $\partial p_B/\partial\mathbf{r} \equiv (\partial p_B/\partial\rho_B)(\partial\rho_B/\partial\mathbf{r})$ we find that the first factor on the right-hand side is the virial expression of the isothermal compressibility modulus, which is given in Hansen *et al.* [26] in terms of the microstructural function of the fluid. Finally, from the flux $\rho_B\mathbf{v}_B$ and Eq. (26) we obtain Fick's law of diffusion $\rho_B\mathbf{v}_B = -D_c\partial\rho_B/\partial\mathbf{r}$, where at low density we recover the general virial expression for the collective diffusion coefficient of the colloidal particles derived by Felderhof [48] and Russel [49],

$$D_c = \frac{k_B T}{\beta_{11}^{tt} m}\left[1 + 4\pi n \int_0^\infty (g(r_{12}) - 1) r_{12}^2 dr_{12}\right]^{-1}. \tag{27}$$

The above equation is valid at low concentrations of particles. The angle-averaged part of the pair-correlation function is [26,50]

$$g(r_{12}) = \frac{1}{\Omega^2}\int g^{(2)}(\mathbf{r}_{12},\Omega_{\mathbf{1}},\Omega_{\mathbf{2}}) d\Omega_1 d\Omega_2 d\mathbf{r}_{12}. \tag{28}$$

It should be noted that in, general, for dipolar fluids, such angle-averaged distribution is distinguishable from the correlation function of an isotropic pure hard-sphere fluid at moderate and high values of dipolar strength [51,52]. For ferrofluids one may use the friction function $\beta_{11}^{tt} = 6\pi\eta\sigma[m(1 + (\chi_T - \chi_F)\Phi)]^{-1}$, where the factors χ_T and χ_F take into account thermodynamic and hydrodynamic interactions [53]. The value $\chi_T - \chi_F \approx -50$ was obtained from an experimental fit of the friction coefficient using a sample of maghemite nanoparticles in n-decane [54]. However, from the experiments reported in Ref. [54] for realistic suspensions, it is apparent that both formulas of theses hydrodynamic friction coefficients remain valid only for volume fractions on the order $\Phi \lesssim 0.01$, see, for instance, Fig. 6 of Ref. [54]. Thus, three-body HI are necessary in order to improve such frictions for higher concentrations leading up to order Φ^2 dependencies, as was demonstrated for monodisperse hard-sphere suspensions [55].

IV. COLLOIDAL SUSPENSION UNDER FLOW CONDITIONS

We are concerned in this section with characterizing colloid dynamics in the long-time regime through the time evolution of the collective density variable $\rho(\mathbf{r},\Omega,t)$ when there are structural relaxations on position and orientation of the particles under a stationary applied external flow $\mathbf{v}_i^0 = \mathbf{v}^0(\mathbf{r}_i,\Omega_i,t)$ that produces a vortex field acting on each particle i, $\omega_i^0 = \omega^0(\mathbf{r}_i,\Omega_i,t) = \nabla \wedge \mathbf{v}^0/2$. From the definition of ρ given below, its diffusion equation is equivalent to the Smoluchowski equation of the probability density $P^{(N)}$. This constitutes the main kinetic equation that provides a quantitative description of the effect of shear on the mean-square displacement of colloidal particles [19,56]. Its angular variable dependence allows us to take into account the relaxation of magnetization in ferrocolloids under external magnetic fields [57]. For concentrated suspensions it is easier to derive the diffusion equation of the collective density by starting, first, from the evolution equation for the single density function associated to particle i since it is not necessary to make the factorization on the probability density into its n-body reduced components, as was done in the previous section. For this purpose, we derive the FP of $P^{(N)}$ under stationary flow. Afterwards, the evolution equation of the first four moments of $P^{(N)}$ for one particle i is generated, thus, resulting in the continuity equation for the density ρ_i, the balance equations of linear and intrinsic angular momentum, and those of the second (for pressure tensor) and third (for change of kinetic energy and stress) centered moments of the velocities, whereas in the last three moments, they involve correlation of the friction tensor of particle i with their partners velocities and, therefore, represent their hydrodynamic interactions. Those hydrodynamical correlations turn out to be expressed as quadratures on configuration space and include sums over distinct particles $j \neq i$ interacting with i. The HI then are included into the collective colloid dynamics described by ρ by using the effective medium approximation, which is an average of dynamical variables pertaining to particle i and attained by performing a sum over i, transforming the discrete particle sums that appear in the correlation of friction and particle velocities as integrals on continuous variables of position and angular coordinates. This confirms that the origin of HI is due to temporal spatial relaxation of the structure of the suspended colloids. At the long-time limit, the so-attained mean linear and angular-momentum equations of the whole colloid fluid yield the diffusion fluxes of particles which, when substituted into the density's continuity equation, provides the effective Smoluchowski description of the collective dynamics of particles in the diffusive regime. Therefore, according to this scheme, let us, first, note that the density function of a single particle i is $\rho_i = m\int P^{(N)}\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)d\Gamma$, which provides a relationship with ρ through

$$\begin{aligned}\rho(\mathbf{r},\Omega,t) = \sum_{i=1}^{N}\rho_i = m\Big[&\int P^{(N)}(\mathbf{r},\Omega,\mathbf{v}_1,\omega_1,\mathbf{r}_2,\Omega_2,\mathbf{v}_2,\omega_2,\ldots,\mathbf{r}_N,\Omega_N,\mathbf{v}_N,\omega_N,t)d\mathbf{v}_1d\omega_1d\mathbf{r}_2d\Omega_2d\mathbf{v}_2d\omega_2\ldots d\mathbf{r}_Nd\Omega_Nd\mathbf{v}_Nd\omega_N\\ &+\cdots+\int P^{(N)}(\mathbf{r}_1,\Omega_1,\mathbf{v}_1,\omega_1,\ldots,\mathbf{r},\Omega,\mathbf{v}_i,\omega_i\ldots,\mathbf{r}_N,\Omega_N,\mathbf{v}_N,\omega_N,t)d\mathbf{v}_id\omega_id\mathbf{r}_1d\Omega_1d\mathbf{v}_1d\omega_1\ldots d\mathbf{r}_Nd\Omega_Nd\mathbf{v}_Nd\omega_N\\ &+\cdots+\int P^{(N)}(\mathbf{r}_1,\Omega_1,\mathbf{v}_1,\omega_1,\ldots,\mathbf{r},\Omega,\mathbf{v}_N,\omega_N,t)d\mathbf{r}_1d\Omega_1d\mathbf{v}_1d\omega_1\ldots d\mathbf{r}d\Omega d\mathbf{v}_Nd\omega_N\Big]\\ = m&\int P^{(1)}(\mathbf{r},\Omega,\mathbf{v}_1,\omega_1,t)d\mathbf{v}_1d\omega_1, \qquad (29)\end{aligned}$$

where in the second equality there appears N repeated terms of the same quadrature of $P^{(N)}$ integrated on just $N-2$ variables of Γ, which is the definition of the one-particle density $P^{(n=1)}$. Equation (29) is identical with ρ_B of Eq. (11) in Sec. II when there is no external flow and for quiescent colloidal fluid under thermal fluctuations only. Following the approach described above, we find that, due to the explicit angular dependence of the density, for a single particle the continuity equation reads

$$\frac{\partial\rho_i}{\partial t} = -\nabla\cdot(\rho_i\overline{\mathbf{v}}_i)-(L_{\mathbf{u}}-\widehat{R})\cdot(\rho_i\overline{\omega}_i), \qquad (30)$$

which is obtained by integrating Eq. (2) over the phase space Γ with the factor $\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)$ and assuming the vanishing of the current fluxes $\mathbf{J}^{(N)}_{\mathbf{v}_i}$, $\mathbf{J}^{(N)}_{\omega_i}$ at high velocities. If we define the baricentric velocities of the colloid suspension

$$\begin{aligned}\rho\overline{\mathbf{v}}(\mathbf{r},\Omega,t) &= m\int \Sigma_{i=1}^{N}\overline{\mathbf{v}}_iP^{(N)}\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)d\Gamma,\\ \rho\overline{\omega}(\mathbf{r},\Omega,t) &= m\int \Sigma_{i=1}^{N}\overline{w}_iP^{(N)}\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)d\Gamma,\end{aligned} \qquad (31)$$

and from (29), Eq. (30) can be written as

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\overline{\mathbf{v}})-(L_{\mathbf{u}}-\widehat{R})\cdot(\rho\overline{\omega}). \qquad (32)$$

The extended version of (30) and (32) differs from that of Sec. II since we are also interested now in relaxation of particles in the real space of translational and orientational degrees of freedom. Similar equations to ours have been used by Caillol [58] and Chandra *et al.* [59] to study relaxation processes in polar solvents, where the mean linear and angular velocities of particle i are, respectively,

$$\begin{aligned}\rho_i\overline{\mathbf{v}}_i(\mathbf{r},\Omega,t) &= m\int \overline{\mathbf{v}}_iP^{(N)}\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)d\Gamma,\\ \rho_i\overline{\omega}_i(\mathbf{r},\Omega,t) &= m\int \omega_iP^{(N)}\delta(\mathbf{r}_i-\mathbf{r})\delta(\Omega_i-\Omega)d\Gamma.\end{aligned} \qquad (33)$$

In order to obtain the FP of the colloid system we shall determine the currents $\mathbf{J}^{(N=1)}_{\mathbf{v}_i} := \mathbf{J}_{\mathbf{v}_i}$, $\mathbf{J}^{(N=1)}_{\omega_i} := \mathbf{J}_{\omega_i}$ of the Liouville equation (2). According to the mesoscopic nonequilibrium thermodynamic approach, these currents can be determined with the use of a canonical structure of the entropy production of the colloid system that is expressed as a product of the fluxes and their conjugated forces. Curi's principle then dictates the form of the phenomenological constitutive relation between fluxes as a function of the forces that, when they are replaced in (2), yields the N-particle Fokker-Planck equation for stationary flow (see Appendix C),

$$\begin{aligned}&\frac{\partial P^{(N)}}{\partial t}+\Sigma_i\mathbf{v}_i\cdot\nabla_{\mathbf{r}_i}P^{(N)}+\Sigma_i\omega_i\cdot\big(L_{\mathbf{u}_i}-\widehat{R}_i\big)P^{(N)}-m^{-1}\Sigma_{i,j=1}^{N}\nabla_{\mathbf{r}_i}\phi_{ij}\cdot\nabla_{\mathbf{v}_i}P^{(N)}-I^{-1}\Sigma_{i,j=1}^{N}\big(L_{\mathbf{u}_i}-\widehat{R}_i\big)\phi_{ij}\cdot\nabla_{\omega_i}P^{(N)}\\ &\quad -m^{-1}\Sigma_{i=1}^{N}\nabla_{\mathbf{r}_i}V_{\text{ext}}\cdot\nabla_{\mathbf{v}_i}P^{(N)}-I^{-1}\Sigma_{i=1}^{N}\big(L_{\mathbf{u}_i}-\widehat{R}_i\big)V_{\text{ext}}\cdot\nabla_{\omega_i}P^{(N)}\\ &=\Sigma_{i,j}\nabla_{\mathbf{v}_i}\cdot\Big[\big(\mathbf{v}_j-\mathbf{v}_j^0\big)\cdot\big(\overleftrightarrow{\alpha}^{tt}_{ij}+\overleftrightarrow{\epsilon}_{ij}\cdot\nabla_{\mathbf{r}_j}\mathbf{v}_j^0\big)P^{(N)}-\overleftrightarrow{\zeta}_{ij}\cdot\mathbf{F}_jP^{(N)}+\frac{k_BT}{m}\overleftrightarrow{\alpha}^{tt}_{ij}\cdot\nabla_{\mathbf{v}_j}P^{(N)}+\big(\omega_j-\omega_j^0\big)\cdot l^2\overleftrightarrow{\alpha}^{tr}_{ij}P^{(N)}\\ &\quad+\frac{k_BT}{I}\Sigma_jl^2\overleftrightarrow{\alpha}^{tr}_{ij}\cdot\nabla_{\omega_j}P^{(N)}\Big]+\Sigma_{i,j}\nabla_{\omega_i}\cdot\Big[\big(\omega_j-\omega_j^0\big)\cdot\big(\overleftrightarrow{\alpha}^{rr}_{ij}+\overleftrightarrow{\epsilon}^{\omega}_{ij}\cdot\big(L_{\mathbf{u}_j}-\widehat{R}_i\big)\omega_j^0\big)P^{(N)}\\ &\quad-\overleftrightarrow{\zeta}^{\omega}_{ij}\cdot\mathbf{T}_jP^{(N)}+\frac{k_BT}{I}\overleftrightarrow{\alpha}^{rr}_{ij}\cdot\nabla_{\omega_j}P^{(N)}+\big(\mathbf{v}_j-\mathbf{v}_j^0\big)\cdot\frac{1}{l^2}\overleftrightarrow{\alpha}^{rt}_{ij}P^{(N)}+\frac{k_BT}{m}\frac{1}{l^2}\overleftrightarrow{\alpha}^{rt}_{ij}\cdot\nabla_{\mathbf{v}_j}P^{(N)}\Big]. \qquad (34)\end{aligned}$$

