Rotational diffusion of nonspherical Brownian particles in a suspension of spheres

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A theory is presented to describe the translational and rotational Brownian motion of a nonspherical tracer particle that interacts with other diffusing spherical particles around it. In order to apply this theory, approximations must be introduced that allow us to express the tracer-diffusion properties of the tracer particle in terms of the static structural properties of the system. We illustrate the application of these results with the calculation of the rotational diffusion coefficient of a Brownian electric dipole that interacts with a Brownian one-component plasma. [S1063-651X(96)06112-0]

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I. INTRODUCTION

The rotational dynamics of nonspherical colloidal particles is a subject of long-standing interest [1,2]. Among the many issues that await systematic study, both from the theoretical and from the experimental side, is the description of the effects of the interactions between many colloidal particles that execute translational and rotational Brownian motion while interacting among themselves by direct and hydrodynamic forces [3]. In this paper we address one aspect of this general problem, as a continuation of our work on this subject contained in the previous paper [4] (hereafter referred to as paper I). There we developed a general theory to describe the effects of the direct interactions between a nonspherical tracer particle and other, also generally nonspherical, particles diffusing around it, on the translational and rotational motion of the former. The main result of that paper is the derivation of a generalized Langevin equation for the linear and angular velocity of the tracer particle. The effects of the direct interactions with the other particles are contained in a time-dependent friction tensor, $\Delta\overleftrightarrow{\zeta}(t)$, for which general and exact expressions were derived. Those formally exact results, however, cannot be used in a concrete application before approximations and simplifications are introduced, and this is what we do in the present work. In order to proceed, however, we first restrict the generality of the results in paper I to the case in which the tracer particle is nonspherical, but the other particles with which it interacts are spherical. For concreteness, we might imagine a system formed by a suspension of interacting spherical colloidal particles (e.g., polystyrene spheres in water), in which a trace of nonspherical particles is added [e.g., tobacco mosaic virus (TMV), or other rigid polyelectrolyte]. Each of these nonspherical tracer particles will execute translational and rotational Brownian motion, while interacting with the many spherical particles around them. The effects of these interactions are contained in the time-dependent friction function $\Delta\overleftrightarrow{\zeta}(t)$ of the nonspherical tracer, and it is this quantity what we want to calculate. As in paper I, here we also neglect hydrodynamic interactions. The main purpose of this paper is to derive, starting from the general and exact results of paper I, approximate expressions for $\Delta\overleftrightarrow{\zeta}(t)$ in terms only of the static properties of the system. These approximate expressions will be, however, still general for the generic conditions to which we restrict ourselves here. As it turns out, introducing approximations leads not to a single expression for $\Delta\overleftrightarrow{\zeta}(t)$, but to a number of different results, which may in general not be consistent. Thus, another important purpose of this work is to monitor the consequences of the order and hierarchy of the approximations that are introduced. The approximate results of this paper will then be ready for their specific application to concrete systems such as the one mentioned above (TMV in polystyrene sphere suspension). Here, however, we shall only describe their application to a simpler and idealized model system, with the purpose of illustrating the protocol to be followed in the process of going from the general and exact results of paper I down to concrete and specific applications.

In the following section we quote the main results of paper I, and in Sec. III we introduce the first simplifying approximation, referred to as the homogeneity approximation. The second important approximation is the use of Fick's diffusion (or short-time) approximation for the collective diffusion propagator for the spherical particles, along with a manner to relate the description of this propagator as observed from the reference frame of the tracer particle, and as observed from the laboratory. This is discussed in Sec. IV. In Sec. V we discuss a general self-consistency test of our results. The extension to multicomponent suspension is described in Sec. VI. In Sec. VII we illustrate their application to a simple idealized model, namely, a Brownian dipole interacting with a Brownian one-component plasma. Section VIII summarizes our results.

II. GENERAL RESULTS

Let us start our discussion by quoting the general and exact results of paper I, as they apply to the generic system considered here (see Sec. VIII of paper I). Thus, consider a

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nonspherical tracer particle whose instantaneous linear and angular velocity $\mathbf{V}(t)$ and $\boldsymbol{\omega}(t)$ are *defined* with respect to the laboratory, but whose components are *referred* to a reference frame whose origin is fixed to the laboratory, but whose orientation follows instantaneously the orientation of the principal axis of the rotating tracer particle. Let M be the mass, and let I_i $(i=1,2,3)$ be the principal moments of inertia of the tracer particle. Then, according to the general results of paper I, and using the compact notation introduced there, the equation of motion of the tracer particle is the following generalized Langevin equation

$$\overset{\Leftrightarrow}{M}\cdot\frac{d\overset{\Rightarrow}{\mathbf{V}}(t)}{dt}=-\overset{\Leftrightarrow}{\zeta}{}^{0}\cdot\overset{\Rightarrow}{\mathbf{V}}(t)+\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)-\int_0^t dt'\,\Delta\overset{\Leftrightarrow}{\zeta}(t-t')\cdot\overset{\Rightarrow}{\mathbf{V}}(t')+\overset{\Rightarrow}{\mathbf{F}}(t), \tag{1}$$

where the six-component vectors $\overset{\Rightarrow}{\mathbf{V}}(t)$, $\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)$, and $\overset{\Rightarrow}{\mathbf{F}}(t)$ are defined as

$$\overset{\Rightarrow}{\mathbf{V}}(t)=\begin{pmatrix}\mathbf{V}(t)\\ \boldsymbol{\omega}(t)\end{pmatrix},\quad \overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)=\begin{pmatrix}\mathbf{f}^{0}(t)\\ \mathbf{t}^{0}(t)\end{pmatrix},\quad \overset{\Rightarrow}{\mathbf{F}}(t)=\begin{pmatrix}\mathbf{F}(t)\\ \mathbf{T}(t)\end{pmatrix}, \tag{2}$$

and the 6×6 matrices $\overset{\Leftrightarrow}{M}$, $\overset{\Leftrightarrow}{\zeta}{}^{0}$, and $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ are defined as

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

$$\Delta\overset{\Leftrightarrow}{\zeta}(t)\equiv\begin{pmatrix}\Delta\overset{\leftrightarrow}{\zeta}(t) & \Delta\overset{\leftrightarrow}{\zeta}_{TR}(t)\\ \Delta\overset{\leftrightarrow}{\zeta}{}^{\dagger}_{RT}(t) & \Delta\overset{\leftrightarrow}{\zeta}_{R}(t)\end{pmatrix}, \tag{3}$$

with $\overset{\Leftrightarrow}{M}_{ij}=M_i\delta_{ij}$, and $M_i=M$ (the mass) for $i=1,2,3$ and $M_i=I_i$ for $i=4,5,6$. In these equations, the vector $\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)$ groups the components of the random force $\mathbf{f}^{0}(t)$ and the random torque $\mathbf{t}^{0}(t)$ that the solvent exerts on the tracer particle. It is modeled as a Gaussian δ-correlated noise, with zero mean and time-dependent correlation function given by the fluctuation-dissipation relation, $\langle\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)\overset{\Rightarrow}{\mathbf{f}}{}^{0}(t)^{\dagger}(0)\rangle=k_BT\overset{\Leftrightarrow}{\zeta}{}^{0}2\,\delta(t)$, where k_B is Boltzmann's constant and T is the temperature. The 3×3 subtensors $\overset{\leftrightarrow}{\zeta}{}^{0}$, $\overset{\leftrightarrow}{\zeta}{}^{0}_{TR}$, $\overset{\leftrightarrow}{\zeta}{}^{0}_{RT}$, and $\overset{\leftrightarrow}{\zeta}{}^{0}_{R}$ are the translational-translational, translational-rotational, rotational-translational, and rotational-rotational free-diffusion (or short-time) friction tensors of the isolated tracer particle. The components of $\overset{\Leftrightarrow}{\zeta}{}^{0}$ are considered here externally-determined phenomenological parameters. The random effects of the direct interactions of the tracer particle with the surrounding spherical particles are contained in the random force $\mathbf{F}(t)$ and random torque $\mathbf{T}(t)$ grouped in $\overset{\Rightarrow}{\mathbf{F}}(t)$. These are stochastic processes, which are not necessarily Gaussian, and are certainly not δ correlated. They do have zero mean, and their time-dependent correlation function is given by the fluctuation-dissipation relation $\langle\overset{\Rightarrow}{\mathbf{F}}(t)\overset{\Rightarrow}{\mathbf{F}}{}^{\dagger}(0)\rangle=k_BT\Delta\overset{\Leftrightarrow}{\zeta}(t)$.

