

Self-diffusion in suspensions of interacting Brownian particles

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We study the short-time and long-time self-diffusion coefficients for a system of interacting, spherical Brownian particles. To first order in the volume fraction occupied by particles, the coefficients are given by exact expressions, first derived by Batchelor [J. Fluid Mech. **83**, 97 (1976); **131**, 155 (1983); **137**, 467 (1983)]. We show that the expression for the long-time self-diffusion coefficient may be cast in a different form by use of a dielectric analogy. The new expression turns out to be advantageous in practical calculations and in qualitative considerations.

I. INTRODUCTION

The self-diffusion coefficient is a quantity of prime interest in the description of the dynamics of interacting Brownian particles. It characterizes the stochastic motion of tracer particles which may be observed in a light-scattering experiment. A time-dependent self-diffusion coefficient $D_S(t)$ may be defined from the mean-square displacement of a particle after time t via the relation

$$\langle [\mathbf{R}(t) - \mathbf{R}(0)]^2 \rangle = 6D_S(t)t. \quad (1.1)$$

For typical Brownian particles the time scale seen in a light-scattering experiment is far longer than the momentum relaxation time τ_B . The latter is of order m/ζ , where m is the mass and ζ is the friction coefficient of a particle. For $t \gg \tau_B$ the self-diffusion coefficient, as defined in (1.1), still varies with time due to relaxation in positions of the surrounding Brownian particles, which occurs on a time scale $\tau_I \gg \tau_B$. The time scale τ_I is of order a^2/D_0 , where a is the radius and $D_0 = k_B T/\zeta$ is the diffusion coefficient of a single particle. The short-time self-diffusion coefficient D_S^S and the long-time self-diffusion coefficient D_S^L are defined by the behavior at short and long times

$$D_S(t) \approx \begin{cases} D_S^S & \text{for } \tau_B \ll t \ll \tau_I \\ D_S^L & \text{for } t \gg \tau_I. \end{cases} \quad (1.2)$$

On the time scale seen in light-scattering experiments the system of Brownian particles is described by the generalized Smoluchowski equation.¹ In Sec. II we give a more formal definition of the self-diffusion coefficients D_S^S and D_S^L based on this equation. The long-time self-diffusion coefficient is related to the steady-state friction coefficient ζ_S of a selected particle via the Einstein relation $D_S^L = k_B T/\zeta_S$.

The short-time and long-time self-diffusion coefficients have been determined in several light-scattering experiments.²⁻⁸ For very dilute suspensions the coefficients both equal the bare diffusion coefficient D_0 . For dilute suspensions Batchelor has derived exact expressions for D_S^S and D_S^L , valid to first order in the volume fraction.^{9,10} Precise numerical results have been obtained for suspensions of hard spheres with⁹⁻¹² and without^{13,14} hydrodynamic interactions. More complicated models have been studied by a number of authors.¹⁵⁻²² All these studies are based on Batchelor's expressions or on a closely related version.

We show in the following that Batchelor's expression for the long-time self-diffusion coefficient D_S^L may be cast in a different form by the use of a dielectric analogy. The new expression turns out to be advantageous in numerical computation and in theoretical discussion. We study some simple models to demonstrate its use.

II. SELF-DIFFUSION COEFFICIENT

We consider N identical spherical particles performing Brownian motion in an incompressible fluid with shear viscosity η . The whole system is enclosed in a volume Ω . To study self-diffusion we consider the Brownian motion of a selected particle labeled 1. The particles interact via a direct pair potential and via hydrodynamic interactions, which are 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, then the configuration of the entire suspension may be described by the $3N$ -dimensional vector $\mathbf{X} = (\mathbf{R}_1, \dots, \mathbf{R}_N)$. The dynamical evolution of the configuration \mathbf{X} is assumed to be described by a time-dependent probability distribution $P(\mathbf{X}, t)$, which obeys the generalized Smoluchowski equation.¹ In abbreviated form this reads

$$\frac{\partial P}{\partial t} = \mathcal{D}P, \quad (2.1)$$

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

$$\mathcal{D}P = \frac{\partial}{\partial \mathbf{X}} \cdot \underline{\mathcal{D}} \cdot \left[\frac{\partial P}{\partial \mathbf{X}} + \beta \frac{\partial \Phi}{\partial \mathbf{X}} P \right]. \quad (2.2)$$

Here $\underline{\mathcal{D}}(\mathbf{X})$ is the $3N \times 3N$ diffusion matrix, which is related by a generalized Einstein relation

$$\underline{\mathcal{D}}(\mathbf{X}) = k_B T \underline{\mu}(\mathbf{X}) \quad (2.3)$$

to the $3N \times 3N$ mobility matrix $\underline{\mu}(\mathbf{X})$. The mobility matrix depends on configuration and may in principle be derived from the steady-state linearized Navier-Stokes equations describing the fluid motion. Furthermore, $\beta = 1/k_B T$ and the potential $\Phi(\mathbf{X})$ in Eq. (2.2) incorporates both a wall potential and the direct pair interactions. The Smoluchowski equation (2.1) describes how the distribution function $P(\mathbf{X}, t)$ tends to the equilibrium distribution

$$P_{\text{eq}}(\mathbf{X}) = \exp[-\beta\Phi(\mathbf{X})]/Z(\beta) \quad (2.4)$$

in the course of time.

