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# Brownian motion of interacting nonspherical tracer particles: General theory

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A general theoretical framework is developed to describe the tracer-diffusion properties of nonspherical Brownian tracer particles that interact with the other particles in a multicomponent colloidal suspension of generally nonspherical particles, in the absence of hydrodynamic interactions. Here we present the derivation of the generalized Langevin equation (GLE) for the linear and angular velocity describing the Brownian motion of the tracer particle. In addition to the dissipative plus the random force and torque exerted by the solvent, this GLE contains the dissipative plus random force and torque due to the direct interactions with the other particles. An exact and general expression is derived for the time-dependent friction tensor that embodies the effects of the latter. Using a generalized Wertheim-Lovett's relation, this expression is cast in two alternative but equivalent forms. The long-time and short-time limits (in reference to the structural relaxation time $\tau_I$) are also discussed. [S1063-651X(96)06012-6]

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## I. INTRODUCTION

Tracer-diffusion experiments in colloidal suspensions record the averaged properties of the Brownian motion of individual labeled particles that do not interact among themselves, but do interact with the many other unlabeled particles of the host suspension [1]. One of the main goals of the theory of colloid dynamics is to explain the observed tracer-diffusion properties in terms of the effective interactions between colloidal particles and/or in terms of the equilibrium static structural properties of the suspension [2]. Among the various theoretical approaches [1–5] proposed to achieve this goal, the generalized Langevin equation (GLE) approach [5] has proved to be one of the most successful in terms of its applications to systems that depart from the particular case corresponding to *self*-diffusion in *monodisperse* suspensions of *spherical* colloidal particles *without* hydrodynamic interactions. Thus, this theory has been applied to rather diverse phenomena and systems such as electrolyte friction effects on charged colloidal particles [6–9], tracer diffusion in dilute but highly interacting colloidal mixtures [10,11], in hydrodynamically concentrated hard-sphere suspensions [12], in two-dimensional [13] and quasi-two-dimensional [14] suspensions, and even in model porous media [15,16]. All of these applications, however, are restricted to the *translational* Brownian motion of *spherical* tracer particles, which interact with other particles that are also assumed spherical. The only extension away from this restriction refers to the description of electrolyte friction effects on the *translational* diffusion of a nonspherical polyion [9] whose rotation, however, was ignored. Since the technical capabilities exist to observe in experimental or computer simulated systems the *rotational* dynamics of interacting nonspherical tracer particles, there is an obvious need to extend the theory of colloid dynamics in this direction. Thus, we have carried out a program [17–20] aimed at extending the GLE approach to describe the effects of the interactions of nonspherical tracer particles with the other particles of the host suspension, on the *translational* and *rotational* Brownian motion of the former, and in this paper we start the systematic presentation of our results.

In this paper we present the most general results of our work in the direction just described. Here we shall have in mind the general situation involving a non-spherical Brownian tracer particle that *translates* and *rotates* while interacting with other diffusing particles that may also be nonspherical, and may belong to more than one species. For the time being, however, we shall not consider hydrodynamic interactions. The main contribution of the present paper is the derivation of a generalized Langevin equation for the linear and angular velocity of the tracer particle. The effects of the interactions with the surrounding particles is embodied in a time-dependent friction tensor, for which an exact expression is derived in terms of the static properties and of the time-dependent correlation function of the local concentration of such particles. Without yet introducing approximations or restriction to particular cases, here we discuss and collect a number of results of a general nature, and analyze some pertinent asymptotic (short- and long-time) limits. Although this will prevent us here from presenting the results of concrete applications, the idea is to separate what is completely general and exact (although at the same time completely formal) from what is the result of approximations and restrictions to particular or generic cases or conditions. In the accompanying paper ([20], hereafter referred to as paper II), however, we illustrate how these general results can be converted into an approximate but still general theory in the context of a more restricted (although still quite relevant) generic case, namely, that in which only the tracer particle remains nonspherical, but all the other particles are assumed spherical. For this generic case concrete applications will become possible and practicable, as paper II will illustrate.

In order to explain the general program of the present extension to suspension of nonspherical Brownian particles,

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in the following section we provide a brief review of the structure of the GLE theory of tracer-diffusion phenomena as it was developed in the context of suspensions of spherical particles. We then write (Secs. III and IV) the basic equations on which we build our extension. The main results of this paper are derived and discussed in Sec. V. General results relevant to the long- and short-time regimes are discussed in Secs. VI and VII. In preparation for paper II, in Sec. VIII we summarize the main results of this paper as they apply to the generic system referred to above. Section IX summarizes our conclusions.

## II. THE GLE THEORY FOR TRACER DIFFUSION OF SPHERICAL PARTICLES

In this section we review the most salient concepts and results of the generalized Langevin equation description of the effects of the direct interactions between a *spherical* tracer Brownian particle (sometimes referred to simply as ''the tracer'') with other interacting Brownian particles (also assumed spherical) diffusing around it. The GLE theory [5] that we review here, and that we extend in this paper, only refers to the effects of these direct interactions on the translational Brownian motion of the tracer particle, which may be identical (''self-diffusion'') or different (''tracer-diffusion'') from the surrounding particles. The Brownian motion of an isolated tracer particle of mass $M$ is described by the ordinary Langevin equation,

$$M\,\frac{d\mathbf{V}(t)}{dt}=-\zeta^0\mathbf{V}(t)+\mathbf{f}^0(t), \tag{1}$$

for its velocity $\mathbf{V}(t)$. Here $\zeta^0$ is the hydrodynamic friction coefficient, and $\mathbf{f}^0(t)$ is a random force, modeled as a Gaussian $\delta$-correlated (white) noise, with zero mean and time-dependent correlation function given by the fluctuation-dissipation relation $\langle\mathbf{f}^0(t)\mathbf{f}^{0\dagger}(0)\rangle=k_BT\zeta^0 2\,\delta(t)\mathbf{1}$, where $\mathbf{1}$ is the $3\times3$ identity diad and $k_B$, $T$, and $\delta(t)$ are Boltzmann's constant, the temperature, and Dirac's $\delta$ function. From these assumptions, all the statistical properties of the velocity $\mathbf{V}(t)$ and the displacement $\Delta\mathbf{R}(t)=\int_0^t\mathbf{V}(t')dt'$ of the particle can be determined [21]. Furthermore, the equivalence between the description of these statistical properties on the basis of Eq. (1) and that provided by the corresponding Fokker-Planck equation is also well established. Let us mention, however, that Eq. (1) assumes that the solvent reacts instantaneously, so that the hydrodynamic friction is instantaneously proprotional to $\mathbf{V}(t)$. In reality, the finite-time response of the solvent leads to memory effects, whose description requires the replacement of the term $-\zeta^0\mathbf{V}(t)$ in Eq. (1) by $-\int_0^t\zeta^0(t-t')\mathbf{V}(t')dt'$. In this case, it is not possible to write a corresponding Fokker-Planck equation, since the stochastic process $\mathbf{V}(t)$ is no longer Markovian. Nevertheless, the generalized Langevin equation that results from this replacement still allows us to write a fluctuation-dissipation relation [now reading $\langle\mathbf{f}^0(t)\mathbf{f}^{0\dagger}(0)\rangle=k_BT\zeta^0(t)\mathbf{1}$], and to express the velocity autocorrelation function in terms of the time-dependent friction function $\zeta^0(t)$. In this work, however, we shall not be interested in this relaxation process, so we assume that $\zeta^0(t)$ can be approximated, as required in Eq. (1), by $\zeta^0(t)=\zeta^0 2\,\delta(t)$, with $\zeta^0$ being the stationary hydrodynamic friction coefficient. From Eq. (1) we have that $\langle\mathbf{V}(t)\cdot\mathbf{V}^\dagger(0)\rangle=(3k_BT/M)\exp(-t/\tau_B)$, with $\tau_B=M/\zeta^0$. This defines the ''Brownian'' relaxation time $\tau_{\mathrm{B}}$. Eq. (1) describes the relaxation of both the velocity and the displacement of the particle [29]. In this paper we shall only be concerned with the so-called diffusive regime, $t\gg\tau_B$, i.e., that in which the velocity has relaxed by hydrodynamic friction, so that we can write $\langle\mathbf{V}(t)\cdot\mathbf{V}^\dagger(0)\rangle=(k_BT/M)\zeta^0 2\,\delta(t)$. In this regime, the mean-squared displacement, for example, is given by $\langle[\Delta\mathbf{R}(t)]^2\rangle=6D^0t$, with $D^0=k_BT/\zeta^0$.

In the presence of direct interactions between the tracer particle and the other colloidal particles in the suspension (but ignoring hydrodynamic interactions), Eq. (1) is modified by the addition of the total direct force $\mathbf{F}_{\mathrm{tot}}(t)$ that the other particles exert on the tracer. The GLE theory starts by noticing that $\mathbf{F}_{\mathrm{tot}}(t)$ can be written exactly as a linear function of the departure $\delta n(\mathbf{r},t)$ of the instantaneous local concentration profile $n(\mathbf{r},t)$ of the other particles around the tracer, from its radial equilibrium average $n^{\mathrm{eq}}(r)$, so that Eq. (1) now reads

$$M\,\frac{d\mathbf{V}(t)}{dt}=-\zeta^0\mathbf{V}(t)+\mathbf{f}^0(t)+\int d^3r[\nabla\psi(r)]\delta n(\mathbf{r},t), \tag{2}$$

with $\psi(r)$ being the pair potential between one of the surrounding particles located at position $\mathbf{r}$ and the tracer particle located at the origin, and where

$$\delta n(\mathbf{r},t)\equiv n(\mathbf{r},t)-n^{\mathrm{eq}}(r). \tag{3}$$

Thus, $\mathbf{V}(t)$ couples dynamically only with the collective variable $\delta n(\mathbf{r},t)$, for which a time-evolution equation must then be written. Such an equation, together with Eq. (2), constitutes a pair of coupled stochastic equations for $\mathbf{V}(t)$ and $\delta n(\mathbf{r},t)$, whose contraction [i.e., the elimination of $\delta n(\mathbf{r},t)$] leads to the main result of GLE theory, namely, the generalized Langevin equation for the tracer particle, which reads

$$\mathrm{M}\frac{d\mathbf{V}(t)}{dt}=-\zeta^0\mathbf{V}(t)+\mathbf{f}^0(t)+\int_0^t dt'\,\Delta\zeta(t-t')\mathbf{V}(t')+\mathbf{F}(t). \tag{4}$$

