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Self-diffusion of small molecules in colloidal systems

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Abstract: The self-diffusion of small molecules in colloidal systems is calculated using the cell model to describe the effect of varying concentration of colloidal particles. The relevant boundary conditions are found using arguments from the thermodynamics of irreversible processes. From a general description of the self-diffusion in systems with spherically symmetrical particles we derive expressions for the concentration dependence of the effective self-diffusion coefficient D^{eff} for several cases of practical importance. It is shown that when the molecule studied is strongly attracted to the particle a minimum in D^{eff} is expected around volume fraction $\Phi = 0.35$. It is also shown that the often made distinction between free and bound molecules is often problematic and a more general description is proposed. The obstruction effect generated by the excluded volume is discussed both for spherical and spheroidal systems. It is pointed out that the often used formula due to Wang ((1954) J Amer Chem Soc 76:4755) is incorrect for self-diffusion and for the obstruction factor for spheres we obtain $(1 + 0.5\ \Phi)^{-1}$. This expresion is tested both by experiments on water diffusion in systems containing latex particles and through computer simulations and it is found valid over a wide concentration range. For prolate ellipsoids the obstruction factor is not greatly different from that for spheres, while for oblate aggregates the limiting obstruction factor of 2/3 can be obtained at low concentrations. It is demonstrated that this effect can be used to distinguish between different aggregate shapes. It is also shown that the disorder present in a solution of colloidal particles leads to a decrease in the obstruction effect.

Key words: Self-diffusion, obstruction factor irreversible processes.

1. Introduction

Studies of the self-diffusion of small, solvent or solute, molecules have been extensively used to investigate colloidal systems containing polymers [1–4], polyelectrolytes [5–7], proteins [8–10], micelles, normal [11, 12] or reversed [13]. The method has also been applied to microemulsions [14, 15], liquid crystals [16, 17] and gels [18], and the self-diffusion is obviously of importance also for the study of porous media [19]. The basic idea in these studies is that the interaction between the particles, or structures, and the small molecule is reflected in the value of the diffusion coefficient. One main difficulty in the application of this technique is to find the theoretical relation between D^{eff} and molecular interactions.

The observed change in the self-diffusion of a small molecule in the colloidal system relative to the ordinary liquid can schematically be attributed to two mechanisms. The colloidal particle excludes a fraction Φ of the total volume for the diffusing molecule and this leads to a lengthening of the diffusion paths. This is often called the obstruction effect. The second factor is related to the direct specific interaction between the particle and the small molecule, which normally leads to a further decrease of D^{eff}. In practic studies of self-diffusion are usually aimed at obtaining information about this specific interaction as, for example, in determinations of solvation numbers [8, 10, 20]. In such applications it is necessary to correct for the obstruction factor using a theoretical estimate. Recently it has been demonstrated [21] that there are also cases where the obstruction factor as such contains interesting information, since it is shape dependent.

The description of the self-diffusion in colloidal systems poses considerable theoretical problems. The particles are distributed in space neither in an ordered nor in a totally random way and the actual diffusion path of a small molecule can thus be very complicated. In addition the particles diffuse themselves, albeit on a much longer timescale. the approach to these problems that is usually adopted consists of starting from the infinite dilution limit and gradually incorporating corrections due to the finite concentration of particles. In this paper we use an alternative approach based on the cell model of liquids. In this way one can derive expressions that are consistent over the entire concentration range without introducing extensive calculations.

The paper is organized so that the cell model is first discussed, then we treat the particular problems associated with a description of self-diffusion. In section 4 a general solution is obtained for spherically symmetrical systems and in the following two sections this solution is applied to the obstruction effect and models for specific interactions. In section 7 the treatment is generalized to systems with spheroidal particles and in section 8 to polydisperse systems. Finally the main conclusions are summarized.

2. The cell model

The cell model was originally devised as a theory of simple liquids [22]. In colloid and polymer chemistry it has been extensively used to describe systems with highly charged particles [23–27], where the electrostatic interactions are dominating. In this case the cell consists of one charged particle surrounded by counterions and solvent to an extent given by the total concentration. It is clear that the cell model gives a good description of the electrostatic effects over a wide concentration range [25–27]. For charged colloidal systems the cell model has also been used to describe the self-diffusion of counterions [28–34]. In this paper we follow this latter tradition and argue that the cell model is very useful for describing the self-diffusion of small molecules in colloidal and locally heterogeneous systems in general [35, 36].

In the cell model the total volume V of the system containing N colloidal particles is divided into N cells as schematically shown in figure 1. The shape of these cells is furthermore idealized to a simple form as, for example, a sphere. This results in a somewhat abstract representation of the total system in terms of cells with simple shapes. There is a considerable freedom in the choice of size and shape of the cells but there is the constraint that volumes of the cells V_i should add up to the total volume

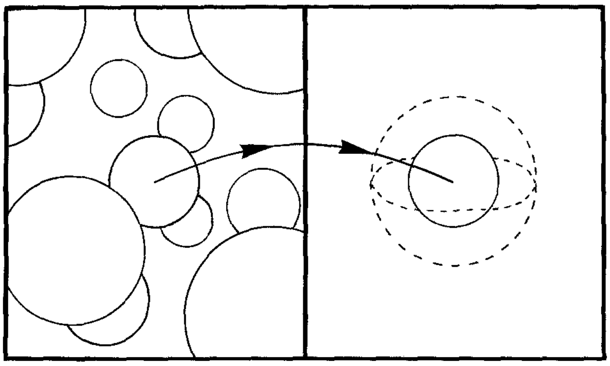

Fig. 1. Illustration of the cell model. The total volume is divided into cells each containing one particle surrounded by the medium in such a way that the sum of the cell volumes adds up to the total volume of the system. The picture shows the special case of spherical particles in spherical cells

$$V = \sum_{i=1}^{N} V_i . \tag{1}$$

This implies that the concentration dependence is modelled through the change in the size of the cells. For identical colloidal particles it is customary to make all cells identical in size but, as we discuss in more detail in the last section of the paper, it could be more appropriate to use a Poisson distribution of the sizes for noninteracting colloidal particles. However, before going into the complications associated with a polydispersity in cell size let us first discuss the monodisperse case where $V_i = V/N$ for all i.