The other important result of paper I is a general and exact expression for the time-dependent friction tensor $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ describing the effects of the direct interactions. This general result can be written in three alternative but formally equivalent manners. Here we shall only be interested in two of them, referred to as the *concentration* equation and the *force* equation. The concentration equation is written as

$$\Delta\overset{\Leftrightarrow}{\zeta}(t)=k_BT\int d^3r_1\int d^3r_2\int d^3r_3\times[\overset{\Rightarrow}{\boldsymbol{\nabla}}_1 n^{\mathrm{eq}}(\mathbf{r}_1)]\sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2)\chi(\mathbf{r}_2,\mathbf{r}_3;t)[\overset{\Rightarrow}{\boldsymbol{\nabla}}_3 n^{\mathrm{eq}}(\mathbf{r}_3)]^{\dagger}, \tag{4}$$

where

$$\overset{\Rightarrow}{\boldsymbol{\nabla}}=\begin{pmatrix}\boldsymbol{\nabla}\\ \mathbf{r}\times\boldsymbol{\nabla}\end{pmatrix}, \tag{5}$$

and where $n^{\mathrm{eq}}(\mathbf{r})$ is the equilibrium local concentration of spherical particles around the tracer particle (here we only consider the case corresponding to a monodisperse suspension of spheres; the extension to polidisperse suspensions will be indicated in Sec. VI below). In Eq. (4), $\sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ is the inverse of the static correlation function

$$\sigma(\mathbf{r}_1,\mathbf{r}_2)\equiv\langle\delta n(\mathbf{r}_1,0)\,\delta n(\mathbf{r}_2,0)\rangle, \tag{6}$$

of the spheres, where $\delta n(\mathbf{r},t)\equiv n(\mathbf{r},t)-n^{\mathrm{eq}}(\mathbf{r})$ is the fluctuation of their instantaneous local concentration $n(\mathbf{r},t)$, around its equilibrium value $n^{\mathrm{eq}}(\mathbf{r})$. σ^{-1} and σ are related by $\int d^3r_2\sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2)\sigma(\mathbf{r}_2,\mathbf{r}_3)=\delta(\mathbf{r}_1-\mathbf{r}_3)$. The collective diffusion propagator $\chi(\mathbf{r}_1,\mathbf{r}_2;t)$ can be defined as

$$\chi(\mathbf{r}_1,\mathbf{r}_2;t)=\int d^3r_3\langle\delta n(\mathbf{r}_1,t)\,\delta n(\mathbf{r}_2,0)\rangle\sigma^{-1}(\mathbf{r}_2,\mathbf{r}_3). \tag{7}$$

The second alternative expression for $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ is what we refer to as the force equation, which can be written as

$$\Delta\overset{\Leftrightarrow}{\zeta}(t)=\beta\int d^3r_1\int d^3r_2\int d^3r_3\times[\overset{\Rightarrow}{\boldsymbol{\nabla}}_1\psi(\mathbf{r}_1)]\chi(\mathbf{r}_1,\mathbf{r}_2;t)\sigma(\mathbf{r}_2,\mathbf{r}_3)[\overset{\Rightarrow}{\boldsymbol{\nabla}}_3\psi(\mathbf{r}_3)]^{\dagger}, \tag{8}$$

where $\beta=1/k_BT$, and $\psi(\mathbf{r})$ is the pair potential of the direct interaction between the tracer particle and one sphere located at position $\mathbf{r}$ referring to the tracer's reference frame. Equations (4) and (8) are equivalent, since they are related to each other by the exact relationship (see Sec. IV of paper I)

$$[\overset{\Rightarrow}{\nabla}_1 n^{\rm eq}(\mathbf{r}_1)] = -\beta \int d^3 r_2 \sigma(\mathbf{r}_1,\mathbf{r}_2)[\overset{\Rightarrow}{\nabla}_2 \psi(\mathbf{r}_2)], \qquad (9)$$

which is a generalization of the well-known Wertheim-Lovett's equation of the equilibrium theory of inhomogeneous fluids [6]. The formal equivalence between these two expressions for $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ will cease to apply as soon as we introduce approximations for $\sigma(\mathbf{r}_1,\mathbf{r}_2)$ and/or $n^{\rm eq}(\mathbf{r})$, which violate the exact relationship in Eq. (9).

III. HOMOGENEITY APPROXIMATION

In order to evaluate $\Delta \overset{\Leftrightarrow}{\zeta}(t)$ according to the general results above, we need to determine first the two static structural properties involved, namely, $n^{\rm eq}(\mathbf{r})$ and $\sigma(\mathbf{r}_1,\mathbf{r}_2)$. Being equilibrium properties, they can be determined in principle by the approaches of the statistical thermodynamic theory of inhomogeneous fluids [5,6]. In fact, this is what we shall do with $n^{\rm eq}(\mathbf{r})$, which is in reality a pair correlation function (between one sphere and the tracer particle). In contrast, the determination of $\sigma(\mathbf{r}_1,\mathbf{r}_2)$, which is in fact a three-particle distribution function (two spheres and the tracer particle), may constitute in practice a rather difficult task. For this reason, at this point we introduce the first simplifying approximation, which consists in approximating $\sigma(\mathbf{r}_1,\mathbf{r}_2)$ by its value in the absence of the tracer particle, i.e., by its bulk value. Ignoring the effects of the field of the tracer on the correlation between the two spheres, reduces $\sigma(\mathbf{r}_1,\mathbf{r}_2)$ to a pair correlation function (now only between the two spheres). In this case, $\sigma(\mathbf{r}_1,\mathbf{r}_2)$ and $\sigma^{-1}(\mathbf{r}_1,\mathbf{r}_2)$ no longer depend separately on $\mathbf{r}_1$ and $\mathbf{r}_2$, but only on the distance $|\mathbf{r}_1-\mathbf{r}_2|$. Another manner to express this approximation, is to write $\sigma(\mathbf{r}_1,\mathbf{r}_2)$ as

$$\sigma(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{(2\pi)^3}\int d^3k \; e^{-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\sigma(k), \qquad (10)$$

where $\sigma(k)$ is the Fourier transform (FT) of the isotropic function $\sigma(|\mathbf{r}_1-\mathbf{r}_2|)$. This is essentially the static structure factor $S(k)$ of the suspension of spheres in the bulk; more precisely, $\sigma(k)=nS(k)$.

In a similar manner, we can also ignore the effects of the field of the tracer on the collective diffusion propagator, and approximate $\chi(\mathbf{r}_1,\mathbf{r}_2;t)$ by its bulk value $\chi(|\mathbf{r}_1-\mathbf{r}_2|,t)$. This allows us to write

$$\chi(\mathbf{r}_1,\mathbf{r}_2;t) = \frac{1}{(2\pi)^3}\int d^3k \; e^{-i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\chi(k,t), \qquad (11)$$

where $\chi(k,t)$ is then defined [see Eq. (7)] as $\chi(k,t)=F(k,t)/S(k)$, where $F(k,t)$ is the intermediate scattering function of the suspension of spheres [7] (referring, however, to the reference frame of the tracer particle, which undergoes Brownian motion; see Sec. IV).

