Structure and rheology of semidilute suspension under shear

J. Bławzdziewicz
Institute of Fundamental Technological Research, Polish Academy of Sciences, Świętokrzyska 21, 00-049 Warsaw, Poland

Grzegorz Szamel*
Instituut voor Theoretische Fysica, Rijksuniversiteit te Utrecht, P.O. Box 80.006, 3508 TA Utrecht, The Netherlands
(Received 10 August 1992)

We study the structure and viscosity of a semidilute colloidal suspension under stationary shear. For a model hard-sphere suspension with no hydrodynamic interactions we obtain accurate results for the low-density limit of the steady-state structure factor and shear-rate-dependent viscosity coefficients. In contrast with predictions of the earlier theories, we find a nonzero distortion of the structure factor in the plane perpendicular to the flow direction. The observed changes of the structure factor are correlated with shear thinning of the suspension.

PACS number(s): 82.70.Dd, 47.50.+d, 47.15.Pn, 51.20.+d

A pioneering work of Clark and Ackerson [1] has been followed by a number of interesting experimental and theoretical investigations of shear-induced distortion of the structure factor [2,3] in colloidal suspensions. Among the most important theoretical approaches are those of Ronis [4], Dhont [5], and Schwarzl and Hess [6]. All these theories involve approximations: Ronis uses a phenomenological approximate method of fluctuating diffusion equation; Schwarzl and Hess introduce a one-relaxation-time approximation into the Kirkwood-Smoluchowski equation; and Dhont's solution of the two-particle Smoluchowski equation is also approximate.

Many features of the experimental data are qualitatively reproduced by the above theories [7]. However, none of the theories reproduces a nonvanishing distortion of the structure factor in the plane perpendicular to the flow direction. Such a distortion has been found both in experiments [8,9] and in Brownian-dynamics simulations [10].

In this paper we present an accurate solution of the two-particle Smoluchowski equation for a simple suspension model. Our calculations yield a nonzero distortion of the structure factor in the plane perpendicular to the flow, in accordance with the experimental findings. Our conclusion is that a zero distortion in Dhont's [5], Schwartzl and Hess's [6], and Ronis's [4] theories results from approximations involved.

We consider a suspension of particles interacting via a hard-sphere potential, with no hydrodynamic interactions. Such a suspension can reasonably be used as a first-approximation model for a charge-stabilized colloidal system. The effective particle diameter should be set equal to the particle separation at which the interaction energy is of the order of k_BT. The steady-state structure factor is calculated in the low-density limit, by a combination of analytical and numerical methods. We also present results for the two-body contributions to the shear-rate-dependent viscosity coefficients. We find that with increasing shear rate the suspension undergoes shear thinning correlated with the structural changes indicated by the nonzero distortion of the structure factor in the plane perpendicular to the flow.

The suspension undergoes a steady shear flow of the form

$$\mathbf{v}(\mathbf{r}) = \gamma y \hat{\mathbf{e}}_x, \tag{1}$$

where γ is the shear rate and $\hat{\mathbf{e}}_x$ is the unit vector in the x direction. The suspension is statistically uniform with mean number density n. The particle volume fraction is denoted by $\phi = n\,4\pi\,a^3/3$, where where a is the particle radius. In addition to the convective drift, suspended particles perform Brownian motion, with the diffusion constant of an isolated particle D_0. The magnitude of the influence of the shear flow on the structure of the suspension is characterized by the Péclet number $\mathrm{Pe} = \gamma a^2/D_0$.

In the low-density limit the shear-induced distortion of the pair distribution $\delta g \equiv g - g^{\mathrm{eq}}$ can be determined from the stationary two-particle Smoluchowski equation. For our model the Smoluchowski equation written in the relative-position coordinates $\mathbf{r}$ takes the form

$$-\boldsymbol{\nabla}\cdot[-2D_0\boldsymbol{\nabla} + \gamma y\hat{\mathbf{e}}_x]\,\delta g(\mathbf{r}) = 0 \text{ for } r > 2a, \tag{2}$$

with the boundary condition

$$\hat{\mathbf{r}}\cdot[-2D_0\boldsymbol{\nabla} + \gamma y\hat{\mathbf{e}}_x]\,\delta g(\mathbf{r}) = -2a\gamma\hat{x}\hat{y} \text{ at } r = 2a, \tag{3}$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$.

