NEWTONIAN VISCOSITY AND VISCO-ELASTIC BEHAVIOR OF CONCENTRATED NEUTRAL HARD-SPHERE COLLOIDAL SUSPENSIONS†

E. G. D. COHEN[1], R. VERBERG[2] and I. M. de SCHEPPER[2]
[1]The Rockefeller University, New York, NY 10021, U.S.A.
[2]I. R. I. Delft University of Technology, 2629 JB Delft, The Netherlands

Abstract—Simple expressions are given for the effective Newtonian viscosity as a function of concentration as well as for the effective visco-elastic behavior as a function of concentration and frequency for neutral monodisperse hard sphere colloidal suspensions over the entire fluid range. The basic physical mechanisms underlying these formulae are discussed. The agreement with existing experiments is very good. Extensions to charged colloidal suspensions and the incorporation of hydrodynamic interactions in the theory are discussed. © 1997 Elsevier Science Ltd.

Key Words: viscosity, viscoelasticity, colloids, suspensions

1. INTRODUCTION

The problem of the computations of the macroscopic properties, such as the viscosity, of a concentrated colloidal suspension from a molecular point of view is a very difficult one, because it deals with a complex strongly interacting many particle system. It is part of a large class of 'effective' behavior problems, where to a relatively simple system (the solvent here) particles or, in general, inclusions are added (Felderhof *et al.* 1982). For low concentrations of the added inclusions, systematic methods are in principle available to obtain corrections to the pure system behavior as a function of the concentration of the inclusions. The prototype of such a method is the virial expansion for computing the equation of state of a moderately dense gas in equilibrium as a correction to that of an ideal gas, in a power series in the (number) density n of the gas at a given temperature T (Kestin and Dorfman 1971, Ch. 7; McQuarrie 1976, Ch. 12; Felderhof 1988). The technique used for this is that of cluster expansions, where the effect on the macroscopic properties of the system (here, the pressure) due to clusters or groups of particles (inclusions) of increasing size are systematically taken into account. A power series in the density then arises since each higher term in the expansion is multiplied by a higher power of the expansion parameter (e.g. the density or concentration) than the previous one, since it includes the effect of a cluster consisting of one more particle (inclusion) than the previous term. In practice one can usually not handle clusters consisting of more than two particles and this restricts the cluster expansion method to low particle (inclusion) densities.

In order to make progress for a high density or a high concentration of inclusions, one has to proceed quite differently. What one has to do is to isolate the physically important effects due to the inclusions and then, hopefully, take these into account quantitatively in a way that leads to a practically usable formula, which gives the density or concentration dependence of the macroscopic properties as observed experimentally. It is this that we have attempted to do for concentrated colloidal suspensions consisting of monodisperse hard sphere neutral particles with diameter σ in a solvent of viscosity η_0. The problem we address is: what is the effective viscosity of such a suspension as a function of the concentration (or density n) of the colloidal particles: $\eta^{\text{eff}}(\phi;\omega)$, where $\phi = \pi n \sigma^3/6$ is the volume fraction of the particles and ω the frequency of an

---

†This paper is an extension of a paper given at the Thirteenth Symposium on Energy Engineering Sciences, 15–17 May 1995 at Argonne National Laboratory, published by Argonne National Laboratory, CONF-9505200, p. 1.

imposed oscillatory shear field of amplitude γ_0: $\gamma(t) = \gamma_0 e^{-i\omega t}$. We shall outline an approximate, yet satisfactory, solution to this problem derived from first principles, but containing a number of physically reasonable, but nevertheless severe approximations. The ultimate justification for these approximations is that they seem to lead to explicit expressions for $\eta^{\text{eff}}(\phi; \omega)$ which agree well with experiment over the entire fluid range of the colloidal suspension. The problem of justifying them theoretically remains largely open.

In section 2 we briefly outline the steps and approximations that lead from the fundamental Smoluchowski equation to the basic equation for the colloidal particle distribution in the suspension and present the solution of this equation to compute $\eta^{\text{eff}}(\phi; \omega)$. In section 3 we give explicit formulae for the effective Newtonian viscosity $\eta_N^{\text{eff}}(\phi) \equiv \eta^{\text{eff}}(\phi; \omega = 0)$ and the full visco-elastic behavior, as contained in $\eta^{\text{eff}}(\phi; \omega)$. In section 4 we compare our theoretical results with experiment and in section 5, we discuss our results and some possible extensions.

2. BASIC EQUATIONS

In this section we discuss the basic equation that describes the spatial distribution of the colloidal particles in a sheared suspension. We start from the N-particle Smoluchowski equation for a colloidal suspension of N identical hard sphere particles in the presence of an applied shear rate $\gamma(t)$, where hydrodynamic interparticle interactions are not explicitly included (Pusey and Tough 1982; Russel *et al.* 1989, pp. 262–266; Pusey 1991, p. 763). Integrating this equation over the positions of all particles but two (1 and 2), one obtains an equation for the nonequilibrium pair distribution function $g_2(\mathbf{R}; \mathbf{r}; \phi; \gamma_0; \omega; t)$ of the suspension, which involves the three-particle distribution function g_3. Neglecting g_3 and the dependence of g_2 on the center of mass $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ of the two particles 1 and 2 at the positions $\mathbf{r}_i (i = 1, 2)$, respectively, and making a Fourier transform of g_2 with respect to the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, one arrives for low concentrations, i.e. for small ϕ, at an equation of the form (de Schepper and Cohen 1994)

$$\left[\frac{\partial}{\partial t} + 2D_0 k^2 - \gamma_0 e^{-i\omega t} k_x \frac{\partial}{\partial k_y} \right] \delta S(\mathbf{k}; \phi; \omega; \gamma_0; t)$$

$$= \gamma_0 e^{-i\omega t} k_x \frac{\partial}{\partial k_y} S_{\text{eq}}(k; \phi). \tag{1}$$