Equations (10) and (11) constitute what we shall refer to as the homogeneity approximation. They allow us to write Eqs. (4) and (8), respectively, as

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = \frac{k_B T n^2}{(2\pi)^3}\int d^3k [\overset{\Rightarrow}{\mathbf{K}} h(\mathbf{k})]\sigma^{-1}(k)\chi(k,t)[\overset{\Rightarrow}{\mathbf{K}} h(-\mathbf{k})]^{\dagger}, \qquad (12)$$

and

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = \frac{\beta}{(2\pi)^3}\int d^3k [\overset{\Rightarrow}{\mathbf{K}}\psi(\mathbf{k})]\chi(k,t)\sigma(k)[\overset{\Rightarrow}{\mathbf{K}}\psi(\mathbf{k})]^{\dagger}, \qquad (13)$$

where

$$h(\mathbf{k}) = \int d^3r e^{i\mathbf{k}\cdot\mathbf{r}} h(\mathbf{r}), \qquad (14)$$

with $h(\mathbf{r}) \equiv n^{\rm eq}(\mathbf{r})/n - 1$,

$$\psi(\mathbf{k}) = \int d^3r e^{i\mathbf{k}\cdot\mathbf{r}} \psi(\mathbf{r}), \qquad (15)$$

and

$$\overset{\Rightarrow}{\mathbf{K}} = \begin{pmatrix} \mathbf{k} \\ \mathbf{k}\times\nabla_k \end{pmatrix}. \qquad (16)$$

Equation (12) is the concentration equation, in which we introduced the homogeneity approximation. For this reason we shall label it as CH. For similar reasons, the force equation in Eq. (13) will be labeled FH. Although they derive, respectively, from the exact results in Eqs. (4) and (8), they are no longer exact. Furthermore, although Eqs. (4) and (8) are equivalent to each other, the equivalence between Eqs. (12) and (13) is no longer guaranteed, due to the introduction of the homogeneity approximation. Thus, we can anticipate possible inconsistencies between the results obtained from them, and we are interested in assessing the degree of inconsistency, at least in particular applications. The two equations remain, however, still general for the generic system considered here, since no assumption has been made concerning the nature of the interaction potentials $u(r)$ and $\psi(\mathbf{r})$ (between two spheres and between the tracer and one sphere, respectively). Given $u(r)$ and $\psi(\mathbf{r})$, one can determine in principle, by statistical thermodynamic methods, the static structure factor $\sigma(k)/n$ of the suspension of spheres, and the equilibrium concentration $n^{\rm eq}(\mathbf{r})$ of spheres around the nonspherical tracer particle [thus leading to $h(\mathbf{k})$]. Thus, the only object that we still have to determine is the collective diffusion propagator $\chi(k,t)$. This is what we do in the following section.

IV. COLLECTIVE DIFFUSION PROPAGATOR AND FICK'S APPROXIMATION

Let us recall the basic definition of the collective diffusion propagator $\chi(\mathbf{r}_1,\mathbf{r}_2;t)$ in Eq. (7), in terms of the time-dependent correlation function of the variable $\delta n(\mathbf{r},t)$. There is an important aspect in this definition, which involves the reference frame in which the position vector $\mathbf{r}$ has been defined, i.e., $\mathbf{r}$ has its origin in the center of mass of the tracer particle, which is not fixed, but is undergoing Brownian motion. This fact introduces an intrinsic dependence of the collective dynamics represented by $\chi(\mathbf{r}_1,\mathbf{r}_2;t)$, on the dynamics of the tracer particle. Making this dependence explicit, even in an approximate manner, is the first aspect of our determination of $\chi(k,t)$. One way to proceed is to recall the microscopic definition of the variable $n(\mathbf{r},t)$, namely [5,7], $n(\mathbf{r},t)=\Sigma_{i=1}{}^{N}\delta(\mathbf{r}-\mathbf{r}_i(t))$, where $\mathbf{r}_i(t)$ is the instantaneous position of particle i at time t with respect to the center of mass of the tracer particle. Thus, within the homogeneity approximation, Eq. (7) can also be written as

$$\chi(k,t)=\left\langle \frac{1}{V}\sum_{i,j}^{N} \exp\{i\mathbf{k}\cdot[\mathbf{r}_i(t)-\mathbf{r}_j(0)]\}\right\rangle \Big/ \sigma(k). \qquad (17)$$

If we denote by $\mathbf{x}_i(t)$ the position of the center of mass of the tracer $(i=T)$ and of each of the N spheres $(i=1,2,\ldots,N)$, with respect to the laboratory, we can write this equation as

$$\chi(k,t)=\left\langle \exp[i\mathbf{k}\cdot\Delta\mathbf{x}_T(t)]\frac{1}{V} \times\sum_{i,j}^{N} \exp\{i\mathbf{k}\cdot[\mathbf{x}_i(t)-\mathbf{x}_j(0)]\}\right\rangle \Big/ \sigma(k), \qquad (18)$$

where $\Delta\mathbf{x}_T(t)\equiv\mathbf{x}_T(t)-\mathbf{x}_T(0)$ is the translational displacement of the tracer particle. This equation suggests a simple decoupling approximation for the ensemble average indicated by $\langle\ \rangle$, which reads

$$\chi(k,t)\approx\langle\exp[i\mathbf{k}\cdot\Delta\mathbf{x}_T(t)]\rangle \times\left\langle \frac{1}{V}\sum_{i,j}^{N} \exp\{i\mathbf{k}\cdot[\mathbf{x}_i(t)-\mathbf{x}_j(0)])\right\rangle \Big/ \sigma(k). \qquad (19)$$

This is what we shall refer to as the "decoupling approximation" (DA), which we then may write as

$$\chi^{(\mathrm{DA})}(k,t)=\chi_T(k,t)\chi^{(B)}(k,t), \qquad (20)$$

with

$$\chi_T(k,t)\equiv\langle e^{i\mathbf{k}\cdot\Delta\mathbf{x}_T(t)}\rangle \qquad (21)$$

being the tracer-diffusion propagator, and where $\chi^{(B)}(k,t)$ is the collective diffusion propagator, now referring to the reference frame of the laboratory, and, according to the homogeneity approximation, in the absence of the tracer particle, i.e., it is the ordinary collective diffusion propagator of the bulk suspension of spheres [7].

Of course, the tracer-diffusion propagator $\chi_T(k,t)$ depends in fact on $\Delta\overset{\Leftrightarrow}{\zeta}(t)$. Thus, we need an independent closure relation, for which we assume at the moment the simplest of them, consisting in approximating $\chi_T(k,t)$ by its free-diffusion, or short-time, expression

$$\chi_T(k,t)=\exp(-k_z^2D_\parallel^0t)\exp[-(k_x^2+k_y^2)D_\perp^0t], \qquad (22)$$

where

$$D_\gamma^0\equiv\frac{k_BT}{\zeta_\gamma^0} \quad (\gamma=\parallel,\perp) \qquad (23)$$

are the longitudinal and transversal free diffusion coefficients of the nonspherical tracer particle, which we assume axisymmetric. In fact, for simplicity, we are assuming that $(\overset{\Leftrightarrow}{\zeta}{}^0)_{\alpha\beta}$ is diagonal, with $\zeta_\perp^0=(\overset{\Leftrightarrow}{\zeta}{}^0)_{11}=(\overset{\Leftrightarrow}{\zeta}{}^0)_{22}$, $\zeta_\parallel^0=(\overset{\Leftrightarrow}{\zeta}{}^0)_{33}$, and $\zeta_R^0=(\overset{\Leftrightarrow}{\zeta}{}^0)_{ii}$, $(i=4,5,6)$.

For the bulk collective diffusion propagator $\chi^{(B)}(k,t)$, we can also resort at this point to its simplest approximation, which we refer to as the short-time, or Fick's diffusion approximation, namely [7,8],

$$\chi^{(B)}(k,t)=\exp\left(-k^2\frac{D^0t}{S(k)}\right), \qquad (24)$$

where D^0 is the short-time diffusion coefficient of the spheres (also an externally determined parameter).

