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LETTER TO THE EDITOR

Self-diffusion coefficient of charged Brownian particles

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Abstract. Starting from a Fokker–Planck equation and using a projection operator formalism and a mode-coupling approximation, the self-diffusion coefficient is calculated for a strongly interacting system of charged spherical Brownian particles.

Charged polystyrene spheres in aqueous solution have served as model systems to study static and dynamic properties of strongly interacting systems of Brownian particles (Pusey and Tough 1982). The results of static and quasi-elastic light scattering experiments can well be accounted for by a model which takes a screened Coulomb law and a hard core as pair potential and uses the Fokker–Planck equation for the distribution function of the momenta p_i and the coordinates r_i as the basic transport equation.

Concerning the static properties, it has been shown (Hayter and Penfold 1981, Hansen and Hayter 1982) that the above-mentioned pair potential and the mean-spherical approximation (MSA) can reproduce well the experimentally determined static structure factors $S(k)$. With regard to the dynamics, it has been possible to calculate the dynamic structure factor $S(k, t)$ by a projection operator technique and within a mode–mode coupling approximation (MMCA), which essentially reduces the dynamical properties to static ones. Using the MSA static structure factors one can therefore calculate $S(k, t)$ without further assumptions. The agreement with the experimental results is quite satisfactory (Klein and Hess 1982). Therefore, we present in this paper a calculation along similar lines for one-particle properties, in particular for the self-diffusion coefficient, which is much more difficult to determine by light scattering. Only preliminary experimental results are known so far (Pusey 1979). They indicate a rather strong reduction of the self-diffusion coefficient due to the strong interactions among the macroions. This fact has also been observed in computer simulations (Gaylor *et al* 1979).

The self-diffusion problem has been treated before by starting from the Smoluchowski equation, where it is assumed that it is sufficient to consider only the coordinates of the macroions as dynamical variables (Hess and Klein 1981, Ohtsuki 1982). There are, however, indications that this procedure is not justified for the strongly interacting systems of polystyrene spheres (Hess 1981). Therefore, we take the more general Fokker–Planck equation as our basic transport equation.

Denoting by Γ the phase space point $\{p_1, \dots, p_N; r_1, \dots, r_N\}$ of our system of macroions, the Fokker–Planck equation reads

$$\partial f(\Gamma, t) / \partial t = \hat{\Omega}(\Gamma) f(\Gamma, t), \quad (1)$$

$$\hat{\Omega}(\Gamma) = -\sum_i \left[\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathbf{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} + \zeta_0 \frac{\partial}{\partial \mathbf{p}_i} \cdot \left(k_B T \frac{\partial}{\partial \mathbf{p}_i} + \frac{\mathbf{p}_i}{m} \right) \right]. \quad (2)$$

Here, m denotes the mass and ζ_0 the friction coefficient of a macroion and \mathbf{F}_i is the sum of forces acting on particle i by all other particles.

The equilibrium distribution is

$$f_0(\Gamma) = Z^{-1} \exp \left[-\beta \left(\frac{1}{2} \sum_i p_i^2 / m + U(\Gamma) \right) \right] \quad (3)$$

where $U(\Gamma)$ is the sum of Verwey-Overbeck pair potentials

$$U(\Gamma) = \sum_{i < j} U(r_{ij}), \quad (4)$$

$$U(r_{ij}) = \pi \epsilon_0 \epsilon d^2 \psi_0^2 (r_{ij})^{-1} \exp[-\kappa(r_{ij} - d)], \quad r_{ij} > d. \quad (5)$$

The dielectric constant of the solvent is ϵ and ψ_0 is the surface potential on the polystyrene spheres of diameter d . The screening constant is denoted by κ and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

The self-diffusion propagator $G(\mathbf{r} - \mathbf{r}', t - t')$ is the probability to find the tagged particle (having the index 1) at time t at \mathbf{r} if it was at time t' at \mathbf{r}' . We are using the solution of (1), which develops out of the constrained initial distribution

$$f(\Gamma, 0) = \delta(\mathbf{r}' - \mathbf{r}_1) f_0(\Gamma). \quad (6)$$

Therefore, $f(\Gamma, t) = \exp(\hat{\Omega}, t) f(\Gamma, 0)$ and

$$G(\mathbf{r} - \mathbf{r}', t - t') = \int d\Gamma \delta(\mathbf{r} - \mathbf{r}_1) f(\Gamma, t) \\ = \langle \delta(\mathbf{r} - \mathbf{r}_1) \exp[\hat{\Omega}(t - t')] \delta(\mathbf{r}' - \mathbf{r}_1) \rangle_0, \quad t \geq t', \quad (7)$$

where $\langle \dots \rangle_0$ denotes an equilibrium expectation value using (3). Fourier transforming gives

$$G(\mathbf{k}, t - t') = \langle c_1(\mathbf{k}) \exp[\hat{\Omega}(t - t')] c_1(-\mathbf{k}) \rangle_0 \quad (8)$$