Here $\delta S(\mathbf{k}; \phi; \omega; \gamma_0; t) = S(\mathbf{k}; \phi; \omega; \gamma_0; t) - S_{\text{eq}}(k; \phi)$, is the deviation of the nonequilibrium structure factor $S(\mathbf{k}; \phi; \omega; \gamma_0; t)$—the Fourier transform of $g_2(\mathbf{r}; \phi; \omega; \gamma_0; t)$—from that in equilibrium: $S_{\text{eq}}(k; \phi)$—the Fourier transform of the equilibrium radial distribution function $g_{\text{eq}}(r; \phi)$—where $r = |\mathbf{r}|$ and $k = |\mathbf{k}|$. The term $2D_0 k^2$ represents the free diffusion of the two colloidal particles, each with the Stokes–Einstein diffusion coefficient $D_0 = k_B T/3\pi\eta_0\sigma$, where k_B is Boltzmann's constant. In deriving [1] the impenetrability of the two hard sphere particles has been neglected (Verberg *et al.* unpublished), while the $S_{\text{eq}}(k; \phi)$ represents, in [1], only its low density approximation: $S_{\text{eq}}(k; \phi) = 1 - 24\phi j_1(k\sigma) + O(\phi^2)$, where $j_1(k\sigma)$ is the first spherical Bessel function.

We now upgrade the low concentration equation [1] to one hopefully physically meaningful and yet mathematically still tractable for high concentrations in two steps, which can be considered as partially accounting for the most important contributions of g_3, which was neglected in the derivation of [1]. These steps are: (1) a static one, by using the full $S_{\text{eq}}(k; \phi)$ on the right side (r.h.s.) of [1] for all ϕ. $S_{\text{eq}}(k; \phi)$ is known theoretically for all densities, since it is identical to that for a (pure) fluid of hard spheres (Henderson and Grundke 1975). It exhibits for $0.3 < \phi < 0.55$ a very sharp maximum at $k \approx k^*$, where $k^*\sigma \approx 2\pi$, implying a periodic particle configuration characterized by a wavelength $\lambda^* = 2\pi/k^* \approx \sigma$ (cf. figure 1). This sharp maximum at these large values of ϕ reflects physically a highly ordered state of the colloidal particles in the suspension on the length scale $\lambda^* \approx \sigma$. This means that each particle finds itself in a cage formed by its nearest neighbors, with a surface to surface distance of neighboring particles of the order of $\sigma/10$, so that the particle can only escape out of its cage with difficulty (Cohen and de Schepper 1992a, p. 387, 1992b, p. 359) (cf. figure 2); (2) a dynamic one, by replacing the low concentration (free) diffusion

coefficient D_0 by a cage-diffusion coefficient $D_c(k)$, which characterizes quantitatively the diffusion (i.e. escape) of a particle out of its cage at high concentrations (de Schepper et al. 1989; Pusey et al. 1990; Cohen and de Schepper 1992a, 1992b)

$$D_0 \rightarrow D_c(k) = \frac{D_0}{\chi(\phi)S_{eq}(k; \phi)}d(k).$$ [2]

Here $\chi(\phi) \equiv g_{eq}(\sigma; \phi)$, is the equilibrium radial distribution function at contact, i.e. $g(r, \phi)$ for $r = \sigma$. $\chi(\phi)$ is given in very good approximation by the Carnahan–Starling approximation $\chi(\phi) = (1 - \phi/2)(1 - \phi)^{-3} = 1 + 2.5\phi + 4.5\phi^2 + O(\phi^3)$ (McQuarrie 1976, pp. 250, 280; Hansen and McDonald 1986, pp. 36, 95) (cf. figure 4), where the $O(\phi)$ term is exact and the $O(\phi^2)$ term differs by 2% from the exact expression $4.59\phi^2$. $d(k) = 1/[1 - j_0(k\sigma) + 2j_2(k\sigma)]$, with $j_l(k\sigma)$ for the lth spherical Bessel function (cf. figure 1). We note that $D_c(k)$ can be identified with the long-time diffusion coefficient (de Schepper et al. 1989).

$D_c(k)k^2$ is sketched and compared with the results from light scattering experiments (Cohen and de Schepper 1991, 1992a, p. 392, 1992b, p. 362) for a typical large ϕ in figure 3.

The crucial cage-diffusion coefficient expression, [2], has been derived from the analogous cage diffusion expression in a (pure) dense hard sphere fluid (de Schepper et al. 1984), by replacing the low density hard sphere Boltzmann self-diffusion coefficient D_B occurring there, by the Stokes–Einstein diffusion coefficient D_0 (de Schepper et al. 1989; Pusey et al. 1990). Since $D_B \approx 10^{-4}\,cm^2/s$ and $D_0 \approx 10^{-7}\,cm^2/s$, this involves a reduction in the value of the cage-diffusion coefficient by three orders of magnitude in the case of colloidal suspensions, i.e. of Brownian particle motion, as compared to ballistic hard sphere motion. We emphasize that this implies that physically the cage diffusion processes in the dense (pure) fluid and the concentrated colloidal suspension proceed qualitatively the same, but quantitatively much slower in the latter than in the former.

Writing $\delta S(\mathbf{k}; \phi; \omega; \gamma_0; t) = \gamma_0 e^{-i\omega t}\delta S(\mathbf{k}; \phi; \omega)$, substituting this in [1] and solving then for $\delta S(\mathbf{k}; \phi; \omega)$ in the limit $\gamma_0 \rightarrow 0$, i.e. of vanishing shear rate amplitude, gives

$$\delta S(\mathbf{k}; \phi; \omega) = \frac{k_x k_y}{k}\frac{S'_{eq}(k; \phi)}{2D_c(k)k^2 - i\omega}$$ [3]
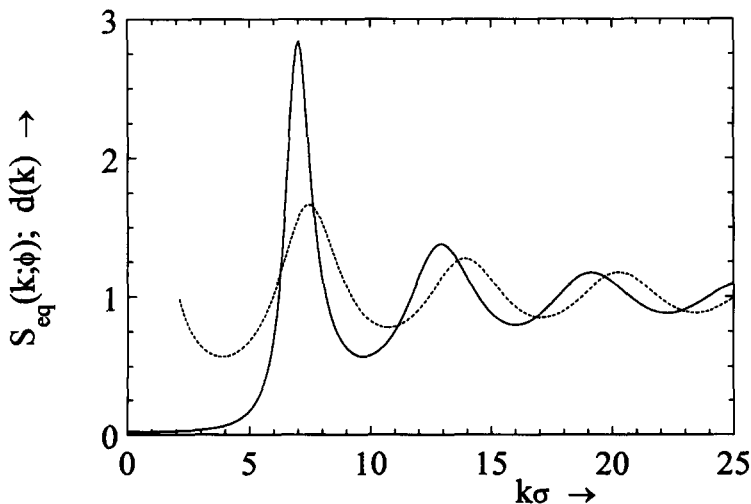
where $S'_{eq}(k; \phi) = dS_{eq}(k; \phi)/dk$.

