Diffusion effects in solutions of Brownian particles

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Abstract. The theory of light scattering from a solution of interacting spherical macro-particles as presented in 1973 by Altenberger and Deutch is re-examined. The Oseen model for the hydrodynamical interaction between the particles, commonly used in statistical mechanical theories of such systems, is shown here to omit a lowest order concentration term to the effective diffusion coefficient. This model is corrected to lowest order in the ratio of particle diameter to interparticle separation and the effective diffusion coefficient re-calculated. We find $D_{\text{eff}} = D^0(1 + 3 \cdot 0\phi)$, where D^0 is the infinite-dilution self-diffusion coefficient for the particles and ϕ is the volume fraction. This is to be compared with earlier results $D_{\text{eff}} = D^0(1 + a\phi)$ where $a = 2$ in the Altenberger–Deutch calculation, $a \approx 1$ for earlier theories, and experiment suggests $a = 2 \cdot 94$.

1. Introduction

An interpretation of the light scattering spectrum from a dilute solution of uncharged spherical macroparticles has been given by Altenberger and Deutch (1973, to be referred to as AD). For high enough dilution so that the interaction between the particles is only hydrodynamic, i.e. the direct short-range forces between them can be ignored, a number of exact results were found for the coherent structure factor. The case in which these short-range forces are included was found to be far less tractable, leading to a coupled hierarchy of equations for the reduced particle distribution functions and thus the need for a closure-effecting *ansatz*. AD point out the need for a detailed analysis of this problem in the context of a more complete model for the hydrodynamic interactions than they have used; for their model they use a simple *ansatz* to produce closure and proceed to generalize their earlier results. The results they find compare well with existing theory and experiment (Altenberger and Deutch 1973, references 17–24). In subsequent work, Phillies (1975) has generalized the model to include some of the effects of solvent backflow, but no direct comparison with the results of AD was made and the work was carried out using a different approach.

Our own interest in this work stems from some related results (Harris 1976) we have obtained in the case of charged particles. For this problem we find that the lowest order concentration correction leads to a reduced effective diffusion coefficient, and that the correction is a self-diffusion effect, AD on the other hand find an enhanced diffusion coefficient containing both self- and cross-diffusional effects. The mechanism for the charged sphere case is quite different (i.e. an electrostatic effect) from those which obtain for uncharged spheres, however it seems quite natural to inquire in this latter case why the effect of self-diffusion appears to be less important. Thus, the concentration diffusion is due to self- and cross-diffusional effects, and we would expect the

former to be reduced as the particle concentration increases from infinite dilution (e.g. due to the increase in viscosity a single particle experiences) while the latter should be enhanced (e.g. due to more particles being available to diffuse). This argument is oversimplistic in that it does not take account of the interference with these effects due to direct particle interactions, but it does seem clear that we can expect two competing effects, however dressed, which must be assessed in a consistent manner if a valid conclusion is to be arrived at concerning which of these is to dominate. This is the basic purpose of this paper. We will show that the model for the hydrodynamic interaction used by AD is not totally consistent in this regard, but that when it is made so their result is in fact more general than it appears. We also offer a conjecture on what appears to be a significant difference between the cases of charged and uncharged spheres in the context of the statistical mechanical description used for the present problem.

2. Theory

Our starting point will be the N-particle Smoluchowski equation which describes the evolution of the particle distribution function in coordinate space, $P(\boldsymbol{R}^N, t)$,

$$\frac{\partial P(\boldsymbol{R}^N, t)}{\partial t} = \left(\sum_{i,j=1}^{N} \boldsymbol{\nabla}_i \cdot \boldsymbol{D}_{ij} \cdot (\boldsymbol{\nabla}_j - \beta \boldsymbol{F}_j) \right) P(\boldsymbol{R}^N, t). \tag{1}$$

