Diffusion of interacting Brownian particles

B U Felderhof

Institut für Theoretische Physik A, RWTH Aachen, TH-Erweiterungsgelände Seffent-Melaten, 5100 Aachen, Germany

Abstract. We develop a theory of Brownian motion for interacting spherical particles suspended in a fluid. Due to potential and hydrodynamic interactions the effective diffusion coefficient depends on the concentration of particles. We derive the correction to the bare diffusion coefficient to first order in the concentration.

1. Introduction

The classical theory of Brownian motion deals with the stochastic motion of a large particle due to random collisions with the much smaller molecules of the surrounding fluid. In macromolecular solutions the concentration of Brownian particles can be sufficiently high that the potential and hydrodynamic interactions between particles can no longer be neglected. Of particular relevance to light scattering studies is the question how the effective diffusion coefficient of the solute particles depends on the concentration.

The diffusion coefficient is related to the friction coefficient by a generalised Einstein relation:

$$D(c) = \frac{c}{1-c} \frac{(\partial \mu / \partial c)_{p,T}}{f(c)}, \qquad (1.1)$$

where μ is the chemical potential and c is the volume fraction of solute particles. The concentration dependence of the friction coefficient $f(c)$ was studied by Burgers (1941, 1942) and later by Pyun and Fixman (1964). These theories were hampered by incomplete knowledge of the hydrodynamic interaction between particles. A more complete theory has recently been presented by Batchelor (1972, 1976), who used exact numerical knowledge concerning the hydrodynamic interaction. The long range of the hydrodynamic interaction gives rise to complications which are resolved by Batchelor by quite subtle considerations. He restricted himself to stick boundary conditions and hard-sphere potential interactions.

We formulate a theory which consistently uses the picture of diffusing interacting particles in the low-density limit. We allow general central potential interactions and extend the treatment of hydrodynamic interactions to include mixed slip–stick boundary conditions at the surface of the spheres. To this purpose we employ recent analytic results concerning the hydrodynamic interaction between two spheres (Felderhof 1977). The integrals involving the long-range part of the hydrodynamic interaction can be handled in a concise and transparent manner. For the case of hard

spheres with stick boundary conditions our results agree with Batchelor's. For this case we can also compare with the numerous other results which have appeared in the literature.

2. Basic equations

We consider a collection of N identical spherical particles suspended in a fluid of much smaller molecules. The fluid motion is assumed to be adequately described by the linear Navier–Stokes equation for steady incompressible flow:

$$\eta \nabla^2 \boldsymbol{v} - \nabla p = 0, \qquad \nabla \cdot \boldsymbol{v} = 0, \tag{2.1}$$

where η is the shear viscosity, $\boldsymbol{v}(r)$ is the flow field and $p(r)$ is the pressure. For given boundary conditions at the surface of the particles and specified translational and rotational velocities there is a uniquely determined flow $(\boldsymbol{v}(r), p(r))$ with corresponding stress tensor from which the forces and torques acting on the particles can be evaluated. We shall assume that the particles are freely rotating so that the torques vanish. The forces $\{\boldsymbol{F}_j\}$ and the translational velocities $\{\boldsymbol{u}_j\}$ are then related by

$$\boldsymbol{F}_j = \sum_{k=1}^{N} \zeta_{jk} \cdot \boldsymbol{u}_k, \qquad j = 1, \ldots, N, \tag{2.2}$$

where the $3N \times 3N$ generalised friction matrix ζ depends on the instantaneous positions $(r_1, \ldots, r_N)$ of the particle centres.