Figure 1. Hard sphere $S_{eq}(k; \phi)$ for $\phi = 0.49$ (solid line, Henderson and Grundke 1975) and $d(k)$ (dashed line, cf. [2], as functions of $k\sigma$.
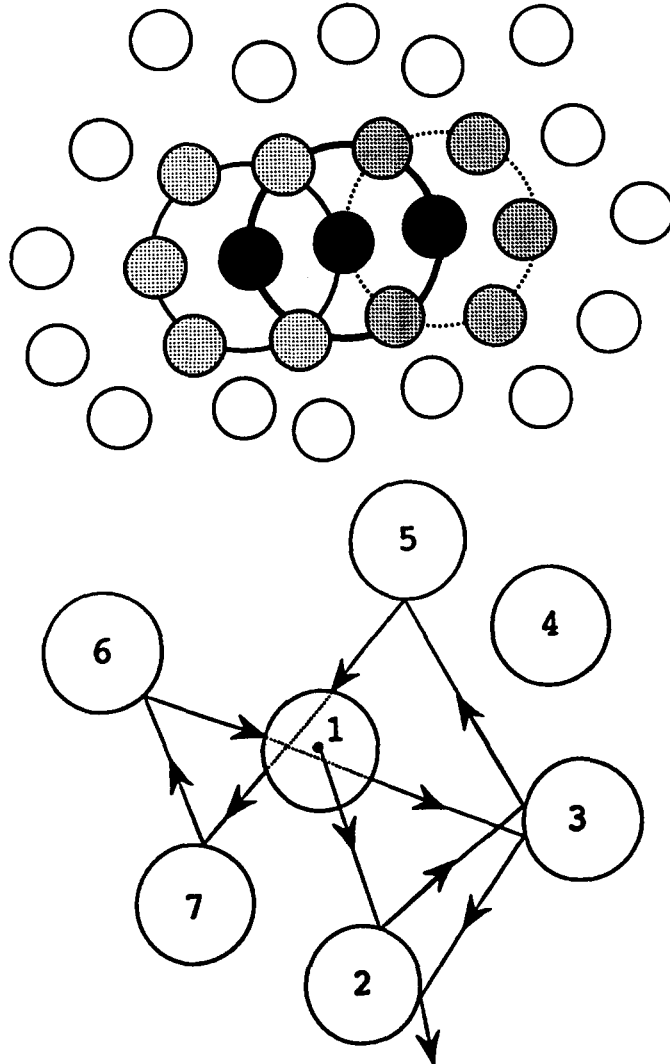
Figure 2. (a) The central particle (black) is in a cage whose wall is formed by the particles connected by the thick black line. Each wall particle is itself the center of a cage, of which the black particle is part of the wall. This is illustrated for two wall particles of the black particle, for which the cage walls are formed by particles connected by a solid line or a dotted line, respectively; (b) cage-diffusion collisions of central particle 1 for fixed wall particles 2–7. The interparticle distances have been considerably enlarged for clarity.

3. EFFECTIVE VISCOSITY

In this section we use the solution for the particle distribution obtained in the previous section to obtain an explicit expression for the effective viscosity. In order to use [3], which is in Fourier form, to obtain an expression for the effective viscosity in the limit $\gamma_0 \to 0$, we adapt the expression for the viscosity of a homogeneous fluid for particles interacting with a general (continuous) potential $V(r)$ (Verberg *et al.* unpublished; de Schepper *et al.* 1993)

$$n^{\text{eff}}(\phi; \omega) = \eta_{\infty}(\phi) + \frac{n^2}{2}\int d\mathbf{r}\,\delta g(\mathbf{r}; \phi; \omega)y\frac{\partial V(r)}{\partial x} \qquad [4]$$

where $\eta_{\infty}(\phi)$ is a static contribution and the dynamic contribution is determined by $\delta g(\mathbf{r}; \phi; \omega)$ defined by

$$g_2(\mathbf{r}; \phi; \omega; \gamma_0; t) = g_{\text{eq}}(r; \phi) + \delta g(\mathbf{r}; \phi; \omega)\gamma_0 e^{-i\omega t} + O(\gamma_0^2) \qquad [5]$$

to one applicable to hard spheres (which cannot be Fourier transformed). This is done in a mean

spherical-like approximation (Verberg *et al.* unpublished; Hansen and McDonald 1986, p. 126) by replacing $V(r)$ in [4] by $-k_BTC_{eq}(r; \phi)$, where $C_{eq}(r; \phi)$ is the equilibrium direct correlation function for hard spheres. Its Fourier transform $C_{eq}(k; \phi)$ is related to $S_{eq}(k; \phi)$ by $nC_{eq}(k; \phi) = 1 - 1/S_{eq}(k; \phi)$. Earlier, Russell and Gast (1986) replaced the hard sphere pair potential by the potential of mean force (see also Hansen and McDonald 1986, p. 113), rather than by the direct correlation function. Subsequently Wagner and Russel found that this approximation does not work at high concentrations, while our replacement does.

Using then [3] in the so-obtained expression for $\eta^{eff}(\phi; \omega)$ one finds

$$\eta^{eff}(\phi; \omega) = \eta_\infty(\phi) + \frac{k_BT}{60\pi^2}\int_0^\infty dk k^4 \left[\frac{S'_{eq}(k; \phi)}{S_{eq}(k; \phi)}\right]^2 \frac{1}{2D_c(k)k^2 - i\omega} \qquad [6]$$

for the general visco-elastic behavior of the suspension. Here $\eta_\infty(\phi)$, the first term on the r.h.s. of [6], is the static (infinite frequency) contribution to the effective viscosity and dominates $\eta^{eff}(\phi; \omega)$ at low concentrations. The second term on the r.h.s. of [6] contains the contributions due to cage diffusion, which come mainly from values $k \approx k^*$ in the integrand and dominate $\eta^{eff}(\phi; \omega)$ at high concentrations.

