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Tracer diffusion of nonspherical colloidal particles

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A general theory is presented to describe the effects of the direct interactions of a labeled nonspherical colloidal particle with other (spherical or nonspherical) particles diffusing around it, on the translational and rotational tracer-diffusion properties of the former. Approximate, but general expressions are derived for these dynamic properties in terms of static structural properties of the system, in the generic case in which the particles with which the nonspherical tracer interacts are spherical. The specific use of these results is illustrated with the calculation of the rotational diffusion coefficient of a Brownian dipole that interacts with a Brownian one-component plasma, and of an ellipsoidal polyion interacting with its own electrical double layer. [S1063-651X(96)50705-1]

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One of the simplest tracer-diffusion phenomena is self-diffusion in monodisperse suspensions of spherical colloidal particles, such as highly charged polystyrene spheres (polyballs) in water [1]. For these systems, scattering techniques allow the determination of properties such as the mean squared displacement $\langle[\Delta\mathbf{r}(t)]^2\rangle$ and self-diffusion coefficient D^L [1–3]. These measurements have been interpreted on the basis of theoretical results expressing these dynamic properties in terms of the static structure factor $S(k)$ of the suspension, and through this quantity, in terms of the effective forces between particles [4,5]. As an illustration, consider one of the simplest approximate expressions for the deviation of D^L from its value D^0 in the absence of direct interactions, namely [6],

$$\frac{D^L}{D^0}=\left[1+\frac{1}{48\pi^3 n}\int d^3k[S(k)-1]^2\right]^{-1}. \tag{1}$$

Although approximate, results of this type are still general, in the sense that no restriction to limiting conditions (weak coupling, low concentration, etc.) is involved, and no assumption is made on the nature of the direct interactions (coulombic, van der Waals, hard-sphere, etc.) [7]. For this reason, they have made a significant contribution to our fundamental understanding of the dynamics of colloidal dispersions, by providing the theoretical interpretation of self-diffusion experiments (or simulations), in model systems such as polyball suspensions [3] and concentrated hard-sphere suspensions (where hydrodynamic interactions are also important) [6]. Furthermore, the extension of these results to polydisperse suspensions have allowed their application to tracer-diffusion in colloidal mixtures [8], and to the description of electrolyte friction effects [9]. However, these results still involve one important restriction, namely, all the pairwise direct forces are assumed to be radially symmetric, and hence, no expression analogous to Eq. (1) exists, applicable to nonspherical tracer particles. The only exception is the description of the *translational* Brownian motion of nonspherical particles interacting with other particles assumed spherical, provided by the generalized Langevin equation (GLE) approach [9], and employed in the description of the electrolyte friction effects on the translational diffusion of a rodlike polyion (tobacco mosaic virus, TMV) [10]. Besides translating, however, a nonspherical tracer particle also executes *rotational* Brownian motion, which is also afected by the direct interactions with other particles diffusing around it. Tracer-diffusion experiments involving nonspherical labeled tracer particles may include phenomena such as the Brownian motion of a rodlike polyion interacting with its own electrical double layer (electrolyte friction), or with other (spherical or not) charged colloidal particles, and self-diffusion in ferrofluids. For this more general class of phenomena, there is a total absence of simple expressions similar to Eq. (1) for quantities such as the rotational diffusion coefficient. The reason for this derives in part from the mathematical complexity of the description of rotational Brownian motion [11], even in the absence of direct interactions with other particles. Thus, a statistical mechanical approach is needed, whose fundamental and general character does not prevent the introduction of sensible approximations leading to results of the quality and practical use as Eq. (1). In this letter we show that the GLE [7] approach lends itself precisely to this purpose.

