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Self-diffusion coefficient for dilute macromolecular solutions

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Abstract. Two distinct procedures have been followed in the literature for determining D , the self-diffusion coefficient for a dilute macromolecular solution. One is a direct statistical mechanical calculation based on the fundamental Einstein relationship; the other consists of averaging the diagonal part of the diffusion tensor which describes the hydrodynamic interactions. Subject to an approximation common to both types of calculation, that the macromolecules remain essentially fixed on the time scale of momentum relaxation, we show that both procedures lead to identical results for D . Our result is valid for any order of approximation to the low-concentration hydrodynamic interaction term. We briefly argue that relaxing the fixed-particle approximation should not lead to appreciably different results.

1. Introduction

The calculation of the self-diffusion coefficient D for a dilute solution of uncharged spherical particles (the macromolecules) has been the subject of a number of papers; the work of Deutch and Oppenheim (1971, to be referred to as DO), Aguirre and Murphy (1973, to be referred to as AM), and Batchelor (1976) is particularly relevant for what follows. Our concern here is with the two seemingly distinct definitions of D that are used in these papers. DO calculate D directly from the fundamental Einstein relationship, written in terms of the momentum autocorrelation function $\phi(t)$,

$$D = \frac{1}{3m^2} \int_0^\infty dt \phi(t). \quad (1)$$

In the other work cited, D is identified as the average over the self-diffusion tensor, \mathbf{D}_{ii} . This definition of D has been used previously in the literature (Riseman and Kirkwood 1956) in the context of the theory of polymers, but we have found no rigorous justification for its use. The purpose of this paper is to demonstrate that, subject to an approximation common to the work cited above, these two definitions do give identical results for D . The results of DO are based on the use of the Oseen model for which $\mathbf{D}_{ii} = D_0 \mathbf{1}$, with D_0 the value of D at infinite dilution; they found $D = D_0$ in accordance with the result obtained by simply averaging \mathbf{D}_{ii} . The results we will obtain here will be general, independent of the specific form of the low-concentration hydrodynamic interaction model.

A number of approximations are used in the work cited above. The most important of these is that the particle locations can be considered as fixed for times over which D can be determined. This assumption is explicit in the work of DO and

Batchelor and appears to be implicit in the work of AM. Another approximation common to all this work is the explicit neglect of effects due to the direct interaction between the particles other than in the averaging. We will not require the use of this approximation, nor the assumption of Batchelor concerning the Gaussian behaviour of the two-particle distribution function or the 'close to equilibrium' assumption of AM. As already mentioned, the correspondence we show between the two definitions of D will depend on the fixed-particle assumption; it is not presently clear whether this correspondence will strictly hold when this assumption is relaxed, but preliminary results for direct hard-sphere interactions indicate that the error involved is small.

The method of approach which we will use here is based on the use of equation (1) and the calculation of the momentum autocorrelation function. Our results will also have a certain relevance for the theory of $\phi(t)$ which we comment on only briefly here. To calculate $\phi(t)$ we will use the generalised Fokker-Planck equation (GFPE) (Murphy and Aguirre 1972). The use of this equation offers several advantages, primary among which is the facility it offers in generating the desired results. Also, use of this equation offers an alternative approach to that given by the generalised Smoluchowski equation (GSE) which has been more widely used in previous applications to the theory of macromolecular solutions (Altenberger and Deutch 1973, Harris 1976, Hess and Klein 1976). The latter equation is embedded in the GFPE and so we would expect a more complete description on the GFPE level. Whether this is accessible *in toto*, or at least beyond what can be done using the GSE, remains for future work to determine, but the present paper is a first step in this direction.

2. Statistical mechanical theory

The notation used in equation (1) will prove inadequate for what follows. To simplify matters we begin by noting that due to the isotropy of the system we can replace $\phi(t)/3$ by $\phi^{xx}(t)$ where the superscripts indicate the components of the momenta whose correlation is being described. We will also have to take into account momentum correlations between different particles, so that $\phi_{11}^{xx}(t)$ will be used to indicate an autocorrelation function and $\phi_{12}^{xx}(t)$ to indicate a joint correlation function:

$$\begin{aligned}\phi_{11}^{xx}(t) &= \langle p_{x1}(0)p_{x1}(t) \rangle = \langle p_{0x1}p_{x1}(t) \rangle \\ \phi_{12}^{xx}(t) &= \langle p_{0x1}p_{x2}(t) \rangle.\end{aligned}\tag{2}$$

The brackets indicate a full equilibrium ensemble average over all the particles in solution. We will also need to refer to momentum-averaged correlation functions, which we define in terms of an equilibrium ensemble average over only the momentum variables, denoted by $\langle \dots \rangle_{p_0}$, as

$$\psi_{ij}^{xx}(t) = \langle p_{0xi}p_{xj}(t) \rangle_{p_0}\tag{3}$$

so that, if the configuration average indicated in equation (2) is denoted by $\langle \dots \rangle_{r_0}$,

$$\phi_{ij}^{xx}(t) = \langle \psi_{ij}^{xx}(t) \rangle_{r_0}.\tag{4}$$

In what follows the superscripts can be dropped, for ease of notation, without causing confusion.