The self-diffusion coefficient may be defined from the time-dependent scattering function at wave vector \mathbf{k}

$$F_S(\vec{\mathbf{k}}, t) = \lim_{\substack{N \rightarrow \infty \\ \Omega \rightarrow \infty}} \langle \exp i\vec{\mathbf{k}} \cdot [\vec{\mathbf{R}}_1(t) - \vec{\mathbf{R}}_1(0)] \rangle, \quad (2.5)$$

where we take the thermodynamic limit $N \rightarrow \infty$, $\Omega \rightarrow \infty$ at constant $n = N/\Omega$. The angle brackets indicate an average over the equilibrium distribution (2.4), and the time dependence of the position $\vec{\mathbf{R}}_1$ is governed by the adjoint Smoluchowski operator \mathcal{L} , such that $\vec{\mathbf{R}}_1(t) = [\exp \mathcal{L} t] \vec{\mathbf{R}}_1(0)$ with $\vec{\mathbf{R}}_1(0) = \vec{\mathbf{R}}_1$. The operator \mathcal{L} is given by

$$\mathcal{L} = \left[\frac{\partial}{\partial \mathbf{X}} - \beta \frac{\partial \Phi}{\partial \mathbf{X}} \right] \cdot \underline{\mathcal{D}} \cdot \frac{\partial}{\partial \mathbf{X}}. \quad (2.6)$$

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

$$G_S(\vec{\mathbf{k}}, \omega) = \int_0^\infty e^{i\omega t} F_S(\vec{\mathbf{k}}, t) dt. \quad (2.7)$$

We define the wave-vector- and frequency-dependent self-diffusion coefficient $D_S(\vec{\mathbf{k}}, \omega)$ from the identity

$$G_S(\vec{\mathbf{k}}, \omega) = \frac{1}{-i\omega + k^2 D_S(\vec{\mathbf{k}}, \omega)}. \quad (2.8)$$

The short-time self-diffusion coefficient is defined as the limit

$$D_S^S = \lim_{\omega \rightarrow \infty} \lim_{\mathbf{k} \rightarrow 0} D_S(\vec{\mathbf{k}}, \omega). \quad (2.9)$$

The long-time self-diffusion coefficient is defined as the limit

$$D_S^L = \lim_{\omega \rightarrow 0} \lim_{\mathbf{k} \rightarrow 0} D_S(\vec{\mathbf{k}}, \omega). \quad (2.10)$$

It is easily shown that the short-time self-diffusion coefficient is given by

$$D_S^S = \lim_{\mathbf{k} \rightarrow 0} \frac{-1}{k^2} \langle e^{-\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}_1} \mathcal{L} e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}_1} \rangle, \quad (2.11)$$

where the thermodynamic limit is implied. Thus the calculation of the short-term self-diffusion coefficient involves only the equilibrium average of a relatively simple quantity. The calculation of the long-term self-diffusion coefficient D_S^L is far more difficult since it involves the solution of the steady-state Smoluchowski equation.

The generalized self-diffusion coefficient $D_S(\vec{\mathbf{k}}, \omega)$ may be expressed as

$$D_S(\vec{\mathbf{k}}, \omega) = D_S(\vec{\mathbf{k}}, \infty) + M_S(\vec{\mathbf{k}}, \omega), \quad (2.12)$$

where $M_S(\vec{\mathbf{k}}, \omega)$ is the Fourier transform of the memory function.²³⁻³⁰ In the long-wavelength limit this is given by

$$M_S(\vec{0}, \omega) = \frac{1}{3} \langle \vec{\mathbf{U}}_1' \cdot (i\omega + \mathcal{L})^{-1} \vec{\mathbf{U}}_1' \rangle, \quad (2.13)$$

where $\vec{\mathbf{U}}_1'(\mathbf{X})$ is the velocity of the selected particle on the Smoluchowski time scale³¹

$$\vec{\mathbf{U}}_1' = \mathcal{L} \vec{\mathbf{R}}_1 = \sum_j \left[\frac{\partial}{\partial \vec{\mathbf{R}}_j} - \beta \frac{\partial \Phi}{\partial \vec{\mathbf{R}}_j} \right] \cdot \vec{\mathbf{D}}_{j1}. \quad (2.14)$$

The velocity $\vec{\mathbf{U}}_1'$ arises naturally in linear response theory applied to the generalized Smoluchowski equation.³² The derivation of Eq. (2.13) for the memory function is the same as that given by Ackerson,^{23,24} which is quoted in the review by Pusey and Tough.¹ However, in the expression presented by these authors the first term in Eq. (2.14), involving the divergence of the diffusion tensor, is missing. In Ackerson's case this is because he approximates the hydrodynamic interaction by the Oseen tensor; in the case of Pusey and Tough it is due to an apparent oversight.

The long-time self-diffusion coefficient may now be expressed as

$$D_S^L = D_S^S + \frac{1}{3} \langle \vec{\mathbf{U}}_1' \cdot \mathcal{L}^{-1} \vec{\mathbf{U}}_1' \rangle. \quad (2.15)$$

The same expression has been derived by Hanna, Hess, and Klein,¹⁴ but expressed with the Smoluchowski operator \mathcal{D} instead of its adjoint \mathcal{L} and with a different interpretation of the brackets. The expressions (2.11) and (2.15) are valid in general. In Sec. III we consider explicit expressions valid at low density.

III. DILUTE SUSPENSIONS

In a very dilute suspension the short-time and long-time self-diffusion coefficients defined in the preceding section are simply identical to the bare single-particle diffusion coefficient D_0 . For a particle with stick boundary conditions and with hydrodynamic radius a this is given by the Stokes-Einstein expression $D_0 = k_B T / 6\pi\eta a$. To first order in the density the short-time self-diffusion coefficient is modified to

$$D_S^S = D_0(1 + \lambda_A \phi), \quad (3.1)$$

where $\phi = (4\pi/3)na^3$ is the volume fraction, and the coefficient λ_A may be expressed in terms of the direct and

hydrodynamic pair interactions. The long-time self-diffusion coefficient is modified to

$$D_S^L = D_0[1 + (\lambda_A + \alpha_S)\phi], \quad (3.2)$$

where the additional coefficient α_S may again be evaluated from a pair problem.