This FP generalizes the one given by Santamaria-Holek *et al.* [19] for translational motion to the case of interacting colloids under external fields and vorticity flow that affects the rotational Brownian motion of particles. Thus, as in Ref. [19], we introduce the effective friction coefficients

$$\begin{aligned}\overleftrightarrow{\alpha}^{tt}_{ij} &:= \overleftrightarrow{\beta}^{tt}_{ij} - \overleftrightarrow{\epsilon}_{ij} \cdot \nabla_{\mathbf{r}_j}\mathbf{v}^0_j,\\ \overleftrightarrow{\alpha}^{rr}_{ij} &:= \overleftrightarrow{\beta}^{rr}_{ij} - \overleftrightarrow{\epsilon}^{\omega}_{ij} \cdot \big(L_{\mathbf{u}_j} - \widehat{R}_i\big)\omega^0_j,\end{aligned} \tag{35}$$

which quantify the departure of the friction due to Brownian motion and HI among particles $\overleftrightarrow{\beta}^{uu}_{ij}$ $(uu = tt,rr)$ from the contribution due to fluid flow, which is linear in $\nabla_{\mathbf{r}_j}\mathbf{v}^0_j$ and $(L_{\mathbf{u}_j} - \widehat{R}_j)\omega^0_j$. In general, $\overleftrightarrow{\beta}^{uu}_{ii}$, $(uu = tt,rr)$, depend on the HI among particles. For spherical particles that experience only translational motion, its analytical form was determined with the Faxén theorem in Ref. [23,62], where it was found that $\overleftrightarrow{\zeta} = \zeta\mathbf{1}$ of Eq. (34) is related to inertial effects due to time variations of $\mathbf{v}^0$, and $\zeta = \rho_p/\rho_s$ with ρ_s the density of the fluid solvent. However, a similar calculation for $uu = rr$ and $\overleftrightarrow{\zeta}^{\omega} = \zeta^{\omega}\mathbf{1}'$ with HI remains to be performed. For spherical particles, if HI are ignored, one can approximate $\overleftrightarrow{\beta}^{tt}_{ii} = \beta_0\mathbf{1}\delta_{ii}$, and $\overleftrightarrow{\beta}^{rr}_{ii} = \beta^r_0\mathbf{1}'\delta_{ii}$, with $\mathbf{1}'$ the second-order unit matrix. $\beta_0 = 6\pi\eta\sigma/m := 1/t^t$ is the inverse of damping time t^t for translational motion, $\beta^r_0 = 8\pi\eta\sigma^3/I := 1/t^r$. The inertial times of translational and angular velocities are of the same order of magnitude $t^t/t^r = 10/3$ [63]. Notice that t^t,t^r is set in a time scale where, for $t \ll t^t,t^r$, inertial effects are dominant, whereas for times much grater than t^t,t^r we enter the diffusion regime. In this long-time regime, relaxation of velocities $\mathbf{v}_i(t),\omega_i(t)$ have occurred, and their constant values in the scale of $t \gg t^t,t^r$ are statistically averaged values at equilibrium $\overline{\mathbf{v}}_i(\mathbf{r},\Omega,t),\overline{\omega_i}(\mathbf{r},\Omega,t)$ whose magnitude depends on the colloid density $\rho(\mathbf{r},\Omega,t)$ and particle's interactions. Thus, these averaged values depend on time through structural relaxations. The mean velocities are susceptible to be measured experimentally and also can be calculated with MNET. Experimentally, thermal fluctuations on density are probed with dynamic and depolarized light scattering due to the slow structural relaxation of the particle configurations $\mathbf{r}(t),\Omega(t)$. From samples of configuration variables, experiments obtain the mean-square translational and angular particle's displacements. Whereas from MNET the averaged velocities of the colloid collective motion are determined from the hydrodynamic equations derived from the FP (34). The result is (see Appendix D)

$$\begin{aligned}\begin{pmatrix}\rho(\overline{\mathbf{v}} - \mathbf{v}^0)\\ \rho(\overline{\omega} - \omega^0)\end{pmatrix} \approx \Bigg[&-\frac{1}{m}\begin{pmatrix}\mathbf{F^d}\\ \frac{1}{l^2}\mathbf{T}^d\end{pmatrix}^{\dagger} + \frac{1}{m}\begin{pmatrix}\rho\nabla V_{\mathrm{ext}}\\ \frac{1}{l^2}\rho(L_{\mathbf{u}} - \widehat{R})V_{\mathrm{ext}}\end{pmatrix}^{\dagger} - \rho\begin{pmatrix}\zeta\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \frac{1}{l^2}\zeta^{\omega}\mathbf{1}'\end{pmatrix}\cdot\begin{pmatrix}\mathbf{F}\\ \mathbf{T}\end{pmatrix}^{\dagger} + k_BT\begin{pmatrix}\overleftrightarrow{A}^{tt} & \mathbf{0}\\ \mathbf{0} & \overleftrightarrow{A}^{rr}\end{pmatrix}\\ &\cdot\begin{pmatrix}\frac{1}{m}\nabla\rho\\ \frac{1}{I}(L_{\mathbf{u}} - \widehat{R})\rho\end{pmatrix}^{\dagger} + k_BT\rho\begin{pmatrix}\frac{1}{m}\nabla\\ \frac{1}{I}(L_{\mathbf{u}} - \widehat{R})\end{pmatrix}^{\dagger}\cdot\begin{pmatrix}\overleftrightarrow{A}^{tt} & \mathbf{0}\\ \mathbf{0} & \overleftrightarrow{A}^{rr}\end{pmatrix}\Bigg]\cdot\begin{pmatrix}(\overleftrightarrow{B}^{tt})^{-1} & \mathbf{0}\\ \mathbf{0} & (\overleftrightarrow{B}^{rr})^{-1}\end{pmatrix}.\end{aligned} \tag{36}$$

Here the density force and torque definitions were used

$$\begin{aligned}&-\frac{1}{2}\Sigma^N_{i\neq j=1}\int P^{(N)}\begin{pmatrix}\nabla_{\mathbf{r}_i}\\ \frac{1}{l^2}(L_{\mathbf{u}_i} - \widehat{R})\end{pmatrix}\phi_{ij}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\Gamma\\ &\quad\approx -\frac{1}{m}\int \rho^{(2)}(\mathbf{r} - \mathbf{r}',\Omega,\Omega',t)\begin{pmatrix}\nabla_{\mathbf{r}}\\ \frac{1}{l^2}(L_{\mathbf{u}} - \widehat{R})\end{pmatrix}\phi(\mathbf{r} - \mathbf{r}',\Omega,\Omega')d\mathbf{r}'d\Omega' = \frac{1}{m}\begin{pmatrix}\mathbf{F^d}\\ \frac{1}{l^2}\mathbf{T}^d\end{pmatrix},\\ &\Sigma^N_{k=1}\int P^{(N)}\begin{pmatrix}\nabla_{\mathbf{r}_k}\\ \frac{1}{l^2}(L_{\mathbf{u}_k} - \widehat{R})\end{pmatrix}V_{\mathrm{ext}}\delta(\mathbf{r}_k - \mathbf{r})\delta(\Omega_k - \Omega)d\Gamma = \frac{1}{m}\begin{pmatrix}\rho\nabla V_{\mathrm{ext}}\\ \frac{1}{l^2}\rho(L_{\mathbf{u}} - \widehat{R})V_{\mathrm{ext}}\end{pmatrix},\end{aligned} \tag{37}$$

which result after using the effective medium approximation. Now the fluxes of Eq. (36) are replaced in (32), resulting in the effective overdamped (diffusion regime) Smoluchowski equation for the average density,

$$\begin{aligned}\frac{\partial\rho}{\partial t} = -\nabla\cdot\big[&\rho\mathbf{v}^0 + D^0\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{tt})^{-1}\big)\beta\cdot(-\rho\nabla V_{\mathrm{ext}} + \mathbf{F}^d) + \rho\beta_0^{-1}\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{tt})^{-1}\big)\cdot\mathbf{f}\\ &+ \rho\zeta\beta_0^{-1}\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{tt})^{-1}\big)\cdot\mathbf{F}\big] + \nabla\cdot(\overleftrightarrow{D}^{tt}\cdot\nabla\rho) - (L_{\mathbf{u}} - \widehat{R})\cdot\big[\rho\omega^0 + D^r_0\big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{tt})^{-1}\big)\beta\\ &\cdot(-\rho(L_{\mathbf{u}} - \widehat{R})V_{\mathrm{ext}} + \mathbf{T}^d) + \rho\big(\beta^r_0\big)^{-1}\big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{rr})^{-1}\big)\cdot\mathbf{t} + \rho\zeta^{\omega}\big(\beta^r_0 l^2\big)^{-1}\big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}}\cdot(\overleftrightarrow{B}^{rr})^{-1}\big)\cdot\mathbf{T}\big]\\ &+ (L_{\mathbf{u}} - \widehat{R})\cdot(\overleftrightarrow{D}^{rr}\cdot(L_{\mathbf{u}} - \widehat{R})\rho),\end{aligned} \tag{38}$$

where $D^0 = k_BT/m\beta_0$, $D^r_0 = k_BT/I\beta^r_0$. Equation (38) coincides with the SE given by Nägele [55] without advective velocities. In the stationary regime and neglecting HI, it coincides with the Yvon-Born-Green equation of molecular fluids [50]. And with the one derived by Rex *et al.* using a time-dependent density functional expansion of an anisotropic fluid [66]. The effective force $\mathbf{f} = -(k_BT/m)\nabla\cdot\overleftrightarrow{A}^{tt}$, torque $\mathbf{t} = -(k_BT/I)(L_{\mathbf{u}} - \widehat{R})\cdot\overleftrightarrow{A}^{rr}$, the mobilities

$\overleftrightarrow{\mu}^{tt} := \beta_0^{-1}\tilde{\mu}^{tt} = (\overleftrightarrow{B}^{tt})^{-1} - \beta_0^{-1}\overleftrightarrow{B}^{tt}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{tt})^{-1}$, $\overleftrightarrow{\mu}^{rr} := (\beta_0^r)^{-1}\tilde{\mu}^{rr} = (\overleftrightarrow{B}^{rr})^{-1} - (\beta_0^r)^{-1}\overleftrightarrow{B}^{rr}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{rr})^{-1}$, and

$$\begin{aligned}\overleftrightarrow{A}^{tt} &= \mathbf{1} - \beta_0^{-1}\overleftrightarrow{B}^{tt}_{\mathrm{dp}} \\ &\quad + \beta_0^{-1}\big(\overleftrightarrow{E}^{tt}_{\mathrm{dp}} - \overleftrightarrow{\epsilon} - \mathbf{1} + \beta_0^{-1}\overleftrightarrow{B}^{tt}_{\mathrm{dp}}\big) \cdot \nabla\mathbf{v}^0 \\ \overleftrightarrow{A}^{rr} &= \mathbf{1}' - \big(\beta_0^r\big)^{-1}\overleftrightarrow{B}^{rr}_{\mathrm{dp}} + \big(\beta_0^r\big)^{-1}\big(\overleftrightarrow{E}^{rr}_{\mathrm{dp}} - \overleftrightarrow{\epsilon}^{\omega} \\ &\quad - \mathbf{1}' + \big(\beta_0^r\big)^{-1}\overleftrightarrow{B}^{rr}_{\mathrm{dp}}\big) \cdot (L_{\mathbf{u}} - \widehat{R})\omega^0. \qquad (39)\end{aligned}$$

