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Shear-flow-induced distortion of the pair-correlation function

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Starting from the appropriate Smoluchowski equation, the pair-correlation function and the associated static structure factor are calculated for a colloidal suspension which undergoes a shear flow. Terms nonlinear in the shear rate are taken into account. The results obtained are in qualitative agreement with the elliptically distorted Debye-Scherrer rings which have recently been observed by Clark and Ackerson.

Recently, Clark and Ackerson[1] observed, for the first time, the shear-flow-induced distortion of the pair-correlation function via its associated structure factor $S(\vec{k})$ in a physical system, viz., in a suspension of interacting colloidal particles (charged monodisperse polymer spheres). Light-scattering techniques were used. Owing to the shear, the Debye-Scherrer rings (which are circles under equilibrium conditions) assume an elliptical shape. It is the purpose of this note to indicate that the experimental findings of[1] can be derived from the appropriate Smoluchowski equation for the pair-correlation function. These experimental results are (i) a shear-rate-induced shift of the maximum of the structure factor for a fixed direction of the scattering wave vector $\vec{k}$ and (ii) the surprising rotation of the principal axes of the elliptical Debye-Scherrer rings versus the principal axes of the (symmetric traceless) shear-rate (velocity gradient) tensor. For the latter effect it is of crucial importance that terms nonlinear in the shear rate are taken into account for the colloidal suspension. In connection with the viscosity problem of simple liquids[2-4] terms of this type are disregarded for good reasons. Thus the colloidal suspensions studied in Ref. 1 not only are model system for simple liquids but exhibit some additional interesting physical phenomena.

It should be mentioned that the shear-flow-induced distortion of the orientational distribution function of a fluid is revealed by the ensuing flow birefringence. In liquids and colloidal solutions of nonspherical particles, this effect has been studied for quite some time.[5,6] Flow birefringence of molecular gases[7] yields information on the orientational distribution of the rotational angular momenta.[8] The velocity distribution function of a heat-conducting gas has been analyzed[9] via the resulting asymmetry of a Doppler profile.[10] Generally speaking, experimental information on pair correlation and molecular distribution functions is of interest for the physical understanding of nonequilibrium phenomena and can provide a test of the kinetic theories used to calculate transport coefficients.

This article proceeds as follows. The Smoluchowski equation for the pair-correlation function g of the interacting colloidal particles is stated for the case where the liquid suspension undergoes a shear flow. Then it is indicated how the deviation of g from its equilibrium value can be determined with the help of the moment method. In an approximation suitable for the present problem, this deviation is characterized by a specific (2nd rank) tensorial expansion function. The pertaining tensorial expansion coefficient (anisotropy tensor) obeys an inhomogeneous relaxation equation. The stationary solution which contains terms nonlinear in the shear rate is stated for a specific geometry. Then, the structure factor $S(\vec{k})$ is calculated. Its angular dependence and its dependence on the magnitude of the wave vector $\vec{k}$ are discussed and compared with the experimental results reported in Ref. 1.

KINETIC EQUATION FOR THE PAIR-CORRELATION FUNCTION

The point of departure is the Smoluchowski equation[4] for the pair-correlation function g which depends on the time t and the relative position vector $\vec{r}$ between two polymer spheres. With the help of the dimensionless position vector $\vec{R}$, defined by $\vec{r} = r_0\vec{R}$, where r_0 is a reference length which can be chosen conveniently (e.g., average distance between the colloidal particles), this equation can be written as

$$\frac{\partial g}{\partial t} + w_\mu \mathfrak{L}_\mu g + \gamma_{\mu\nu} \frac{\partial}{\partial R_\mu}(R_\nu g) - \tau_0^{-1} \frac{\partial}{\partial R_\mu}\left(\frac{\partial}{\partial R_\mu} g - g g_0^{-1} \frac{\partial g_0}{\partial R_\mu}\right) = 0 . \qquad (1)$$

Greek indices refer to Cartesian components and the summation convention is used. In (1) $g_0 = e^{-w/k_B T}$ is the equilibrium pair-correlation function and w is the effective potential for the interacting polymer spheres. The relaxation time coefficient τ_0 is related to the diffusion coefficient $D=2k_BT/\xi$ (ξ is a friction coefficient) occurring in the Smoluchowski equation by

$$\tau_0^{-1}=Dr_0^{-2}\,. \tag{2}$$

The second and third terms in (1) describe the change of g due to the presence of a flow field v which is characterized by

$$\nabla_\mu v_\mu=0,\quad w_\mu=\tfrac{1}{2}(\vec\nabla\times\vec v)_\mu,\quad \gamma_{\mu\nu}=\tfrac{1}{2}(\nabla_\mu v_\nu+\nabla_\nu v_\mu)\,. \tag{3}$$

