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On the distortion of the static structure factor of colloidal fluids in shear flow

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It is shown that the shear-induced distortion of the static structure factor (or equivalently, the pair distribution function) of colloidal fluids is a non-analytic function of the shear rate. The Smoluchowski equation shows boundary-layer behaviour at zero wave vector (large separations). The width of this boundary layer is proportional to the square-root of the shear rate. An explicit perturbation analysis of the two-particle Smoluchowski equation without hydrodynamic interactions is given. The onset of the non-Newtonian behaviour of the effective vicosity is due to the boundary-layer behaviour of the structure factor.

1. Introduction

In recent years the question of how the pair-distribution function for colloidal fluids changes as a shear flow is applied has been the subject of an increase of interest. The shear-rate dependence of the pair-distribution function is interesting in itself as a non-equilibrium quantity and is an ingredient for the calculation of the effective viscosity of colloidal fluids.

It has not been recognized before that the Smoluchowski equation with shear flow is singularly perturbed for small shear rates. The problem addressed in this paper is thus the singular perturbation analysis of the Smoluchowski equation with shear flow for small shear rates, where the two-particle equation without hydrodynamic interactions is treated explicitly.

The Smoluchowski equation, being the basic equation for the statistical mechanical description of colloidal fluids, is not an equation that is encountered amongst the many singularly perturbed fluid mechanical equations. The Smoluchowski equation exhibits boundary-layer behaviour at large values of its argument $\boldsymbol{r}$. Some singular perturbed equations from fluid mechanics have a boundary layer at small values of their argument (the position vector $\boldsymbol{r}$) such as the steady Navier–Stokes equation for large Reynolds numbers. Others have a boundary layer of large values of their argument, like the Smoluchowski equation, as for example the Navier–Stokes equation for small Reynolds numbers (van Dyke 1964). The difference between the Smoluchowski equation and the latter is not only the structure of the differential equation itself, but more so its boundary condition. For the solution of the Smoluchowski equation there is no prefixed boundary value as for the solution of, for example, the Navier–Stokes equation. Instead we know that for vanishing shear rates the solution of the Smoluchowski equation is equal to the known equilibrium pair-distribution function. In $\boldsymbol{r}$-space the singularity of the Smoluchowski equation can be recognized in a manner similar to that of Oseen in connection with the Stokes paradox (van Dyke 1964). This point is discussed further in §2. The 'boundary condition' pertaining to the Smoluchowski equation has the consequence that the singular inner solution reduces to the outer solution outside the boundary layer, so that the inner solution is actually valid throughout $\boldsymbol{r}$-space. This is quite different to solutions of singularly perturbed equations from fluid mechanics where inner and outer solutions must be asympotically matched. This is discussed in §§ 4 and 5. In this paper we shall be concerned with the solution of the Fourier-transformed Smoluchowski equation rather than the Smoluchowski equation in $\boldsymbol{r}$-space. The Fourier-transformed solution of the equation in $\boldsymbol{r}$-space is the static structure factor, which is measured by light scattering. The singular behaviour in $\boldsymbol{r}$-space at large values of r results in singular behaviour of the structure factor at small values of its argument $\boldsymbol{k}$. In $\boldsymbol{k}$-space the Fourier-transformed Smoluchowski equation attains the 'standard form' of a singular perturbed differential equation, where the highest-order derivative is multiplied with the small parameter.

For effective viscosity calculations of colloidal systems, an often made Ansatz is that the pair-distribution function in shear flow at low shear rates γ, can be written as (Russel 1976; Russel & Gast 1986; Felderhof 1983; Batchelor 1977)

$$g(\boldsymbol{R},\gamma) = g_e(R)+\gamma g^{(1)}(\boldsymbol{R})+\gamma^2 g^{(2)}(\boldsymbol{R})+\dots \tag{1.1}$$

Here, $g_e(R)$ is the equilibrium pair-distribution function. The first-order distortion $g^{(1)}(\boldsymbol{R})$ is then calculated by substitution of (1.1) into the two-particle Smoluchowski equation. Fourier transforming (1.1) yields

$$S(\boldsymbol{k},\gamma) = S_e(k)+\gamma S^{(1)}(\boldsymbol{k})+\gamma^2 S^{(2)}(\boldsymbol{k})+\dots, \tag{1.2}$$