Using the decoupling approximation, Eq. (20), in either the concentration or the force equations [Eqs. (12) and (13)], we may now write $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ in terms of the tracer and collective diffusion propagators. The resulting expressions, which we would then label as CHD and FHD, to recall the order and hierarchy of the approximations introduced, still require specific approximations for $\chi_T(k,t)$ and $\chi^{(B)}(k,t)$, such as those in Eqs. (22)–(24). These, however, are about the simplest of such approximations, and more refined options could, and will, also be considered. For simplicity, in the present work we decide to adopt this level of approximation for $\chi_T(k,t)$ and $\chi^{(B)}(k,t)$, which, when employed in either the CHD or the FHD schemes, finally leads to closed and explicit expressions for $\Delta\overset{\Leftrightarrow}{\zeta}(t)$ in terms only of the short-time transport parameters D^0, $D_\parallel^0$, and $D_\perp^0$, and the equilibrium structural properties $S(k)$, $h(\mathbf{k})$, and/or $\psi(\mathbf{k})$. These two schemes, which we shall denote by CHDF and FHDF (to include the reminder of the use of the rather accessorial Fick's approximation for the collective propagator) are now ready for concrete applications, as we shall illustrate in Sec. VII.

V. SELF-CONSISTENCY TEST OF THE THEORY

Before illustrating the concrete use of these results, let us discuss how other results in the literature happen to be contained as particular cases, and let us describe an interesting self-consistency test of the theory. Consider first the case in which our tracer particle is also spherical (although different, in general, from the surrounding spheres). For this we mean that $\psi(\mathbf{r})$ [and also $n^{\mathrm{eq}}(\mathbf{r})$] only depends on the magnitude $|\mathbf{r}|$, and hence, $\psi(\mathbf{k})$ and $h(\mathbf{k})$ only depend on the magnitude of $\mathbf{k}$. Then, $\psi(\mathbf{k})=u_{TS}(k)$ and $h(\mathbf{k})=h_{TS}(k)$, where $u_{TS}(k)$ and $h_{\mathrm{TS}}(k)$ are, respectively, the Fourier transform of the pair potential $u_{TS}(r)$ and of the total correlation function $h_{TS}(\mathbf{r})$, between the spherical tracer particle (T) and one of the surrounding spheres (S). It is not difficult to see that in this case,

$$\mathbf{k}\times\nabla_k\psi(\mathbf{k})=\mathbf{k}\times\nabla_kh(\mathbf{k})=0, \qquad (25)$$

and hence, from either Eq. (12) or Eq. (13), we find that $\Delta\zeta_{ij}(t)=0$ if $i,j=4,5,6$. This simply tells us that a spherical tracer particle can rotate without additional friction due to its *direct* interactions with the other spherical particles around it. Furthermore, $\Delta\zeta_{ij}(t)$ also vanishes if either i or j is 4, 5, or 6. Thus, the only possibly nonzero elements of $\Delta\overleftrightarrow{\zeta}(t)$ are $\Delta\zeta_{ij}(t)$ with $i,j=1,2,3$, which define the components of a 3×3 subtensor that we denote simply as $\Delta\overleftrightarrow{\zeta}(t)$. On the other hand, we also find that $\Delta\overleftrightarrow{\zeta}(t)$ is isotropic, i.e., $\hat{\mathbf{n}}\cdot\Delta\overleftrightarrow{\zeta}(t)\cdot\hat{\mathbf{n}}$ has the same value for any unit vector $\hat{\mathbf{n}}$. Therefore, using the representation $\Delta\zeta_{ij}(t)=\hat{\mathbf{n}}_i\cdot\Delta\overleftrightarrow{\zeta}(t)\cdot\hat{\mathbf{n}}_j$, with $\hat{\mathbf{n}}_i$ $(i=1,2,3)$ being the unit vectors $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}})$ of a Cartesian system, we have that $\Delta\zeta_{ij}(t)=\delta_{ij}\Delta\zeta^{\mathrm{sph}}(t)$ $(i,j=1,2,3)$, where $\Delta\zeta^{\mathrm{sph}}(t)\equiv\mathrm{Tr}[\Delta\overleftrightarrow{\zeta}(t)/3]$ is given, according, for example, to the concentration equation, Eq. (12), by

$$\Delta\zeta^{\mathrm{sph}}(t)=\frac{k_BTn}{(2\pi)^3}\int d^3k\frac{[k_zh_{TS}(k)]^2}{S(k)}\chi(k,t). \tag{26}$$

This expression only involves the homogeneity approximation employed in the concentration equation (which we labeled as CH). Within the decoupling approximation, Eq. (20), and in the still more restricted case in which the tracer particle is identical to the other spheres ($T=S$, and hence, $h_{TS}(k)=[S(k)-1]/n$), Eq. (26) coincides with the expression for $\Delta\zeta^{\mathrm{sph}}(t)$ derived by Hess and Klein [9] for self-diffusion. Their derivation, however, employed a completely different approach, involving mode-mode coupling arguments. The particular version of such result, labeled MMC1 by Nägele *et al.* [10], corresponds, in our language, to the use of the additional approximations of Eqs. (22) and (24), i.e., to what we have labeled here as CHDF. Thus, our CHDF results of the previous section constitute a generalization of Hess and Klein's self-diffusion expression for $\Delta\zeta^{\mathrm{sph}}(t)$, which allows for the tracer to be different from the other spheres around it [11]. Furthermore, our results of the previous section (both CHDF and FHDF) also describe the rotational Brownian motion of the tracer particle when it actually is nonspherical.

Let us now explain an interesting self-consistency test of our theory. For this, consider first just the same system discussed above, namely, a spherical tracer particle whose solvent friction coefficent is ζ_T^0, and whose isotropic time-dependent friction function representing its direct interactions with the surrounding spheres is described by $\Delta\zeta^{\mathrm{sph}}(t)$. Now imagine that two of these tracer particles are rigidly bound to each other, with a center-to-center separation l thus constituting a dumbell. This dumbell can now be viewed as our nonspherical tracer particle, which undergoes translational and rotational Brownian motion. For an infinitely elongated dumbell, $l\to\infty$, we expect that the translational and rotational friction forces and torques will be the simple superposition of the friction forces and torques on each of the two spheres of the dumbell. This means that if $\zeta_\perp$ and $\zeta_\parallel$ are the transversal and parallel translational friction coefficients of the dumbell, then $\zeta_\perp=\zeta_\parallel=2\zeta^{\mathrm{sph}}$, where ζ^{sph} is the friction coefficient of each of its spheres. Similarly, if ζ_R is the rotational friction coefficient (for rotations around an axis perpendicular to the dumbell axis), then $\zeta_R=(l^2/2)\zeta^{\mathrm{sph}}$. What we now prove is the dynamical version of these expectations, referring to the contributions $\Delta\zeta_\parallel(t)$, $\Delta\zeta_\perp(t)$, and $\Delta\zeta_R(t)$ of the direct interactions of the dumbell with the surrounding spherical particles. To see this, let us notice that when the dumbell is highly elongated, such that $l\gg\lambda$, where λ is the correlation length of the radial distribution function $g_{TS}(r)$ of the spheres (S) around a sphere (T) of the dumbell, then the local concentration $n^{\mathrm{eq}}(\mathbf{r})$ of the spheres around the dumbell can be written as

$$n^{\mathrm{eq}}(\mathbf{r})=ng_{TS}(|\mathbf{r}-\mathbf{l}/2|)g_{TS}(|\mathbf{r}+\mathbf{l}/2|), \tag{27}$$

where $\mathbf{l}\equiv l\hat{\mathbf{n}}$, with $\hat{\mathbf{n}}$ being a unit vector in the direction of the symmetry axis. Thus, since $h(\mathbf{r})\equiv n^{\mathrm{eq}}(\mathbf{r})/n-1$, and using $h_{TS}(r)=g_{TS}(r)-1$, we have that Eq. (27) can also be written as

$$\begin{aligned}h(\mathbf{r})=&h_{TS}(|\mathbf{r}-\mathbf{l}/2|)+h_{TS}(|\mathbf{r}+\mathbf{l}/2|)\\&+h_{TS}(|\mathbf{r}-\mathbf{l}/2|)h_{TS}(|\mathbf{r}+\mathbf{l}/2|).\end{aligned} \tag{28}$$

