

On the calculation of the self-diffusion coefficient of interacting Brownian particles

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We consider two ways to calculate the self-diffusion coefficient of interacting Brownian particles. The first approach is based on the calculation of the mean square displacement of a Brownian particle starting from the Smoluchowski equation. In the second approach the self-diffusion coefficient is obtained as the product of the thermodynamic driving force and the mobility. The advantages and limitations of the two methods are discussed.

I. INTRODUCTION

In the last few years there has been considerable interest both theoretically as well as experimentally in the concentration dependence of the diffusion coefficient of interacting colloidal particles.¹ As far as the first-order concentration dependence on concentration of the collective diffusion coefficient is concerned, there is now full agreement on the expressions to describe this effect.^{2,3} Furthermore, the theoretical predictions have been confirmed by experiment.⁴ The concentration dependence of the self-diffusion coefficient has been the subject of several recent theoretical investigations,⁵⁻¹² unfortunately leading to a variety of different results. The problem is that self-diffusion is complicated by what some people call the memory effect and others refer to as the relaxation effect. The point being that, as first recognized clearly by Pusey,¹³ for times $t \gg (a^2/D_0)$ (a : radius of the colloidal particles, D_0 diffusion coefficient of the colloidal particles at infinite dilution) the relative positions of a particle and its neighbors change significantly. This change in configuration will have an influence on the Brownian motion of colloidal particles and thus on their diffusion coefficient.

This effect can be taken into account in two different ways. In the first approach the mean square displacement of a tagged colloidal particle surrounded by other particles is calculated from the Smoluchowski equation and the self-diffusion coefficient is found from the relation

$$D_s = \lim_{t \rightarrow \infty} \frac{\langle [\Delta x(t)]^2 \rangle}{2t} \quad (1)$$

The fact that the motion of the tagged particle is influenced by the slowly changing configuration of the other particles gives rise to a memory effect.

In the second approach, the self-diffusion coefficient is obtained as the product of the thermodynamic driving force $k_B T$ (k_B : Boltzmann constant) and the appropriate mobility B_s :

$$D_s = k_B T B_s \quad (2)$$

In the case of self-diffusion, the appropriate mobility to be employed is the mobility for the case where one exerts a force F on one tagged particle and no force on the other particles.

Due to the imbalance of forces, the pair distribution function between the tagged particle and the other particles will be deformed. This deformation gives rise to the so-called relaxation effect. This relaxation effect was first clearly recognized about 60 yr ago by Debye and Hückel¹⁴ in their treatment of electrolytic conduction.

So far the more popular approach has been the calculation via the memory effect.⁶⁻¹⁰ The relaxation effect approach has been championed by Batchelor.¹² Obviously the memory effect and the relaxation effect describe the same physical effect and therefore the result for the self-diffusion coefficient obtained by the two approaches should be same. Unfortunately, in the results published so far the numerical end products obtained by the two approaches differ. One explanation for this discrepancy appears to be the fact that the results obtained depend very sensitively on the accuracy of the expressions employed to describe the hydrodynamic interaction between the particles. We therefore decided, in order to resolve the problem of the diverging results obtained by the memory effect calculation and the relaxation effect calculation, to consider the hypothetical case of hard spheres without hydrodynamic interaction. For this case Ackerson and Fleishman,⁸ and Hanna, Hess, and Klein⁹ find by calculating the memory effect

$$D_s = D_0(1 - 2\phi), \quad (3)$$

where ϕ is the volume fraction of the colloidal particles. Here we will show that the calculation of the relaxation effect also yields the result given above.

In Sec. II we summarize the memory effect calculation and in Sec. III we present the calculation of the relaxation effect along the lines set forth by Batchelor.¹² In Sec. IV we conclude by considering the advantages and limitations of the two methods.

II. CALCULATION OF THE MEMORY EFFECT

A particularly clear account of the calculation of the memory effect calculation has been given by Ackerson and Fleishman.⁸ We will give a brief summary of their work here. The starting point of the calculation is the Smoluchowski equation for two particles interacting through a pair poten-

tial $\Phi(|\mathbf{r}_1 - \mathbf{r}_2|)$ but without hydrodynamic interaction

$$\frac{\partial P}{\partial t} = D_0 \nabla_1 \cdot (\nabla_1 P + \beta P \nabla_1 \Phi) + D_0 \nabla_2 \cdot (\nabla_2 P + \beta P \nabla_2 \Phi). \quad (4)$$

