Long-Time Self-Diffusion of Rigid Rods at Low Concentrations: A Variational Approach

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ABSTRACT: No theoretical predictions exist for the concentration dependence of long-time self-diffusion coefficients of rod-shaped Brownian particles with a finite aspect ratio. The reason for this is that the relevant Smoluchowski equation is extremely complicated and cannot be solved explicitly, even on the two-particle level. We present an alternative approach where the Smoluchowski equation is solved in approximation by a variational method. The variational principle is applied to calculate the dependence of the long-time translational self-diffusion coefficient of spherocylinders with hard-core interaction to leading order in concentration, with the neglect of hydrodynamic interactions, up to aspect ratios of 30. The first order in concentration coefficient α is found to depend on the aspect ratio p as $\alpha = 2 + {}^{10}/_{32}(p-1) + {}^{1}/_{53}(p-1)^2$.

1. Introduction

There is a large body of literature dedicated to the prediction of the concentration dependence of transport coefficients of *spherical* Brownian particles to leading order in concentration, which is a field that was initiated and explored in detail by Batchelor[1] (for an overview of relevant literature, see the books of Russel[2] and Dhont[3]). As yet there are no analogous theoretical results for rigid *rod-shaped* Brownian particles. Existing theories on long-time diffusion of rod-like particles are based on assumptions which only apply to rods with an extremely large aspect ratio.[4−9] For rod- shaped particles of aspect ratios of less than, e.g., 50, no theoretical developments as for spherical colloids have been reported.

Theoretical results for the concentration dependence of long-time self-diffusion coefficients for rods with a finite aspect ratio do not exist because the Smoluchowski equation one should solve is extremely complicated. In the present paper, we present a variational approach to long-time self-diffusion which is applied to translational diffusion of rigid rodlike particles with aspect ratios up to 30, to leading order in concentration. We consider spherocylindrical rods with a hard-core interaction.

The leading order concentration dependence of the long-time self-diffusion coefficient D_s^l is described by the coefficient α in its Taylor expansion with respect to the concentration,

$$D_s^l = \bar{D}\,[1 - \alpha\varphi + O(\varphi^2)] \qquad (1)$$

where $\varphi = v_p\bar{\rho}$ is the volume fraction of rods (with v_p being the volume of a single rod and $\bar{\rho} = N/V$ being the number density of rods) and $\bar{D}$ is the translational diffusion coefficient at infinite dilution. The coefficient α is of course a function of the aspect ratio L/D, where L is the length (including the two hemispherical caps) and D the thickness of the rods.

For spherical particles, for which $L/D = 1$, the first order in concentration coefficient α is known to be equal to $\alpha = 2$ when hydrodynamic interactions (HI) are neglected, and $\alpha = 2.10$ when HI are included. The effect of HI on the translational long-time self-diffusion coefficient is thus not so important, and beyond experimental accuracy. For long rodlike particles the effect of HI on the translational diffusion coefficient is probably even less important than for spheres, since the average distance between the segments of two distinct rods is large. Furthermore, the precise form of hydrodynamic interaction tensors for rods is unknown. We shall therefore neglect HI in the present paper, although the variational principle does straightforwardly allow the inclusion of HI.

Long-time self-diffusion coefficients can be calculated as follows.[1] Consider the Langevin equation for a single Brownian particle, interacting both with solvent molecules and other Brownian particles, where the random force now includes the interaction with the remaining Brownian particles. This random force is only δ-correlated on the so-called interaction time scale τ_I, which time is large compared to relaxation times of the microstructure of Brownian particles. On this time scale the self-diffusion coefficient, which is by definition the *long-time* self-diffusion coefficient, can be obtained from the Langevin equation as $D_s^l = k_BT/\gamma$, where k_B is Boltzmann's constant and T is the temperature. The friction coefficient γ is the proportionality constant between a weak external force $\mathbf{F}^{ext}$, acting only on a single rod (the tracer particle), and its resulting thermally averaged translational velocity $\langle\mathbf{v}\rangle$. The friction coefficient γ now includes friction with the solvent *and* resistence due to interaction with the remaining Brownian particles (the host particles). Hence

$$D_s^l = k_BT/\gamma, \quad \text{with } \mathbf{F}^{ext} = \gamma\langle\mathbf{v}\rangle \qquad (2)$$

The long-time self-diffusion coefficient for translational motion is thus obtained by evaluation of the thermally averaged translational velocity of the tracer rod. In order to evaluate that average velocity, one needs the

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solution of the Smoluchowski equation in the presence of a force acting on the tracer rod. The approach here is to obtain an approximate solution from a variational principle.

2. The Variational Principle

The relevant Smoluchowki equation for the calculation of the coefficient α in eq 1 is the stationary two-particle equation where an external force $F^{ext}\hat{\mathbf{e}}_3$ acts on the tracer rod (where $\hat{\mathbf{e}}_3 = (0, 0, 1)$ is the unit vector along the z-axis). We shall take rod number 1 to be the tracer rod.

The Smoluchowski equation for the probability density function $P(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$ of the center-of-mass position $\mathbf{R}_j = \mathbf{r}_j/D$ in units of the thickness D of the rods and the orientations $\hat{\mathbf{u}}_j$ of the two rods reads

$$0 = \{\hat{L}^{(0)} + \beta D F^{ext}\hat{L}^{(1)}\}\, P(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2), \qquad (3)$$

where the operator $\hat{L}^{(0)}$ is the two-particle Smoluchowski operator without the external force

$$\hat{L}^{(0)}v = \sum_{j=1}^{2}\Big\{\nabla_j\cdot[\nabla_j v + \beta v[\nabla_j V]] + \epsilon_t\nabla_j\cdot\Big[\hat{\mathbf{u}}_j\hat{\mathbf{u}}_j - \frac{1}{3}\hat{\mathbf{I}}\Big]\cdot[\nabla_j v + \beta v[\nabla_j V]] + \epsilon_r\hat{R}_j\cdot[\hat{R}_j v + \beta v[\hat{R}_j V]]\Big\} \qquad (4)$$