Here we address mostly the general aspects of this theory, which in principle describes the effects of the direct interactions on the translational *and* rotational Brownian motion of a *nonspherical* tracer particle interacting with other, in general non-spherical, particles. We show, for example, that, upon the introduction of an adequate extended notation, the general results of the theory [Eqs. (4a) and (4b)] are remarkably similar to those of the previous version referring only to suspensions of spherical particles [7]. Thus, the next task is to introduce approximations that render these general results useful in practice. This we do for a simple but interesting generic case, namely, a translating-rotating nonspherical tracer particle interacting with other spherical particles, for which case we end up with general approximate expresions, analogous to Eq. (1) (which then happens to follow as a particular case). In order to illustrate its use down to specific results, here we describe its application to two simple model systems, namely, the rotational diffusion of a Brownian electric dipole interacting with a Brownian one-component plasma, and the problem of rotational electrolyte friction of a rodlike polyion (tobacco mosaic virus). Let us first start our discussion with the general aspects of our theory.

Consider a nonspherical tracer particle in a suspension of other nonspherical particles belonging to species $\alpha=1,2,\ldots,\nu$, present at bulk concentration n_α. Let $\psi_\alpha(\mathbf{r},\Omega)$ be the potential energy of the direct interactions between the tracer and one of such particles of species α located at position $\mathbf{r}$ relative to the tracer's center of mass, and with principal axis rotated by a rotation Ω with respect to the orientation of the tracer particle [represented, for example, by the three Euler angles $\Omega=(\phi,\theta,\chi)$]. Let $n_\alpha(\mathbf{r},\Omega;t)$ be the instantaneous local concentration of particles of species α for the configuration $\mathbf{r}_i^{(\alpha)}(t)$, $\Omega_i^{(\alpha)}(t)$ ($i=1,\ldots,N_\alpha$; $\alpha=1,\ldots,\nu$; N_α=number of particles of species α) of the other particles, whose equilibrium ensemble average $n_\alpha^{eq}(\mathbf{r},\Omega)\equiv\langle n_\alpha(\mathbf{r},\Omega;t)\rangle$ equals n_α/Ω far from the tracer particle ($\Omega=\int d\Omega$). Then, one can show that if the total interaction energy is pairwise additive, the instantaneous total direct force $\mathbf{F}(t)$ and total direct torque $\mathbf{T}(t)$ on the tracer particle exerted by all the other particles can be written *exactly* as

$$\mathbf{F}(t)=\Sigma_{\alpha=1}^{\nu}\int d\mathbf{r}\int d\overline{\Omega}[\nabla\psi_\alpha(\mathbf{r},\overline{\Omega})]n_\alpha(\mathbf{r},\overline{\Omega};t)$$

and

$$\mathbf{T}(t)=\Sigma_{\alpha=1}^{\nu}\int d\mathbf{r}\int d\overline{\Omega}[\boldsymbol{\nabla}_{ROT}\psi_\alpha(\mathbf{r},\overline{\Omega})]n_\alpha(\mathbf{r},\overline{\Omega};t)$$

with $\boldsymbol{\nabla}_{ROT}\equiv\mathbf{r}\times\boldsymbol{\nabla}+\boldsymbol{\nabla}_\Omega$, $\boldsymbol{\nabla}_\Omega$ being the angular gradient operator [12]. On the other hand, let $\mathbf{V}(t)$ and $\mathbf{W}(t)$ be the linear and angular velocity of the tracer observed from the laboratory, but with components referred to a cartesian system with origin fixed to the laboratory, but whose orientation coincides instantaneously with the orientation of the principal axis of the tracer particle. Then, ignoring kinetic terms quadratic in $\mathbf{V}(t)$ and $\mathbf{W}(t)$ [11], the time-evolution equation for $\mathbf{V}(t)$ and $\mathbf{W}(t)$ can be written, grouping the components of $\mathbf{V}(t)$ and $\mathbf{W}(t)$ in a single vector $\vec{\mathbf{V}}(t)=(\mathbf{V}(t),\mathbf{W}(t))$, as

$$\overleftrightarrow{M}\cdot\frac{d\vec{\mathbf{V}}(t)}{dt}=-\overleftrightarrow{\zeta}^{s}\cdot\vec{\mathbf{V}}(t)+\vec{\mathbf{f}}(t)+[\vec{\nabla}\underline{\psi}]\circ\delta\underline{n}(t) \tag{2}$$