To calculate D from the fundamental Einstein relationship, equation (1), we require an expression for $\phi_{11}(t)$, or more simply $\tilde{\phi}_{11}(0)$, where the tilde denotes a

Laplace transform. In terms of the distribution function $f_1(\mathbf{r}_1, \mathbf{p}_1, t)$ for a single particle in solution we have

$$\psi_{11}(t) = \left\langle p_{01x} \int d\mathbf{r}_1 d\mathbf{p}_1 p_{1x} f_1(\mathbf{r}_1, \mathbf{p}_1, t) \right\rangle_{p_0} \quad (5)$$

Differentiating equation (5) leads to an equation for $\psi_{11}(t)$ that contains $\partial f_1(\mathbf{r}_1, \mathbf{p}_1, t)/\partial t$. The latter quantity can be obtained by reducing the GFPE, which describes the N -particle distribution function for the particles in solution since in general we have

$$\frac{(N-n)!}{N!} f_n(\mathbf{r}_n, \mathbf{p}_n, t) = \int \frac{d\mathbf{r}_N d\mathbf{p}_N}{d\mathbf{r}_n d\mathbf{p}_n} f_N(\mathbf{r}_N, \mathbf{p}_N, t) \quad (6)$$

where $\mathbf{r}_N, \mathbf{p}_N$ denote the configuration and momenta of N particles and the differential notation is obvious.

The GFPE is (Murphy and Aguirre 1973)

$$\frac{\partial f_N}{\partial t} + \sum_{i=1}^N \left(\frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} + \mathcal{F}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \right) f_N = \beta^{-1} \sum_{i,j=1}^N \frac{\partial}{\partial \mathbf{p}_i} \cdot \boldsymbol{\zeta}_{ij} \cdot \left(\frac{\partial}{\partial \mathbf{p}_j} + \frac{\beta \mathbf{p}_j}{m} \right) f_N \quad (7)$$

with $\beta = 1/kT$, \mathcal{F}_i the direct force of interaction experienced by particle i , assumed to be the sum of pairwise additive terms, and $\boldsymbol{\zeta}_{ij}$ is the friction tensor. Reduction of the GFPE to an equation for f_1 follows from equation (6), and we find

$$\begin{aligned} \frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} + \int d\mathbf{r}_2 d\mathbf{p}_2 \frac{\partial}{\partial \mathbf{p}_1} \cdot \mathcal{F}_1 f_2 \\ = \beta^{-1} \frac{\partial}{\partial \mathbf{p}_1} \cdot \boldsymbol{\zeta}_{11}^0 \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} + \frac{\mathbf{p}_1}{m} \beta \right) f_1 \\ + \beta^{-1} \frac{\partial}{\partial \mathbf{p}_1} \cdot \int d\mathbf{r}_2 d\mathbf{p}_2 \left[\bar{\boldsymbol{\zeta}}_{11} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} + \frac{\mathbf{p}_1}{m} \beta \right) + \boldsymbol{\zeta}_{12} \cdot \frac{\mathbf{p}_2}{m} \beta \right] f_2. \end{aligned} \quad (8)$$

Here we have used the low-concentration form for $\boldsymbol{\zeta}_{ij}$, so that it too is written as the sum of pairwise additive terms, and we have written the diagonal part as $\boldsymbol{\zeta}_{11} = \boldsymbol{\zeta}_{11}^0 + \bar{\boldsymbol{\zeta}}_{11}$ with $\boldsymbol{\zeta}_{11}^0 = \boldsymbol{\zeta}_{11}^0$ the infinite-dilution friction tensor.

In what follows we will have to close equation (8) in order to use this, with equation (5) to obtain a set of equations for the ψ_{ij} . The closure which we use is described in the following section and is based on the fixed-particle approximation discussed earlier. One point that might be noted here regarding equation (8) is that, unlike the reduced GSE, the direct force is not explicitly coupled with the friction tensor (Altenberger and Deutch 1973). Even in the context of the fixed-particle approximation we will see that this is illusory, and that this coupling does occur in the description of the ψ_{ij} . However, in arriving at equation (8) there is no need to consider (or drop) three-body terms as is the case with the GSE. A problem that might be anticipated in using equation (8) as the basis for a specific calculation is that the $\boldsymbol{\zeta}_{ij}$ converge much slower than the \mathbf{D}_{ij} which appear in the GSE (Felderhof 1977).