where $S(\boldsymbol{k},\gamma)$ is the (static) structure factor in shear flow, and $S_e(k)$ is the equilibrium structure factor. We show that the structure factor is *not* an analytic function in γ for small γ, in contrast to what is assumed in (1.1) and (1.2). Actually, $S(\boldsymbol{k};\gamma)$ shows boundary-layer behaviour at $\boldsymbol{k} = \boldsymbol{0}$. The width of this boundary layer varies as $\gamma^{\frac{1}{2}}$. Thus, *for extremely small* γ the width of the boundary layer is very small, and the Ansatz (1.2) yields good results if it is used to calculate averages (such as the effective stress tensor). As the width of the boundary layer increases with increasing γ, averages calculated from (1.2) differ from their correct values. The contribution of the shear-flow-induced distortion of the pair-distribution function to the effective vicosity is not simply linear in γ as would follow from (1.2). Since the width of the boundary layer increases as $\gamma^{\frac{1}{2}}$, as a first guess the above-mentioned contribution to the effective viscosity would be linear in $\gamma^{\frac{1}{2}}$. The onset of non-Newtonian behaviour of the viscosity is thus related to the change of the boundary-layer structure with increasing γ.

In the following section of this paper, we review the Smoluchowski equation with shear flow. The third section deals with the asymptotic expansion of $S(\boldsymbol{k};\gamma)$ for small γ inside the boundary layer, the inner solution, and §4 deals with the expansion outside the boundary layer, the outer solution. In §5 it is shown that the inner solution outside the boundary layer simply reduces to the outer-solution (to first iteration), so that the inner solution is actually valid throughout $\boldsymbol{k}$-space. A well-known result from linear-response theory (where (1.2) is assumed from the outset) is recovered. Some numerical results are also presented in this section. We conclude with a summary and discussion.

2. The two-particle Smoluchowski equation with shear flow

In this paper we restrict our attention to the two-particle Smoluchowski equation with the neglect of hydrodynamic interactions. As will become clear, the solution of this 'simple' equation shows interesting properties. Qualitatively the same properties must be expected for solutions of more complete Smoluchowski equations in which, for example, hydrodynamic interactions are taken into account, since the interaction part of the diffusion tensors tend to zero as $R \to \infty$. The steady-state two-particle Smoluchowski equation without hydrodynamic interaction is

$$\nabla \cdot \left[\boldsymbol{\Gamma} \boldsymbol{R} P - 2D_0 \left\{ \frac{(\nabla V)}{k_B T} P + \nabla P \right\} \right] = 0. \tag{2.1}$$

$\boldsymbol{\Gamma}$ is the velocity-gradient tensor which depends linearly on the shear rate γ, $\boldsymbol{R}$ is the relative distance between two Brownian particles, V is their interaction potential and D_0 is the Stokes–Einstein diffusion coefficient. P is the probability density function for $\boldsymbol{R}$, which depends parametrically on the rate-of-strain tensor $\boldsymbol{\Gamma}$, or, equivalently, on the shear rate γ. If P is normalized as

$$\lim_{R \to \infty} P = 1, \tag{2.2}$$

it is usually named the 'radial- or pair-distribution function' denoted as g.

If $\boldsymbol{\Gamma} = \boldsymbol{0}$ it is easily seen that the canonical probability density function,

$$P \sim \exp\left\{ -\frac{V}{k_B T} \right\}, \tag{2.3}$$

is a solution of (2.1), since the quantity within the curly braces vanishes for this P. In contrast, if $\boldsymbol{\Gamma} \neq \boldsymbol{0}$, it is not possible to find appropriate solutions for which the quantity within the square brackets in (2.1) vanishes, since as $R \to \infty$ one has $\nabla V \to \boldsymbol{0}, \nabla P \to \boldsymbol{0}, P \to 1$. Thus, what remains between the square brackets for large R is $\boldsymbol{\Gamma} \boldsymbol{R}$. The divergence of this field is zero owing to the assumption that the fluid in which the Brownian particles are suspended is an incompressible fluid. This incompressibility assumption is entailed in the creeping-flow equations, which are needed to derive the Smoluchowski equation (2.1). Thus, the solution we seek is a function for which the quantity within the square brackets in (2.1) is non-zero.

For arbitarily small shear-rates γ, that is, for 'small' $\boldsymbol{\Gamma}$, the first term in the square brackets in (2.1), as was mentioned above, is *not* small compared to the second term (the quantity within the curly brackets) for large enough R. This is in conflict with the Ansatz (1.1), since for small γ this Ansatz predicts that the solution of (2.1) is approximately equal to the solution for $\gamma = 0$, that is, $\boldsymbol{\Gamma} = \boldsymbol{0}$. The Ansatz (1.1) is only valid for those $\boldsymbol{R}$ for which the second term is dominant over the first term. An analogous observation led Oseen to the solution of the Stokes paradox (van Dyke 1964). This singular behaviour for large R shows up in the small-k region for the Fourier transform of P, which is essentially the static structure factor. In singular perturbation theory this is called 'boundary-layer behaviour at wave vector $\boldsymbol{k} = \boldsymbol{0}$'. The phrase 'boundary layer' is a mathematical nomenclature from singular perturbation theory. In this case it does not have an interpretation as a physical boundary layer in real space, that is, in $\boldsymbol{r}$-space.