The Brownian motion of the particles is assumed to be described by a Smoluchowski equation for the probability distribution $P_N(r_1, \ldots, r_N, t)$ in configuration space (Zwanzig 1969, Deutch and Oppenheim 1971, Murphy and Aguirre 1972). The equation reads

$$\frac{\partial P_N}{\partial t} = \nabla_N \cdot \mathbf{D} \cdot [\nabla_N P_N + \beta (\nabla_N \Phi) P_N], \tag{2.3}$$

where $\mathbf{D}$ is a generalised diffusion matrix related to the friction matrix ζ by the Einstein relation

$$\mathbf{D} = kT\zeta^{-1}. \tag{2.4}$$

Furthermore $\beta = 1/kT$, and $\Phi(r_1, \ldots, r_N)$ describes the potential interactions. We assume pair interactions of the form

$$\Phi(r_1, \ldots, r_N) = \tfrac{1}{2} \sum_i \sum_{j \neq i} \phi(r_{ij}). \tag{2.5}$$

In the low-density limit the diffusion matrix $\mathbf{D}$ can be approximated as a sum of single-particle and pair contributions:

$$\mathbf{D} = D_0 \mathbf{I} + \sum_i \sum_j (\mathbf{A}(i, j) + \mathbf{B}(i, j)), \tag{2.6}$$

where D_0 is the diffusion coefficient for a single particle, and $\mathbf{A}(i, j)$ and $\mathbf{B}(i, j)$ are modifications to the diffusion coefficient due to hydrodynamic interactions. More precisely, the coefficients are defined from the solution of the hydrodynamic two-body

problem in the following manner:

$$u_1 = \beta(D_0\mathbf{1} + \mathbf{A}(1, 2)) \cdot F_1 + \beta \mathbf{B}(1, 2) \cdot F_2$$

$$u_2 = \beta \mathbf{B}(2, 1) \cdot F_1 + \beta(D_0\mathbf{1} + \mathbf{A}(2, 1)) \cdot F_2. \tag{2.7}$$

In §4 we shall give explicit expressions for the coefficients in terms of a series expansion in powers of the inverse distance between centres. With the approximation (2.6) the Smoluchowski equation (2.3) becomes

$$\frac{\partial P_N}{\partial t} = D_0 \sum_j \nabla_j \cdot \left(\nabla_j P_N + \beta \sum_{k \neq j} (\nabla_j \phi(r_{jk})) P_N \right)$$

$$+ \sum_j \sum_{k \neq j} \nabla_j \cdot \mathbf{A}(j, k) \cdot \left(\nabla_j P_N + \beta \sum_{l \neq j} (\nabla_j \phi(r_{jl})) P_N \right)$$

$$+ \sum_j \sum_{k \neq j} \nabla_j \cdot \mathbf{B}(j, k) \cdot \left(\nabla_k P_N + \beta \sum_{l \neq k} (\nabla_k \phi(r_{kl})) P_N \right). \tag{2.8}$$

Although this equation is simpler than (2.3), where the diffusion matrix **D** is not known explicitly, it still represents a complicated many-body problem. The restriction to hydrodynamic pair interactions is customary in polymer problems and presumably does not represent too drastic a simplification even for higher densities.

3. One-body and two-body equations

From the N-body Smoluchowski equation (2.8) one can derive a coupled hierarchy of equations for the set of s-body distribution functions ($s = 1, \ldots, N$). To this hierarchy one can apply the method of kinetic gas theory by taking the thermodynamic limit in the manner of Bogoliubov: $N \to \infty$, $V \to \infty$, $N/V = n_0$ constant, where V is the volume of the system (Bogoliubov 1946, translated in de Boer and Uhlenbeck 1962). Keeping terms to linear order in n_0 the equation for the particle density $n(r, t)$ becomes

$$\frac{\partial n(r_1, t)}{\partial t} = D_0 \nabla_1 \cdot \left(\nabla_1 n + \beta \int (\nabla_1 \phi(r_{12})) n_2 \, dr_2 \right)$$

$$+ \nabla_1 \cdot \int \mathbf{A}(1, 2) \cdot [\nabla_1 n_2 + \beta(\nabla_1 \phi(r_{12})) n_2] \, dr_2$$

$$+ \nabla_1 \cdot \int \mathbf{B}(1, 2) \cdot [\nabla_2 n_2 + \beta(\nabla_2 \phi(r_{12})) n_2] \, dr_2 \tag{3.1}$$

where $n_2(r_1, r_2, t)$ is the pair density. To lowest order in n_0 the latter satisfies

