Journal of Statistical Physics, Vol. 63, Nos. 1/2, 1991

Note on Transport Processes in Dense Colloidal Suspensions

E. G. D. Cohen[1] and I. M. de Schepper[2]

Received August 24, 1990; final November 5, 1990

A new approach to transport processes in dense charged as well as neutral colloidal suspensions is presented. It is based on a far-reaching analogy between dense colloidal suspensions and dense hard-sphere fluids, implying, in turn, an analogy with atomic liquids. As a result, new expressions valid for a number of colloidal transport coefficients are predicted.

KEY WORDS: Transport coefficients; cage diffusion; viscosity; colloidal suspensions; hard-sphere fluids; intermediate scattering function.

Recently it was shown$^{(1)}$ for dense *charged* colloidal suspensions that the intermediate scattering function $F(k, t)$ can be represented, for $t \approx t_l$ and for k near the maximum k^* of the static structure factor $S(k)$, by the expression

$$F(k, t) = S(k) e^{-\Gamma(k) t} \tag{1a}$$

where the decay constant $\Gamma(k)$ is given by

$$\Gamma(k) = D_s k^2 \frac{d(k)}{S(k)} \tag{1b}$$

with D_s, the single (tagged)-particle diffusion constant:

$$D_s = \frac{D_0}{\chi} \tag{1c}$$

---

[1] The Rockefeller University, New York, New York 10021.

[2] IRI, University of Delft, 2629 JB Delft, The Netherlands.

0022-4715/91/0400-0241$06.50/0

Here t_I is the average time between two successive interactions (collisions) of the Brownian particles. This expression was obtained from an assumed analogy of dense charged colloidal suspensions and corresponding dense hard-sphere fluids based on the hard-sphere-like behavior of $S(k)$. Thus, in Eq. (1), χ is the radial distribution function at contact in a hard-sphere fluid and $d(k) = [1 - j_0(x) + 2j_2(x)]^{-1}$, where $j_n(x)$ is the spherical Bessel function of order n and $x = k\sigma$,(2) with σ the diameter of the *Debye* spheres of the colloidal particles, determined such that k^* for the colloidal suspension and the hard-sphere fluid coincide.(1) D_0 is the single (tagged)-particle diffusion coefficient at infinite dilution.

In proposing Eq. (1) for $F(k, t)$ it was argued that at high concentrations, i.e., for volume fractions $\phi = n\pi\sigma^3/6 > 0.3$ (n is the number density), the separation of the Debye spheres of the charged colloidal particles is small, so that the diffusion process, which dominates the decay of $F(k, t)$, is determined by the direct interactions between the colloidal particles, which can be modeled by those in a hard-sphere fluid at the same volume fraction ϕ. There are two important differences between the two systems due to the presence of the solvent in the colloidal fluid: (1) the colloidal particles move with Brownian dynamics, the hard spheres with Newtonian; (2) in a collision, only the particle number is conserved for colloidal particles, while particle number, momentum, and energy are conserved in the hard-sphere fluid. In spite of these differences, the very good agreement(1) of Eq. (1) with experiment vindicates the above assumption for the decay of $F(k, t)$. Since at these high densities each particle finds itself in a cage formed by its neighbors, the diffusion process described by Eq. (1) can be called *cage diffusion*. This diffusion is characterized by a new diffusion coefficient $\Gamma(k)/k^2 = D_s d(k)/S(k)$, which differs fundamentally from the hydrodynamic diffusion coefficient for $k = 0$, since it takes into account that each particle moves not only in a cage formed by its neighbors (on a length scale $\approx 2\pi/k^*$), but is itself part of the (moving) walls of the cages in which its neighbors are. Thus Eq. (1), derived from a solution of a linear Boltzmann-like equation,(2) incorporates the collective diffusion of the particles out of their cages in a dynamically consistent manner. Equation (1) for a colloidal suspension follows from the corresponding expression for a dense (pure) hard-sphere fluid,(2) i.e., from

