

## Orientational relaxation in a colloidal suspension of spheres

B. U. Felderhof

*Institut für Theoretische Physik A, Rheinisch-Westfälische Technische Hochschule Aachen, Templergraben 55,  
52056 Aachen, Germany*

R. B. Jones

*Department of Physics, Queen Mary and Westfield College, Mile End Road, London E1 4NS, Great Britain*

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We study orientational relaxation in a colloidal suspension of spheres on the basis of the generalized Smoluchowski equation. The time dependence of the polarization correlation function is characterized by a wave-vector- and frequency-dependent rotational-diffusion tensor. In the absence of hydrodynamic interactions the short-time decay of the correlation function is governed by free translational and rotational diffusion. This observation leads to a simple expression for the high-frequency limit of the rotational-diffusion tensor. We also derive a concise and transparent expression for the wave-vector- and frequency-dependent rotational-diffusion tensor of a semidilute suspension.

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### I. INTRODUCTION

Orientational relaxation is an important feature of the dynamics of liquids. It governs the frequency dependence of the dielectric constant of polar liquids [1], and manifests itself in nuclear magnetic resonance, Raman scattering, and other instances [2]. A liquid suspension of spheres constitutes a useful model for the study of orientational relaxation. In such a system inertial effects may be neglected. On a slow time scale the dynamics of the macroparticles is governed by translational and rotational diffusion [3]. The time dependence of the configurational probability distribution is described by a generalized Smoluchowski equation [4–7]. Ferrofluids consist of ferromagnetic particles suspended in a liquid [8], and constitute an important example of the system under study.

In this paper we consider general features of orientational relaxation of a single particle, as well as collective reorientation, on the basis of the generalized Smoluchowski equation. The time dependence of the polarization correlation function is characterized by a wave-vector- and frequency-dependent diffusion tensor. We show that in the absence of hydrodynamic interactions the initial decay of the correlation function is governed by free translational and rotational diffusion. This observation leads to a simple expression for the high-frequency limit of the rotational-diffusion tensor. The result is important, because it shows that the short-time relaxation time depends strongly on wave vector, and may be calculated from the equilibrium structure. Though the expression for the short-time rotational-diffusion tensor is a straightforward generalization of an analogous expression for translational diffusion [4,6], it seems not to have been derived before.

We also derive a concise and transparent expression for the wave-number- and frequency-dependent rotational-diffusion tensor of a semidilute suspension. For such a

suspension the diffusion tensor may be calculated from a solution of the pair Smoluchowski equation.

The theory of orientational relaxation in dipolar liquids has been reviewed by Adelman and Deutch [9], Böttcher and Bordewijk [1], McConnell [10], Alder and Pollock [11], Madden and Kivelson [12], and Bagchi and Chandra [13]. More general aspects have been discussed by Madden [14] and Hansen and McDonald [15]. We generally follow the latter monograph in our notation.

Brilliantov *et al.* [16] have determined a concentration-dependent rotational-diffusion coefficient of spherical proteins from nuclear-magnetic-resonance measurements. Recently it has become possible to measure the rotational-diffusion constant more directly by depolarized light scattering from a suspension of spherical particles with intrinsic optical anisotropy [17–19].

### II. TRANSLATIONAL AND ROTATIONAL DIFFUSION

We consider  $N$  spherical particles of radius  $a$  immersed in an incompressible fluid of shear viscosity  $\eta$  and at temperature  $T$ . The whole system is enclosed in a volume  $\Omega$ . The orientation of a sphere is indicated by the direction of a unit vector at its center. The translational-diffusion coefficient of a single sphere is  $D_0 = k_B T / 6\pi\eta a$ , and its rotational-diffusion coefficient is  $D_R = k_B T / 8\pi\eta a^3$ . The spheres interact via a direct pair potential which depends on orientation. In addition there may be many-body hydrodynamic interactions mediated by the Stokes flow response of the solvent fluid to the motion of the suspended macroparticles. If  $\mathbf{R}_i$  denotes the position of the center of the  $i$ th sphere, and  $\mathbf{u}_i$  its orientation, then the locations of all spheres are described by the  $3N$ -dimensional vector  $\mathbf{X}_T = (\mathbf{R}_1, \dots, \mathbf{R}_N)$ , and the orientations are described by the  $3N$ -dimensional vector  $\mathbf{X}_R = (\mathbf{u}_1, \dots, \mathbf{u}_N)$ . The total configuration is summa-

rized in the  $6N$ -dimensional vector  $\mathbf{X}=(\mathbf{X}_T, \mathbf{X}_R)$ , corresponding to  $5N$  degrees of freedom.