where, with similar notation, $\vec{\nabla}=(\boldsymbol{\nabla},\boldsymbol{\nabla}_{ROT})$, $\overleftrightarrow{M}_{ij}=M\delta_{ij}$ ($i,j=1,2,3$), $\overleftrightarrow{M}_{ij}=\delta_{ij}I_{i-3}$ ($i,j=4,5,6$), with M, I_1, I_2, I_3 being the mass and principal moments of inertia of the tracer particle, and $\overleftrightarrow{\zeta}_{ij}^{s}$ ($i,j=1,2,\ldots,6$) being the friction coefficients coupling the solvent force and torque with the linear and angular velocity, and where $\vec{\mathbf{f}}(t)$ groups the corresponding random force and torque. The last term in Eq.(2) is just ($\mathbf{F}(t)$, $\mathbf{T}(t)$), in which we introduced the inner product "$\circ$" (which denotes "$\Sigma_{\alpha=1}^{\nu}\int d\mathbf{r}\int d\Omega$") between the "vectors" $\underline{\psi}$ and $\delta\underline{n}(t)$ with "components" $\psi_\alpha(\mathbf{r},\Omega)$ and $\delta n_\alpha(\mathbf{r},\Omega;t)$ [$\equiv n_\alpha(\mathbf{r},\Omega;t)-n_\alpha^{eq}(\mathbf{r},\Omega)$], and where we have recognized that $n_\alpha^{eq}(\mathbf{r},\Omega)$ does not contribute to the total force and torque.

Equation (2) is the basis of our theory, and expresses a very simple physical idea: the force and the torque on the tracer due to *direct* interactions can be written *exactly* as a linear function of the instantaneous fluctuations $\delta n_\alpha(\mathbf{r},\overline{\Omega};t)$ of the local concentration, whereas the force and torque exerted by the solvent can be written just as in the ordinary Langevin equation, i.e., as a dissipative plus a random term, the latter assumed to have zero mean and time-correlation function given by $\langle\vec{\mathbf{f}}(t)\vec{\mathbf{f}}(0)\rangle=k_BT\overleftrightarrow{\zeta}^{s}2\delta(t)$. In the present theory, the friction coefficients $\overleftrightarrow{\zeta}_{ij}^{s}$ enter as phenomenological parameters, determined either experimentally or from external theoretical considerations or assumptions. At the moment, we focus on the term representing direct interactions. Since $[d\vec{\mathbf{V}}(t)/dt]$ couples to $\delta\underline{n}(t)$, we need a time-evolution equation for the latter. For this, one appeals to the principles of the linear irreversible thermodynamic theory of fluctuations [7,13,14], which allow us to write the structure of the most general (and exact) time evolution equation for $\delta n_\alpha(\mathbf{r},\Omega;t)$ consistent with Eq. (2) above (in the sense explained in Ref. [7]). Such an equation, together with Eq. (2) itself, constitute a closed system of stochastic equations describing the coupled time evolution equation of $\vec{\mathbf{V}}(t)$ and $\delta\underline{n}(t)$. Eliminating $\delta\underline{n}(t)$ from this description [7] finally leads to the desired GLE

$$\overleftrightarrow{M}\cdot\frac{d\vec{\mathbf{V}}(t)}{dt}=-\overleftrightarrow{\zeta}^{s}\cdot\vec{\mathbf{V}}(t)+\vec{\mathbf{f}}(t)-\int_0^t\Delta\overleftrightarrow{\zeta}(t-t')\cdot\vec{\mathbf{V}}(t')dt'+\vec{\mathbf{j}}(t) \tag{3}$$