with v being an arbitrary phase function; ∇_j is the gradient operator with respect to the position coordinate $\mathbf{R}_j$, $\hat{\mathbf{I}}$ is the identity, $V \equiv V(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)$ is the pair-interaction potential, and $\hat{R}_j = \hat{\mathbf{u}}_j \times \nabla_{\hat{u}j}$, is the rotation operator. Furthermore

$$\epsilon_t = \Delta D/\bar{D}, \quad \epsilon_r = D^2 D_r/\bar{D} \qquad (5)$$

where ΔD is the difference between the diffusion coefficients $D_{||}$ and $D_\perp$ for Brownian motion parallel and perpendicular to the rods long axis, respectively, while $\bar{D}$ is the average translational diffusion coefficient $^1/_3[D_{||} + 2D_\perp]$ and D_r is the rotational diffusion coefficient. These coefficients relate to Brownian motion of a single rod, not interacting with other rods. The dimensionless quantities ϵ_t and ϵ_r depend on the aspect ratio $p = L/D$ as[10]

$$\epsilon_t = \frac{3}{4}\frac{\ln\{p\} - 1.253 + 1.775/p - 0.552/p^2}{\ln\{p\} + 0.316 + 0.582/p + 0.102/p^2} \qquad (6)$$

$$\epsilon_r = \frac{9}{p^2}\frac{\ln\{p\} - 0.662 + 0.917/p + 0.078/p^2}{\ln\{p\} + 0.316 + 0.582/p + 0.102/p^2} \qquad (7)$$

The operator $\hat{L}^{(1)}$ is the part of the Smoluchowski operator that accounts for the external force on the tracer rod 1

$$\hat{L}^{(1)}v = -\Big\{\nabla_1\cdot[\hat{\mathbf{e}}_3 v] + \epsilon_t\nabla_1\cdot\Big[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\Big]\cdot[\hat{\mathbf{e}}_3 v]\Big\}. \qquad (8)$$

where the external force $\mathbf{F}^{ext} = F^{ext}\mathbf{e}_3$ (with $\hat{\mathbf{e}}_3 = (0, 0, 1)$) is taken along the z-direction.

For our purpose, without loss of generality, the following linear form for the solution of the Smoluchowski equation (eq 3) can be used

$$P(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = P^{eq}(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)[1 + \beta D F^{ext}\Psi(\mathbf{R}_1 - \mathbf{R}_2, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)] \qquad (9)$$

where the factor βD is used to render the solution Ψ dimensionless, and $P^{eq} \sim \exp\{-\beta V\}$ is the equilibrium solution of the Smoluchowski equation without the external force. Substitution of this form into the Smoluchowski equation (eq 3) and linearization with respect to $\beta D F^{ext}$ leads to

$$\hat{L}^{(0)}[P^{eq}\Psi] = -\hat{L}^{(1)}P^{eq} \qquad (10)$$

where the position and orientation dependences are not denoted for brevity.

The aim is now to find a functional of which the Euler−Lagrange equation is precisely the Smoluchowski equation (eq 10). The following theorem can be used to achieve this.[11] Consider the operator equation $\hat{A}\,\Psi = f$, with $\hat{A} : F \to F$ a linear operator defined on a vector space F of real-valued functions, with inner product $\langle\cdots|\cdots\rangle$, and with $f \in F$ a known function. Suppose that $\hat{A}$ is Hermitian and negative definite, that is, $\langle u|\hat{A}\,v\rangle = \langle\hat{A}\,u|v\rangle$ for all $u, v \in F$, and $\langle v|\hat{A}\,v\rangle < 0$ for all $v \in F$, $v \neq 0$. Define the functional

$$F[v] \equiv \langle v|\hat{A}\,v\rangle - 2\langle v|f\rangle \qquad (11)$$

This functional has the following properties: (i) Ψ is a stationary element of $F \Leftrightarrow \hat{A}\,\Psi = f$; (ii) every stationary element maximizes F; (iii) there is at most one, unique stationary element. Hence, when F has a stationary element, this element is a unique maxixum of F and this element Ψ is the solution of $\hat{A}\,\Psi = f$. The elementary proof of this theorem is given in Appendix A.

The Smoluchowski equation (eq 10) must be reformulated in order to apply the above theorem. To this end the backward Smoluchowski operator $\hat{L}_B^{(0)}$ is introduced as the Hermitian conjugate operator of $\hat{L}^{(0)}$ with respect to the unweighted innerproduct, that is, $\langle u||\hat{L}^{(0)}v\rangle = \langle v||\hat{L}_B^{(0)}u\rangle$, where the unweighted innerproduct is defined as, $\langle u||v\rangle = \int d\mathbf{R}_1 \int d\mathbf{R}_2 \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2\, uv$, with u and v real-valued phase functions of $\mathbf{R}_1$, $\mathbf{R}_2$, $\hat{\mathbf{u}}_1$, and $\hat{\mathbf{u}}_2$, and where the integrals $\oint$ range over the unit spherical surface, that is, over all directions of the corresponding unit vectors $\hat{\mathbf{u}}_j$. Partial integration leads to (see Appendix B for mathematical details)

$$\hat{L}_B^{(0)}v = \sum_{j=1}^{2}\Big\{[\nabla_j - \beta[\nabla_j V]]\cdot\nabla_j v + \epsilon_t[\nabla_j - \beta[\nabla_j V]]\cdot\Big[\hat{\mathbf{u}}_j\hat{\mathbf{u}}_j - \frac{1}{3}\hat{\mathbf{I}}\Big]\cdot\nabla_j v + \epsilon_r[\hat{R}_j - \beta[\hat{R}_j V]]\cdot\hat{R}_j v\Big\} \qquad (12)$$