We consider an ensemble of configurations  $\mathbf{X}$ , described by a time-dependent probability distribution  $P(\mathbf{X}, t)$ , which obeys the generalized Smoluchowski equation [4–7]. In abbreviated form this reads

$$\frac{\partial P}{\partial t} = \mathcal{D}P, \quad (1)$$

where  $\mathcal{D}$  is the Smoluchowski operator defined by

$$\mathcal{D}P = \frac{\partial}{\partial \mathbf{X}} \cdot \mathbf{D} \cdot \left[ \frac{\partial P}{\partial \mathbf{X}} + \beta \frac{\partial \Phi}{\partial \mathbf{X}} P \right]. \quad (2)$$

Here  $\mathbf{D}(\mathbf{X})$  is the  $6N \times 6N$  diffusion matrix, which depends on configuration due to hydrodynamic interactions. Furthermore,  $\beta = 1/k_B T$  and the potential  $\Phi(\mathbf{X})$  incorporates both a wall potential and direct pair interactions. The rotational part of the gradient operator is defined as  $\partial/\partial \mathbf{X}_R = (\partial/\partial \mathbf{u}_1, \dots, \partial/\partial \mathbf{u}_N)$  with

$$\frac{\partial}{\partial \mathbf{u}_j} = \mathbf{e}_{\theta_j} \frac{\partial}{\partial \theta_j} + \mathbf{e}_{\varphi_j} \frac{1}{\sin \theta_j} \frac{\partial}{\partial \varphi_j}, \quad (3)$$

in spherical coordinates  $(\theta_j, \varphi_j)$  with corresponding unit vectors  $\mathbf{e}_{\theta_j}$  and  $\mathbf{e}_{\varphi_j}$ . Alternatively, the rotational diffusion may be expressed [2,3,20] with the aid of operators  $\mathbf{L}_j = \mathbf{u}_j \times (\partial/\partial \mathbf{u}_j)$ . The concise form (2) is convenient for formal calculation. The Smoluchowski equation (1) describes how the distribution function  $P(\mathbf{X}, t)$  tends to the equilibrium distribution

$$P_{\text{eq}}(\mathbf{X}) = \exp[-\beta \Phi(\mathbf{X})] / Z(\beta) \quad (4)$$

in the course of time. The partition function  $Z(\beta)$  normalizes the distribution to unity.

We consider thermal-equilibrium fluctuations of polarization at wave vector  $\mathbf{k}$ . The corresponding variable is

$$\mathbf{M}(\mathbf{k}) = \mu \sum_{j=1}^N \mathbf{u}_j e^{-i\mathbf{k} \cdot \mathbf{R}_j}, \quad (5)$$

where  $\mu$  is the dipole strength. The time-dependent orientational scattering function is defined by

$$\mathbf{F}_R(\mathbf{k}, t) = \lim_{\substack{N \rightarrow \infty \\ \Omega \rightarrow \infty}} \frac{1}{N} \langle \mathbf{M}(\mathbf{k}, t) \mathbf{M}(-\mathbf{k}) \rangle, \quad (6)$$

where the time dependence is governed by the adjoint Smoluchowski operator  $\mathcal{L}$  such that

$$\mathbf{M}(\mathbf{k}, t) = \exp(\mathcal{L}t) \mathbf{M}(\mathbf{k}, 0), \quad \mathbf{M}(\mathbf{k}, 0) = \mathbf{M}(\mathbf{k}). \quad (7)$$

The operator  $\mathcal{L}$  is given by

$$\mathcal{L} = \left[ \frac{\partial}{\partial \mathbf{X}} - \beta \frac{\partial \Phi}{\partial \mathbf{X}} \right] \cdot \mathbf{D} \cdot \frac{\partial}{\partial \mathbf{X}}. \quad (8)$$

The angle brackets in Eq. (6) indicate an average over the equilibrium distribution (4). Finally, we take the thermodynamic limit  $N \rightarrow \infty$ ,  $\Omega \rightarrow \infty$  at constant  $n_0 = N/\Omega$ . In the absence of applied fields, the system is homogeneous and isotropic in the thermodynamic limit.

The one-sided Fourier transform of the scattering function is given by

$$\mathbf{G}_R(\mathbf{k}, \omega) = n_0 \int_0^\infty e^{i\omega t} \mathbf{F}_R(\mathbf{k}, t) dt. \quad (9)$$

From Eqs. (6) and (7) we find the expression

$$G_{R\alpha\beta}(\mathbf{k}, \omega) = \lim_{\substack{N \rightarrow \infty \\ \Omega \rightarrow \infty}} \frac{-1}{\Omega} \langle M_\beta(-\mathbf{k})(i\omega + \mathcal{L})^{-1} M_\alpha(\mathbf{k}) \rangle. \quad (10)$$

In linear-response theory, the polarization response to an applied field, varying as a plane wave with wave vector  $\mathbf{k}$  and frequency  $\omega$ , is described by the dimensionless susceptibility tensor  $\chi^0(\mathbf{k}, \omega)$ . This is related to the tensor in Eq. (9) by

$$\chi^0(\mathbf{k}, \omega) = \chi^0(\mathbf{k}, 0) + i\omega \beta \mathbf{G}_R(\mathbf{k}, \omega). \quad (11)$$

The zero-frequency susceptibility is given by

$$\chi^0(\mathbf{k}, 0) = \frac{\beta}{\Omega} \langle \mathbf{M}(\mathbf{k}) \mathbf{M}(-\mathbf{k}) \rangle. \quad (12)$$

Here and in the following the thermodynamic limit is understood. In the case of electric- or magnetic-dipole interactions one requires the response of the polarization to the average Maxwell field, rather than the applied field. The corresponding susceptibility tensor is given by

$$\chi(\mathbf{k}, \omega) = \chi^0(\mathbf{k}, \omega) [1 - 4\pi \hat{\mathbf{k}} \hat{\mathbf{k}} \cdot \chi^0(\mathbf{k}, \omega)]^{-1}, \quad (13)$$

where  $\hat{\mathbf{k}} = \mathbf{k}/k$ .