The vorticity w_μ and the symmetric traceless shear-rate tensor $\gamma_{\mu\nu}$ are assumed to be (approximately) constant. The quantity $\vec{\mathfrak{L}}$ is the anti-Hermitian operator

$$\vec{\mathfrak{L}}=\vec r\times\frac{\partial}{\partial\vec r}=\vec R\times\frac{\partial}{\partial\vec R}\,. \tag{4}$$

Notice that both the second and third terms of (1) stem from the single term $\nabla_\nu v_\mu\partial/\partial R_\mu(R_\nu g)$. In (1), the velocity gradient tensor $\nabla_\nu v_\mu$ has been decomposed into its symmetric part $\gamma_{\mu\nu}$ and its antisymmetric part involving w_μ. This decomposition is not only a matter of mathematical convenience; the physical effects associated with these terms are rather different. More specifically, the $\gamma_{\mu\nu}$ term leads to a kind of alignment (preferential orientation) of the unit vector $\hat{\vec r}=\hat{\vec R}$ between a pair of particles whereas the $\vec w$ term induces a rotation of $\hat{\vec r}$ about an axis parallel to $\vec w$. The ansatz

$$g=g_0(1+\psi) \tag{5}$$

where ψ characterizes the deviation of g from its equilibrium value g_0 leads to the following equation for ψ:

$$g_0\left(\frac{\partial\psi}{\partial t}+w_\mu\mathfrak{L}_\mu\psi\right)+\gamma_{\mu\nu}\frac{\partial}{\partial R_\mu}(R_\nu g_0\psi)-\tau_0^{-1}\frac{\partial}{\partial R_\mu}\left(g_0\frac{\partial\psi}{\partial R_\mu}\right)=-\gamma_{\mu\nu}R_\nu\frac{\partial g_0}{\partial R_\mu}\,. \tag{6}$$

Clearly this is an inhomogeneous equation for ψ. The inhomogeneity term vanishes for practically noninteracting colloidal particles where $g_0\approx1$. In connection with the viscosity problem for simple liquids[2-4] the terms containing w_μ and $\gamma_{\mu\nu}$ on the left-hand side of (6) can be disregarded. At least as far as the $\vec w$ term is concerned, this is no longer true for the colloidal suspension to be considered here.

Next, it is indicated how an approximate solution of (6) can be obtained with the help of the moment method which has previously been used successfully to obtain approximate solutions of kinetic equations, e.g., for molecular gases and liquids.[11,12]

MOMENT METHOD, RELAXATION EQUATIONS

Let $\varphi^i=\varphi^i(\vec R)$ be a set of orthonormalized functions with $\int\varphi^i g_0\,d^3R=0$ and

$$\langle i|j\rangle\equiv\int\varphi^i g_0\varphi^j\,d^3R=\delta_{ij}\,. \tag{7}$$

Then ψ can be written as

$$\psi=\sum_j a^j\varphi^j\,, \tag{8}$$

with the expansion coefficients a^i given by

$$a^i=\int\varphi^i g\,d^3R=\int\varphi^i g_0\psi\,d^3R\equiv\langle i|\psi\rangle\,. \tag{9}$$

Multiplication of (6) by φ^i and subsequent integration leads to the following set of coupled relaxation equations for the moments $a^i(t)$:

$$\frac{\partial a^i}{\partial t}+\sum_j\left(w_\mu\langle i|\mathfrak{L}_\mu|j\rangle+\gamma_{\mu\nu}\left\langle i\left|g_0^{-1}\frac{\partial}{\partial R_\mu}R_\nu g_0\right|j\right\rangle+\tau_0^{-1}\langle i,\lambda|j,\lambda\rangle\right)a^j=-\gamma_{\mu\nu}\left\langle i\left|g_0^{-1}R_\nu\frac{\partial g_0}{\partial R_\mu}\right.\right\rangle\,, \tag{10}$$

where

$$\langle i,\lambda|j,\lambda\rangle\equiv\int\left(\frac{\partial}{\partial R_\lambda}\varphi^i\right)g_0\left(\frac{\partial}{\partial R_\lambda}\varphi^j\right)d^3R\,. \tag{11}$$

Notice that, in general, Eq. (10) stands for an infinite set of equations, which for practical purposes, is approximated by a finite set.