3. Asymptotic expansion of the static structure factor for small shear rates

The Fourier transform of the probability density function $P(\boldsymbol{R})$ is related to the static structure factor as follows:

$$\int \mathrm{d}\boldsymbol{R}\, P(\boldsymbol{R}) \exp\{\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{R}\} = (2\pi)^3 \delta(\boldsymbol{k}) + \frac{S(\boldsymbol{k}, \gamma) - 1}{n}, \tag{3.1}$$

where n is the particle number density of Brownian particles, $S(\boldsymbol{k},\gamma)$ is the static structure factor, where γ is the shear rate, which for simple shear is defined as

$$\boldsymbol{\Gamma} = \gamma\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.2}$$

Fourier transformation of (2.1) using (3.1) and (3.2) gives

$$\gamma k_1 \frac{\partial}{\partial k_2}[S(\boldsymbol{k},\gamma)-1] = 2D_0 k^2\left\{[S(\boldsymbol{k},\gamma)-1]+n\frac{\tilde{V}(k)}{k_B T}\right\} + \frac{2D_0}{k_B T(2\pi)^3}\boldsymbol{k}\cdot\int \mathrm{d}\boldsymbol{k}'\,\boldsymbol{k}'\tilde{V}(k')\,[S(\boldsymbol{k}-\boldsymbol{k}',\gamma)-1] \tag{3.3}$$

with $\boldsymbol{k} = (k_1, k_2, k_3)$ and $\tilde{V}$ is the Fourier transform of V.

If $\tilde{V}$ does not exist the following procedure should be used in order to calculate averages from $S(\boldsymbol{k},\gamma)$. First find a sequence V_m, so that $V_m \to V$ as $m \to \infty$, and so that $\tilde{V}_m$ exists for all integers m. Solve (3.3) with $\tilde{V}$ replaced by $\tilde{V}_m$. The solution of course depends on m, $S_m(\boldsymbol{k},\gamma)$. For the calculation of averages the limit $m\to\infty$ can be taken in a distributional sense, that is, calculate *first* the average using S_m, *then* take the limit $m \to \infty$,

$$\lim_{m\to\infty}\int \mathrm{d}\boldsymbol{k}(S_m(\boldsymbol{k},\gamma)-1)(\ldots).$$

For example, for a hard-sphere potential one could use

$$V_m = m; \quad R \leqslant 2a,$$
$$= 0; \quad R > 2a.$$

For $\gamma = 0$ (3.3) is easily seen to be satisfied by

$$S_e(k) = 1+n\int \mathrm{d}\boldsymbol{R}\left[\exp\left\{-\frac{V(R)}{k_B T}\right\}-1\right]\exp\{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}\}, \tag{3.4}$$

as it should be. Subtracting (3.3) with $\gamma = 0$ from the full (3.3) gives

$$\gamma k_1 \frac{\partial}{\partial k_2}[S(\boldsymbol{k},\gamma)-1] = 2D_0 k^2\{S(\boldsymbol{k},\gamma)-S_e(k)\} + \frac{2D_0}{k_B T(2\pi)^3}\boldsymbol{k}\cdot\int \mathrm{d}\boldsymbol{k}'\,\boldsymbol{k}'\tilde{V}(k')\{S(\boldsymbol{k}-\boldsymbol{k}',\gamma)-S_e(|\boldsymbol{k}-\boldsymbol{k}'|)\} \tag{3.5}$$

In order to expand $S(\boldsymbol{k};\gamma)$ for small γ, (3.5) is rewritten in dimensionless form. Let

$$\boldsymbol{K} = (K_1, K_2, K_3) = \boldsymbol{k}a, \tag{3.6}$$

$$\gamma^* = \frac{\gamma a^2}{D_0}. \tag{3.7}$$

Equation (3.5) reads in terms of these dimensionless variables

$$\gamma^* K_1 \frac{\partial}{\partial K_2}[S(\boldsymbol{K},\gamma^*)-1] = 2K^2\{S(\boldsymbol{K},\gamma^*)-S_e(K)\} \times \frac{2}{k_B T(2\pi)^3}\boldsymbol{K}\cdot\int \mathrm{d}\boldsymbol{K}'\,\boldsymbol{K}'\tilde{V}(K')\{S(\boldsymbol{K}-\boldsymbol{K}',\gamma^*)-S_e(|\boldsymbol{K}-\boldsymbol{K}'|)\}. \tag{3.8}$$