Thus, we recover the known result first derived by Santamaria-Holek *et al.* in Ref. [19] for the translational diffusion part of Eq. (38) with effective diffusion $\overleftrightarrow{D}^{tt}$, and we obtained a new expression for the rotational diffusion coefficient $\overleftrightarrow{D}^{rr}$,

$$\begin{aligned}\overleftrightarrow{D}^{tt} &= D^0\big[\tilde{\mu}^{tt} + \beta_0^{-1}\big[\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{tt})^{-1}\big) \\ &\quad \cdot \big(\overleftrightarrow{E}^{tt}_{\mathrm{dp}} - \overleftrightarrow{\epsilon} - \mathbf{1} + \beta_0^{-1}\overleftrightarrow{B}^{tt}_{\mathrm{dp}}\big) \cdot \nabla\mathbf{v}^0\big]^s\big], \\ \overleftrightarrow{D}^{rr} &= D_0^r\big[\tilde{\mu}^{rr} + \big(\beta_0^r\big)^{-1}\big[\big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{rr})^{-1}\big) \\ &\quad \cdot \big(\overleftrightarrow{E}^{rr}_{\mathrm{dp}} - \overleftrightarrow{\epsilon}^{\omega} - \mathbf{1}' + \overleftrightarrow{B}^{rr}_{\mathrm{dp}}\big) \cdot (L_{\mathbf{u}} - \widehat{R})\omega^0\big]^s\big]. \qquad (40)\end{aligned}$$

The factors $\overleftrightarrow{B}^{u}_{\mathrm{dp}}$, $\overleftrightarrow{B}^{u}$ and their diverse products that appear in the definition of the mobility tensor $\overleftrightarrow{\mu}^{u}$, $u = tt,rr$ are given, for instance, at two-body HI in (D9). At very low density and no stationary flow $\overleftrightarrow{B}^{u}_{\mathrm{dp}} = \mathbf{0}$, $\overleftrightarrow{B}^{tt} = \beta_0\mathbf{1}$, $\overleftrightarrow{B}^{rr} = \beta_0^r\mathbf{1}'$, $\overleftrightarrow{E}^{u}_{\mathrm{dp}} = \mathbf{0}$, $\overleftrightarrow{\mu}^{tt} = \beta_0^{-1}\mathbf{1}$, and, therefore, $\overleftrightarrow{D}^{tt} = D^0\mathbf{1}$ and similarly for $\overleftrightarrow{D}^{rr} = D_0^r\mathbf{1}'$. The rotational diffusion coefficient (40) contains two contributions; the first one is the thermal rotational diffusion that includes HI, whereas the second part adds the effect of vortex flow. In addition, from (D12) and (D13) of Appendix D we are led to the rotational viscosity $\overleftrightarrow{\eta}^{rr}_{\mathrm{HI}} = D_0^r\rho(\overleftrightarrow{\epsilon}^{\omega} - \overleftrightarrow{E}^{rr}_{\mathrm{dp}})$ due to the particles' HI and external flow field. Another contribution to rotational viscosity has been shown to occur in ferrofluid suspensions without shear flow in the presence of moderate magnetic fields. This magnetoviscous effect changes the fluid's viscous behavior by counteracting the rotational Brownian viscosity due to thermal fluctuations and direct interactions among particles [67,68]. Integrating (38) in the spatial coordinates and using $\int d\mathbf{r}\nabla \cdot [\ldots] = 0$ for ρ vanishing at the system boundaries [55], and $\rho(\theta,\phi,t) := \int d\mathbf{r}\rho(\mathbf{r},\Omega,t)$ the angular dependence SE is attained,

$$\begin{aligned}\frac{\partial\rho(\theta,\phi,t)}{\partial t} &= -(L_{\mathbf{u}} - \widehat{R}) \cdot \Big[\int \rho\omega^0 d\mathbf{r} + D_0^r \int \big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}} \\ &\quad \cdot (\overleftrightarrow{B}^{rr})^{-1}\big)\beta \cdot (-\rho(L_{\mathbf{u}} - \widehat{R})V_{\mathrm{ext}} + \mathbf{T}^d)d\mathbf{r} \\ &\quad + \big(\beta_0^r\big)^{-1}\int \big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{rr})^{-1}\big)\beta \cdot \rho\mathbf{t}d\mathbf{r} \\ &\quad + \zeta^{\omega}\big(\beta_0^r l^2\big)^{-1}\int \big(\tilde{\mu}^{rr} + \overleftrightarrow{B}^{rr}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{rr})^{-1}\big) \cdot \rho d\mathbf{r}\Big] \\ &\quad + (L_{\mathbf{u}} - \widehat{R}) \cdot \int [\overleftrightarrow{D}^{rr} \cdot (L_{\mathbf{u}} - \widehat{R})\rho]d\mathbf{r}. \qquad (41)\end{aligned}$$

It extends similar SE given by Nägele [55] to the case of a particle's HI and direct interactions. From this equation we can see that we obtain the same kinetic equation of Martsenyuk *et al.* [57] that describes the magnetization of suspensions of ferromagnetic particles (see Appendix E).

Alternatively, using that $\int d\Omega(L_{\mathbf{u}} - \widehat{R})[\ldots] = 0$, $\rho(\mathbf{r},t) := \int d\Omega\rho(\mathbf{r},\Omega,t)$ we get from (38)

$$\begin{aligned}\frac{\partial\rho(\mathbf{r},t)}{\partial t} &= -\nabla \cdot \Big[\int \rho\mathbf{v}^0 d\Omega + D^0\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{tt})^{-1}\big)\beta \\ &\quad \cdot \int (-\rho\nabla V_{\mathrm{ext}} + \mathbf{F}^d)d\Omega \\ &\quad + \beta_0^{-1}\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{tt})^{-1}\big)\beta \cdot \rho\mathbf{f} \\ &\quad + \zeta\beta_0^{-1}\big(\tilde{\mu}^{tt} + \overleftrightarrow{B}^{tt}_{\mathrm{dp}} \cdot (\overleftrightarrow{B}^{tt})^{-1}\big) \cdot \rho\Big] \\ &\quad + \nabla \cdot [\overleftrightarrow{D}^{tt} \cdot \nabla\rho], \qquad (42)\end{aligned}$$

which is the SE given before by Santamaria-Holek *et al.* [19] for the translational degree of freedom and coincides with one given by Nägele [55].

V. CONCLUSIONS

In this paper we derived the Fokker-Planck equations for one- and two-particle probability densities of suspensions of particles with anisotropic interactions using the MNET approach. In the hydrodynamic regime we obtained the balance equations of linear, angular momentum, and energy conservation. In the long-time limit and for *orientational isotropic* colloidal suspensions at thermal equilibrium, the former equation for the average translational velocity yields the collective diffusion coefficient D_c. It depends on the microstructure of the suspension through the equilibrium pair-correlation function and the single-particle hydrodynamic translational friction coefficient, which is a function of the concentration. Furthermore, we considered that an external flow field is imposed in the suspension and derived with MNET the FP equation under arbitrary flow conditions. In the diffusive regime we derived the Smoluchowski equation for particle's average density. This equation extended previous works [19] on translational degree of freedom of particles in order to encompass its rotational motion and effect of their direct and hydrodynamics interactions. Therefore, the result is an expression for the rotational diffusion coefficient of particles under the action of applied shear. In the diffusive regime, the balance equation of angular momentum leads to the derivation of a rotational viscosity that adds to the one that originates from thermal fluctuations of the particles in a quiescent fluid.

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APPENDIX A

The steps to derive the expressions for the currents are provided. The dynamical evolution of the suspension will be made through the one- and two-particle distribution functions.

Using the definitions of $P^{(n)}$ and $J_{\mathbf{v}_i}^{(n)}$ and $J_{\omega_i}^{(n)}$ for $n = 1,2$ we integrate the Liouville equation (2) on the remaining N-n coordinates and obtain the continuity equation,

$$
\begin{aligned}
&\frac{\partial P^{(n)}}{\partial t} + \sum_{i=1}^{n} \mathbf{v}_i \cdot \frac{\partial P^{(n)}}{\partial \mathbf{r}_i} + \sum_{i=1}^{n} \omega_i \cdot \left(L_{\mathbf{u}_i} - \widehat{R}_i\right) P^{(N)} \\
&\quad -m^{-1} \frac{N!}{(N-n)!} \sum_{i,j=1}^{N} \int \frac{\partial \phi_{ij}}{\partial \mathbf{r}_i} \cdot \frac{\partial P^{(N)}}{\partial \mathbf{v}_i} d\mathbf{x}_{n+1} \dots d\mathbf{x}_N \\
&\quad -m^{-1} \sum_{j=1}^{n} \frac{\partial V_{\text{ext}}}{\partial \mathbf{r}_j} \cdot \frac{\partial P^{(N)}}{\partial \mathbf{v}_j} \\
&\quad -I^{-1} \frac{N!}{(N-n)!} \sum_{i,j=1}^{N} \left(L_{\mathbf{u}_i} - \widehat{R}_i\right) \phi_{ij} \\
&\quad \cdot \frac{\partial P^{(N)}}{\partial \omega_i} d\mathbf{x}_{n+1} \dots d\mathbf{x}_N - I^{-1} \sum_{j=1}^{n} (L_{\mathbf{u}} - \widehat{R}) V_{\text{ext}} \cdot \frac{\partial P^{(n)}}{\partial \omega_j} \\
&= -\sum_{i=1}^{n} \frac{\partial}{\partial \mathbf{v}_i} \cdot J_{\mathbf{v}_i}^{(n)} - \sum_{i=1}^{n} \frac{\partial}{\partial \omega_i} \cdot J_{\omega_i}^{(n)},
\end{aligned}
\tag{A1}
$$

a relationship that will be used further. We note that Eq. (A1) ignores the triplet distribution function $P^{(3)}$ [26] and, thus, it is valid at the low-density limit. On the other hand, it is assumed that at local equilibrium the factorization of $P^{(N)}$ is valid in the same way as for its thermodynamic equilibrium counterpart [22,30],

$$
P^{(N)}(\mathbf{x}_N,t) = P^{(1)}(\mathbf{x}_1,t) P^{(2)}(\mathbf{x}_2,t) \dots P^{(1)}(\mathbf{x}_1,t) g^{(N)}(\mathbf{x}_N,t),
\tag{A2}
$$

with the dynamical correlation function

$$
\begin{aligned}
g^{(N)} = {} & g^{(2)}(\mathbf{x}_1,\mathbf{x}_2,t) \dots g^{(2)}(\mathbf{x}_{N-1},\mathbf{x}_N,t) \delta g^{(3)}(\mathbf{x}_1,\mathbf{x}_2,\mathbf{x}_3,t) \dots \\
& \times \delta g^{(3)}(\mathbf{x}_{N-2},\mathbf{x}_{N-1},\mathbf{x}_N,t) \dots \delta g^{(N)}(\mathbf{x}_1,\dots,\mathbf{x}_N,t).
\end{aligned}
\tag{A3}
$$

It should be noted that there are N factors $P^{(1)}$, $N(N-1)/2$ factors $g^{(2)}$, $N(N-1)(N-2)/3!$ factors $g^{(3)}$, and so on [30]. Within MNET the Gibbs equation of the solvent and colloids is [12]

$$
\delta S = -\frac{k_B m}{T} \int \mu(\Gamma,t) \delta P^{(N)} d\Gamma,
\tag{A4}
$$

where μ is the nonequilibrium chemical potential per unit mass that can be derived by comparing (A4) with the variation of (5) and using that $\delta S_{\text{LE}} = (m/T) \int \mu_B \delta P^{(N)} d\Gamma$ [12]. Thus, we find

$$
\mu(\mathbf{r},\Omega,\mathbf{v},\omega,t) = \mu_B + \frac{k_B T}{m} \ln \frac{P^{(N)}}{P_{\text{LE}}^{(N)}},
\tag{A5}
$$

where T is the local thermodynamic temperature. Substituting (A2) and (A3) in the above equation yields

$$
\mu = \frac{k_B T}{m} \ln \frac{P^{(1)}}{P_{\text{LE}}^{(1)}} + \frac{k_B T}{m} \frac{1}{2} \ln \frac{g^{(2)}}{g_{\text{LE}}^{(2)}} + \dots + \mu_B.
\tag{A6}
$$