We construct the solution of Eqs. (2) and (3) by the induced-sources method. Namely we consider the solution of (2) generated in the whole space by a set of multipole sources inserted at $\mathbf{r} = 0$. The strength of the

*Present address: Dept. of Materials Science and Engineering, University of Illinois, 1304 W. Green St., Urbana, IL 61801. Permanent address: Institute of Theoretical Physics, Warsaw University, Warsaw, Poland.

1063-651X/93/48(6)/4632(5)/$06.00

sources is adjusted to fulfill the boundary condition at $\mathbf{r} = 2a$. The solution constructed in this way is identical to the pair distribution δg for $r \geq 2a$.

We start from defining a set of solutions $T_{\alpha\beta}$ to Eq. (2), corresponding to multipole sources $(\partial/\partial x)^{\alpha}(\partial/\partial y)^{\beta}\delta(\mathbf{r})$. The functions $T_{\alpha\beta}$ can be obtained from the fundamental solution of Eq. (2), found by Erlick [11]. They are given by the following equation:

$$T_{\alpha\beta}(\mathbf{r}) = \frac{\mathrm{Pe}^{1/2}}{32\pi^{3/2} a D_0} \int_0^{\infty} \frac{dt}{\left(1+\frac{1}{3}t^2\right)^{1/2} t^{3/2}} \left(\frac{\partial}{\partial x}\right)^{\alpha} \left(\frac{\partial}{\partial y} + 2t\,\frac{\partial}{\partial x}\right)^{\beta} \exp\left\{-\frac{\mathrm{Pe}}{16a^2 t}\left[\frac{(x-t\,y)^2}{1+\frac{1}{3}t^2} + y^2 + z^2\right]\right\}. \quad (4)$$

We express the pair distribution g as a linear combination of $T_{\alpha\beta}$:

$$\delta g(\mathbf{r}) = \sum_{\alpha,\beta=0}^{\infty} C^{\alpha\beta}\, T_{\alpha\beta}(\mathbf{r}) \text{ for } r \geq 2a. \quad (5)$$

The coefficients $C^{\alpha\beta}$ are determined by the boundary condition (3). To derive explicit equations for $C^{\alpha\beta}$ we expand the left-hand side of (3) into spherical harmonics. We define the expansion coefficients $j^{lm}_{\alpha\beta}(r)$:

$$\hat{\mathbf{r}} \cdot [-2D_0 \boldsymbol{\nabla} + \gamma y \hat{\mathbf{e}}_x]\, T_{\alpha\beta}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} j^{lm}_{\alpha\beta}(r) Y_{lm}(\hat{\mathbf{r}}). \quad (6)$$

The boundary condition can be then rewritten as a set of linear equations for $C^{\alpha\beta}$:

$$\sum_{\alpha,\beta=0}^{\infty} j^{lm}_{\alpha\beta}(2a) C^{\alpha\beta} = A\gamma a \delta_{2,l}\,(\delta_{2,m} - \delta_{-2,m}), \quad (7)$$

where $A = 2i\,(2\pi/15)^{1/2}$.

Equations (4)–(7) have been approximately solved by considering a sequence of truncations obtained by setting $j^{lm}_{\alpha\beta} = 0$ if $\alpha+\beta > l_{\max}$ or $l > l_{\max}$. We have used $l_{\max} = 10$ at Pe $= 12.5$; for Pe ≤ 2 the truncation at $l_{\max} = 4$ appears to be sufficient. The convergence was monitored by calculating viscosity coefficients corresponding to the subsequent truncations.

The solution of Eqs. (2) and (3) obtained in this way has been used to calculate the distortion of the structure factor $S(\mathbf{k}) - S^{\mathrm{eq}}(\mathbf{k}) = n \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\,\delta g(\mathbf{r})$. Our results are presented in Figs. 1–4, along with the results of the theories of Refs. [4–6], adopted for our model system. Before we go on to the presentation of our findings we briefly discuss these theories.