In this equation, $\mathbf{F}(t)$ is a fluctuating force deriving from the spontaneous departures from zero of the net direct force exerted by the other particles on the tracer. It has zero mean, but it is non-Markovian, and satisfies the fluctuation-dissipation relation $\langle\mathbf{F}(t)\mathbf{F}^\dagger(0)\rangle=k_BT\Delta\zeta(t)\mathbf{1}$. The memory function $\Delta\zeta(t)$ contains the dissipative friction effects derived from the direct interactions of the tracer with the particles around it. Its relaxation time is determined by the structural relaxation of the cage formed by the surrounding particles, and is characterized by the time $\tau_I$ within which the particles diffuse a mean distance between them. In general, $\tau_I\gg\tau_B$. Thus, in the diffusive regime ($t\gg\tau_B$) there is a time-scale separation in reference to $\tau_I$. ''Long times'' means $t \gg \tau_I$, while ''short times'' means $t \ll \tau_I$ (but still in the diffusive regime, i.e., such that $t \gg \tau_B$). At short times, the effects of the interactions involved in $\Delta\zeta(t)$ are still not perceptible, and the movement of the tracer is essentially free diffusion. On the other hand, at asymptotically long times, the function $\Delta\zeta(t)$ can be approximated by a Dirac $\delta$ function (Markovian limit) times the time integral of $2\Delta\zeta(t)$, that is, Eq. (4) can be rewritten just as Eq. (1), but with $\zeta^0$ replaced by the total friction coefficient $\zeta$ given by $\zeta = \zeta^0 + \Delta\zeta$, with $\Delta\zeta$ given by $\Delta\zeta \equiv \int_0^\infty \Delta\zeta(t)dt$. Thus, the long-time diffusion coefficient $D^L$ is given by the Einstein relation $D^L = k_B T/(\zeta^0 + \Delta\zeta)$. The determination of $\Delta\zeta$, or its dynamical extension $\Delta\zeta(t)$, is precisely one of the main purposes of the theories of Brownian motion of interacting colloidal particles.

This being a typical many-body problem, such theories cannot be but approximate. First, however, the GLE theory [5] leads to the following exact and general expression for $\Delta\zeta(t)$:

$$\Delta\zeta(t) = \frac{\beta}{3}\,\mathrm{Tr}\left[\int d^3r \int d^3r' [\boldsymbol{\nabla}\psi(r)] \times \langle \delta n(\mathbf{r},t)\,\delta n(\mathbf{r}',0)\rangle [\boldsymbol{\nabla}'\psi(r')]\right]. \tag{5}$$

The van Hove function, $\langle \delta n(\mathbf{r},t)\,\delta n(\mathbf{r}',0)\rangle$, is the time-dependent correlation function of the fluctuations of the local concentration of the surrounding particles. In this function all the information about the relaxation by diffusive processes of the cloud of particles around the tracer resides, and it is here where important approximations must be made, before the exact and general result of Eq. (5) may be useful in practice. There exists a variety of approximations that lead to a diversity of approximate expressions for $\Delta\zeta(t)$. For the purpose of illustration, we quote here one of the simplest approximate expressions [12] derived in this way for self-diffusion, namely,

$$\Delta\zeta(t) = \frac{k_B T n}{8\pi^3}\int d^3k \frac{[k_z h(k)]^2}{1+nh(k)} \exp\left[\frac{-2k^2 D^0 t}{1+nh(k)}\right], \tag{6}$$

where $h(k)$ is the Fourier transform (FT) of the total correlation function [22] $h(r) = g(r) - 1$ with $g(r) = n^{\mathrm{eq}}(r)/n$, $n$ being the bulk concentration of the suspension. Approximate expressions such as this are general, in the sense that we have not yet specified the pair interaction potential $u(r)$. Its application to specific systems may involve, however, additional approximations, which are not of a dynamic nature, but which refer to the precise calculation of $h(r)$, given $\psi(r)$. References [5]–[16] illustrate the application of these general results to a variety of specific systems and conditions.

## III. LANGEVIN EQUATION FOR AN INTERACTING NONSPHERICAL TRACER

The general system we have in mind consists of a volume $V$, containing the solvent in which a labeled tracer particle, plus $N$ other colloidal particles of the same species (all of them in general nonspherical) are suspended. The case of several species will be considered at the end of Sec. V, since it is only a matter of careful and adequate notation.

Let $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$ be the linear and angular velocity of the tracer particle defined with respect to the laboratory. The vectors $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$ can be written in terms of their components (projections) along the axis of a given reference system whose origin and orientation are fixed with respect to the laboratory. Such a description of $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$ is, however, not the most convenient for our purposes. Let us consider instead the projections of $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$ along a coordinate system whose origin is certainly fixed to the laboratory, but whose orientation changes with time, and in fact, follows instantaneously the orientation of the main symmetry axis of the tracer particle. Within this description, the extension of Eq. (1) above to an isolated nonspherical Brownian particle reads [23]

$$M\,\frac{d\mathbf{V}(t)}{dt} + \boldsymbol{\omega}(t)\times M\mathbf{V}(t) = -\overleftrightarrow{\zeta}^{0}\cdot\mathbf{V}(t) - \overleftrightarrow{\zeta}^{0}_{\mathrm{TR}}\cdot\boldsymbol{\omega}(t) + \mathbf{f}^0(t), \tag{7}$$

$$\mathbf{I}\cdot\frac{d\boldsymbol{\omega}(t)}{dt} + \boldsymbol{\omega}(t)\times[\mathbf{I}\cdot\boldsymbol{\omega}(t)] = -\overleftrightarrow{\zeta}^{0}_{\mathrm{RT}}\cdot\mathbf{V}(t) - \overleftrightarrow{\zeta}^{0}_{R}\cdot\boldsymbol{\omega}(t) + \mathbf{t}^0(t). \tag{8}$$

These are just the equations of motion of a rigid body in the reference system just decribed, in which the tensor of inertia $\mathbf{I}$ is diagonal [24]. Thus, Eq. (8) is the well-known Euler-Langevin equation for a rigid body. The kinematic terms on the left-hand side also derive from the particular choice of this reference system. However, they are quadratic in $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$, and, hence, must be neglected in building up a linear theory [25,26] for the fluctuations of these quantities around their vanishing equilibrium value. The right-hand side of these equations thus expresses the total force and total torque on the tracer particle. In the linear regime the friction force and torque must in general be linear in all the components of $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$. The proportionality constants are grouped in the translational-translational (TT), translational-rotational ($TR$), $RT$, and $RR$ $3\times3$ friction tensors $\overleftrightarrow{\zeta}^{0}_{TT}(\equiv\overleftrightarrow{\zeta}^{0})$, $\overleftrightarrow{\zeta}^{0}_{TR}$, $\overleftrightarrow{\zeta}^{0}_{RT}$, $\overleftrightarrow{\zeta}^{0}_{RR}(\equiv\overleftrightarrow{\zeta}^{0}_{R})$, respectively. Finally, $\mathbf{f}^0(t)$ and $\mathbf{t}^0(t)$ are the corresponding random force and torque, respectively, assumed Gaussian, and $\delta$ correlated, with zero mean, and time-correlation function given by the following fluctuation-dissipation relation:

$$\begin{pmatrix} \langle \mathbf{f}^0(t)\mathbf{f}^{0\dagger}(0)\rangle & \langle \mathbf{f}^0(t)\mathbf{t}^{0\dagger}(0)\rangle \\ \langle \mathbf{t}^0(t)\mathbf{f}^{0\dagger}(0)\rangle & \langle \mathbf{t}^0(t)\mathbf{t}^{0\dagger}(0)\rangle \end{pmatrix} = k_B T \begin{pmatrix} \overleftrightarrow{\zeta}^{0} & \overleftrightarrow{\zeta}^{0}_{TR} \\ \overleftrightarrow{\zeta}^{0}_{RT} & \overleftrightarrow{\zeta}^{0}_{R} \end{pmatrix} 2\,\delta(t). \tag{9}$$

Strictly speaking, these relations cannot be satisfied by Eqs. (7) and (8). This is so because these are nonlinear equations, due to the terms $\boldsymbol{\omega}(t)\times\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)\times[\mathbf{I}\cdot\boldsymbol{\omega}(t)]$. However, as indicated before, the linearization of the transport equations describing spontaneous fluctuations of the dynamic variables around their equilibrium values is a key aspect in the general theory of equilibrium time-dependent fluctuations [25,26]. The assumptions above concerning $\mathbf{f}^0(t)$ and $\mathbf{t}^0(t)$ are enough to characterize completely the stochastic process $[\mathbf{V}(t),\boldsymbol{\omega}(t)]$, which then turns out to be stationary, Gaussian, Markovian, of zero mean and time-dependent correlation function given by

$$\langle \overset{\Rightarrow}{\mathbf{V}}(t)\overset{\Rightarrow}{\mathbf{V}}^{\dagger}(0)\rangle=[\exp(-\overset{\Leftrightarrow}{M}^{-1}\cdot\overset{\Leftrightarrow}{\zeta}^{0}t)]\cdot\overset{\Leftrightarrow}{M}^{-1}k_BT, \tag{10}$$

where we have introduced a compact notation in terms of the six-component vectors

$$\overset{\Rightarrow}{\mathbf{V}}(t)=\begin{pmatrix}\mathbf{V}(t)\\ \boldsymbol{\omega}(t)\end{pmatrix},\quad \overset{\Rightarrow}{\mathbf{f}}^{0}(t)=\begin{pmatrix}\mathbf{f}^{0}(t)\\ \mathbf{t}^{0}(t)\end{pmatrix}, \tag{11}$$

and of the 6×6 matrices

$$\overset{\Leftrightarrow}{M}=\begin{pmatrix}\mathrm{M}\mathbf{1} & \mathbf{0}\\ \mathbf{0}^{\dagger} & \mathbf{I}\end{pmatrix},\quad \overset{\Leftrightarrow}{\zeta}^{0}=\begin{pmatrix}\overset{\leftrightarrow}{\zeta}^{0} & \overset{\leftrightarrow}{\zeta}^{0}_{TR}\\ \overset{\leftrightarrow}{\zeta}^{0}_{RT} & \overset{\leftrightarrow}{\zeta}^{0}_{R}\end{pmatrix} \tag{12}$$