Here $\beta = (k_B T)^{-1}$ and $P(\mathbf{r}_1, \mathbf{r}_2, t; \mathbf{r}_{10}, \mathbf{r}_{20})$ is the conditional probability for finding the two particles at positions \mathbf{r}_1 and \mathbf{r}_2 at time t given that their positions at time $t = 0$ are \mathbf{r}_{10} and \mathbf{r}_{20} . From the solution P of Eq. (4), the self-intermediate scattering function can be calculated

$$\begin{aligned} F_s(k, t) &= \langle e^{ik \cdot [\mathbf{r}(t) - \mathbf{r}(0)]} \rangle \\ &= \frac{1}{2} \int \{ e^{ik \cdot [\mathbf{r}_1 - \mathbf{r}_{10}] + e^{ik \cdot [\mathbf{r}_2 - \mathbf{r}_{20}]} \} \\ &\quad \times P(\mathbf{r}_1, \mathbf{r}_2, t; \mathbf{r}_{10}, \mathbf{r}_{20}) P(\mathbf{r}_{10}, \mathbf{r}_{20}) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_{10} d\mathbf{r}_{20}. \end{aligned} \quad (5)$$

In order to clearly display the memory effect it is helpful to write the self-intermediate scattering function in the form

$$\frac{\partial F_s(k, t)}{\partial t} = K_1(k) F_s(k, t) + \int_0^t M(k, \tau) F_s(k, t - \tau) d\tau, \quad (6)$$

where $K_1(k)$ is the first cumulant

$$K_1(k) = \lim_{t \rightarrow 0} \frac{\partial \ln F_s(k, t)}{\partial t}, \quad (7)$$

and $M(k, \tau)$ is the memory function. For the case of hard spheres, Ackerson and Fleishman find for the first cumulant

$$K_1(k) = -D_0 k^2 \quad (8)$$

and for the memory function (up to terms of order k^2)

$$\begin{aligned} M(k, t) &= (16/3) \pi a c D_0^2 k^2 \left\{ \frac{1}{\pi \alpha} - [1/2 - S(\alpha)] \cos\left(\frac{\pi \alpha^2}{2}\right) \right. \\ &\quad \left. + [1/2 - C(\alpha)] \sin\left(\frac{\pi \alpha^2}{2}\right) \right\}. \end{aligned} \quad (9)$$

Here $c = N/V$ is the number density of the colloidal particles, $\alpha = (2D_0 t / \pi a^2)^{1/2}$ and $C(\alpha)$ and $S(\alpha)$ are the Fresnel cosine and sine integrals. Without loss of generality we may assume that the \mathbf{k} vector is parallel to the x axis. Then we may write

$$\begin{aligned} F_s(k, t) &= \langle e^{ik[x(t) - x(0)]} \rangle \\ &= 1 - \frac{1}{2} k^2 \langle [x(t) - x(0)]^2 \rangle + O(k^4). \end{aligned} \quad (10)$$

From Eq. (10) it follows that:

$$\langle [\Delta x(t)]^2 \rangle = \lim_{k \rightarrow 0} \frac{2}{k^2} [1 - F_s(k, t)]. \quad (11)$$

Using Eqs. (6) and (11) and taking into account that from the definition of the self-intermediate scattering function it follows that $F_s(k, 0) = 1$ one obtains:

$$\langle [\Delta x(t)]^2 \rangle = - \lim_{k \rightarrow 0} \left[\frac{2K_1 t + 2 \int_0^t (t - \tau) M(k, \tau) d\tau}{k^2} \right]. \quad (12)$$

From Eq. (12) the following expression for the self-diffusion coefficient is obtained:

$$\begin{aligned} D_s &= \lim_{t \rightarrow \infty} \frac{\langle [\Delta x(t)]^2 \rangle}{2t} \\ &= - \lim_{k \rightarrow 0} \left[\frac{K_1 + \int_0^\infty M(k, \tau) d\tau}{k^2} \right]. \end{aligned} \quad (13)$$

Substituting the expressions in Eqs. (8) and (9) for the first cumulant and the memory function in Eq. (13) one obtains

$$D_s = D_0(1 - 2\phi), \quad (14)$$

where $\phi = (4\pi/3)a^3 c$ is the volume fraction of the colloidal particles. We see that the memory effect leads to a decrease of the self-diffusion coefficient.

III. CALCULATION OF THE RELAXATION EFFECT

The self-diffusion coefficient can be written as

$$D_s = k_B T B_s,$$

where the mobility B_s is defined by the relation

$$\langle \mathbf{u} \rangle = B_s \mathbf{F}. \quad (15)$$

Here $\langle \mathbf{u} \rangle$ is the average velocity of a tagged particle 1 on which a force \mathbf{F} acts surrounded by particles 2 on which no forces act. In the stationary state the pair distribution function $g(\mathbf{r}_2 - \mathbf{r}_1)$ of the particles 2 with respect to the tagged particle 1 will be deformed due to this difference in applied forces. This deformation can be calculated from the Smoluchowski equation for the case where a force \mathbf{F} is applied to the tagged particle

$$\frac{\partial g(\mathbf{r})}{\partial t} = 2D_0 \nabla_r \cdot [\nabla_r g(\mathbf{r}) + \beta g(\mathbf{r}) \nabla_r \Phi] + \beta D_0 \mathbf{F} \cdot \nabla_r g(\mathbf{r}). \quad (16)$$

Here $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$.