The starting point of Dhont's theory [5] is the two-particle Smoluchowski equation for continuous interparticle potentials:

$$-\boldsymbol{\nabla} \cdot [-2D_0 \boldsymbol{\nabla} + 2\beta D_0 \mathbf{F}(\mathbf{r}) + \gamma y \hat{\mathbf{e}}_x]\, \delta g(\mathbf{r}) = \gamma y \nabla_x g^{\mathrm{eq}}(\mathbf{r}), \quad (8)$$

where $\beta = 1/(k_B T)$, the interparticle force $\mathbf{F} = -\boldsymbol{\nabla}\psi$ with ψ, the pair potential, and $g^{\mathrm{eq}} = \exp(-\beta\psi)$ is the equilibrium pair distribution function. In the hard-sphere limit $\psi \to \psi_{\mathrm{HS}}$, with $\psi_{\mathrm{HS}}(r) = \infty$ for $r < 2a$ and $\psi_{\mathrm{HS}}(r) = 0$ for $r > 2a$, Eq. (8) is equivalent to the boundary-value problem (2) and (3).

Dhont's approximation amounts to neglecting the force term on the left-hand side of Eq. (8). The simplified equation can be then solved analytically in the Fourier space. It describes independent diffusion of two particles after initial interaction, with no further interaction taken into account. Therefore Dhont's approximation is equivalent to the mode-mode coupling approximation applied

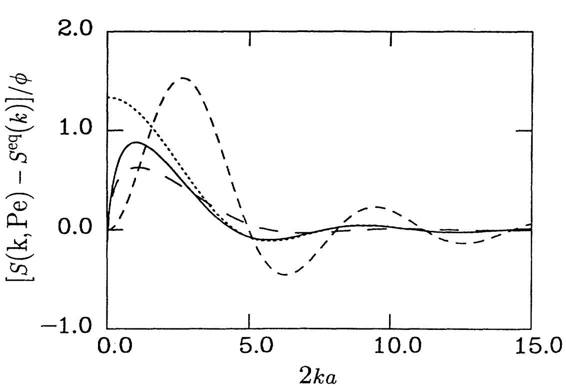

FIG. 1. Distortion $[S(\mathbf{k},\mathrm{Pe}) - S^{\mathrm{eq}}(k)]/\phi$ of the reduced steady-state structure factor from its equilibrium form, along the dilatation axis $\mathbf{k} = k(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y)/\sqrt{2}$, for the Péclet number Pe $= 0.5$. Solid line, present theory; long-dashed line, Dhont's approximation [5]; dashed line, Schwarzl and Hess's approximation [6]; dotted line, linear-response result.

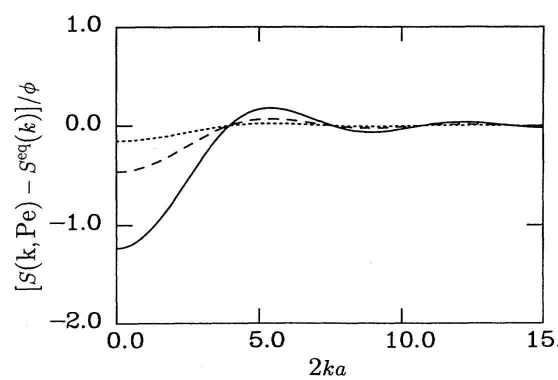

FIG. 2. Distortion $[S(\mathbf{k},\mathrm{Pe}) - S^{\mathrm{eq}}(k)]/\phi$ of the reduced steady-state structure factor from its equilibrium form, along the gradient direction $\mathbf{k} = k\hat{\mathbf{e}}_y$. Dotted line, Pe $= 0.5$; dashed line, Pe $= 1$; solid line, Pe $= 2$.

at low densities.

The analysis of Schwarzl and Hess [6] begins with the Kirkwood-Smoluchowski equation. In the low-density limit discussed in the present paper the Kirkwood-Smoluchowski equation is equivalent to Eq. (8). The approximation of Schwarzl and Hess consists in replacing the term $-\nabla \cdot [-2D_0\nabla + 2\beta D_0\mathbf{F}(\mathbf{r})]$ by the inverse of the relaxation time τ^{-1}, a free parameter. We have used $\tau = a^2/D_0$ when applying the theory to our model system.

Ronis's theory [4] is based on the phenomenological fluctuating diffusion equation for the one-particle density. It is known that in the theory of simple fluids the analogous approach, i.e., that of the fluctuating hydrodynamics, gives results equivalent to the mode-coupling approximation [12]. One can show that the same also holds for diffusive systems [13]. As we have discussed above, Dhont's result is equivalent to the low-density mode-mode coupling approximation. Therefore, in the low-density limit Dhont's and Ronis's results for the structure factor are equivalent, which can be checked by explicit calculation.