$$\frac{\partial n_2(r_1, r_2, t)}{\partial t} = D_0 \nabla_1 \cdot [\nabla_1 n_2 + \beta(\nabla_1 \phi) n_2] + D_0 \nabla_2 \cdot [\nabla_2 n_2 + \beta(\nabla_2 \phi) n_2]$$

$$+ \nabla_1 \cdot \mathbf{A}(1, 2) \cdot [\nabla_1 n_2 + \beta(\nabla_1 \phi) n_2] + \nabla_2 \cdot \mathbf{A}(2, 1) \cdot [\nabla_2 n_2 + \beta(\nabla_2 \phi) n_2]$$

$$+ \nabla_1 \cdot \mathbf{B}(1, 2) \cdot [\nabla_2 n_2 + \beta(\nabla_2 \phi) n_2] + \nabla_2 \cdot \mathbf{B}(2, 1) \cdot [\nabla_1 n_2 + \beta(\nabla_1 \phi) n_2].$$

$$\tag{3.2}$$

Due to the low-density approximation equations (3.1) and (3.2) decouple from the rest of the hierarchy. The pair density $n_2(r_1, r_2, t)$ must satisfy $n_2(r_1, r_2, t) \approx n(r_1, t) n(r_2, t)$ for $|r_1 - r_2| \to \infty$, but the integral of $n_2(r_1, r_2, t)$ over r_2 does not necessarily equal $n(r_1, t)$.

The equations (3.1) and (3.2) have the time-independent equilibrium solution

$$n(r_1) = n_0, \qquad n_2(r_1, r_2) = n_0^2 g_0(r_1 - r_2) \tag{3.3}$$

where n_0 is a constant, with pair correlation

$$g_0(r) = \exp(-\beta \phi(r)). \tag{3.4}$$

We write

$$n_2(r_1, r_2, t) = n(r_1, t) n(r_2, t) g(r_1, r_2, t) \tag{3.5}$$

and consider deviations n_1 and g_1 from the equilibrium solution

$$n(r_1, t) = n_0 + n_1(r_1, t), \qquad g(r_1, r_2, t) = g_0(r_{12}) + g_1(r_1, r_2, t). \tag{3.6}$$

To terms linear in n_1 and g_1 the pair density becomes

$$n_2(r_1, r_2, t) \approx n_0^2 g_0(r_{12}) + n_1(r_1, t) n_0 g_0(r_{12}) + n_0 n_1(r_2, t) g_0(r_{12}) + n_0^2 g_1(r_1, r_2, t). \tag{3.7}$$

Substituting in equation (3.1) and linearising one obtains

$$\frac{\partial n_1(r_1, t)}{\partial t} = D_0 \nabla_1 \cdot \left(\nabla_1 n_1 + n_0 \beta \int (\nabla_1 \phi) g_0 n_1(r_2, t) \, dr_2 + n_0^2 \beta \int (\nabla_1 \phi) g_1 \, dr_2 \right)$$

$$+ n_0 \nabla_1 \cdot \int A(1, 2) g_0 \, dr_2 \cdot \nabla_1 n_1(r_1, t)$$

$$+ n_0^2 \nabla_1 \cdot \int A(1, 2) \cdot [\nabla_1 g_1 + \beta (\nabla_1 \phi) g_1] \, dr_2$$

$$+ n_0 \nabla_1 \cdot \int B(1, 2) g_0 \cdot \nabla_2 n_1(r_2, t) \, dr_2$$

$$+ n_0^2 \nabla_1 \cdot \int B(1, 2) \cdot [\nabla_2 g_1 + \beta (\nabla_2 \phi) g_1] \, dr_2. \tag{3.8}$$