From the classical statistical theory of liquids, the equilibrium electrochemical potential μ_B has two contributions; an ideal μ^{id} reference potential and μ^{exc} excess term due to direct interactions among particles, whereas the fundamental equation of state reads $\mu_B := \mu^{\text{id}} + \mu^{\text{exc}}$. It is also known that $P_{\text{LE}}^{(1)}$ is a Maxwell profile velocity [26],

$$
\begin{aligned}
P_{\text{LE}}^{(1)} = \exp\Bigg[& \frac{m}{k_B T} \left(\mu_{B\text{eq}}^{\text{id}} - \frac{\mathbf{v}_1^2}{2} \right) - \frac{I \omega_1^2}{2 k_B T} \\
& - \frac{1}{k_B T} \sum_j \phi_{1j} - \frac{V_{\text{ext}}}{k_B T} \Bigg],
\end{aligned}
\tag{A7}
$$

and the pair-correlation function $g^{(2)}$ contains the excess part [31]. There are several approximations in a diagrammatic expansion on the number of interacting particles for this static structural property which serve our purpose to show its explicit dependence on only μ^{exc}, aside from the direct interaction, for instance, in the hypernetted chain approximation [26,31]

$$
\begin{aligned}
g^{(2)}(\mathbf{r}_1,\Omega_1,\mathbf{r}_2,\Omega_2)_{\text{LE}} = \exp\Bigg[& \frac{1}{k_B T} \Big(m \mu_{B\text{eq}}^{\text{exc}}(\mathbf{r}_1,\Omega_1,\mathbf{r}_2,\Omega_2) \\
& - \phi_{12}(\mathbf{r}_1,\Omega_1,\mathbf{r}_2,\Omega_2) - V_{\text{ext}} \Big) \Bigg].
\end{aligned}
\tag{A8}
$$

Using both equilibrium functions in (A6) we get, for the local equilibrium chemical potential at the two-particle level,

$$
\begin{aligned}
\mu = {} & \frac{k_B T}{m} \ln P^{(1)} + \frac{\mathbf{v}_1^2}{2} + \frac{I^2 \omega_1^2}{2} + \frac{k_B T}{m} \ln g^{(2)} \\
& + \frac{\phi_{12}}{m} + \frac{V_{\text{ext}}}{m} + \cdots
\end{aligned}
\tag{A9}
$$

or, equivalently, $\mu = \mu^{(1)} + \mu^{(2)} + \dots$, where $\mu_1 = (k_B T/m) \ln(P^{(1)}/P_{\text{LE}}^{(1)}) + \mu^{id}$, $\mu_2 = (k_B T/m) \ln(g^{(2)}/g_{\text{LE}}^{(2)}) + \mu^{\text{exc}}$. Now, by replacing (A9) and (A2) in (A4) yields

$$
\delta S = -\frac{m}{T} \int \delta P^{(1)} \mu^{(1)} d\mathbf{x}_1 - \frac{m}{2T} \int \delta P^{(2)} \mu^{(2)} d\mathbf{x}_2 + \cdots .
\tag{A10}
$$

From the above equation we attain the time rate of change of entropy per unit volume as

$$
\begin{aligned}
\frac{\partial S(\mathbf{r},t)}{\partial t} = {} & -\frac{m}{T} \int \mu^{(1)} \frac{\partial P^{(1)}}{\partial t} d\mathbf{v}_1 d\Omega_1 d\omega_1 \\
& - \frac{m}{2T} \int \mu^{(2)} \frac{\partial P^{(2)}}{\partial t} d\mathbf{v}_1 d\Omega_1 d\omega_1 d\mathbf{r}_2 d\mathbf{v}_2 d\Omega_2 d\omega_2.
\end{aligned}
\tag{A11}
$$

The first term on the right-hand side is rewritten with the use of (A1) with $n = 1$, thus,

$$
\begin{aligned}
& -\frac{m}{T} \int \mu^{(1)} \frac{\partial P^{(1)}}{\partial t} d\mathbf{v}_1 d\omega_1 d\Omega_1 \\
& = -\frac{\partial}{\partial \mathbf{r}_1} \cdot J_s^{(1)} - \int \left(L_{\mathbf{u}_1} - \widehat{R}_1\right) \cdot J_{s,\omega_1}^{(1)} d\Omega_1 + \sigma^{(1)}(\mathbf{r}_1,t),
\end{aligned}
\tag{A12}
$$

where, using Refs. [27,32], it yields

$$\begin{aligned}
J^{(1)}_{s,\omega_1} &= k_B \int \omega_1 P^{(1)}\left(\frac{\mu^{(1)}m}{k_BT}-1\right)d\mathbf{v}_1 d\omega_1 - \frac{1}{4Tl^2}\int \mathbf{r}_{12}\big(L_{\mathbf{u}_1}-\widehat{R}_1\big)\phi_{12}\int_0^1 P^{(2)}d\alpha\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{r}_{12}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
&\quad + \frac{1}{Tl^2}\int \big[\big(L_{\mathbf{u}_1}-\widehat{R}_1\big)V_{\text{ext}}\big]P^{(2)}\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2,\\
J^{(1)}_{s} &= k_B \int \mathbf{v}_1 P^{(1)}\left(\frac{\mu^{(1)}m}{k_BT}-1\right)d\mathbf{v}_1 d\omega_1 d\Omega_1 - \frac{1}{2T}\int \frac{\mathbf{r}_{12}\mathbf{r}_{12}}{r_{12}}\phi'_{12}\cdot\int_0^1 P^{(2)}d\alpha\frac{\partial\mu^{(1)}}{\partial\mathbf{v}_1}d\mathbf{r}_{12}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
&\quad + \frac{1}{T}\int\left[\frac{\partial}{\partial\mathbf{r}_1}V_{\text{ext}}\right]P^{(2)}\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2,\\
\sigma^{(1)} &= -k_B\int\left[J^{(1)}_{\mathbf{v}_1}\cdot\frac{\partial}{\partial\mathbf{v}_1}\ln\frac{P^{(1)}}{P^{(1)}_{\text{LE}}} + J^{(1)}_{\omega_1}\cdot\frac{\partial}{\partial\omega_1}\ln\frac{P^{(1)}}{P^{(1)}_{\text{LE}}}\right]d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2
\end{aligned} \tag{A13}$$

The last term above contains the first contribution to the entropy production at the one-particle level $\sigma^{(1)}$. Similarly, the second term in (A11) can be calculated to give

$$-\frac{m}{2T}\int \mu^{(2)}\frac{\partial P^{(2)}}{\partial t}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{r}_2 d\mathbf{v}_1 d\omega_2 d\Omega_2 = -\frac{\partial}{\partial\mathbf{r}_1}\cdot J^{(2)}_s - \int\big(L_{\mathbf{u}_1}-\widehat{R}_1\big)\cdot J^{(2)}_{s,\omega}d\Omega_1 + \sigma^{(2)}(\mathbf{r}_1,t), \tag{A14}$$

where now

$$\begin{aligned}
J^{(2)}_{s} &= -\frac{m}{2T}\int \mathbf{v}_1 P^{(1)}\left(\frac{\mu^{(1)}m}{k_BT}-1\right)d\mathbf{v}_1 d\omega_1 d\Omega_1 - \frac{1}{2T}\sum_{i,j=1}^{2}\int \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}}\phi'_{ij}\cdot\int_0^1 P^{(2)}d\alpha\frac{\partial\mu^{(1)}}{\partial\mathbf{v}_1}d\mathbf{r}_{ij}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
&\quad + \frac{1}{T}\int\left[\frac{\partial}{\partial\mathbf{r}_1}V_{\text{ext}}\right]P^{(2)}\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
&\quad + \frac{m}{2T}\int(\mathbf{v}_1+\mathbf{v}_2)\cdot\frac{\mathbf{r}_{12}\mathbf{r}_{ij}}{r_{12}}\cdot\int_0^1 P^{(2)}d\alpha\frac{\partial\mu^{(2)}}{\partial\mathbf{r}_{12}}d\mathbf{r}_{12}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
J^{(2)}_{s,\omega} &= -\frac{1}{4Tl^2}\int \mathbf{r}_{12}\big(L_{\mathbf{u}_1}-\widehat{R}_1\big)\phi_{12}\cdot\int_0^1 P^{(2)}d\alpha\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{r}_{12}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2,\\
&\quad + \frac{1}{Tl^2}\int \big[\big(L_{\mathbf{u}_1}-\widehat{R}_1\big)V_{\text{ext}}\big]P^{(2)}\frac{\partial\mu^{(1)}}{\partial\omega_1}d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\Omega_2\\
\sigma^{(2)} &= -k_B\int\left[J^{(2)}_{\mathbf{v}_1}\cdot\frac{\partial}{\partial\mathbf{v}_1}\ln\frac{g^{(2)}}{g^{(2)}_{LE}} + J^{(2)}_{\omega_1}\cdot\frac{\partial}{\partial\omega_1}\ln\frac{P^{(2)}}{P^{(2)}_{\text{LE}}}\right]d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_2 d\omega_1 d\omega_2 d\Omega_1 d\Omega_2\\
&\quad - k_B\int\left[J^{(2)}_{\mathbf{v}_2}\cdot\frac{\partial}{\partial\mathbf{v}_2}\ln\frac{g^{(2)}}{g^{(2)}_{\text{LE}}} + J^{(2)}_{\omega_2}\cdot\frac{\partial}{\partial\omega_2}\ln\frac{g^{(2)}}{g^{(2)}_{\text{LE}}}\right]d\mathbf{v}_1 d\mathbf{v}_2 d\mathbf{r}_2 d\omega_1 d\omega_2 d\Omega_1 d\Omega_2,
\end{aligned} \tag{A15}$$

and we can identify in the last term the contribution to the entropy production of two particles $\sigma^{(2)}$. Therefore, the total entropy production is the sum of those two contributions found,

$$\begin{aligned}
\sigma(t) &= k_B\int J^{(1)}_{\mathbf{v}_1}\cdot\frac{\partial}{\partial\mathbf{v}_1}\ln\frac{P^{(1)}}{P^{(1)}_{\text{LE}}}d\mathbf{x}_1\\
&\quad + \frac{1}{2}\sum_i^2\int J^{(2)}_{\mathbf{v}_i}\cdot\frac{\partial}{\partial\mathbf{v}_i}\ln\frac{g^{(2)}}{g^{(2)}_{\text{LE}}}d\mathbf{x}_2\\
&\quad + k\int J^{(1)}_{\omega_1}\cdot\frac{\partial}{\partial\omega_1}\ln\frac{P^{(1)}}{P^{(1)}_{\text{LE}}}d\mathbf{x}_1\\
&\quad + \frac{1}{2}\sum_i^2\int J^{(2)}_{\omega_i}\cdot\frac{\partial}{\partial\omega_i}\ln\frac{g^{(2)}}{g^{(2)}_{\text{LE}}}d\mathbf{x}_2 + \dots,
\end{aligned} \tag{A16}$$

which constitute an extension of similar expression found by Mayorga *et al.* [22] and Rubi *et al.* [12] for translational velocity of spherical particles. According to Curi's principle [29] the unknown fluxes satisfy a linear relationship with the thermodynamic forces throughout Onsager coefficients. However, Snider and Lewchuck [33] demonstrated that for systems with spin as in our case here, if the Onsager coefficients do not depend on the spin variable $\mathbf{s}_B$, a generic class of isotropic system where the constitutive relations between forces and fluxes can be written as [33]

$$\begin{aligned}
J^{(N)}_{\mathbf{v}_i} &= -k_B\sum_{i\neq j,j=1}^{N}L_{\mathbf{v}_1\mathbf{v}_j}\frac{\partial}{\partial\mathbf{v}_j}\ln\frac{P^{(N)}}{P^{(N)}_{\text{LE}}}\\
&\quad - k_B\sum_{i\neq j,j=1}^{N}L_{\mathbf{v}_1\omega_j}\frac{\partial}{\partial\omega_j}\ln\frac{P^{(N)}}{P^{(N)}_{\text{LE}}}
\end{aligned}$$

$$J_{\omega_i}^{(N)} = -k_B \sum_{i\neq j, j=1}^{N} L_{\omega_i\omega_j} \frac{\partial}{\partial \omega_j} \ln \frac{P^{(N)}}{P_{\mathrm{LE}}^{(N)}} - k_B \sum_{i\neq j, j=1}^{N} L_{\omega_i \mathbf{v}_j} \frac{\partial}{\partial \mathbf{v}_j} \ln \frac{P^{(N)}}{P_{\mathrm{LE}}^{(N)}}, \qquad \text{(A17)}$$

where $\overleftrightarrow{L}_{\mathbf{a}_i\mathbf{a}_j}$ are Onsager coefficients that may depend on the variables of configuration and therefore represent hydrodynamics interaction among particles. Moreover, according to the general form of the above currents there appears a hydrodynamic coupling of the rotational and translational movement of the particles. For $\mathbf{a}_i = (\mathbf{v}_i,\omega_i)$, $\mathbf{a}_j = (\mathbf{v}_j,\mathbf{r}_j,\omega_j,\Omega_j)$ the unknown reciprocal relations $\overleftrightarrow{L}_{\mathbf{v}_i\mathbf{r}_j} = -\overleftrightarrow{L}_{\mathbf{r}_j\mathbf{v}_i}$, $\overleftrightarrow{L}_{\omega_i\Omega_j} = -\overleftrightarrow{L}_{\Omega_j\omega_i}$ [22,29] is satisfied. We will not consider in this paper the anisotropic case for the spin dependence of Onsager coefficients as given by Snider *et al.* [33]. Thus, we define the spin-independent static (but configurational dependent) hydrodynamic friction tensors as

$$\overleftrightarrow{\beta}^{tt}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\mathbf{v}_j}}{P^{(N)}T}, \quad \overleftrightarrow{\beta}^{tr}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\omega_j}}{P^{(N)}Tl^2}$$
$$\overleftrightarrow{\beta}^{rt}_{ij} = \frac{ml^2\overleftrightarrow{L}_{\omega_i\mathbf{v}_j}}{P^{(N)}T}, \quad \overleftrightarrow{\beta}^{rr}_{ij} = \frac{I\overleftrightarrow{L}_{\omega_i\omega_j}}{P^{(N)}T}, \qquad \text{(A18)}$$

which, when replaced in (A17), yield the currents of (7) and (8) in the main text.