By substitution it is easily verified that $\hat{L}^{(0)}[P^{eq}v] = P^{eq}\hat{L}_B^{(0)}v$, so that eq 10 can be rewritten as

$$\hat{L}_B^{(0)}\Psi = -[P^{eq}]^{-1}\hat{L}^{(0)}[P^{eq}] \qquad (13)$$

The reason for writing the Smoluchowski equation in this form is that the backward Smoluchowski operator $\hat{L}_B^{(0)}$ is Hermitian with respect to the innerproduct weighted by P^{eq}, that is, $\langle u|\hat{L}_B^{(0)}v\rangle = \langle\hat{L}_B^{(0)}u|v\rangle$, with $\langle u|v\rangle = \int d\mathbf{R}_1 \int d\mathbf{R}_2 \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2\, P^{eq}uv$. Furthermore, as is shown in Appendix C, $\hat{L}_B^{(0)}$ is negative definite with respect to the same weighted innerproduct. Applying

the above theorem to the Smoluchowski equation in the form of eq 13 leads to the functional

$$F[v] \equiv \langle v|\hat{L}_{\mathrm{B}}^{(0)}v\rangle + 2\langle v|[P^{\mathrm{eq}}]^{-1}\hat{L}^{(1)}P^{\mathrm{eq}}\rangle \qquad (14)$$

Its unique maximum element solves the Smoluchowski equation.

Substitution of the explicit forms of the operators yields the following form for the functional for identical rods, apart from a factor involving the volume V of the system (see Appendix D for mathematical details)

$$F[v] = -\sum_{j=1}^{2}\int \mathrm{d}\mathbf{R}\oint \mathrm{d}\hat{\mathbf{u}}_1\oint \mathrm{d}\hat{\mathbf{u}}_2\,\chi\left\{\left(1-\frac{1}{3}\epsilon_{\mathrm{t}}\right)\left|\nabla_j v\right|^2 + \epsilon_{\mathrm{t}}\left|\hat{\mathbf{u}}_j\cdot\nabla_j v\right|^2 + \epsilon_{\mathrm{r}}\left|\hat{R}_j v\right|^2\right\} + 2\int_{R<L/D} d\mathbf{R}\oint \mathrm{d}\hat{\mathbf{u}}_1\oint \mathrm{d}\hat{\mathbf{u}}_2\,\chi\left\{\left(1-\frac{1}{3}\epsilon_{\mathrm{t}}\right)(\hat{\mathbf{e}}_3\cdot\nabla_1 v) + \epsilon_{\mathrm{t}}\hat{\mathbf{u}}_z(\hat{\mathbf{u}}_1\cdot\nabla_1 v)\right\} - 2\left(\frac{L}{D}\right)^2\oint \mathrm{d}\hat{\mathbf{R}}\oint \mathrm{d}\hat{\mathbf{u}}_1\oint \mathrm{d}\hat{\mathbf{u}}_2\left\{\left(1-\frac{1}{3}\epsilon_{\mathrm{t}}\right)\frac{z}{R} + \epsilon_{\mathrm{t}}\hat{\mathbf{u}}_z(\hat{\mathbf{u}}_1\cdot\hat{R})\right\}v_{|R=L/D}. \qquad (15)$$

where $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, $\hat{\mathbf{R}} = \mathbf{R}/R$ is the unit vector along the center-to-center line, and z and $\hat{\mathbf{u}}_z$, are the z-components of $\mathbf{R}$ and $\hat{\mathbf{u}}_1$, respectively. Furthermore, $\chi = \exp\{-\beta V\} = VP^{\mathrm{eq}}$. In case of hard-core interaction this is the characteristic function for the excluded volume, that is, $\chi = 0$ in case the hard cores of the two rods overlap and $\chi = 1$ in case there is no overlap.

The first integral in eq 15 corresponds to the first term in the formal expression (eq 14) for the functional, while the last two integrals stem from the second term in eq 14. The last two integrals are responsible for a finite drift velocity in the z-direction. Without those terms, maximization of the functional leads to $\hat{L}^{(0)}v = 0$, which is the unperturbed stationary Smoluchowski equation, of which the solution on the two-particle level is simply given by $v = P^{\mathrm{eq}}$. Note, however, that the first integral in eq 15 does contribute to the drift velocity once the stationary solution v of the full, perturbed Smoluchowski equation exhibits a preferred z-dependence. We were not able to assign a clear physical meaning to each of the terms in eq 15 or to the entire functional.

Proper normalization of the pdf in eq 9 requires that the trial function v for Ψ satisfies the normalization condition

$$\int \mathrm{d}\mathbf{R}\oint \mathrm{d}\hat{\mathbf{u}}_1\oint \mathrm{d}\hat{\mathbf{u}}_2\,\chi v(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = 0 \qquad (16)$$

This is a constraint on maximizing the functional (eq 15). Notice that this constraint excludes all functions v which are identically equal to some constant. Constants (except for the trivial zero element $v \equiv 0$) are therefore not in the function space of admissible solutions of the Smoluchowski equation.

3. Trial Functions

Let us now consider the form of appropriate trial functions. For spherical Brownian particles the exact solution of the Smoluchowski equation pertaining to long-time translational diffusion is given by $\Psi = (\partial/\partial z)\phi$ where "the potential" is equal to, $\phi = 1/R$, and where the direction of the external force on the tracer sphere is chosen in the positive z-direction. For spherical particles the equipotential surfaces, where ϕ is a constant, are spherical. For elongated Brownian particles the equipotential surfaces will have an ellipsoidal-like geometry with an orientation that is approximately that of the tracer rod. With increasing distance between the tracer and host rod, the trial function must tend to the solution for spheres. Now think of the two rods as being a rigid string of spherical subunits, "the beads" of the rods. The simplest trial function for the potential that satisfies the above basic features is a superposition of solutions for spheres over all beads of the two rods. Replacing the summations over beads by integrals, which is allowed for long and thin rods, leads to the following trial function as a linear combination of the solution for a sphere and the superposition over beads:

$$v = \frac{\partial}{\partial z}\left\{a_1\frac{1}{R} + a_2\int_{-(1/2)((L/D)-1)}^{(1/2)((L/D)-1)}\mathrm{d}l_1\int_{-(1/2)(L/D-1)}^{(1/2)(L/D-1)}\mathrm{d}l_2\,\frac{1}{|\mathbf{R} - l_1\hat{\mathbf{u}}_1 + l_2\hat{\mathbf{u}}_2|}\right\} \qquad (17)$$

The parameters a_1 and a_2 are the variational parameters.