From the isotropy of the system it follows that the susceptibility tensor takes the form

$$\chi^0(\mathbf{k}, \omega) = \chi_l^0(k, \omega) \hat{\mathbf{k}} \hat{\mathbf{k}} + \chi_t^0(k, \omega) (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}). \quad (14)$$

For systems with dipolar interactions the tensor  $\chi(\mathbf{k}, \omega)$  takes the same form, as follows from Eq. (13). The scalar susceptibilities are related by

$$\chi_l(k, \omega) = \frac{\chi_l^0(k, \omega)}{1 - 4\pi \chi_l^0(k, \omega)}, \quad \chi_t(k, \omega) = \chi_t^0(k, \omega). \quad (15)$$

For systems with short-range interactions the longitudinal and transverse susceptibilities are equal in the long-wavelength limit,

$$\chi_l^0(0, \omega) = \chi_t^0(0, \omega). \quad (16)$$

For systems with dipolar interactions one has instead

$$\chi_l(0, \omega) = \chi_t(0, \omega). \quad (17)$$

In Eqs. (16) and (17) it is understood that the thermodynamic limit is taken before the limit  $k \rightarrow 0$ .

At zero frequency

$$\chi_l^0(k, 0) = \frac{1}{3} \beta n_0 \mu^2 S_l(k), \quad \chi_t^0(k, 0) = \frac{1}{3} \beta n_0 \mu^2 S_t(k), \quad (18)$$

where  $S_l(k)$  and  $S_t(k)$  are longitudinal and transverse static structure factors. In conventional notation

$$\begin{aligned} S_l(k) &= 1 + \frac{1}{3} n_0 [\hat{h}_\Delta(k) + 2\bar{h}_D(k)], \\ S_t(k) &= 1 + \frac{1}{3} n_0 [\hat{h}_\Delta(k) - \bar{h}_D(k)], \end{aligned} \quad (19)$$

where  $\hat{h}_\Delta(k)$  is the Fourier transform of the pair-correlation function  $h_\Delta(r)$ , and  $\hat{h}_D(k)$  is the Hankel transform of the pair-correlation function  $h_D(r)$ , as defined in Hansen and McDonald [15].

We shall also study the single-particle orientational time-correlation function

$$C^{(1)}(t) = \langle \mathbf{u}_1(t) \cdot \mathbf{u}_1(0) \rangle, \quad (20)$$

where the time dependence is governed by the adjoint Smoluchowski operator, as in Eq. (7).

### III. RELAXATION TIMES

In this section we recall formal definitions of relaxation times characterizing the process of reorientation. We consider first reorientation of a single particle, and subsequently collective reorientation.

The integral correlation time  $\tau_1$  is defined by

$$\tau_1 = \int_0^\infty C^{(1)}(t) dt. \quad (21)$$

From Eq. (20) we find the formal expression

$$\tau_1 = -\langle \mathbf{u}_1 \cdot \mathcal{L}^{-1} \mathbf{u}_1 \rangle. \quad (22)$$

More generally, we may consider the one-sided Fourier transform of the time-correlation function

$$\hat{C}^{(1)}(\omega) = \int_0^\infty e^{i\omega t} C^{(1)}(t) dt, \quad (23)$$

and define a frequency-dependent relaxation time  $\tau_S(\omega)$  from the expression

$$\hat{C}^{(1)}(\omega) = \frac{1}{-i\omega + \tau_S^{-1}(\omega)}. \quad (24)$$

Clearly  $\tau_1 = \tau_S(0)$ .

It follows from the generalized Smoluchowski equation that at short times the correlation function  $C^{(1)}(t)$  decays linearly with time. Evaluating the time derivative at  $t=0$  one finds for the high-frequency limit of  $\tau_S(\omega)$

$$\tau_S^S \equiv \tau_S(\infty) = \frac{-1}{\langle \mathbf{u}_1 \cdot \mathcal{L} \mathbf{u}_1 \rangle}. \quad (25)$$

In general, the short-time relaxation time  $\tau_S^S$  differs from the integral relaxation time  $\tau_1$ .

Analogous relaxation times may be defined for collective reorientation. On the basis of the generalized Smoluchowski equation the time evolution of the orientational scattering function may be expressed by means of the equation of motion

$$\frac{d\mathbf{F}_R(\mathbf{k}, t)}{dt} = -2\mathbf{D}_R^S \mathbf{F}_R(\mathbf{k}, t) - \int_0^t \mathbf{M}_R(\mathbf{k}, t-t') \mathbf{F}_R(\mathbf{k}, t') dt', \quad (26)$$

with short-time diffusion tensor  $\mathbf{D}_R^S(\mathbf{k})$  given by

$$\mathbf{D}_R^S(\mathbf{k}) = -\frac{1}{2} \langle [\mathcal{L} \mathbf{M}(\mathbf{k})] \mathbf{M}(-\mathbf{k}) \rangle \langle \mathbf{M}(\mathbf{k}) \mathbf{M}(-\mathbf{k}) \rangle^{-1} \quad (27)$$

and with memory function  $\mathbf{M}_R(\mathbf{k}, t)$ . The one-sided Fourier transform defined in Eq. (9) may be expressed as

$$\mathbf{G}_R(\mathbf{k}, \omega) = k_B T [-i\omega \mathbf{1} + 2\mathbf{D}_R(\mathbf{k}, \omega)]^{-1} \cdot \chi^0(\mathbf{k}, 0), \quad (28)$$