In the same way as for the sizes there is a certain degree of arbitrariness in the choice of the shape of the cells. However, the natural procedure is to make the shape of the cell reflect the shape of the particle so that for spherical particles one has spherical cells, while for cylindrical particles the cells are cylindrical. For less symmetrical particles the choice of the shape is somewhat more problematic.

In the application of the cell model to diffusion problems a third complication arises. In the real system the colloidal particles themselves undergo a diffusional motion, while in the cell model they are treated as stationary. For many applications it is reasonable to assume that diffusive motion of the small molecule is independent of that of the colloidal particle. In such a case one has approximately for species α

$$D_\alpha(\text{total}) = D_\alpha\ (\text{fixed cell}) + D(\text{particle}). \tag{2}$$

In equation (2) we have introduced an artefact in that the motion of the particle leads to a displacement of the cell without really changing the positions of the small molecules close to the cell boundary. However, since D(particle) is normally very small the second term in equation (2) is only important when the first term is small due to a strong interaction between the molecules studied and the colloidal particle. In such a case the error is small in equation (2).

3. Self-diffusion in the cell model

In the typical self-diffusion experiment we have a system that is at equilibrium except that some molecular species has been labelled radioactively or through the nuclear spin, so that there is a gradient of the labelled molecules. Since there is a macroscopically homogeneous concentration of the molecule studied there is also a compensating gradient of the unlabelled compound. Let us denote the total concentration of the studied species as C. It will be assumed that C is constant averaged over macroscopic dimensions but C is allowed to vary locally due to the inhomogeneity generated by the colloidal particles. This means that the local concentrations of labelled molecules C_a can also vary substantially, while the relative amount of $X_a = C_a/C$ of labelled compound changes over a much larger length scale.

It is assumed that the diffusional flows J_i, local and global are described by Fick's first law in a general from

$$\vec{J}_i(\vec{r}) = -\,D(\vec{r})\,C_i(\vec{r})\,\nabla\mu_i/kT \tag{3}$$

where the local diffusion constant is scalar but varying in space. In the chemical potential μ_i we include local potentials of mean force so that equation (3) combined with the equation of continuity leads to a Smoluchowski equation.

Equation (3) provides a basic equation for the calculation of the diffusion in the cells. To obtain the globally averaged diffusion coefficient one needs a relation between the local and global diffusional properties. One way is to identify the effective macroscopic self-diffusion coefficient through the relation

$$\langle r^2 \rangle = 6D^{\text{eff}}\,t \tag{4}$$

where the root mean square displacement $\langle r^2 \rangle^{1/2}$ should be much larger than the range of the local inhomogeneities. Another alternative is to relate the average flow to the average concentration gradient

$$\langle \vec{J}_i \rangle = -\,D^{\text{eff}} \cdot \nabla \langle C_i \rangle \tag{5}$$

or for a particular direction $\vec{e}_\eta$

$$\langle \vec{J}_i \cdot \vec{e}_\eta \rangle = -\,D^{\text{eff}}_\eta \cdot \nabla_\eta \langle C_i \rangle\,. \tag{6}$$

In applying equation (5) it is necessary to make a clear distinction between the case where the concentration is counted per total volume or only per accessible volume (excluding the volume of the colloidal particles). Depending on this choice the diffusion coefficient will differ by a factor $(1 - \Phi)$ where Φ is the volume fraction of particles. Only when $\langle C_i \rangle$ is calculated relative to the total volume are the definitions of the diffusion coefficients in equations (4) and (5) equivalent. It is essential to make this distinction [18, 30] and there is a considerable confusion in the literature concerning this particular point [4, 37].

In order to apply equation (5) to the calculation of D^{eff} it is necessary to relate the average flow and the average concentration gradient to the corresponding local (cell) properties. For identical cells the macroscopic flow in the direction z is simply the average flow in the cell

$$\langle J_z \rangle = \frac{1}{V_{\text{cell}}} \int J_z\,dV = \frac{1}{V_{\text{cell}}} \int_{S_{\text{cell}}} z\vec{J}_z \cdot d\vec{S} \tag{7}$$

where the second equality is obtained for a stationary process using Gauss theorem.

It is more problematic to obtain a relation between global concentration gradient and local quantities. The basic difficulty is that the cell model is a somewhat abstract representation of the real system and there is no strict geometrical relation between the real system and the model representation. Instead of obtaining $\nabla \langle C_i \rangle$ intuitively, which is usually done, we will make a digression into irreversible thermodynamics to obtain a volume averaged quantity that can replace $\nabla \langle C_i \rangle$ for the calculation of D^{eff}. This approach was first used for transport phenomena in the cell model in reference [35].

For a transport process there exists a function, often called a Ljapunov function [38], that is minimized at the steady state. In the linear regime the entropy production $\frac{dS}{dt}$ is the proper Ljapunov function [39]. For the case of diffusional processes where equation (3) applies it is possible to find a proper Ljapunov function also outside the linear regime [40, 41] and

$$L = \int X_a X_b \sigma \, dV \tag{8}$$

is steadily decreasing as the stationary state is approached. Here $X_b = 1 - X_a$ is the relative concentration C_b/C of unlabelled compound, and σ is an entropy production density. Now the entropy production is the flow times the conjugate force so that

$$T\sigma = -\vec{J}^a \nabla \mu_a - \vec{J}^b \nabla \mu_b . \tag{9}$$

Combined with equation (3) a Gibbs-Duhem relation and $\vec{J}^a = -\vec{J}^b$ equation (9) results in

$$\begin{aligned} X_a X_b T\sigma &= \vec{J}^a \cdot (X_a X_b \nabla \mu_a + X_a^2 \nabla \mu_a) \\ &= (\vec{J}^a)^2 \cdot kT/CD \end{aligned} \tag{10}$$

