

## Relationship between short-time self-diffusion and high-frequency viscosity in charge-stabilized dispersions

J. Bergholtz\*

*Faculty of Physics, University of Konstanz, P.O. Box 5560, D-78457 Konstanz, Germany*

F. M. Horn and W. Richtering

*Institute for Macromolecular Chemistry, University of Freiburg, Stefan-Meier Strasse 31, D-79104 Freiburg, Germany*

N. Willenbacher

*Polymer Research Division, BASF Aktiengesellschaft, D-67056 Ludwigshafen, Germany*

N. J. Wagner

*Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716*

(Received 8 April 1998)

Experimental determination of both the short-time self-diffusion coefficient and the high-frequency viscosity are reported for model charge-stabilized dispersions. Despite the charged nature of the particles, we find that both quantities are insensitive to direct interparticle interactions. Quantitative agreement between the experimental data and micromechanical hard sphere theory is observed for a range of particle sizes and added salt content. However, while the reciprocal of the short-time self-diffusion coefficient shows a similar concentration dependence as the high-frequency viscosity, the two do not obey a generalized Stokes-Einstein relation. The violation is due to subtle differences in hydrodynamic interactions between the two particle motions, in agreement with theory and simulation. [S1063-651X(98)50310-8]

PACS number(s): 82.70.Dd, 83.50.Fc, 83.85.Jn

The structural relaxations in colloidal dispersions are governed by slow diffusive processes. The viscosity of a dispersion is related to the response due to the structural deformation caused by flow, while the self diffusion coefficient results from the relaxational response to the deformation caused by the diffusing particle [1]. Researchers are thus prompted to search for extensions of the celebrated Stokes-Einstein relation [2-4], relating the self-diffusivity to the shear viscosity in the dilute particle limit, to concentrated dispersions. The Stokes-Einstein relation is given by the familiar formula  $D_0 = k_B T / 6\pi\mu_0 a$ , where  $D_0$  is the diffusion coefficient of the single Brownian particle,  $\mu_0$  is the solvent shear viscosity,  $a$  is the particle radius, and  $k_B T$  is the temperature.

In concentrated dispersions particle diffusion is slowed due to hydrodynamic and thermodynamic interactions among the suspended particles. As a consequence of these many-body interactions, the Stokes-Einstein formula no longer represents the particle diffusivity. The dynamics of interacting colloidal dispersions is complicated by memory effects such that additional, so-called generalized Stokes-Einstein relations can be postulated. Many attempts, both theoretical and experimental, have been made to identify such generalizations valid for concentrated colloidal dispersions. For example, the generalized Stokes-Einstein relation given by

$$D_S^L(\phi) = k_B T / 6\pi\eta(\phi)a, \quad (1)$$

with the long-time self-diffusion coefficient  $D_S^L(\phi)$  and the zero-shear viscosity  $\eta(\phi)$ , both functions of the particle volume fraction  $\phi$ , has been widely explored. It has been found to agree well for a variety of systems, such as hard sphere dispersions [5,6], microemulsions [7], micellar solutions [8], and protein dispersions [9]. Imhof and co-workers [10] found, however, strong deviations from Eq. (1) for charge-stabilized dispersions. Also, more recent measurements of both quantities for the same hard sphere dispersions [11] show measurable deviations from Eq. (1). Thus, while both quantities qualitatively correlate, Eq. (1) does not provide a universal quantitative relation for concentrated colloidal dispersions.

There is no theoretical basis for such a generalization of the Stokes-Einstein relation to concentrated dispersions. Indeed, the dilute limiting hard sphere expansions of  $D_S^L(\phi)$  and  $\eta(\phi)$ , calculated by Batchelor [12,13] and Cichocki and Felderhof [14] show that the two quantities differ in the dilute limit. Upon removing the hydrodynamic interactions among the particles, as in many Brownian dynamics computer simulations, the generalized Stokes-Einstein relation in Eq. (1) is found to hold reasonably well both at rest and under shear flow [15]. Thus, it can be inferred that the hydrodynamic interactions, due to the suspending solvent which couples particle motions in real dispersions, drive deviations from the generalized Stokes-Einstein relation quoted in Eq. (1).

Other generalizations have also been investigated. For instance, Richtering and co-workers [16,17] examined the relationship between the short-time self-diffusion coefficient  $D_S^S(\phi)$  and both the zero-shear and high-shear limiting vis-

\*Author to whom correspondence should be addressed.

cosity  $\eta_\infty(\phi)$ . Neither viscosity was found to correlate quantitatively with  $D_S^S$ , reflecting the sensitivity of  $\eta(\phi)$  to direct interparticle interactions [10,18,19] and the distorted microstructure characteristic of  $\eta_\infty(\phi)$  [1,20].