The second integral in the trial function (eq 17) is probably a good approximation for the solution of the Smoluchowski equation for very long and thin rods. Inserting this form into the Smoluchowski equation (eq 3) reveals that it is not an exact solution. Note that for large distances both terms within the curly brackets vary like $\sim 1/R$, but clearly their behaviour at shorter distances is completely different. The parameters a_1 and a_2 interpolate between the exact solution for spheres and the probably good approximation for very long rods.

To take the connectedness of the beads on the two rods into account, the constant a_2 can be made a function of the bead indices l_1 and l_2, that is, the "charge" a_2 on the center lines of the rods is now variable. This will be done to first order in a formal Taylor expansion of the line charges with respect to l_{j}. The leading term varies as $\sim(l_1^2 + l_2^2)$. Furthermore, the connectedness can be taken into account by Taylor expansion of a_2 with respect to angular coordinates. The leading order terms are: $\sim(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2)^2$, $(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{R}})^2 + (\hat{\mathbf{u}}_2\cdot\hat{\mathbf{R}})^2$, $(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{e}}_3)^2 + (\hat{\mathbf{u}}_2\cdot\hat{\mathbf{e}}_3)^2$, and $(\hat{\mathbf{R}}\cdot\hat{\mathbf{e}}_3)^2$. We thus arrive at a trial function which is a linear combination of 6 functions. The trial function in eq 17, which is a linear combination of just two functions, will here after be referred to as "*the simple trial function*", while the trial function consisting of a linear combination of the 6 functions mentioned above will be referred to as "*the advanced trialfunction*". The difference between the variational results using these two trial functions can be considered an estimate for their accuracy. The trial functions are anti-symmetric on reflection in the xy-plane, so that proper normalization (see eq 16) is assured.

Another way to proceed would be to expand Ψ in a triple spherical-harmonics series and to use the expansion parameters as variational parameters or to optimize the functional on a grid with the grid-values of the trial function as variational parameters. These would both lead to exact solutions (to within numerical accuracy). The effort to implement such optimizations is much more involved than using trial functions of the form in eq 17.

Our trial functions $v = \sum_{n=1}^{M} a_n\psi_n$ are linear combinations of $M = 2$ or $M = 6$ functions. Substitution

into eq 14 replaces the functional $F[v]$ by a function $F(\mathbf{a})$ of the vector $\mathbf{a} = (a_1, ..., a_M)$

$$F(\mathbf{a}) = \sum_{n,m=1}^{M} M_{nm} a_n a_m + 2 \sum_{n=1}^{M} a_n f_n \tag{18}$$

where the matrix elements M_{nm} are equal to

$$M_{nm} = \langle \psi_n | \hat{L}\ {}^{(0)}_{\mathrm{B}} \psi_m \rangle \tag{19}$$

and the vector elements f_n are equal to

$$f_n = \langle \psi_n | [P^{\mathrm{eq}}]^{-1} \hat{L}\ {}^{(1)} P^{\mathrm{eq}} \rangle \tag{20}$$

The coefficients a_n, which maximize the function in eq 18, are given by

$$a_n = -\sum_{m=1}^{M} {M_{nm}}^{-1} f_m \tag{21}$$

where ${M_{nm}}^{-1}$ are the matrix elements of the inverse of the matrix M_{nm}.

Substitution of the explicit form (eq 12) of the backward Smoluchowski operator leads to the following explicit expression for the matrix elements:

$$M_{nm} = -\sum_{j=1}^{2} \int \mathrm{d}\mathbf{R} \oint \mathrm{d}\hat{\mathbf{u}}_1 \oint \mathrm{d}\hat{\mathbf{u}}_2 \, \chi \Big\{ \Big(1 - \frac{1}{3}\epsilon_{\mathrm{t}}\Big) [\nabla_j \psi_n] \cdot [\nabla_j \psi_m] + \epsilon_{\mathrm{t}} \hat{\mathbf{u}}_j \hat{\mathbf{u}}_j : [\nabla_j \psi_n][\nabla_j \psi_m] + \epsilon_{\mathrm{r}} [\hat{R}_j \psi_n] \cdot [\hat{R}_j \psi_m] \Big\} \tag{22}$$

Substitution of the form in eq 8 for $\hat{L}\ {}^{(1)}$ gives

$$f_n = \int_{R<L/D} \mathrm{d}\mathbf{R} \oint \mathrm{d}\hat{\mathbf{u}}_1 \oint \mathrm{d}\hat{\mathbf{u}}_2 \, \chi \Big\{ \Big(1 - \frac{1}{3}\epsilon_{\mathrm{t}}\Big) \frac{\partial \psi_n}{\partial z} + \epsilon_{\mathrm{t}} \hat{\mathbf{u}}_z (\hat{\mathbf{u}}_1 \cdot \nabla \psi_n) \Big\} - \Big(\frac{L}{D}\Big)^2 \oint \mathrm{d}\hat{\mathbf{R}} \oint \mathrm{d}\hat{\mathbf{u}}_1 \oint \mathrm{d}\hat{\mathbf{u}}_2 \Big\{ \Big(1 - \frac{1}{3}\epsilon_{\mathrm{t}}\Big) \frac{z}{R} + \epsilon_{\mathrm{t}} \hat{\mathbf{u}}_z (\hat{\mathbf{u}}_1 \cdot \hat{R}) \Big\} \psi_{n|_{R=L/D}} \tag{23}$$

The numerical scheme is thus to calculate the matrix elements M_{nm} and the vector elements f_n, to invert the matrix M_{nm}, and to obtain the optimal values for the coefficients a_n from eq 21. The variational solution $v = \sum_{n=1}^{M} a_n \psi_n$ can then be used to calculate the first order in volume fraction coefficient for the long-time translational self-diffusion coefficient.