The Ljapunov function for a cell may now be calculated from equations (8) and (10)

$$\begin{aligned} L_{\text{cell}} &= \int X_a X_b \sigma \, dV = k \int (\vec{J}^a)^2 / DC \, dV \\ &= -k \int \nabla \cdot \{X_a \vec{J}^a\} \, dV = -k \int_{S_{\text{cell}}} X_a \vec{J}^a \cdot d\vec{S} \end{aligned} \tag{11 a}$$

where equation (3) combined with $\nabla \cdot \vec{J}^a = 0$ has been used to obtain the third equality. Since all the cells in the macroscopic system are equal the Ljapunov function for the macroscopic system becomes

$$L = N \cdot L_{\text{cell}} = -Nk \int_{S_{\text{cell}}} X_a \vec{J}^a \cdot d\vec{S} \tag{11 b}$$

where N is the number of cells.

However, the Ljapunov function for the macroscopic system may also be written as

$$L = V \cdot k \frac{\langle \vec{J}^a \rangle^2}{D^{\text{eff}} \cdot \langle C \rangle} \tag{12}$$

where V is the volume of the system and D^{eff} the effective macroscopic diffusion coefficient. The assertion that gives an explicit formula for D^{eff} is now that the value of the Ljapunov function for the macroscopic system in the two description (11 b) and (12) shall be the same. Then combining equations (7), (11) and (12)

$$D^{\text{eff}} = -\frac{1}{\langle C \rangle \cdot V_{\text{cell}}} \frac{\left(\int_{S_{\text{cell}}} z \cdot \vec{J}^a \cdot dS \right)^2}{\int_{S_{\text{cell}}} X_a \vec{J}^a \cdot d\vec{S}} \tag{13}$$

which shows that it is sufficient to know the flow $\vec{J}^a$ and the relative concentration X_a at the border of the cell to calculate D^{eff}. These quantities are obtained through the solution of the diffusion equation for stationary states

$$\begin{aligned} \vec{\nabla} \cdot J^a = 0 &\Rightarrow \nabla(DC) \cdot \nabla X_a + DC \nabla^2 X_a = 0 \\ &\Rightarrow \nabla^2 X_a = -\nabla X_a \cdot \nabla \ln(DC) . \end{aligned} \tag{14}$$

This demonstrates that it is only the product of the local diffusion coefficient and the local total concentration $C(\vec{r})$ that determines the effective self-diffusion coefficient.

Since equation (14) is a second order differential equation two boundary conditions are needed to specify the solution. One of these follows from the requirement that the concentrations remain finite at the center of the cell, or from a requirement of zero normal flows at the surface of a totally obstructing particle. In a conventional diffusion problem the second boundary conditions follows from a specification of the concentration or the flow at the surface of the cell. However, since the cell model is an abstract representation of the real system it is not possible to find such a boundary condition in a strict way. Usually one invokes an intuitive argument [30, 33] but this can pose severe difficulties in more complex situations. To avoid these difficulties we again refer to the principles of irreversible thermodynamics and require that the boundary values are chosen so that the Ljapunov function of equation (8) is minimized under the given constraints. How this principle is applied in practice is demonstrated in the next section.

4. Spherically symmetric systems

The simplest application of the cell model is to systems with spherical symmetry containing monodisperse particles. It is then natural to choose the cells as spheres. To solve equation (14) the fraction of labelled compound $X_a(\vec{r})$ is expanded in spherical harmonics

$$X_a = \sum_{l=o}^{\infty} \sum_{m=-l}^{l} f_{lm}(r) \, Y_2^m(\Theta, \phi) . \tag{15}$$

Since the C and D only depend on r due to the spherical symmetry equation (14) reduces to an ordinary differential equation for the quantities f_{lm}

$$\frac{d}{dr}(r^2 f'_{lm}) - l(l+1) f_{lm} = -r^2 f'_{lm} \frac{d}{dr} \ln(DC) . \quad (16)$$

The flow at the surface $\vec{J}^a \cdot d\vec{S}$ can be determined once the $f_{lm}(R)$ are known

$$\vec{J}^a \cdot d\vec{S} = -D(R)\,C(R)\,R^2 \sum_{l,m} f'_{lm}(R)\,Y_l^m\,d\cos\Theta\,d\phi \quad (17)$$

and the average flow in the z-direction is

$$\langle J_z^a \rangle = -\sqrt{\frac{3}{4\pi}}\,D(R)\,C(R)\,f'_{10}(R) . \quad (18)$$

For the Ljapunov function we find

$$L = \int X_a X_b \sigma dV = kD(R)\,C(R) \sum_{l,m} f^*_{lm}(R)\,f'_{lm}(R) . \quad (19)$$

It is possible to show that

$$R^2 D(R)\,C(R)\,f^*_{lm}(R)\,f'_{lm}(R) \geq 0 \text{ all } l, m \quad (20)$$

by observing that $r^2 DC f^*_{lm}(r) f'_{lm}(r)$ is monotonically increasing with increasing r, but zero at $r = 0$. The inequality in equation (20) means that L is minimized by minimizing each term in the sum in equation (19) separately, since there are no couplings between the different terms. The only constraints are that there is a nonzero concentration and a nonzero flow so that $f_{00}, f_{10} \neq 0$, while the other f_{lm} are allowed to become zero and they are consequently chosen as zero to minimize L.