Similarly one derives a lengthy linearised equation for $g_1(r_1, r_2, t)$. However, if one uses the fact that $A(1, 2) = A(2, 1)$ and $B(1, 2) = B(2, 1)$ depend only on r_{12}, and if one restricts attention to small density gradients so that $\nabla_2 n_1(r_2) \approx \nabla_1 n_1(r_1)$, then one sees that g_1 is of order n_0^0. Hence to terms linear in n_0 the terms with g_1 can be omitted from (3.8) and this equation simplifies to

$$\frac{\partial n_1(r_1, t)}{\partial t} = D_0 \nabla_1 \cdot \left(\nabla_1 n_1 + n_0 \beta \int (\nabla_1 \phi) g_0 n_1(r_2, t) \, dr_2 \right)$$

$$+ n_0 \nabla_1 \cdot \int A(1, 2) g_0 \, dr_2 \cdot \nabla_1 n_1(r_1, t) + n_0 \nabla_1 \cdot \int B(1, 2) g_0 \cdot \nabla_2 n_1(r_2, t) \, dr_2. \tag{3.9}$$

As we shall show, for intermolecular potentials ϕ of short range this amounts to a diffusion equation for $n_1(r_1, t)$ with a modified diffusion coefficient.

4. Derivation of modified diffusion coefficient

For mixed slip–stick boundary conditions at the surface of the spheres the bare single-particle diffusion coefficient is

$$D_0 = kT/6\pi\eta a(1-\xi) \tag{4.1}$$

where the parameter ξ characterises the boundary condition. It takes values in the range $0 \leqslant \xi \leqslant \frac{1}{3}$, the value $\xi = 0$ corresponding to stick, and $\xi = \frac{1}{3}$ to pure slip. We have earlier derived expressions for the diffusion tensors $\mathbf{A}(1, 2)$ and $\mathbf{B}(1, 2)$ in an expansion in inverse powers of the centre-to-centre distance (Felderhof 1977). For the tensor $\mathbf{A}(1, 2)$ we found

$$
\begin{aligned}
\mathbf{A}(1, 2) = D_0(1-\xi)\Bigg[&-\frac{15}{4}\frac{1-\xi}{1+2\xi}\frac{a^4}{r_{12}^4}\mathbf{P} + 12\frac{1-3\xi}{1+2\xi}\frac{a^6}{r_{12}^6}\mathbf{P} \\
&-\frac{21}{80}\frac{1-\xi}{1+4\xi}\frac{a^6}{r_{12}^6}(1+23\mathbf{P}) - \frac{3}{4}\frac{1-4\xi}{1+\xi}\frac{a^6}{r_{12}^6}(1-\mathbf{P}) \\
&-\frac{1}{20}\frac{1-6\xi}{1-\xi}\frac{a^6}{r_{12}^6}(1+3\mathbf{P}) + O\left(\frac{a^8}{r_{12}^8}\right)\Bigg]
\end{aligned}
\tag{4.2}
$$

where $\mathbf{P} = r_{12}r_{12}/r_{12}^2$. For the tensor $\mathbf{B}(1, 2)$ we found

$$\mathbf{B}(1, 2) = \mathbf{B}_L(1, 2) + \mathbf{B}_S(1, 2) \tag{4.3}$$

where the long-range part $\mathbf{B}_L(1, 2)$ is given by

$$\mathbf{B}_L(1, 2) = D_0\left((1-\xi)\frac{3a}{4r_{12}}(1+\mathbf{P}) + (1-3\xi)\frac{a^3}{2r_{12}^3}(1-3\mathbf{P})\right), \tag{4.4}$$

and the short-range part $\mathbf{B}_S(1, 2)$ by

$$\mathbf{B}_S(1, 2) = D_0\frac{75}{4}\frac{(1-\xi)^3}{(1+2\xi)^2}\frac{a^7}{r_{12}^7}\mathbf{P} + O\left(\frac{a^8}{r_{12}^8}\right). \tag{4.5}$$

The long-range part $\mathbf{B}_L(1, 2)$ can be further split into an Oseen part $\mathbf{B}_O(1, 2)$ and a dipole part $\mathbf{B}_D(1, 2)$, corresponding to the two terms in equation (4.4).