The short-time self-diffusion coefficient is a purely hydrodynamic quantity that reflects the local small-displacement mobility of a tracer particle in the equilibrium dispersion. The rheological property most akin to  $D_S^S(\phi)$  is the high-frequency viscosity  $\eta'_\infty(\phi)$ . It reflects the bulk dissipation due to a high frequency, low amplitude shear oscillation of the dispersion in the linear viscoelastic regime. Note that both "short-time" and "high-frequency" are relative to the structural relaxation time  $\approx a^2/D_0$ , and represent diffusive motion on time scales long relative to momentum relaxation and vorticity propagation times. Thus, both  $D_S^S$  and  $\eta'_\infty$  probe the local hydrodynamic environment of the colloidal particles at equilibrium.

Previous work by Shikata and Pearson [21] and Zhu *et al.* [22] tested the relationship between  $D_S^S(\phi)$  and  $\eta'_\infty(\phi)$  for hard sphere dispersions. They found, to within experimental accuracy, that the following generalized Stokes-Einstein relation holds:

$$D_S^S(\phi) = k_B T / 6\pi \eta'_\infty(\phi) a. \quad (2)$$

It is noteworthy that the comparisons by Shikata and Pearson were made on different hard sphere dispersions and those of Zhu *et al.* were made with Beenakker's many-body hard sphere theory [23]. Inspection of the results from the theories by Beenakker and Mazur [23,24], the dilute limiting hard sphere expansions [30–32], and computer simulations [25,26] suggests that there should be small but measurable differences between  $D_S^S$  and  $\eta'_\infty$ , in contrast to the conclusions drawn.

In this work we examine the generalized Stokes-Einstein relation between  $D_S^S$  and  $\eta'_\infty$  for model, charge-stabilized polystyrene spheres over a substantial range of particle concentrations, particle sizes, and ionic strengths. The short-time self-diffusion coefficient is measured using fiber-optic quasi-elastic light scattering (FOQELS) and the high-frequency viscosity is determined using torsional resonance oscillation. We demonstrate experimentally the insensitivity of these two quantities to direct interparticle interactions, also showing that  $\eta'_\infty$  can be captured by hard sphere theory. We show that the deviations from the generalized Stokes-Einstein relation are in agreement with those predicted from theory and computer simulations. These results not only provide insight into the microhydrodynamics of concentrated colloidal dispersions, but also impact both interpretations of dynamic light scattering measurements [27] and "hydrodynamic rescaling" theories proposed for handling concentrated dispersions [28,29].

Monodisperse poly(styrene) (PS) dispersions were prepared by soap-free emulsion polymerization using potassium persulfate (KPS) as initiator and styrenesulfonate as comonomer, imparting strong acid sulfonate groups on the particle surface. The dispersions were filtered and dialysed against pure water until the conductivity of the dialyzate reached 10  $\mu\text{S}/\text{cm}$ . The dispersion ionic strength was adjusted by further dialysis against KCl solutions of desired ionic strength. Concentration series were obtained by diluting the dispersions

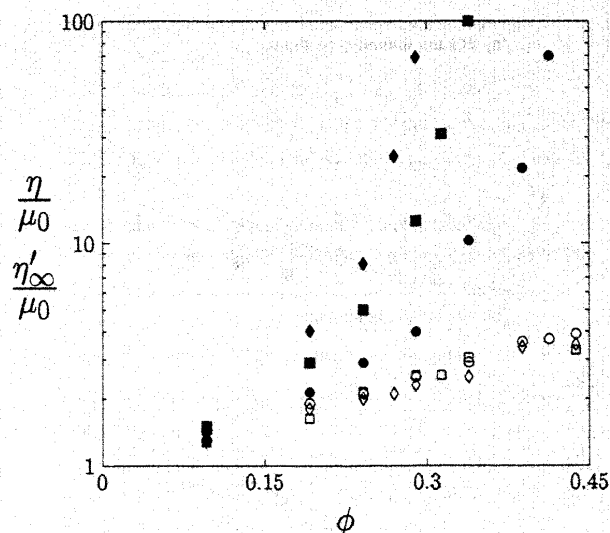


FIG. 1. Relative zero-shear rate viscosity (closed symbols) and high-frequency viscosity (open symbols) as functions of particle volume fraction and ionic strength for 200-nm-diameter particles: ( $\diamond$ )  $10^{-4}$  M; ( $\square$ )  $10^{-3}$  M; ( $\circ$ )  $10^{-2}$  M KCl. Note that the ionic strength quoted is that of the dialysate.