APPENDIX B

The momentum balance equation results from differentiating (12) and using the conservation probability equation (9). Additionally, using that the probability density $P^{(1)}$ decays quickly for large velocities, we obtain

$$\begin{aligned}\frac{\partial \rho_B \mathbf{v}_B}{\partial t} &+ m\frac{\partial}{\partial \mathbf{r}_1}\cdot \int d\mathbf{v}_1 d\omega_1 d\Omega_1 \mathbf{v}_1\mathbf{v}_1 P^{(1)} \\ &+ m\big(L_{\mathbf{u}_1} - \widehat{R}_1\big)\cdot \int d\mathbf{v}_1 d\omega_1 d\Omega_1 \mathbf{v}_1 \omega_1 P^{(1)} \\ &= \int d\mathbf{v}_1 d\omega_1 d\Omega_1 d\mathbf{v}_2 d\omega_2 d\mathbf{r}_2 d\Omega_2 \mathbf{v}_1 \frac{\partial\phi_{12}}{\partial \mathbf{r}_1}\cdot\frac{\partial P^{(2)}}{\partial \mathbf{v}_1} \\ &+ m\overleftrightarrow{\beta}^{tt}_{11}\cdot \int d\mathbf{v}_1 d\omega_1 d\Omega_1 \mathbf{v}_1 \frac{\partial}{\partial \mathbf{v}_1}(P^{(1)}\mathbf{u}_1) \\ &+ m\overleftrightarrow{\beta}^{tr}_{11}\cdot \int d\mathbf{v}_1 d\omega_1 d\Omega_1 \mathbf{v}_1 \frac{\partial}{\partial \mathbf{v}_1}(P^{(1)}\omega_1). \qquad \text{(B1)}\end{aligned}$$

Introducing now the definitions (11), (12), (15), and (16) we arrive at

$$\begin{aligned}\frac{\partial \rho_B \mathbf{v}_B}{\partial t} &+ \frac{\partial}{\partial \mathbf{r}_1}\cdot\big(\overleftrightarrow{P}^{K,\mathbf{vv}}_B + \rho_B\mathbf{v}_B\mathbf{v}_B\big) + \big(L_{\mathbf{u}_1} - \widehat{R}_1\big) \\ &\cdot\big(\overleftrightarrow{P}^{K,\mathbf{v}\omega}_B + \rho_B\mathbf{v}_B\omega_B\big) + \mathbf{F}^d - \rho_B\overleftrightarrow{\beta}^{tt}_{11}\cdot\mathbf{v}_B - \rho_B\overleftrightarrow{\beta}^{tr}_{11}\cdot\mathbf{s}_B, \qquad \text{(B2)}\end{aligned}$$

If we define the total time derivative $d/dt = \partial/\partial t + \mathbf{v}_B\cdot\nabla$ we obtain (14). In order to derive Eq. (19) we need to multiply component γ of Eq. (14) by $\mathbf{r}_\delta$ and subtract the symmetric equation [29,44], yielding

$$\begin{aligned}\frac{d}{dt}&[\rho_B(\mathbf{r}_\gamma\mathbf{v}_{B,\delta} - \mathbf{r}_\delta\mathbf{v}_{B,\gamma})] \\ &= -\frac{\partial}{\partial \mathbf{r}_r}(\mathbf{r}_\gamma P_{\delta r} - \mathbf{r}_\delta P_{\gamma r}) + P_{\delta\gamma} - P_{\gamma\delta} \\ &- \frac{\rho_B}{m}\left(\mathbf{r}_\gamma\frac{\partial}{\partial \mathbf{r}_\delta} - \mathbf{r}_\delta\frac{\partial}{\partial \mathbf{r}_\gamma}\right)V_{\mathrm{ext}} \\ &+ \rho_B\big[\mathbf{r}_\delta\big(\overleftrightarrow{\beta}^{tt}_{11}\big)_{\gamma r} - \mathbf{r}_\gamma\big(\overleftrightarrow{\beta}^{tt}_{11}\big)_{\delta r}\big]\mathbf{v}_{B,r} \\ &+ \rho_B\big[\mathbf{r}_\delta\big(\overleftrightarrow{\beta}^{tr}_{11}\big)_{\gamma r} - \mathbf{r}_\gamma\big(\overleftrightarrow{\beta}^{tr}_{11}\big)_{\delta r}\big]\mathbf{s}_{B,r}. \qquad \text{(B3)}\end{aligned}$$

Finally, it results as follows:

$$\begin{aligned}\frac{d}{dt}[\rho_B\mathbf{r}\times\mathbf{v}_B] &= -\frac{\partial}{\partial \mathbf{r}}\cdot(\mathbf{r}\times\overleftrightarrow{P}_B) + 2\overleftrightarrow{P}^a - \frac{\rho_B}{m}\mathbf{r}\times\nabla V_{\mathrm{ext}} \\ &- \rho_B\mathbf{r}\times\overleftrightarrow{\beta}^{tt}_{11}\cdot\mathbf{v}_B - \rho_B\mathbf{r}\times\overleftrightarrow{\beta}^{tr}_{11}\cdot\mathbf{s}_B, \qquad \text{(B4)}\end{aligned}$$

where we added the coefficient 2 in the second term on the right-hand side in order to conform with the anisotropic contribution defined by Evans [27,45]. This term couples the equations of motion of orbital angular momentum above with that of the intrinsic angular momentum. It must, therefore, be added to the dynamic equation for $\rho_B d\mathbf{s}_B/dt$. The other remaining terms in such an equation are derived by taking the time derivative of (13) and using $\partial P^{(1)}/\partial t$ from (9), yielding

$$\begin{aligned}\rho_B\frac{d\mathbf{s}_B}{dt} &= -\frac{\partial}{\partial \mathbf{r}_1}\cdot l^2\overleftrightarrow{P}^{K,\mathbf{v}\omega}_B + \mathbf{T}^d(t) - \frac{l^2\rho_B}{I}(L_{\mathbf{u}_1} - \widehat{R}_1)V_{\mathrm{ext}} \\ &- 2P^a - \rho_B\overleftrightarrow{\beta}^{rr}_{11}\cdot\mathbf{s}_B - \rho_B\overleftrightarrow{\beta}^{rt}_{11}\cdot\mathbf{v}_B, \qquad \text{(B5)}\end{aligned}$$

where we have defined the torque's density of pairs interaction,

$$\begin{aligned}\mathbf{T}^d(t) &= -\int \big[(L_{\mathbf{u}_1} - \widehat{R}_1)\phi_{12}(\mathbf{r}_1,\mathbf{r}_2,\Omega_1,\Omega_2)\big]P^{(2)} \\ &\times d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\omega_1 d\mathbf{v}_2 d\omega_2 \\ &\approx -\frac{\partial}{\partial \mathbf{r}}\cdot\overleftrightarrow{Q}^{\phi}_B. \qquad \text{(B6)}\end{aligned}$$

The potential component of the torque tensor is [27]

$$\begin{aligned}\overleftrightarrow{Q}^{\phi}_B = -\frac{1}{4}\int \mathbf{r}_{12}(L_{\mathbf{u}_1} - \widehat{R}_1)\phi(r_{12},\Omega_1,\Omega_2)\int_0^1 P^{(2)} \\ \times(\mathbf{r}_1 - (1-\alpha)\mathbf{r}_{12}, \mathbf{r}_1 + \alpha\mathbf{r}_{12}, \mathbf{v}_1,\mathbf{v}_2,\omega_1,\omega_2,\Omega_1,\Omega_2,t) \\ \times d\alpha d\mathbf{r}_{12} d\Omega_1 d\Omega_2 d\mathbf{v}_1 d\omega_1 d\mathbf{v}_2 d\omega_2. \qquad \text{(B7)}\end{aligned}$$

We also introduced the symmetric kinetic pressure tensor for the particles,

$$\overleftrightarrow{P}^{K,\mathbf{v}\omega}_B = m\int P^{(1)}(\mathbf{v}_1 - \mathbf{v}_B)(\omega_1 - \omega_B)d\mathbf{v}_1 d\omega_1 d\Omega_1. \qquad \text{(B8)}$$

Thus, the final result is (19). Note that its general form is dictated by the evolution equation for the density of total angular momentum $\mathbf{L} = \mathbf{s}_B + \rho_B\mathbf{r}\times\mathbf{v}_\mathbf{B}$ that is attained using similar methods as those explained in Refs. [33,44,46]

$$\begin{aligned}\frac{d\mathbf{L}}{dt} = {} & \frac{d}{dt}[\mathbf{s}_B + \rho_B \mathbf{r} \times \mathbf{v}_B] \\ & - \frac{\rho_B}{m}\left[\mathbf{r} \times \nabla V_{\text{ext}} + \frac{l^2 \rho_B}{I}(L_{\mathbf{u}} - \widehat{R})V_{\text{ext}}\right] + \mathbf{r} \times \mathbf{F}^d \\ & + \nabla \cdot (\mathbf{r} \times \overleftrightarrow{P}_B + \overleftrightarrow{Q}_B) - \rho_B \mathbf{r} \times \overleftrightarrow{\beta}^{tt}_{11} \cdot \mathbf{v}_B \\ & - \rho_B \mathbf{r} \times \overleftrightarrow{\beta}^{tr}_{11} \cdot \mathbf{s}_B + \rho_B \overleftrightarrow{\beta}^{rr}_{11} \cdot \mathbf{s}_B + \overleftrightarrow{\beta}^{rt}_{11} \cdot \mathbf{v}_B .\end{aligned} \tag{B9}$$

Subtracting (B4) from this equation yields Eq. (19).

APPENDIX C

We follow the methods of MNET, Refs. [12,19,20], and calculate the entropy production of the system from the Gibbs entropy postulate

$$S = -k_B \int \Sigma_{i=1}^N P^{(N)} \ln \frac{P^{(N)}}{P_{\text{LE}}^{(N)}} \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma + S_{\text{LE}}, \tag{C1}$$

where S_{LE} is the reference local equilibrium entropy with

$$\begin{aligned}P_{\text{LE}}^{(N)} = {} & \exp\left[\frac{m}{k_B T}\left(\mu_B - \Sigma_{i=1}^N \frac{1}{2}\left(\mathbf{v}_i - \mathbf{v}_i^0\right)^2\right)\right. \\ & - \frac{ml^2}{k_B T}\Sigma_{i=1}^N \frac{1}{2}\left(\omega_i - \omega_i^0\right)^2 - \frac{1}{2k_B T}\Sigma_{i,j=1}^N \phi_{ij} \\ & \left. - \frac{1}{k_B T}\Sigma_{i=1}^N V_{\text{ext}}\right],\end{aligned} \tag{C2}$$

where μ_B is the local equilibrium chemical potential.