The pair hydrodynamic interactions may be defined in terms of the two-body mobility matrix $\mu(1,2)$ composed of the four tensors $\vec{\mu}_{ij}^{\prime\prime}(1,2)$. The tensor $\vec{\mu}_{11}^{\prime\prime}(1,2)$ has the form

$$\vec{\mu}_{11}^{\prime\prime}(1,2) = \mu_0 \vec{1} + \alpha_{11}^{\prime\prime}(r) \hat{r}\hat{r} + \beta_{11}^{\prime\prime}(r) (\vec{1} - \hat{r}\hat{r}), \quad (3.3)$$

where $\mu_0 = 1/6\pi\eta a$ and $\vec{r} = \vec{R}_2 - \vec{R}_1$. The tensor $\vec{\mu}_{12}^{\prime\prime}(1,2)$ has the form

$$\vec{\mu}_{12}^{\prime\prime}(1,2) = \alpha_{12}^{\prime\prime}(r) \hat{r}\hat{r} + \beta_{12}^{\prime\prime}(r) (\vec{1} - \hat{r}\hat{r}). \quad (3.4)$$

The remaining two tensors follow by an interchange of labels and the symmetry properties

$$\alpha_{12}^{\prime\prime}(r) = \alpha_{21}^{\prime\prime}(r), \quad \beta_{12}^{\prime\prime}(r) = \beta_{21}^{\prime\prime}(r). \quad (3.5)$$

We define the dimensionless functions

$$A_{ij}^{\prime\prime}(x) = 6\pi\eta a \alpha_{ij}^{\prime\prime}(r), \quad B_{ij}^{\prime\prime}(x) = 6\pi\eta a \beta_{ij}^{\prime\prime}(r), \quad (3.6)$$

where $x = r/2a$.

The coefficient λ_A in Eq. (3.1) is given by the integral^{9,33}

$$\lambda_A = 8 \int_1^\infty g(x) [A_{11}^{\prime\prime}(x) + 2B_{11}^{\prime\prime}(x)] x^2 dx, \quad (3.7)$$

where $g(r)$ is the radial distribution function. In a dilute system this is given by

$$g(r) = \exp[-\beta v(r)], \quad (3.8)$$

where $v(r)$ is the direct pair interaction. It has been shown by Batchelor¹⁰ that the coefficient α_S in Eq. (3.2) may be expressed as

$$\alpha_S = 4 \int_1^\infty g(x) \left[W(x) - \frac{1}{2} \beta \frac{dv}{dx} G(x) \right] f(x) x^2 dx, \quad (3.9)$$

where the hydrodynamic function $W(x)$ is given by

$$W(x) = \frac{G-H}{x} + \frac{1}{2} \frac{dG}{dx}, \quad (3.10)$$

in terms of the functions $G(x)$ and $H(x)$ defined by

$$\begin{aligned} G(x) &= 1 + A_{11}^{\prime\prime}(x) - A_{12}^{\prime\prime}(x), \\ H(x) &= 1 + B_{11}^{\prime\prime}(x) - B_{12}^{\prime\prime}(x). \end{aligned} \quad (3.11)$$

The function $f(x)$ in Eq. (3.9) is a solution of a radial differential equation which originates from the two-sphere Smoluchowski equation. The radial differential equation reads

$$\frac{1}{x^2} \frac{d}{dx} \left[x^2 G \frac{df}{dx} \right] - \beta \frac{dv}{dx} G \frac{df}{dx} - \frac{2H}{x^2} f = 4W - 2\beta \frac{dv}{dx} G. \quad (3.12)$$

The solution $f(x)$ satisfies the boundary conditions

$$G \frac{df}{dx} = 0 \text{ at } x=1, \quad f \rightarrow 0 \text{ as } x \rightarrow \infty. \quad (3.13)$$

The behavior of the hydrodynamic function G near touching is given by⁹

$$G(x) \approx 4(x-1). \quad (3.14)$$

The coefficient λ_A may be evaluated straightforwardly from Eq. (3.7). The calculation of the coefficient α_S from Eq. (3.9) is more difficult. We show in the following that an alternative expression for the coefficient α_S may be found which is more convenient in practical calculations.

IV. LINEAR RESPONSE THEORY

In order to find the alternative expression for the coefficient α_S we return to the linear response theory from which the expression (3.9) was derived. Batchelor¹⁰ considered an applied force \vec{E}_0 acting on particle 1 and studied the resulting change in the pair distribution function. In linear response theory the steady-state Smoluchowski equation in the relative space of two particles reads

$$\vec{\nabla} \cdot \vec{D}_r(\vec{r}) \cdot [\vec{\nabla} P_1 + \beta(\vec{\nabla} v) P_1 + \frac{1}{2} \beta \vec{E}_0 g] = 0, \quad (4.1)$$

where $\vec{r} = \vec{R}_2 - \vec{R}_1$ is the relative coordinate $\vec{\nabla} = \partial/\partial\vec{r}$ and P_1 is the change of the pair distribution function from its equilibrium value g . The relative diffusion tensor is given by

$$\vec{D}_r(\vec{r}) = 2[\vec{D}_{11}(1,2) - \vec{D}_{12}(1,2)], \quad (4.2)$$

with $\vec{D}_{ij}(1,2) = k_B T \vec{\mu}_{ij}^{\prime\prime}(1,2)$. By angular symmetry the perturbed distribution function takes the form

$$P_1(\vec{r}) = -\frac{1}{2} a \beta g(r) f(r) \hat{r} \cdot \vec{E}_0, \quad (4.3)$$

with a radial function $f(r)$, which satisfies the differential equation (3.12). The linear equation (4.1) may be expressed formally as

$$\mathcal{D}_r P_1 = \beta g \vec{U}'_1 \cdot \vec{E}_0, \quad (4.4)$$

with the velocity \vec{U}'_1 given by

$$\vec{U}'_1 = -\frac{1}{2} [\vec{\nabla} \cdot \vec{D}_r - \beta(\vec{\nabla} v) \cdot \vec{D}_r]. \quad (4.5)$$