3. Momentum correlation functions

To use equation (8) with equation (5) we require a closure *ansatz*. For the purposes of

the present paper we use the approximation that the particle locations remain fixed on the time scale required to determine D . Batchelor (1976) has shown this to be a reasonable assumption for systems of physical interest; we will comment briefly on relaxing this assumption in the concluding section. On the basis of this assumption we can combine the equation for $\partial\psi_{11}(t)/\partial t$ and equation (8) to obtain

$$\frac{\partial\psi_{11}(t)}{\partial t} = -\frac{\zeta_{11}^0}{m}\psi_{11}(t) + \psi_{11}^F(t) - \psi_{11}(t)\frac{\bar{\zeta}_{11}^{xx}(r_{012})}{m} - \psi_{12}(t)\frac{\zeta_{12}^{xx}(r_{012})}{m} \quad (9)$$

where

$$\psi_{11}^F(t) = \langle p_{01x} \mathcal{F}_{1x}(r_{012}) \rangle_{p_0} \quad (10)$$

and $\zeta_{ij}^{xx}(r_{012})$ is the xx component of the tensor $\zeta_{ij}(r)$ evaluated at the (yet to be averaged over) initial separation r_{012}^\dagger . In what follows we again simplify our notation by writing ζ_{ij} for $\zeta_{ij}^{xx}(r_{012})$.

An equation for $\psi_{12}(t)$ can be obtained from equation (5) by changing labels from 1 to 2 in the integral and using the appropriate form of equation (8) for this change; we find

$$\frac{\partial\psi_{12}(t)}{\partial t} = -\psi_{12}(t)\frac{\zeta_{22}}{m} - \psi_{12}(t)\frac{\zeta_{21}}{m} - \psi_{11}^F(t). \quad (11)$$

Solving equations (9) and (11) for $\psi_{11}(t)$ by Laplace transforms we find

$$\begin{aligned} \tilde{\psi}_{11}(s) = & \left[\frac{\psi_{11}(0)}{s + (\zeta_{11}/m)} + \frac{\tilde{\psi}_{11}^F(s)}{s + (\zeta_{11}/m)} \left(1 + \frac{\zeta_{12}/m}{s + (\zeta_{11}/m)} \right) \right] \\ & \times \left(1 - \frac{(\zeta_{12}/m)(\zeta_{21}/m)}{[s + (\zeta_{11}/m)][s + (\zeta_{22}/m)]} \right)^{-1} \end{aligned} \quad (12)$$

where s is the transform variable.

4. The self-diffusion coefficient

The self-diffusion coefficient is given by $\tilde{\phi}_{11}(0)$, which follows from equation (12) after performing the averaging indicated in equation (4). In the fixed-particle approximation the average of the term containing $\tilde{\psi}^F(s)$ will be identically zero since the ζ_{ij} are functions of r_{012} , not r_{012} ; it is important to note that the proper procedure for determining D requires first averaging and then taking the limit $s \rightarrow 0$. Thus a separate assumption is not required to neglect the contribution to D of the direct interactions, rather this follows as a direct consequence of the fixed-particle approximation as used here. For $\tilde{\phi}_{11}(0)$ we have

$$\frac{\tilde{\phi}_{11}(0)}{m} = \left\langle \frac{\phi_{11}(0)}{\zeta_{11} - (\zeta_{12}\zeta_{21}/\zeta_{22})} \right\rangle = \langle D_{11} \rangle \quad (13)$$

where the last equality is valid for any order of approximation to the hydrodynamic interaction terms (cf AM equation (17)). This is the main difference between our result and that of DO which is based on the use of Oseen's model for the hydrodynamic interaction.

[†] We use a coordinate system like that of DO, where the off-diagonal components vanish.

Preliminary calculations indicate that relaxing the fixed-particle approximation will not lead to significant numerical corrections for the case of hard-sphere direct interactions. To see why the direct interaction term might be expected to be small we briefly consider a linearised theory which does not use the fixed-particle approximation. To obtain closure in equation (8) we will write $f_2 = f_1(1)f_1(2)g(r, t)$ where the correlation function g is a function of r as in equilibrium, but we do not require that $g = g^0$, the equilibrium value, as has been done in the closure of the GSE (Harris 1976, Hess and Klein 1976). Linearising $f_1 = f_1^0 + \bar{f}_1$, the linearised equation for \bar{f}_1 contains the direct interaction term

$$I^F = \int d\mathbf{r}_2 d\mathbf{p}_2 \frac{\partial}{\partial \mathbf{p}_1} \cdot \mathcal{F}_1(f_1^0(1)\bar{f}_1(2) + f_1^0(2)\bar{f}_1(1))g(r, t) \quad (14)$$

which leads to

$$\psi_{11}^F(t) = \frac{1}{3} \left\langle \mathbf{p}_{01} \cdot \int d\mathbf{r}_1 d\mathbf{p}_1 d\mathbf{r}_2 d\mathbf{p}_2 \mathcal{F}_1 f_1^0(1)\bar{f}_1(2)g(r, t) \right\rangle_{p_0} = 0. \quad (15)$$

One final point should be made concerning the results found here, namely that they can be used to determine the time dependence of $\phi_{ij}(t)$. We will not pursue this here other than to mention that this does not seem to be a simple exponential dependence, as is found at infinite dilution. If so this would be in accord with results currently being prepared for publication based on an extension of our earlier solution for the GSE (Harris 1976). We have already found (Harris 1973) similar results for systems of charged spheres.

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