The last term in this equation, however, must be ignored, since either $h_{TS}(|\mathbf{r}-\mathbf{l}/2|)$ or $h_{TS}(|\mathbf{r}+\mathbf{l}/2|)$ vanish for all $\mathbf{r}$ when $l\gg\lambda$. Thus, the FT of Eq. (28) is given by

$$h(\mathbf{k})=[e^{i\mathbf{k}\cdot\mathbf{l}/2}+e^{-i\mathbf{k}\cdot\mathbf{l}/2}]h_{TS}(k), \tag{29}$$

where $h_{TS}(k)$ is the FT of $h_{TS}(r)$. This expression for $h(\mathbf{k})$ can now be substituted in Eq. (12). For the subtensor $\Delta\overleftrightarrow{\zeta}(t)$ [i.e., $\zeta_{ij}(t)$, with $i,j=1,2,3$), we then find that

$$\Delta\overleftrightarrow{\zeta}(t)=2\left[\frac{k_BTn}{(2\pi)^3}\int d^3k\ \mathbf{kk}h_{TS}^2(k)\frac{\chi(k,t)}{S(k)}+\frac{k_BTn}{(2\pi)^3}\int d^3k\ \mathbf{kk}\cos(k_zl)h_{TS}^2(k)\frac{\chi(k,t)}{S(k)}\right], \tag{30}$$

where we used the identity $\cos^2x=(1+\cos 2x)/2$. Now, we observe that the second term on the right-hand side of this equation vanishes for $l\gg\lambda$. This is so because the factor $\cos(k_zl)$ becomes rapidly oscillatory when k_z varies in the range where the rest of the integrand is slowly varying (i.e., where $|k_z|\approx\lambda^{-1}$). Hence, this integral tends to zero, and $\Delta\overleftrightarrow{\zeta}(t)$ tends to a value given by the first term of this equation. This, however, can be written as

$$\lim_{l\to\infty}\Delta\overleftrightarrow{\zeta}(t)=2\Delta\overleftrightarrow{\zeta}^{\mathrm{sph}}(t), \tag{31}$$

with

$$\Delta\overleftrightarrow{\zeta}^{\mathrm{sph}}(t)=\frac{2k_BTn}{(2\pi)^3}\int d^3k\ \mathbf{kk}h_{TS}^2(k)\frac{\chi(k,t)}{S(k)}, \tag{32}$$

which is precisely twice the expression we would get from Eq. (12) when the tracer is a spherical particle. As indicated before, $\Delta \overleftrightarrow{\zeta}^{\rm sph}(t)$ is isotropic, i.e., $\Delta \zeta_{ij}^{\rm sph}(t) = \delta_{ij} \Delta \zeta^{\rm sph}(t)$ with $\Delta \zeta^{\rm sph}(t)$ given by Eq. (26). Therefore, from Eq. (32), we have that $\Delta \zeta_{xx}(t) = \Delta \zeta_{zz}(t) = 2 \Delta \zeta^{\rm sph}(t)$, which, with the notation "$xx \rightarrow \perp$" and "$zz \rightarrow \parallel$," is expressed as

$$\lim_{t\to\infty} \Delta \zeta_{\perp}(t) = \lim_{t\to\infty} \Delta \zeta_{\parallel}(t) = 2 \Delta \zeta^{\rm sph}(t). \tag{33}$$

In a similar manner, let us consider the subtensor $\Delta \overleftrightarrow{\zeta}_R(t)$, defined by the components of $[\Delta \overset{\Leftrightarrow}{\zeta}(t)]_{ij}$ with $i,j = 4,5,6$. This is the time-dependent contribution of the direct interactions to the friction tensor coupling the total torque on the tracer with its angular velocity. For an axisymmetric tracer particle, we can define the components of $\Delta \overleftrightarrow{\zeta}_R(t)$ by $\hat{\mathbf{n}}_i \cdot \Delta \overleftrightarrow{\zeta}_R(t) \cdot \hat{\mathbf{n}}_j$, with $\hat{\mathbf{n}}_1$, $\hat{\mathbf{n}}_2$, $\hat{\mathbf{n}}_3$ being the Cartesian unit vectors, $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$, and with $\hat{\mathbf{z}}$ pointing in the symmetry axis of the dumbell. From Eq. (12), with Eq. (29), we find that $\Delta \overleftrightarrow{\zeta}_R(t)$ is diagonal. Furthermore, we find that $\hat{\mathbf{z}} \cdot \Delta \overleftrightarrow{\zeta}_R \cdot \hat{\mathbf{z}}$ also vanishes. This means that the rotation of the dumbell around its symmetry axis causes no friction due to the direct interactions with the surrounding spheres. We also find that $\hat{\mathbf{x}} \cdot \Delta \overleftrightarrow{\zeta}_R(t) \cdot \hat{\mathbf{x}} = \hat{\mathbf{y}} \cdot \Delta \overleftrightarrow{\zeta}_R(t) \cdot \hat{\mathbf{y}} \equiv \Delta \zeta_R(t)$, which indicates the equivalence of the rotations around any of the two axis orthogonal to $\hat{\mathbf{z}}$. In order to evaluate $\Delta \zeta_R(t)$ from Eq. (12), let us notice, using Eq. (29), that $\hat{\mathbf{x}} \cdot [\mathbf{k} \times \nabla_k h(\mathbf{k})] = k_y h_{TS}(k) \sin(k_z l/2)$. With this result, along with the identity $\sin^2 x = (1 - \cos 2x)/2$, we obtain for $\Delta \zeta_R(t)$

$$\Delta \zeta_R(t) = \frac{l^2}{2} \left[\frac{k_B T n}{(2\pi)^3} \int d^3k \; k_y^2 h_{TS}^2(k) \frac{\chi(k,t)}{S(k)} - \frac{k_B T n}{(2\pi)^3} \int d^3k \; k_y^2 h_{TS}^2(k) \cos(k_z l) \frac{\chi(k,t)}{S(k)} \right]. \tag{34}$$

By the same argument used for the translational motion, the second term on the right-hand side vanishes in the limit $l \rightarrow \infty$. In addition, the first term inside the brackets of Eq. (34) is precisely the expresion for $\Delta \zeta^{\rm sph}(t)$ in Eq. (26). Thus, we find that $\Delta \zeta_R(t)$ is given, for $l \rightarrow \infty$, by

$$\Delta \zeta_R(t) = \frac{l^2}{2} \Delta \zeta^{\rm sph}(t). \tag{35}$$

Summarizing, the general expression for $\Delta \overleftrightarrow{\zeta}(t)$ and $\Delta \overleftrightarrow{\zeta}_R(t)$ implicit in Eq. (12), together with Eq. (29), and in the limit considered here ($l \gg \lambda$), leads to predictions [Eqs. (33) and (35)] in accordance with the expected results, based on reasonable superposition arguments. These predictions provide confidence on the general validity and formal consistency of the theory. Finally, let us note that this demonstration only required the homogeneity approximation, and no use was made of Fick's approximation. Furthermore, although the discussion was based on the concentration equation [Eq. (12)], similar arguments can be given starting from the force equation, Eq. (13).