Solving for the perturbed distribution function P_1 and evaluating the mean of \vec{U}'_1 , one finds for the coefficient α_S ,

$$\alpha_S = \frac{1}{4\pi D_0 a^3} \int \vec{U}'_1 \cdot \mathcal{D}_r^{-1} (\vec{U}'_1 g) d\vec{r}. \quad (4.6)$$

This may be expressed alternatively as

$$\alpha_S = \frac{1}{4\pi D_0 a^3} \int g \vec{U}'_1 \cdot \mathcal{L}_r^{-1} \vec{U}'_1 d\vec{r}, \quad (4.7)$$

where \mathcal{L}_r is the adjoint Smoluchowski operator

$$\mathcal{L}_r = [\vec{\nabla} - \beta(\vec{\nabla} v)] \cdot \vec{D}_r \cdot \vec{\nabla}. \quad (4.8)$$

There is an obvious relation with the memory function given by Eq. (2.15). By performing the angular integrations in Eq. (4.6) one arrives at the expression (3.9). We

note that it is evident from Eq. (4.7) that the coefficient α_S is negative definite.

V. DIELECTRIC ANALOGY

In this section we show that the expression (4.7) for the coefficient α_S may be cast in an alternative form by use of a dielectric analogy. We introduce two functions $\psi_0(\vec{r})$ and $\psi_1(\vec{r})$ by the definitions

$$\psi_0 = -\vec{E}_0 \cdot \vec{r}, \quad P_1 = -\frac{1}{2}\beta g \psi_1. \quad (5.1)$$

By substitution we find that Eq. (4.1) may be written alternatively as

$$\vec{\nabla} \cdot \vec{\epsilon} \cdot \vec{\nabla} \psi = 0, \quad (5.2)$$

with

$$\psi = \psi_0 + \psi_1, \quad (5.3)$$

and the abbreviation

$$\vec{\epsilon} = g \vec{D}_r / 2D_0. \quad (5.4)$$

We may interpret $\psi(\vec{r})$ as the electrostatic potential in a dielectric described by the dielectric tensor $\vec{\epsilon}(\vec{r})$. Correspondingly, we define the electric field and the electric polarization from the electrostatic equations

$$\vec{E} = -\vec{\nabla} \psi, \quad \vec{P} = \frac{1}{4\pi} (\vec{\epsilon} - \vec{1}) \cdot \vec{E}. \quad (5.5)$$

The dielectric tensor vanishes identically for $r < 2a$, corresponding to a perfectly insulating sphere.

The integral evaluated in linear response theory is given by

$$I_S = 2 \frac{k_B T}{D_0} \int \vec{E}_0 \cdot \vec{U}'_1 P_1 d\vec{r}, \quad (5.6)$$

where we have chosen a convenient prefactor. Substituting Eqs. (4.5) and (5.1) we find that in the dielectric analogy the integral may be expressed as

$$I_S = \int \psi_1 \vec{\nabla} \cdot (\vec{\epsilon} \cdot \vec{E}_0) d\vec{r}. \quad (5.7)$$

The direct interaction potential $v(r)$ tends to zero at large distances, and the relative diffusion tensor $\underline{D}_r(\vec{r})$ tends to $2D_0 \vec{1}$, so that the dielectric tensor, defined by Eq. (5.4), tends to the unit tensor as the distance r tends to infinity. For realistic hydrodynamic interactions the decay of the diffusion tensor is slow, and $\vec{\epsilon}(\vec{r})$ tends to the unit tensor in proportion to the inverse of the distance r . As a consequence the same is true of the polarization given by Eq. (5.5). It follows from the detailed form of the radial equation corresponding to Eq. (5.2) that, nonetheless, the perturbed potential ψ_1 has the asymptotic form

$$\psi_1(\vec{r}) = \alpha \frac{\hat{r} \cdot \vec{E}_0}{r^2} + O(r^{-3}), \quad (5.8)$$

with electric polarizability α . We shall show that the integral I_S , given by Eq. (5.7), may be expressed in terms of the polarizability α . The derivation is somewhat delicate,

because of the slow decay of the dielectric tensor $\vec{\epsilon}$, and we present it in detail.

Since \vec{E}_0 is a constant, we may write

$$\begin{aligned} \psi_1 \vec{\nabla} \cdot (\vec{\epsilon} \cdot \vec{E}_0) &= \psi_1 \vec{\nabla} \cdot [(\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0] \\ &= \vec{\nabla} \cdot [\psi_1 (\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0] - (\vec{\nabla} \psi_1) \cdot (\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0. \end{aligned} \quad (5.9)$$

We perform the integral in Eq. (5.7) for a large spherical volume V centered at the origin and subsequently take the limit of infinite radius. For realistic hydrodynamic interactions the divergence $\vec{\nabla} \cdot (\vec{\epsilon} \cdot \vec{E}_0)$ decays in proportion to r^{-5} , so that the integral converges fast and does not depend on the chosen shape of integration volume. By use of Gauss's theorem we find that the first term on the right-hand side of Eq. (5.9) gives zero contribution. In the second term we write $\vec{E}_0 = -\nabla \psi_0$ and perform an integration by parts to find

$$I_S = \int \psi_0 \vec{\nabla} \cdot [(\vec{\epsilon} - \vec{1}) \cdot (\vec{E} - \vec{E}_0)] d\vec{r}. \quad (5.10)$$