(i.e., $\overset{\Leftrightarrow}{M}_{ij}=M_i\delta_{ij}$, with $M_i=M$ for $i=1,2,3$, and $M_i=I_i$ for $i=4,5,6$, with $I_1$, $I_2$, $I_3$ being the principal moments of inertia) and

$$\langle \overset{\Rightarrow}{\mathbf{V}}(t)\overset{\Rightarrow}{\mathbf{V}}^{\dagger}(0)\rangle=\begin{pmatrix}\langle\mathbf{V}(t)\mathbf{V}^{\dagger}(0)\rangle & \langle\mathbf{V}(t)\boldsymbol{\omega}^{\dagger}(0)\rangle\\ \langle\boldsymbol{\omega}(t)\mathbf{V}^{\dagger}(0)\rangle & \langle\boldsymbol{\omega}(t)\boldsymbol{\omega}^{\dagger}(0)\rangle\end{pmatrix}. \tag{13}$$

We now may use this compact notation to rewrite Eqs. (7)–(9) (which describe the Brownian motion of a freely diffusing nonspherical tracer particle) but now including the direct interactions of this tracer particle with other Brownian particles diffusing around it. In the absence of hydrodynamic interactions, the Brownian motion of the tracer particle is still described by Eqs. (7) and (8) to which we add, respectively, the instantaneous total direct force $\mathbf{F}_{\mathrm{tot}}(t)$ and total direct torque $\mathbf{T}_{\mathrm{tot}}(t)$ that those other particles exert on the tracer. Grouping together $\mathbf{F}_{\mathrm{tot}}(t)$ and $\mathbf{T}_{\mathrm{tot}}(t)$ in the six-component vector

$$\overset{\Rightarrow}{\mathbf{F}}_{\mathrm{tot}}(t)=\begin{pmatrix}\mathbf{F}_{\mathrm{tot}}(t)\\ \mathbf{T}_{\mathrm{tot}}(t)\end{pmatrix}, \tag{14}$$

Eqs. (7)–(9) will now read, in our compact notation, as

$$\overset{\Leftrightarrow}{M}\cdot\frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt}=-\overset{\Leftrightarrow}{\zeta}^{0}\cdot\overset{\Rightarrow}{\mathbf{V}}(t)+\overset{\Rightarrow}{\mathbf{f}}^{0}(t)+\overset{\Rightarrow}{\mathbf{F}}_{\mathrm{tot}}(t) \tag{15}$$

and

$$\langle\overset{\Rightarrow}{\mathbf{f}}^{0}(t)\overset{\Rightarrow}{\mathbf{f}}^{0\dagger}(0)\rangle=k_BT\overset{\Leftrightarrow}{\zeta}^{0}2\,\delta(t). \tag{16}$$

It is worth emphasizing that, within the condition of the absence of hydrodynamic interactions, there exists no additional approximation in writing Eqs. (15) and (16) for an interacting tracer. Let us also mention that, within the context of the theory developed here, the hydrodynamic friction coefficients $\overset{\Leftrightarrow}{\zeta}^{0}$ are considered phenomenological coefficients, assumed to be given, and in terms of which, among other things, we will have to express the final effects of the direct interactions represented in Eq. (15) by the ''force'' $\overset{\Rightarrow}{\mathbf{F}}_{\mathrm{tot}}(t)$ that the other particles exert on the tracer.

Let us now write $\overset{\Rightarrow}{\mathbf{F}}_{\mathrm{tot}}(t)$ in terms of the collective dynamical variable that represents the local concentration of particles. We assume that the total energy $U$ of the direct interaction between the $N+1$ particles of the system is pairwise additive. Therefore, the forces and torques are also pairwise additive. Thus,

$$\mathbf{F}_{\mathrm{tot}}(t)=\sum_{i=1}^{N}\mathbf{F}_i^{(T)}, \tag{17}$$

that is, the total force on the tracer is the sum of the forces $\mathbf{F}_i^{(\mathrm{T})}$ that the $i$th particle $(i=1,\ldots,N)$ exert on the tracer (denoted by the index ''$T$''). It can be shown (third law of Newton) that $\mathbf{F}_i^{(T)}=-\mathbf{F}_T^{(i)}$ where $\mathbf{F}_T^{(i)}$ is the total force on the $i$th particle due to its interaction with the tracer particle. Thus, the total direct force on the tracer particle can be written as

$$\mathbf{F}_{\mathrm{tot}}(t)=-\sum_{i=1}^{N}\mathbf{F}_T^{(i)}. \tag{18}$$

In the same way, it can be shown that the total torque on the tracer due to its direct interactions with the $N$ particles, can be written as

$$\mathbf{T}_{\mathrm{tot}}(t)=-\sum_{i=1}^{N}\mathbf{T}_T^{(i)}, \tag{19}$$

where $\mathbf{T}_T^{(i)}$ is the total (orbital plus intrinsic) torque on particle $i$ due to its direct interaction with the tracer particle.

Let us now express $\mathbf{F}_T^{(i)}$ and $\mathbf{T}_T^{(i)}$ in terms of the pair interaction energy between the tracer particle and the $i$th particle. For this purpose, we express this pair interaction in terms of positions and orientations of all the particles referred to a reference system fixed to the tracer particle. Thus, the location of particle $i$ will be denoted by the position vector $\mathbf{r}^{(i)}$, whose origin is fixed at the tracer's center of mass (c.m.), and the orientation of the same particle will be determined by a set of three angular variables $(\Omega_1^{(i)},\Omega_2^{(i)},\Omega_3^{(i)})\equiv\overline{\Omega}^{(i)}$ describing the orientation of the principal axis of that particle relative to the principal axis of the tracer particle. The variables $\Omega_1$, $\Omega_2$, and $\Omega_3$ may be the Euler angles of the corresponding rotation, or any other equivalent description. Obviously, the tracer's position and orientation in this coordinate system remain constant [we assume, in fact, $\mathbf{r}^{(T)}=\mathbf{0}$, and $\overline{\Omega}^{(T)}=(0,0,0)$]. Thus, the pair interaction energy of the tracer particle with another particle located at $\mathbf{r}$, and with orientation $\Omega$, will only depend on $\mathbf{r}$

and $\overline{\Omega}$, and will be denoted by $\psi_T(\mathbf{r},\overline{\Omega})$. Thus, we now can express $\mathbf{F}_T^{(i)}$ and $\mathbf{T}_T^{(i)}$ in terms of the linear and angular gradients of $\psi_T(\mathbf{r}^{(i)},\overline{\Omega}^{(i)})$ in the following manner:

$$\mathbf{F}_T^{(i)} = -\left(\frac{\partial \psi_T(\mathbf{r}^{(i)},\overline{\Omega}^{(i)})}{\partial \mathbf{r}^{(i)}}\right) \equiv -\boldsymbol{\nabla}^{(i)}\psi_T(\mathbf{r}^{(i)},\overline{\Omega}^{(i)}) \qquad (20)$$

and

$$\mathbf{T}_T^{(i)} = \mathbf{r}^{(i)}\times\mathbf{F}_T^{(i)} + \mathbf{T}^{(i)}, \qquad (21)$$

where $\mathbf{r}^{(i)}\times\mathbf{F}_T^{(i)}$ is the orbital torque on particle $i$ due to the force $\mathbf{F}_T^{(i)}$ on its center of mass, capable of producing a translation around the tracer's CM. The intrinsic torque $\mathbf{T}^{(i)}$ can be denoted as

$$\mathbf{T}^{(i)} = -\left(\frac{\partial \psi_{\mathrm{T}}(\mathbf{r}^{(i)},\overline{\Omega}^{(i)})}{\partial \vec{\phi}}\right), \qquad (22)$$

which means that if particle $i$ rotates with an infinitesimal angular displacement $d\vec{\phi}$ of magnitude $d\phi$ in the direction $\hat{\mathbf{n}}$, then, the change in the energy of its interaction with the tracer is

$$d\psi_T = -\left(\frac{\partial \psi_T}{\partial \vec{\phi}}\right)\cdot d\vec{\phi}, \qquad (23)$$

where $(\partial\psi_T/\partial\vec{\phi})$ is merely a symbol [24]. Here we only quote, for example, that for axially symmetric particles, whose orientation can be defined by the components $\Omega_i = u_i$ $(i=1,2,3)$ of the unitary vector along its axis, the angular gradient $[\partial\psi_T(\mathbf{r},\overline{\Omega})/\partial\vec{\phi}]$ now reads $[\partial\psi_T(\mathbf{r},\hat{\mathbf{u}})/\partial\vec{\phi}] = \hat{\mathbf{u}}\times\partial\psi_T(\mathbf{r},\hat{\mathbf{u}})/\partial\hat{\mathbf{u}}$. Going back to Eq. (18), and using Eq. (20), the total direct force on the tracer can be rewritten as

$$\mathbf{F}_{\mathrm{tot}} = \sum_{i=1}^{N}\left(\frac{\partial \psi_{\mathrm{T}}(\mathbf{r}^{(i)},\overline{\Omega}^{(i)})}{\partial \mathbf{r}^{(i)}}\right) = \int d^3r \int d\overline{\Omega}[\boldsymbol{\nabla}\psi_T(\mathbf{r},\overline{\Omega})]n(\mathbf{r},\overline{\Omega};t), \qquad (24)$$

with

$$n(\mathbf{r},\overline{\Omega};t) \equiv \sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}^{(i)}(t))\,\delta(\overline{\Omega}-\overline{\Omega}^{(i)}(t)), \qquad (25)$$

being the instantaneous local concentration of particles at position $\mathbf{r}$ and orientation $\Omega$, respectively referred to the c.m., and to the orientation of the principal axis, of the tracer. In a similar fashion, we can rewrite the total torque $\mathbf{T}_{\mathrm{tot}}(t)$ in Eq. (19), using Eqs. (21), (22), and (25), as

$$\mathbf{T}_{\mathrm{tot}}(t) = \int d^3r \int d\overline{\Omega}\left[\mathbf{r}\times\boldsymbol{\nabla}\psi_T(\mathbf{r},\overline{\Omega}) + \frac{\partial\psi_T(\mathbf{r},\overline{\Omega})}{\partial\vec{\phi}}\right]\cdot n(\mathbf{r},\overline{\Omega};t). \qquad (26)$$

We now come back to Eq. (15), and write it, in the compact notation introduced before, as

$$\overset{\Leftrightarrow}{M}\cdot\frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt} = -\overset{\Leftrightarrow}{\zeta^0}\cdot\overset{\Rightarrow}{\mathbf{V}}(t) + \overset{\Rightarrow}{\mathbf{f}^0}(t) + \int d^3r\int d\overline{\Omega}[\overset{\Rightarrow}{\boldsymbol{\nabla}}\psi_T(\mathbf{r},\overline{\Omega})]n(\mathbf{r},\overline{\Omega};t), \qquad (27)$$

with

$$\overset{\Rightarrow}{\boldsymbol{\nabla}} = \begin{pmatrix}\boldsymbol{\nabla}\\ \boldsymbol{\nabla}_{\mathrm{rot}}\end{pmatrix} \qquad (28)$$

and

$$\boldsymbol{\nabla}_{\mathrm{rot}} \equiv \mathbf{r}\times\boldsymbol{\nabla} + \frac{\partial}{\partial\vec{\phi}}. \qquad (29)$$

Equation (27) tells us that the equation of motion of the tracer couples, in fact, with the positions and orientations of the other particles surrounding it, but solely through the collective variable $n(\mathbf{r},\overline{\Omega};t)$ defined in Eq. (25). This is an enormous simplification in our further development since we do not need to be concerned about the details of the position and motion of each and all individual particles. Instead, we will find that only the essential features of the time-evolution equation for $n(\mathbf{r},\overline{\Omega};t)$ turn out to be important in determining the most relevant features of the effective equation of motion of the tracer particle, [i.e., the generalized Langevin equation for $\overset{\Rightarrow}{\mathbf{V}}(t)$, that we are aimed at deriving].