Inserting the solution for f_{lm} into the expression for D^{eff} in equation (13) gives

$$D^{\text{eff}} = D(R)\,C(R)\,U(R)/\bar{C} \quad (21)$$

where

$$U(R) \equiv r f'_{10}(r)/f_{10}(r) \quad (22)$$

satifies the differential equation

$$r \cdot \frac{dU}{dr} = 2 - U - U^2 - r \cdot U \frac{d}{dr} \{\ln(D(r)\,C(r))\} ;$$
$$U(o) = 1 \quad (23)$$

according to equation (16). An equation equivalent to equation (23) has previously been derived for the special case of ion diffusion around a charged particle (see eq. (23) of ref. [30]). In equation (23) we can insert a number of model expressions for the concentration profile $C(r)$ and the radial variation of the diffusion constant $D(r)$ and obtain the effective self diffusion constant by simply solving the first order differential equation (23) for $U(R)$ which gives D^{eff} through equation (21). In the next two sections we use this procedure for a couple of cases of particular practical importance.

5. The obstruction factor for spherical particles

When the colloid particle is obstructing the diffusion of the studied species but otherwise not influencing the concentration profile nor the local diffusion coefficient we have a case where $CD = 0$ for $r < b$ (the particle radius) and $C(r)\,D(r) = C_2 D_2$ otherwise. It is straightforward to find $U(R) = (1 - \Phi)/(1 + \Phi/2)$ observing that the flow $\vec{J}^a$ is continuous at $r = b$, and

$$D^{\text{eff}} = \frac{D_2 C_2}{\bar{C}} \frac{(1-\Phi)}{1+\Phi/2} = D_2 \frac{1}{1+\Phi/2} . \quad (24)$$

To obtain the second equality we have used the convention that the average concentration is calculated relative to the total volume. We note that the often cited expression for the obstruction effect due to Wang [8] is obtained by setting $C_2 = \bar{C}$ and linearizing the denominator. This is normally not correct when discussing the self diffusion. Expressions similar to equation (24) have a long history in connection with electromagnetic properties such as electrical permittivity, magnetic susceptibility and electrical conductivity [42–44]. The similarity between the different properties arises from the fact that they all relate to solutions of the Laplace equation, but there are differences due to the difference in boundary conditions.

Equation (24) and its counterpart for other properties is usually derived on the basis of an infinite dilution approach, but the fact that it applies reasonable well also for concentrated systems has already been discussed by Rayleigh [45]. One of the virtues of the cell model is that it is applicable over the whole concentration range. One can note that the obstruction factor $(1 + \Phi/2)^{-1}$ gives 2/3 at $\Phi = 1$ when the system is completely filled with particles. Within the physical model this is the correct limit and one can hope that equation (24) is in fact good over the total concentration range.

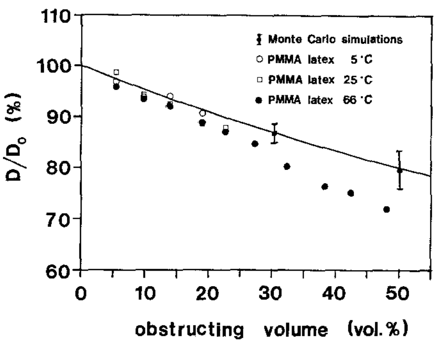

Fig. 2. The effective self-diffusion coefficient for water in a PMMA latex. The marks ○, □ and ● represent experimental values and I represents values from computer simulations. The theoretical estimation (eq. (24)) is the full drawn line

To test this supposition further the water self-diffusion was measured in a system containing reasonably monodisperse ($r \sim 100$ nm) polymethylmethacrylate latex particles by means of the NMR spin-echo pulsed field gradient method [20]. The results given in figure 2 show that up to $\Phi = 0.2$ there is a good agreement between equation (24) and the experimental value of D^{eff}/D_2. Above this concentration the measured values fall below the theoretical curve. However, this deviation is more likely to be an effect of the swelling of the particles and of a direct interaction between water and polymer segments on the particle surface rather than an effect of the approximation of the cell model. To further support this conclusion we performed a series of Monte Carlo simulations, where a test particle is performing a random walk in a face centered lattice of obstructing spheres. The effective diffusion coefficient is evaluated using equation (4) [46]. The simulated values of D^{eff} fall right on the theoretical curve. As will be shown in section 8 the effect of going to a less ordered structure is to increase D^{eff} and this effect cannot explain the difference between the theoretical estimate and the experimental points in figure 2.

6. The effect of specific interactions on the self-diffusion

Measurements of the self-diffusion are often used to study the interaction between a colloidal particle and a small molecule. The simplest model for interpreting the experimental data is based on a distinction between free and bound small molecules so that (cf. eq. (2))

$$D = P_{\text{free}} D_{\text{free}} + P_{\text{bound}} D_{\text{bound}} \,. \tag{25}$$

This model implies a strong association of the small molecule to the particle but with weaker interactions the distinction between free and bound molecules becomes problematic. For ion diffusion equations (21) and (23) have been used to interpret experimental data, but the cell model has not been used in the general case.

On the basis of equations (21) and (23) one can identify two different mechanisms affecting D^{eff}. For a constant local diffusion coefficient $D(r)$ an inhomgeneous distribution $C(r)$ gives rise to a lowering of D^{eff}. The obstruction effect discussed in the previous section gives an example of this mechanism, but it appears that it is also the basic mechanism for lowering the diffusion coefficient of monovalent ions in the presence of charged particles [31, 34]. For systems with divalent ions the picture seems more complex [33, 34]. In the other mechanism, which is often the most important one for solvent diffusion, the decrease in D^{eff} is generated by a low local value of $D(r)$. In equation (23) it is only the variation in the product $D(r) \cdot C(r)$ that determines the effective diffusion coefficient. It is consequently not always easy to distinguish between the two mechansims.