The expression for $\eta_\infty(\phi)$ we use

$$\eta_\infty(\phi) = \eta_0\chi(\phi) \qquad [7]$$

agrees very well with experiment over the entire fluid range (cf. figure 4) (Cohen and de Schepper 1995). Physically, [7] implies that the effective viscosity of the suspension at very high frequencies, or very short times (in fact: instantaneously) is increased above that of the pure solvent η_0 by the fraction of colloidal particle pairs at contact $\chi(\phi)$, i.e. that are colliding, exchange momentum and therefore contribute to the dissipation. The second term on the r.h.s. of [6], due to cage diffusion, is due to effects that basically take place on the much longer time scale of the Péclet time $\tau_P = \sigma^2/4D_0$, the characteristic time for a Brownian particle to displace itself diffusively over its diameter σ.
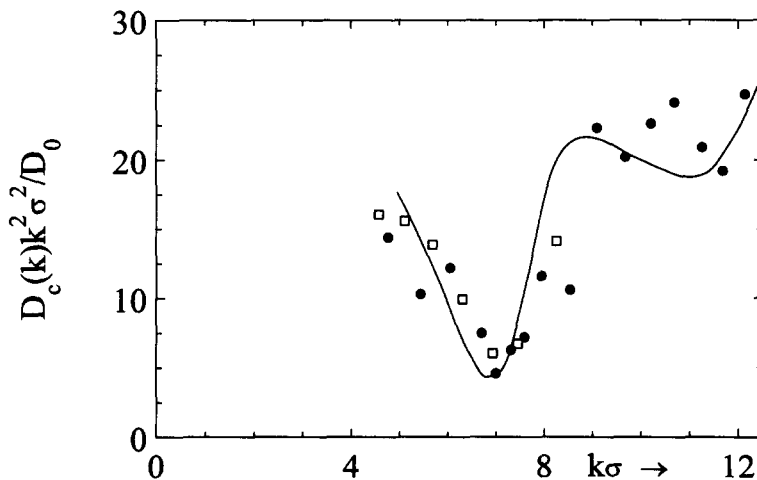

Figure 3. Reduced cage diffusion coefficient $D_c(k)k^2\sigma^2/D_0$ as a function of $k\sigma$ from light scattering for a charged colloid (●$\sigma = 600$ nm, $\phi = 0.48$), a neutral colloid (□$\sigma = 335$ nm, $\phi = 0.49$) (Cohen and de Schepper 1991, 1992a, 1992b) and from theory (solid line, [2]). The two minima correspond to the first two maxima of $S_{eq}(k; \phi)$. Here the diameter of the Debye sphere of the charged colloid is replaced by an effective hard sphere diameter which is determined by making a best fit of the experimental behavior of $S_{eq}(k; \phi)$ of the charged colloid near k^*, with an $S_{eq}(k; \phi)$ of a corresponding hard sphere fluid (de Schepper *et al.* 1989).
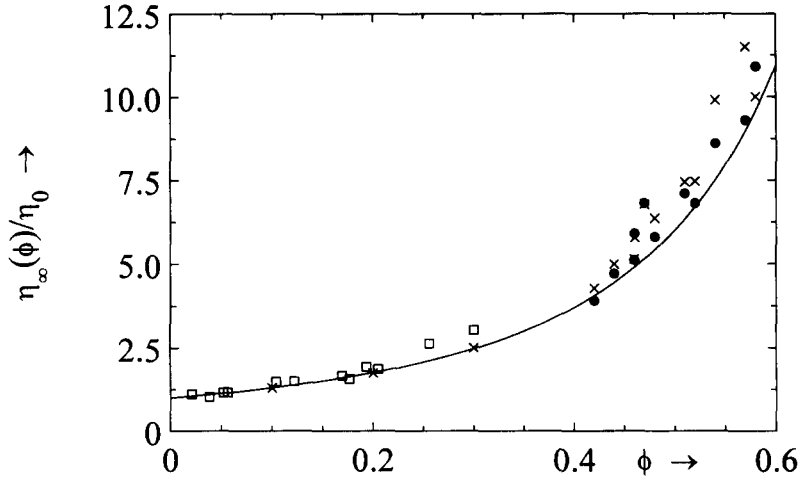
Figure 4. Relative infinite frequency viscosity $\eta_\infty(\phi)/\eta_0$ as a function of ϕ. □ Zhu *et al.* (1992); × van der Werff *et al.* (1989); ● Cichocki and Felderhof (1994), whose points were obtained by a different analysis of van der Werff *et al.*'s data (1989) than by the authors themselves. The solid line corresponds to [7].

The effective Newtonian viscosity $\eta_N^{\text{eff}}(\phi)$ can be obtained directly from [6] by setting $\omega = 0$, leading, with [2] and [7] to

$$\eta_N^{\text{eff}}(\phi) = \eta_0\chi(\phi)\left[1 + \frac{1}{40\pi}\int_0^\infty d\kappa\kappa^4\frac{[S'_{\text{eq}}(\kappa;\phi)]^2}{S_{\text{eq}}(\kappa;\phi)d(\kappa)}\right] \qquad [8]$$

with $\kappa = k\sigma$. Explicit formulae for $S_{\text{eq}}(k;\phi)$ for hard sphere fluids for all ϕ can be found in the literature (Henderson and Grundke 1975). A useful Padé approximation of [8], good to within 0.25%, is

$$\eta_N^{\text{eff}}(\phi) = \eta_0\chi(\phi)\left[1 + \frac{1.44\phi^2\chi(\phi)^2}{1 - 0.1241\phi + 10.46\phi^2}\right] \qquad [9]$$

where the Carnahan–Starling expression for $\chi(\phi) = (1 - \phi/2)(1 - \phi)^{-3}$ can be used.