Taking the time derivative of Eq. (C1) and performing a partial integration with the use of (2) results in a balance equation for the entropy, from which the entropy production reads

$$\begin{aligned}\sigma = {} & -\frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_{\mathbf{v}_i} \cdot \frac{\partial \mu}{\partial \mathbf{v}_i} \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & - \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_{\omega_i} \cdot \frac{\partial \mu}{\partial \omega_i} \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_i \cdot \left(\mathbf{v}_i - \mathbf{v}_i^0\right) \cdot \frac{\partial}{\partial \mathbf{r}_i}\mathbf{v}_i^0 \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_i \cdot l^2\left(\omega_i - \omega_i^0\right) \\ & \cdot \frac{\partial}{\partial \mathbf{r}_i}\omega_i^0 \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_i^\omega \\ & \cdot \left(\mathbf{v}_i - \mathbf{v}_i^0\right) \cdot (L_{\mathbf{u}_i} - \widehat{R}_i)\mathbf{v}_i^0 \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_i^\omega \cdot l^2\left(\omega_i - \omega_i^0\right) \\ & \cdot \left(L_{\mathbf{u}_i} - \widehat{R}_i\right)\omega_i^0 \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_0^i \cdot \mathbf{F}_i \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma \\ & + \frac{m}{T}\int \Sigma_{i=1}^N \mathbf{J}_0^{i,\omega} \cdot \mathbf{T}_i \delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega) d\Gamma,\end{aligned} \tag{C3}$$

where the first two terms are diffusion processes in phase space. $\mathbf{F}_i = \partial \mathbf{v}_i^0/\partial t$, $\mathbf{T}_i = \partial \omega_i^0/\partial t$ are forces and torques due to the flow [19]. $\mathbf{J}_i = (\mathbf{v}_i - \overline{\mathbf{v}}_i)P^N$, $\mathbf{J}_i^\omega = (\omega_i - \overline{\omega_i})P^N$, $\mathbf{J}_0^i = (\mathbf{v}_i - \mathbf{v}_i^0)P^N$, $\mathbf{J}_0^{i,\omega} = (\omega_i - \omega_i^0)P^N$. The last two terms are diffusion with respect to the flow velocity [19]. We define the nonequilibrium chemical potential as follows:

$$\begin{aligned}\mu(\Gamma,t) = {} & \frac{k_B T}{m}\ln P^{(N)} + \frac{1}{2}\Sigma_{i=1}^N \left(\mathbf{v}_i - \mathbf{v}_i^0\right)^2 \\ & + \frac{l^2}{2}\Sigma_{i=1}^N \left(\omega_i - \omega_i^0\right)^2 + \frac{1}{2m}\Sigma_{i,j=1}^N \phi_{ij} + \frac{1}{m}\Sigma_{i=1}^N V_{\text{ext}}.\end{aligned} \tag{C4}$$

Since the entropy production is a positive defined property, nonequilibrium thermodynamics implies [29], from Eq. (C3), that there exist linear relationships between the fluxes $\mathbf{J}_{\mathbf{v}_i}$, $\mathbf{J}_{\omega_i}$ and forces $\partial\mu/\partial\mathbf{v}_i$, $\partial\mu/\partial\omega_i$, respectively. According to Curi's principle, these vectorial quantities are given by the constitutive relations

$$\begin{aligned}\mathbf{J}_{\mathbf{v}_i} = {} & -\Sigma_j \overleftrightarrow{\alpha}^{tt}_{ij} \cdot \left(\mathbf{v}_j - \mathbf{v}_j^0\right) P^{(N)} - \frac{k_B T}{m}\Sigma_j \overleftrightarrow{\alpha}^{tt}_{ij} \cdot \nabla_{\mathbf{v}_j} P^{(N)} \\ & - \Sigma_j \overleftrightarrow{\epsilon}_{ij} \cdot \left(\mathbf{v}_j - \mathbf{v}_j^0\right) \cdot \nabla_{\mathbf{r}_j}\mathbf{v}_j^0 P^{(N)} - \Sigma_j l^2 \overleftrightarrow{\alpha}^{tr}_{ij} \\ & \cdot \left(\omega_i - \omega_i^0\right) P^{(N)} - \frac{k_B T}{I}\Sigma_j l^2 \overleftrightarrow{\alpha}^{tr}_{ij} \cdot \nabla_{\omega_j} P^{(N)} \\ & + \Sigma_j \overleftrightarrow{\zeta}_{ij} \cdot \mathbf{F}_j P^{(N)},\end{aligned} \tag{C5}$$

with $\nabla_\gamma = \frac{\partial}{\partial\gamma}$, $\gamma = \mathbf{v}_j, \mathbf{r}_j, \omega_j$,

$$\begin{aligned}\mathbf{J}_{\omega_i} = {} & -\Sigma_j \frac{1}{l^2}\overleftrightarrow{\alpha}^{rt}_{ij} \cdot \left(\mathbf{v}_i - \mathbf{v}_i^0\right) P^{(N)} - \frac{k_B T}{m}\Sigma_j \frac{1}{l^2}\overleftrightarrow{\alpha}^{rt}_{ij} \\ & \cdot \nabla_{\mathbf{v}_j} P^{(N)} - \Sigma_j \overleftrightarrow{\epsilon}^{\omega}_{ij} \cdot \left(\omega_j - \omega_j^0\right) \cdot \left(L_{\mathbf{u}_j} - \widehat{R}_j\right)\omega_j^0 P^{(N)} \\ & - \Sigma_j \overleftrightarrow{\alpha}^{rr}_{ij} \cdot \left(\omega_j - \omega_j^0\right) P^{(N)} - \frac{k_B T}{ml^2}\Sigma_j \overleftrightarrow{\alpha}^{rr}_{ij} \cdot \nabla_{\omega_j} P^{(N)} \\ & + \Sigma_j \overleftrightarrow{\zeta}^{\omega}_{ij} \cdot \mathbf{T}_j P^{(N)}.\end{aligned} \tag{C6}$$

The following tensors were defined in terms of the Onsager coefficients $\overleftrightarrow{L}_{\mathbf{a}_i\mathbf{a}_j}$, with $\mathbf{a}_i = (\mathbf{v}_i,\omega_i)$, $\mathbf{a}_j = (\mathbf{v}_j,\mathbf{r}_j,\overline{\mathbf{v}}_j,\omega_j,\Omega_j,\overline{\omega}_j)$,

$$\begin{gathered}\overleftrightarrow{\alpha}^{tt}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\mathbf{v}_j}}{TP^{(N)}}, \quad \overleftrightarrow{\alpha}^{tr}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\omega_j}}{TP^{(N)}l^2}, \quad \overleftrightarrow{\epsilon}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\mathbf{r}_j}}{TP^{(N)}}, \\ \overleftrightarrow{\alpha}^{rr}_{ij} = \frac{ml^2\overleftrightarrow{L}_{\omega_i\omega_j}}{TP^{(N)}}, \quad \overleftrightarrow{\alpha}^{rt}_{ij} = \frac{ml^2\overleftrightarrow{L}_{\omega_i\omega_j}}{TP^{(N)}}, \\ \overleftrightarrow{\epsilon}^{\omega}_{ij} = \frac{ml^2\overleftrightarrow{L}_{\omega_i\Omega_j}}{TP^{(N)}}, \quad \overleftrightarrow{\zeta}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\overline{\mathbf{v}}_j}}{TP^{(N)}}, \\ \overleftrightarrow{\zeta}^{\omega}_{ij} = \frac{m\overleftrightarrow{L}_{\mathbf{v}_i\overline{\omega}_j}}{TP^{(N)}}.\end{gathered} \tag{C7}$$

These Onsager coefficients satisfy the reciprocal relations $\overleftrightarrow{L}_{\mathbf{v}_i\mathbf{r}_j} = -\overleftrightarrow{L}_{\mathbf{r}_j\mathbf{v}_i}$, $\overleftrightarrow{L}_{\omega_i\Omega_j} = -\overleftrightarrow{L}_{\Omega_j\omega_i}$ [19,60], which can depend on flow. The mesoscopic nonequilibrium approach breaks down for Onsager reciprocal relations are not valid far from equilibrium states. Such states are reached with strong flows. Another limitation of MNET is that, in general, $\rho^{(2)}$ depends on applied flow and its functional form is not known. At low concentration it can be approximated through the pair-correlation function [61].

Replacing the currents, Eqs. (C5)–(C6), in (2), we obtain the N-particle Fokker-Planck equation (34) for stationary flow.

APPENDIX D

In the inertial regime ($t \ll t^t, t^r$) the out-of-equilibrium dynamics of the system is provided by the continuity equation Eq. (32), and the balance equation of linear momentum is obtained by differentiating (33) and using (34),

$$\begin{aligned}\rho_i \frac{d_i \overline{\mathbf{v}}_i}{dt} =& -\nabla \cdot \overleftrightarrow{P}^{\mathbf{vv}}_i - (L_{\mathbf{u}} - \widehat{R}) \cdot \overleftrightarrow{P}^{\omega\mathbf{v}}_i - \int \Sigma_j P^{(N)} \nabla_{\mathbf{r}_i} \phi_{ij} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma - \int P^{(N)} \nabla_{\mathbf{r}_i} V_{\mathrm{ext}} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma \\ & - \int \Sigma_j \overleftrightarrow{\beta}^{tt}_{ij} \cdot \big(\mathbf{v}^{(2)}_j - \mathbf{v}^0_j\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\ & - \int \Sigma_j l^2 \overleftrightarrow{\alpha}^{tr}_{ij} \cdot \big(\omega^{(2)}_j - \omega^0_j\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j + \rho_i \overleftrightarrow{\zeta} \cdot \mathbf{F}_i . \end{aligned} \tag{D1}$$

Similarly, we deduce the balance equation of intrinsic angular momentum,

$$\begin{aligned}\rho_i \frac{d_i l^2 \overline{\omega}_i}{dt} =& -\nabla \cdot l^2 \overleftrightarrow{P}^{\mathbf{v}\omega}_i - (L_{\mathbf{u}} - \widehat{R}) \cdot l^2 \overleftrightarrow{P}^{\omega\omega}_i - m l^2 I^{-1} \int \Sigma_j P^{(N)} (L_{\mathbf{u}_i} - \widehat{R}_i) \phi_{ij} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma \\ & - \int P^{(N)} \big(L_{\mathbf{u}_i} - \widehat{R}_i\big) V_{\mathrm{ext}} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma - \int \Sigma_j l^2 \overleftrightarrow{\beta}^{rr}_{ij} \cdot \big(\omega^{(2)}_j - \omega^0_j\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\ & - \int \Sigma_j \overleftrightarrow{\alpha}^{rt}_{ij} \cdot \big(\mathbf{v}^{(2)}_j - \mathbf{v}^0_j\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j + \rho_i \overleftrightarrow{\zeta}^{\omega} \cdot \mathbf{T}_i - 2 \overleftrightarrow{P}^{a}_i , \end{aligned} \tag{D2}$$

where $\rho^{(2)}(\mathbf{r}_i, \Omega_i, \mathbf{r}_j, \Omega_j, t) = m \int P^{(N)} d\Gamma^{N-2}_{ij}$, $d\Gamma^{N-2}_{ij} = d\mathbf{r}_1 d\Omega_1 d\mathbf{v}_1 d\omega_1 \ldots d\mathbf{v}_i d\omega_i d\mathbf{v}_j d\omega_j$ of $N-2$ particles, and the convective derivative $\frac{d_i}{dt} = \frac{\partial}{\partial t} + \overline{\mathbf{v}}_i \cdot \nabla + \overline{\omega}_i \cdot (L_{\mathbf{u}} - \widehat{R})$. Here $\mathbf{v}^{(2)}$ and $\omega^{(2)}$ depend on $\mathbf{r_i} \mathbf{r}_j \Omega_i \Omega_j$. The first terms on the right-hand side of the above equations are the drag forces and torques on the particles mediated by HI which modify their velocities due to the distribution of particles [19]. Equations (D1) and (D2) depend on the pressure tensors for the particles,

$$\begin{aligned}\overleftrightarrow{P}^{\mathbf{vv}}_i &= m \int P^{(N)} (\mathbf{v}_i - \overline{\mathbf{v}}_i)(\mathbf{v}_i - \overline{\mathbf{v}}_i) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma, \\ \overleftrightarrow{P}^{\mathbf{v}\omega}_i &= m \int P^{(N)} (\mathbf{v}_i - \overline{\mathbf{v}}_i)(\omega_i - \overline{\omega}_i) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma, \\ \overleftrightarrow{P}^{\omega\omega}_i &= m \int P^{(N)} (\omega_i - \overline{\omega}_i)(\omega_i - \overline{\omega}_i) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma, \\ \overleftrightarrow{P}^{\omega\mathbf{v}}_i &= m \int P^{(N)} (\omega_i - \overline{\omega}_i)(\mathbf{v}_i - \overline{\mathbf{v}}_i) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma. \end{aligned} \tag{D3}$$