We now discuss the various terms in equation (3.9). The second term gives a virial correction. Since the integrand is short range we can expand $n_1(r_2, t)$ about r_1. Keeping only the first non-vanishing term we get

$$\beta \int (\nabla_1\phi)g_0 n_1(r_2, t)\,dr_2 \approx C_V\nabla_1 n_1(r_1, t) \tag{4.6}$$

with

$$C_V = -\int [\exp(-\beta\phi(r_{12}))-1]\,dr_2. \tag{4.7}$$

For the integral in the third term of (3.9) we obtain after performing the angular integrations

$$\int \mathbf{A}(1, 2)g_0\,dr_2 = D_0 C_A\mathbf{1} \tag{4.8}$$

with

$$C_A = 4\pi(1-\xi) \int_{2a}^{\infty} \left(-\frac{5}{4} \frac{1-\xi}{1+2\xi} \frac{a^4}{r^4} + 4 \frac{1-3\xi}{1+2\xi} \frac{a^6}{r^6} - \frac{91}{40} \frac{1-\xi}{1+4\xi} \frac{a^6}{r^6} \right.$$

$$\left. - \frac{1}{2} \frac{1-4\xi}{1+\xi} \frac{a^6}{r^6} - \frac{1}{10} \frac{1-6\xi}{1-\xi} \frac{a^6}{r^6} \right) e^{-\beta\phi} r^2 \, dr. \tag{4.9}$$

In the last integral in (3.9) we treat the Oseen part, the dipole part and the short-range part separately. Starting with the latter we have

$$\int \mathbf{B}_S(1, 2) g_0 \cdot \nabla_2 n_1(r_2, t) \, dr_2 \approx D_0 C_S \nabla_1 n_1(r_1, t) \tag{4.10}$$

with

$$C_S = \frac{75}{4} \frac{(1-\xi)^3}{(1+2\xi)^2} \frac{4\pi}{3} a^7 \int_{2a}^{\infty} r^{-5} e^{-\beta\phi} \, dr. \tag{4.11}$$

For the Oseen part we write

$$\int \mathbf{B}_O(1, 2) g_0 \cdot \nabla_2 n_1(r_2, t) \, dr_2 = \int \mathbf{B}_O(1, 2) \cdot \nabla_2 n_1(r_2, t) \, dr_2$$

$$+ \int \mathbf{B}_O(1, 2)(g_0 - 1) \cdot \nabla_2 n_1(r_2, t) \, dr_2. \tag{4.12}$$

The first term on the right does not contribute in (3.9) since

$$\nabla_1 \cdot \int \mathbf{B}_O(1, 2) \cdot \nabla_2 n_1(r_2, t) \, dr_2 = 0, \tag{4.13}$$

where we have used the fact that the Oseen tensor is the Green function of the linear Navier-Stokes equation for incompressible flow. The integrand of the second integral in equation (4.12) has short range and one can approximate

$$\int \mathbf{B}_O(1, 2)(g_0 - 1) \cdot \nabla_2 n_1(r_2, t) \, dr_2 \approx D_0 C_O \nabla_1 n_1(r_1, t) \tag{4.14}$$

with

$$C_O = (1-\xi) 4\pi a \int_0^{\infty} (e^{-\beta\phi} - 1) r \, dr. \tag{4.15}$$

For the dipole part we write

$$\mathbf{B}_D(1, 2) = -\tfrac{1}{2} D_0(1 - 3\xi) a^3 \mathbf{F}(1, 2) \tag{4.16}$$

where

$$\mathbf{F}(1, 2) = -(\mathbf{1} - 3\mathbf{P})/r_{12}^3 \tag{4.17}$$

is the electrostatic dipole–dipole tensor. Proceeding in the same way as in (4.12) but cutting out an infinitesimal sphere of radius ϵ about r_1 we get a contribution

$$\int_{\epsilon} \mathbf{F}(1, 2) \cdot \nabla_2 n_1(r_2, t) \, dr_2 = \mathbf{E}_L(r_1), \tag{4.18}$$

where we have used the electrostatic analogy to introduce a 'Lorentz local field' $\mathbf{E}_L$

due to the 'polarisation' $P = \nabla n_1$. Hence $E_L = E + \frac{4}{3}\pi P$, where E satisfies $\nabla \cdot E = -4\pi \nabla \cdot P$. Therefore we obtain

$$\nabla_1 \cdot \int_\epsilon F(1, 2) \cdot \nabla_2 n_1(r_2, t) \, dr_2 = -\frac{8}{3}\pi \nabla_1^2 n_1(r_1, t). \tag{4.19}$$