It might be of interest to outline how the representation [9] of [8] was obtained. Using the asymptotic expressions for large k of $S(\kappa;\phi) = 1 + O(\kappa^{-2})$; $d(\kappa) = 1 + O(\kappa^{-2})$ and $S'_{\text{eq}}(\kappa;\phi) = 24\phi\chi(\phi)[j_2(\kappa)/\kappa][1 + O(\kappa^{-2})]$, one obtains: $\eta_N^{\text{eff}}(\phi) = \eta_0\chi(\phi)[1 + 1.44\phi^2\chi(\phi)^2 + O(\phi^3)]$. Dividing then the second term in the square brackets of this expression for $\eta_N^{\text{eff}}(\phi)$ by a polynomial of the second degree in ϕ, one adjusts the coefficients of this polynomial so that they agree with those obtained from [8].

For $\omega \neq 0$ one obtains the visco-elastic behavior of the suspension with a complex $\eta^{\text{eff}}(\phi;\omega) = \eta_R^{\text{eff}}(\phi;\omega) + i\eta_I^{\text{eff}}(\phi;\omega)$ or equivalently $\eta_R^*(\phi;\omega) = [\eta_R^{\text{eff}}(\phi;\omega) - \eta_\infty(\phi)]/[\eta_N^{\text{eff}}(\phi) - \eta_\infty(\phi)]$ and $\eta_I^*(\phi;\omega) = \eta_I^{\text{eff}}(\phi;\omega)/[\eta_N^{\text{eff}}(\phi) - \eta_\infty(\phi)]$, respectively.

We remark that [6] with [7] and all equations following from them, like [8], do not contain any adjustable parameters and are completely determined by those that determine the system: the viscosity η_0 of the solvent, the concentration n and the volume fraction ϕ (or the diameter σ) of the colloidal particles.

4. COMPARISON WITH EXPERIMENT

$\eta_N^{\text{eff}}(\phi)$ is compared with experiment in figure 5 and $\eta_R^*(\phi;\omega)$ as well as $\eta_I^*(\phi;\omega)$ in figure 6. In figure 5 the contributions of $\eta_\infty(\phi)$ are plotted separately and represent—on the scale used in figure 5—the low concentration behavior for $0 < \phi < 0.35$ well. The steep increase in η_N^{eff} for $0.35 < \phi < 0.55$ is due to the increasing difficulty for colloidal particles to escape from, i.e. diffuse out of, their cages. The total increase in the relative effective viscosity $\eta_r^{\text{eff}} = \eta_N^{\text{eff}}(\phi)/\eta_0$ over the entire

fluid range $0 < \phi < 0.55$ is about a factor 60. We note that the good agreement with experiment is not restricted to the benchmark experiments of van der Werff and de Kruif (1989), but also includes those of Jones et al. (1991, 1992) and Papir and Krieger (1970), which are all very well consistent with each other.

Figure 6 shows, in agreement with van der Werff et al.'s (1989) observation, that the concentration dependence of the visco-elasticity as a function of $\omega \tau_1(\phi)$ is weak.

Figure 7 gives a more detailed comparison for four concentrations. Here the phenomenological time $\tau_1(\phi)$ is determined from the experimental asymptotic behavior of $\eta_R^*(\phi; \omega)$ for large ω by setting (van der Werff et al. 1989): $\eta_R^*(\phi; \omega) = (3\sqrt{2}/2\pi)[\omega \tau_1(\phi)]^{-1/2}$, where $\tau_1(\phi) \approx \tau_P/4$ for $0 < \phi < 0.50$ (cf. de Schepper et al., figure 2).

The asymptotic, large ω, behavior of $\eta_R^{\text{eff}}(\phi; \omega)$ and $\eta_I^{\text{eff}}(\phi; \omega)$ is both theoretically and experimentally as $A(\omega\tau_P)^{-1/2}$. The theoretical and experimental values of A differ, however, in good approximation by a factor $2/\chi(\phi)$, so that $A^{\text{th}}/A^{\text{exp}} \approx 2/\chi(\phi)$. This, combined with the similarity in shape of the theoretical and experimental $\eta_R^{\text{eff}}(\phi; \omega)$ and $\eta_I^{\text{eff}}(\phi; \omega)$, allows a determination of $\eta_R^{\text{eff}}(\phi; \omega)$ and $\eta_I^{\text{eff}}(\phi; \omega)$ even when the experimental asymptotic ω-behavior is unknown. For, one can then simply shift the theoretical curves for $\eta_R^{\text{eff}}(\phi; \omega)$ and $\eta_I^{\text{eff}}(\phi; \omega)$ plotted as a function of $\omega\tau_P$, horizontally over an amount $2/\chi(\phi)$, to obtain a good representation of the corresponding experimental curves (cf. figure 8) (Verberg et al. unpublished).

5. DISCUSSION

(1) The rheological behavior, defined as the shear rate γ_0 dependence of the viscosity, i.e. $\eta^{\text{eff}}(\phi; \gamma_0)$, for dense colloidal suspensions of hard spheres has been studied theoretically before (de Schepper and Cohen 1994). However, the relation of the theoretical results to those found experimentally is not unambiguous and needs further study. We mention in particular the very interesting work on the rheology of colloidal suspensions of Ronis (1986). He considered $\eta^{\text{eff}}(\phi; \gamma_0)$ for soft charged particles interacting through a screened Coulomb potential at low densities. Then the cage-diffusion ([2]) is still relevant to describe the particle motions (Verberg et al. unpublished).

(2) Recently Brady (1993) has published a different model for the Newtonian as well as the frequency dependent viscosity. His results can be obtained by scaling the low density solution of the two particle Smoluchowski equation (Cichocki and Felderhof 1991) and an adjustment of the pair correlation function at contact using experimental and computer simulation results. This leads to an excellent agreement of the Newtonian viscosity with experiment (virtually indistinguishable from our results for $0 < \phi < 0.55$), but not of the visco-elastic behavior (Brady 1994; Cichocki and Felderhoff 1994). The underlying physics is, however, very different from ours, since the
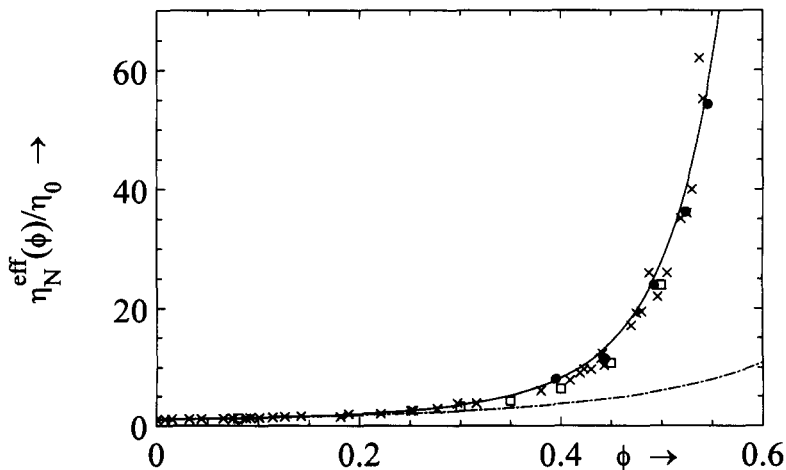