To illustrate the use of equations (21) and (23) we assume that

$$D(r)\,C(r) \begin{array}{ll} = D_1 C_1 & r < b \\ = D_2 C_2 & b < r < R \end{array} . \tag{26}$$

It is straightforward to solve equation (23) in the two regions and match the solutions at $r = b$. This leads to

$$U(R) = \frac{1 - \beta\Phi}{1 + \beta\Phi/2}\,; \quad \beta = \frac{1 - D_1 C_1/D_2 C_2}{1 + D_1 C_1/2D_2 C_2} \tag{27}$$

and

$$D^{\text{eff}} = D_2 \frac{1}{1 - (1 - C_1/C_2)\,\Phi} \, \frac{1 - \beta\Phi}{1 + \beta\Phi/2} \,. \tag{28}$$

In the limit $C_1 = 0$ this reduces to equation (24) as it should. An interesting application of equation (28) is when the studied species is highly attracted to the particle so that $D_1 C_1/D_2 C_2 \gg 1$. If D_1 and D_2 are of the same magnitude equation (28) reduces to

$$D^{\text{eff}} = D_2 \cdot \frac{1}{1 + \dfrac{C_1}{C_2} \cdot \Phi} \cdot \frac{1 + 2\Phi}{1 - \Phi} \,. \tag{29}$$

This shows that D^{eff} has a minimum around $\Phi = 0.35$. As Φ is increased above this value the diffusion within the aggregates as well as the reduction of the distance between the aggregate and the cell boundary contributes sufficiently to D^{eff} for it to increase with increasing Φ. This result has interesting applications for micellar systems of both the normal and reversed type. For example in studies of nonionic surfactant systems Nilsson et al. [47] found a minimum in D^{eff} at around $\Phi = 0.3$ for both pentaethylene glycol dodecyl ether ($C_{12}E_5$) and octaethylene glycol dodecyl ether ($C_{12}E_8$) under conditions where nearly spherical micelles are expected. Similarly for reversed micelles of Aerosol OT Stilbs and Lindman [48] found a minimum of the self diffusion at $\Phi = 0.3$–0.4. It leads too far to go into detailed interpretation of these data but we point out that there is the additional complication that the particle diffusion is not negligible so that equation (2) must also be incorporated in a full description.

To obtain a deeper understanding of the range of validity of equation (25) for the study of binding to the colloidal particle we construct a three-region model

$$\begin{aligned} &= 0 && r < b \\ D(r)\,C(r) &= D_1 C_1 && b < r < b + \Delta \\ &= D_2 C_2 && b + \Delta < r < R. \end{aligned} \tag{30}$$

Here there is an excluded region $r < b$, a binding region with D_1 small and/or C_1 large up to a small distance, Δ, outside the particle and finally an unperturbed region for $r < b + \Delta$. Also for this case it is straightforward to solve equations (21) and (23) and

$$D^{\mathrm{eff}} = P_{\mathrm{free}} D_2 \frac{1}{1 + 0.5\,\Phi_2} \frac{\Phi_2 + Y \cdot (0.5 + \Phi_2)}{\Phi_2 + Y \cdot (1 - \Phi_2)^2/(2 + \Phi_2)} \tag{31}$$

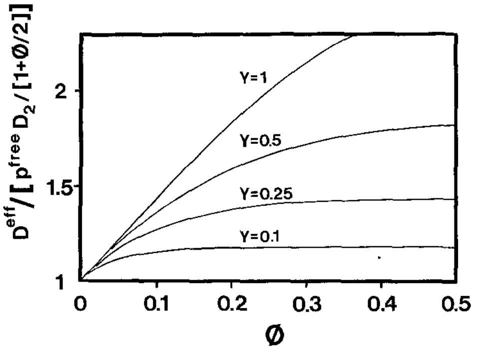

Fig. 3. The effect of the mobility of the "bound" water molecules on the effective self-diffusion coefficient of water in a system with colloidal spherical particles. $Y = 0.67 \cdot (D \cdot P)_{\mathrm{bound}}/(D \cdot P)_{\mathrm{free}}$

where

$$Y = \frac{D_1}{D_2} \cdot \frac{1}{1 + 0.5\,\Phi_1} \cdot \frac{P_{\mathrm{bound}}}{P_{\mathrm{free}}} \tag{32}$$

Φ_1 is $(b/(b + \Delta))^3$ and Φ_2 is $((b + \Delta)/R)^3$, the volume fraction inside $r = b + \Delta$. In equation (25) D_{free} is usually interpreted as $D_2/(1 + 0.5\,\Phi_2)$ and this is correct only when D_1 is small enough to make Y in equation (32) negligibly small. In figure 3 we have plotted $D^{\mathrm{eff}}/[P_{\mathrm{free}} D_2/(1 + 0.5\,\Phi)]$ assuming $\Phi_2 \approx \Phi$, as a function of the volume fraction Φ for varying values of Y. Except when Y is very small this ratio is concentration dependent. A direct application of equation (25) would then artificially give a concentration dependent P_{free}. This effect has for example, been observed for water diffusion in polyethyleneoxide and nonionic micellar solutions [20]. Although retarded by the presence of the colloidal particle the "bound" water molecule still seems to be mobile enough to contribute significantly to the diffusional flow. It can be noted that a similar physical picture emerges from a careful analysis of NMR water relaxation data [49].

7. Cells of spheroidal symmetry

When the colloidal particles are markedly dissymmetric it is no longer appropriate to use spherical cells, particularly at higher concentrations. It is then a useful generalization to consider spheroidal particles in cells of spheroidal symmetry. Consider the coordinates ξ_1, ν and ϕ defined through the relations

$$\begin{aligned} x &= a(\xi_1^2 \mp 1)^{1/2} \sin\nu \cos\phi \\ y &= a(\xi_1 \mp 1)^{1/2} \sin\nu \sin\phi \\ z &= a\,\xi_1 \cos\nu \end{aligned} \tag{33}$$

where $2a$ is the distance between the two foci of the prolate (− sign) or oblate (+ sign) ellipsoid. The diffusion problem can be solved using the same principles as in the spherically symmetrical case and the expansion of X_a in terms of spherical harmonics, equation (15), still applies with the variables r, θ, ϕ replaced by ξ_1, ν and ϕ, respectively. In the differential equation (14) for X_a we find for the r.h.s. assuming that $D * C$ only depends on ξ_1