Substituting Eq. (5.5) we obtain

$$I_S = 4\pi \int \psi_0 \vec{\nabla} \cdot \vec{P} d\vec{r} - \int \psi_0 \vec{\nabla} \cdot [(\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0] d\vec{r}. \quad (5.11)$$

The first integral on the right-hand side may be transformed to

$$\begin{aligned} 4\pi \int_V \psi_0 \vec{\nabla} \cdot \vec{P} d\vec{r} &= - \int_V \psi_0 \vec{\nabla} \cdot \vec{E} d\vec{r} \\ &= - \int_S \psi_0 \vec{E}_1 \cdot \hat{r} dS - \int_V \vec{E}_0 \cdot \vec{E}_1 d\vec{r}, \end{aligned} \quad (5.12)$$

where we have used $\vec{\nabla} \cdot \vec{E} = \vec{\nabla} \cdot \vec{E}_1$ with $\vec{E}_1 = -\vec{\nabla} \psi_1$. The last term may be transformed to a surface integral

$$\int_V \vec{E}_0 \cdot \vec{E}_1 d\vec{r} = - \int_V \vec{\nabla} \cdot (\vec{E}_0 \psi_1) d\vec{r} = - \int_S \psi_1 \hat{r} \cdot \vec{E}_0 dS. \quad (5.13)$$

Using the asymptotic form (5.8) to evaluate the surface integrals in Eqs. (5.12) and (5.13) we find, finally,

$$I_S = 4\pi \alpha \vec{E}_0^2 - \int \psi_0 \vec{\nabla} \cdot [(\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0] d\vec{r}. \quad (5.14)$$

The coefficient α_S , given by Eq. (4.6), may now be expressed as

$$\alpha_S = \frac{3}{2} \frac{\alpha}{a^3} + J_S, \quad (5.15)$$

where J_S is defined by

$$J_S = -\frac{3}{8\pi a^3 \vec{E}_0^2} \int \psi_0 \vec{\nabla} \cdot [(\vec{\epsilon} - \vec{1}) \cdot \vec{E}_0] d\vec{r}. \quad (5.16)$$

It follows from Eqs. (3.3), (3.4), (4.2), and (5.4) that the dielectric tensor has the spherical symmetry

$$\vec{\epsilon}(\vec{r}) = \epsilon_n(r) \hat{r} \hat{r} + \epsilon_t(r) (\vec{1} - \hat{r} \hat{r}). \quad (5.17)$$

Substituting into Eq. (5.16) and performing the angular integrations we obtain

$$J_S = \frac{1}{2a^3} \int_0^\infty \left[r^3 \frac{d\epsilon_n}{dr} + 2r^2 (\epsilon_n - \epsilon_t) \right] dr. \quad (5.18)$$

For realistic hydrodynamic interactions the integrand varies in proportion to $1/r^2$ at large r .

The expression (5.15) together with Eq. (5.18) is the

main result of this article. It allows the calculation of the coefficient α_S from a calculation of the electric polarizability α , which characterizes the asymptotic form of the perturbed distribution function and the single integral (5.18). The explicit form of the perturbed distribution function is not needed, unlike in Batchelor's expression (3.9). It turns out that the expression (5.15) is of great help in practical calculations. It also facilitates the qualitative discussion.

VI. MODEL CALCULATIONS

In this section we show that the expression (5.15) for the coefficient α_S may be used conveniently in simple model calculations. We note first that for models in which the radial dielectric constant ϵ_n tends to unity faster than $1/r^3$, we may perform an integration by parts in Eq. (5.18) to obtain

$$J_S = 4 - \frac{1}{2a^3} \int_{2a}^{\infty} (\epsilon_n + 2\epsilon_t - 3)r^2 dr, \quad (6.1)$$

where we have used also that ϵ_n and ϵ_t vanish for $r < 2a$. This transformation cannot be used in the case of realistic hydrodynamic interactions, since then ϵ_n tends to unity only in proportion to $1/r$.

As a first application we consider hard spheres of radius a without hydrodynamic interactions. For this model the equivalent dielectric tensor vanishes for $r < 2a$ and equals the unit tensor for $r > 2a$. The polarizability of a perfectly insulating sphere of radius $2a$ in vacuum equals $\alpha = -4a^3$. The integral in Eq. (6.1) vanishes for this model. Therefore we find $\alpha_S = -2$, the well-known value for the hard-sphere model.^{13,14} Note that Batchelor's expression (3.9) requires a subtle limit consideration for this model.³⁴

Next we consider hard spheres of radius a with a shell of radius b , with interaction potential

$$v(r) = \begin{cases} \infty & \text{for } 0 < r < 2a \\ v_1 & \text{for } 2a < r < 2b \\ 0 & \text{for } 2b < r. \end{cases} \quad (6.2)$$

Furthermore, we assume that the relative diffusion tensor \bar{D}_r is a scalar with value $2D_1$ in the shell $2a < r < 2b$ and with value $2D_0$ for $r > 2b$. From Eq. (5.4) we find therefore a scalar dielectric constant ϵ with values

$$\epsilon = \begin{cases} 0 & \text{for } 0 < r < 2a \\ g_1 D_1 / D_0 & \text{for } 2a < r < 2b \\ 1 & \text{for } 2b < r, \end{cases} \quad (6.3)$$

where $g_1 = \exp(-\beta v_1)$. The polarizability for this shell model is easily evaluated and found to be

$$\alpha = 4\rho \frac{2(\epsilon_1 - 1)\rho - 2\epsilon_1 - 1}{(\epsilon_1 + 2)\rho - \epsilon_1 + 1} a^3, \quad (6.4)$$

with the abbreviations

$$\rho = (b/a)^3, \quad \epsilon_1 = g_1 D_1 / D_0. \quad (6.5)$$

The integral J_S is given by

$$J_S = 4 - 4(\epsilon_1 - 1)(\rho - 1). \quad (6.6)$$

In total we find for the coefficient α_S ,

$$\alpha_S = -2 + 2(\epsilon_1 - 1)(\rho - 1) \frac{2\rho + 1 - 2(\rho - 1)\epsilon_1}{2\rho + 1 + (\rho - 1)\epsilon_1}. \quad (6.7)$$

