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LETTER TO THE EDITOR

Theory of self-diffusion of highly charged spherical Brownian particles

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Abstract. Starting from the N -particle Smoluchowski equation without hydrodynamic interactions we derived an expression for the mean square displacement by modelling the memory function entered in the equation for the incoherent scattering function. The numerical evaluation of that expression is done for the case of spherical particles interacting via a screened Coulombic potential. The results of this theory compare favourably with computer simulation results.

The phenomenon of self-diffusion in a suspension of interacting spherical Brownian particles can be described (Pusey and Tough 1982, Hess and Klein 1983) by the mean square displacement, $\langle(\Delta\mathbf{x}(t))^2\rangle$, of a tagged particle. One can define a time-dependent self-diffusion coefficient $D(t)$ as

$$D(t) = \langle[\Delta\mathbf{x}(t)]^2\rangle/6t \quad (1)$$

such that

$$\lim_{t \rightarrow \infty} D(t) = D_s \quad (2)$$

where D_s is referred to (Hess and Klein 1983) as the 'tracer' (or 'self-') diffusion coefficient. In general, D_s is found to be smaller than the free-particle diffusion coefficient, D_0 , due to the additional friction originated by the interaction of the tagged particle with the other diffusing macroparticles through hydrodynamic (Pusey and Van Megen 1983, Beenakker and Mazur 1983) and direct interactions (Ackerson and Fleishman 1982, Hanna *et al* 1982, Lekkerkerker and Dhont 1984, Van Den Broeck 1985, Hess and Klein 1982, Ohtsuki 1982, Tough 1982) and, for charged particles, with their own ionic atmosphere (Gorti *et al* 1984, Schurr 1980, Medina-Noyola and Vizcarra-Rendón 1985). The understanding of each of these effects presents its own difficulties. In particular, the effect of the strong repulsive interactions present in dilute suspensions of highly charged colloidal particles at low ionic strength has been studied by several authors (Pusey and Tough 1982, Hess and Klein 1982, 1983, Ohtsuki 1982, Tough 1982, Gaylor *et al* 1980, Van Megen and Snook 1977). However, specific numerical results for this contribution to D_s have only been derived from computer

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simulations (Gaylor *et al* 1980) and from two, rather involved, approximate theories (Hess and Klein 1982, Ohtsuki 1982). In this letter we describe an additional approach to the calculation of $D(t)$ which is exact at short times, and which, under additional simplifying assumptions, is particularly simple and accurate.

It can be shown that, in the absence of hydrodynamic interactions, and if the diffusion of the N interacting macroparticles is governed by the Smoluchowski equation (Ackerson 1978), $D(t)$ can be expressed as (Ackerson and Fleishman 1982, Lekkerkerker and Dhont 1984)

$$D(t) = D_0 - \lim_{k \rightarrow 0} \int_0^t (1 - \tau/t) [M_s(k, \tau)/k^2] d\tau \quad (3)$$

where $M_s(k, \tau)$ is the memory function associated with the incoherent scattering function (Ackerson 1978) $F_s(k, t)$, i.e.

$$\frac{\partial F_s(k, t)}{\partial t} = -k^2 D_0 F_s(k, t) + \int_0^t M_s(k, t - \tau) F_s(k, \tau) d\tau \quad (4)$$

As in the theory of simple liquids (Boon and Yip 1980), one could attempt to model the time dependence of $M_s(k, t)$ by some simple functional form. A two-parameter model memory could be useful if two exact conditions were available for $M_s(k, t)$, such as the exact initial values of $M_s(k, t)$ and its time derivative. Let us notice that such initial values can be related to those of $F_s(k, t)$. From (4), one can see that

$$M_s(k, 0) = m_s^{(2)}(k) - k^4 D_0^2 \quad (5)$$

and

$$M_s'(k, 0) = [\partial M_s(k, t)/\partial t]_{t=0} = m_s^{(3)}(k) + 2k^2 D_0 m_s^{(2)}(k) - k^6 D_0^6 \quad (6)$$

where

$$m_s^{(n)}(k) \equiv [\partial^n F_s(k, t)/\partial t^n]_{t=0} \quad (7)$$

An exact condition for $m_s^{(2)}(k)$ was first derived by Ackerson (1976) and it reads

$$m_s^{(2)}(k) = D_0^2 \left(k^4 + (n/k_B T) \int d\mathbf{r} g(r) (k \cdot \nabla)^2 u(r) \right) \quad (8)$$

whereas we have derived a similar result (Arauz-Lara 1985) for $m_s^{(3)}(k)$, namely

$$\begin{aligned} m_s^{(3)}(k) = & -D_0^3 k^6 - 3 \frac{D_0^3 k^2 n}{k_B T} \int d\mathbf{r} g(r) (k \cdot \nabla)^2 u(r) - 2 \frac{D_0^3 n}{(k_B T)^2} \int d\mathbf{r} g(r) [(k \cdot \nabla) \nabla u(r)]^2 \\ & - \frac{D_0^3 n^2}{(k_B T)^2} \iint d\mathbf{r} d\mathbf{r}' g^{(3)}(\mathbf{r}, \mathbf{r}') (k \cdot \nabla) (k \cdot \nabla') (\nabla \cdot \nabla') u(r) u(r'). \end{aligned} \quad (9)$$