VI. EXTENSION TO MULTICOMPONENT SUSPENSION

As explained in paper I (end of Sec. V), extending the results of the present theory to the case in which the particles with which the nonspherical tracer interacts belong to more than one species, is quite a simple matter, involving only adequate notation. In our case, we refer to the case in which the other particles are spherical, but belong to species $\alpha = 1,2, \ldots, \nu$. The corresponding extension of Eqs. (12) and (13) can be written, respectively, as

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = \frac{k_B T}{(2\pi)^3} \int d^3k [\overset{\Rightarrow}{\mathbf{K}} H(\mathbf{k})] \bigcirc \sigma^{-1} \times (k) \bigcirc \chi(k,t) \bigcirc [\overset{\Rightarrow}{\mathbf{K}} H(-\mathbf{k})]^{\dagger}, \tag{36}$$

and

$$\Delta \overset{\Leftrightarrow}{\zeta}(t) = \frac{\beta}{(2\pi)^3} \int d^3k [\overset{\Rightarrow}{\mathbf{K}} \psi(\mathbf{k})] \bigcirc \chi(k,t) \bigcirc \times \sigma(k) \bigcirc [\overset{\Rightarrow}{\mathbf{K}} \psi(\mathbf{k})]^{\dagger}, \tag{37}$$

provided that $\sigma(k)$ and $\chi(k,t)$ are considered $\nu \times \nu$ matrices, and $H(\mathbf{k})$ and $\psi(\mathbf{k})$ are considered vectors with ν components, and "$\bigcirc$" indicates the corresponding inner product (i.e., summation over common species indices). More concretely, the components of $\psi(\mathbf{k})$ will be $\psi_\alpha(\mathbf{k})$ ($\alpha = 1,2, \ldots, \nu$), the Fourier transform of the pair potential $\psi_\alpha(\mathbf{r})$ between the tracer particle and one sphere at position $\mathbf{r}$ with respect to the tracer's center of mass, and $H_\alpha(\mathbf{k})$ is the FT of $n_\alpha h_{T\alpha}(\mathbf{r}) \equiv n_\alpha^{\rm eq}(\mathbf{r}) - n_\alpha$. Similarly, $\sigma_{\alpha\beta}(k) = \sqrt{n_\alpha n_\beta}[\delta_{\alpha\beta} + \sqrt{n_\alpha n_\beta} h_{\alpha\beta}(k)]$, and $\chi_{\alpha\beta}(k,t)$ is the FT of the multicomponent version of the (isotropic) collective propagator.

It is also not difficult to see that the arguments leading to the decoupling approximation in Eq. (20) go through unchanged, leading to

$$\chi_{\alpha\beta}^{(\rm DA)}(k,t) = \chi_T(k,t) \chi_{\alpha\beta}^{(B)}(k,t), \tag{38}$$

with $\chi_T(k,t)$ still given by Eq. (21), and for which we can still use the short-time approximation in Eq. (22). The multicomponent extension of the bulk collective diffusion propagator $\chi_{(\alpha\beta)}^{(B)}(k,t)$, within Fick's approximation, can be written in matrix notation as [11]

$$\chi^{(B)}(k,t) = \exp[-k^2 L^0 \bigcirc \sigma^{-1}(k) t], \tag{39}$$

with the $\nu \times \nu$ matrix L^0 defined as $L_{\alpha\beta}^0 = n_\alpha D_\alpha^0 \delta_{\alpha\beta}$, where D_α^0 is the short-time diffusion coefficient of the spheres of species α.

VII. A BROWNIAN DIPOLE INTERACTING WITH THE BROWNIAN ONE-COMPONENT PLASMA

In this section we describe the protocol to be followed in applying the approximate but general results of Sec. V to a concrete system involving a nonspherical tracer particle interacting with a suspension of spheres. In the Introduction, we referred to TMV tracer particles in a polystyrene sphere suspension, as a simple experimental realization of the generic system considered here. This could be modeled by a Brownian Yukawa fluid with which a nonspherical charged tracer particle interacts. The tracer-sphere interactions could be modeled, for example, assuming the tracer particle to be a line of Yukawa forces. The application of our results to such a model is the subject of current work, and will be reported separately [12]. Here, however, we shall consider instead the simplest idealized model system that retains the basic features of our generic system, and that lends itself to an almost fully analytical treatment.

Consider a system of pointlike particles at bulk concentration n, interacting by purely Coulombic forces, so that their pair potential is just

$$u(r)=\frac{q^2}{r}. \tag{40}$$

This system, which requires a rigid background of uniform charge density $\rho_{\mathrm{el}}=-qn$ to guarantee charge neutrality, is referred to as the one-component plasma [5]. If we assume, in addition, that each pointlike ion executes Brownian motion with a free-diffusion coefficient given by D^0, we refer to it as the *Brownian* one-component plasma (BOP) [9], and this is our idealization of the suspension of spherical Brownian particles with which a nonspherical tracer particle will interact. The model for the nonspherical tracer particle is defined by its nonradially symmetric interaction potential $\psi(\mathbf{r})$ with the ''spheres'' of the BOP. The analytically simplest such interaction is the point-dipole–point-ion interaction. Thus, let us adopt a Brownian point dipole as our model nonspherical tracer particle, so that

$$\psi(\mathbf{r})=\begin{cases}\dfrac{q}{r^3}\,\vec{\mu}\cdot\hat{\mathbf{r}}, & r>a\\ \infty, & r<a,\end{cases} \tag{41}$$

where $\vec{\mu}$ is the electrical dipole, and where we have also allowed for a finite spherical hard core around this pointlike dipole. Thus, our tracer particle is a hard sphere of radius a with a point dipole located in its center. We will also assume that in the absence of interactions with the ''spheres,'' the Brownian motion of this dipolar tracer particle is characterized by the free-diffusion coefficients D_T^0 and D_R^0 characterizing its translational and rotational diffusion, so that its short-time friction tensor $\overleftrightarrow{\zeta}^0$ has components $[\overleftrightarrow{\zeta}^0]_{ij}=\delta_{ij}\zeta_i^0$ with $\zeta_i^0=k_BT/D_T^0$ for $i=1,2,3$, and $\zeta_i^0=k_BT/D_R^0$ for $i=4,5,6$. In this manner, we have defined the fundamental parameters that constitute the basic input of our theory, namely, the free diffusion coefficient D^0 of the spherical particles, the free-diffusion friction tensor $\overleftrightarrow{\zeta}^0$ of the tracer particle, the sphere-sphere interaction potential $u(r)$, and the tracer-sphere interaction potential $\psi(\mathbf{r})$. This is the very first step in attempting to apply the general results of our theory to a particular system. The second step is the determination of the static properties $n^{\mathrm{eq}}(\mathbf{r})$ and $\sigma(\mathbf{r},\mathbf{r}')$, in terms of which we have expressed the time-dependent friction tensor $\Delta\overleftrightarrow{\zeta}(t)$. For this we may resort to the methods of the statistical thermodynamics of fluids, and here we adopt the simplest approximation available to calculate these properties, namely, the Debye-Hückel approximation [5,6]. The calculation of $\sigma(\mathbf{r},\mathbf{r}')$, within the homogeneity approximation, is a rather simple problem, since its Fourier tranform, $\sigma(k)=nS(k)$, is known analytically [9] for the BOP, and is given by

$$\sigma(k)=nS(k)=n\left[\frac{\kappa^2}{k^2+\kappa^2}\right], \tag{42}$$

where $\kappa=\sqrt{4\pi\beta nq^2}$. The calculation of $n^{\mathrm{eq}}(\mathbf{r})$ is a little bit more involved, and it amounts to the calculation of the structure of the ''electrical double layer'' around a dipolar particle. Carrying out this calculation in the Debye-Hückel approximation (in quite an analogous manner as in the Debye-Hückel calculation of the spherical double layer around a charged spherical particle, see Ref. [13]), we get

$$n^{\mathrm{eq}}(\mathbf{r})=n\left(1-\beta q\frac{\exp(\kappa a)}{1+\kappa a+(\kappa a)^2/3}\,\frac{\exp(-\kappa r)}{r}\times(1+\kappa r)\vec{\mu}\cdot\hat{\mathbf{r}}\right)\theta(r-a), \tag{43}$$

where $\theta(x)$ is Heaviside's step function. What we actually need, however, is the FT $h(\mathbf{k})$ of $h(\mathbf{r})\equiv n^{\mathrm{eq}}(\mathbf{r})/n-1$. This is given by

$$h(\mathbf{k})=\frac{4\pi i\beta q}{1+\kappa a+(\kappa a)^2/3}\,\frac{\vec{\mu}\cdot\hat{\mathbf{k}}}{k}\left[\frac{\kappa^2}{k^2+\kappa^2}\times\left(\cos(ka)+\frac{\kappa}{k}\sin(ka)\right)-(1+\kappa a)\frac{\sin(ka)}{ka}\right]. \tag{44}$$