Figure 5. Relative effective Newtonian viscosity $\eta_N^{\text{eff}}(\phi)/\eta_0$ as a function of ϕ. × van der Werff and de Kruif (1989); ● Jones et al. (1991, 1992), □ Papir and Krieger (1970). —— theory ([8] or [9]), —·—·— $\eta_\infty(\phi)/\eta_0 = \chi(\phi)$.
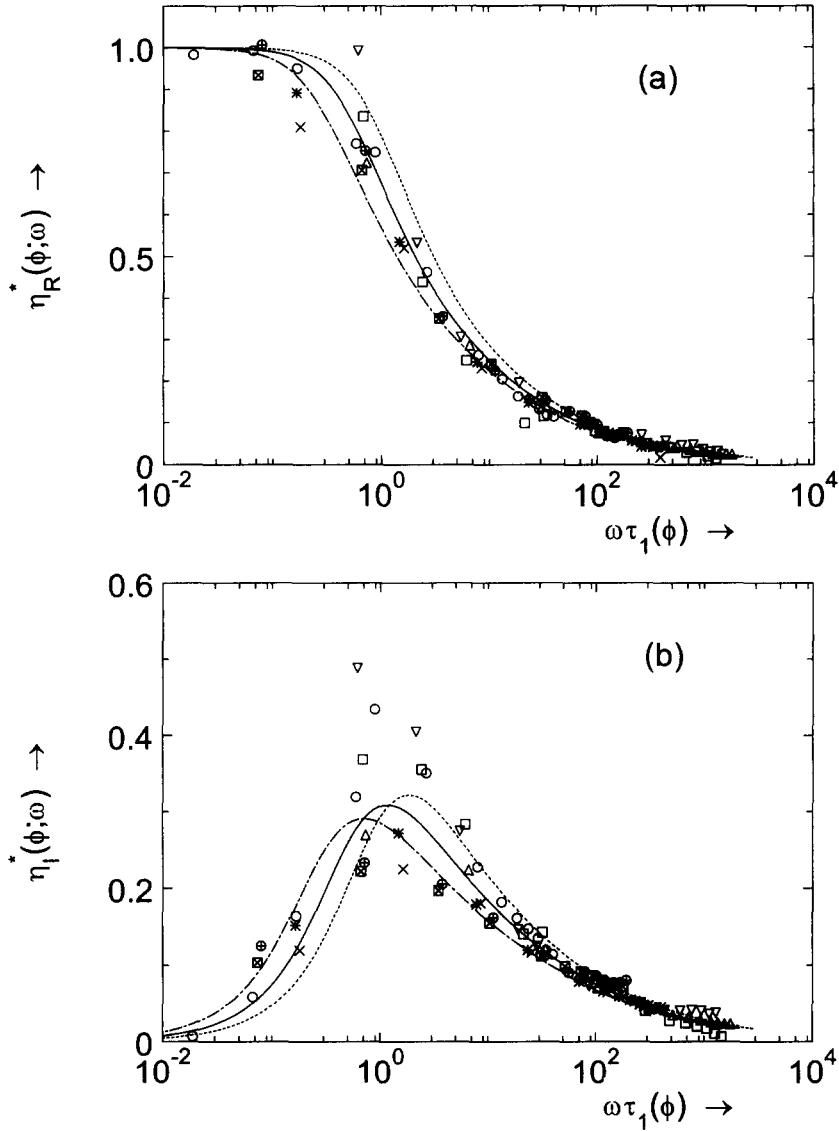
Figure 6. (a) $\eta_R^*(\phi; \omega)$ and (b) $\eta_I^*(\phi; \omega)$ as a function of $\omega\tau_1(\phi)$. Experimental points from Jones *et al.* (1991). ⊕ for $\phi = 0.44$; ○ for $\phi = 0.46$; □ for $\phi = 0.47$; ⊠ for $\gamma = 0.48$; ▽ for $\phi = 0.51$; * for $\phi = 0.52$; × for $\phi = 0.54$ and △ for $\phi = 0.57$. Theory from [6]: —·—·— $\phi = 0.55$; ——— $\phi = 0.50$ and ···· $\phi = 0.45$. The cloud of points in (b) near $\omega\tau_1(\phi) = 1$ should be discarded since they do not satisfy the Kramers–Kronig relation (Cichocki and Felderhof 1994).

cage-diffusion mechanism, crucial for high densities, is missing. It appears therefore that only our theory is able to account for the full frequency behavior of $\eta(\phi; \omega)$.

(3) We note that we have not explicitly considered here any hydrodynamic interactions between the colloidal particles as transmitted by the solvent. While we believe that at high concentrations $0.3 < \phi < 0.55$ the hydrodynamic interactions are quenched to a very high extent due to the extreme proximity of the colloidal particles, they are certainly present at lower concentrations, as the calculations of Batchelor (1977) and Cichocki and Felderhof (1988) have shown. However, there is an increasing number of indications that at the very least part of these hydrodynamic interactions can be taken into account via the function $\chi(\phi)$ (Verberg *et al.* unpublished). As an example, we note that the theoretical result of Freed and Muthukumar (1982) and Beenakker (1984) for $\eta_\infty(\phi)$ to $O(\phi^2)$