where

$$c_1(\mathbf{k}) = \exp(-i\mathbf{k} \cdot \mathbf{r}_1) \quad (9)$$

and G depends only on k due to the isotropy of the system. From a knowledge of $G(k, t)$ one can calculate a number of one-particle properties. The mean-square displacement is defined by

$$W(t) = \frac{1}{6} \int d^3 r r^2 G(r, t) = -\frac{1}{2} \partial^2 G(k, t) / \partial k^2 |_{k=0} \quad (10)$$

and the velocity autocorrelation function is

$$Z(t) = \frac{1}{3} \langle \mathbf{v}_1(t) \cdot \mathbf{v}_1(0) \rangle_0 = \frac{d^2}{dt^2} W(t) = -\lim_{k \rightarrow 0} \frac{\partial^2}{\partial t^2} \frac{1}{k^2} G(k, t). \quad (11)$$

The self-diffusion coefficient is given by

$$D_s = \lim_{t \rightarrow \infty} \frac{W(t)}{t} = \int_0^\infty dt Z(t) \equiv \dot{Z}(0), \quad (12)$$

where $\dot{Z}(z)$ is the Laplace transform of $Z(t)$.

We now calculate the self-diffusion propagator. For the Laplace transform of (8) one finds

$$z\tilde{G}(k, z) = 1 + \langle c_1(\mathbf{k})\hat{\Omega}[z - \hat{\Omega}]^{-1}c_1(-\mathbf{k}) \rangle_0. \quad (13)$$

Using the operator identity

$$[z - \hat{\Omega}]^{-1} = [z - \hat{\Omega}\hat{Q}_c]^{-1}(1 + \hat{\Omega}\hat{P}_c[z - \hat{\Omega}]^{-1}) \quad (14)$$

with $\hat{P}_c = c_1(-\mathbf{k})\langle c_1(\mathbf{k})$ the projector onto $c_1(\mathbf{k})$ and $\hat{Q}_c = 1 - \hat{P}_c$, we obtain

$$\tilde{G}(k, z) = [z + \tilde{D}(k, z)k^2]^{-1} \quad (15)$$

where the generalised self-diffusion function

$$\tilde{D}(k, z) = \frac{1}{3}\langle j_{1z}(\mathbf{k})[z - \hat{\Omega}\hat{Q}_c]^{-1}j_{1z}(-\mathbf{k}) \rangle_0 \quad (16)$$

has been introduced and

$$j_1(\mathbf{k}) = (\mathbf{p}_1/m)c_1(\mathbf{k}). \quad (17)$$

From (11), (12) and (15) the self-diffusion coefficient is

$$D_s = \tilde{D}(0, 0), \quad (18)$$

and $\tilde{Z}(z) = \tilde{D}(0, z)$.

Since $j_1(k)$, equation (17), is orthogonal to $c_1(\mathbf{k})$ we introduce the projector

$$\hat{P}_j = \hat{\mathbf{k}} \cdot j_1(-\mathbf{k})\langle m/k_B T \rangle \langle \hat{\mathbf{k}} \cdot j_1(\mathbf{k}), \quad \hat{\mathbf{k}} = \mathbf{k}/k, \quad (19)$$

and use it for the calculation of $\tilde{D}(k, z)$ in the same manner as \hat{P}_c was applied for $\tilde{G}(k, z)$. The result is a generalised Stokes-Einstein relation for self-diffusion

$$\tilde{D}(k, z) = (k_B T/m)/(z + m^{-1}\tilde{\zeta}(k, z)) \quad (20)$$

with

$$\tilde{\zeta}(k, z) = \zeta_0 + \frac{1}{3}\beta\langle f_{1z}(\mathbf{k})\hat{Q}_{c,j}[z - \hat{\Omega}\hat{Q}_{c,j}]^{-1}\hat{Q}_{c,j}f_{1z}(-\mathbf{k}) \rangle_0. \quad (21)$$

Here, $\hat{Q}_{c,j} = \hat{Q}_c - \hat{P}_j$ and

$$f_{1z}(\mathbf{k}) = [-ik(mv_{1z}^2 - k_B T) + F_{1z}]c_1(\mathbf{k}). \quad (22)$$

Therefore, the velocity autocorrelation function is given by

$$\tilde{Z}(z) = (k_B T/m)[z + \zeta_0/m + (\beta/3m)\langle F_{1z}[z - \hat{\Omega}\hat{Q}_{c,j}]^{-1}F_{1z} \rangle]^{-1}. \quad (23)$$

The remaining calculation of the correlation function is performed by using a MMCA (Keyes 1977). Introducing the bilinear variable

$$b(\mathbf{k}) = c_1(\mathbf{k}) \sum_{i=2}^N c_i(-\mathbf{k}) \quad (24)$$

and the projection operator

$$\hat{P}_b = \frac{V}{(2\pi)^3} \int d^3k b(-\mathbf{k})\langle \frac{1}{NS(\mathbf{k})} \rangle b(\mathbf{k}), \quad (25)$$

we approximate $\hat{Q}_{c,j}f_{1z}(0)\rangle_0 = \hat{Q}_{c,j}F_{1z}\rangle_0 \approx \hat{P}_bF_{1z}\rangle_0$ in (21). The result for $k = 0$ is

$$\tilde{\zeta}(0, z) = \zeta_0 + \frac{k_B T}{3(2\pi)^3} \int d^3k \int d^3k' \frac{k_z k'_z h(k)h(k')}{S(k)S(k')} \langle b(\mathbf{k}') (z - \hat{\Omega}\hat{Q}_{c,j})^{-1} b(-\mathbf{k}) \rangle, \quad (26)$$

where $S(k) = 1 + ch(k)$ is the static structure factor.