This function, together with $\sigma(k)$, is the static input of the concentration equation, Eq. (12). For the force equation, we require $\sigma(k)$, along with the FT $\psi(\mathbf{k})$ of the tracer-sphere interaction potential $\psi(\mathbf{r})$. In our case, Fourier transforming Eq. (41), we get

$$\psi(\mathbf{k})=i\frac{q}{2\epsilon}\sqrt{\frac{\pi}{2}}\frac{aJ_{1/2}(ka)\vec{\mu}\cdot\hat{\mathbf{k}}}{(ka)^{3/2}}, \tag{45}$$

where $J_{1/2}(x)$ is the Bessel function of order 1/2.

The third step is to use these static structural inputs in either of the two approximate schemes defined in Sec. IV, and referred to as FHDF and CHDF. For this, let us summarize here the expressions for $\Delta\overleftrightarrow{\zeta}(t)$ that result from employing Fick's approximation for the collective diffusion propagator [Eq. (24), along with the short-time tracer-diffusion propagator (Eq. (22)] in the decoupling approximation, Eq. (20), together with either the concentration [Eq. (12)] or the force [Eq. (13)] equation. Let us write this summary, however, in terms of the relevant elements of the tensor $\Delta\overleftrightarrow{\zeta}(t)$, which we denote as $\Delta\zeta_\perp(t)$, $\Delta\zeta_\parallel(t)$, and $\Delta\zeta_R(t)$.

The resulting expressions for these functions, denoted collectively as $\Delta\zeta_\gamma(t)$, (with $\gamma=\perp$, $\|$, and R), are given, within the CHDF scheme, by

$$\Delta\zeta_\gamma^{\rm CHDF}(t)=\frac{k_BT}{(2\pi)^3}\int d^3k\left|\frac{K_\gamma h(\mathbf{k})}{S(k)}\right|^2 \times\exp[-k_z^2D_\|^0t-(k_x^2+k_y^2)D_\perp^0t] \times\exp\left(-\frac{k^2D^0t}{S(k)}\right), \tag{46}$$

whereas in the FHDF scheme, they are given by

$$\Delta\zeta_\gamma^{\rm FHDF}(t)=\frac{\beta}{(2\pi)^3}\int d^3k|K_\gamma\psi(\mathbf{k})|^2\sigma(k) \times\exp[-k_z^2D_\|^0t-(k_x^2+k_y^2)D_\perp^0t] \times\exp\left(-\frac{k^2D^0t}{S(k)}\right). \tag{47}$$

In both cases, K_γ is defined as

$$K_\gamma=\begin{cases}k_x, & \gamma=\perp\\ k_z, & \gamma=\|\\ [\mathbf{k}\times\boldsymbol{\nabla}_k]_x, & \gamma=R.\end{cases} \tag{48}$$

The time-dependent friction function $\Delta\zeta_\perp(t)$ describes the effects of the direct interactions on the translational motion of the tracer particle in the direction transversal to its symmetry axis. From $\Delta\zeta_\perp(t)$ we could calculate the mean squared (transversal) displacement, and the corresponding diffusion coefficient $D_\perp$. In a similar manner, $\Delta\zeta_\|(t)$ describes the corresponding effects referring to the translational motion of the tracer particle in the direction parallel to its axis, whereas $\Delta\zeta_R(t)$ refers to the rotational motion around any axis perpendicular to its symmetry axis. This completes our summary, which is in fact applicable for any system in the generic type considered in this paper.

The specific application to the particular model system considered in this section amounts to substituting the approximate expression for $S(k)$, $h(\mathbf{k})$, and $\psi(\mathbf{k})$ [Eqs. (42), (44), and (45)] in either the CHDF or FHDF expressions for $\Delta\zeta_\gamma(t)$ in Eqs. (46) and (47). This reduces to quadratures the calculation of these properties. In general, the integral on $\mathbf{k}$ involved in these expressions cannot always be calculated analytically, and in our specific application, the resulting analytic expressions are not particularly instructive. For this reason, let us analyze here only one important quantity derived from $\Delta\zeta_\gamma(t)$, namely, its time integral, denoted simply by

$$\Delta\zeta_\gamma\equiv\int_0^\infty\Delta\zeta_\gamma(t)dt \quad (\gamma=\perp,\|,R), \tag{49}$$

which is the static friction coefficient from which the corresponding (long-time) tracer-diffusion coefficient D_γ follows using Eintein's relation

$$D_\gamma=\frac{k_BT}{\zeta_\gamma^0+\Delta\zeta_\gamma}. \tag{50}$$

The calculation of $\Delta\zeta_\perp$ and $\Delta\zeta_\|$ can be carried out fully analytically within both the CHDF and the FHDF schemes, and the results, and limiting cases, will be discussed elsewhere [14], within the context of the description of electrolyte friction phenomena. Here we only present our results for $\Delta\zeta_R$, for which we find, using the Debye-Hückel statics in the CHDF scheme,

$$\Delta\zeta_R^{\rm CHDF}=\left(\frac{\mu^2}{D_T^0\epsilon a}\right)\left[\frac{1}{2\pi^2}\frac{x(1-c^2)}{(1+x+x^2/3)^2} \times\int_0^\infty dy\frac{1}{y^2}\left(\frac{1+y^2}{y^2+c^2}\right)\left\{\frac{1}{1+y^2}\left(\cos(yx)+\frac{1}{y}\sin(yx)\right)-(1+x)\frac{\sin(yx)}{yx}\right\}^2\right], \tag{51}$$

where $x=\kappa a$ and $c=(1+D_T^0/D^0)^{-1/2}$. Unfortunately, we could not reduce this result to a closed analytic form for arbitrary asymmetries in the free diffusion coefficients of the tracer (D_T^0) and the surrounding ions (D^0). However, in the extreme limit where $D_T^0/D^0\to 0$, we have

$$\Delta\zeta_R^{\rm CHMF}=\left(\frac{\mu^2}{D^0\epsilon a}\right)\frac{1}{9}\frac{x(2/3+x)}{(1+x+x^2/3)^2} \tag{52}$$

On the other hand, within the CHDF scheme, the results corresponding to Eqs. (51) and (52) are obtained in closed analytical form, and are given by

$$\Delta\zeta_R^{\rm PHDF}=\left(\frac{\mu^2}{D_T^0\epsilon a}\right)\frac{1}{12}\left[\frac{1}{x}\left(-\frac{1}{2}+\frac{1}{2}e^{-2x}+\frac{1}{2c}-\frac{1}{2c}e^{-2xc}\right)\right], \tag{53}$$

and

$$\Delta\zeta_R^{\rm PHMF}=\left(\frac{\mu^2}{D^0\epsilon a}\right)\frac{1}{48}\left[\frac{\exp(-2x)}{x}(e^{2x}-1-2x)\right]. \tag{54}$$

With these results at hand, we can compare the extent of the expected inconsistencies between the CHDF and FHDF results. This is illustrated in Fig. 1, where the results in Eq. (51) and (53) for $\Delta\zeta_R$ are plotted as a function of κa for the case in which $D_T^0=D^0$. As we can see from this figure, in spite of the different analytic appearance of the two expressions for $\Delta\zeta_R$, the qualitative behavior is quite similar. This we found to be the case for all the other cases where $1>D_T^0/D^0\geqslant 0$. In the limit in which the tracer particle is highly immobile compared to the surrounding ions [$D_T^0/D^0\to 0$, see Eq. (52) and (53)], the analytic expressions for $\Delta\zeta_R$ obtained from the two schemes are clearly different. Nevertheless, the qualitative behavior is also quite similar. Although some of these observations may be interesting, our purpose here was only to describe the protocol to be followed in going from the general and exact results of the previous paper down to a concrete application, and in this sense, the results discussed in this section should suffice.