The above theories have been used to evaluate the low-density steady-state structure factor for our model system. We compare the results with our accurate solution of Eqs. (2) and (3).

In Fig. 1 we show the distortion of the structure factor for Pe = 0.5, along the extensional axis $\mathbf{k} = k(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y)/\sqrt{2}$. We compare the present solution of Eqs. (2)

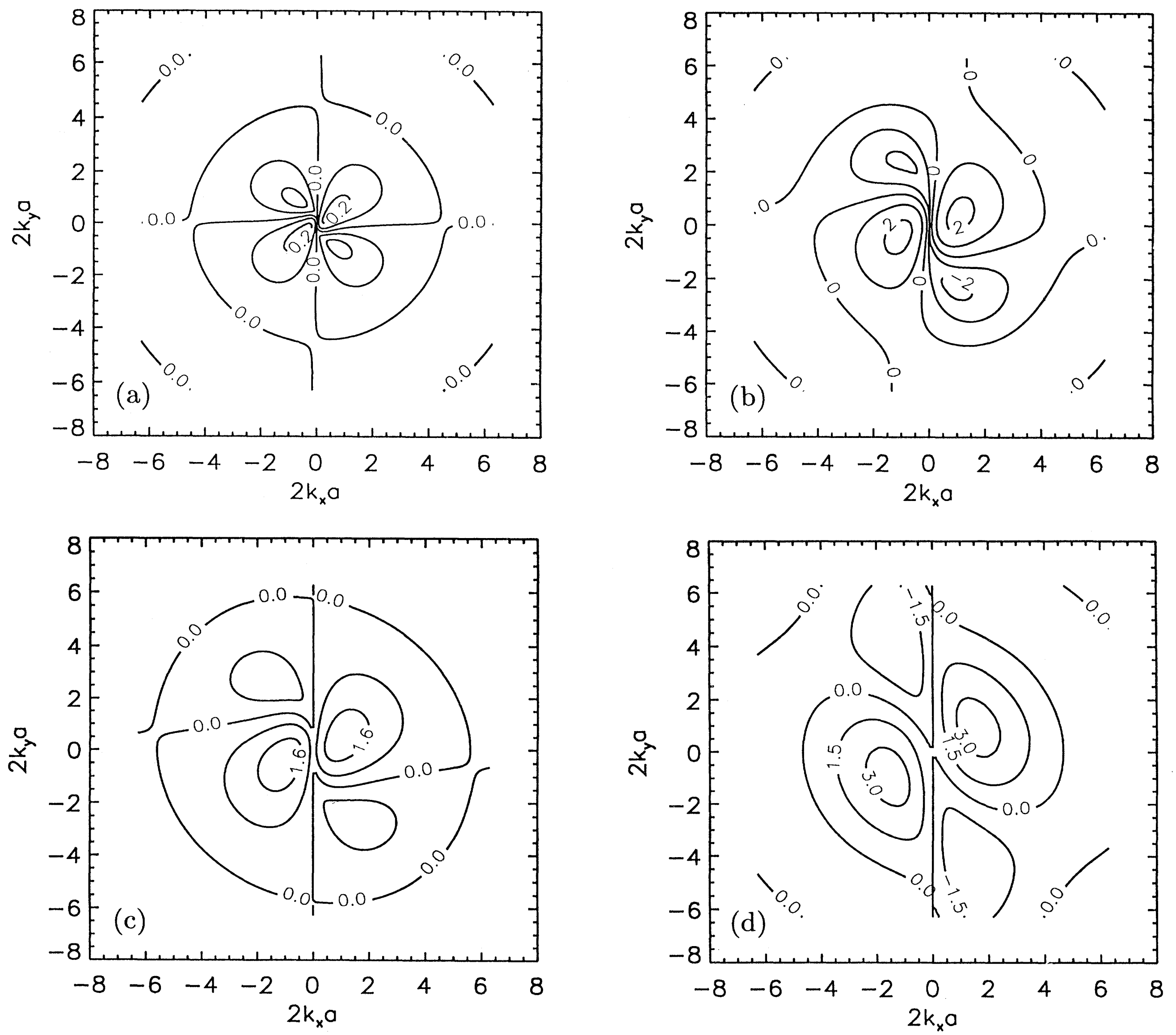

FIG. 3. Contour maps of $[S(\mathbf{k},\mathrm{Pe}) - S^{\mathrm{eq}}(k)]/\phi$ in the gradient-velocity plane. (a) Present theory, Pe = 0.1; (b) present theory, Pe = 2; (c) Dhont's approximation [5], Pe = 2; (d) Schwarzl and Hess's theory [6], Pe = 2.