$$\begin{aligned} &-\nabla X_a \cdot \nabla \ln(DC) \\ &= h_1^{-2} \frac{d}{d\xi_1} \ln(DC) \sum_{l,m} f_{lm}(\xi_1)\, Y_l^m(\nu, \phi) \end{aligned} \tag{34}$$

and for the l.h.s. of equation (14)

$$\nabla^2 X_a = (h_1 h_2 h_3)^{-1} \sum_{l,m} \left\{ \frac{\partial}{\partial \xi_1} \left(\frac{h_2 h_3}{h_1} f'_{lm} \right) Y_l^m + \frac{\partial}{\partial \xi_2} \left(\frac{h_2 h_3}{h_2} f_{lm} \frac{\partial Y_l^m}{\partial \xi_2} \right) + \frac{\partial^2}{\partial \phi^2} \left(\frac{h_1 h_2}{h_3} f_{lm} Y_l^m \right) \right\} \qquad (35)$$

where $\xi_2 \equiv \cos \nu$. Here the h_i are the scale factors of the coordinate transformation

$$h_1 = a \cdot \left(\frac{\xi_1^2 \mp \xi_2^2}{\xi_2^2 \mp 1} \right)^{1/2}$$

$$h_2 = a \cdot \left(\frac{\xi_1^2 \mp \xi_2^2}{1 - \xi_2^2} \right)^{1/2}$$

$$h_3 = a \cdot (\xi_1^2 \mp 1)^{1/2} (1 - \xi_2^2)^{1/2} \qquad (36)$$

where the optional minus and plus signs refer to the prolate and oblate case, respectively. Using these explicit expressions for the scale factors and the properties of spherical harmonics we arrive at

$$\nabla^2 X_a = a^{-2} (\xi_1^2 \pm \xi_2^2)^{-1} \sum_{l,m} \left\{ \frac{d}{d\xi_1} [(\xi_1^2 \pm 1) f'_{lm}] - \left[l(l+1) + \frac{-m^2}{\xi_1^2 \pm 1} \right] f_{lm} \right\} Y_l^m . \qquad (37)$$

By identifying the coefficient of the spherical harmonics in equations (34) and (37) we arrive at an ordinary differential equation for the quantities f_{lm}

$$\frac{d}{d\xi_1} [(\xi_1^2 \pm 1) f'_{lm}] = [l(l+1) \mp m^2/(\xi_1^2 \pm 1)] f_{lm} - (\xi_1^2 \pm 1) f'_{lm} \frac{d}{d\xi_1} \ln(DC) \qquad (38)$$

for all l and m. For the cases with optional signs the upper sign refers to the prolate and the lower to the oblate case. Once the f_{lm}'s have been determined through a solution of equation (38) the flow at the cell boundary is determined and

$$J^a \cdot d\vec{S} = -D(\xi_R)\, C(\xi_R)\, a(\xi_R^2 \pm 1) \sum_{l,m} f'_{lm}(\xi_R)\, Y_l^m \qquad (39)$$

where ξ_R is the value of ξ_1 at the cell boundary. Averaging over the surface of the cell leads to

$$\langle J_z^a \rangle = -D(\xi_R)\, C(\xi_R) \sqrt{\frac{3}{4\pi}}\, a^{-1} f'_{10}(\xi_R) \qquad (40\,\mathrm{a})$$

$$\langle J_x^a \rangle = D(\xi_R)\, C(\xi_R) \sqrt{\frac{3}{8\pi}}\, (a\xi_R)^{-1} (\xi_R^2 \mp 1)^{1/2} \{f'_{11}(\xi_R) - f'_{1-1}(\xi_R)\} \qquad (40\,\mathrm{b})$$

and for the Ljapunov function

$$L = \int X_a X_b \sigma dV = k D(\xi_R)\, C(\xi_R)\, a(\xi_R^2 \pm 1) \sum_{l,m} \sum f^*_{lm}(\xi_R)\, f'_{lm}(\xi_R) . \qquad (41)$$

As in the spherically symmetrical case one can show that each term in the sum in equation (41) gives a positive contribution and all f_{lm} are consequently chosen as zero except where imposed constraints require a nonzero term. In analogy with equation (21) the diffusion coefficient for the z direction is

$$D_z^{\mathrm{eff}} = D(\xi_R) \frac{C(\xi_R)}{\bar{C}} \xi_R \frac{f'_{10}(\xi_R)}{f_{10}(\xi_R)} \equiv D(\xi_R) \frac{C(\xi_R)}{\bar{C}} U_z(\xi_R) \qquad (42)$$

where U_z is determined by the differential equation

$$\xi_1 \frac{dU_z}{d\xi_1} = (1 - U_z)\,[U_z + 2\xi_1^2/(\xi_1^2 \pm 1)] - \xi_1 U \frac{d}{d\xi_1} \ln(DC) \qquad (43)$$

with $U_z = 1$ at the center of the cell. For the diffusion in the x direction an expression analogous to equation (42) is obtained but with $U_z(\xi_R)$ replaced by $U_x(\xi_R)$ determined through the equation

$$\xi_1 \frac{dU_x}{d\xi_1} = (1 - U_x)\,[1 + (1 + U_x)\,\xi_1^2/(\xi_1^2 \pm 1)] - \xi_1 U_x \frac{d}{d\xi_1} \ln(DC) . \qquad (44)$$

Due to the cylindrical symmetry $D_y^{\mathrm{eff}} = D_x^{\mathrm{eff}}$. Equations (43) and (44) can now be solved once the product $D(\xi_1)\, C(\xi_1)$ is specified.