That satisfies the corresponding evolution equations

$$\begin{aligned} & \frac{d_i}{dt} \overleftrightarrow{P}^{\mathbf{vv}}_i + 2\bigg[\bigg(\beta_0 \mathbf{1} + \nabla \overline{\mathbf{v}}_i + \frac{1}{2} \nabla \cdot \overline{\mathbf{v}}_i \mathbf{1} + \frac{1}{2}(L_{\mathbf{u}} - \widehat{R}) \cdot \overline{\omega}_i \mathbf{1}\bigg) \cdot \overleftrightarrow{P}^{\mathbf{vv}}_i\bigg]^s + 2\big[\big(l^2 \overleftrightarrow{\alpha}^{tr}_{ii} + (L_{\mathbf{u}} - \widehat{R}) \overline{\mathbf{v}}_i\big) \cdot \overleftrightarrow{P}^{\omega\mathbf{v}}_i\big]^s \\ &= 2 k_B T \frac{\rho_i}{m} (\overleftrightarrow{\alpha}^{tt})^s - 2\bigg(\int \Sigma_{j, i \neq j} \overleftrightarrow{\beta}^{tt}_{ij} \cdot \big(\mathbf{v}^{(2)}_j - \mathbf{v}^0_j\big)\big(\mathbf{v}^{(2)}_i - \mathbf{v}^0_i\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s \\ &\quad - 2\bigg(\int \Sigma_{j, i \neq j} l^2 \overleftrightarrow{\alpha}^{tr}_{ij} \cdot \big(\omega^{(2)}_j - \omega^0_j\big)\big(\mathbf{v}^{(2)}_i - \mathbf{v}^0_i\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s , \end{aligned} \tag{D4}$$

$$\begin{aligned} & \frac{d_i}{dt} \overleftrightarrow{P}^{\omega\omega}_i + 2\bigg[\bigg(\beta^{rr}_{ii} \mathbf{1}' + (L_{\mathbf{u}} - \widehat{R}) \overline{\omega}_i + \frac{1}{2} \nabla \cdot \overline{\mathbf{v}}_i \mathbf{1}' + \frac{1}{2}(L_{\mathbf{u}} - \widehat{R}) \cdot \overline{\omega}_i \mathbf{1}'\bigg) \cdot \overleftrightarrow{P}^{\omega\omega}_i\bigg]^s + 2\bigg[\bigg(\frac{1}{l^2} \overleftrightarrow{\alpha}^{rt}_{ii} + \nabla \overline{\omega}_i\bigg) \cdot \overleftrightarrow{P}^{\mathbf{v}\omega}_i\bigg]^s \\ &= 2 k_B T \frac{\rho_i}{I} (\overleftrightarrow{\alpha}^{rr})^s - 2\bigg(\int \Sigma_{j, i \neq j} \overleftrightarrow{\beta}^{rr}_{ij} \cdot \big(\omega^{(2)}_j - \omega^0_j\big)\big(\omega^{(2)}_i - \omega^0_i\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s \\ &\quad - 2\bigg(\int \Sigma_{j, i \neq j} \frac{1}{l^2} \overleftrightarrow{\alpha}^{rt}_{ij} \cdot \big(\mathbf{v}^{(2)}_j - \mathbf{v}^0_j\big)\big(\omega^{(2)}_i - \omega^0_i\big) \rho^{(2)} \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s . \end{aligned} \tag{D5}$$

The last terms on (D4) and (D5) add HI to the pressure tensor [19]. This cross-correlation of velocities of distinct particles (dp) implies that stresses in the system are modified by HI [19]. In Eqs. (D1) and (D2) we used the values of friction tensors without HI $\overleftrightarrow{\beta}^{tt}_{ii} \approx \beta_0 \mathbf{1} \delta_{ii}$, $\overleftrightarrow{\beta}^{rr}_{ii} \approx \beta^{rr}_{ii} \mathbf{1}' \delta_{ii} = \beta^r_0 \mathbf{1}' \delta_{ii}$, and Eq. (35). The superscript s denotes the symmetric part of a tensor. Following the method of Ref. [19], in order to rewrite the quadrature terms of (D1) and (D2) and then (D4) and (D5) it is necessary to derive also the evolution equations for the cross-correlation of velocities for distinct particles,

$$\begin{aligned}\overleftrightarrow{C}^{\mathbf{vv}}_{ij} &= m \int P^{(N)} (\mathbf{v}_i - \overline{\mathbf{v}}_i)(\mathbf{v}_j - \overline{\mathbf{v}}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma \\ \overleftrightarrow{C}^{\omega\omega}_{ij} &= m \int P^{(N)} (\omega_i - \overline{\omega}_i)(\omega_j - \overline{\omega}_j) \delta(\mathbf{r}_i - \mathbf{r}) \delta(\Omega_i - \Omega) d\Gamma, \end{aligned} \tag{D6}$$

whose result is

$$\begin{aligned}
&\frac{d_i}{dt}\overleftrightarrow{C}^{\mathbf{vv}}_{ij} + 2\left[\left(\nabla\overline{\mathbf{v}}_i + \frac{1}{2}\nabla\cdot\overline{\mathbf{v}}_i\mathbf{1} + \frac{1}{2}(L_{\mathbf{u}} - \widehat{R})\cdot\overline{\omega}_i\mathbf{1}\right)\cdot\overleftrightarrow{C}^{\mathbf{vv}}_{ij}\right]^s + 2\big[(L_{\mathbf{u}} - \widehat{R})\overline{\mathbf{v}}_i\cdot\overleftrightarrow{C}^{\omega\mathbf{v}}_{ij}\big]^s \\
&\quad = \frac{2k_BT}{m}\int \Sigma_{k=1}^N \overleftrightarrow{\alpha}^{tt,s}_{ij}\delta_{jk}\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\
&\qquad - 2\bigg(\int \Sigma_{k=1}^N \overleftrightarrow{\beta}^{tt}_{ik}\cdot\big(\mathbf{v}_k^{(2)} - \mathbf{v}_k^0\big)\big(\mathbf{v}_j^{(2)} - \mathbf{v}_j^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_i\bigg)^s \\
&\qquad - 2\bigg(\int \Sigma_{k=1}^N l^2\overleftrightarrow{\alpha}^{tr}_{ik}\cdot\big(\omega_j^{(2)} - \omega_j^0\big)\big(\mathbf{v}_i^{(2)} - \mathbf{v}_i^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s, \qquad \text{(D7)}
\end{aligned}$$

$$\begin{aligned}
&\frac{d_i}{dt}\overleftrightarrow{C}^{\omega\omega}_{ij} + 2\left[\left((L_{\mathbf{u}} - \widehat{R})\overline{\omega}_i + \frac{1}{2}\nabla\cdot\overline{\mathbf{v}}_i\mathbf{1}' + \frac{1}{2}(L_{\mathbf{u}} - \widehat{R})\cdot\overline{\omega}_j\mathbf{1}'\right)\cdot\overleftrightarrow{C}^{\omega\omega}_{ij}\right]^s + 2\big[\nabla\overline{\omega}_i\cdot\overleftrightarrow{C}^{\mathbf{v}\omega}_{ij}\big]^s \\
&\quad = \frac{2k_BT}{I}\int \Sigma_{k=1}^N \overleftrightarrow{\alpha}^{rr,s}_{ij}\delta_{jk}\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\
&\qquad - 2\bigg(\int \Sigma_{k=1}^N \overleftrightarrow{\beta}^{rr}_{ik}\cdot\big(\omega_k^{(2)} - \omega_k^0\big)\big(\omega_j^{(2)} - \omega_j^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s \\
&\qquad - 2\bigg(\int \Sigma_{k=1}^N \frac{1}{l^2}\overleftrightarrow{\alpha}^{rt}_{ik}\cdot\big(\mathbf{v}_j^{(2)} - \mathbf{v}_j^0\big)\big(\omega_i^{(2)} - \omega_i^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j\bigg)^s. \qquad \text{(D8)}
\end{aligned}$$

Both equations are valid for $k \neq i$. Higher-order moments of velocities are not considered since they relax faster than the ones considered here [19]. The friction tensors for two particles are related to the mobility $\overleftrightarrow{\mu}$ through [64]

$$\begin{aligned}
&\begin{pmatrix} \overleftrightarrow{\beta}^{tt} & \overleftrightarrow{\beta}^{tr} \\ \overleftrightarrow{\beta}^{rt} & \overleftrightarrow{\beta}^{rr} \end{pmatrix}^{-1} = \begin{pmatrix} \overleftrightarrow{\mu}^{tt} & \overleftrightarrow{\mu}^{tr} \\ \overleftrightarrow{\mu}^{rt} & \overleftrightarrow{\mu}^{rr} \end{pmatrix}, \\
&\beta_0\overleftrightarrow{\mu}^{tt}_{ij} := \widetilde{\mu}^{tt}_{ij} \approx \mathbf{1}\delta_{ij} + \frac{3}{4}\frac{\sigma}{r_{ij}}(\mathbf{1} + \hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij})(1 - \delta_{ij}) - \frac{3}{4}\frac{\sigma}{r_{ij_s}}(\mathbf{1} + \hat{\mathbf{r}}_{ij_s}\hat{\mathbf{r}}_{ij_s}) + \dots, \\
&\beta_0^r\overleftrightarrow{\mu}^{rr}_{ij} := \widetilde{\mu}^{rr}_{ij} \approx \mathbf{1}'\delta_{ij} + \frac{3}{2}\left(\frac{\sigma}{r_{ij}}\right)^3\left(\hat{\mathbf{r}}_{ij}\hat{\mathbf{r}}_{ij} - \frac{1}{3}\mathbf{1}'\right)(1 - \delta_{ij}) \\
&\qquad - \frac{3}{2}\left(\frac{\sigma}{r_{ij_s}}\right)^3\left[\hat{\mathbf{r}}_{i_sj}\hat{\mathbf{r}}_{ij_s} - \frac{1}{3}\mathbf{1}' - 2(\hat{\mathbf{r}}_{ij_s}\wedge\hat{\mathbf{n}})(\hat{\mathbf{r}}_{ij_s}\wedge\hat{\mathbf{n}})\right] + \dots, \qquad \text{(D9)}
\end{aligned}$$

where we kept terms up to first and third order in σ/r_{ij} for $uu = tt,rr$, respectively. r_{ij_s} is the distance between particle i and the image of j with respect to an infinite plane. $\hat{\mathbf{n}}$ is a unit vector normal to the surface of the sphere. We shall not consider the HI couplings $uu = tr,rt$, $\overleftrightarrow{P}^{\omega\mathbf{v}}$, $\overleftrightarrow{P}^{\mathbf{v}\omega}$. At very low densities $\overleftrightarrow{\mu}^{tt}_{ij} = (\overleftrightarrow{\beta}^{tt})^{-1}_{ij} \approx \beta_0^{-1}\mathbf{1}\delta_{ij}$ and $\overleftrightarrow{\mu}^{rr}_{ij} = (\overleftrightarrow{\beta}^{rr})^{-1}_{ij} \approx (\beta_0^r)^{-1}\mathbf{1}'\delta_{ij}$ but, in general, for concentrated suspensions they are nonzero for distinct particles as seen in (D9). In the long-time limit this amounts to neglecting inertial terms [19,56] $d_i\overline{\mathbf{v}}_i/dt$, $d_i\overline{\omega}_i/dt$, $d_i\overleftrightarrow{C}^{\mathbf{vv}}_{ij}/dt$, $d_i\overleftrightarrow{C}^{\omega\omega}_{ij}/dt$, $d_i\overleftrightarrow{C}^{\mathbf{vv}}_{ij}/dt$, $d_i\overleftrightarrow{C}^{\omega\omega}_{ij}/dt$, $\nabla\overline{\mathbf{v}}_i\beta_0^{-1} \ll 1$, $\nabla\cdot\overline{\mathbf{v}}_i\beta_0^{-1} \ll 1$, $(L_{\mathbf{u}} - \widehat{R})\cdot\overline{\omega}_i\beta_0^{-1} \ll 1$, $(L_{\mathbf{u}} - \widehat{\mathbf{R}})\overline{\omega}_i(\beta_0^r)^{-1} \ll 1$, $\nabla\cdot\overline{\mathbf{v}}_i(\beta_0^r)^{-1} \ll 1$, $(L_{\mathbf{u}} - \widehat{R})\cdot\overline{\omega}_i(\beta_0^r)^{-1} \ll 1$ in Eqs. (D1) and (D2) and then (D4) and (D5). One may show that, for distinct particles, $i \neq j$ to the lowest order in σ/r_{ij} equations (D7) and (D8), yielding