The dynamical variable $n(\mathbf{r},\overline{\Omega};t)$ depends on the instantaneous configuration $\mathbf{r}^{(i)}(t)$, $\overline{\Omega}^{(i)}(t)$ $(i=1,2,\ldots,N)$ of the $N$ particles around the tracer. Its equilibrium ensemble average, denoted as $n^{\mathrm{eq}}(\mathbf{r},\overline{\Omega}) \equiv \langle n(\mathbf{r},\overline{\Omega};t)\rangle$, is, however, independent of time, and has the following important property. Taking an ensemble average of Eq. (27), we conclude that

$$\int d^3r\int d\overline{\Omega}[\overset{\Rightarrow}{\boldsymbol{\nabla}}\psi_T(\mathbf{r},\overline{\Omega})]n^{\mathrm{eq}}(\mathbf{r},\overline{\Omega}) = 0, \qquad (30)$$

where use has been made of the fact $\langle\overset{\Rightarrow}{\mathbf{V}}(t)\rangle = \langle\overset{\Rightarrow}{\mathbf{f}^0}(t)\rangle = \mathbf{0}$. Therefore, Eq. (27) can be rewritten as

$$\overset{\Leftrightarrow}{M} \cdot \frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt} = -\overset{\Leftrightarrow}{\zeta}{}^{0} \cdot \overset{\Rightarrow}{\mathbf{V}}(t) + \overset{\Rightarrow}{\mathbf{f}}{}^{0}(t) + \int d^3r \int d\overline{\Omega}[\overset{\Rightarrow}{\boldsymbol{\nabla}} \psi_T(\mathbf{r},\overline{\Omega})]\delta n(\mathbf{r},\overline{\Omega};t), \tag{31}$$

that is, in terms of the fluctuations $\delta n(\mathbf{r},\overline{\Omega};t)$ of the local concentration around its equilibrium value,

$$\delta n(\mathbf{r},\overline{\Omega};t) \equiv n(\mathbf{r},\overline{\Omega};t) - n^{\mathrm{eq}}(\mathbf{r},\overline{\Omega}). \tag{32}$$

The next step is to write up the time-evolution equation for this collective variable.

## IV. TIME EVOLUTION EQUATION FOR THE LOCAL CONCENTRATION

The time rate of change of $n(\mathbf{r},\overline{\Omega};t)$ is due to two fundamentally different mechanisms. The first is purely kinematic, and is due to the fact that the position $\mathbf{r}$ and orientation $\Omega$ in $n(\mathbf{r},\Omega;t)$ are referred to the reference system attached to the tracer particle. The tracer moves instantaneously with linear velocity $\mathbf{V}(t)$, and rotates with angular velocity $\boldsymbol{\omega}(t)$. Thus, even if the other particles are kept fixed (with respect to the laboratory), $n(\mathbf{r},\Omega;t)$ will change, due to the movement of the tracer. To quantify this effect, imagine a displacement $\Delta\mathbf{R}$ of the tracer's c.m., taking place without changing orientation in a time $\Delta t$, such that $\Delta\mathbf{R} = \mathbf{V}(t)\Delta t$. If the concentration profile at time $t$ is $n(\mathbf{r},\Omega;t)$ at time $t+\Delta t$ the profile should be the same as at time $t$, but with $\mathbf{r}$ displaced by $\Delta\mathbf{R}$, that is

$$n(\mathbf{r},\overline{\Omega};t+\Delta t) = n(\mathbf{r}+\Delta\mathbf{R},\overline{\Omega};t). \tag{33}$$

Hence, we can calculate the change of $\Delta n(\mathbf{r},\overline{\Omega};t)$ originated by the displacement $\Delta\mathbf{R}$, as

$$\begin{aligned}\Delta n(\mathbf{r},\overline{\Omega};t) &\equiv n(\mathbf{r},\overline{\Omega};t+\Delta t) - n(\mathbf{r},\overline{\Omega};t)\\ &= n(\mathbf{r}+\Delta\mathbf{R},\overline{\Omega};t) - n(\mathbf{r},\overline{\Omega};t)\\ &= [n(\mathbf{r},\overline{\Omega};t)]\cdot\Delta\mathbf{R} + O(\Delta\mathbf{R})^2\\ &= [\boldsymbol{\nabla} n(\mathbf{r},\overline{\Omega};t)]\cdot\mathbf{V}(t)\Delta t + O(\Delta t)^2.\end{aligned} \tag{34}$$

Therefore, the rate of change of $n(\mathbf{r},\overline{\Omega},t)$ due to this infinitesimal displacement, is given by

$$\frac{\partial n(\mathbf{r},\overline{\Omega};t)}{\partial t} = [\boldsymbol{\nabla} n(\mathbf{r},\overline{\Omega};t)]\cdot\mathbf{V}(t). \tag{35}$$

Similarly, if the tracer rotates by an angular displacement $\Delta\vec{\phi} = \boldsymbol{\omega}(t)\Delta t$ (without a displacement of its c.m.), we find that the concentration profile at time $t+\Delta t$ is the same as at time $t$, but with $\mathbf{r}$ displaced by $\Delta\mathbf{r} = -\mathbf{r}\times\Delta\vec{\phi}$ and $\overline{\Omega}$ displaced by $\Delta\overline{\Omega} = (\partial\overline{\Omega}/\partial\vec{\phi})\cdot\Delta\vec{\phi}$. Thus,

$$n(\mathbf{r},\overline{\Omega};t+\Delta t) = n(\mathbf{r}+\Delta\mathbf{r},\overline{\Omega}+\Delta\overline{\Omega};t). \tag{36}$$

Hence,

$$\begin{aligned}\Delta n(\mathbf{r},\Omega;t) &\equiv n(\mathbf{r},\overline{\Omega};t+\Delta t) - n(\mathbf{r},\overline{\Omega};t)\\ &= n(\mathbf{r}+\Delta\mathbf{r},\overline{\Omega}+\Delta\overline{\Omega};t) - n(\mathbf{r},\overline{\Omega};t)\\ &= [\boldsymbol{\nabla} n(\mathbf{r},\overline{\Omega};t)]\cdot\Delta\mathbf{r} + \left(\frac{\partial n}{\partial\Omega}\right)\cdot\Delta\overline{\Omega} + O(\Delta t)^2\\ &= -[\boldsymbol{\nabla} n(\mathbf{r},\overline{\Omega};t)]\cdot(\mathbf{r}\times\Delta\vec{\phi})\\ &\quad + \left(\frac{\partial n}{\partial\Omega}\right)\cdot\left(\frac{\partial\overline{\Omega}}{\partial\vec{\phi}}\right)\cdot\Delta\vec{\phi} + O(\Delta t)^2\\ &= [\mathbf{r}\times\boldsymbol{\nabla} n(\mathbf{r},\overline{\Omega};t)]\cdot\Delta\vec{\phi}\\ &\quad + \left(\frac{\partial n(\mathbf{r},\overline{\Omega};t)}{\partial\vec{\phi}}\right)\cdot\Delta\vec{\phi} + O(\Delta t)^2.\end{aligned} \tag{37}$$

Thus, we can write the rate of change of $n(\mathbf{r},\overline{\Omega};t)$, due to this infinitesimal angular displacement, as

$$\frac{\partial n(\mathbf{r},\overline{\Omega};t)}{\partial t} = \left[\left(\mathbf{r}\times\boldsymbol{\nabla} + \frac{\partial}{\partial\vec{\phi}}\right)n(\mathbf{r},\overline{\Omega};t)\right]\cdot\boldsymbol{\omega}(t). \tag{38}$$

Collecting the contributions in Eqs. (35) and (38), we finally arrive at

$$\frac{\partial n(\mathbf{r},\overline{\Omega};t)}{\partial t} = [\overset{\Rightarrow}{\boldsymbol{\nabla}} n(\mathbf{r},\overline{\Omega};t)]\cdot\overset{\Rightarrow}{\mathbf{V}}(t) + \left(\frac{\partial n}{\partial t}\right)_{\mathrm{diff}}, \tag{39}$$

where the term $(\partial n/\partial t)_{\mathrm{diff}}$ represents the rate of change of $n(\mathbf{r},\Omega;t)$ due to the second fundamental mechanism for the change in $n(\mathbf{r},\Omega;t)$, namely, the diffusive processes that change the local concentration according to a relaxation law that we now discuss.