In these equations, $u(r)$ is the interparticle potential, $g(r)$ the radial distribution function, $g^{(3)}(\mathbf{r}, \mathbf{r}')$ the three-particle distribution function and T is the temperature. In this manner, the equations above reduce the determination of the self-diffusion properties to the calculation of these static quantities. Although the time dependence of $M_s(k, t)$ may be, in general, rather involved (for example Hess and Klein (1983) have found an asymptotic power law decay), a simpler functional form could be used in the approach above. For instance, if $M_s(k, t)$ is modelled by

$$M_s(k, t) = a(k) \exp[-b(k)t] \quad (10)$$

then

$$D(t) = D_0 \left(1 - \frac{nA^2}{2B + nC} \right) + \frac{nA^3 k_B T}{(2B + nC)^2} \{ 1 - \exp[-D_0(2B + nC)t / Ak_B T] \} t^{-1} \quad (11)$$

with

$$A = \int d\mathbf{r} g(r) (\hat{\mathbf{k}} \cdot \nabla)^2 u(r) \quad (12)$$

$$B = \int d\mathbf{r} g(r) [(\hat{\mathbf{k}} \cdot \nabla) \nabla u(r)]^2 \quad (13)$$

$$C = \iint d\mathbf{r} d\mathbf{r}' g^{(3)}(\mathbf{r}, \mathbf{r}') (\hat{\mathbf{k}} \cdot \nabla) (\hat{\mathbf{k}} \cdot \nabla') (\nabla \cdot \nabla') u(r) u(r') \quad (14)$$

and where n is the number concentration of macroparticles.

We have evaluated $D(t)$ for the hard sphere plus repulsive Yukawa potential under the following additional approximations. (i) We have neglected the contributions involving three-body correlations, which are of higher order in n (i.e. we have set $nC = 0$ —this is strictly valid only at very low concentrations; in a more accurate approximation, nC could be evaluated using Kirkwood's superposition approximation). (ii) We approximate $g(r)$ by the solution of the 'rescaled' mean spherical approximation suggested by Hansen and Hayter (1982), in which, however, the use of the results of Høye and Blum (1977) for $g^{\text{MSA}}(r)$ allows an (essentially) analytic evaluation of A and B in (12) and (13). The details of these derivations (Arauz-Lara 1985) will be published elsewhere, but the results are now illustrated.

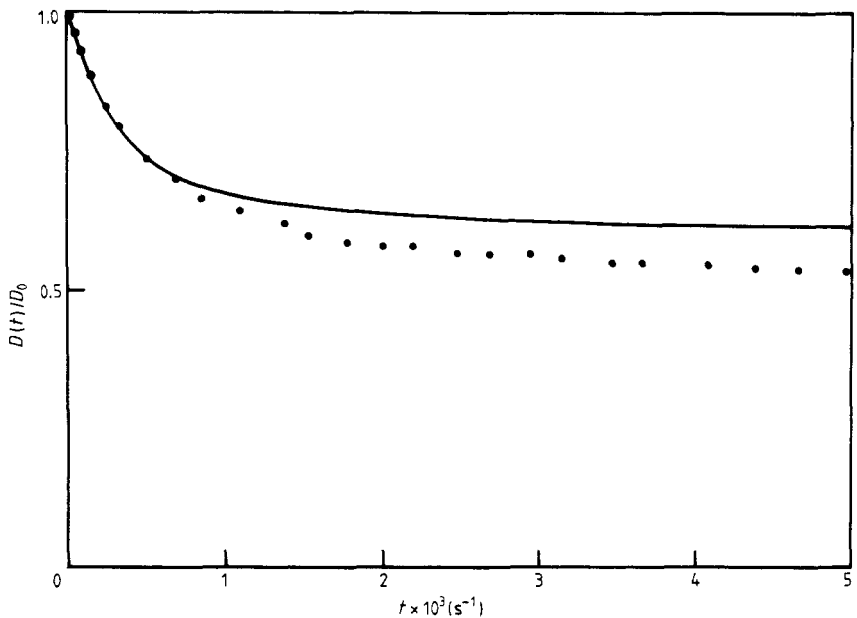


Figure 1. $D(t)$ against t for a system of spherical particles; $z = 0.15$, $K = 200$ and $D_0 = 9.35 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. The dots are the computer simulation data (Gaylor *et al* 1980).