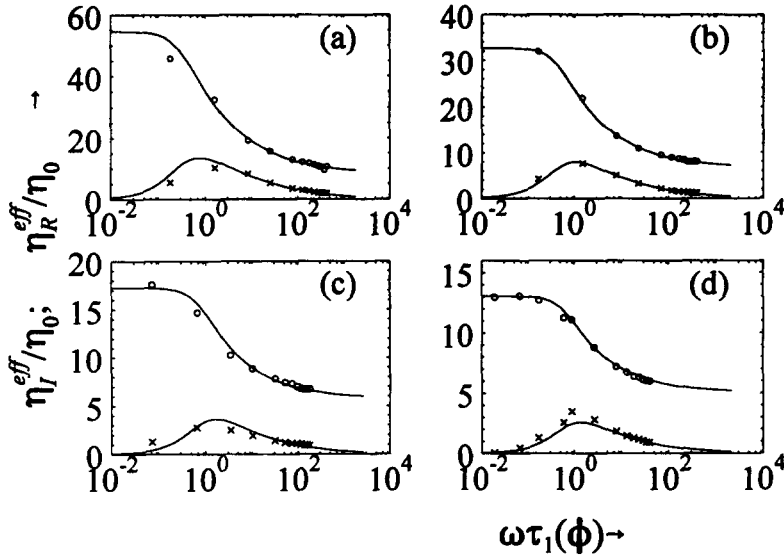$$\eta_\infty(\phi) = \eta_0[1 + \frac{5}{2}\phi + 4.84\phi^2] \tag{10}$$

Figure 7. Relative real and imaginary parts of the visco-elastic $\eta(\phi; \omega)$: $\eta_R^{\text{eff}}(\phi; \omega)/\eta_0$ (O) and $\eta_I^{\text{eff}}(\phi; \omega)/\eta_0$ (×), respectively (cf. figure 6(a), (b)), as a function of $\omega\tau_1(\phi)$ for four suspensions studied experimentally by van der Werff and de Kruif (1989): (a) $\phi = 0.54$; (b) $\phi = 0.52$; (c) $\phi = 0.48$; (d) $\phi = 0.46$. Solid lines: theory from [6].

which was computed on the basis of hydrodynamic particle interactions alone, is very close—within experimental accuracy—to our expression [7] for $\eta_\infty(\phi)$ to $O(\phi^2)$

$$\eta_\infty(\phi) = \eta_0[1 + \frac{5}{2}\phi + 4.59\phi^2] \qquad [11]$$

as well as to a resummed expression of Beenakker's for $\eta_\infty(\phi)$, which takes into account more complicated hydrodynamic interactions than contained in [10] (Beenakker 1984).

4. In view of the previous point, we conjecture that the theoretical expression [8] for $\eta^{\text{eff}}(\phi; \omega)$ can also be used for concentrated charged colloidal suspensions, where hydrodynamic interactions are supposed to be negligible, on condition that: (a) one identifies the hard sphere diameter σ with the diameter of the Debye sphere; and (b) that ω does not cause relevant deformations of the Debye spheres. The few experimental data for charged colloidal suspensions available so far—mainly for
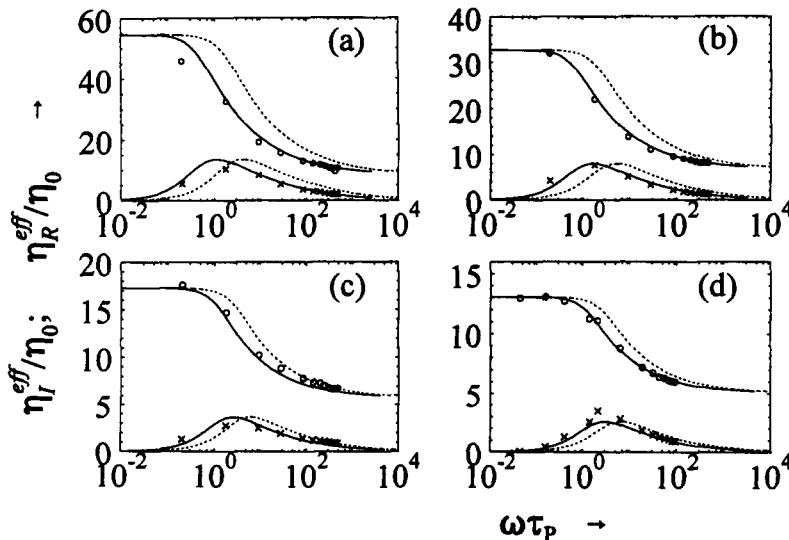

Figure 8. Same as in figure 7 as a function of $\omega\tau_P$. $\cdots\cdot$ theory from [6]; —— theory shifted over $2/\chi(\phi)$.

diffusion—seem to confirm a similarity of concentrated hard sphere and charged colloidal suspensions (Verberg *et al.* unpublished; de Schepper *et al.* 1989; Pusey *et al.* 1990; Cohen and de Schepper 1992a, 1992b).

(5) Applications to more complicated colloidal suspensions, relevant for technology or biology, such as binary mixtures of colloidal particles, micelles (Liu and Sheu 1996; Liu 1996), micro-emulsions, etc. appear to be feasible.

REFERENCES

Batchelor, G. K. (1977) The effect of brownian motion on the bulk stress in a suspension of spherical particles. *J. Fluid Mech.* **83**, 97–117.

Beenakker, C. W. J. (1984) The effective viscosity of a concentrated suspension of hard spheres (and its relation to diffusion). *Physica A* **128**, 48–81.

Brady, J. F. (1993) The rheological behavior of concentrated colloidal suspensions. *J. Chem. Phys.* **99**, 567–581.

Brady, J. F. (1994) Response to "Comment on 'The rheological behavior of concentrated colloidal suspensions' " [*J. Chem. Phys.* **101**, 1757 (1994)]. *J. Chem. Phys.* **101**, 1758.

Cichocki, B. and Felderhof, B. U. (1988) Long-time self-diffusion coefficient and zero-frequency viscosity of dilute suspensions of spherical brownian particles. *J. Chem. Phys.* **89**, 3705–3709.

Cichocki, B. and Felderhof, B. U. (1991) Linear viscoelasticity of semidilute hard-sphere suspensions. *Phys. Rev. A* **43**, 5405–5411.

Cichocki, B. and Felderhof, B. U. (1994) Comment on 'The rheological behavior of concentrated colloidal suspensions' [*J. Chem. Phys.* **99**, 567 (1993)]. *J. Chem. Phys.* **101**, 1757.