The term $(\partial n/\partial t)_{\mathrm{diff}}$ in Eq. (39) refers to the change in $n(\mathbf{r},\Omega;t)$ due to the (translational and rotational) diffusion of the particles around the tracer. Clearly, if the tracer itself were not moving [i.e., if $\overset{\Rightarrow}{\mathbf{V}}(t)=0$], this would be the only mechanism for $n(\mathbf{r},\Omega;t)$ to change with time. In such a case, Eq. (39) would be just the diffusion equation describing the change in $n(\mathbf{r},\Omega;t)$ due to the translational and rotational diffusion of the surrounding particles in the presence of the static field $\psi_T(\mathbf{r},\Omega)$ produced by the immobile tracer particle. If, in addition, we were to neglect the effect of this field of force, we would still need the most general diffusion equation for $n(\mathbf{r},\Omega;t)$. This, however, is in itself one of the most basic problems that the theory of colloid dynamics faces (which involves, in fact, our tracer-diffusion phenomenon as a particular problem). Such a problem is not yet completely solved, even in the more specific case of spherical particles (no rotational diffusion). Thus, if we do not want to commit to approximations or particular cases, we have to write up the most general form of the diffusion equation for $n(\mathbf{r},\Omega;t)$, or, better, for the fluctuations $\delta n(\mathbf{r},\Omega;t)$, which is what we need in Eq. (31). In this regard, the general principles of the linear irreversible thermodynamic (LIT) theory of dynamic fluctuations [25,26] dictates the most general structure of the linearized version of Eq. (39) for $\delta n(\mathbf{r},\Omega;t)$. According to these principles, if the variables $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta n(\mathbf{r},\Omega;t)$ constitute the components of a multivariate stochastic process describing spontaneous fluctuations around the thermodynamic equilibrium state, then such a stochastic process must satisfy a generalized Langevin equation with a very rigid structure [27]. Equation (31), together with the linearized version of Eq. (39), constitutes such a generalized Langevin equation, expressing $d\overset{\Rightarrow}{\mathbf{V}}(t)/dt$ and $\partial\delta n(\mathbf{r},\Omega;t)/\partial t$ as linear combinations of both variables $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta n(\mathbf{r},\Omega;t)$. Due to time-reversal symmetry considerations, many of those linear couplings are absent [5]. In fact, the nonvanishing terms in the equation for $d\overset{\Rightarrow}{\mathbf{V}}(t)/dt$ are already exhibited by Eq. (31), and similar symmetry considerations determine the absence or presence of the various possible terms coupling $\partial\delta n(\mathbf{r},\Omega;t)/\partial t$ to the components of $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta n(\mathbf{r},\Omega;t)$. The result of this analysis finally leads us to the conclusion that the most general time-evolution equation for $\delta n(\mathbf{r},\Omega;t)$ can be written as

$$\begin{aligned}\frac{\partial\delta n(\mathbf{r},\Omega;t)}{\partial t}=&[\overset{\Rightarrow}{\boldsymbol{\nabla}}n^{\mathrm{eq}}(\mathbf{r},\Omega)]\cdot\overset{\Rightarrow}{\mathbf{V}}(t)\\&-\int_0^t dt'\int d^3r'\int d\Omega'\int d^3r''\int d\Omega'' L\\&\times(\mathbf{r},\Omega;\mathbf{r}',\Omega';t-t')\sigma^{-1}(\mathbf{r}',\Omega';\mathbf{r}'',\Omega'')\\&\times\delta n(\mathbf{r}'',\Omega'';t')+h(\mathbf{r},\Omega;t),\end{aligned}\tag{40}$$

with $\sigma^{-1}(\mathbf{r},\Omega;\mathbf{r}',\Omega')$ being the inverse function of the static correlation function

$$\sigma(\mathbf{r},\Omega,\mathbf{r}',\Omega')\equiv\langle\delta n(\mathbf{r},\Omega;0)\delta n(\mathbf{r}',\Omega';0)\rangle,\tag{41}$$

in the sense that

$$\begin{aligned}\int d^3r'\int d\Omega'\sigma(\mathbf{r},\Omega;\mathbf{r}',\Omega')\sigma^{-1}(\mathbf{r}',\Omega';\mathbf{r}'',\Omega'')\\=\delta(\mathbf{r}-\mathbf{r}''),\\\delta(\Omega-\Omega''),\end{aligned}\tag{42}$$

whereas $L(\mathbf{r},\Omega,\mathbf{r}',\Omega';t)$ is a generalized temporally, spatially, and orientationally nonlocal diffusion kernel (a generalized ``matrix'' of Onsager coefficients). $h(\mathbf{r},\Omega;t)$ is a stationary random term, originating from the random diffusion fluxes. It has zero mean, and a time-dependent correlation function given by the Onsager ``matrix'' $L(\mathbf{r},\Omega,\mathbf{r}',\Omega';t)$, according to the following fluctuation-dissipation relation:

$$\langle h(\mathbf{r},\Omega;t)h(\mathbf{r}',\Omega';t')\rangle=L(\mathbf{r},\Omega;\mathbf{r}',\Omega';t-t').\tag{43}$$

To simplify the notation, let us indicate the convolutions in the equations above as inner products between the ``vectors'' and/or ``matrices'' $\delta\underline{n}(t)$, $\underline{n}^{\mathrm{eq}}$, $\underline{h}(t)$, $\underset{\approx}{L}(t)$, $\underset{\approx}{\sigma}$, etc., whose components are $\delta n(\mathbf{r},\Omega;t)$, $n^{\mathrm{eq}}(\mathbf{r},\Omega)$, $h(\mathbf{r},\Omega;t)$, $L(\mathbf{r},\Omega;\mathbf{r}',\Omega';t)$, $\sigma(\mathbf{r},\Omega;\mathbf{r}',\Omega')$, etc., in such a way that, for example, Eqs. (40) and (43) above can be rewritten still more economically as

$$\begin{aligned}\frac{\partial\delta\underline{n}(t)}{\partial t}=&[\overset{\Rightarrow}{\boldsymbol{\nabla}}n^{\mathrm{eq}}]\cdot\overset{\Rightarrow}{\mathbf{V}}(t)-\int_0^t dt\underset{\approx}{L}(t-t')\bigcirc\underset{\approx}{\sigma}^{-1}\bigcirc\delta\underline{n}(t')\\&+\underline{h}(t),\end{aligned}\tag{44}$$

and

$$\langle\underline{h}(t)\underline{h}^{\dagger}(0)\rangle=\underset{\approx}{L}(t).\tag{45}$$

Thus, the inner product in these equations, indicated by ``$\bigcirc$,'' implies integration over the common position and orientation indices $(\mathbf{r},\Omega)$ of the corresponding vectors and/or matrices, i.e., ``$\bigcirc$''↔ ``$\int d^3r\int d\Omega$.''

Unfortunately, no more can be extracted further from the principles of the LIT theory concerning the detailed structure of the generalized diffusion kernel $\underset{\approx}{L}(t)$. Thus, it will be on this object where the most important approximations and simplifications will eventually have to be introduced. On the other hand, $n^{\mathrm{eq}}(\mathbf{r},\Omega)$ and $\sigma(\mathbf{r},\Omega;\mathbf{r}',\Omega')$ are well defined equilibrium static structural properties, amenable in principle to statistical thermodynamic determination, starting from the pair potential $\underline{\psi}_T(\mathbf{r},\Omega)$ between the tracer and one of the surrounding particles, and the pair potential $u(\mathbf{r},\Omega;\mathbf{r}',\Omega')$ between two of those particles. Here, too, one may have to resort to approximations or simplifications, but for reasons that are not as fundamental, as in the case of $\underset{\approx}{L}(t)$. As it happens, $n^{\mathrm{eq}}(\mathbf{r},\Omega)$ and $\sigma(\mathbf{r},\Omega;\mathbf{r}',\Omega')$ are in reality two- and three-particle distribution functions, respectively (one of them being the tracer particle), and their exact statistical thermodynamic determination may prove impossible in practice, even with the assistance of computer simulations. Nevertheless, we shall continue our discussion without regard to these eventual practical concerns, so as to keep our present discussion at a formally exact level.

In this respect, an interesting observation can be made, and it refers to a beautiful side product of the reasoning that led us to Eq. (44) above. Clearly, the first term on the right-hand side of that equation is just the linearization of the streaming term in Eq. (39), whose meaning and origin were discussed at the beginning of this section. Thus, this term in Eq. (44) can be written exactly, attending to purely kinematic considerations. However, in considering Eqs. (44) and (31) as a closed system of linear stochastic equations for the variable $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta n(\mathbf{r},\Omega;t)$, we find that this nondissipative term of Eq. (44) is not independent of the other nondissipative coupling term appearing in this system of equations, namely, the force term in Eq. (31) (reading $[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]\cdot\delta n(t)$ in our notation). These two terms are related to each other by a very stringent symmetry condition [5]. One can check that such a symmetry condition is satisfied if and only if the following relationship between $[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]$ and $[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{n}^{\mathrm{eq}}]$ holds:

$$[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]=-k_BT\underset{\approx}{\sigma}^{-1}\bigcirc[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{n}^{\mathrm{eq}}].\tag{46}$$

This, however, is nothing else but the generalization of an exact relationship between $\underline{n}^{eq}$ and $\underset{\approx}{\sigma}$, well established in the statistical thermodynamic theory of inhomogeneous fluids. The restricted version of this equation, referring to fluids of spherical particles, is known as the Wertheim-Lovett relation [28]. Notice that Eq. (46) can also be written, using Eq. (42), as

$$[\overset{\Rightarrow}{\nabla}\underline{n}^{eq}] = -\beta\underset{\approx}{\sigma}\bigcirc[\overset{\Rightarrow}{\nabla}\underline{\psi}_T], \tag{47}$$

with $\beta = 1/k_BT$. These two exact relations will prove useful later on.

## V. CONTRACTION OF THE DESCRIPTION

The main results of Secs. III and IV are the time-evolution equations for the stochastic variables $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta\underline{n}(t)$, namely, Eqs. (31) and (44). Together, these equations constitute a stationary process, and therefore, the stationarity condition requires that the fluctuation-dissipation relations in Eqs. (16) and (43), complemented with the condition of independence between $\overset{\Rightarrow}{\mathbf{F}}_{tot}(t)$ and $\underline{h}(t)$, i.e., $\langle\overset{\Rightarrow}{\mathbf{F}}_{tot}(t)\underline{h}^{\dagger}(0)\rangle = \mathbf{0}$, to be satisfied [27]. From these two time-evolution equations we must now eliminate $\delta\underline{n}(t)$, and this should lead us to an effective equation involving only the variable $\overset{\Rightarrow}{\mathbf{V}}(t)$, which is the GLE we wish to derive. Such a procedure constitutes what is referred to as the contraction of the description [5,27]. Formally, we solve Eq. (44) for $\delta\underline{n}(t)$, and substitute in Eq. (31). The solution of Eq. (44) can be written as

$$\delta\underline{n}(t) = \underset{\approx}{\chi}(t)\bigcirc\delta\underline{n}(0) + \int_0^t dt'\underset{\approx}{\chi}(t-t')\bigcirc[\overset{\Rightarrow}{\nabla}\underline{n}^{eq}]\cdot\overset{\Rightarrow}{\mathbf{V}}(t) + \int_0^t dt'\underset{\approx}{\chi}(t-t')\bigcirc\underline{h}(t'), \tag{48}$$

where $\underset{\approx}{\chi}(t)$ is the solution of

$$\frac{\partial\underset{\approx}{\chi}(t)}{\partial t} = -\int_0^t dt'\underset{\approx}{L}(t-t')\bigcirc\underset{\approx}{\sigma}^{-1}\bigcirc\underset{\approx}{\chi}(t'), \tag{49}$$