As an illustrative example consider a case analogous to that of equation (26)

$$D(\xi_1)\,C(\xi_1) \begin{array}{ll} = D_1 C_1 & \xi_1 < \xi_b \\ = D_2 C_2 & \xi_b \le \xi_1 \le \xi_R . \end{array} \tag{45}$$

The solution of equation (43) leads to

$$U_z(\xi_R) = \frac{y - h(\xi_b) + \Phi\,\{h(\xi_R) - 1\}}{y - h(\xi_b) + \Phi\, h(\xi_R)} \tag{46}$$

where $y = D_2 C_2/(D_2 C_2 - D_1 C_1)$ and

$$h(\xi_1) = \begin{array}{l} (\xi_1^2 + 1)\left(\xi_1 \arctan \xi_1 + 1 - \dfrac{\pi}{2}\,\xi_1\right) \text{ for an oblate} \\ -\,(\xi_1^2 - 1)\left(\dfrac{\xi_1}{2} \cdot \ln \dfrac{\xi_1 - 1}{\xi_1 + 1} + 1\right) \text{ for a prolate.} \end{array} \tag{47}$$

For equation (44) the solution is

$$U_x(\xi_R) = \frac{1 - 2y - h(\xi_b) + \Phi\,[h(\xi_R) + 1]}{1 - 2y - h(\xi_b) + \Phi\,[h(\xi_R) - 1]} . \tag{48}$$

For an isotropic system the diffusion over large distances is obtained as an average

$$\begin{aligned} D^{\text{eff}} &= \frac{1}{3}\,(D_x^{\text{eff}} + D_y^{\text{eff}} + D_z^{\text{eff}}) \\ &= \frac{1}{3}\, D_2\, \frac{C(\xi_R)}{\bar{C}} \\ &\quad \left\{ 2 \cdot \frac{1 - 2y - h(\xi_b) + \Phi\,[h(\xi_R) + 1]}{1 - 2y - h(\xi_b) + \Phi\,[h(\xi_R) - 1]} \right. \\ &\quad \left. + \frac{y - h(\xi_b) + \Phi\,[h(\xi_R) - 1]}{y - h(\xi_b) + \Phi\, h(\xi_R)} \right\} . \end{aligned} \tag{49}$$

This is the explicit expression for the effective diffusion coefficient in this fairly complex geometry. When $C_1 = 0$ ($y = 1$) the obstruction effect is obtained from equation (49). The calculated dependence of the obstruction factor D^{eff}/D_2 on the volume fraction Φ is shown in figure 4. For prolate ellipsoids there is a minor decrease in the obstruction factor, while for oblate aggregates it can reach the limiting value of 2/3 even at fairly low concentrations. In figure 5 we show an example where a determination of the obstruction factor has been used to determine the shape of a micellar aggregate. The limiting value 2/3 is obtained at low concentrations strongly suggesting large disclike aggregates.

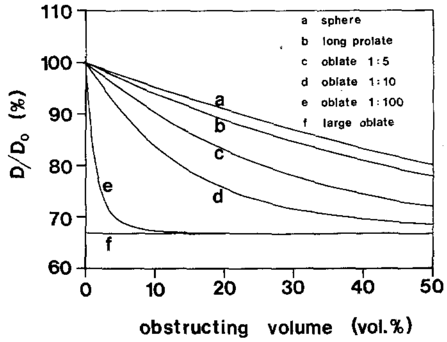

Fig. 4. The theoretical obstruction term (D/D_0) for some different particle shapes vs. the volume fraction obstructing particles

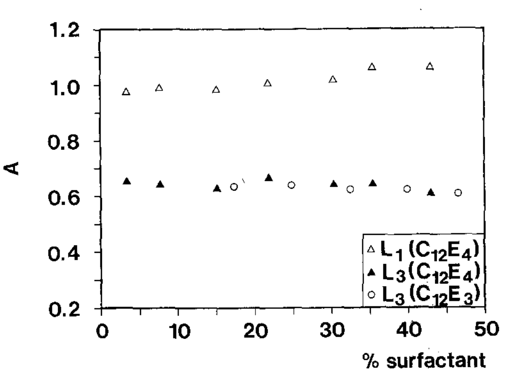

Fig. 5. The obstruction factor $A(A = D/D_0)$ in three different isotropic solutions of nonionic surfactants (see ref. [21])

As with the obstruction factor for spherical systems the problem has also been extensively studied with spheroidal aggregates. For a comprehensive review related to dielectrical properties see reference [44]. Fricke derived an equation analogous to equation (49) for conductivity, but it is applicable to the diffusion problem only for small volume fractions and they do not approach the correct limit at $\Phi = 1$. With the cell model we obtain equations that are consistent over the entire concentration range.

Another application of equation (49) is for the case of strong binding to the particles so that $C_2 \ll C_1$ and $D_2 > D_1$. Then $y \approx 0$ and there is a considerably reduced diffusion rate with a minimum at intermediate values of Φ as shown in figure 6a and 6b.

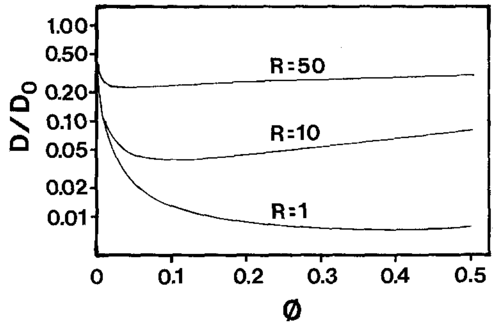

Fig. 6 a. The effective self-diffusion coefficient for a component in a colloidal system with 1000 times higher concentration in the prolate aggregate then in the surroundings. R is the axial ratio of the aggregate. The self-diffusion coefficient is assumed to be constant in the system