with the same solution as dialysed against. Extensive characterization of the dispersions has been done and will be reported in detail in a future publication. FOQELS measurements were conducted using a self-built instrument previously described by Wiese and Horn [33], modified to yield two different wavelengths:  $\lambda = 632.8$  and  $457.9$  nm. The light is detected in backscattering mode and results in two wave vectors:  $q = 4\pi n/\lambda = 0.0268$  and  $0.0366$   $\text{nm}^{-1}$ . For sufficiently large particles these wavevectors are larger than that corresponding to the maximum of the structure factor, thus providing a probe of self-diffusion. This was verified by the equivalence of the determined self-diffusivity at both wavelengths. The short-time self-diffusion coefficient was determined from a cumulant fit to ten separate measurements of the auto-correlation function. The torsional resonance oscillation measurements were conducted using a torsional resonator (Rheoswing, Physica). This instrument and the analysis procedure have been described elsewhere [18].

In Fig. 1 we compare the relative zero-shear rate viscosity  $\eta/\mu_0$  with the high-frequency viscosity  $\eta'_\infty/\mu_0$  as functions of volume fraction for a series of ionic strengths: 0.1, 1, and 10 mM KCl. As seen,  $\eta$  increases strongly with decreasing ionic strength. The apparent divergence of the zero-shear rate viscosity at volume fractions well below random close packing ( $\phi \approx 0.64$ ), shows that these dispersions are far from being hard-sphere-like [34]. The strong effect of ionic strength on  $\eta$  is a known consequence of its dependency on direct interparticle interactions [19]. In contrast,  $\eta'_\infty$  shows essentially no ionic strength dependence and only a modest increase with increasing volume fraction. This demonstrates the hydrodynamic character of  $\eta'_\infty$ ; it depends only indirectly, through the colloidal microstructure, on the interaction potential [19,30]. The results in Fig. 1 were obtained for 200-nm-diameter particles and similar results were found for other particle sizes (310- and 120-nm-diameter particles). However, when the diffuse double layer is large compared to the particle size, characterized by a large dimensionless Debye length  $(\kappa a)^{-1}$ , ionic strength effects on  $\eta'_\infty$  can be detected experimentally [18].

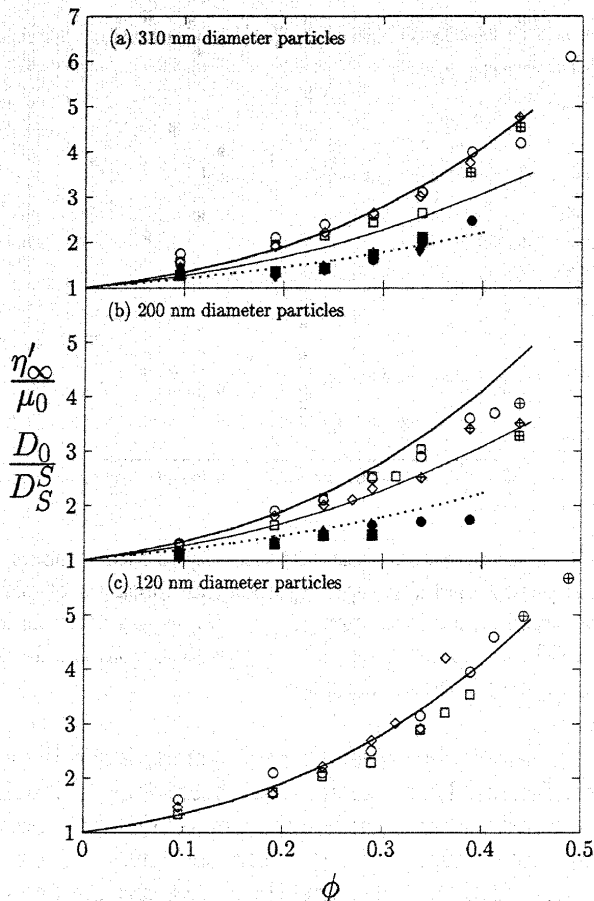


FIG. 2.  $\eta'_{\infty}/\mu_0$  (open symbols) and  $D_0/D_S^S$  (closed symbols) as functions of particle volume fraction, ionic strength, and particle size. (a): ( $\diamond$ )  $10^{-4}$  M, ( $\square$ )  $10^{-3}$  M, ( $\circ$ )  $10^{-2}$  M KCl. (b): same legend as top graph. (c): ( $\diamond$ )  $5 \times 10^{-3}$  M, ( $\square$ )  $10^{-2}$  M, ( $\circ$ )  $10^{-2}$  M KCl. Lines are (—),  $\eta'_{\infty}/\mu_0$  many-body hard sphere theory [23]; (—),  $D_0/D_S^S$  many-body hard sphere theory [24]; and ( $\cdots$ ),  $D_0/D_S^S$  hard sphere virial expansion [36]. Note that symbols marked with a + correspond to solid dispersions.