The remaining correlation function is now factorised as

$$\langle b(\mathbf{k}') \exp(\hat{\Omega} \hat{Q}_{c,t}) b(-\mathbf{k}) \rangle \approx (2\pi)^3 V^{-1} \delta(\mathbf{k} - \mathbf{k}') G(\mathbf{k}, t) NS(\mathbf{k}, t). \quad (27)$$

In order to calculate D_s from (18) and (20), it is sufficient to know $\tilde{\zeta}(0, 0)$. From (26) and (27)

$$\tilde{\zeta}(0, 0) = \zeta_0 + \frac{k_B T}{3(2\pi)^3} \int d^3 k \left(\frac{k_z h(\mathbf{k})}{S(\mathbf{k})} \right)^2 \int_0^\infty dt G(\mathbf{k}, t) S(\mathbf{k}, t). \quad (28)$$

The self-diffusion propagator under the time integral is approximated by its free-particle expression $G_0(\mathbf{k}, t) = \exp(-D_0 k^2 t)$ and for $S(\mathbf{k}, t)$ we use the mean-field form (Hess and Klein 1981), $S_{MF}(\mathbf{k}, t) = S(\mathbf{k}) \exp[-D_0 k^2 t/S(\mathbf{k})]$. Here, $D_0 = k_B T/\zeta_0$ is the diffusion constant of a free particle. In this way the self-diffusion coefficient becomes

$$D_s = D_0 \left(1 + \frac{c}{6\pi^2} \int_0^\infty d^3 k \frac{(kh(\mathbf{k}))^2}{1+S(\mathbf{k})} \right)^{-1}. \quad (29)$$

D_s is now completely reduced to static properties of the system.

Static light scattering experiments (Brown *et al* 1975, Dahlberg *et al* 1978, Grüner and Lehmann 1979) on polystyrene spheres in aqueous solution show clearly that these systems are strongly interacting even at volume fractions as low as 0.001; there is a well developed first diffraction peak in $S(k)$ and $S(0)$ is as small as 0.1. It is therefore not possible to use in (29) the Debye-Hückel expression for $S(k)$. Hansen and Hayter (1982) have extended an earlier theoretical approach developed by Hayter and Penfold (1981) who had calculated $S(k)$ using the MSA on the basis of the pair potential (5).

We have used this approach for the static structure factors measured by Grüner and Lehmann (1979). The spheres in these systems have a diameter of 900 Å. By fitting the rescaled MSA to the experiments at one concentration, the surface potential was determined to $\psi_0 = 73$ mV and the screening parameter to $\kappa^{-1} = 5000$ Å. In this way good agreement was found between the results of the rescaled MSA and experiments at other concentrations (Hansen and Hayter 1982). The concentration dependent structure factor obtained by this procedure is now used in (29); the result is the

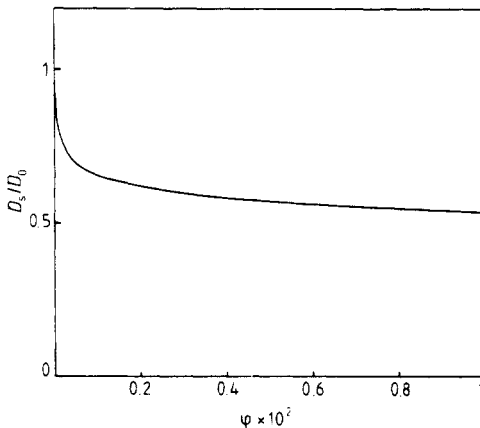


Figure 1. Self-diffusion coefficient D_s as a function of volume concentration for a system of charged hard spheres of diameter 900 Å, surface potential 73 mV and a screening length of 5000 Å.

concentration dependent self-diffusion coefficient shown in figure 1. There is at first a fast, limiting-law-like drop in D_s , followed by a rather large region of concentrations, where D_s is only slowly decreasing. The numerical values of D_s in this interval depend, of course, on the magnitude of ψ_0 and κ .

In view of the fact that a similar MMCA approach for the dynamical structure factor (Klein and Hess 1982) has given satisfactory agreement with the quasi-elastic light scattering experiments, it is believed that the calculation of the self-diffusion coefficient presented in this paper is a prediction of similar accuracy. More experimental work on D_s for strongly interacting charged spherical macroparticles would be most welcome.

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