The remaining term from the dipole part can be approximated by

$$\int_\epsilon B_D(1, 2)(g_0 - 1)\nabla_2 n_1(r_2, t) \, dr_2 \approx \int_\epsilon B_D(1, 2)(g_0 - 1) \, dr_2 \cdot \nabla_1 n_1(r_1, t) \tag{4.20}$$

which vanishes by integration over angles. Thus we obtain in total for the dipolar term

$$\nabla_1 \cdot \int B_D(1, 2)g_0 \cdot \nabla_2 n_1(r_2, t) \, dr_2 \approx D_0 C_D \nabla_1^2 n_1(r_1, t) \tag{4.21}$$

with

$$C_D = \frac{4}{3}\pi(1 - 3\xi)a^3. \tag{4.22}$$

Note that one would be free to cut out an infinitesimal ellipsoid instead of a sphere in (4.18). That would give a different result in (4.19), but the integral in (4.20) would not vanish and compensate for the difference. The choice of a sphere is the simplest and most obvious one. Combining the results of this section we find that equation (3.9) can be approximated by the diffusion equation

$$\frac{\partial n_1(r_1, t)}{\partial t} = D\nabla_1^2 n_1(r_1, t) \tag{4.23}$$

with

$$D = D_0[1 + n_0(C_V + C_O + C_D + C_S + C_A)] \tag{4.24}$$

where the coefficients C_i are given by (4.7), (4.9), (4.11), (4.15) and (4.22).

5. Results for hard spheres

We specialise the results of the preceding section to the case of hard spheres. Conventionally the effective diffusion coefficient is written in the form

$$D = D_0(1 + \lambda c) \tag{5.1}$$

where $c = \frac{4}{3}\pi a^3 n_0$ is the volume fraction. From (4.24) we have

$$\lambda = \lambda_V + \lambda_O + \lambda_D + \lambda_S + \lambda_A \tag{5.2}$$

where $C_i = \frac{4}{3}\pi a^3 \lambda_i$. For the various coefficients we find

$$\lambda_V = 8, \qquad \lambda_O = -6(1 - \xi),$$

$$\lambda_D = 1 - 3\xi, \qquad \lambda_S = \frac{75}{256}\frac{(1 - \xi)^3}{(1 + 2\xi)^2},$$

$$\lambda_A = (1 - \xi)\left(-\frac{15}{8}\frac{1 - \xi}{1 + 2\xi} + \frac{1}{2}\frac{1 - 3\xi}{1 + 2\xi} - \frac{91}{320}\frac{1 - \xi}{1 + 4\xi} - \frac{1}{16}\frac{1 - 4\xi}{1 + \xi} - \frac{1}{80}\frac{1 - 6\xi}{1 - \xi}\right). \tag{5.3}$$

For stick ($\xi = 0$) one gets $\lambda_S = 0\cdot29$, $\lambda_A = -1\cdot73$ so that