with initial condition

$$\underset{\approx}{\chi}(0) = \underset{\approx}{\mathbf{U}} \tag{50}$$

[where $U(\mathbf{r},\overline{\Omega},\mathbf{r}',\overline{\Omega}') = \delta(\mathbf{r}-\mathbf{r}')\delta(\overline{\Omega}-\overline{\Omega}')$]. Hence, $\underset{\approx}{\chi}(t)$ is the Green's function of the generalized diffusion equation in Eq. (44). Substituting Eq. (48) in Eq. (31), we obtain

$$\overset{\Leftrightarrow}{M}\cdot\frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt} = -\overset{\Leftrightarrow}{\zeta}^0\cdot\overset{\Rightarrow}{\mathbf{V}}(t) + \overset{\Rightarrow}{\mathbf{f}}^0(t) - \int_0^t dt'\Delta\overset{\Leftrightarrow}{\zeta}(t-t')\cdot\overset{\Rightarrow}{\mathbf{V}}(t') + \overset{\Rightarrow}{\mathbf{F}}(t), \tag{51}$$

with

$$\Delta\overset{\Leftrightarrow}{\zeta}(t) = -[\overset{\Rightarrow}{\nabla}\underline{\psi}_T]\bigcirc\underset{\approx}{\chi}(t)\bigcirc[\overset{\Rightarrow}{\nabla}\underline{n}^{eq}] \tag{52}$$

and

$$\overset{\Rightarrow}{\mathbf{F}}(t) = [\overset{\Rightarrow}{\nabla}\underline{\psi}_T]\bigcirc\underset{\approx}{\chi}(t)\bigcirc\delta\underline{n}(0) + \int_0^t dt'\underset{\approx}{\chi}(t-t')\bigcirc\underline{h}(t'). \tag{53}$$

$\overset{\Rightarrow}{\mathbf{F}}(t)$ is a linear function of the stochastic variables $\delta\underline{n}(t)$ and $\underline{h}(t)$, and it is, therefore, a stochastic force, with zero mean, and time correlation function given by the following fluctuation-dissipation relation,

$$\langle\overset{\Rightarrow}{\mathbf{F}}(t)\overset{\Rightarrow}{\mathbf{F}}^{\dagger}(0)\rangle = k_BT\Delta\overset{\Leftrightarrow}{\zeta}(t). \tag{54}$$

This relation can be demonstrated by using a theorem [27] that assures us that a contracted description of a *stationary* stochastic process is also stationary, provided that the static cross correlations between the remaining and the eliminated variables vanish. This is satisfied in our case, due to the different time-reversal symmetry of the variables $\overset{\Rightarrow}{\mathbf{V}}(t)$ and $\delta\underline{n}(t)$, which implies that $\langle\overset{\Rightarrow}{\mathbf{V}}(0)\delta\underline{n}^{\dagger}(0)\rangle = \mathbf{0}$. On the other hand, another general theorem establishes [27] that the stationarity of a linear stochastic process is a necessary and sufficient condition for the fluctuation-dissipation relation to be satisfied. In our case, such a relation is precisely Eq. (54).

Equations (51), (52), and (54) are the most fundamental results of this paper. From Eq. (51), the velocity autocorrelation functions, and other relevant time-dependent properties, could in principle be derived in terms of the components of the solvent friction tensor $\overset{\Leftrightarrow}{\zeta}^0$ (which in our theory are considered externally determined phenomenological parameters) and of the time-dependent friction tensor $\Delta\overset{\Leftrightarrow}{\zeta}(t)$. Thus, $\Delta\overset{\Leftrightarrow}{\zeta}(t)$, which describes the additional friction effects on the tracer due to its direct interactions with the other particles, now becomes the most important object, whose determination is the immediate goal in any concrete application of our theory. For this reason, let us now focus our attention on Eq. (52), which expresses $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ in terms of three objects: the pair potential $\psi_T(\mathbf{r},\Omega)$ (assumed known), the equilibrium concentration profile $n^{eq}(\mathbf{r},\Omega)$ (assumed caculable by statistical thermodynamic methods), and the collective-diffusion propagator $\underset{\approx}{\chi}(t)$. The latter is defined as the solution of Eq. (49) with initial condition given by Eq. (50). Equation (49), in its turn, involves the static correlation matrix $\underset{\approx}{\sigma}$ (assumed calculable by statistical thermodynamic methods), and the collective-diffusion kernel $\underset{\approx}{L}(t)$. Thus, in order to be able to use Eq. (52) either $\underset{\approx}{L}(t)$ or $\underset{\approx}{\chi}(t)$ must be provided. This will only be possible in an approximate manner, and the following paper deals with this aspect of our theory. For the time being, however, it is convenient to use the exact (Wertheim-Lovett's) relation in Eqs. (46) and (47) to derive two additional equivalent expressions for $\Delta\overset{\Leftrightarrow}{\zeta}(t)$, namely,

$$\Delta\overset{\Leftrightarrow}{\zeta}(t) = k_BT[\overset{\Rightarrow}{\nabla}\underline{n}^{eq}]\bigcirc\underset{\approx}{\sigma}^{-1}\bigcirc\underset{\approx}{\chi}(t)\bigcirc[\underline{n}^{eq}]^{\dagger}, \tag{55}$$

and

$$\Delta \overset{\Leftrightarrow}{\zeta}(t)=\beta[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]\bigcirc\underset{\approx}{\chi}(t)\bigcirc\underset{\approx}{\sigma}\bigcirc[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]^{\dagger}. \tag{56}$$

Although these two expressions for $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ are formally equivalent to the original result in Eq. (52), either of them may prove to be more convenient under particular conditions. For example, if the static structural properties $\underline{n}^{\mathrm{eq}}$ and $\underset{\approx}{\sigma}$ are more directly accessible (either theoretically or experimentally) than the pair potential $\underline{\psi}_T$, then Eq. (55) is a better starting point for the determination of $\Delta \overset{\Leftrightarrow}{\zeta}(t)$. On the other hand, for softer and longer-ranged potentials $\underline{\psi}_T$, Eq. (56) may be more useful. Let us also notice that the equivalence between Eqs. (55) and (56) is only guaranteed as long as no approximation is involved that breaks the connection between $\underline{\psi}_T$, $\underline{n}^{\mathrm{eq}}$, and $\underset{\approx}{\sigma}$ represented by Wertheim-Lovett's relation. In any other case, one should be prepared to find inconsistencies between results calculated from Eq. (55) (that we shall refer to as the "concentration equation") or from Eq. (56) (referred to as the "force equation"). This situation is similar to the inconsistencies found in the theory of liquids [22], when the same thermodynamic property is calculated from the energy, virial, or compressibility equations, using as an input an approximate radial distribution function. This will be illustrated in the following paper. In reference to the brief review in Sec. II, let us notice that our main results in this section [Eqs. (51) and (52)] correspond to Eqs. (4) and (5) of Sec. II. More precisely, Eq. (5) is the particular version for spherical particles of the "force" equation [Eq. (56)]. To see this, notice that multiplying Eq. (44) by $\delta n^{\dagger}(0)$, and taking the ensemble average, we get the time-evolution equation for the van Hove function $\langle \delta n(\mathbf{r},\Omega,t)\,\delta n(\mathbf{r}',\Omega',0)\rangle$. This is just the time-evolution equation that $\underset{\approx}{\chi}(t)$ satisfies [since there are no correlations between $\overset{\Rightarrow}{\mathbf{V}}(t)$ or $\underline{h}(t)$ with $\delta\underline{n}(0)$]. Thus, $\langle \delta\underline{n}(t)\,\delta\underline{n}^{\dagger}(0)\rangle$ differs from $\underset{\approx}{\chi}(t)$ only in the initial condition [$\underset{\approx}{\chi}(t=0)=\underset{\approx}{\mathbf{U}}$ and $\langle \delta\underline{n}(t=0)\,\delta\underline{n}^{\dagger}(0)\rangle=\underset{\approx}{\sigma}$], and hence, $\langle \delta\underline{n}(t)\,\delta\underline{n}^{\dagger}(0)\rangle=\underset{\approx}{\chi}(t)\bigcirc\underset{\approx}{\sigma}$. Using this result in Eq. (56), it should now be easy to recognize Eq. (5) as a particular result of Eq. (56).

To close this section on the most general results of our theory, let us now go back to the begining of Sec. III, where we indicated that the consideration of a single species of particles interacting with the tracer was only a convenient but nonessential simplification. At this point, however, it is easy to indicate the way in which all our previous discussion applies when we consider an arbitrary number $\nu$ of species of particles around the tracer. This is possible due to our compact notation, which allowed us to denote the functions $n(\mathbf{r},\Omega,t)$, $\psi_T(\mathbf{r},\Omega)$, etc., as the vectors $\underline{n}(t)$, $\underline{\psi}_T$, etc. In the multicomponent case, the species can be indicated by means of an additional index in all of these functions. Thus, we speak of $n_\alpha(\mathbf{r},\Omega;t)$ ($\alpha=1,2,\ldots,\nu$) as the concentration of particles of specie $\alpha$ in $(\mathbf{r},\Omega)$ at time $t$, of $\psi_{T\alpha}(\mathbf{r},\Omega)$ as the pair potential between the tracer and one particle of species $\alpha$ in ($\mathbf{r}$, $\Omega$), etc. In this manner, wherever we integrate over common position and orientation variables, we should also sum over the common species index. Thus, the inner product "$\bigcirc$" now implies "$\Sigma_{\alpha=1}^{\nu}\int d^3r\int d\Omega$." With this understanding, all the derivations and results in this paper extend to multicomponent suspensions.