In contrast to the zero-shear viscosity, we find that  $\eta'_{\infty}$  shows hard sphere behavior for all volume fractions. This is demonstrated in Fig. 2, where the agreement between the data for  $\eta'_{\infty}$  for our charge-stabilized dispersions and the theoretical predictions of Beenakker's hard sphere theory [23] is shown. Note that the  $\eta'_{\infty}$  data in Fig. 2 superpose on the hard sphere prediction independent of particle size and ionic strength, both of which determine the Debye length  $(\kappa a)^{-1}$ . Figure 2 also shows that  $\eta'_{\infty}$  varies smoothly into the solid phase, demonstrating an insensitivity to the microstructure. This can be understood by the fact that a small amplitude shear oscillation, unlike steady shear flow, does not force particles to move past one another.

In Fig. 2 we also examine the dependence of the short-time self diffusion coefficient  $D_S^S$  on volume fraction, particle size, and ionic strength. We plot the data in Fig. 2 as

$\eta'_{\infty}/\mu_0$  and  $(D_S^S/D_0)^{-1}$  versus  $\phi$  in anticipation of a similar concentration dependence according to the generalized Stokes-Einstein relation given by Eq. (2). Figure 2 demonstrates that  $D_S^S$  is unaffected by the changes in particle size and ionic strength, i.e., changes in the interparticle potential. Similar observations have been made by van Veleuwen *et al.* [35], who studied charge- and sterically stabilized silica dispersions. Moreover, while  $\eta'_{\infty}/\mu_0$  and  $(D_S^S/D_0)^{-1}$  show a similar dependence on  $\phi$ , they do not obey the generalized Stokes-Einstein relation in Eq. (2). We find instead that the quantity  $\eta'_{\infty}/\eta_0$  lies above  $(D_S^S/D_0)^{-1}$  for all volume fractions. The data for the reciprocal short-time self-diffusion coefficient lie somewhat below the many-body hard sphere theory of Beenakker and Mazur [24] (and the computer simulation results [25,26]), and agree better with their virial expansion [36] also shown in Fig. 2. The fact that the short-time self-diffusion coefficient for our charge-stabilized dispersions is higher than that for hard sphere dispersions reflects the depletion of neighboring particles near contact due to electrostatic repulsion, and agrees with the predictions of Nägele and co-workers [37,38].

These results show that short-time diffusion of particles in concentrated charge-stabilized dispersions is close to that in hard sphere dispersions. Furthermore, they demonstrate that the violation of the generalized Stokes-Einstein relation is caused by subtle differences in the hydrodynamic flows caused by the diffusing particle and that resulting from the suspension being exposed to a high-frequency oscillatory shear flow.

Our measurements of  $\eta'_{\infty}$  for charge-stabilized dispersions can be described by hard sphere theory when  $\kappa a \gg 1$ . These observations make it possible to apply the "hydrodynamic rescaling" theories developed by Medina-Noyola [28] and Brady [29] also to charge-stabilized systems. These theories and others, such as the mode-coupling theory for linear viscoelasticity [39], require  $\eta'_{\infty}$  and  $D_S^S$  as inputs. The assumption is that hydrodynamic interactions in concentrated dispersions can be accounted for by simply rescaling the particle mobility, i.e., replacing  $D_0$  by  $D_S^S$  [28,29], which has been shown to work well empirically [40]. Other similar theories incorporate also  $\eta'_{\infty}$  [41]. As  $\eta'_{\infty}$  and  $D_S^S$  are not generally known for charge-stabilized dispersions, the present results show that hard sphere correlations, for instance those given by Lionberger and Russel [41], can be used for the former but not the latter.

F.M.H. and W.R. thank the BMBF (Grant No. 03D0039D7) and the DFG for financial support. N.J.W. acknowledges support from the NSF (Grant No. CTS-9523968) and the Fulbright Commission. Discussions with G. Nägele and R. Klein are gratefully acknowledged.

[1] J. F. Brady, *Curr. Opin. Colloid Interface Sci.* **1**, 472 (1996).  
 [2] G. Stokes, *Trans. Cambridge Philos. Soc.* **9**, 5 (1856).  
 [3] A. Einstein, *Ann. Phys. (Leipzig)* **19**, 289 (1906); **34**, 591 (1911).