$$F(k, t) = S(k) e^{-z(k)t} \tag{2a}$$

with

$$z(k) = D_E k^2 \frac{d(k)}{S(k)} \tag{2b}$$

where the first Enskog approximation to the diffusion coefficient D_E is given by[1]

$$D_E = \frac{D_B}{\chi} \tag{2c}$$

To obtain from Eq. (2) the corresponding expression for charged colloidal suspensions, i.e., Eq. (1), one only has to replace the low-density (Boltzmann) diffusion coefficient $D_B = 0.214/(\beta m)^{1/2} n\sigma^2$ by the corresponding coefficient D_0 for a dilute colloidal suspension (m is the mass of a hard sphere and $\beta = 1/k_B T$, with k_B Boltzmann's constant and T the temperature). This implies that the main difference between the colloidal and the hard-sphere fluid is that the Brownian versus the Newtonian dynamics introduces a difference in time scales (t_l) of the two systems of σ^2/D_0: $\sigma^2/D_B = 10^9:1$.[1]

In this note we first show that Eq. (1) can also be used to describe $F(k, t)$ for $t = t_l$ and $k = k^*$ for dense *neutral* colloidal suspensions, implying that the usual large difference in hydrodynamic interactions between charged and neutral colloidal particles (see, e.g., ref. 3) is not important at these high concentrations. This is indeed borne out in Fig. 1, where data for $\Gamma(k)$ of both charged and neutral colloidal suspensions are compared with Eq. (1). The same similarity is illustrated in Fig. 2, where the minimum value $\Gamma(k^*)$ of $\Gamma(k)$ is plotted as a function of ϕ. The minimum of $\Gamma(k)$ is due to the maximum of $S(k)$ for $\phi > 0.3$. The agreement between the data for both charged and neutral colloidal suspensions and Eq. (1) is excellent.

Second, in addition to the collective or many-particle $F(k, t)$, we also considered the self (s)- or single (tagged)-particle $F_s(k, t)$, for which one has for $t \approx t_l$ and $k \approx k^*$

$$F_s(k, t) = e^{-\Gamma_s(k)t} \tag{3a}$$

where

$$\Gamma_s(k) = D_s k^2 \tag{3b}$$

Equation (3b) follows from Eq. (1b) by using that $F(k, t) = F_s(k, t)$ for very large k [consistent with $\lim_{k\to\infty} d(k) = \lim_{k\to\infty} S(k) = 1$].[1-3] In Fig. 3 we compare D_s/D_0 for charged and neutral colloiodal suspensions and $D_E/D_B = 1/\chi$ for the corresponding hard-sphere fluids. The agreement at high densities is very good.

Third, Eqs. (1)–(3) do not contain any mode–mode coupling effects that would appear in $\Gamma(k)$ and $\Gamma_s(k)$ for measurements on longer time scales $t \gg t_l$ than those used in Figs. 1–3 and Eqs. (1)–(3). Thus, Medina-

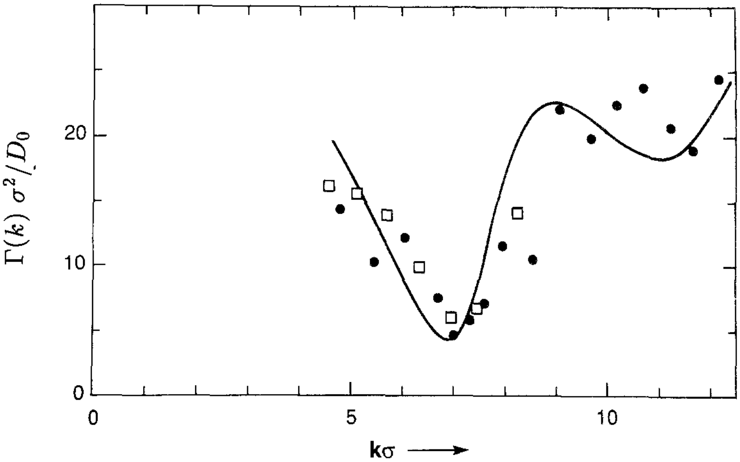

Fig. 1. Reduced decay rate $\Gamma(k)\sigma^2/D_0$ as function of $k\sigma$ for a charged colloid (circles; ref. 9, $\sigma = 600$ nm, $\phi = 0.48$, $\sigma^2/D_0 = 82$ ms), a neutral colloid (squares; ref. 10, $\sigma = 335$ nm, $\phi = 0.49$, $\sigma^2/D_0 = 123$ ms), and from theory [curve; Eq. (1b)].