with $\vec{\mathbf{j}}(t)$ grouping a random force and torque on the tracer, which turns out to have zero mean and time-correlation function given by $\langle\vec{\mathbf{j}}(t)\vec{\mathbf{j}}(0)\rangle=k_BT\Delta\overleftrightarrow{\zeta}(t)$, and with the time-dependent friction function given by $\Delta\overleftrightarrow{\zeta}(t)=\beta[\vec{\nabla}\underline{\psi}]\circ C(t)\circ[\vec{\nabla}\underline{\psi}]$, with $C(t)$ being the matrix of van Hove functions, $C_{\alpha\beta}(\mathbf{r},\Omega,\mathbf{r}',\Omega';t)\equiv\langle\delta n_\alpha(\mathbf{r},\Omega;t)\delta n_\beta(\mathbf{r}',\Omega';0)\rangle$, *referred to the tracer's position and orientation*. Thus, $C(t)$ is the solution of the linearized diffusion equation that governs the *diffusive* relaxation of $\delta n_\alpha(\mathbf{r},\Omega;t)$, as described from the tracer's reference frame, and whose initial condition is $C(0)=\langle\delta\underline{n}(0)\delta\underline{n}(0)\rangle\equiv\sigma$. Thus, the matrix σ is the static correlation of the variables $\delta n_\alpha(\mathbf{r},\Omega;t)$. The matrices $C(t)$ and σ define the collective-diffusion propagator as $\chi(t)\equiv C(t)\circ\sigma^{-1}$, where σ^{-1} is the inverse of σ in the sense that $\sigma^{-1}\circ\sigma=U$, $U_{\alpha\beta}(\mathbf{r},\Omega,\mathbf{r}',\Omega')=\delta_{\alpha\beta}\delta(\mathbf{r}-\mathbf{r}')\delta(\Omega-\Omega')$. In terms of $\chi(t)$, this result for $\Delta\overleftrightarrow{\zeta}(t)$ can be written in two alternative equivalent forms, by means of the extended version of the exact (Wertheim-Lovett's) equation [7,15], $[\vec{\nabla}\underline{\psi}]=-k_BT\sigma^{-1}\circ[\vec{\nabla}\underline{n}^{eq}]$, which read

$$\Delta\overleftrightarrow{\zeta}(t)=\beta[\vec{\nabla}\underline{\psi}]\circ\chi(t)\circ\sigma\circ[\vec{\nabla}\underline{\psi}], \tag{4a}$$

$$\Delta\overleftrightarrow{\zeta}(t)=k_BT[\vec{\nabla}\underline{n}^{eq}]\circ\sigma^{-1}\circ\chi(t)\circ[\vec{\nabla}\underline{n}^{eq}]. \tag{4b}$$