and (3) to the linear-response result [14], the approximate result of Dhont's theory [5] (this result is equivalent to that of Ronis [4]), and the one-relaxation-time approximation of Schwarzl and Hess [6]. Even at this rather low Péclet number there is a significant disagreement of the results based on the approximate solutions of the Smoluchowski equation with our calculations. The theory of Dhont underestimates the distortion whereas the theory of Schwarzl and Hess overestimates it substantially, especially for large k. (Perhaps a better fit of Schwarzl and Hess's approximation can be obtained by using a shorter relaxation time.) Finally, we note that the linear-response result describes correctly the large-k behavior of the distortion but fails to do so for small k. This corresponds to the small-k boundary layer behavior of $S(\mathbf{k})$, discussed by Dhont [5].

In Fig. 2 we show the distortion of the structure factor along the gradient direction $\mathbf{k} = k\hat{\mathbf{e}}_y$, for several Péclet numbers. The approximate theories of Refs. [4–6] do not give any distortion along this line. In contrast, we find a nonzero distortion. The distortion is small for Pe up to 0.5, but is already significant at Pe = 2. It is interesting to note that these structural changes are correlated with the shear-thinning behavior of the suspension (see below). In the vicinity of the first maximum of the equilibrium structure factor the distortion is positive. This agrees qualitatively with the Brownian-dynamics simulation results [10]. The simulations, however, have been performed at much higher densities and Péclet numbers. Our theory yields a nonzero distortion not only in the gradient direction but also in other directions in the plane perpendicular to the flow.

In Fig. 3 we show the contour maps of the distortion of the steady state structure factor for $\mathbf{k}$ in the gradient-velocity plane. The results for two values of the Péclet number Pe = 0.1 and Pe = 2 are given. At Pe = 2 our present results are compared with the predictions of Dhont's and Schwarzl and Hess's theories. At this Péclet number the results of their theories differ considerably from ours. For lower Péclet numbers the difference is smaller, but it remains nonzero even in the low-Pe limit.

In order to illustrate the relative magnitude of the structural distortion caused by the flow we plot, in Fig. 4, the equilibrium static structure factor $S^{\mathrm{eq}}(k)$, along with $S(\mathbf{k}, \mathrm{Pe} = 2)$ for $\mathbf{k}$ in the extentional axis direction $(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y)/\sqrt{2}$ and in the velocity gradient direction $\hat{\mathbf{e}}_y$.

The steady-state pair distribution function g has been used to evaluate the two-particle contribution $\sigma_{ij}^{(2)}$ to the ensemble-averaged stress tensor of a suspension under shear. For suspension with no hydrodynamic interactions the only nonvanishing contribution to $\sigma_{ij}^{(2)}$ is the direct-interaction contribution, which for hard-spheres takes the form [14]

$$\sigma_{ij}^{(2)} = -\frac{9k_{\mathrm{B}}T\phi^2}{4\pi^2a^5}\int d^2\hat{\mathbf{a}}\; a_i\, a_j\, g(2\mathbf{a}), \tag{9}$$

where integration is over the unit sphere and $\mathbf{a} = a\hat{\mathbf{a}}$. For the flow (1) the traceless part of the steady-state stress-tensor can be fully characterized by three γ-dependent transport coefficients. Here we choose to present the results for the coefficients introduced by Hess [15]:

$$\eta_+^{(2)} = \gamma^{-1}\,\sigma_{xy}^{(2)}, \tag{10}$$

$$\eta_-^{(2)} = \gamma^{-1}\left(\sigma_{xx}^{(2)} - \sigma_{yy}^{(2)}\right)/2, \tag{11}$$

$$\eta_0^{(2)} = \gamma^{-1}\left[\sigma_{zz}^{(2)} - \frac{1}{2}\left(\sigma_{xx}^{(2)} - \sigma_{yy}^{(2)}\right)\right]\Big/2, \tag{12}$$

where only the two-particle contributions have been taken into account. In the low-shear-rate limit $\eta_+^{(2)}$ reduces to the two-body contribution to the low-shear-rate viscosity and $\eta_-^{(2)}, \eta_0^{(2)} = O(\mathrm{Pe})$.