with  $(\mathbf{k}, \omega)$ -dependent diffusion tensor

$$\mathbf{D}_R(\mathbf{k}, \omega) = \mathbf{D}_R(\mathbf{k}, \infty) + \frac{1}{2} \hat{\mathbf{M}}_R(\mathbf{k}, \omega), \quad (29)$$

where  $\mathbf{D}_R(\mathbf{k}, \infty) = \mathbf{D}_R^S(\mathbf{k})$ , and  $\hat{\mathbf{M}}_R(\mathbf{k}, \omega)$  is the one-sided Fourier transform of the memory function. By isotropy the diffusion tensor takes the form

$$\mathbf{D}_R(\mathbf{k}, \omega) = D_{Rl}(k, \omega) \hat{\mathbf{k}} \hat{\mathbf{k}} + D_{Rt}(k, \omega) (1 - \hat{\mathbf{k}} \hat{\mathbf{k}}). \quad (30)$$

We may define the corresponding  $k, \omega$ -dependent relaxation times

$$\begin{aligned} \tau_l(k, \omega) &= [2D_{Rl}(k, \omega)]^{-1}, \\ \tau_t(k, \omega) &= [2D_{Rt}(k, \omega)]^{-1}. \end{aligned} \quad (31)$$

It follows from Eq. (16) that for systems with short-range interactions the diffusion tensor is proportional to the unit tensor in the limit of zero wave number,  $D_{Rl}(0, \omega) = D_{Rt}(0, \omega)$ . From Eq. (17) it follows that for systems with electric-dipole interactions the two coefficients are related by

$$D_{Rl}(0, \omega) = \epsilon(0, 0) D_{Rt}(0, \omega), \quad (32)$$

where  $\epsilon(0, 0) = 1 + 4\pi\chi_l(0, 0)$  is the dielectric constant at zero wave number and zero frequency.

In the limit of large wave number only single-particle terms survive. The zero-frequency susceptibility tends to

$$\chi^0(\infty, 0) = \frac{1}{3} \beta n_0 \mu^2 \mathbf{1}. \quad (33)$$

The tensor  $\mathbf{G}_R(\mathbf{k}, \omega)$  tends to

$$\mathbf{G}_R(\mathbf{k}, \omega) \approx \frac{1}{3} n_0 \mu^2 (-i\omega + D_S^S k^2)^{-1} \mathbf{1} \quad \text{as } k \rightarrow \infty, \quad (34)$$

where  $D_S^S$  is the short-time translational self-diffusion coefficient. Both  $\tau_l(k, \omega)$  and  $\tau_t(k, \omega)$  tend to  $1/(D_S^S k^2)$  in the limit of large  $k$ .

### IV. SHORT-TIME DIFFUSION

In the absence of hydrodynamic interactions the expression (27) for the short-time diffusion tensor simplifies, in analogy to that for the translational diffusion coefficient [4,6]. The first average on the right in Eq. (27) reads explicitly in the absence of hydrodynamic interactions

$$\begin{aligned} \langle [\mathcal{L} M_\alpha(\mathbf{k})] M_\beta(-\mathbf{k}) \rangle &= \frac{D_0}{Z(\beta)} \int e^{-\beta\Phi} M_\beta(-\mathbf{k}) \left[ \frac{\partial}{\partial \mathbf{X}_T} - \beta \frac{\partial \Phi}{\partial \mathbf{X}_T} \right] \cdot \frac{\partial}{\partial \mathbf{X}_T} M_\alpha(\mathbf{k}) d\mathbf{X} \\ &+ \frac{D_R}{Z(\beta)} \int e^{-\beta\Phi} M_\beta(-\mathbf{k}) \left[ \frac{\partial}{\partial \mathbf{X}_R} - \beta \frac{\partial \Phi}{\partial \mathbf{X}_R} \right] \cdot \frac{\partial}{\partial \mathbf{X}_R} M_\alpha(\mathbf{k}) d\mathbf{X}. \end{aligned} \quad (35)$$

Integrating the first term in each integral by parts we transform this to

$$\begin{aligned} \langle [\mathcal{L}M_\alpha(\mathbf{k})]M_\beta(-\mathbf{k}) \rangle &= -\frac{D_0}{Z(\beta)} \int e^{-\beta\Phi} \left[ \frac{\partial}{\partial \mathbf{X}_T} M_\beta(-\mathbf{k}) \right] \cdot \left[ \frac{\partial}{\partial \mathbf{X}_T} M_\alpha(\mathbf{k}) \right] d\mathbf{X} \\ &\quad - \frac{D_R}{Z(\beta)} \int e^{-\beta\Phi} \left[ \frac{\partial}{\partial \mathbf{X}_R} M_\beta(-\mathbf{k}) \right] \cdot \left[ \frac{\partial}{\partial \mathbf{X}_R} M_\alpha(\mathbf{k}) \right] d\mathbf{X}. \end{aligned} \quad (36)$$

The integrals are easily evaluated and we find

$$\begin{aligned} \langle [\mathcal{L}M(\mathbf{k})]M(-\mathbf{k}) \rangle &= -N\mu^2[D_0k^2\langle \mathbf{u}_1\mathbf{u}_1 \rangle \\ &\quad + D_R(1 - \langle \mathbf{u}_1\mathbf{u}_1 \rangle)]. \end{aligned} \quad (37)$$