Equations (3) and (4) are the most general and important results of the present theory. With the notation employed to write them, they are remarkably similar to the corresponding results of the original GLE theory [7], in which only translational diffusion of spherical tracers was considered. If $\overleftrightarrow{\zeta}^{s}$ were provided, and if we could evaluate $\Delta\overleftrightarrow{\zeta}(t)$, other tracer-diffusion properties could be calculated, and compared with experimental measurements. Thus, the relevance of these general results now depends on the actual possibility of evaluating $\Delta\overleftrightarrow{\zeta}(t)$ starting from either of Eqs.(4). This result is exact, and writes $\Delta\overleftrightarrow{\zeta}(t)$ in terms only of the equilibrium static quantities $\underline{\psi}$, $\underline{n}^{eq}$ and σ, and of the collective propagator $\chi(t)$. The static properties are in principle amenable to experimental measurement or to theoretical calculation. In contrast, $\chi(t)$ is conceptually a well defined object, but its determination does not seem straighforward even in principle. Thus, sooner or latter we have to resort to some form of approximation or assumption for this quantity, with the hope that even a simple but sensible guess for $\chi(t)$ will lead to reasonably accurate results for $\Delta\overleftrightarrow{\zeta}(t)$. There is not, however, a unique and systematic manner to approximate $\chi(t)$, and different ansatz will lead to different results for $\Delta\overleftrightarrow{\zeta}(t)$. At this early stage of development of the present theory, we can only illustrate the manner to proceed, by adopting the simplest approximation for $\chi(t)$, namely, Fick's diffusion approximation. This is defined by $\chi(t)=\exp[-L\circ\sigma^{-1}t]$, with $L_{\alpha\beta}(\mathbf{r},\overline{\Omega},\mathbf{r}',\overline{\Omega}') = \delta_{\alpha\beta}\vec{\nabla}^*\cdot\overleftrightarrow{D}_\alpha^* n_\alpha^{eq}(\mathbf{r},\overline{\Omega})\cdot\vec{\nabla}^*\delta(\mathbf{r}-\mathbf{r}')\delta(\overline{\Omega}-\overline{\Omega}')$, in which $\vec{\nabla}^*=(\boldsymbol{\nabla},\mathbf{r}\times\boldsymbol{\nabla})$, and $\overleftrightarrow{D}_\alpha^*$ are phenomenological parameters, for which a sensible assumption must be made. If we adopt this or a similar closure, we finally have a closed expression for $\Delta\overleftrightarrow{\zeta}(t)$ in terms only of the static quantities $\underline{\psi}$, $\underline{n}^{eq}$ and σ, and of the phenomenological parameters $\overleftrightarrow{\zeta}^s$ and $\overleftrightarrow{D}_\alpha^*$. In this manner, we have established an approximate, but completely general connection between equilibrium static properties and the dynamic properties describing tracer-diffusion of nonspherical particles.

The practical application of the general results above to specific systems and conditions is still not straightforward, mainly because the determination of $\underline{n}^{eq}$ and σ constitutes by itself a highly nontrivial statistical mechanical problem [12,16]. Thus, at this stage, we can only illustrate the type of results that can be obtained from our theory by restricting ourselves to the simplest nontrivial generic case, with the purpose of illustrating the protocol to be followed in particular applications. With this aim, let us consider from now on the most symmetric but still important case, in which the tracer particle is nonspherical, but is axisymmetric, and the other particles are spherical. In addition, let us approximate σ and $\chi(t)$ by their value far from the tracer particle (homogeneity approximation). For axisymmetric tracers interacting with spheres, $\Delta\overleftrightarrow{\zeta}(t)$ in Eq.(4b) turns out to be diagonal, with $\Delta\zeta_{11}=\Delta\zeta_{22}=\Delta\zeta_\perp$, $\Delta\zeta_{33}=\Delta\zeta_\parallel$, $\Delta\zeta_{44}=\Delta\zeta_{55}=\Delta\zeta_{ROT}$ and $\Delta\zeta_{66}=0$. The use of the homogeneity approximation allows us to rewrite Eq.(4b) in terms of the nonzero elements of $\Delta\overleftrightarrow{\zeta}(t)$ as

$$\Delta\zeta_i(t)=\frac{k_BTn}{(2\pi)^3}\int d^3k f_i(\mathbf{k})\frac{\chi(k,t)}{S(k)}f_i(\mathbf{k}) \tag{5}$$

with $f_i(\mathbf{k})=k_xh(\mathbf{k})$ $(i=\perp)$, $k_zh(\mathbf{k})$ $(i=\parallel)$, and $[\mathbf{k}\times\boldsymbol{\nabla}_\mathbf{k}h(\mathbf{k})]_x$ $(i=ROT)$, where $h(\mathbf{k})$ is the Fourier transform (FT) of $h(\mathbf{r})\equiv n^{eq}(\mathbf{r})/n-1$, $S(k)$ the static structure factor of the fluid of spheres, i.e, the FT of $\sigma(|\mathbf{r}-\mathbf{r}'|)/n$, and $\chi(k,t)$ is the FT of $\chi(|\mathbf{r}-\mathbf{r}'|;t)$. We only display the results for a monodisperse suspension of spheres; the extension to mixtures $(\nu>1)$ is straightforward. In order to use Eq. (5) for specific calculations we require approximating $\chi(k;t)$. We adopt Fick's approximation, which for our case reads