$$\lambda = 8 - 6 + 1 + 0\cdot29 - 1\cdot73 = 1\cdot56. \tag{5.4}$$

This result can be compared with values from the literature. The values $\lambda_S = 0\cdot29$, $\lambda_A = -1\cdot73$ obtained from our series expansion are close to the values $\lambda_S = 0\cdot28$, $\lambda_A = -1\cdot83$ quoted by Batchelor (1976) as resulting from numerical integration of exact results for the hydrodynamic two-body problem. Batchelor gave a completely different derivation for the long-range hydrodynamic effects but also arrived at $\lambda_O + \lambda_D = -5$. Thus the result (5.4) is essentially identical to Batchelor's. An earlier derivation along similar lines was given by Pyun and Fixman (1964), who found however $\lambda_O + \lambda_D = -5\cdot5$ and $\lambda_S + \lambda_A = -1\cdot66$ leading to $\lambda = 0\cdot84$. It was pointed out by Batchelor that a term is missing from the calculation of Pyun and Fixman, the corrected value being $\lambda_O + \lambda_D = -5$. Altenberger and Deutch (1973) derived an equation (their equation (4.9)) similar to our equation (3.9). Note that (3.9) also holds for the total density $n = n_0 + n_1$ since n_0 cancels on both sides. The equation of Altenberger and Deutch differs in that the term with $\mathbf{A}(1, 2)$ is missing and $\mathbf{B}(1, 2)$ is approximated by the Oseen part. Correspondingly, they obtained $\lambda_V + \lambda_O = 8 - 6 = 2$. Harris (1976) added the dipole part and using the Fourier transform method of Altenberger and Deutch found $\lambda = \lambda_V + \lambda_O + \lambda_D = 8 - 6 + 1 = 3$. Phillies (1973) neglects hydrodynamic interactions altogether and therefore arrives at $\lambda = \lambda_V = 8$. Anderson and Reed (1975) derived a modified diffusion equation which for hard spheres leaves only the contribution corresponding to λ_A. Thus they find $\lambda = \lambda_A = -1\cdot83$. Their derivation is not systematic and they have omitted certain terms which appear in our derivation. Aguirre and Murphy (1973) also have only the contribution corresponding to λ_A, but by erroneous calculation they arrive at $\lambda_A = -\frac{21}{8} = -2\cdot625$. Hess and Klein (1977) used a diagrammatic method which is difficult to compare with the other approaches. For hard spheres they obtain $\lambda = 1$.

There seems to be no calculation in the literature corresponding to mixed slip–stick boundary conditions. If Batchelor's calculation is modified to take account of mixed boundary conditions one obtains† for the long-range contributions the sum $-(\frac{11}{2} - \frac{9}{2}\xi) + \frac{1}{2}(1 - 3\xi) = -5 + 3\xi$ (where the terms correspond to Batchelor's $V' + V''$) identical to our $\lambda_O + \lambda_D = -6(1 - \xi) + (1 - 3\xi) = -5 + 3\xi$. The numerical value for λ for the pure slip boundary condition is

$$\lambda = 8 - 4 + 0 + 0\cdot03 - 0\cdot53 = 3\cdot50. \tag{5.5}$$

As expected the hydrodynamic contributions are smaller in this case and therefore the total effect is larger.

6. Light scattering

In conclusion we calculate the spectrum of light scattered from the solution. The intensity of light scattered with wavevector transfer $\mathbf{k}$ and frequency change ω is proportional to the scattering function

$$S(\mathbf{k}, \omega) = \frac{1}{2\pi} \int\int \langle n_1(\mathbf{r}, t + \tau) n_1(\mathbf{r}', t) \rangle \exp[-\mathrm{i}\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') + \mathrm{i}\omega\tau] \, \mathrm{d}(\mathbf{r} - \mathbf{r}') \, \mathrm{d}\tau. \tag{6.1}$$

† R Schmitz, private communication.

According to the general formalism of irreversible thermodynamics the density correlation function can be evaluated from the linear equation (4.23). Hence the scattering function is

$$S(k, \omega) = \frac{1}{\pi} S(k) \frac{Dk^2}{\omega^2 + D^2 k^4} \tag{6.2}$$

where D is given by (4.24) and $S(k)$ is the static structure factor,

$$S(k) = n_0 + n_0^2 \int (e^{-\beta\phi} - 1) e^{-i k \cdot r} \, dr, \tag{6.3}$$

in the low-density limit. Therefore the linewidth of the scattered light is determined by the effective diffusion coefficient (4.24).

The short-time behaviour of the density correlation function has been studied by Ackerson (1976). Hydrodynamic corrections are taken into account in the Oseen approximation.

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