This equation is singularly perturbed for small γ^*, since γ^* appears as a factor in front of the derivative. This is the common situation in singular perturbation theory.† Equation (2.1) is singularly perturbed for small $\boldsymbol{\Gamma}$, since however small $\boldsymbol{\Gamma}$ is, the term $\boldsymbol{\Gamma}\boldsymbol{R}P$ in (2.1) can be made arbitrarily large by taking $\boldsymbol{R}$ large (note that (2.1) is only valid for systems of infinite extent, since the potential and hydrodynamic influences of the boundaries of the system are neglected *for all values of* $\boldsymbol{R}$). Thus for large separations $\boldsymbol{R}$, the pair-distribution function significantly differs from the function that is obtained from the Ansatz (1.1). These differences may contribute significantly to averages as calculated from the pair-distribution function. The behaviour of the pair-distribution function at large $\boldsymbol{R}$ shows up in the small-$\boldsymbol{k}$ behaviour of the structure factor. We have here a singular perturbation problem, with boundary-layer behaviour at $\boldsymbol{k} = \boldsymbol{0}$. Therefore we introduce the boundary-layer variable (Eckhaus 1979)

$$\boldsymbol{q} = \boldsymbol{K}(\gamma^*)^{-\nu}; \quad \nu \in \mathbb{R}^+, \quad \gamma^* > 0. \tag{3.9}$$

Here ν is to be taken such that, after transforming (3.8) to an equation in $\boldsymbol{q}$, setting $\gamma^* = 0$ does not lead to divergences and yields an equation 'as rich in structure as possible'. These conditions are satisfied if

$$\nu = \tfrac{1}{2}. \tag{3.10}$$

The asymptotic expansion of $S(\boldsymbol{q};\gamma^*)$ inside the boundary layer thus reads (Eckhaus 1979)

$$S(\boldsymbol{q},\gamma^*) = S_0(\boldsymbol{q},\gamma^*) + (\gamma^*)^{\frac{1}{2}} S_1(\boldsymbol{q},\gamma^*) + \ldots; \quad 0 < \gamma^* \ll 1. \tag{3.11}$$

We used the same symbol for the $\boldsymbol{k}$-, $\boldsymbol{K}$- and $\boldsymbol{q}$-dependent structure factors. The equation for S_0 is

$$q_1 \frac{\partial}{\partial q_2}[S_0(\boldsymbol{q},\gamma^*) - 1] = 2q^2\{S_0(\boldsymbol{q},\gamma^*) - S_e(q)\}. \tag{3.12}$$

Henceforth we shall assume that γ^* is small enough to neglect second- and higher-order terms in (3.11), and we concentrate on the properties of S_0. The solution of (3.12) in terms of the original $\boldsymbol{K}$-variable is

$$S_0(\boldsymbol{K},\gamma^*) - 1 = \frac{2}{\gamma^* K_1} \exp\left\{\frac{2K_2}{K_1}\frac{K_1^2 + \frac{1}{3}K_2^2 + K_3^2}{\gamma^*}\right\}$$
$$\times \int_{K_2}^{\pm\infty} \mathrm{d}Q (K_1^2 + Q^2 + K_3^2)\,[S_e((K_1^2 + Q^2 + K_3^2)^{\frac{1}{2}}) - 1] \exp\left\{-\frac{2Q}{K_1}\frac{K_1^2 + \frac{1}{3}Q^2 + K_3^2}{\gamma^*}\right\}; \quad \gamma^* > 0. \tag{3.13}$$

Here $+(-)$ in the integration limit is to be used if K_1 is positive (negative). The above expression was also obtained by Ronis (1984) in a completely different way (his equation (16) with $t = 0$ and $D(K) = D_0$, *not* $D(K) = D_0/S_e(K)$ as is assumed by Ronis). Ronis states the validity of (3.13) for arbitrary shear rates. From the above analysis it is clear that this equation is valid only for small shear rates, since it represents the first term in an asymptotic expansion of the structure factor for low shear rates.