In figure 1 we compare the time dependence of $D(t)$ resulting from our calculations, with the simulation results of Gaylor *et al* (1980), for the pair potential

$$\frac{u(r)}{k_B T} = K \frac{\exp[-z(x-1)]}{x} \quad r/\sigma = x > 1$$

$$= \infty \quad x < 1$$
(15)

with $z = 0.15$, $K = 200$, and hard-sphere volume fraction $\phi = \pi n \sigma^3 / 6 = 4.4 \times 10^{-4}$. We notice that the initial decay of $D(t)$ is very accurately predicted by our theory, whereas the long-time limit of $D(t)$ seems to be somewhat larger than the simulation results. Figure 2 shows the dependence of $D(t)$ at $t = 5 \times 10^{-4}$ s on ϕ for a fixed potential, with $z = 0.15$ and $K = 556$. For this potential, the 'fluid' of macroparticles crystallises at $\phi_m \approx 0.7 \times 10^{-3}$. From figure 2, we see that even for this more demanding system, our results compare quite well with the simulation data for values of ϕ up to about half the volume fraction of melting. This is more interesting considering that the calculations above do not involve any adjustable parameter, and that they correspond to the simplest approximation within the scheme suggested here. We have made additional comparisons with simulation results and with the results of other theories, and expect to extend this method to treat polydispersity effects.

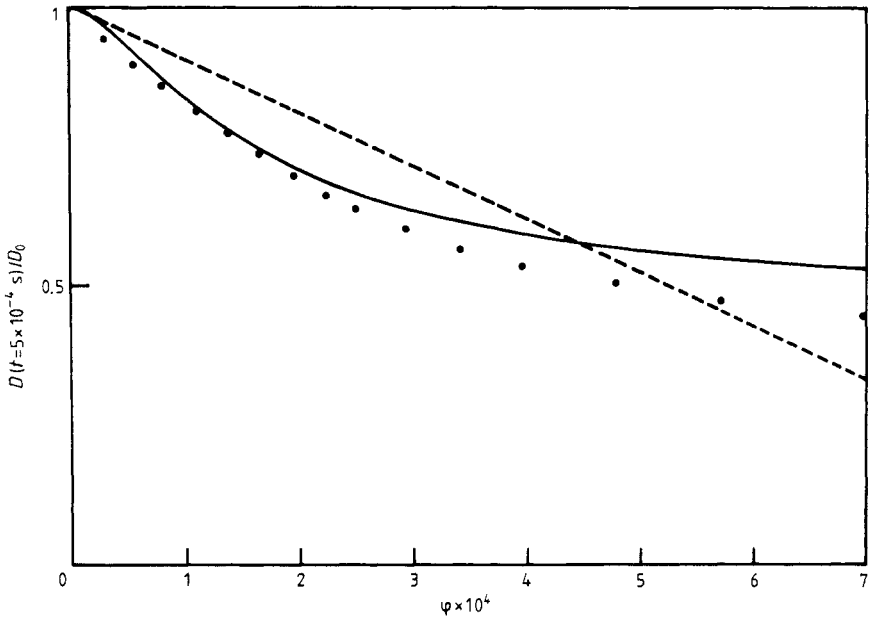


Figure 2. $D(t = 5 \times 10^{-4}$ s) against ϕ for the same system as in figure 1 but with $K = 556$. The broken line is the linear limit which can be obtained if one uses $g(r) = e^{-\beta u(r)}$ rather than the MSA. The dots represent the simulation data (Gaylor *et al* 1980).

References

- Ackerson B J 1976 *J. Chem. Phys.* **64** 242
 — 1978 *J. Chem. Phys.* **69** 684
 Ackerson B J and Fleishman L 1982 *J. Chem. Phys.* **76** 2675

- Arauz-Lara B J L 1985 *Thesis* CINVESTAV, IPN, Mexico
- Beenakker C W J and Mazur P 1983 *Physica* **120A** 388
- Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)
- Gaylor K J, Snook I K, Van Megen W J and Watts R O 1980 *J. Chem. Soc. Faraday Trans. II* **76** 1067
- Gorti S, Plank L and Ware B R 1984 *J. Chem. Phys.* **81** 909
- Hanna S, Hess W and Klein R 1982 *Physica* **11A** 181
- Hansen J P and Hayter J B 1982 *Mol. Phys.* **46** 651
- Hess W and Klein R 1982 *J. Phys. A: Math. Gen.* **15** L669
— 1983 *Adv. Phys.* **32** 173
- Høye J S and Blum L 1977 *J. Stat. Phys.* **16** 399
- Lekkerkerker H N W and Dhont J 1984 *J. Chem. Phys.* **80** 5790
- Medina-Noyola M and Vizcarra-Rendón A 1985 *Phys. Rev. A* in press
- Ohtsuki T 1982 *Physica* **110A** 606
- Pusey P N and Tough R J A 1982 *Dynamic Light Scattering and Velocimetry: Applications of Photon Correlation Spectroscopy* ed R Pecora (New York: Plenum)
- Pusey P N and Van Megen W 1983 *J. Physique* **44** 285
- Schurr J M 1980 *Chem. Phys.* **45** 119
- Tough R J A 1982 *Mol. Phys.* **46** 465
- Van Den Broeck C 1985 *J. Chem. Phys.* **82** 4248
- Van Megen W and Snook I 1977 *J. Chem. Phys.* **66** 813