4. Expression for the Linear Concentration Coefficient

There are four forces on rod 1 to be considered: the external force $\mathbf{F}^{\mathrm{ext}}$, the interaction force $\mathbf{F}^{\mathrm{I}} = -\nabla_1 \Phi$, with Φ the total potential energy of an assembly of N rods, the Brownian force $\mathbf{F}^{\mathrm{Br}} = -k_{\mathrm{B}} T \nabla_1 \ln\{P\}$, with P the N-particle probability density function for the positions and orientations, and the hydrodynamic force $\mathbf{F}^{\mathrm{h}}$ which results from friction with the solvent. Without hydrodynamic interactions, the hydrodynamic force is equal to

$$\mathbf{F}^{\mathrm{h}} = -(\gamma_{\parallel} \hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1 + \gamma_{\perp} [\hat{\mathbf{I}} - \hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1]) \cdot \mathbf{v} \tag{24}$$

where $\gamma_{\parallel}$ and $\gamma_{\perp}$ are the friction coefficients for motion parallel and perpendicular to the rods long axis, respectively. On the Brownian time scale these four forces balance, that is, the inertial force is very small in comparison to each of the other forces. Thus

$$\mathbf{F}^{\mathrm{ext}} + \mathbf{F}^{\mathrm{I}} + \mathbf{F}^{\mathrm{Br}} + \mathbf{F}^{\mathrm{h}} = \mathbf{0} \tag{25}$$

Using the above expressions for the forces yields the thermally averaged velocity of rod 1

$$\langle \mathbf{v} \rangle = \langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot [\beta \mathbf{F}^{\mathrm{ext}} - \beta \nabla_1 \Phi - \nabla_1 \ln\{P\}] \rangle \tag{26}$$

where

$$\mathbf{D}(\hat{\mathbf{u}}_1) = D_{\parallel} \hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1 + D_{\perp} [\hat{\mathbf{I}} - \hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1] = \bar{D} \hat{\mathbf{I}} + \Delta D \Big[\hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1 - \frac{1}{3} \hat{\mathbf{I}} \Big] \tag{27}$$

with $D_{\parallel,\perp} = k_{\mathrm{B}} T / \gamma_{\parallel,\perp}$, while $\bar{D}$ and ΔD are defined just below eq 5. For a pairwise additive potential Φ and identical rods we have (remember that $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ is the center-to center distance in units of the thickness D of the rods)

$$\langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \nabla_1 \Phi \rangle = \frac{N-1}{D} \langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \nabla V(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \rangle \tag{28}$$

The N-particle probability density function P, on the pair level, is equal to

$$P \equiv \frac{1}{V^N} g_N = \frac{1}{V^N} \prod_{\substack{i,j=1 \\ i<j}}^{N} g(\mathbf{R}_{\mathrm{i}} - \mathbf{R}_{\mathrm{j}}, \hat{\mathbf{u}}_{\mathrm{i}}, \hat{\mathbf{u}}_{\mathrm{j}}) \tag{29}$$

where g_N is the N-particle correlation function, and g is the pair-correlation function. Hence, for identical rods

$$\langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \nabla_1 \ln\{P\} \rangle = \frac{N-1}{D} \langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \nabla \ln\{P(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)\} \rangle \tag{30}$$

where P is related to the function Ψ in eq 9 for which we constructed a variational solution in the previous section. On the two-particle level the thermally averaged translational velocity of the tracer rod thus follows from substitution of eqs 28, 30 into eq 26 as

$$\langle \mathbf{v} \rangle = \Big\langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \Big(\beta \mathbf{F}^{\mathrm{ext}} - \frac{N-1}{D} [\beta \nabla V(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) + \nabla \ln\{P(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)\}] \Big) \Big\rangle = \bar{D} \beta \mathbf{F}^{\mathrm{ext}} - (N-1) \beta \mathbf{F}^{\mathrm{ext}} \langle \mathbf{D}(\hat{\mathbf{u}}_1) \cdot \nabla \Psi(\mathbf{R}, \hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) \rangle_0 \tag{31}$$

where in the second equation, eq 9 has been inserted, and where $\langle \cdots \rangle_0$ is the average with respect to P^{eq}. From eq 2 that relates $\langle \mathbf{v} \rangle$ to $D_{\mathrm{s}}^{\mathrm{l}}$ the following expression for the first order in concentration coefficient α (see eq 1) is found

$$\alpha = \frac{1}{4\pi^3 \frac{L}{D}\left(1 - \frac{1}{3}\frac{D}{L}\right)}\Bigg[\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi \frac{\partial \psi}{\partial z} - \left(\frac{L}{D}\right)^2 \oint d\hat{\mathbf{R}} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \frac{z}{R} \Psi_{|_{R=L/D}} + \frac{\Delta D}{\bar{D}} \int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi \hat{\mathbf{e}} \cdot \left[\hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right] \cdot \nabla \psi - \frac{\Delta D}{\bar{D}} \left(\frac{L}{D}\right)^2 \oint d\hat{\mathbf{R}} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \hat{\mathbf{e}}_3 \cdot \left[\hat{\mathbf{u}}_1 \hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right] \cdot \hat{\mathbf{R}} \psi_{|_{R=L/D}} \Bigg] \quad (32)$$

For mathematical details see Appendix E. We used here that the volume v_p of a single sphero-cylindrical rod is equal to $(\pi/4)D^2L[1 - (1/3)(D/L)]$, in order to express the volume fraction $\varphi = v_p N/V$ in terms of L and D. The first two integrals between the square brackets in eq 32 correspond to the term $\sim\bar{D}$ in eq 27, while the last two integrals correspond to the term $\sim\Delta D$. The last two terms in eq 32 thus account for coupling between translational and rotational motion on the one-particle level; that is, they account for the orientation dependence of the translational friction coefficient of a single rod.