$$\chi(k,t)=\exp[-k^2D^*t/S(k)]. \tag{6}$$

Equation (5) is still quite general for the generic system considered, and only involves the approximation of homogeneity. Along with Fick's approximation, Eq. (5) now writes $\Delta\zeta_i(t)$ in terms only of the structure factor of the host suspension and of the local concentration $\underline{n}^{eq}$ of spheres around the tracer. The only other input required is D^*, a simple proposal for which, is to write $D^*=D_1^s+\overline{D}_{c.m.}^s$, with D_1^s being the short-time diffusion coefficient of the spheres, and $\overline{D}_{c.m.}^s$ being the short-time mean diffusion coefficient of the tracer's center of mass. Eq. (5) with (6) constitute the extention of Eq. (1), as we now see.

We are now ready to apply the approximate but general results in Eqs. (5) and (6) to specific systems. But before proceeding, let us mention that Eq. (5) alone fulfills a nice and simple self-consistency test. Consider first the particular case in which the tracer particle is also spherical. Then, from Eq. (5) we find that $\Delta\zeta_{ROT}(t)=0$, and that $\Delta\zeta_\perp(t)=\Delta\zeta_\parallel(t)\equiv\Delta\zeta^{sph}(t)$. From $\Delta\zeta^{sph}(t)$ one can then calculate the other relevant tracer-diffusion properties of the spherical tracer, in particular its long-time tracer-diffusion coeficient $D^L\equiv k_BT/[\zeta^s+\Delta\zeta^{sph}]$, with $\Delta\zeta^{sph}=\int_0^\infty dt\Delta\zeta^{sph}(t)$. [In fact, if the tracer is identical to the other spheres, this result is precisely Eq. (1).] Let us now imagine that two of these spherical tracers are now rigidly bound to each other to constitute a dumbbell, with a center-to-center distance l. Now consider that this is our non-spherical tracer particle, diffusing in the same host suspension of spheres. If l is sufficiently large, $n^{eq}(\mathbf{r})\approx ng(|\mathbf{r}-(l/2)\hat{\mathbf{z}}|)g(|\mathbf{r}+(l/2)\hat{\mathbf{z}}|)$, where $n_{sph}^{eq}(r)=ng(r)$ is the local concentration of host spheres around a single sphere of the type in the dumbbell. Using this result for $n^{eq}(\mathbf{r})$ in Eq. (5), we find that the functions $\Delta\zeta_i(t)$ for the long dumbbell can be expressed, to leading order in l^{-1}, in terms of $\Delta\zeta^{sph}(t)$ for a single sphere. In particular, we find that the dumbbell's static friction coefficients $\Delta\zeta_i\equiv\int_0^\infty\Delta\zeta_i(t)dt$ are given, in terms of $\Delta\zeta^{sph}$, by $\Delta\zeta_\perp=\Delta\zeta_\parallel=2\Delta\zeta^{sph}$, and $\Delta\zeta_{ROT}=(l^2/2)\Delta\zeta^{sph}$. This result is, however, intuitively expected.

Now let us apply the generic results above to a relatively simple and idealized problem, to illustrate the use of the present theory down to specific results. Consider a point electric dipole of magnitude μ embedded in a hard sphere of radius a, which diffuses with a short-time friction coefficient ζ^s, in a suspension of charged spheres modelled by the Brownian one-component plasma (BOP), i.e., pointlike particles of charge Q in a rigid background of opposite charge to ensure electroneutrality. Although pointlike with respect to interactions [their pair potential is just $u(r)=Q^2/r$], we assume that their short-time diffusion coefficient D^0 is finite. Within the Debye-Hückel approximation for this system, $S(k)$ and $n^{eq}(\mathbf{r})$ can be calculated analytically, thus allowing us to evaluate the integrals in Eq. (5) with (6). The results for $\Delta\zeta_i(t)$ cannot be expressed in closed analytic form, although they are reduced to quadratures. For the static friction coefficients, however, we find that