Note that we have not used isotropy. Substituting into Eq. (27) we obtain

$$\begin{aligned} D_R^S(\mathbf{k}) &= \frac{1}{2}\beta n_0\mu^2[D_0k^2\langle \mathbf{u}_1\mathbf{u}_1 \rangle \\ &\quad + D_R(1 - \langle \mathbf{u}_1\mathbf{u}_1 \rangle)][\chi^0(\mathbf{k},0)]^{-1}. \end{aligned} \quad (38)$$

In the absence of applied fields the system is isotropic and the expression becomes

$$D_R^S(\mathbf{k}) = \frac{D_R + \frac{1}{2}D_0k^2}{S_t(k)} \widehat{\mathbf{k}}\widehat{\mathbf{k}} + \frac{D_R + \frac{1}{2}D_0k^2}{S_l(k)} (1 - \widehat{\mathbf{k}}\widehat{\mathbf{k}}). \quad (39)$$

We therefore find slowing down at the peaks of the static structure factors, in analogy to de Gennes narrowing of the dynamic structure factor of a dense liquid [21].

For a system with strong dipolar interactions the transverse structure factor  $S_t(k)$  is much larger at small  $k$  than the longitudinal factor  $S_l(k)$ . For such a system transverse-polarization fluctuations decay much more slowly than longitudinal-polarization fluctuations. The ratio of short-time relaxation times equals the ratio  $S_t(k)/S_l(k)$ .

The result in Eq. (39) was proposed by Chandra and Bagchi as an approximation in a theory of dipolar suspensions [22]. The expression (39) is exact for isotropic systems in the absence of hydrodynamic interactions and with time evolution governed by the generalized Smoluchowski equation. In the presence of applied fields the more general expression (38) holds. One can derive a generalization in the presence of hydrodynamic interactions by performing an integration by parts in Eq. (27) in analogy to that in Eq. (36). The result (39) implies that the initial rate of change of the scattering function is governed by free diffusion. The static structure factors appear as a consequence of the initial value  $F_R(\mathbf{k},0) = (k_B T/n_0)\chi^0(\mathbf{k},0)$ . For a discussion of the mechanism and a comparison with corresponding results for atomic liquids we refer to Pusey [6].

## V. MEMORY FUNCTION

The memory function appearing in Eq. (26) may be studied in the framework of the Mori-Zwanzig projection-operator formalism, which allows convenient mathematical formulation [15]. We define the projection  $P_{\mathbf{k}}A$  of a configuration variable  $A(\mathbf{X})$  onto the polarization fluctuation by

$$P_{\mathbf{k}}A = \langle A\mathbf{M}(-\mathbf{k}) \rangle \langle \mathbf{M}(\mathbf{k})\mathbf{M}(-\mathbf{k}) \rangle^{-1} \mathbf{M}(\mathbf{k}). \quad (40)$$

The orthogonal projector  $Q_{\mathbf{k}}$  is defined by

$$Q_{\mathbf{k}} = 1 - P_{\mathbf{k}}. \quad (41)$$

The memory function  $\mathbf{M}_R(\mathbf{k},t)$  may be written as the autocorrelation function of a random force,

$$\mathbf{M}_R(\mathbf{k},t) = -\langle \mathbf{f}_R(\mathbf{k},t)\mathbf{f}_R(-\mathbf{k}) \rangle \langle \mathbf{M}(\mathbf{k})\mathbf{M}(-\mathbf{k}) \rangle^{-1}, \quad (42)$$

where

$$\mathbf{f}_R(\mathbf{k},t) = \exp(Q_{\mathbf{k}}\mathcal{L}t)Q_{\mathbf{k}}\mathcal{L}\mathbf{M}(\mathbf{k}), \quad (43)$$

and  $\mathbf{f}_R(-\mathbf{k}) = \mathbf{f}_R(-\mathbf{k},0)$ . The one-sided Fourier transform of the memory function is therefore given by

$$\begin{aligned} \widehat{\mathbf{M}}_R(\mathbf{k},\omega) &= \langle [(i\omega + Q_{\mathbf{k}}\mathcal{L})^{-1}\mathbf{f}_R(\mathbf{k})]\mathbf{f}_R(-\mathbf{k}) \rangle \\ &\quad \times \langle \mathbf{M}(\mathbf{k})\mathbf{M}(-\mathbf{k}) \rangle^{-1}. \end{aligned} \quad (44)$$

This may be transformed to a form involving the actual time-evolution operator, rather than the projected one. Following the procedure developed by Mori [23] we find

$$\widehat{\mathbf{M}}_R(\mathbf{k},\omega) = \widehat{\Phi}_R(\mathbf{k},\omega) \{ 1 + [i\omega\mathbf{1} - 2D_R^S(\mathbf{k})]^{-1} \widehat{\Phi}_R(\mathbf{k},\omega) \}^{-1}, \quad (45)$$

where the tensor  $\widehat{\Phi}_R(\mathbf{k},\omega)$  is given by

$$\begin{aligned} \widehat{\Phi}_R(\mathbf{k},\omega) &= \langle [(i\omega + \mathcal{L})^{-1}\mathbf{J}_R(\mathbf{k})]\mathbf{J}_R(-\mathbf{k}) \rangle \\ &\quad \times \langle \mathbf{M}(\mathbf{k})\mathbf{M}(-\mathbf{k}) \rangle^{-1} \end{aligned} \quad (46)$$

with the current variable  $\mathbf{J}_R(\mathbf{k})$  defined by

$$\mathbf{J}_R(\mathbf{k}) = Q_{\mathbf{k}}\mathcal{L}\mathbf{M}(\mathbf{k}). \quad (47)$$

We note that the current variable may be replaced by

$$\mathbf{J}_R(\mathbf{k}) = Q_{\mathbf{k}}(\mathcal{L} - \mathcal{L}_f)\mathbf{M}(\mathbf{k}), \quad (48)$$

where  $\mathcal{L}_f$  is the free-diffusion operator. The current variable differs from zero because of interactions.