$$\begin{aligned}
&\frac{k_BT}{m}\int \Sigma_j\overleftrightarrow{\alpha}^{tt}_{ij}\cdot\overleftrightarrow{\beta}^{tt}_{ij}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\
&\quad \approx \int \Sigma_{j=1,i\neq j}^N \beta_0\overleftrightarrow{\beta}^{tt}_{ij}\cdot\big(\mathbf{v}_i^{(2)} - \mathbf{v}_i^0\big)\big(\mathbf{v}_j^{(2)} - \mathbf{v}_j^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j, \\
&\frac{k_BT}{I}\int \Sigma_j\overleftrightarrow{\alpha}^{rr}_{ij}\cdot\overleftrightarrow{\beta}^{rr}_{ij}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j \\
&\quad \approx \int \Sigma_{j=1,i\neq j}^N \beta_0^r\overleftrightarrow{\beta}^{rr}_{ij}\cdot\big(\mathbf{v}_i^{(2)} - \mathbf{v}_i^0\big)\big(\mathbf{v}_j^{(2)} - \mathbf{v}_j^0\big)\rho^{(2)}\delta(\mathbf{r}_i - \mathbf{r})\delta(\Omega_i - \Omega)d\mathbf{r}_i d\mathbf{r}_j d\Omega_i d\Omega_j. \qquad \text{(D10)}
\end{aligned}$$

Also using the effective medium approximation valid at intermediate volume fractions [19], where dynamical properties are obtained from a configurationally averaged suspension. Thus, a test particle i performs its hydrodynamic and Brownian motion in the averaged colloidal fluid [19,65]. This amounts to replacing $\int f(\mathbf{r}',\Omega')d\mathbf{r}'d\Omega' \longrightarrow \int \Sigma_i f(\mathbf{r}_i,\Omega_i)d\mathbf{r}_i d\Omega_i$ in the above equations, which are finally used in Eqs. (D1) and (D2) and then (D4) and (D5), yielding the effective pressure tensors

$$\overleftrightarrow{P}^{\mathbf{vv}} \approx \frac{k_BT}{m}\left[\rho\beta_0^{-1}\overleftrightarrow{\alpha}^{tt} - \beta_0^{-2}\int\overleftrightarrow{\alpha}^{*tt}(\mathbf{r}',\Omega')\rho^{(2)}d\mathbf{r}'d\Omega'\right]^s, \qquad \text{(D11)}$$

with $\overleftrightarrow{\alpha}^{*tt}(\mathbf{r},\Omega) = \overleftrightarrow{\beta}^{tt}(\mathbf{r},\Omega) \cdot \overleftrightarrow{\alpha}^{tt}(\mathbf{r},\Omega)$,

$$\overleftrightarrow{P}^{\omega\omega} \approx \frac{k_B T}{I}\left[\rho\left(\beta_0^r\right)^{-1}\overleftrightarrow{\alpha}^{rr} - \left(\beta_0^r\right)^{-2}\int \overleftrightarrow{\alpha}^{*rr}(\mathbf{r}',\Omega')\rho^{(2)}d\mathbf{r}'d\Omega'\right]^s, \tag{D12}$$

where $\overleftrightarrow{\alpha}^{*rr}(\mathbf{r},\Omega) = \overleftrightarrow{\beta}^{rr}(\mathbf{r},\Omega) \cdot \overleftrightarrow{\alpha}^{rr}(\mathbf{r},\Omega)$. These pressure tensors can be recast into another form after assuming small spatial gradients in the velocity [19] $(\overline{\mathbf{v}})$; $\overline{\omega}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t) - \omega^0(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t) \approx \overline{\omega}(\mathbf{r},\Omega,t) - \omega^0(\mathbf{r},\Omega,t)$ [19,22] and using the distinct particles expressions of (D10) to define

$$\begin{aligned}
\overleftrightarrow{B}^{tt}_{\mathrm{dp}}(\mathbf{r},\Omega,t) &= (\beta_0\rho^2)^{-1}\int \overleftrightarrow{\beta}^{tt}(\mathbf{r}'\Omega') \cdot \overleftrightarrow{\beta}^{tt}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega'\\
\overleftrightarrow{B}^{rr}_{\mathrm{dp}}(\mathbf{r},\Omega,t) &= \left(\beta_0^r\rho^2\right)^{-1}\int \overleftrightarrow{\beta}^{rr}(\mathbf{r}'\Omega') \cdot \overleftrightarrow{\beta}^{rr}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega'\\
\overleftrightarrow{E}^{tt}_{\mathrm{dp}}(\mathbf{r},\Omega,t) &= (\beta_0\rho^2)^{-1}\int \overleftrightarrow{\beta}^{tt}(\mathbf{r}'\Omega') \cdot \overleftrightarrow{\epsilon}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega'\\
\overleftrightarrow{E}^{rr}_{\mathrm{dp}}(\mathbf{r},\Omega,t) &= \left(\beta_0^r\rho^2\right)^{-1}\int \overleftrightarrow{\beta}^{rr}(\mathbf{r}'\Omega') \cdot \overleftrightarrow{\epsilon}^{\omega}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega',
\end{aligned} \tag{D13}$$

where, for all particles,

$$\begin{aligned}
\overleftrightarrow{B}^{tt}(\mathbf{r},\Omega,t) &= \rho^{-2}\int \overleftrightarrow{\beta}^{tt}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega'\\
\overleftrightarrow{B}^{rr}(\mathbf{r},\Omega,t) &= \rho^{-2}\int \overleftrightarrow{\beta}^{rr}(\mathbf{r}'\Omega')\rho^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega',t)d\mathbf{r}'d\Omega'
\end{aligned} \tag{D14}$$

is valid. The very low density limit of no HI of (D13) reduce to tensor zero in all cases, whereas for (D14) they reduce to $\beta_0\mathbf{1}$, $\beta_0^r\mathbf{1}'$, respectively. Replacing (D13) and (D14) into (D11) and (D12) and using (D1) and (D2), the effective currents (36) follow

$$\begin{aligned}
&\begin{pmatrix} \overleftrightarrow{B}^{tt} & \mathbf{0}\\ \mathbf{0} & \overleftrightarrow{B}^{rr}\end{pmatrix} \cdot \begin{pmatrix}\rho(\overline{\mathbf{v}}-\mathbf{v}^0)\\ \rho(\overline{\omega}-\omega^0)\end{pmatrix}\\
&\approx -\frac{1}{m}\begin{pmatrix}\mathbf{F}^{\mathbf{d}}\\ \frac{1}{l^2}\mathbf{T}^d\end{pmatrix} + \frac{1}{m}\begin{pmatrix}\rho\nabla V_{\mathrm{ext}}\\ \frac{1}{l^2}\rho(L_{\mathbf{u}}-\widehat{R})V_{\mathrm{ext}}\end{pmatrix} - \rho\begin{pmatrix}\zeta\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \frac{1}{l^2}\zeta^{\omega}\mathbf{1}'\end{pmatrix}\cdot\begin{pmatrix}\mathbf{F}\\ \mathbf{T}\end{pmatrix} + k_B T\begin{pmatrix}\overleftrightarrow{A}^{tt} & \mathbf{0}\\ \mathbf{0} & \overleftrightarrow{A}^{rr}\end{pmatrix}\cdot\begin{pmatrix}\frac{1}{m}\nabla\rho\\ \frac{1}{I}(L_{\mathbf{u}}-\widehat{R})\rho\end{pmatrix}\\
&\quad + k_B T\rho\left(\frac{1}{m}\nabla,\frac{1}{I}(L_{\mathbf{u}}-\widehat{R})\right)\cdot\begin{pmatrix}\overleftrightarrow{A}^{tt} & \mathbf{0}\\ \mathbf{0} & \overleftrightarrow{A}^{rr}\end{pmatrix}.
\end{aligned} \tag{D15}$$

APPENDIX E

Here we demonstrate the SE for the density $\rho(\theta,\Omega,t)$ of Martensyuk *et al.* [57]. The system is a diluted ferromagnetic ideal gas made of identical spherical particles of diameter σ and magnetic moment $\overrightarrow{\mu}$ under a constant external magnetic field H independent of time, and there is no flow field $\mathbf{v}^0 = \mathbf{0}$. Martsenyuk *et al.* determined the SE governing the purely rotational relaxation of the particles without taking into account their translational motion in order to explain the kinetic magnetization of the particles. Since there are no particle interactions $\mathbf{T}^d = \mathbf{0}$, $\overleftrightarrow{B}^{rr}_{\mathrm{dp}} = \mathbf{0}$, at low colloid density the effective inverse rotational friction $(\overleftrightarrow{B}^{rr})^{-1} = (\beta_0^r)^{-1}\mathbf{1}$ and $\widetilde{\mu}^{tt} = \mathbf{1}'$. Thus, $\overleftrightarrow{\mu}^{rr} = (\beta_0^r)^{-1}\mathbf{1}'$, therefore, we have the product $\overleftrightarrow{B}^{rr}_{\mathrm{dp}} \cdot \overleftrightarrow{B}^{rr} = \mathbf{0}$. From (40) the rotational diffusion coefficient reduces to $\overleftrightarrow{D}^{rr} = D_0^r\widetilde{\mu}^{rr}\mathbf{1}' = (\beta_0^r)^{-1}\frac{k_B T}{I}\mathbf{1}' = \frac{1}{\beta I\beta_0^r}\mathbf{1}' = \frac{1}{\beta 8\pi\eta\sigma^3}\mathbf{1}' = \frac{1}{2\tau_B}\mathbf{1}'$, whereas from the definition of $\overleftrightarrow{A}^{rr} = \mathbf{1}'$ at low densities, $\nabla\cdot\overleftrightarrow{A}^{rr} = \mathbf{0}$, and then the torque $\mathbf{t} = \mathbf{0}$. The external torque due to vortex flow $\mathbf{T} = \frac{\partial\omega^0}{\partial t} = \mathbf{0}$. The external field is $V_{\mathrm{ext}} = -\overrightarrow{\mu}\,\widehat{\mathbf{e}}\mathbf{H}$, with $\widehat{\mathbf{e}} = \overrightarrow{\mu}/|\overrightarrow{\mu}|$ [57]. Thus, $-\beta L_{\mathbf{u}}V_{\mathrm{ext}} = \beta\overrightarrow{\mu}\,\widehat{\mathbf{e}}\times\mathbf{H}\delta(\mathbf{r}) := \overrightarrow{\xi}\,\delta(\mathbf{r})$. Substituting into the diffusion Eq. (41) yields

$$\frac{\partial\rho(\theta,\phi,t)}{\partial t} = \frac{1}{2\tau_B}\left[L_{\mathbf{u}}^2\rho + L_{\mathbf{u}}\cdot(\rho\overrightarrow{\xi})\right]. \tag{E1}$$

As in Martsenyuk *et al.* [57], using the projection of $\overrightarrow{\xi}$ along the unitary angle $\widehat{\theta}$, that is, $\rho\overrightarrow{\xi}\cdot\widehat{\theta} = \xi\sin\theta\rho$, $\xi = |\overrightarrow{\xi}|$, and the spherical coordinates representation of the Laplacian and divergence angular operators $L_{\mathbf{u}}^2, L_{\mathbf{u}}$ yields

$$\begin{aligned}
&\frac{\partial\rho(\theta,\phi,t)}{\partial t}\\
&= \frac{1}{2\tau_B\sin\theta}\left\{\frac{\partial}{\partial\theta}\left[\sin\theta\left(\frac{\partial\rho}{\partial\theta} + \rho\xi\sin\theta\right)\right] + \frac{1}{\sin\theta}\frac{\partial^2\rho}{\partial\phi^2}\right\},
\end{aligned} \tag{E2}$$

which is the main kinetic equation in Martsenyuk *et al.* [57].

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