$$\Delta\zeta_{\perp}=\frac{1}{3}\Delta\zeta_{\parallel}=\frac{\mu^2}{30D^*a^3}\,\frac{(\kappa a)^2(2+\kappa a)}{[1+\kappa a+(\kappa a)^2/3]^2}\,, \tag{7}$$

$$\Delta\zeta_{ROT}=\frac{\mu^2}{9D^*a}\,\frac{\kappa a(2/3+\kappa a)}{[1+\kappa a+(\kappa a)^2/3]^2}\,, \tag{8}$$

where $\kappa=\sqrt{4\pi\beta n Q^2}$ is the inverse Debye length and $D^*=D^0+D_T^0$ ($D_T^0=k_BT/\zeta^s$). Let us mention that the same result is obtained if instead of the BOP we consider a point-like model of an electrolyte (Brownian *multi*component plasma), only that now $\kappa=\sqrt{4\pi\beta\Sigma_{\alpha=1}^{\nu}n_\alpha q_\alpha^2/\epsilon}$, q_α being the charge of ions of species α and ϵ the dielectric constant of the solvent. Thus, if a tracer particle of radius a bears an electric dipole of magnitude μ, and diffuses in an electrolyte solution, Eqs. (7) and (8) allow us to calculate the effect of the friction due to the interaction between the dipole and its electrical double layer (electrolyte friction) on the translational and rotational diffusion coefficients.

We have also calculated the electrolyte friction effects on another simple but experimentally more relevant model nonspherical tracer particle, namely, a hard ellipsoid with a line of charge between its foci. The results of the present theory, at the same level of approximation as the previous example (homogeneity, Fick's diffusion, and Debye-Hückel approximations), cannot be written in closed analytic form [17]. For $\Delta\zeta_{\perp}$ and $\Delta\zeta_{\parallel}$, however, we recover the results of Vizcarra-Rendon *et al.* [9], which already have been compared with experimental measurements of the (average) translational diffusion coefficient $D_{c.m.}$ of the tobacco mosaic virus (TMV) [10]. The result for $\Delta\zeta_{ROT}$ can be written as $\Delta\zeta_{ROT}=Q^2a'G(\kappa b,\phi)/12\epsilon D^*$ where Q is the total charge along the distance $2a'$ between the foci of the ellipsoid, whose minor and major semiaxis are b and $a(=\phi b)$. The dependence on the (electrolyte) ionic charge and concentration is only through the function $G(\kappa b,\phi)$, defined in detail elsewhere [17], which has a maximun at a certain value κ_m of the inverse Debye length κ. Applied to TMV, this result predicts a deviation of $D_{ROT}\equiv k_BT/(\zeta_{ROT}^0+\Delta\zeta_{ROT})$ from its value $D_{ROT}^0\equiv k_BT/\zeta_{ROT}^0$ which is stronger than that predicted (and observed [10]) for the translational diffusion coefficient $D_{c.m.}$, and which occurs at an electrolyte concentration around 10 times larger. These are rather distinct quantitative predictions whose experimental testing is certainly accessible [10].

We are also in the process of applying the GLE theory to the description of translational and rotational diffusion of a rodlike tracer particle (e.g., TMV) in a suspension of highly charged colloidal particles (e.g., polyballs). Similarly we are extending the realm of the practical applications of this general theory to the simplest example of a less symmetric generic case, namely, self-diffusion in a model ferrofluid (a Brownian dipolar fluid), in which case the particles around the tracer interact through a nonradially symmetric potential. In both cases we pretend to compare first with Brownian dynamics simulations, but we believe that there are no fundamental difficulties for the eventual comparison with the measurement of these effects in real experimental systems. We consider, however, that already the general results and the specific illustrations presented here constitute an important step in the process of building a solid theoretical description of the effects of the direct interactions on the Brownian motion of nonspherical tracer particles.

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