Noyola[4] recently derived under a number of assumptions for the long (L)-time (self-) decay constant $\Gamma_{s,L}(k)$ of a tagged particle in neutral colloidal suspensions on this long time scale the expression

$$\Gamma_{s,L}(k) = D_{s,L}k^2 \tag{4a}$$

with

$$D_{s,L} = \frac{D_s}{1 + \Sigma^C} \tag{4b}$$

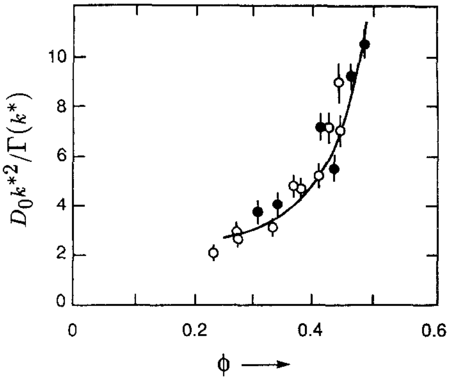

Fig. 2. Reduced minimum value $D_0k^{*2}/\Gamma(k^*)$ as function of ϕ for charged colloids (closed circles; ref. 1), neutral colloids (open circles; ref. 12), and from theory [curve; Eq. (1b)].

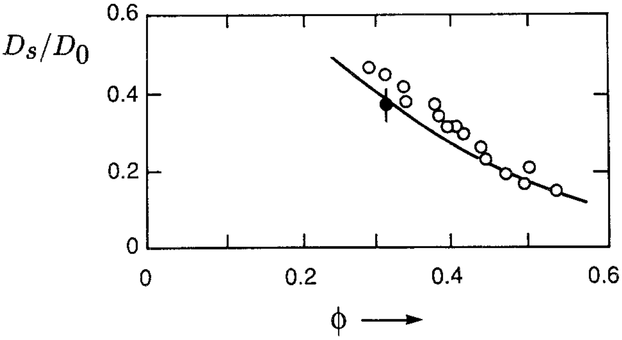

Fig. 3. Reduced diffusion coefficient D_s/D_0 as function of ϕ for a charged colloid (closed circles; ref. 3), for neutral colloids (open circles; ref. 11), and from theory [curve; Eq. (1c)].

where

$$\Sigma^C = \frac{D_s}{6\pi^2 n}\int_0^\infty dk\, \frac{k^4}{S(k)}\, \frac{[S(k)-1]^2}{\Gamma_s(k)+\Gamma(k)} \tag{4c}$$

is a mode coupling contribution due, in our language, to the coupling of a colloidal self-diffusion $[\Gamma_s(k)]$ and a cage diffusion mode $[\Gamma(k)]$.

Equation (4) can be understood immediately on the basis of our assumption of hard-sphere-fluidlike behavior of the colloidal suspension, since it follows from a corresponding expression for a pure, dense, hard-sphere fluid, given earlier by Kirkpatrick and Niewoudt(5):

$$D = D_E/[1 + \Sigma^C + \Sigma^V] \tag{5}$$

Here Σ^C is also due to the coupling of a self-diffusion and a cage diffusion mode in a dense, hard-sphere fluid and is identical to Σ^C of Eq. (4c) except that D_0 is replaced by D_B. The term Σ^V, the long-time-tail contribution to D, related to a coupling between a diffusive and a viscous mode, is absent in Eq. (4b); this is because of the absence of a viscous mode in the colloidal particle system, due to the absence of momentum conservation of the colloidal particles in collisions. In Fig. 4 experimental values of $D_{s,L}/D_0$ and D/D_B are compared with Eqs. (4) and (5).[3] We note that at very high concentrations ($\phi > 0.55$), Σ^V does not contribute to D either, so that then $D_{s,L}/D_0 = D/D_B$.