This is an extension of the result obtained by Van Den Broeck,¹⁷ who considered the case $D_1 = D_0$. It is to be noted that the potential and the diffusion coefficient appear only in the combination $\epsilon_1 = g_1 D_1 / D_0$, so that both quantities can vary while α_S remains constant.

The expression (6.7) shows some interesting features. It may be cast in the form

$$\alpha_S = -2 - \frac{\rho - 1}{2\rho} (\epsilon_1 - 1) \frac{\alpha}{a^3}. \quad (6.8)$$

For $\epsilon_1 = 0$, corresponding to impenetrable spheres of radius b , we recover the hard-sphere result $\alpha_S = -2\rho = -2(b^3/a^3)$. For large ϵ_1 the polarizability α equals $8\rho a^3$, so that α_S decreases in proportion to ϵ_1 . As ϵ_1 varies from zero to positive values, the factor $1 - \epsilon_1$ decreases, but α increases, and the net effect is an increase of α_S . Starting at -2ρ , the coefficient α_S passes through the value -2 at $\epsilon_1 = 1$. It then increases further, goes through a maximum, and finally decreases to large negative values. This is a surprising effect. If we consider the case $D_1 = D_0$, then ϵ_1 varies only through the change of potential v_1 . The value $\epsilon_1 = 1$ for this case corresponds to zero potential and $\epsilon_1 > 1$ to an attractive potential. As the attraction is turned on, α_S at first increases, but then decreases. This corresponds to the change of sign of the sum $\alpha_S + 2$ noted by Van Den Broeck.¹⁷ For $0 < \epsilon_1 < 1$ the sum $\alpha_S + 2$ is always negative. For $\epsilon_1 > 1$ the sum is positive for small values of ϵ_1 , but changes sign at $\epsilon_{10} = (2\rho + 1)/2(\rho - 1)$, as determined by the sign of the numerator in Eq. (6.7). In Fig. 1 we plot α_S as a function of ϵ_1 for fixed $\rho = 1.5$. In Fig. 2 we plot α_S as a function

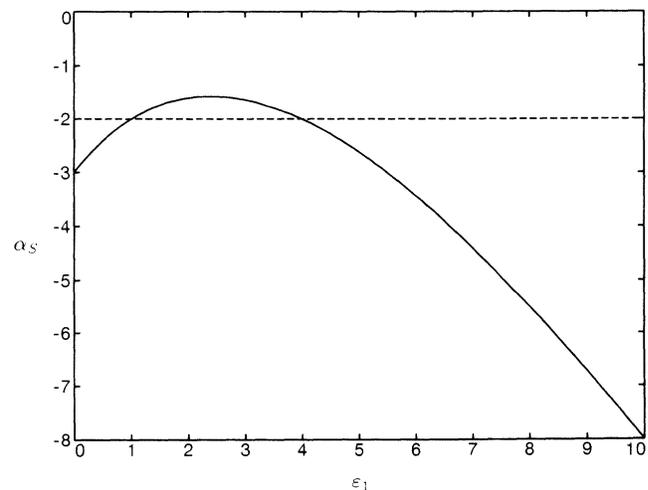


FIG. 1. Plot of α_S vs ϵ_1 for fixed $\rho = 1.5$, as given by Eq. (6.7).

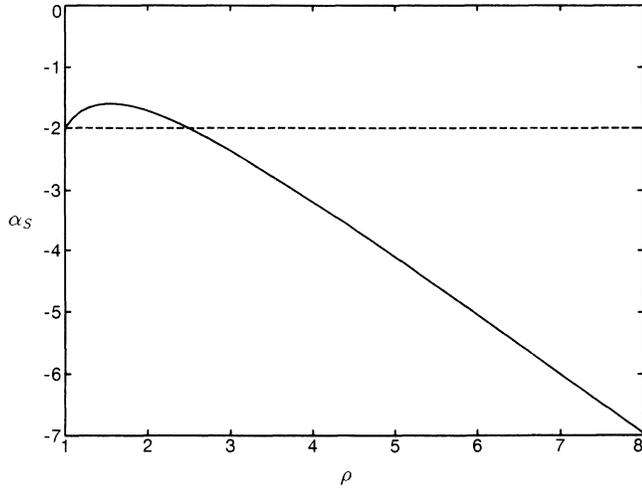


FIG. 2. Plot of α_S vs ρ for fixed $\epsilon_1=2$, as given by Eq. (6.7).

of ρ for fixed $\epsilon_1=2$.

The simple model defined by Eqs. (6.2) and (6.3) provides a good qualitative impression of the effects of the direct interaction potential and the speed of relative diffusion of pairs of particles on the self-diffusion coefficient.

VII. STEPWISE VARYING INTERACTIONS

In this section we consider more complicated models in which the interaction potential and the relative diffusion tensor vary stepwise at a number of specified radii and have constant values in between. The number of steps may be arbitrarily large. One may evaluate results for a continuum profile by approximating it by a large number of small steps.