RELAXATION EQUATION FOR THE ANISOTROPY TENSOR

The simplest approximation for the deviation of g from g_0 is a single term description where just one expansion function is taken into account which, however, is chosen such that the inhomogeneity term in (10) becomes extremal. This implies the use of the 2nd rank tensorial expansion function

$$\varphi_{\mu\nu}=-\kappa^{-1}g_0^{-1}R_\nu*\frac{\partial g_0}{\partial R_\mu}=-\kappa^{-1}h(R)\hat r_\mu*\hat r_\nu\,, \tag{12}$$

with the normalization factor κ determined by

$$\kappa^2=\tfrac{2}{15}\langle h(R)|h(R)\rangle,\quad h(R)=g_0^{-1}R\frac{\partial g_0}{\partial R}\,. \tag{13}$$

The centered asterisk refers to the symmetric traceless part of a tensor, e.g., $a_\mu*b_\nu=\frac{1}{2}(a_\mu b_\nu+a_\nu b_\mu)-\frac{1}{3}a_\lambda b_\lambda\delta_{\mu\nu}$; $\hat{\vec r}$ is the unit vector parallel to $\vec r$ and $\vec R$. In this case, ψ is given by

$$\psi=a_{\mu\nu}\varphi_{\mu\nu}\,. \tag{14}$$

The tensorial expansion coefficient

$$a_{\mu\nu}=\int\varphi_{\mu\nu}g\,d^3R=\langle\varphi_{\mu\nu}|\psi\rangle \tag{15}$$

is referred to as the (2nd rank) anisotropy tensor since it characterizes the (anisotropic) deviation of g from the isotropic g_0. Note, that the normalization (13) has been chosen such that

$$\langle \varphi_{\mu\nu} | \varphi_{\mu'\nu'} \rangle a_{\mu'\nu'} = a_{\mu\nu} .$$

Within the approximation (14), the relaxation equation for $a_{\mu\nu}$ as it can be inferred from (10) is

$$\frac{\partial a_{\mu\nu}}{\partial t} + 2(\vec{\mathrm{w}} \times a)_{\mu\nu} + \sigma \gamma_{\mu\lambda} * a_{\lambda\nu} + \tau^{-1} a_{\mu\nu} = \kappa \gamma_{\mu\nu} . \tag{15'}$$

The effective relaxation time τ is given by

$$\tau^{-1} = \tau_0^{-1} \tfrac{1}{5} \langle \varphi_{\mu\nu,\lambda} | \varphi_{\mu\nu,\lambda} \rangle , \tag{16}$$

cf. (10) and (11). The scalar coefficient

$$\sigma = \frac{12}{25} \left\langle \varphi_{\mu\nu} \middle| g_0^{-1} \frac{\partial}{\partial R_\nu} R_\lambda g_0 \middle| \varphi_{\lambda\mu} \right\rangle \tag{17}$$

can also be expressed in terms of an integral involving g_0 and its derivatives with respect to R. It should be mentioned that the influence of the shear flow on the diffusion process which is described by a term proportional to

$$\gamma_{\mu\nu} \frac{\partial}{\partial R_\mu} \left(g_0 \frac{\partial \psi}{\partial R_\nu} \right)$$

has been disregarded in (1) and (6). Inclusion of this term leads to a renormalization of the coefficient σ in (15′) but does not affect the $\vec{\mathrm{w}}$ term.

Formally, (15′) is analogous to the equation governing the alignment tensor which occurs in connection with flow birefringence in molecular gases[8,12,13] and in liquids or colloidal solutions of nonspherical particles.[14]

Next, a special geometry is considered where the tensorial Eq. (15′) can be reduced to three equations for scalar functions.

SPECIAL GEOMETRY

For a linear velocity profile (planar Couette flow) with $\vec{\mathrm{v}}$ parallel to the x axis and its gradient parallel to the y axis, one has

$$\gamma_{\mu\nu} = \gamma \hat{e}^x_\mu * \hat{e}^y_\nu , \quad \vec{\mathrm{w}} = -\tfrac{1}{2} \gamma \vec{\mathrm{e}}^z , \quad \gamma = \frac{\partial v_x}{\partial y} , \tag{18}$$

where the $\hat{e}^{x,y,z}$ are unit vectors. Insertion of the ansatz

$$a_{\mu\nu} = a \hat{e}^x_\mu * \hat{e}^y_\nu + b \tfrac{1}{2} (\hat{e}^x_\mu e^x_\nu - \hat{e}^y_\mu \hat{e}^y_\nu) + c \hat{e}^z_\mu * \hat{e}^z_\nu \tag{19}$$

into (15′) and comparison of the terms in front of the various (linearly independent) tensors yields three coupled equations for the coefficients a, b, c, viz.,

$$\begin{aligned} &\frac{\partial a}{\partial t} - \gamma b - \tfrac{1}{3} \sigma \gamma c + \tau^{-1} a = \kappa \gamma , \\ &\frac{\partial b}{\partial t} + \gamma a + \tau^{-1} b = 0 , \\ &\frac{\partial c}{\partial t} - \tfrac{1}{4} \sigma \gamma a + \tau^{-1} c = 0 . \end{aligned} \tag{20}$$