---

[3] The Σ^C and Σ^V used in Eq. (5) are evaluated by integrating the leading terms in $\zeta_D^H(t)$ and $\zeta_D^S(t)$ of Eq. (3.2) in ref. 5 from 6 and 3 mean free times, respectively, to infinity. The Σ^C used in Eq. (4c) is evaluated with $\Gamma(k)$ of Eq. (1b); the numerical difference with the $\Gamma(k)$ used in ref. 4, where $d(k)$ is taken to be 1, is negligible.

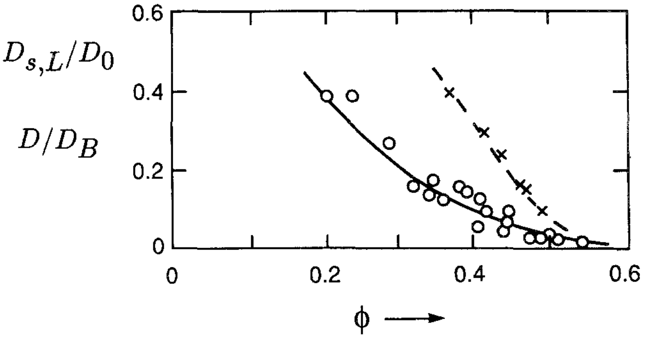

Fig. 4. Reduced long-time diffusion coefficient $D_{s,L}/D_0$ of neutral colloids [circles, ref. 11; curve, Eq. (4b)] and $D/D_{\rm B}$ of hard spheres [crosses, refs. 13, 14; dashed curve, Eq. (5)] as functions of ϕ.

On the basis of the similarity of neutral and charged colloids at high densities, we predicted$^{(6)}$ that Eq. (4) also holds for charged colloids, on condition that one takes the Debye sphere diameter as σ. Since σ can be chemically controlled, a systematic investigation of D as a function of σ seems feasible. Similarly, we predict, for both neutral and charged suspensions, that the long-time (collective) decay constant is given by $\Gamma_L(k) = D_L(k)k^2$, which $D_L(k) = D_{s,L}d(k)/S(k)$, in analogy with Eqs. (1b) and (3b).

Finally, on the basis of our analogy, we can make, for the first time, a prediction of the shear viscosities η of *concentrated* neutral and charged colloids, in that both will behave as in dense, hard-sphere fluids. In that case,

$$\eta = \eta_{\rm E}(1 + \Sigma_\eta^C + \textstyle\sum_\eta^V) \tag{6a}$$

where

$$\Sigma_\eta^C = \frac{k_{\rm B}T}{60\pi^2\eta_{\rm E}} \int_0^\infty dk \left[\frac{k^2}{S(k)} \frac{dS(k)}{dk}\right]^2 \frac{1}{2z(k)} \tag{6b}$$

is the mode coupling contribution to η, due to the coupling of two cage diffusion modes$^{(5,7)}$ and $\eta_{\rm E}$ is the Enskog shear viscosity. The contribution of the coupling of two viscous modes (Σ_η^V) to η is negligible for all $\phi > 0.3$.$^{(7)}$ Thus, η/η_0 for dense charged as well as neutral colloidal suspensions (η_0 is the viscosity at infinite dilution, i.e., of the solvent) should behave as $\eta/\eta_{\rm B}$ for dense, hard-sphere fluids ($\eta_{\rm B}$ is the Boltzmann viscosity). One sees in Fig. 5 that the experimental η_0/η for neutral colloids$^{(8)}$ agree indeed well with the hard-sphere values of $\eta_{\rm B}/\eta$. It would clearly be of interest to compare also experimental data for the viscosity of