We set

$$\psi_1(\vec{r}) = af(r)\hat{r}\cdot\vec{E}_0, \quad (7.1)$$

as in Eq. (4.3). By substitution in Eq. (5.2) we find the radial equation

$$\frac{d}{dx} \left[x^2 \epsilon_n \frac{df}{dx} \right] - 2\epsilon_n f = 2 \frac{d}{dx} (x^2 \epsilon_n) - 4\epsilon_n x \quad (7.2)$$

in dimensionless units $x=r/2a$. Clearly $f=2x$ is a solution of the inhomogeneous equation.

We assume that the whole range $1 \leq x < \infty$ is divided into $N+1$ intervals by points $\{x_j\}$, ordered such that $1 < x_1 < x_2 < \dots < x_N < \infty$. For simplicity we consider only the isotropic case for which $\epsilon_n = \epsilon_t = \text{const}$ in each layer. Let ϵ_j be the value of the dielectric constant in the interval $x_{j-1} < x < x_j$. For $x > x_N$ the value is $\epsilon_{N+1}=1$. At x_j the radial function $f(x)$ must satisfy the jump conditions

$$\begin{aligned} f(x_{j+}) &= f(x_{j-}), \\ -2\epsilon_{j+1} + \epsilon_{j+1} f'(x_{j+}) &= -2\epsilon_j + \epsilon_j f'(x_{j-}). \end{aligned} \quad (7.3)$$

In each interval the functions x and x^{-2} are solutions of the homogeneous differential equation. We therefore put

$$f(x) = 2x + X_j x + Y_j x^{-2} \quad \text{for } x_{j-1} < x < x_j. \quad (7.4)$$

The jump conditions (7.3) become relations between the coefficients in successive intervals, which may be written in the matrix form

$$\begin{bmatrix} X_j \\ Y_j \end{bmatrix} = \underline{M}_j \begin{bmatrix} X_{j+1} \\ Y_{j+1} \end{bmatrix}, \quad (7.5)$$

with the 2×2 matrix

$$\underline{M}_j = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{1}{3} x_j^2 \frac{\epsilon_{j+1} - \epsilon_j}{\epsilon_j} \begin{bmatrix} 1/x_j^2 & -2/x_j^5 \\ -x_j & 2/x_j^2 \end{bmatrix}. \quad (7.6)$$

By repeated application of Eq. (7.5) we find the relation between the first and last coefficients

$$\begin{bmatrix} X_1 \\ Y_1 \end{bmatrix} = \underline{T} \begin{bmatrix} X_{N+1} \\ Y_{N+1} \end{bmatrix}, \quad (7.7)$$

with the transfer matrix

$$\underline{T} = \underline{M}_1 \underline{M}_2 \cdots \underline{M}_N. \quad (7.8)$$

Applying the conditions (7.3) at $x_0=1$, we find that the coefficients X_1 and Y_1 are related by

$$X_1 = 2Y_1, \quad (7.9)$$

in order to satisfy the boundary condition on the normal derivative. In dielectric language this condition implies that the normal component of the electric displacement vanishes. In our original problem it corresponds to the vanishing of the normal component of the probability current. The final coefficients are

$$X_{N+1} = -2, \quad Y_{N+1} = \frac{\alpha}{4a^3}, \quad (7.10)$$

as follows from Eqs. (5.8), (7.1), and (7.4). Solving for the polarizability α , we therefore find from Eqs. (7.7), (7.9), and (7.10),

$$\alpha = 8a^3 \frac{T_{XX} - 2T_{YX}}{T_{XY} - 2T_{YY}}. \quad (7.11)$$

As a check one easily recovers the result (6.4).

The integral J_S , as given by Eq. (6.1), may be replaced by a sum. Finally, one finds the coefficient α_S from Eq. (5.15). Since all coefficients $\{X_j, Y_j\}$ may be evaluated, one can also find the perturbed distribution function.

VIII. HYDRODYNAMIC INTERACTIONS

In this section we show how the coefficient α_S may be evaluated in the case of realistic hydrodynamic interactions. We first consider the case of hard spheres without additional direct interaction $v(r)$. Subsequently, we investigate the effect of the direct interaction.

For hard spheres with hydrodynamic interactions we have $\epsilon_n = G(x)$ and $\epsilon_t = H(x)$ in the notation of Eq. (3.11). The differential equation for the radial function

$f(x)$ is given by Eq. (3.12) with $v(x)=0$. By use of Eqs. (5.15) and (5.18) the coefficient α_S may be expressed as

$$\alpha_{S,HS} = \frac{3}{2} \frac{\alpha_{HS}}{a^3} + 8 \int_1^\infty W(x) x^3 dx, \quad (8.1)$$

where the hydrodynamic function $W(x)$ is given by Eq. (3.10). The polarizability α_{HS} may be obtained from the asymptotic behavior of the perturbed distribution function. The solution of the differential equation satisfying the boundary conditions (3.13) is written¹²

$$Q(x) = \gamma Q_1(x) + Q_2(x), \quad (8.2)$$

where $Q_1(x)$ is the solution of the homogeneous differential equation which tends to $1/x^2$ for large x , and $Q_2(x)$ is the solution of the inhomogeneous equation with asymptotic behavior

$$Q_2(x) = \frac{15}{64x^3} + O(x^{-4}) \quad (8.3)$$

for hydrodynamic stick boundary conditions. The functions $Q_1(x)$ and $Q_2(x)$ may be constructed¹² as series expansions in inverse powers of x . Both functions have a logarithmic divergence at $x=1$. The coefficient γ in Eq. (8.2) must be chosen such that the boundary condition (3.13) at $x=1$ is satisfied. The polarizability α_{HS} in Eq. (8.1) is related to γ according to

$$\alpha_{HS} = 4a^3 \gamma. \quad (8.4)$$

From the series expansion of the solution $Q(x)$ in inverse powers of x we find $\gamma = -0.47067$. The integral in Eq. (8.1) is given by

$$J_{S,HS} = 8 \int_1^\infty W(x) x^3 dx = 2.5583. \quad (8.5)$$

Hence we find $\alpha_S = -0.2657$, in agreement with the result found previously¹² from Eq. (3.9). The convergence of the series expansions to the limiting value of γ and the integral in Eq. (8.5) is very rapid, so that the present method is convenient.