In this connection, it should be noticed that $\pm ia + b$ and c are essentially the spherical components a^m of $a_{\mu\nu}$ for $m = \pm 2$ and $m = 0$, respectively, where the z axis is chosen as the reference axis. The equations for the $m = \pm 1$ components are not coupled with the components which are taken into account here. The solution of (20) for a stationary situation can be written as

$$\begin{aligned} &a = \kappa \epsilon \alpha \cos 2\chi , \quad b = - \kappa \epsilon \alpha \sin 2\chi , \\ &c = \tfrac{1}{4} \sigma \epsilon \alpha , \\ &\epsilon = \tau \gamma , \quad \alpha = (1 + \epsilon^2)^{1/2} [1 + (1 - \tfrac{1}{12} \sigma^2) \epsilon^2]^{-1} . \end{aligned} \tag{21}$$

The angle χ is determined by

$$\tan 2\chi = \tau \gamma \equiv \epsilon . \tag{22}$$

The ansatz (19) with (21) implies that one of the principal axes of the tensor $a_{\mu\nu}$ is parallel to the z axis; the other two are in the plane determined by $\vec{\mathrm{v}}$ and the direction of its gradient and they enclose the angles $\tfrac{1}{4}\pi - \chi$ and $\tfrac{3}{4}\pi - \chi$ with the x axis (flow direction).

In the limit $(\epsilon)^2 \ll 1$ which is always fulfilled in simple liquids where the relaxation time τ is very short, (21) and (22) reduce to

$$a = \kappa \epsilon , \quad b \approx c \approx 0 , \quad \chi \approx 0 .$$

This result can also be obtained from

$$a_{\mu\nu} = \kappa \tau \gamma_{\mu\nu} , \tag{23}$$

the corresponding stationary solution of (15′) in the small shear-rate limit. The approximation (23), however, is not appropriate for the colloidal suspensions under consideration as will become apparent from a comparison of the structure factor with the light scattering observed in Ref. 1.

STRUCTURE FACTOR

The ansatz (5) with (12) and (14) implies that the structure factor (spectral density)

$$S(\vec{\mathrm{k}}) = \int (g - 1) e^{i \vec{\mathrm{k}} \cdot \vec{\mathrm{r}}} d^3 r \tag{24}$$

becomes

$$\begin{aligned} S &= S_0 + \kappa^{-1} a_{\mu\nu} \frac{\partial}{\partial k_\nu} (k_\mu S_0) \\ &= S_0 + \kappa^{-1} k \frac{\partial S_0}{\partial k} a_{\mu\nu} \hat{k}_\mu \hat{k}_\nu , \end{aligned} \tag{25}$$

where S_0 is the static structure factor for an equilibrium situation and $\hat{k}$ is the unit vector parallel to $\vec{k}$. For the light-scattering experiments as in Ref. 1, the relevant wave vector $\vec{k}$ is the difference between the wave vectors of incident and scattered light.

For $a_{\mu\nu} \neq 0$, the Debye-Scherrer rings become ellipses with their principal axes determined by those of the tensor $a_{\mu\nu}$. The strength of this ellipsoidal distortion is determined by the "magnitude" of $a_{\mu\nu}$ and by $k\partial S_0/\partial k$.

In particular, for the special geometry considered in the previous section, where $a_{\mu\nu}$ is given by (19) with (21) and (22), (25) leads to

$$S = S_0 + \epsilon\alpha k \frac{\partial S_0}{\partial k} Q \,, \qquad (26)$$

$$Q = \sin 2(\varphi - \chi)\sin^2\nu + \tfrac{1}{4}\sigma\epsilon\cos 2\chi(\cos^2\nu - \tfrac{1}{3}) \,,$$

where ν and φ are the polar angles of $\vec{k}$.