As far as possible we will use notation similar to that of AD, but some differences will be unavoidable. Thus in (1) $\boldsymbol{D}_{ij}$ is the entire diffusion tensor; its diagonal elements are the self-diffusion tensors and its off-diagonal elements are the cross-diffusional tensors. In AD the former are given by $D^0\boldsymbol{I}$, with D^0 the self-diffusion coefficient at infinite dilution, and the latter by $\beta^{-1}\boldsymbol{T}_{ij}$ where $\boldsymbol{T}_{ij}$ is Oseen's tensor, but for the time being we will not specify these beyond requiring that they both depend at most on the coordinates of two particles. The latter requirement restricts us to low concentrations and will eliminate some part of the solvent counterflow effect (Friedman 1965). The quantity $\boldsymbol{F}_i = \Sigma_{j \neq i} \boldsymbol{F}_{ij}$ in the above equation is the direct force of interaction on particle i due to the other particles.

Integrating (1) over the coordinates of all but one of the particles we find

$$\frac{\partial p^{(1)}(\boldsymbol{R}_1, t)}{\partial t} = D^0\nabla_1^2 p^{(1)}(\boldsymbol{R}_1, t) + (N-1) \int \mathrm{d}\boldsymbol{R}_2 \boldsymbol{\nabla}_1 \cdot \boldsymbol{D}'_{11} \cdot (\boldsymbol{\nabla}_1 - \beta \boldsymbol{F}_{12}) p^{(2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t)$$

$$+ (N-1) \int \mathrm{d}\boldsymbol{R}_2 \boldsymbol{\nabla}_1 \cdot D^0\boldsymbol{I} \cdot (-\beta \boldsymbol{F}_{12}) p^{(2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t)$$

$$+ (N-1) \int \mathrm{d}\boldsymbol{R}_2 \boldsymbol{\nabla}_1 \cdot \boldsymbol{D}_{12} \cdot (-\beta \boldsymbol{F}_{21}) p^{(2)}(\boldsymbol{R}_1, \boldsymbol{R}_2, t) \tag{2}$$

where we have written $\boldsymbol{D}_{ii} = D^0\boldsymbol{I} + \boldsymbol{D}'_{ii}$. In arriving at this equation we have made use of the fact that $\boldsymbol{\nabla}_2 \cdot \boldsymbol{D}_{12} = 0$ (the argument given in AD still holds; this is also verifiable by direct calculation from equation (4)). We have also neglected three-body terms in the first integral, $(N-2)(N-1) \int \mathrm{d}\boldsymbol{R}_2 \, \mathrm{d}\boldsymbol{R}_3 \boldsymbol{\nabla}_1 \cdot \boldsymbol{D}'_{11} \cdot (-\beta \boldsymbol{F}_{13}) p^{(3)}(\boldsymbol{R}_1, \boldsymbol{R}_2, \boldsymbol{R}_3, t)$ where $\boldsymbol{D}'_{11} = \boldsymbol{D}'_{11}(\boldsymbol{R}_1 - \boldsymbol{R}_2)$. It is interesting to note that even in the low concentration approximation used here the first hierarchy equation explicitly couples the first three distribution functions; the three-body terms are probably of higher order, and thus

would not appear in a low concentration theory based on a more rigorous treatment, but their presence signals the extreme difficulty which such a theory is likely to involve.

If we set $\mathbf{D}'_{11} = 0$, $\mathbf{F}_{12} = -\nabla_1 U = \nabla_2 U = -\mathbf{F}_{21}$ (U the potential of direct interaction) in (2) and take note of a misprint in equation (4.5) of AD we then recover their equation (4.4). But this does not seem to us to be a consistent description, since only part of the self-diffusion concentration correction, that given by the second integral term on the right-hand side of (2), is included. However, to include the gradient correction in a consistent manner also requires including the force term, and both of these have thus been included together in the first integral term on the right-hand side of (2). Within the context of the AD calculation, including the closure *ansatz* which has yet to be introduced, this will make no direct difference regardless of the degree of approxima-tion (in the ratio of particle diameter to particle separation) which is used to specify $\mathbf{D}'_{11}$. This follows from the AD *ansatz*,

$$p^{(2)}(\mathbf{R}_1, \mathbf{R}_2, t) = V^{-1}g(R_{12})p^{(1)}(\mathbf{R}_2, t) \tag{3}$$