The dependence of the transport coefficients $\eta_+^{(2)}$, $\eta_-^{(2)}$,

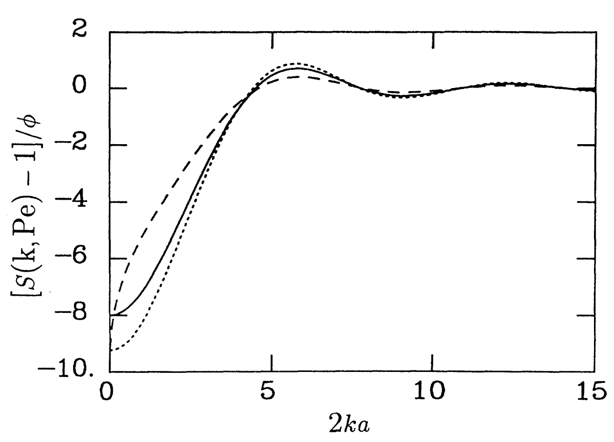

FIG. 4. Reduced structure factor $[S(\mathbf{k}, \mathrm{Pe}) - 1]/\phi$. Solid line, the equilibrium structure factor, Pe = 0; dashed line, structure factor along the dilatation line $\mathbf{k} = k(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y)/\sqrt{2}$, for Pe = 2; dotted line, structure factor along the gradient direction $\mathbf{k} = k\,\hat{\mathbf{e}}_y$, for Pe = 2.

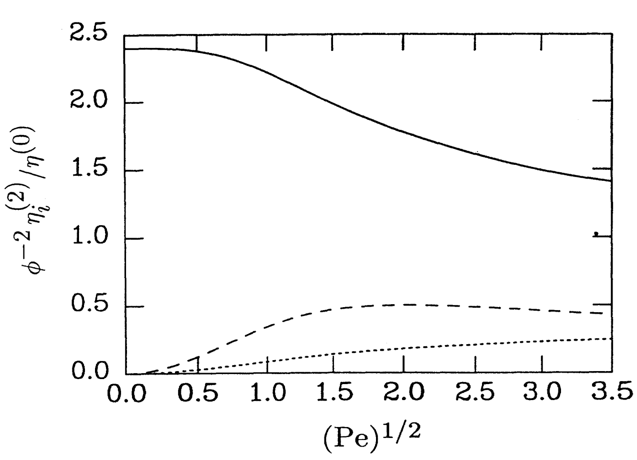

FIG. 5. Reduced viscosity coefficients $\eta_i^{(2)}$, where $i = +, -, 0$, defined in Eqs. (10)–(12), plotted as functions of $\sqrt{\mathrm{Pe}}$. Solid line, $\phi^{-2}\,\eta_+^{(2)}/\eta^{(0)}$; dashed line, $\phi^{-2}\,\eta_-^{(2)}/\eta^{(0)}$; dotted line, $\phi^{-2}\,\eta_0^{(2)}/\eta^{(0)}$, where $\eta^{(0)} = k_BT/(6\pi\,D_0\,a)$.

and $\eta_0^{(2)}$ on $\sqrt{\mathrm{Pe}}$ is shown in Fig. 5. For small Péclet numbers $\eta_+^{(2)}$ is approximately constant; for Pe above 1 the coefficient decreases significantly with the increasing shear rate. This is in qualitative agreement with the experimentally observed shear-thinning behavior of colloidal suspensions [14,16–18]. It follows from our data that $\sigma_{yy}^{(2)}$ is the smallest diagonal element of the stress tensor, the often observed pattern [20]. (For other theoretical approaches see Refs. [15] and [19–22].)

To summarize, we have shown that the the two-particle Smoluchowski equation for a suspension under shear yields a nonzero distortion of the structure factor in the plane perpendicular to the flow direction. We find that the structural changes are correlated with shear thinning.

We would like to acknowledge useful discussions with J. Dhont, M. Ernst, and H. van Beijeren. J.B. thanks Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) for supporting his stay in Utrecht where part of this work was done and G.S. acknowledges the financial support by the Stichting voor Fundamenteel Onderzoek der Materie which is sponsored by NWO.

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