Explicit results for the memory function may be evaluated at low density by cluster expansion [24] of the first average in Eq. (46). Because of the property (48) there is no single-particle contribution. To lowest order in density, the projection operator  $Q_{\mathbf{k}}$  may be omitted in (48), and we find a contribution from the two-particle term

$$\begin{aligned} \widehat{\Phi}_R(\mathbf{k},\omega) &= \lim_{\substack{N \rightarrow \infty \\ \Omega \rightarrow \infty}} \frac{3}{32\pi^2 N} \int d\mathbf{R}_1 d\mathbf{R}_2 d\mathbf{u}_1 d\mathbf{u}_2 n_0(1,2) \\ &\quad \times \{ [i\omega + \mathcal{L}(1,2)]^{-1} \mathbf{U}_{R\mathbf{k}}(1,2) \} \\ &\quad \times \mathbf{U}_{R-\mathbf{k}}(1,2) + O(n_0^2), \end{aligned} \quad (49)$$

with

$$U_{\mathbf{R}\mathbf{k}}(1,2) = [\mathcal{L}(1,2) - \mathcal{L}_f(1,2)](\mathbf{u}_1 e^{-i\mathbf{k}\cdot\mathbf{R}_1} + \mathbf{u}_2 e^{-i\mathbf{k}\cdot\mathbf{R}_2}) . \quad (50)$$

Furthermore,  $n_0(1,2)$  is the low-density limit of the two-particle distribution function, and  $\mathcal{L}(1,2)$  is the adjoint Smoluchowski operator specialized to two particles. We introduce center-of-mass and relative coordinates

$$\mathbf{R} = \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2), \quad \mathbf{r} = \mathbf{R}_2 - \mathbf{R}_1 . \quad (51)$$

Taking the thermodynamic limit in Eq. (49) we find

$$\begin{aligned} \hat{\Phi}_{\mathbf{R}}(\mathbf{k}, \omega) = & \frac{3}{32\pi^2} n_0 \int d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2 g(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) \\ & \times \{ [i\omega + \mathcal{L}_r(\mathbf{k})]^{-1} \mathbf{U}_r(\mathbf{k}) \} \\ & \times \mathbf{U}_r(-\mathbf{k}) + O(n_0^2) , \end{aligned} \quad (52)$$

where the distribution function  $g(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$  is given by

$$g(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \exp[-\beta v(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)] \quad (53)$$

for two-particle direct interaction  $v(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ . The operator  $\mathcal{L}_r(\mathbf{k})$  differs from the operator  $\mathcal{L}(1,2)$  only in the replacement of the gradient operator  $\partial/\partial\mathbf{R}_1$  by  $-\frac{1}{2}i\mathbf{k} - (\partial/\partial\mathbf{r})$ , and of the gradient operator  $\partial/\partial\mathbf{R}_2$  by  $-\frac{1}{2}i\mathbf{k} + (\partial/\partial\mathbf{r})$ . The current variable  $\mathbf{U}_r(\mathbf{k})$  may be expressed as

$$\mathbf{U}_r(\mathbf{k}) = V_r(\mathbf{k})(\mathbf{u}_1 e^{i\mathbf{k}\cdot\mathbf{r}/2} + \mathbf{u}_2 e^{-i\mathbf{k}\cdot\mathbf{r}/2}) , \quad (54)$$

with an operator

$$V_r(\mathbf{k}) = \mathcal{L}_r(\mathbf{k}) - \mathcal{L}_{f_r}(\mathbf{k}) , \quad (55)$$

which differs from zero only due to hydrodynamic and direct pair interactions.

## VI. ROTATIONAL-DIFFUSION COEFFICIENT

We are now in a position to write down expressions for the  $(\mathbf{k}, \omega)$ -dependent rotational-diffusion tensor of a semi-dilute suspension. We consider first the high-frequency limit.