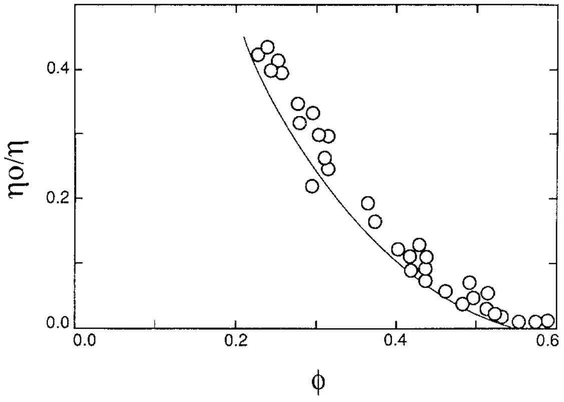

Fig. 5. Reduced inverse viscosity η_0/η of a neutral colloid (circles, ref. 8) and η_B/η of hard spheres (curve, ref. 7) as functions of ϕ.

dense, charged colloidal suspensions with Eq. (6) and study their dependence on the Debye sphere diameter σ. In addition, the agreement of colloidal and hard-sphere viscosities suggests a possible connection of the onset of the glass transition in both systems.(5) A discussion of the rheological behavior of the viscosity in dense colloidal suspensions has been given elsewhere.(15)

In previous publications(1,2) we have discussed in detail the close analogy between atomic liquids and dense hard-sphere fluids for $k \approx k^*$. Thus, the more general analogy discussed here between dense colloids and dense, hard-sphere fluids implies one between dense neutral colloids and atomic liquids as well. These analogies therefore allow predictions of the diffusive properties of one system from the other by a simple scaling procedure. We remark that a different approach to predict the behavior of the viscosity, in particular the rheological behavior, of dense neutral suspensions, using a different scaling procedure as well as nonequilibrium molecular dynamics simulations, has been discussed by Woodcock.(16)

ACKNOWLEDGMENT

Part of this work was performed under contract DE-FG01-88-ER13847 of the Department of Energy.

REFERENCES

1. I. M. de Schepper, E. G. D. Cohen, P. N. Pusey, and H. N. W. Lekkerkerker, *J. Phys. Cond. Mat.* **1**:6503 (1989); P. N. Pusey, H. N. W. Lekkerkerker, E. G. D. Cohen, and I. M. de Schepper, *Physica A* **164**:12 (1990).
2. E. G. D. Cohen, I. M. de Schepper, and M. J. Zuilhof, *Physica B* **127**:282 (1984).
3. P. N. Pusey and R. J. A. Tough, in *Dynamic Light Scattering*, R. Pecora, ed. (Plenum, New York, 1985).
4. M. Medina-Noyola, *Phys. Rev. Lett.* **60**:2705 (1988); and in *Lectures on Thermodynamic and Statistical Mechanics*, A. E. Gonzalez and G. Varea, eds. (World Scientific, Singapore, 1988), p. 1.
5. T. R. Kirkpatrick and J. C. Niewoudt, *Phys. Rev. A* **33**:2651, 2658 (1986).
6. E. G. D. Cohen and I. M. de Schepper, preprint (January 1990).
7. I. M. de Schepper, A. F. E. M. Haffmans, and H. van Beijeren, *Phys. Rev. Lett.* **57**:1715 (1986).
8. J. C. van der Werff and C. G. de Kruif, *J. Rheol.* **33**:421 (1989).
9. T. W. Taylor and B. J. Ackerson, *J. Chem. Phys.* **83**:2441 (1985).
10. P. N. Pusey and W. van Megen, *Phys. Rev. Lett.* **59**:2083 (1987).
11. W. van Megen, S. M. Underwood, R. H. Ottewill, N. S. J. Williams, and P. N. Pusey, *Faraday Disc. Chem. Soc.* **47**:21 (1987).
12. W. van Megen, R. H. Ottewill, S. M. Owens, and P. N. Pusey, *J. Chem. Phys.* **82**:508 (1985).
13. B. J. Alder and T. E. Wainwright, *Phys. Rev. A* **1**:18 (1970).
14. J. J. Erpenbeck and W. W. Wood, *J. Stat. Phys.* **24**:455 (1981).
15. I. M. de Schepper and E. G. D. Cohen, *Phys. Lett. A* **150**:308 (1990).
16. L. V. Woodcock, *Mol. Simulation* **2**:253 (1989).