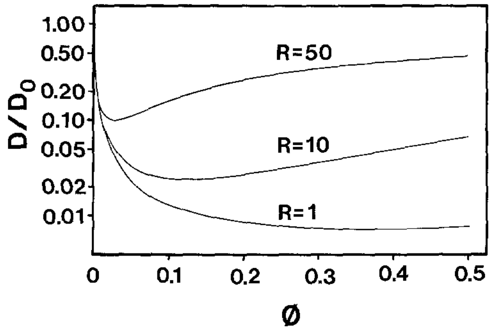

Fig. 6 b. Same as in figure 6 a except that the aggregate is oblate

8. Polydisperse systems

So far the discussion has been based on a cell model with monodisperse particles in monodisperse cells. One virtue of the approach based on irreversible thermodynamics is that the generalization to a polydisperse situation follows in a straightforward way. Assume that there is a variation in cell volume V_c and in some other parameters y with a given distribution function $n(V_c, y)$. For each cell there is a flow in the η-direction.

$$\langle \vec{J}^a \cdot \vec{e}_\eta \rangle_{\text{cell}} = f(V_c, y) \tag{50}$$

and an effective local diffusion constant

$$D_\eta^{\text{eff}}(V_c, y) = g(V_c, y)/\bar{C}. \tag{51}$$

At the present stage the function $f(V_c, y)$ is unknown, since it is not obvious how the flows in the different types of cells adjust relative to one another. The principle is again that the total Ljapunov function should be minimized under the given constraints. For each cell we have

$$\langle X_a X_b \sigma \rangle_{\text{cell}} = k f^2(V_c, y)/g(V_c, y) \tag{52}$$

using equation (11). Averaging over the total system the Ljapunov function is

$$L = \iint n(V_c, y)\, f^2(V_c, y)/g(V_c, y)\, dV_c\, dy \tag{53}$$

which should be minimized with respect to the local flows $f(V_c, y)$ under the constraint of a given total flow

$$\langle \vec{J}^a \cdot \vec{e}_\eta \rangle_{\text{total}} = \iint n(V_c, y)\, f(V_c, y)\, dV_c\, dy. \tag{54}$$

Thus the integral

$$\iint n(V_c, y) \{f^2(V_c, y)/g(V_c, y) + \lambda f(V_c, y)\}\, dV_c\, dy \tag{55}$$

should be stationary with respect to variations in f. Here λ is a undetermined Lagrangian multiplier. This leads to the Euler equation

$$n(V_c, y)\, \{2f/g + \lambda\} = 0 \tag{56}$$

and at optimum

$$f(v_c, y) = -\frac{1}{2} \lambda g(v_c, y). \tag{57}$$

Using the general formula of equation (11) and averaging over the total system we find the nearly self-evident expression

$$D_\eta^{\text{eff}} = \iint n(V_c, y)\, D(V_c, y)\, dV_c\, dy. \tag{58}$$

If one can determine the diffusion coefficient in each type of cell, i. e. $g(V_c, y)$, equation (58) gives the global self-diffusion coefficient.

As a first example consider a system with polydisperse hard spheres. If the cell volumes are chosen so that the particles occupy a constant volume fraction of the cells equation (58) gives the same as for the monodisperse case. This follows from the fact the local diffusion coefficient only depends on the volume fraction in the cell so that the average in equation (58) is trivial.

Another instructive example is obtained by considering monodisperse spherical particles but letting the cell size vary. This is one way of taking into account

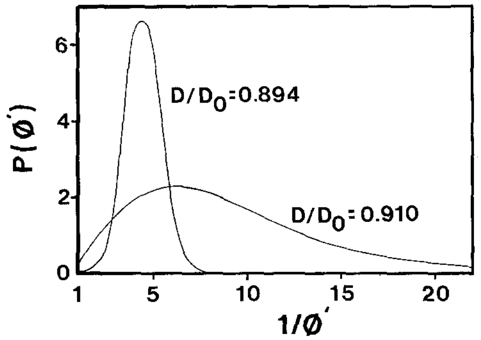

Fig. 7. The calculated obstruction factor D/D_0 for the cases of a size distribution in cell volumes but with equal size particles. The figure illustrates two distributions $n(V_c) = P(\Phi')$ where Φ' is the particle volume fraction in the particular cell. The overall particle concentration is $\Phi' = 0.25$

the positional disorder present in a real solution of colloidal particles. The result obviously depends on the assumed size distribution $n(V_c)$ but for the obstruction effect there is always an increase in D^{eff}, as illustrated in figure 7. The largest obstruction is obtained by distributing the obstruction objects regularly in space. An effect that is often seen also in every day life. However for reasonable distributions $n(V_c)$ the increase in D^{eff} is only moderate.

9. Conclusions

The self-diffusion of a small molecule in a system containing colloidal particles has been described using the cell model and the formalism of irreversible thermodynamics. The main advantages with this approach are

i) by using the cell model one obtains a description of the concentration effects that is consistent over the whole concentration range $0 < \Phi < 1$.

ii) After the identification of the proper Ljapunov function for the diffusional process, the boundary conditions at the steady state flow follow through an objective procedure.

iii) Through the Ljapunov function we obtain an objective criterion for the relation between the local diffusion and the averaged overall diffusion.

iv) For several important cases the specific characteristics of the system in terms of the potential of mean force and the local diffusion coefficient only enter into a first order differential equation (eqs. (23), (43) and (44)). Even for a complicated potential of mean force one can often find a reasonable analytical or numerical approximation for $C(r)$ so that a solution of the differential equation is feasible.

v) By using simple model expressions for $D(r)$ $C(r)$ the qualitative behaviour of the effective diffusion constant D^{eff} is revealed so that different mechanisms can be clearly illustrated.

vi) Through an explicit solution of a particular model a generalization of the often used equation (25) is obtained. It is demonstrated that when the "bound" species has a low, but non-negligible diffusion constant the use of equation (25) can lead to an artificial concentration dependence of the fraction of bound species.

vii) By solving the diffusion problem for spheroidal obstructing particles it is shown that large oblate particle can give an obstruction factor of 2/3 even at low concentrations. This effect can be used to determine aggregate shape.

viii) The treatment of a polydispersity in cell volume reveals that the maximum obstruction factor is obtained for regularly arranged spheres.

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