To investigate the behaviour of the structure factor at $\gamma^* = 0^+$, the following

† A similar (but not equivalent) singular perturbation problem is found in the calculation of the orientational probability density function for a single rod-like Brownian particle in simple shear (Leal & Hinch 1971; Hinch & Leal 1972).

lemma are needed: if $f(Q)$ is a differentiable function with $f'(Q) > 0$ on (Q_0, ∞), and $\lim_{Q\to\infty} f(Q) = \infty$, then,

$$\lim_{\epsilon\downarrow 0} \frac{f'(Q)}{\epsilon} H(Q-Q_0) \exp\left\{-\frac{f(Q)-f(Q_0)}{\epsilon}\right\} = \delta(Q-Q_0), \tag{3.14}$$

where H is the Heaviside step function. If $K_1 > 0$ with $\epsilon = \gamma^*$, $f(Q) = 2Q(K_1^2+\frac{1}{3}Q^2+K_3^2)/K_1$ and $Q_0 = K_2$, then it follows from the lemma and from (3.11) and (3.13) that

$$\lim_{\gamma^*\downarrow 0} S(\boldsymbol{K}, \gamma^*) = S_e(K), \tag{3.15}$$

as it should be. Actually, (3.15) serves as the 'boundary value' to (3.12); there is no prescribed boundary value for the solution at $\boldsymbol{k} = \boldsymbol{0}$. As is shown in the next section, the inner solution (3.13) reduces outside the boundary layer to the outer solution, so that (3.13) is valid throughout $\boldsymbol{k}$-space (to first iteration).

Using (3.14) with $\epsilon = K_1$ we find from (3.13),

$$\lim_{K_1\downarrow 0} S_0(\boldsymbol{K}, \gamma^*) = S_e((K_2^2+K_3^2)^{\frac{1}{2}}) \tag{3.16}$$

independent of $\gamma^* > 0$. A similar relation can be obtained for $K_1 = 0^-$. Equation (3.16) predicts that there is no distortion of the structure factor in the (K_2, K_3)-plane. Of course the higher-order terms in (3.11) may give rise to a non-zero distortion in the (K_2, K_3)-plane. It is therefore to be expected that for low shear rates the distortion in the (K_2, K_3)-plane is small.

Since (3.13) is valid for $\gamma^* \ll 1$, the exponent in the integral drops to zero over a Q-range which is so small that $S_e((K_1^2+Q^2+K_3^2)^{\frac{1}{2}})$ hardly changes in this range. The delta-distribution-like behaviour given in (3.14) is therefore almost valid. Thus we expect that the distortion of the structure factor is quite small. Physically this is of course the result of considering both small shear rates and small volume fractions. For the numerical evaluation and further investigation of the distortion it is therefore convenient to rewrite (3.13) as

$$\Delta S(\boldsymbol{K}, \gamma^*) = S_0(\boldsymbol{K}, \gamma^*) - S_e(K) = \frac{2}{\gamma^* K_1} \exp\left\{\frac{2K_2}{K_1}\frac{K_1^2+\frac{1}{3}K_2^2+K_3^2}{\gamma^*}\right\}$$
$$\times \int_{K_2}^{\pm\infty} dQ (K_1^2+Q^2+K_3^2)\,[S_e((K_1^2+Q^2+K_3^2)^{\frac{1}{2}}) - S_e(K)] \exp\left\{-\frac{2Q}{K_1}\frac{K_1^2+\frac{1}{3}Q^2+K_3^2}{\gamma^*}\right\}; \quad \gamma^* > 0. \tag{3.17}$$

In the following section some of the properties of this equation are discussed. In particular the boundary-layer behaviour of the distortion $\Delta S(\boldsymbol{K}, \gamma^*)$ is considered and a comparison with the linear-response theory result is made.

4. The linear-response result

Outside the boundary layer, that is for large enough values of $\boldsymbol{K}$, or equivalently, small enough values of $\boldsymbol{r}$, where the perturbation of the Smoluchowski equation (2.1) becomes regular, the structure factor should have a γ-dependence as given in (1.2). This is the outer solution. Substitution of (1.2) into (3.8) and comparing the lowest order in γ^* coefficients gives the following integral equation for $S^{(1)}$:

$$K_1 \frac{\partial}{\partial K_2} S_e(K) = 2K^2 S^{(1)}(\boldsymbol{K}) + \frac{2}{k_B T (2\pi)^3} \boldsymbol{K}\cdot \int d\boldsymbol{K}'\, \boldsymbol{K}' \tilde{V}(K')\, S^{(1)}(\boldsymbol{K}-\boldsymbol{K}'). \tag{4.1}$$

The solution of this equation is a well-known result from linear-response theory (Ronis 1984),

$$S^{(1)}(K) = \frac{K_1 K_2}{2K^3} \frac{\partial S_e(K)}{\partial K}. \tag{4.2}$$

Notice that the integral in (4.1) vanishes for the solution (4.2) owing to the angular dependence of $S^{(1)}$ on $\boldsymbol{K}$. Here it is essential that V depends only on the magnitude of $\boldsymbol{K}$.