where $g = \exp(-\beta U(R_{12}))$ is the low concentration equilibrium radial distribution function for the particles in solution. Thus from (2) it follows that the self-diffusion correction from the $\mathbf{D}'_{11}$ term is identically zero independent of the choice of $\mathbf{D}'_{11}$. This does not imply that the results obtained by AD are valid for arbitrary $\mathbf{D}'_{11}$ however, since a level of approximation for this quantity implies a corresponding level for $\mathbf{D}_{12}$, and it is this term which then determines the degree of approximation being used.

3. Results and conclusions

In equation (2) the self-diffusion contribution is given by the first three terms while the cross-diffusion contribution is given by the last term. Note particularly that the first integral term contains the concentration dependent gradient correction which we feel must be included in the equation in order to account for the complete contribution of the self-diffusion term. Thus we require a model for $\mathbf{D}_{ij}$ which includes $\mathbf{D}'_{ii}$ at least to lowest order in $(R_0/R) = $ (particle radius/particle separation), i.e. which includes the first correction beyond the infinite dilution expression in $\mathbf{D}_{ii}$. Such results have been given by Aguirre and Murphy (1973) and Batchelor (1976). The correction to $D^0\mathbf{I}$ is of $O(R_0/R)^4$, which means we must also retain terms of comparable order in the off-diagonal terms. This will then specify the lowest order consistent model for use in equation (2). The explicit expression for $\mathbf{D}'_{11}$ need not be written here since we are going to use equation (3), in which case the term in equation (2) with $\mathbf{D}'_{11}$ (but not $\mathbf{D}'_{11}$) is identically zero. For $\mathbf{D}_{12}$ the model gives

$$\mathbf{D}_{12}(R) = \frac{1}{6\pi\eta\beta}\left[\frac{3}{4R}\left(1 + \frac{\mathbf{R}^2}{R^2}\right) + \frac{\sigma^2}{8R^3}\left(1 - \frac{3\mathbf{R}^2}{R^2}\right)\right] \tag{4}$$

with σ the sphere diameter and η the solvent viscosity. This includes a term of $O(R_0/R)^3$ not present in the model used by AD (note that whereas Aguirre and Murphy (1973) and Batchelor (1976) are in slight disagreement concerning $\mathbf{D}'_{11}$ they do agree on the expression for $\mathbf{D}_{12}$).

To see how the use of this model for $\mathbf{D}_{ij}$ would alter the results of AD we repeat their calculation for the concentration correction to the wavelength-dependent diffusion

coefficient. Using equation (4) in equation (2) with equation (3), Fourier transforming and repeating the calculations of AD we find

$$D_1(k) = 1 \cdot 5\pi\sigma\left(-\cos k\sigma + \frac{\sin k\sigma}{k\sigma}\right)D^0. \tag{5}$$

The result of AD has a numerical prefactor of π, so our result represents an enhancement effect in accordance with our earlier intuitive argument. The remaining results of AD now follow directly; in particular for small $k\sigma$ we find

$$D_{eff} = D^0(1 + 3\phi)$$

where ϕ is the volume fraction $(4\pi\sigma^3/24)c$. Other theoretical results cited by AD find the coefficient of ϕ to be around 1, AD find this exactly 2, and experiment cited by AD suggests 2·94.

The basis for the several simplifying features of the above calculation is the closure *ansatz*, (3). Note that this violates an obvious symmetry requirement and is, at best, a very rough approximation. The vanishing of the direct self-diffusion contribution in (2), which occurs here, would not take place in a system of charged spheres in the context of a similar approximation since the direct potential of interaction (screened by the solvent) is not related to the radial distribution function in so simple a fashion due to the inclusion in the latter of the shielding effects of the other particles and counter-ions. These terms will in fact contribute in lower order, $c^{1/2}$, than those considered above. Despite the fact that existing derivations of the generalized Smoluchowski equation are only valid for short-range forces, it has been used with notable success in describing charged systems (Murphy 1972).

References

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