## VI. LONG TIMES

Let us now write some results that may be useful when particular time regimes are considered. The generalized Langevin equation that we have just derived, Eq. (51), describes the relaxation of $\overset{\Rightarrow}{\mathbf{V}}(t)$ at all time regimes referring to the relaxation time $\tau_B$ of the tracer's velocity by hydrodynamic friction. The relevant time scales in many experiments, however, are associated with the direct interactions, and are concerned with the relaxation time of the function $\Delta \overset{\Leftrightarrow}{\zeta}(t)$. Leaving aside possible anomalous conditions in which $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ does not decay sufficiently fast (long-time tails), the relaxation of $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ defines a characteristic relaxation time, denoted as $\tau_I$ ($\gg\tau_B$), such that for asymptotically long times $t\gg\tau_I$, the decay of $\overset{\Rightarrow}{\mathbf{V}}(t)$ can be described by a simpler form of the generalized Langevin equation, in which $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ is approximated by

$$\Delta \overset{\Leftrightarrow}{\zeta}(t)=\Delta \overset{\Leftrightarrow}{\zeta}\,2\,\delta(t), \tag{57}$$

where the tensor $\Delta \overset{\Leftrightarrow}{\zeta}$ (without temporal argument) is defined as

$$\Delta \overset{\Leftrightarrow}{\zeta}\equiv\int_0^{\infty}\Delta \overset{\Leftrightarrow}{\zeta}(t)\,dt. \tag{58}$$

Using Eq. (57) in Eq. (51), we have the so-called Markovian limit, in which the GLE becomes

$$\overset{\Leftrightarrow}{M}\cdot\frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt}=-\overset{\Leftrightarrow}{\zeta}\cdot\overset{\Rightarrow}{\mathbf{V}}(t)+\overset{\Rightarrow}{\mathbf{f}}(t), \tag{59}$$

with

$$\overset{\Leftrightarrow}{\zeta}=\overset{\Leftrightarrow}{\zeta}{}^{0}+\Delta \overset{\Leftrightarrow}{\zeta}, \tag{60}$$

and with

$$\overset{\Rightarrow}{\mathbf{f}}(t)=\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)+\overset{\Rightarrow}{\mathbf{F}}(t), \tag{61}$$

satisfying

$$\langle \overset{\Rightarrow}{\mathbf{f}}(t)\,\overset{\Rightarrow}{\mathbf{f}}{}^{\dagger}(0)\rangle=k_BT\overset{\Leftrightarrow}{\zeta}\,2\,\delta(t). \tag{62}$$

Thus, we see that in this limit, the description of the Brownian motion of the interacting tracer is formally identical to the case of a free tracer [Eqs. (7) and (8)]. In some experiments this is the relevant time regime. In such a case, it is enough to calculate $\Delta \overset{\Leftrightarrow}{\zeta}$. Integrating the general results for

$\Delta\overset{\Leftrightarrow}{\zeta}(t)$ in Eqs. (52), (55,) and (56), we can find general expressions for $\Delta\overset{\Leftrightarrow}{\zeta}$. Note first that from Eqs. (49) and (50), we find that

$$\int_0^\infty \underset{\approx}{\chi}(t)dt=\underset{\approx}{\sigma}\bigcirc\underset{\approx}{L}^{-1}, \tag{63}$$

where $\underset{\approx}{L}^{-1}\bigcirc\underset{\approx}{L}=\underset{\approx}{\mathbf{U}}$, and

$$\underset{\approx}{L}\equiv\int_0^\infty \underset{\approx}{L}(t)dt. \tag{64}$$

Using Eq. (63) in Eqs. (52), (55), and (56), we get the following three exact equivalent expressions for the static friction tensor $\Delta\overset{\Leftrightarrow}{\zeta}$:

$$\Delta\overset{\Leftrightarrow}{\zeta}=-[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]\bigcirc\underset{\approx}{\sigma}\bigcirc\underset{\approx}{L}^{-1}\bigcirc[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{n}^{\text{eq}}]^\dagger, \tag{65}$$

$$\Delta\overset{\Leftrightarrow}{\zeta}=k_BT[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{n}^{\text{eq}}]\bigcirc\underset{\approx}{L}^{-1}\bigcirc[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{n}^{\text{eq}}]^\dagger, \tag{66}$$

and

$$\Delta\overset{\Leftrightarrow}{\zeta}=\beta[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]\bigcirc\underset{\approx}{\sigma}\bigcirc\underset{\approx}{L}^{-1}\bigcirc\underset{\approx}{\sigma}\bigcirc[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]^\dagger. \tag{67}$$

From these expressions, the seemingly most convenient one, in principle, is the ‘‘concentration’’ equation, Eq. (66), since, even though it depends on $\underset{\approx}{L}$, it only involves $\underline{n}^{\text{eq}}$, which is a static property easier to determine than $\underset{\approx}{\sigma}$. Once again, in later work we shall make use of some of these results.

## VII. SHORT-TIME REGIME

Let us now consider the regime opposite to that discussed in the previous section. We recall that for short times we refer to the regime $t\ll\tau_I$, but still in the diffusive regime $t\gg\tau_B$. To zeroth order in $(t/\tau_I)$, $\underset{\approx}{\chi}(t)=\underset{\approx}{\mathbf{U}}$, and the memory term in the generalized Langevin equation in Eq. (51) is negligible. Thus, this equation only differs from Eqs. (7) and (8), which describe free diffusion, by the additional term $\overset{\Rightarrow}{\mathbf{F}}(t=0)=[\overset{\Rightarrow}{\boldsymbol{\nabla}}\underline{\psi}_T]\bigcirc\delta\underline{n}(0)$. This is the total force that the surrounding particles exert on the tracer for a given initial configuration. On the average, however, this total force vanishes, since $\langle\delta\underline{n}(0)\rangle=0$. Thus, in this regime the tracer moves, on the average (over initial configurations of the surrounding particles), as a freely diffusing Brownian particle. The fact that the averaged effect of the direct interactions vanishes at short times can be interpreted saying that in this regime, a ‘‘representative’’ tracer particle undergoes local Brownian motion at the local minimun of the field of force exerted by the average ‘‘cage’’ of the surounding particles, described by the equilibrium profile $\underline{n}^{\text{eq}}=\langle\underline{n}(0)\rangle$. Thus, as long as the tracer particle does not displace itself from this local minimum, we have free diffussion. The very initial effects of the direct interactions on the tracer's motion occur at first order in $(t/\tau_I)$, where the tracer has displaced itself by $\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\equiv\int_0^t\overset{\Rightarrow}{\mathbf{V}}(t')dt'$ from the equilibrium minimum, but the cage has not yet evolved in time. This first-order effects are also described by the GLE in Eq. (51), which, to linear order in $t$, reads

$$\overset{\Leftrightarrow}{M}\cdot\frac{\overset{\Rightarrow}{\mathbf{V}}(t)}{dt}=-\overset{\Leftrightarrow}{\zeta}{}^0\cdot\overset{\Rightarrow}{\mathbf{V}}(t)+\overset{\Rightarrow}{\mathbf{f}}{}^0(t)-\Delta\overset{\Leftrightarrow}{\zeta}(0)\cdot\Delta\overset{\Rightarrow}{\mathbf{R}}(t)+\overset{\Rightarrow}{\mathbf{F}}(t). \tag{68}$$

Once again, $\overset{\Rightarrow}{\mathbf{F}}(t)$ vanishes on the average [over all possible realizations of $\overset{\Rightarrow}{\mathbf{F}}(t)$, i.e., over an ensemble of tracer particles]. Without this last term, Eq. (68) describes Brownian motion of the tracer particle displaced from the local minimum, by a displacement $\Delta\overset{\Rightarrow}{\mathbf{R}}(t)$, and subjected to a ‘‘restoring’’ force linear in $\Delta\overset{\Rightarrow}{\mathbf{R}}(t)$. The spring constants of the corresponding harmonic potential are precisely the components of the initial value of $\Delta\overset{\Leftrightarrow}{\zeta}(t)$. From Eq. (68), we see that $\Delta\overset{\Leftrightarrow}{\zeta}(0)$ can be written, in terms only of $\underline{\psi}_T$ and $\underline{n}^{\text{eq}}$, as

$$\Delta\overset{\Leftrightarrow}{\zeta}(0)=-[\boldsymbol{\nabla}\underline{\psi}_T]\bigcirc[\boldsymbol{\nabla}\underline{n}^{\text{eq}}]^\dagger. \tag{69}$$

This quantity determines the very early deviations (up to $t^2$), from its initial linear (free diffusion) dependence of the generalized mean-squared displacement $\langle\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\Delta\overset{\Rightarrow}{\mathbf{R}}{}^\dagger(t)\rangle$ on time. If a well-defined separation of time scales exists for a given system (i.e., if $t\ll\tau_I$), in such a way that the free-diffussion regime $\tau_B\ll t\ll\tau_I$ can be observed, then the initial linear behavior of $\langle\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\Delta\overset{\Rightarrow}{\mathbf{R}}{}^\dagger(t)\rangle$ will determine the phenomenological parameters involved in $\overset{\Leftrightarrow}{\zeta}{}^0$ [since the corresponding short-time diffusion coefficients $\overset{\Leftrightarrow}{D}{}^0$ will be related to $(\overset{\Leftrightarrow}{\zeta}{}^0)^{-1}$]. In addition, the very early departure from this short-time, or free diffusion regime will appear at order $t^2$ in $\langle\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\Delta\overset{\Rightarrow}{\mathbf{R}}{}^\dagger(t)\rangle$, and will be related to $\Delta\overset{\Leftrightarrow}{\zeta}(0)$. How useful these observations can be in practice will depend, of course, on the particular system and on the specific experimental approach employed to monitor the averaged motion of the tracer particles. In principle, light scattering or video microscopy could be tunned to measure those short-time properties (as has been the case for spherical particles). In the most general case, however, it may be that the experimental measurement records time-dependent correlation functions different from $\langle\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\Delta\overset{\Rightarrow}{\mathbf{R}}{}^\dagger(t)\rangle$, which is defined in terms of $\overset{\Rightarrow}{\mathbf{V}}(t)$, which, in its turn, is best described in the reference frame with orientation following the tracer particle's orientation. Thus, additional work must be made to find the appropriate connection between the measurable time-dependent correlation functions and $\langle\Delta\overset{\Rightarrow}{\mathbf{R}}(t)\Delta\overset{\Rightarrow}{\mathbf{R}}{}^\dagger(t)\rangle$, or $\langle\overset{\Rightarrow}{\mathbf{V}}(t)\overset{\Rightarrow}{\mathbf{V}}(0)^\dagger\rangle$. In the meanwhile, computer simulations should provide a useful test of the general scenario for the short-time diffusion properties just described.