To first order in \mathbf{F} the stationary state solution of Eq. (16) can be written as

$$g(\mathbf{r}) = \exp(-\beta\Phi) \left[1 + \frac{\beta a Q(\mathbf{r}) \mathbf{r} \cdot \mathbf{F}}{2r} \right], \quad (17)$$

where $Q(r)$ must satisfy the equation

$$\frac{d}{dr} \left[e^{-\beta\Phi} r^2 \frac{dQ}{dr} \right] - 2e^{-\beta\Phi} Q + \frac{r^2}{a} \frac{de^{-\beta\Phi}}{dr} = 0. \quad (18)$$

For a hard sphere interaction $e^{-\beta\Phi} = 1$ for $r > 2a$ and Eq. (18) reduces to

$$\frac{d}{dr} \left(r^2 \frac{dQ}{dr} \right) - 2Q = 0. \quad (19)$$

The general solution of Eq. (19) is

$$Q(r) = \frac{A_1}{r^2} + A_2 r. \quad (20)$$

Physically it is clear that $Q \rightarrow 0$ for $r \rightarrow \infty$ and thus we must put $A_2 = 0$. In order to find A_1 we integrate Eq. (18) from $2a$ to $2a + \epsilon$. This yields

$$\begin{aligned} e^{-\beta\Phi} r^2 \frac{dQ}{dr} \Big|_{2a}^{2a+\epsilon} - 2 \int_{2a}^{2a+\epsilon} Q dr \\ + \int_{2a}^{2a+\epsilon} \frac{r^2}{a} \frac{de^{-\beta\Phi}}{dr} dr = 0. \end{aligned} \quad (21)$$

Taking into account that $e^{-\beta\Phi}$ is a unit step function at $r = 2a$ and that Q is well behaved for $r > 2a$ we obtain from Eq. (21):

$$4a^2 \frac{dQ}{dr} \Big|_{2a+\epsilon} - 0(\epsilon) + 4a = 0,$$

and thus

$$\lim_{\epsilon \rightarrow 0} \frac{dQ}{dr} \Big|_{2a+\epsilon} = -\frac{1}{a}. \quad (22)$$

Using this result together with Eq. (20) we get

$$A_1 = 4a^2. \quad (23)$$

This completes the calculation of the deformed pair distribution function. With this deformed pair distribution function we are in a position to calculate the relaxation effect. Since the pair distribution given by Eq. (17) is not spherically symmetric the interaction of the tagged particle with the other particles leads to a net force on the tagged particle. This is precisely the relaxation force that can be written as

$$\begin{aligned} \mathbf{F}_{\text{relax}} &= c \int g(\mathbf{r}) \frac{d\Phi}{dr} \frac{\mathbf{r}}{r} d\mathbf{r} \\ &= -c \int \frac{de^{-\beta\Phi}}{dr} \frac{2a^3}{r^4} \mathbf{r} \mathbf{r} \cdot \mathbf{F} d\mathbf{r} \\ &= -2\phi \mathbf{F}. \end{aligned} \quad (24)$$

This means that the total force acting on the tagged particles is given by

$$\mathbf{F}_{\text{total}} = \mathbf{F} + \mathbf{F}_{\text{relax}} = (1 - 2\phi) \mathbf{F}. \quad (25)$$

The average velocity of the tagged particle will be given by

$$\begin{aligned} \langle \mathbf{u} \rangle &= B_0 \mathbf{F}_{\text{total}} \\ &= B_0 (1 - 2\phi) \mathbf{F}. \end{aligned} \quad (26)$$

Here B_0 is the mobility at infinite dilution. Comparing Eqs. (15) and (26) we see that

$$B_s = B_0 (1 - 2\phi). \quad (27)$$

Substituting this result in the expression for the self-diffusion coefficient we find

$$D_s = k_B T B_0 (1 - 2\phi) = D_0 (1 - 2\phi). \quad (28)$$

This result is in complete agreement with the result (14) obtained from the calculation of the memory effect.

IV. DISCUSSION

Comparing the two approaches it appears that each of them has its specific advantages and disadvantages. If one is

only interested in the self-diffusion coefficient the relaxation approach requires less calculational effort than the memory approach. In addition the relaxation force allows one to make a mental picture of the physical mechanism that gives rise to the contribution $2\phi D_0$ in the self-diffusion coefficient. On the other hand, from the memory function the mean square displacement of a tagged particle at all times can be obtained. This information is conceptually important in seeing how the neighboring particles influence the motion of a tagged particle and for the interpretation of light scattering measurements.

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¹For comprehensive reviews see P. N. Pusey and R. J. A. Tough, in *Dynamic Light Scattering and Velocity: Applications of Photon Correlation Spectroscopy*, edited by R. Pecora (Plenum, New York, 1982); W. Hess and R. Klein, *Adv. Phys.* **32**, 173 (1983).

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