5. Results and Discussion

Integrals are evaluated using Gaussian integration quadratures. For the trial functions that we used, we found that the two last integrals within the square brackets in eq 32 for α are negligibly small. After integration with respect to $\hat{\mathbf{u}}_2$ and $\mathbf{R}$ or $\hat{\mathbf{R}}$, respectively, the result was found to be virtually independent of $\hat{\mathbf{u}}_1$. The integration with respect to $\hat{\mathbf{u}}_1$ then yields a zero result, since $\oint d\hat{\mathbf{u}}_1 \, [\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - {}^1/_3\hat{\mathbf{I}}] = \mathbf{0}$. Physically this means that the orientation dependence of the translational friction coefficient of a single rod hardly affects the long-time translational friction coefficient. This is probably due to the fact that for long times the rods probed many independent orientations, so that on average the orientation dependence of the friction coefficient does not come into play. Results for the first order in concentration coefficient α as a function of the aspect ratio L/D are presented in parts a and b of Figure 1. The dashed curves are the results obtained with the simple trial function, the solid lines with the advanced trial function. The difference between these two curves is an indication for the accuracy of the trial functions. Up to $L/D = 10$ the accuracy is thus estimated to be about 4%, for $10 < L/D < 20$ about 8% and for $20 < L/D < 30$ about 12%. The filled circles in Figure 1a are computer simulation results[12] of which the accuracy is about 5%, as indicated by the error bars (computer simulations do not go further than $L/D = 6$ because of increasing computation times). The errors in the computer simulation results are rather large because these are obtained by an exponential fit of the tail of a correlation function. It may seem that the variational results are less accurate for intermediate aspect ratios. However, the uncertainty in the computer simulation results, which is only *estimated* to be 5%, could very well be larger for the given result at the intermediate aspect ratio. We feel that the apparent mismatch at the intermediate aspect ratio is statistically not significant. The open circle is an experimental result for colloidal silica rods.[13] The experimental results and computer simulation data are in good agreement with the results obtained from the variational principle.

A simple formula that fits the result for the advanced trial function to within a few percent reads (with $p = L/D$)

$$\alpha = 2 + \frac{10}{32}(p - 1) + \frac{1}{53}(p - 1)^2 \quad (33)$$

Note that the result $\alpha = 2$ for spheres is an exact result, but for larger aspect ratios the results for the two trial functions differ, due to the fact that the second term between the curly brackets in eq 17 for our trial function is not an exact solution for very long and thin rods.

In obtaining the above results, we have neglected hydrodynamic interactions between the rods. The validity of the arguments as given in the introduction that these interactions are not so important for the numerical value of the long-time self-diffusion coefficient could be assessed by extending the variational principle to include these interactions. This is straightforward due to the symmetry of the hydrodynamic interaction functions. The difficulty here will be not only that integrands become more involved but also that proper approximations for these hydrodynamic interaction functions, for which so far no exact results are known as for spherical particles, are difficult to find.

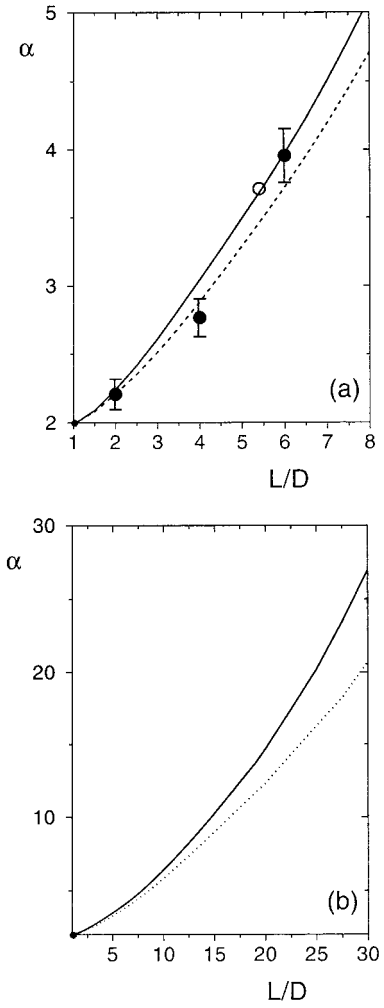

Figure 1. First order in concentration coefficient α as a function of the aspect ratio L/D: (a) for $L/D < 8$ and (b) for $L/D < 30$. The dashed line is obtained from the simple trial function; the solid line is obtained from the advanced trial function. Filled circles in part a are computer simulation results,[12] and the open circle is an experimental result.[13]

The variational technique can be used to calculate long-time *rotational* diffusion coefficients as well, where the problem will be to find appropriate trial functions. The variational approach presented here also applies to more concentrated systems, where the additional problem is to find an appropriate closure for the three-particle probability density function. In addition it can be applied to diffusion in restricted geometries as far as the geometrical hindrance of the confining geometry is concerned.

Appendix A. Proof of the Variational Principle

In this appendix the variational theorem mentioned in the main text (see eq 11) is proven.