In the absence of hydrodynamic interactions, the short-time diffusion tensor is given by the simple expression (39). In the more general case we return to Eq. (27). In the first average on the right we write  $\mathcal{L} = \mathcal{L} - \mathcal{L}_f + \mathcal{L}_f$  and use

$$\mathcal{L}_f \mathbf{M}(\mathbf{k}) = -(D_0 k^2 + 2D_R) \mathbf{M}(\mathbf{k}) . \quad (56)$$

Hence we find

$$\begin{aligned} \mathbf{D}_{\mathbf{R}}^S(\mathbf{k}) = & (D_R + \frac{1}{2}D_0 k^2) \mathbf{1} \\ & - \frac{1}{2} \langle [(\mathcal{L} - \mathcal{L}_f) \mathbf{M}(\mathbf{k})] \mathbf{M}(-\mathbf{k}) \rangle \\ & \times \langle \mathbf{M}(\mathbf{k}) \mathbf{M}(-\mathbf{k}) \rangle^{-1} . \end{aligned} \quad (57)$$

The first average on the right may be evaluated by cluster expansion. The single-particle term vanishes. To first order in the density we find as in Eq. (52)

$$\begin{aligned} \langle [(\mathcal{L} - \mathcal{L}_f) \mathbf{M}(\mathbf{k})] \mathbf{M}(-\mathbf{k}) \rangle = & \frac{N}{32\pi^2} n_0 \int d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2 g \\ & \times [V_r(\mathbf{k}) \mathbf{M}_r(\mathbf{k})] \\ & \times \mathbf{M}_r(-\mathbf{k}) \\ & + O(n_0^2) , \end{aligned} \quad (58)$$

with the variable

$$\mathbf{M}_r(\mathbf{k}) = \mu(\mathbf{u}_1 e^{i\mathbf{k}\cdot\mathbf{r}/2} + \mathbf{u}_2 e^{-i\mathbf{k}\cdot\mathbf{r}/2}) . \quad (59)$$

To lowest order the second average in Eq. (57) may be replaced by  $\frac{1}{3}N\mu^2 \mathbf{1}$ , in the absence of applied fields. To first order in density we therefore find

$$\mathbf{D}_{\mathbf{R}}^S(\mathbf{k}) = (D_R + \frac{1}{2}D_0 k^2) [1 + \lambda_{\mathbf{R}}(\mathbf{k}) \phi] , \quad (60)$$

where  $\phi = (4\pi/3)n_0 a^3$  is the volume fraction and the tensor  $\lambda_{\mathbf{R}}(\mathbf{k})$  is given by

$$\begin{aligned} (D_R + \frac{1}{2}D_0 k^2) \lambda_{\mathbf{R}}(\mathbf{k}) = & - \frac{9}{4(4\pi a)^3 \mu^2} \\ & \times \int g \mathbf{M}_r(-\mathbf{k}) V_r(\mathbf{k}) \\ & \times \mathbf{M}_r(\mathbf{k}) d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2 . \end{aligned} \quad (61)$$

We have used the symmetry of the tensor. It is convenient to use a shorthand notation. We introduce the scalar product between two functions  $A(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$  and  $B(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$  by

$$\begin{aligned} (A|B) = & \frac{1}{16\pi^2} \int g(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) A^*(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) \\ & \times B(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2 , \end{aligned} \quad (62)$$

and abbreviate

$$|\mathbf{k}\rangle = \mathbf{u}_1 e^{i\mathbf{k}\cdot\mathbf{r}/2} + \mathbf{u}_2 e^{-i\mathbf{k}\cdot\mathbf{r}/2} . \quad (63)$$

We find

$$\lambda_{\mathbf{R}}(\mathbf{k}) = - \frac{9}{8\pi a^3 (2D_R + D_0 k^2)} (\mathbf{k} | V_r(\mathbf{k}) | \mathbf{k}) . \quad (64)$$

This is similar to an expression derived for translational diffusion [25]. In the limit  $k \rightarrow 0$  the tensor reduces to a scalar  $\lambda_{\mathbf{R}}$  multiplying the unit tensor for systems with short-range interactions. The value of  $\lambda_{\mathbf{R}}$  has been calculated for hard spheres with mixed slip-stick boundary conditions [3,26]. For systems with dipolar interactions the tensor  $\lambda_{\mathbf{R}}(\mathbf{k})$  remains anisotropic in the limit  $k \rightarrow 0$ . The difference of the longitudinal and transverse coefficients  $\lambda_{Rl}(k)$  and  $\lambda_{Rt}(k)$  for this case is given by

$$\lambda_{Rl}(0) - \lambda_{Rt}(0) = \frac{\beta \mu^2}{a^3} , \quad (65)$$

as follows from Eq. (32).

In analogy to Eq. (60) we write the  $\mathbf{k}, \omega$ -dependent diffusion tensor as

$$\mathbf{D}_{\mathbf{R}}(\mathbf{k}, \omega) = (D_R + \frac{1}{2}D_0 k^2) \{ 1 + [\lambda_{\mathbf{R}}(\mathbf{k}) + \alpha_{\mathbf{R}}(\mathbf{k}, \omega)] \phi \} , \quad (66)$$

with a tensor  $\alpha_R(\mathbf{k}, \omega)$  which tends to zero at high frequency. We abbreviate

$$|V\mathbf{k}\rangle = V_r(\mathbf{k})|\mathbf{k}\rangle = \mathbf{U}_r(\mathbf{k}). \quad (67)$$

Using symmetry of the tensor we find from Eqs. (29), (45), and (52)

$$\alpha_R(\mathbf{k}, \omega) = \frac{9}{8\pi a^3(2D_R + D_0 k^2)} \left[ V\mathbf{k} \left| \frac{1}{i\omega + \mathcal{L}_r(\mathbf{k})} \right| V\mathbf{k} \right]. \quad (68)$$

Again this is quite similar to an analogous expression for translational diffusion [25].

## VII. SINGLE-PARTICLE RELAXATION TIME

We may find analogous expressions for the frequency-dependent single-particle relaxation time  $\tau_S(\omega)$  of a semidilute suspension. We consider first the high-frequency limit in the general case.