Cichocki, B. and Felderhof, B. U. (1994) Linear viscoelasticity of dense colloidal suspensions. *J. Chem. Phys.* **101**, 7850–7855.

Cohen, E. G. D. and de Schepper, I. M. (1991) Note on transport processes in dense colloidal suspensions. *J. Stat. Phys.* **63**, 241–248.

Cohen, E. G. D. and de Schepper, I. M. (1992a) The colloidal many-body problem: colloidal suspensions as hard sphere fluids. In *Recent Progress in Many-body Theories*, eds T. L. Ainsworth, C. E. Campbell, B. E. Clements and E. Krotscheck, Vol. 3, pp. 387–395. Plenum, New York.

Cohen, E. G. D. and de Schepper, I. M. (1992b) Transport properties of concentrated colloidal suspensions. In *Slow Dynamics in Condensed Matter*, eds K. Kawasaki, M. Tokuyama and T. Kawakatsu, AIP Conference Proceedings, No. 256, pp. 359–369.

Cohen, E. G. D. and de Schepper, I. M. (1995) Comment on 'Scaling of transient hydrodynamic interactions in concentrated suspensions'. *Phys. Rev. Lett.* **75**, 2252–2252.

Felderhof, B. U. (1988) The contribution of brownian motion to the viscosity of suspensions of spherical particles. *Physica A* **147**, 533–543.

Felderhof, B. U., Ford, G. W. and Cohen, E. G. D. (1982) Cluster expansion for the dielectric constant of a polarizable suspension. *J. Stat. Phys.* **28**, 135–164.

Freed, K. F. and Muthukumar, M. (1982) Cluster theory for concentration dependence of shear viscosity for suspensions of interacting spheres—I. *J. Chem. Phys.* **76**, 6186–6194.

Hansen, J. P. and McDonald, J. R. (1986) *Theory of Simple Liquids*. Academic Press, London.

Henderson, D. and Grundke, E. W. (1975) Direct correlation function: hard sphere fluid. *J. Chem. Phys.* **63**, 601–607.

Jones, D. A. R., Leary, B. and Boger, D. V. (1991) The rheology of a concentrated colloidal suspension of hard spheres. *J. Colloid Interface Sci.* **147**, 479–495.

Jones, D. A. R., Leary, B. and Boger, D. V. (1992) The rheology of a sterically stabilized suspension at high concentration. *J. Colloid Interface Sci.* **150**, 84–96.

Kestin, J. and Dorfman, J. R. (1971) *A Course in Statistical Thermodynamics*. Academic Press, New York.

Liu, Y. C., Chen, S. H. and Huang, J. S. (1996) Relationship between microstructure and rheology of micellar solutions formed by a tri-block copolymer surfactant. *Phys. Rev. E* **54**, 1698–1708.

Liu, Y. C. and Shue, E. Y. (1996) Low shear viscosity of a dense ionic micellar solution. *Phys. Rev. Lett.* **76**, 700–703.

McQuarrie, D. A. (1976) *Statistical Mechanics*. Harper and Row, New York.

Papir, Y. S. and Krieger, I. M. (1970) Rheological studies on dispersions of uniform colloidal spheres—II. Dispersions in nonaqueous media. *J. Colloid Int. Sci.* **34**, 126–130.

Pusey, P. N. (1991) *Liquids, Freezing and Glass Transition*, eds J. P. Hansen, D. Levesque and J. Zinn-Justin. North-Holland, Amsterdam.

Pusey, P. N., Lekkerkerker, H. N. W., Cohen, E. G. D. and de Schepper, I. M. (1990) Analogies between the dynamics of concentrated charged colloidal suspensions and dense atomic liquids. *Physica A* **164**, 12–27.

Pusey, P. N. and Tough, R. J. A. (1982) *Dynamic Light Scattering and Velocimetry: Applications of Photon Correlation Spectroscopy*, ed. R. Pecora. Plenum, New York.

Ronis, D. (1986) Configurational viscosity of dilute colloidal suspensions. *Phys. Rev. A* **34**, 1472–1480.

Russel, W. B. and Gast, A. P. (1986) Nonequilibrium statistical mechanics of concentrated colloidal dispersions: hard spheres in weak flows. *J. Chem. Phys.* **84**, 1815–1826.

Russel, W. B., Saville, D. A. and Schowalter, W. R. (1989) *Colloidal Suspensions*. Cambridge University Press, Cambridge.

de Schepper, I. M. and Cohen, E. G. D. (1994) Viscoelastic and rheological behavior of concentrated colloidal suspensions. *Int. J. of Thermoph.* **15**, 1179–1188.

de Schepper, I. M., Cohen, E. G. D., Pusey, P. N. and Lekkerkerker, H. N. W. (1989) Long time diffusion in suspensions of interacting charged colloids. *J. Phys. Condens. Matter* **1**, 6503–6506.

de Schepper, I. M., Cohen, E. G. D. and Zuilhof, M. J. (1984) The width of neutron spectra and the heat mode of fluids. *Phys. Lett. A* **101**, 399–404.

de Schepper, I. M., Smorenburg, H. E. and Cohen, E. G. D. (1993) Viscoelasticity in dense hard sphere suspensions. *Phys. Rev. Lett.* **70**, 2178–2181.

Verberg, R., de Schepper, I. M. and Cohen, E. G. D. Viscosity of colloidal suspensions. *Phys. Rev. E* (to appear).

Wagner, J. and Russel, W. B. (1989) Nonequilibrium statistical mechanics of concentrated colloidal dispersions: hard spheres in weak flows with many body thermodynamic interactions. *Physica A* **155**, 475–518.

van der Werff, J. C. and de Kruif, C. G. (1989) Hard-sphere colloidal dispersions: the scaling of rheological properties with particle size, volume fraction and shear rate. *J. Rheol.* **33**, 421–454.

van der Werff, J. C., de Kruif, C. G., Blom, C. and Mellema, J. (1989) Linear viscoelastic behavior of dense hard sphere dispersions. *Phys. Rev. A* **39**, 795–807.

Zhu, J. X., Durian, D. J., Müller, J., Weitz, D. A. and Pine, D. J. (1992) Scaling of transient hydrodynamic interactions in concentrated suspensions. *Phys. Rev. Lett.* **68**, 2559–2562.