Of course, computer simulations, light scattering, or video microscopy are also in principle capable of describing the dynamics at a time regime beyond the one just described, i.e, at times $t \approx \tau_I$. For this intermediate regime, the short-time expansion is no longer useful, and the full time dependence of $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ is required. The determination of $\Delta \overset{\Leftrightarrow}{\zeta}(t)$, however, must wait until we introduce approximations, such as those that will be defined in the following paper. Recalling, however, that in the context of suspensions of spherical particles a very useful strategy [4] has been to approximate by an exponential function the memory function corresponding essentially to $\Delta \overset{\Leftrightarrow}{\zeta}(t)$, it is worthwhile to indicate a general result for $\Delta \overset{\Leftrightarrow}{\zeta}^{(1)}(0) \equiv [d\Delta \overset{\Leftrightarrow}{\zeta}(t)/dt]_{t=0}$. From $\Delta \overset{\Leftrightarrow}{\zeta}(0)$ and $\Delta \overset{\Leftrightarrow}{\zeta}^{(1)}(0)$, such a simple approximation for $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ could be defined. From Eq. (52), we have that

$$\Delta \overset{\Leftrightarrow}{\zeta}^{(1)}(0) = -[\boldsymbol{\nabla} \underline{\psi}_T] \bigcirc \underset{\approx}{\chi}^{(1)}(t) \bigcirc [\boldsymbol{\nabla} \underline{n}^{\mathrm{eq}}]^{\dagger}, \qquad (70)$$

and from Eq. (49) we find that

$$\underset{\approx}{\chi}^{(1)}(t) \equiv \left( \frac{d\underset{\approx}{\chi}(t)}{dt} \right)_{t=0} = \underset{\approx}{L}^{0} \bigcirc \underset{\approx}{\sigma}^{-1}, \qquad (71)$$

where we have assumed (extending what is well established in the context of spherical particles) that $\underset{\approx}{L}(t)$ has a temporally local term $\underset{\approx}{L}^{0} 2\delta(t)$, such that

$$\underset{\approx}{L}(t) = \underset{\approx}{L}^{0} 2\delta(t) + \Delta \underset{\approx}{L}(t), \qquad (72)$$

where $\Delta \underset{\approx}{L}(t)$ embodies the dynamic effects of the direct interactions among the particles of the suspension. At this point, these results constitute another aspect of our present general discussion. We expect that they will be useful in further developments of the present theory, which might parallel those that occurred in the more restricted case of suspensions of spherical particles.

## VIII. A RELEVANT GENERIC SYSTEM

Besides being exact, in the sense that we have not yet introduced approximations in $\underset{\approx}{\chi}(t)$ [or, equivalently, in $\underset{\approx}{L}(t)$], our results are also still general. Thus, they should apply to the general condition involving a nonspherical tracer interacting with other nonspherical particles of a multicomponent suspension. In order to apply these results to concrete systems, it is convenient to retrict ourselves to systems that present some of the complexities, but not all, that are involved in the most general case. One possibility is to consider a generic system with a higher degree of symmetry in the interparticle interactions. The simplest such generic system corresponds to that in which only the tracer particle remains nonspherical, while the other particles are spherical. By this we mean that the interaction $u_{\alpha\beta}(\mathbf{r},\Omega;\mathbf{r}',\Omega')$ between two of the latter (of species $\alpha,\beta = 1,2,\ldots,\nu$) does not depend on their orientations $\Omega$ and $\Omega'$, and that the pair potential $\psi_T(\mathbf{r},\Omega)$ between the tracer and one of those particles of species $\alpha$ does not depend on the orientation of the latter, but only on its relative position $\mathbf{r}$ with respect to the center of mass of the tracer, whose (fixed) orientation, however, does matter. Thus, for this generic system, $u_{\alpha\beta}(\mathbf{r},\Omega;\mathbf{r}',\Omega') = u_{\alpha\beta}(|\mathbf{r}-\mathbf{r}|)$ and $\psi_{T\alpha}(\mathbf{r},\Omega) = \psi_{T\alpha}(\mathbf{r})$, and the local concentration profile $n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega)$ is also independent of $\Omega$, and can be written as $n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega) = n_{\alpha}^{\mathrm{eq}}(\mathbf{r})/\Omega$ where $\Omega \equiv \int d\Omega$. In general we have implicitly assumed that $n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega)$ is normalized in such a way that $\int d\mathbf{r} \int d\Omega\, n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega) = N_{\alpha}$, such that $N_{\alpha}$ is the total number of particles in volume $V$, and that in the bulk $n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega) = n_{\alpha}/\Omega$, with $n_{\alpha}$ being the bulk concentration $n_{\alpha} \equiv N_{\alpha}/V$ of species $\alpha$. In addition, for similar reasons, we must have that $\sigma(\mathbf{r},\Omega;\mathbf{r}',\Omega') = \sigma(\mathbf{r},\mathbf{r}')/\Omega^2$, whereas $\sigma_{\alpha\beta}^{-1}(\mathbf{r},\Omega;\mathbf{r}',\Omega') = \sigma_{\alpha\beta}^{-1}(\mathbf{r},\mathbf{r}')/\Omega^2$, and $\chi_{\alpha\beta}(\mathbf{r},\Omega;\mathbf{r}',\Omega';t) = \chi_{\alpha\beta}(\mathbf{r},\mathbf{r}';t)/\Omega^2$.

With this understanding, it is not difficult to see that all the results in this paper are to be read, for this generic system, just as they are, provided that for $\underline{\psi}_T$, $\underline{n}^{\mathrm{eq}}$, $\underset{\approx}{\sigma}$, and $\underset{\approx}{\chi}(t)$ we understand the vectors and matrices with orientation-independent components $\psi_{T\alpha}(\mathbf{r})$, $n_{\alpha}(\mathbf{r})$, $\sigma_{\alpha\beta}(\mathbf{r},\mathbf{r}')$, and $\chi_{\alpha\beta}(\mathbf{r},\mathbf{r}';t)$, and that the inner product ‘‘$\bigcirc$’’ only indicates ‘‘$\sum_{\alpha=1}^{\nu} \int d^3r$.’’ In addition, since $[\partial \psi_T(\mathbf{r},\Omega)/\partial \vec{\phi}] = [\partial n_{\alpha}^{\mathrm{eq}}(\mathbf{r},\Omega)/\partial \vec{\phi}] = 0$, the operator $\boldsymbol{\nabla}_{\mathrm{rot}}$ is just $\boldsymbol{\nabla}_{\mathrm{rot}} = \mathbf{r} \times \boldsymbol{\nabla}$. As a result, for this generic system, although the GLE in Eq. (51) exhibits no notational modification, the other main results of this paper, namely, the expressions for $\Delta \overset{\Leftrightarrow}{\zeta}(t)$, can be written in a simpler manner. For example, the ‘‘concentration’’ and the ‘‘force’’ equations in Eqs. (55) and (56) now read, respectively,

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = k_B T \int d^3r_1 \int d^3r_2 \int d^3r_3 \left[ \begin{pmatrix} \boldsymbol{\nabla}_1 \\ \mathbf{r}_1 \times \boldsymbol{\nabla}_1 \end{pmatrix} n^{\mathrm{eq}}(\mathbf{r}_1) \right] \sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2) \chi(\mathbf{r}_2,\mathbf{r}_3;t) [(\boldsymbol{\nabla}_3, \mathbf{r}_3 \times \boldsymbol{\nabla}_3) n^{\mathrm{eq}}(\mathbf{r}_3)], \qquad (73)$$

and

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = \beta \int d^3r_1 \int d^3r_2 \int d^3r_3 \left[ \begin{pmatrix} \boldsymbol{\nabla}_1 \\ \mathbf{r}_1 \times \boldsymbol{\nabla}_1 \end{pmatrix} \psi_T(\mathbf{r}_1) \right] \chi(\mathbf{r}_1,\mathbf{r}_2;t) \sigma(\mathbf{r}_2,\mathbf{r}_3) [(\boldsymbol{\nabla}_3, \mathbf{r}_3 \times \boldsymbol{\nabla}_3) \psi_T(\mathbf{r}_3)]. \qquad (74)$$

These are the results from which we shall start our discussion in the following paper on the application of our theory to this generic system. Once again, these results are still exact, but they are the most general only in the context of the generic system considered. Other generic systems may also be considered (for example, a spherical tracer diffusing in a suspension of nonspherical particles). The one described here, however, will be used immediately as a simple prototype that will allow us to explain the protocol to be followed in applying our theory to concrete systems and conditions.

## IX. CONCLUSIONS

Here we have presented the formal derivation of the GLE that describes the Brownian motion of a nonspherical tracer particle that interacts with other diffusing particles in a suspension, which are in general nonspherical, and of different species. This is Eq. (51) of Sec. V. A relevant aspect of this result is the fluctuation-dissipation relation in Eq. (54). However, the most important result is the exact and general expression derived for the time-dependent friction tensor $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ in Eq. (52), or its alternative expressions in Eqs. (55) and (56) (the ‘‘concentration’’ and the ‘‘force’’ equations). These are expressions in terms of equilibrium static properties $[n_\alpha^{\text{eq}}(\mathbf{r},\Omega)$ and $\sigma_{\alpha\beta}(\mathbf{r},\Omega,\mathbf{r}',\Omega')]$ and of the collective diffusion propagator $\chi_{\alpha\beta}(\mathbf{r},\Omega,\mathbf{r}',\Omega';t)$ [or through Eq. (49), of the time-dependent diffusion kernel $L_{\alpha\beta}(\mathbf{r},\Omega,\mathbf{r}',\Omega';t)$]. The latter is still to be determined in an approximate manner, and in the context of a concrete application. For the time being, we also included in this paper results referring to the long-time and to the short-time regimes (Secs. VI and VII). These are equally formal results, that we shall refer to in future applications of the general theoretical framework established in this paper. In preparation for the first such application, in the previous section we wrote explicitly how these general results simplify when particular restricting symmetries are introduced in the definition of a generic system. While the following paper, that deals with such generic system, will start from these still exact but less general results, future applications [17] to systems outside that generic case will force us to go back to the most general formulation of the theory. This justifies having developed a formal but general framework, from which a number of possible applications will branch. Paper II contains the first and most inmediate of such branches. As a final remark, let us mention that the GLE approach presented here leads to results for the tracer-diffusion properties, which turn out to be equivalent to results derived starting from the Fokker-Planck or the Smoluchowski equation. An example will be given in the following paper, where we will show that Hess and Klein's result for self-diffusion of spherical particles (whose derivation starts from the many-particle Fokker-Planck equation) follows as a particular result of the GLE theory. This should not be surprising, since at least in the absence of hydrodynamic interactions, the statistical information contained in the many-particle Fokker-Planck equation is the same as that contained in the many-particle Langevin equation. Thus, Eq. (2) [or its extended version in Eq. (15)] is just one of the $(N+1)$ coupled Langevin equations, except that it is written in the precise form needed to proceed with our method. Spelling out the equivalences and differences with other approaches is indeed an interesting topic, which falls, however, outside the scope and length of the present paper. In this regard, we refer the reader to a recent paper, [29], where some of these topics are discussed in more detail.

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