Since there are no adjustable integration constants in $S^{(1)}$, the inner solution determined in §3 should reduce to the outer solution (1.2) and (4.2) outside the boundary layer. This is shown in the next section, where the boundary-layer behaviour is further investigated.

5. The boundary-layer behaviour of the distortion

The boundary layer at $\boldsymbol{K} = \boldsymbol{0}$ is defined as the neighbourhood of $\boldsymbol{K} = \boldsymbol{0}$ where the Ansatz that the structure factor is analytic in γ^*, (1.2), does *not* yield a good approximation for the exact structure factor for small shear rates. That is, *outside* the boundary layer for small shear rates, the structure factor equals, to a good approximation, the analytic function which, to first order, is calculated in §4. Or, the boundary layer is the region in $\boldsymbol{K}$-space where solutions of (3.8) for small γ^* obtained from singular and regular perturbation theory significantly differ. The fact that the boundary-layer variable scales with $(\gamma^*)^{\frac{1}{3}}$, (3.9), implies that the width of the boundary layer is proportional to $(\gamma^*)^{\frac{1}{3}}$. This is illustrated explicitly below, where it is shown that in a region in $\boldsymbol{K}$-space where K is 'large enough', (3.17) reduces, to a good approximation, to the analytic function in γ^*, obtained in §4. The equations that specify the region where K is 'large enough', (5.2)–(5.5), are easily seen to be invariant with respect to the transformation $\boldsymbol{K} \rightarrow (\alpha \boldsymbol{K})^{\frac{1}{3}}, \gamma^* \rightarrow \alpha\gamma^*$ for any $\alpha > 0$, or, taking $\alpha = 1/\gamma^*, \boldsymbol{K} \rightarrow \boldsymbol{K}/(\gamma^*)^{\frac{1}{3}}, \gamma^* \rightarrow 1$. This invariance illustrates the $(\gamma^*)^{\frac{1}{3}}$-scaling of the width of the boundary layer. Notice that from (3.16) it follows that the (K_2, K_3)-plane lies outside the boundary layer.

Let us first rewrite (3.17) by introducing the new integration variable $X = Q - K_2$

$$\Delta S(\boldsymbol{K}, \gamma^*) = \frac{2}{\gamma^* K_1} \int_0^{\pm\infty} \mathrm{d}X (K^2 + X^2 + 2XK_2) [S_e((K^2 + X^2 + 2XK_2)^{\frac{1}{2}}) - S_e(K)]$$

$$\times \exp\left\{ -\frac{2X}{K_1} \frac{K_1^2 + \frac{1}{3}K_2^2 + K_3^2 + \frac{1}{3}(X^2 + 2XK_2)}{\gamma^*} - \frac{2K_2}{3K_1} \frac{X^2 + 2XK_2}{\gamma^*} \right\}; \quad \gamma^* > 0. \tag{5.1}$$

If

$$\left| \frac{2(K_1^2 + \frac{1}{3}K_2^2 + K_3^2)}{K_1 \gamma^*} \right| \gg 1 \tag{5.2}$$

and/or

$$\left| \frac{2K_2^2}{3K_1 \gamma^*} \right| \gg 1 \tag{5.3}$$

then only $X = 0^{\pm}$ contributes to the integral in (5.1). If all X-values that contribute significantly to the integral satisfy

$$\frac{2}{3} \left| \frac{X(X^2 + 2XK_2)}{K_1 \gamma^*} \right| + \frac{2}{3} \left| \frac{K_2 X^2}{K_1 \gamma^*} \right| \ll 1 \tag{5.4}$$

and

$$X^2 \ll 2|XK_2| \tag{5.5}$$

then (5.1) may be approximated by

$$\Delta S(\boldsymbol{K},\gamma^*) = \frac{2}{\gamma^* K_1}\int_0^{\pm\infty} \mathrm{d}X (K^2+2XK_2)\,[S_e((K^2+2XK_2)^{\frac{1}{2}})-S_e(K)] \times \exp\left\{-\frac{2XK^2}{K_1\gamma^*}\right\};\quad \gamma^*>0. \quad (5.6)$$

Expanding the equilibrium structure factor at K^2+2XK_2 around $X=0^{\pm}$ and keeping only leading terms in X yields

$$\Delta S(\boldsymbol{K},\gamma^*) = \frac{2}{\gamma^* K_1} K_2 K \frac{\partial S_e(K)}{\partial K}\int_0^{\pm\infty} \mathrm{d}X X \exp\left\{-\frac{2XK^2}{K_1\gamma^*}\right\}+\ldots;\quad \gamma^*>0. \quad (5.7)$$