It is convenient to consider the tensor correlation function

$$C_{11}(t) = \langle \mathbf{u}_1(t) \mathbf{u}_1(0) \rangle, \quad (69)$$

and the corresponding short-time relaxation time tensor  $\tau_S^S$  given by

$$(\tau_S^S)^{-1} = -\langle (\mathcal{L}\mathbf{u}_1)\mathbf{u}_1 \rangle \langle \mathbf{u}_1\mathbf{u}_1 \rangle^{-1}. \quad (70)$$

By the method explained in Sec. IV one finds for the first average on the right

$$\langle (\mathcal{L}\mathbf{u}_1)\mathbf{u}_1 \rangle = -\langle (1 - \mathbf{u}_1\mathbf{u}_1) \cdot \mathbf{D}_{RR11} \cdot (1 - \mathbf{u}_1\mathbf{u}_1) \rangle. \quad (71)$$

In the absence of applied fields the suspension is isotropic. In that case  $\tau_S^S = \tau_S^S \mathbf{1}$  and  $\langle \mathbf{u}_1\mathbf{u}_1 \rangle = \frac{1}{3}\mathbf{1}$ . In the absence of hydrodynamic interactions the rotational part of the diffusion matrix is just the unit matrix multiplied by the coefficient  $D_R$ , so that then the short-time relaxation time is simply

$$\tau_S^S = \frac{1}{2D_R}, \quad (72)$$

independent of the nature of the direct interactions. More generally, the short-time relaxation time of an isotropic suspension is given by

$$\frac{1}{\tau_S^S} = \text{Tr} \langle (1 - \mathbf{u}_1\mathbf{u}_1) \cdot \mathbf{D}_{RR11} \cdot (1 - \mathbf{u}_1\mathbf{u}_1) \rangle. \quad (73)$$

In order to obtain an explicit expression for the short-time relaxation time in the presence of hydrodynamic interactions, and valid to first order in volume fraction, we return to Eq. (70) and replace the operator  $\mathcal{L}$  in the average by  $\mathcal{L} - \mathcal{L}_f + \mathcal{L}_f$ . This yields

$$\langle (\mathcal{L}\mathbf{u}_1)\mathbf{u}_1 \rangle = -\frac{2}{3}D_R \mathbf{1} + \langle [(\mathcal{L} - \mathcal{L}_f)\mathbf{u}_1]\mathbf{u}_1 \rangle. \quad (74)$$

We evaluate the average on the right by rooted cluster expansion. To first order in density we find

$$\begin{aligned} \langle [(\mathcal{L} - \mathcal{L}_f)\mathbf{u}_1]\mathbf{u}_1 \rangle &= \frac{1}{16\pi^2} n_0 \\ &\times \int d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2 g[V_r(\mathbf{0})\mathbf{u}_1]\mathbf{u}_1 \\ &+ O(n_0^2). \end{aligned} \quad (75)$$

To first order in density the short-time relaxation time is therefore given by

$$\tau_S^S = \frac{1}{2D_R} (1 + \lambda_T \phi) \quad (76)$$

with coefficient

$$\lambda_T = \frac{3}{2(4\pi a)^3 D_R} \int g \mathbf{u}_1 \cdot V_r(\mathbf{0}) \mathbf{u}_1 d\mathbf{r} d\mathbf{u}_1 d\mathbf{u}_2. \quad (77)$$

In shorthand notation

$$\lambda_T = \frac{3}{8\pi a^3 D_R} (\mathbf{u}_1 \cdot |V_r(\mathbf{0})|\mathbf{u}_1). \quad (78)$$

In analogy to Eq. (76) we write the frequency-dependent relaxation time as

$$\tau_S(\omega) = \frac{1}{2D_R} \{1 + [\lambda_T + \alpha_T(\omega)]\phi\}, \quad (79)$$

with a coefficient  $\alpha_T(\omega)$  which tends to zero at high frequency. We abbreviate

$$|V\mathbf{u}_1\rangle = V_r(\mathbf{0})\mathbf{u}_1. \quad (80)$$

By the same method as used for the rotational diffusion tensor we find

$$\alpha_T(\omega) = \frac{-3}{8\pi a^3 D_R} \left[ V\mathbf{u}_1 \cdot \left| \frac{1}{i\omega + \mathcal{L}_r(\mathbf{0})} \right| V\mathbf{u}_1 \right]. \quad (81)$$

The expressions (78) and (81) are analogous to Eqs. (64) and (68).

## VIII. DISCUSSION

We have discussed relaxation of orientation for a suspension of spheres on the basis of the generalized Smoluchowski equation. An important result is embodied in Eq. (39), which shows that in the absence of hydrodynamic interactions the initial decay of the polarization correlation function is governed by free diffusion. The short-time diffusion coefficient shows a strong wave-vector dependence due to the equilibrium structure of the suspension at the initial time. The result is a straightforward generalization of an analogous expression for the translation diffusion coefficient, but seems not to have been derived before.

We have also derived convenient expressions for the wave-vector- and frequency-dependent rotational diffusion tensor and the single-particle relaxation time of a semidilute suspension. The expressions are valid to first order in volume fraction and are a convenient starting point for explicit calculation. In a forthcoming paper we shall use these expressions to study orientational relaxation in a colloidal Heisenberg model.

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