Now (26) is discussed for (small-angle) scattering with the direction of the incident light, firstly, parallel to the z axis (normal to the plane determined by $\vec{v}$ and its gradient) and, secondly, parallel to the y direction. These cases correspond to the experimental situations studied in Ref. 1. In the first case one has $\nu \approx \frac{1}{2}\pi$ and (26) reduces to

$$S = S_0 + \epsilon\alpha k \frac{\partial S_0}{\partial k} \left[\sin 2(\varphi - \chi) - \tfrac{1}{12}\sigma\epsilon\cos 2\chi\right] . \qquad (27)$$

The resulting Debye-Scherrer rings are ellipses as observed in Ref. 1. Their principal axes enclose the angles $\frac{1}{4}\pi - \chi$ and $\frac{3}{4}\pi\chi$ with the x axis. The approximation (23) implies $\chi = 0$. The experimental results of Ref. 1 indicate that one has $\chi \neq 0$. It should be possible to determine the relaxation time τ from the observed values of χ with the help of relaxation (22). Notice that it is the term involving $\vec{w}$ in (1), (6), or (15) which leads to a rotation of the principal axes of $a_{\mu\nu}$ versus those of $\gamma_{\mu\nu}$ and thus to $\chi \neq 0$. In the limit of small ϵ ($\epsilon^2 \ll 1$, $\alpha \approx 1$) where (27) is approximated by

$$S = S_0 + \epsilon k \frac{\partial S_0}{\partial k} \sin 2(\varphi - \chi) \,, \qquad (28)$$

the angle χ can still be of measurable size, e.g., one has $\chi = 5°$ (10°) for $\epsilon = \tau\gamma = 0.18$ (0.36).

For incident light parallel to the y axis, $\vec{k}$ practically lies in the x-z plane ($\varphi \approx 0$). Thus the deviation of S from S_0 as it can be inferred from (26) is considerably smaller in this case. This fact has also been noticed in Ref. 1.

Next, the dependence of S on k is studied for fixed direction of $\vec{k}$. Special attention is paid to S in the vicinity of $k = k_0$ where S_0 assumes the maximum value S_m. Insertion of the ansatz $S_0 = S_m + \frac{1}{2}S_0''(k - k_0)^2$ (with $S_0'' = \partial^2 S_0/\partial k^2$ at $k = k_0$, $S_0'' < 0$) into (26) yields

$$S = S_m + \tfrac{1}{2}S_0''(k - k_0)(k - k_0 + 2k\epsilon\alpha Q) \,.$$

This relation implies a shear-induced shift of the maximum of S from k_0 to

$$k_m = k_0[1 - \epsilon\alpha Q(1 + 2\epsilon\alpha Q)^{-1}] \,. \qquad (29)$$

The shift of the maximum of S (towards smaller values of k) has indeed been observed experimentally.[1]

For $\nu \approx \frac{1}{2}\pi$ and with the approximation which led from (26) to (28), (29) reduces to $k_m = k_0[1 - \epsilon\sin 2(\varphi - \chi)]$. In this case, k_m is shifted towards smaller (larger) values as compared with k_0 for $\varphi > \chi$ ($\varphi < \chi$). Notice that the shift of the maximum of S essentially stems from the expression (12) for the tensorial expansion function $\varphi_{\mu\nu}$ and it already can be found in the small shear-rate limit where the approximation (23) can be used.

CONCLUDING REMARKS

In this article, it has been demonstrated that the shear-flow-induced distortion of the structure factor as observed in colloidal suspensions can be derived from the appropriate Smoluchowski equation. In contradistinction to simple liquids, terms nonlinear in the shear rate have to be taken into consideration.

Finally, however, a few qualifying remarks are in order. The result (26) is based in the approximation (14) for the deviation of g from g_0. In principle, additional expansion functions and moments of two types have to be included. Firstly, there are 2nd rank tensorial functions (orthogonal to $\varphi_{\mu\nu}$) which affect the radial dependence of ψ. It is hoped that the resulting modifications of the effective relaxation time and of the dependence of S-S_0 on the magnitude of $\vec{k}$ are insignificant for practical purposes. Secondly, expansion tensors of higher rank have to be included in ψ. In particular, the term involving the shear-rate tensor $\gamma_{\mu\nu}$ on the left-hand side of (6) leads to a coupling of $a_{\mu\nu}$ with a 4th rank anisotropy tensor and thus additional terms contribute to (26) which are nonlinear in $\epsilon = \tau\gamma$. For the suspensions studied in Ref. 1 these contributions are negligible for small values of ϵ where (28) applies. This is no longer true for suspensions with a crystal-like structure.[15] There, higher rank anisotropy tensors[16] play an important role.

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