This gives exactly the well-known result from linear-response theory,

$$\Delta S(\boldsymbol{K},\gamma^*) = \gamma^* \frac{K_1 K_2}{2K^3}\frac{\partial S_e(K)}{\partial K}+\ldots;\quad \gamma^*>0. \quad (5.8)$$

As shown in §4, (5.8) is found from linear-response theory, where (1.2) is assumed from the outset, so that the outer solution is recovered from the inner solution (3.17). Thus (3.17) is valid throughout $\boldsymbol{K}$-space, up to the first-order iteration. The region in $\boldsymbol{K}$-space where this equation is *not* a good approximation is, as was pointed out before, the boundary layer. It is clear that the boundary layer has a complicated structure; it is the union of the complements of the region defined by (5.2)–(5.5) and other regions where (5.8) is a good approximation for (5.1). Equations (5.2)–(5.5) are sufficient conditions for the correctness of (5.8), but they are not necessary conditions. There may exist additional sufficient conditions for the validity of (5.8).

Some numerical results are presented in figure 1. The results in figure 1 are obtained from (5.1) by numerical integration, where the hard-sphere equilibrium structure factor is used (see (3.4)),

$$S_e(K) = 1-3\phi\frac{\sin(K)-K\cos(K)}{K^3}, \quad (5.9)$$

where ϕ is the volume fraction of hard core,

$$\phi = \tfrac{4}{3}\pi a^3 n. \quad (5.10)$$

As expected, if one moves away from $\boldsymbol{K}=\boldsymbol{0}$, the difference between ΔS as given by (3.17) and (5.8) decreases. For screened Coulomb systems the same behaviour of the boundary layer is observed in Ronis (1984). Thus, the boundary layer is essentially concentrated at $\boldsymbol{K}=\boldsymbol{0}$.

Notice that the distortion for the hard-core system is of the order 10^{-3}, which is too small to have any experimental significance, both for a direct measurement and for its influence on the effective viscosity. Significant effects arise for larger concentrations and larger shear rates. The theory described here is valid only for small shear rates and is accurate only to first order in concentration (second order for the effective viscosity). Larger effects are found from (3.17) by taking a larger γ^* (in figure 1, $\gamma^*=0.05$, which is quite small). The question then is, up to which value for γ^* in equation (3.11), is S well approximated by S_0? It may well be that the integral in (3.8) is small even for larger shear rates owing to symmetry properties of the structure factor. In that case the structure factor is well approximated by S_0 for larger shear rates also. For charged systems ΔS for $\gamma^*=0.05$ is much larger than for hard-core systems; ΔS is $\leqslant 0.05$ (Dhont 1987). Results of future theories on the

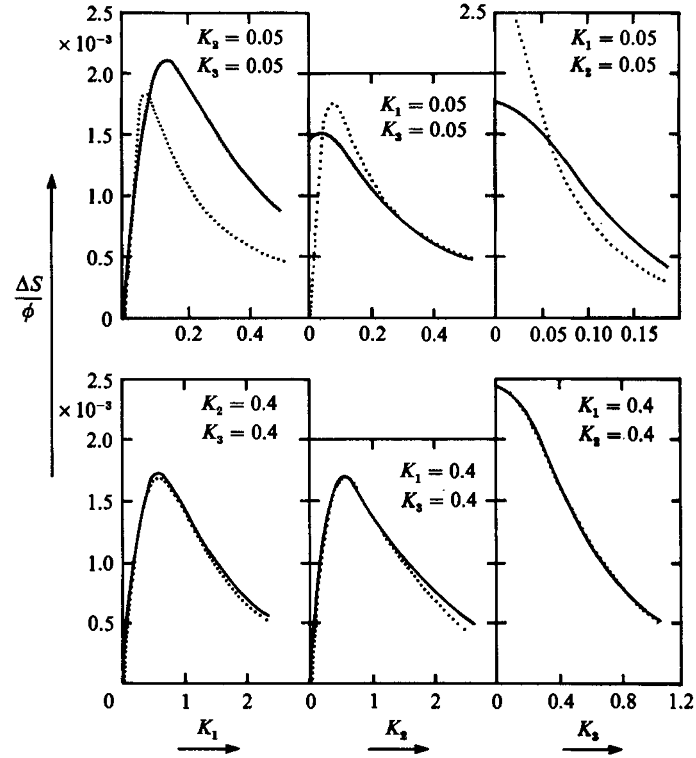

FIGURE 1. The distortion ΔS of the static structure factor divided by the volume fraction ϕ as a function of K_1, K_2 and K_3 for the two fixed values 0.05 and 0.4 of respectively (K_2, K_3), (K_1, K_3) and (K_1, K_2). The dimensionless shear rate γ^* is 0.05. For 50 nm particles in water this corresponds to a shear rate of $\gamma \approx 90\ \mathrm{s}^{-1}$. ——, The correct distortion as given by equation (3.13) or (3.17); ---, the linear-response result given by equation (5.8).

distortion of the structure factor in shear flow which are valid for higher shear rates and/or larger volume fractions, should reduce to the results obtained in the present paper to 'leading order' in the shear rate and the volume fraction.