[4] A. Einstein, *Investigation on the Theory of Brownian Movement* (Dover, New York, 1956).  
 [5] M. M. Kops-Werkhoven and H. M. Fijnaut, *J. Chem. Phys.* **77**, 2242 (1982).

- [6] A. van Blaaderen, J. Peetermans, G. Maret, and J. K. G. Dhont, *J. Chem. Phys.* **96**, 4591 (1992).
- [7] D. L. Cebula, R. H. Ottewill, J. Ralston, and P. N. Pusey, *J. Chem. Soc., Faraday Trans. 1* **77**, 2585 (1981).
- [8] D. Chatenay, W. Urbach, R. Messenger, and D. Langevin, *J. Chem. Phys.* **86**, 2343 (1987).
- [9] P. Licino and M. Delaye, *J. Phys. (Paris)* **49**, 975 (1988).
- [10] A. Imhof, A. van Blaaderen, G. Maret, J. Mellema, and J. K. G. Dhont, *J. Chem. Phys.* **100**, 2170 (1994).
- [11] P. N. Segre, S. P. Meeker, P. N. Pusey, W. C. K. Poon, *Phys. Rev. Lett.* **75**, 958 (1995).
- [12] G. K. Batchelor, *J. Fluid Mech.* **131**, 155 (1983); **137**, 467 (1983).
- [13] G. K. Batchelor, *J. Fluid Mech.* **83**, 97 (1977).
- [14] B. Cichocki and B. U. Felderhof, *J. Chem. Phys.* **89**, 3705 (1988).
- [15] S. R. Rastogi, N. J. Wagner, and S. Lustig, *J. Chem. Phys.* **104**, 9234 (1996).
- [16] K. Berend and W. Richtering, *Colloids Surf., A* **99**, 101 (1995).
- [17] W. Richtering and H. Müller, *Langmuir* **11**, 3699 (1995).
- [18] J. Bergenholtz, N. Willenbacher, N. J. Wagner, B. Morrison, D. van den Ende, and J. Mellema, *J. Colloid Interface Sci.* **202**, 430 (1998).
- [19] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge, New York, 1989).
- [20] J. W. Bender and N. J. Wagner, *J. Colloid Interface Sci.* **172**, 171 (1995).
- [21] T. Shikata and D. S. Pearson, *J. Rheol.* **38**, 601 (1994).
- [22] J. K. Zhu, D. J. Durian, J. Müller, D. A. Weitz, and D. J. Pine, *Phys. Rev. Lett.* **68**, 2559 (1992).
- [23] C. W. J. Beenakker, *Physica A* **128**, 48 (1984).
- [24] C. W. J. Beenakker and P. Mazur, *Physica A* **126**, 349 (1984).
- [25] R. J. Phillips, J. F. Brady, and G. Bossis, *Phys. Fluids* **31**, 3462 (1988).
- [26] A. J. C. Ladd, *J. Chem. Phys.* **93**, 3484 (1990).
- [27] T. G. Mason and D. A. Weitz, *Phys. Rev. Lett.* **74**, 1250 (1995).
- [28] M. Medina-Noyola, *Phys. Rev. Lett.* **60**, 2705 (1988).
- [29] J. F. Brady, *J. Chem. Phys.* **99**, 567 (1993).
- [30] G. K. Batchelor and J. T. Green, *J. Fluid Mech.* **56**, 401 (1972).
- [31] G. K. Batchelor, *J. Fluid Mech.* **74**, 1 (1976).
- [32] B. Cichocki and B. U. Felderhof, *J. Chem. Phys.* **89**, 1049 (1988).
- [33] H. Wiese and D. Horn, *J. Chem. Phys.* **94**, 6429 (1991).
- [34] J. C. van der Werff, C. G. de Kruif, C. Blom, and J. Mellema, *Phys. Rev. A* **39**, 795 (1989).
- [35] A. van Veluwen, H. N. W. Lekkerkerker, C. G. de Kruif, and A. Vrij, *J. Chem. Phys.* **87**, 4873 (1987).
- [36] C. W. J. Beenakker and P. Mazur, *Physica A* **120**, 388 (1983).
- [37] G. Nägele, B. Mandl, and R. Klein, *Prog. Colloid Polym. Sci.* **98**, 117 (1995).
- [38] M. Watzlawek and G. Nägele, *Phys. Rev. E* **56**, 1258 (1997).
- [39] G. Nägele and J. Bergenholtz, *J. Chem. Phys.* **108**, 9893 (1998).
- [40] S. R. Rastogi and N. J. Wagner, *J. Rheol.* **41**, 893 (1997).
- [41] R. A. Lionberger and W. B. Russel, *J. Rheol.* **38**, 1885 (1994).