Let us write $v = \Psi + \epsilon\eta$, with Ψ a stationary element of the functional, ϵ a real number, and η an arbitrary function (in F). Substitution of this form for v into the functional (eq 11) gives

$$F\ [\Psi + \epsilon\eta] - F\ [\Psi] = 2\epsilon\langle\eta|\hat{A}\ \Psi - f\rangle + \epsilon^2\langle\eta|\hat{A}\ \eta\rangle$$

For Ψ to be a stationary element of the functional, the leading order term in ϵ must vanish, that is, $\langle\eta|\hat{A}\ \Psi - f\rangle = 0$. Since η is an arbitrary function, it follows that $\hat{A}\ \Psi - f = 0$.

That all stationary elements Ψ actually maximizes the functional (eq 11) follows from the fact that the last term in the above equation $\sim\epsilon^2$ is negative, since $\hat{A}$ is negative definite. Notice that the above expression is exact and not the result of a truncated series expansion with respect to ϵ.

Now suppose that both Ψ_1 and Ψ_2 are solutions of the Smoluchowski equation, and let $\eta = \Psi_1 - \Psi_2$. From the above equation, with $\epsilon = 1$, we find that

$$F\ [\Psi_1] - F\ [\Psi_2] = \langle\eta|\hat{A}\ \eta\rangle < 0$$

provided that $\Psi_1 \neq \Psi_2$; that is, $\eta \neq 0$. On the other hand, interchanging Ψ_1 and Ψ_2, we find that

$$F\ [\Psi_2] - F\ [\Psi_1] = \langle\eta|\hat{A}\ \eta\rangle < 0$$

These two results are in contradiction, from which it follows that $\eta = 0$, so that the solution of the Smoluchowski equation is unique, within the space F of admissible functions.

Appendix B. The Backward Smoluchowski Operator

Consider the last term in the Smoluchowski operator (eq 4)

$$\hat{L}\ v \equiv \hat{R}_j\cdot[\hat{R}_j v + \beta v[\hat{R}_j V]]$$

From Stokes's integral theorem we have

$$\oint \mathrm{d}\hat{\mathbf{u}}_j\ \hat{R}_j v = \mathbf{0}$$

since the rim of the closed unit spherical surface is empty. Hence

$$\langle u||\hat{R}_j v\rangle = -\langle\hat{R}_j u||v\rangle \tag{34}$$

and

$$\langle u||\hat{R}_j\cdot\hat{R}_j v\rangle = \langle\hat{R}_j\cdot\hat{R}_j u||v\rangle \tag{35}$$

It follows immediately from the two above identities that the Hemitian conjugate $\hat{L}^{\dagger}$ of $\hat{L}$ with respect to the unweighted innerproduct is equal to

$$\hat{L}^{\dagger} v = [\hat{R}_j - \beta[\hat{R}_j V]]\cdot\hat{R}_j v$$

This corresponds to the last term in eq 12 for the backward Smoluchowski operator. The remaining terms follow similarly from the spatial analogues of eqs 34 and 35

$$\langle u||\nabla_j v\rangle = -\langle\nabla_j u||v\rangle \tag{36}$$

$$\langle u||\nabla_j\cdot\nabla_j v\rangle = \langle\nabla_j\cdot\nabla_j u||v\rangle \tag{37}$$

which identities are a consequence of Gauss's integral theorem. This concludes the derivation of the expression (eq 12) for the backward Smoluchowski operator.

Appendix C. Proof of Negative Definiteness of $\hat{L}^{(0)}_{B}$

Consider the last term in eq 12, corresponding to the operator

$$\hat{L}\ v \equiv [\hat{R}_j - \beta[\hat{R}_j V]]\cdot\hat{R}_j v$$

Since $P^{\mathrm{eq}} \sim \exp\{-\beta V\}$ we have

$$P^{\mathrm{eq}}[\hat{R}_j - \beta[\hat{R}_j V]]\cdot\hat{R}_j v = \hat{R}_j\cdot[P^{\mathrm{eq}}\hat{R}_j v] \tag{38}$$

From the definitions of the weighted and unweighted innerproducts it thus follows that

$$\langle v|\hat{L}\ v\rangle = \langle v||\hat{R}_j\cdot[P^{\mathrm{eq}}\hat{R}_j v]\rangle$$
$$= -\int \mathrm{d}\mathbf{R}_1 \int \mathrm{d}\mathbf{R}_2 \oint \mathrm{d}\hat{\mathbf{u}}_1 \oint \mathrm{d}\hat{\mathbf{u}}_2\ P^{\mathrm{eq}}|\hat{R}_j v|^2$$

In the second equation we used eq 34. Since P^{eq} is positive, it follows that $\hat{L}$ is negative definite with respect to the weighted innerproduct. The remaining terms in the expression 4 for the Smoluchowski operator are shown to be negative definite in a similar way, using the spatial analoque of eq 38

$$P^{\mathrm{eq}}[\nabla_j - \beta[\nabla_j V]]\cdot\nabla_j v = \nabla_j\cdot[P^{\mathrm{eq}}\nabla_j v] \tag{39}$$

together with eq 36. This concludes the proof of negative definiteness of $\hat{L}^{(0)}_{B}$ with respect to the weighted inner product.

Appendix D. The Explicit Form of the Functional

The first integral in eq 15 is already found in Appendix C in connection with positive definiteness of the backward Smoluchowski operator.

Consider now the evaluation of the second term $\langle v|[P^{\mathrm{eq}}]^{-1}\hat{L}^{(1)}P^{\mathrm{eq}}\rangle$ in eq 14. By definition we have

$$\langle v|[P^{\mathrm{eq}}]^{-1}\hat{L}^{(1)}P^{\mathrm{eq}}\rangle = -\int \mathrm{d}\mathbf{R}_1 \int \mathrm{d}\mathbf{R}_2 \oint \mathrm{d}\hat{\mathbf{u}}_1 \oint \mathrm{d}\hat{\mathbf{u}}_2$$
$$v\left\{\nabla_1\cdot[\hat{\mathbf{e}}_3 P^{\mathrm{eq}}] + \epsilon_t\nabla_1\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot[\hat{\mathbf{e}}_3 P^{\mathrm{eq}}]\right\}$$

Now note that on the pair-level, P^{eq} is a constant whenever $R = |\mathbf{R}_1 - \mathbf{R}_2| > L/D$, so that the above integral extends only over center-to-center distances $R < L/D$ (remember that $\mathbf{R}$ is the center-to-center distance of two rods in units of their thickness D).