In order to take the effect of additional direct interaction into account we proceed in the same manner as in Sec. VII. We divide the range $1 \leq x < \infty$ into $N+1$ intervals by points $\{x_j\}$ and assume that in each interval the direct potential $v(x)$ may be approximated by a constant. Let v_j be the value of the potential in the interval $x_{j-1} < x < x_j$, with the corresponding value $g_j = \exp(-\beta v_j)$ of the radial distribution function. We assume that for $x > x_{N+1}$ we may set $g_{N+1} = 1$. At x_j the radial function $f(x)$ must satisfy the jump conditions

$$\begin{aligned} f(x_{j+}) &= f(x_{j-}), \\ -2g_{j+1} + g_{j+1} f'(x_{j+}) &= -2g_j + g_j f'(x_{j-}). \end{aligned} \quad (8.6)$$

As before $f=2x$ is a solution of the inhomogeneous equation (3.12). Let $Q_0(x)$ be the solution of the homogeneous equation for hard spheres which tends to x for large x and which satisfies the boundary condition (3.13) at $x=1$. Then in each interval the functions $Q_0(x)$ and $Q_1(x)$ are independent solutions of the homogeneous differential equation. We therefore set

$$f(x) = 2x + X_j Q_0(x) + Y_j Q_1(x) \quad \text{for } x_{j-1} < x < x_j. \quad (8.7)$$

The jump conditions (8.6) become relations between the coefficients in successive intervals, which may be written in the matrix form

$$\begin{pmatrix} X_j \\ Y_j \end{pmatrix} = \underline{M}_j \begin{pmatrix} X_{j+1} \\ Y_{j+1} \end{pmatrix}, \quad (8.8)$$

with the 2×2 matrix

$$\begin{aligned} \underline{M}_j &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \\ &+ \frac{1}{3} x_j^2 G(x_j) \frac{g_{j+1} - g_j}{g_j} \\ &\times \begin{pmatrix} Q_0'(x_j) Q_1(x_j) & Q_1(x_j) Q_1'(x_j) \\ -Q_0(x_j) Q_0'(x_j) & -Q_0(x_j) Q_1'(x_j) \end{pmatrix}. \end{aligned} \quad (8.9)$$

Here we have used that the Wronskian of the solutions of the homogeneous differential equation is given by

$$Q_0 \frac{dQ_1}{dx} - \frac{dQ_0}{dx} Q_1 = -\frac{3}{x^2 G(x)}. \quad (8.10)$$

By repeated application of Eq. (8.8) we find the relation between the first and last coefficients

$$\begin{pmatrix} X_1 \\ Y_1 \end{pmatrix} = \underline{T} \begin{pmatrix} X_{N+1} \\ Y_{N+1} \end{pmatrix}, \quad (8.11)$$

with the transfer matrix

$$\underline{T} = \underline{M}_1 \underline{M}_2 \cdots \underline{M}_N. \quad (8.12)$$

The coefficient Y_1 must vanish since the function $Q_1(x)$ diverges logarithmically at $x=1$. The final coefficients are

$$X_{N+1} = -2, \quad Y_{N+1} = \frac{\alpha}{4a^3} - \gamma. \quad (8.13)$$

Solving for the polarizability α we therefore find

$$\alpha = 4a^3 \gamma + 8a^3 \frac{T_{YX}}{T_{YY}}. \quad (8.14)$$

Since all coefficients $\{X_j, Y_j\}$ may be evaluated, one can also find the complete perturbed distribution function. The hard-sphere solution (8.2) is given by $Q(x) = 2x - 2Q_0(x)$.

The integral J_S , as given by Eq. (5.18), may be expressed as

$$J_S = J_{S,HS} - 4 \int_1^\infty (g-1)(G+2H)x^2 dx. \quad (8.15)$$

Finally, the coefficient α_S is found as

$$\alpha_S = \alpha_{S,HS} + 12 \frac{T_{YX}}{T_{YY}} - 4 \int_1^\infty (g-1)(G+2H)x^2 dx. \quad (8.16)$$

As a first application of the expression (8.16) we con-

sider sticky hard spheres.³⁵ These are defined by a single step at x_1 with an attractive potential v_1 for $1 < x < x_1$ in the limit $x_1 \rightarrow 1$, $v_1 \rightarrow -\infty$ such that

$$(x_1 - 1)g_1 = \frac{1}{12\tau} \quad (8.17)$$

remains constant. In this limit the matrix \underline{M}_1 tends to the unit matrix, as is easily seen from Eq. (8.9). Hence $T_{YX} = 0$ and $T_{YY} = 1$ for this model and we find with use of Eq. (3.14)

$$\alpha_S = \alpha_{S,HS} - \frac{2H(1)}{3\tau}, \quad (8.18)$$

in agreement with our earlier result²² based on Eq. (3.9). The present derivation is far simpler.

IX. DISCUSSION

We have shown that Batchelor's expression for the long-time self-diffusion coefficient, valid to first order in the volume fraction, may be cast in a different form by the use of a dielectric analogy. The new form is convenient in practical calculations, as we have demonstrated for several models. In future publications we shall apply the method to other models of interest. It may be expected that a similar method may be used for the zero-frequency effective viscosity of suspensions, as well as for the frequency-dependent self-diffusion coefficient and effective viscosity.

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