6. Summary and discussion

We have shown that for small shear rates the structure factor in shear flow is non-analytic in the shear rate γ. That is, it is not correct to assume that for small γ

$$S(\boldsymbol{k}, \gamma) = S_e(\boldsymbol{k}) + \gamma S^{(1)}(\boldsymbol{k}) + \gamma^2 S^{(2)}(\boldsymbol{k}) + \dots . \tag{6.1}$$

Outside a neighbourhood of $\boldsymbol{k} = \boldsymbol{0}$, the extent of which scales as $\gamma^{\frac{1}{2}}$, (6.1) is approximately correct. Inside this neighbourhood, the so-called boundary layer, (6.1) is very different from the true structure factor for small shear rates.

The analysis as given in this paper is based on the two-particle Smoluchowski equation without hydrodynamic interaction. This is the simplest form of the general Smoluchowski equation. More complete Smoluchowski equations, in which for example hydrodynamic interactions are included, exhibit the same kind of singular behaviour. Solutions of these equations, which are much more difficult to calculate, will show the same kind of boundary-layer behaviour.

We note that the phrase 'boundary layer' is a mathematical nomenclature from singular perturbation theory. Here it does not have the physical interpretation as, for example, the boundary layer for fluids with a 'small' viscosity flowing along a large object, although the mathematics is the same in both cases, except that the 'boundary-value', (3.15), is of a different nature.

Ronis (1984) derives a series expansion of the distortion with respect to γ^* from (3.13) by partial integrations. Equation (5.8) is the first term in this expansion. In this way it seems as if the structure factor *is* analytic in γ^*, which is clearly not the case. The point is that the series obtained by partial integrations has a zero radius of convergence (for γ^*). A simpler but completely analogous and classic example of such partial integrations which formally leads to a series expansion is due to Euler. Consider the integral

$$I(\gamma^*) = \int_0^\infty \mathrm{d}x \frac{\exp\{-x\}}{1+x\gamma^*}. \tag{6.2}$$

Partial integrations give

$$I(\gamma^*) = \sum_{n=0}^{\infty} (-1)^n n!(\gamma^*)^n. \tag{6.3}$$

The radius of convergence of this series is zero, since for any $\gamma^* \neq 0$ the terms in it do not tend to zero as $n \to \infty$, thus violating a necessary condition for convergence. Equation (6.3), and for exactly the same reason Ronis' expansion, has no meaning as it stands. The significance of the first term in this non-converging series, (5.8), is clarified in §5; it is the approximate expression for the distortion for low shear rates outside the (non-empty) boundary layer at $\boldsymbol{k} = \boldsymbol{0}$. The distortion inside the boundary layer is properly described by (5.1), *not* by (5.8). The series (6.3) is an asympotic expansion of $I(\gamma^*)$ for small γ^*, that is, for every different γ^* the sum of a different finite number of terms of the series yields a good approximation for $I(\gamma^*)$. Similarly, within the boundary layer Ronis' expansion should be summed up to a finite number of terms, depending on the value of $\boldsymbol{K}$ and γ^*. Only outside the boundary layer is it sufficient to approximate the structure factor with the first term in the linear-in-γ^* expansion of Ronis. Thus, even at low shear rates it is not sufficient to keep only the first term in the non-converging series expansion obtained by partial integrations.

For extremely small shear rates the width of the boundary layer is so small that it does not contribute to the effective viscosity significantly. Or, equivalently, for extremely small shear rates the non-analytic distortion of the pair-distribution function $g(\boldsymbol{R}, \gamma)$ occurs at values of $\boldsymbol{R}$ so large that this function is almost equal to 1, so the averages calculated from an analytic $g(\boldsymbol{R}, \gamma)$ will yield accurate results. Thus, for the calculation of the Newtonian viscosity, the Ansatz that the shear-induced distortion is analytic, equations (1.1) and (1.2), may be used. For the non-Newtonian behaviour of the viscosity, however, the non-analytic behaviour of the pair-distribution function is essential.

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