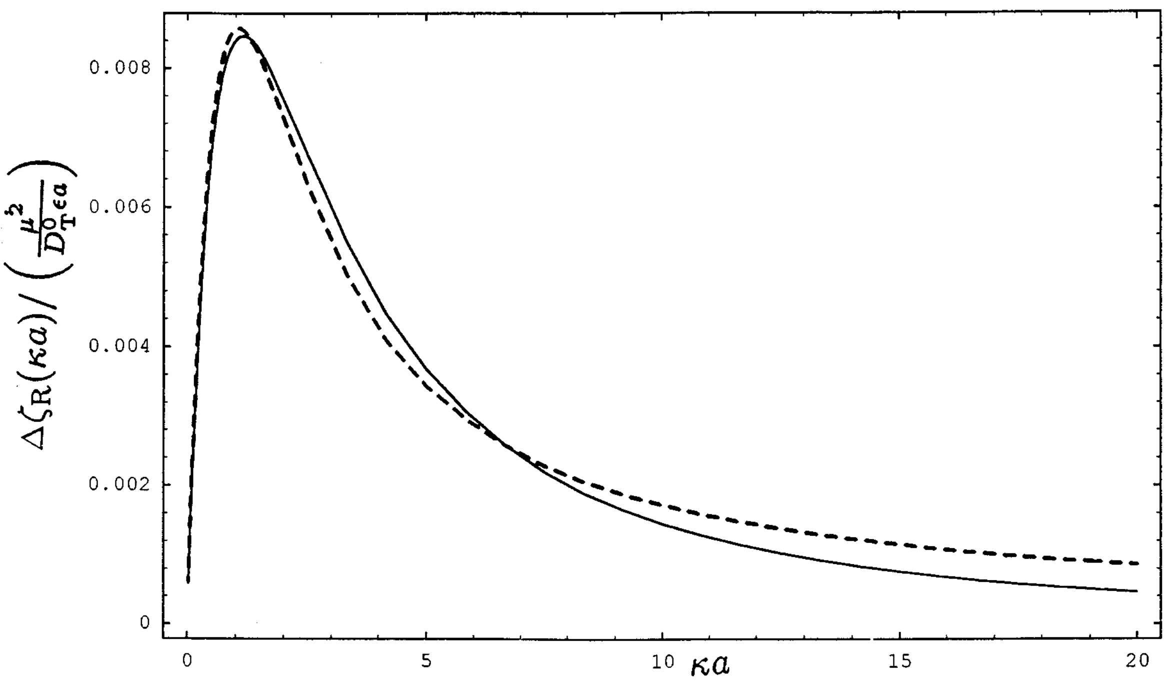

FIG. 1. Electrostatic contribution to the static rotational friciton coefficient $\Delta\zeta_R$ of a Brownian dipolar hard sphere interacting with a Brownian one-component plasma, as a function of the inverse Debye length k (scaled with the radius a of the dipolar hard sphere). $\Delta\zeta_R$ has been scaled with $(\mu^2/D_T^0\epsilon a)$, where μ is the magnitude of the electric dipole D_T^0 the free diffusion coefficient of the tracer, and ϵ the solvent dielectric constant. The solid line corresponds to the use of the concentration equation (CHDF scheme), and the dashed line to the force equation (FHDF scheme).

VIII. SUMMARY

In this paper we have started from the exact results of our previous work, as they apply to the generic system in which a nonspherical tracer particle interacts with other diffusing particles that are spherical. Besides restricting in this manner the general results of the previous paper, here we introduced two important approximations, referred to as the homogeneity approximation (Sec. III) and the decoupling approximation (Sec. IV). With the introduction of an additional, rather accessorial approximation (the ''short-time'' or ''Fick's'' approximation), we finally succeeded in expressing $\Delta\overleftrightarrow{\zeta}(t)$ in terms solely of the static properties and the elementary (short-time) transport properties of the system. The actual application of the resulting approximate expressions for $\Delta\overleftrightarrow{\zeta}(t)$ was illustrated in the previous section, where a very simple model system (a Brownian point dipole interacting with the Brownian one-component plasma) was considered. As illustrated there, the actual application of our approximate results in Sec. V requires that the fundamental properties defining our system are given. These fundamental properties are the pair interaction potentials $\psi(\mathbf{r})$ (between the tracer particle, one surrounding sphere) and $u(\mathbf{r})$ (between two spheres), and the short-time tracer-diffusion tensor $\overleftrightarrow{D}_T^0 = k_B T(\overleftrightarrow{\zeta}^0{}_T)^{-1}$ of the tracer particle and the tracer diffusion coefficient D^0 of the surrounding spheres. The next step in to determine the static properties $n^{\mathrm{eq}}(\mathbf{r})$ and $\sigma(\mathbf{r},\mathbf{r}')$ from $\psi(\mathbf{r})$ and $u(r)$. This proved to be an easy matter in our illustrative application due to the use of a particularly simple approximation of the theory of simple liquids (the Debye-Hückel approximation). In other applications however, this step will in general require numerical approaches that may constitute a rather severe limitation in some specific applications of our theory. Once the static information is available, however, the calculation of the relevant elements of $\Delta\overleftrightarrow{\zeta}(t)$ is reduced to an integration in the Fourier variable $\mathbf{k}$, as we indicated in our illustrative example. Let us mention that the most difficult aspect in the determination of the static properties is the calculation of $n^{\mathrm{eq}}(\mathbf{r})$. Notice, however, that it is only the *concentration* equation that requires $n^{\mathrm{eq}}(\mathbf{r})$ as the static input. Thus, when the calculation of $n^{\mathrm{eq}}(\mathbf{r})$ proves to be particularly difficult, we can still employ the *force* equation, which only requires the pair interaction $\psi(\mathbf{r})$. According to our illustrative example, both schemes will differ quantitatively, but the qualitative agreement may be expected to be satisfactory. In this manner we have completed our program, aimed at (i) establishing a general theoretical framework to describe the Brownian motion of a nonspherical tracer particle interacting with other, in general also nonspherical, particles (this was the subject of paper I), (ii) producing approximate expressions for $\Delta\overleftrightarrow{\zeta}(t)$ for a generic system (a nonspherical tracer interacting with other, spherical particles) (these expresions were written in terms, essentially, of the static properties of the system), and (iii) applying the resulting expressions for $\Delta\overleftrightarrow{\zeta}(t)$ to specific systems. Here we only attempted to illustrate this point with a rather simple model. Shortly we shall report our work on a second, far less trivial, application to a more realistic model system, employing more sophisticated approximations to determine the static inputs of our theory [12]. In addition, the extension of the second aspect [(ii) above] to the case in which the other particles besides the tracer particle are also nonspherical, is also in progress [15]. As a final remark, let us mention that other approximate general schemes, besides CHDF and FHDF discussed here, are also possible. Thus, if instead of the decoupling approximation in Eq. (20) we approximate $\chi(k,t)$ in Eqs. (12) and (13) directly with Fick's approximation in Eq. (24) with an effective mobility βD^* replacing βD^0, we can define two other approximate schemes, which we might label as CHMF and FHMF, respectively. The MF label refers to the use of this modified version of Fick approximation. In recent short accounts of our present work [16,17], these approximate schemes were considered for simplicity.

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