Hence,

$$\langle v|[P^{eq}]^{-1}\hat{L}\ {}^{(1)}P^{eq}\rangle = -VD^3 \int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, v\left\{\nabla_1\cdot[\hat{\mathbf{e}}_3 P^{eq}] + \epsilon_t \nabla_1\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot[\hat{\mathbf{e}}_3 P^{eq}]\right\}$$

An application of Gauss's integral theorem gives

$$\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, v\left\{\nabla_1\cdot[\hat{\mathbf{e}}_3 P^{eq}] + \epsilon_t \nabla_1\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot[\hat{\mathbf{e}}_3 P^{eq}]\right\} = -\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\left\{\nabla_1\cdot[\hat{\mathbf{e}}_3 v] + \epsilon_t \nabla_1\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot[\hat{\mathbf{e}}_3 v]\right\} + \oint_{R=L/D} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq} v\left\{\hat{\mathbf{e}}_3 + \epsilon_t\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\hat{\mathbf{e}}_3\right\}$$

where d$\mathbf{S}$ points away from the origin. Using $P^{eq} = 1/(4\pi V)^2$ for $R = L/D$, the surface integral in the above result can be rewritten as

$$\oint_{R=L/D} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq} v\left\{\hat{\mathbf{e}}_3 + \epsilon_t\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\hat{\mathbf{e}}_3\right\} = \left(\frac{L}{D}\right)^2 \frac{1}{(4\pi V)^2} \oint d\hat{\mathbf{R}} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, v\left\{\left(1 - \frac{1}{3}\epsilon_t\right)\frac{z}{R} + \epsilon_t \hat{\mathbf{u}}_z(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{R}})\right\}_{v|_{R=L/D}}$$

where the latter integral ranges over the unit spherical surface. This immediately leads to the last two integrals in eq 15.

Appendix E. Mathematical Details for the Derivation of Eq 32

Since only the z-component of $\langle\mathbf{v}\rangle$ is of importance, the following two terms in the average in eq 31 must be considered

$$A_1 \equiv \langle\hat{\mathbf{e}}_3\cdot\nabla\Psi\rangle_0 = \left\langle\frac{\partial}{\partial z}\Psi\right\rangle_0 \tag{40}$$

and

$$A_2 \equiv \left\langle\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi\right\rangle_0 \tag{41}$$

Consider first the evaluation of A_1. By definition we have

$$A_1 = D^2 V \int d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\frac{\partial}{\partial z}\Psi$$

To avoid mathematical complications due to the jump discontinuities of P^{eq} upon overlap of hard-cores, the volume integral is split into two parts

$$A_1 = \frac{D^2}{16\pi^2 V}\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi\frac{\partial}{\partial z}\Psi + D^2 \int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\frac{\partial}{\partial z}\Psi$$

where we used $P^{eq} = \chi/(4\pi V)^2$. The last integral is rewritten with the help of Gauss's integral theorem as

$$\int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\hat{\mathbf{e}}_3\cdot\nabla\Psi = -\int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \Psi\hat{\mathbf{e}}_3\cdot\nabla P^{eq} - \oint_{R=L/D} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \hat{\mathbf{e}}_3 P^{eq}\Psi + \oint_{R\in\partial V} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \hat{\mathbf{e}}_3 P^{eq}\Psi$$

with d$\mathbf{S}$ pointing away from the origin and ∂V the surface that bounds the volume V. The volume integral on the right hand-side in the first line is zero, since P^{eq} = constant within the volume V for $R > L/D$. The last surface integral in the second line is zero because $P^{eq} = 0$ on ∂V. We thus find that

$$A_1 = \frac{D^2}{16\pi^2 V}\left[\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi\frac{\partial}{\partial z}\Psi - \left(\frac{L}{D}\right)^2 \oint_{R=L/D} d\hat{\mathbf{R}} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \frac{z}{R}\Psi_{|_{R=L/D}}\right]$$

where the surface integral now ranges over the unit spherical surface. In this way the first two terms between the square brackets in eq 32 are reproduced.

Consider now A_2. By definition we have

$$A_2 = D^2 V \int d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi$$

Again we split the volume integral into two parts

$$A_2 = \frac{D^2}{16\pi^2 V}\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi + D^2 V \int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi$$

The second integral is rewritten, as before, with the help of Gauss's integral theorem as

$$\int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, P^{eq}\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi = \int_{R>L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \Psi\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla P^{eq} - \oint_{R=L/D} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\hat{\mathbf{e}}_3 P^{eq}\Psi + \oint_{R\in\partial V} d\mathbf{S}\cdot\oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\hat{\mathbf{e}}_3 P^{eq}\Psi$$

For the same reasons as before, the volume integral and the surface integral ranging over the boundary ∂V of V are zero. Hence

$$A_2 = \frac{D^2}{16\pi^2 V}\left[\int_{R<L/D} d\mathbf{R} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \chi\hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\nabla\Psi - \left(\frac{L}{D}\right)^2 \oint d\hat{\mathbf{R}} \oint d\hat{\mathbf{u}}_1 \oint d\hat{\mathbf{u}}_2 \, \hat{\mathbf{e}}_3\cdot\left[\hat{\mathbf{u}}_1\hat{\mathbf{u}}_1 - \frac{1}{3}\hat{\mathbf{I}}\right]\cdot\hat{\mathbf{R}}\Psi_{|_{R=L/D}}\right]$$

These two terms correspond to the last two integrals in eq 32 for the coefficient α.

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