Theory of tracer diffusion in concentrated hard-sphere suspensions

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A phenomenological theory of diffusion and cross-diffusion of tracer particles in concentrated hard-sphere suspensions is developed within the context of Batchelor’s theory of multicomponent diffusion. Expressions for the diffusion coefficients as functions of the host particle volume fraction are obtained up to the close-packing limit. In concentrated systems the tracer diffusivity decreases because of the reduced pore space available for diffusion. Tracer diffusion, and segregation during sedimentation, ceases at a critical trapping volume fraction. The tracer diffusivity can be modelled by a Stokes-Einstein equation with an effective viscosity that depends on the pore size. The tracer cross-diffusion coefficient increases near the glass transition and diverges in the close-packed limit.

Key words: colloidal suspensions, diffusion, sedimentation

1. Introduction

In contrast to normal Brownian diffusion in liquids, tracer diffusion in complex systems such as colloidal suspensions is strongly hindered and anomalous (Wang et al. 2012; Metzler et al. 2014). Modelling such systems is challenging owing to competing nonlinear effects, including long-range viscous interactions between the tracer particles and host matrix. In this work some progress is made in the case of a hard-sphere suspension containing spherical tracer particles in the pore fluid. Batchelor (1976, 1983, 1986) solved the hydrodynamic equations describing this system in the dilute limit and obtained expressions for the diffusion coefficients to first order in the particle volume fractions. Later researchers obtained similar results starting from the Smoluchowski and Fokker-Planck equations (Zhang & Nagele 2002; Bruna & Chapman 2012) or by using thermodynamic methods (Vergara et al. 2001; Annunziata 2008), while recent efforts have employed Stokesian and molecular dynamics simulations (Wang & Brady 2015; Hannam et al. 2017). In many ‘crowded’ systems the host particles are at non-dilute volume fractions near to and above the glass transition, where long-range viscous effects and nonlinear particle-particle interactions are predominant (Wang et al. 2012; Guan et al. 2014; Sentjabrskaja et al. 2016). In order to obtain expressions for the diffusion coefficients at these high concentrations, here a phenomenological approach is used, in which nonequilibrium thermodynamics is combined with capillary flow models and empirical data.

In Section 2 the irreversible thermodynamics equations describing cross diffusion are described, and Batchelor’s theory of multicomponent diffusion is briefly reviewed. In Section 3 the equations are written in a membrane transport framework in order to obtain expressions for the diffusion coefficients in terms of experimentally convenient quantities such as the permeability and osmotic pressure. Expressions for these quantities are combined in Section 4 with Batchelor’s results to obtain the diffusion coefficients.
2. Diffusion and cross-diffusion in hard-sphere suspensions

2.1. Flux equations

From irreversible thermodynamics (deGroot & Mazur 1962; Batchelor 1986) the diffusion fluxes in a binary hard-sphere suspension can be written as

\[ J_1 = -L_{11} \nabla \mu_1 - L_{12} \nabla \mu_2, \quad (2.1a) \]
\[ J_2 = -L_{21} \nabla \mu_1 - L_{22} \nabla \mu_2, \quad (2.1b) \]

where the \( L_{ij} \) are phenomenological coefficients, \( J_i = n_i (u_i - \bar{u}) \) is the flux of \( i \) moving at average velocity \( u_i \) relative to the volume-average velocity \( \bar{u} \) of the mixture, and \( n_i \) is the concentration of \( i \) (number of particles per unit volume of mixture). If the system is not too far from equilibrium, the \( L_{ij} \) obey the Onsager relation (deGroot & Mazur 1962; Batchelor 1986)

\[ L_{12} = L_{21}. \quad (2.2) \]

In (2.1) \( \mu_i = \mu_i^0 - v_i \mu_i^0 / \nu_0 \) are effective (reduced) chemical potentials, where \( \mu_i^0 \) is the actual chemical potential per particle of component \( i \) (0 is the fluid, assumed incompressible, 1 is the host particles and 2 is the tracer particles), and \( v_i = \frac{4}{3} \pi R_i^3 \) is the volume of a particle of radius \( R_i \). When the suspending fluid is incompressible and composed of molecules that are much smaller than the hard-sphere particles, the reduced chemical potentials in a hard-sphere suspension are equivalent to the chemical potentials of a hard-sphere gas at the same volume fractions (Russel et al. 1989; Batchelor 1983; Annunziata 2008).

At constant mixture pressure \( P \) and temperature \( T \) the chemical potentials depend on the concentrations \( n_1 \) and \( n_2 \), so that

\[ \nabla \mu_1 = \mu_{11} \nabla n_1 + \mu_{12} \nabla n_2, \quad (2.3a) \]
\[ \nabla \mu_2 = \mu_{21} \nabla n_1 + \mu_{22} \nabla n_2, \quad (2.3b) \]

where \( \mu_{ij} = (\partial \mu_i / \partial n_j)_{T,P,n_k \neq j} \). Equations (2.1) can then be written as

\[ J_1 = -D_{11} \nabla n_1 - D_{12} \nabla n_2, \quad (2.4a) \]
\[ J_2 = -D_{21} \nabla n_1 - D_{22} \nabla n_2, \quad (2.4b) \]

where the diffusion coefficients \( D_{ij} \) are

\[ D_{11} = L_{11} \mu_{11} + L_{12} \mu_{21}, \quad D_{12} = L_{11} \mu_{12} + L_{12} \mu_{22}, \quad (2.5a,b) \]
\[ D_{21} = L_{21} \mu_{11} + L_{22} \mu_{21}, \quad D_{22} = L_{21} \mu_{12} + L_{22} \mu_{22}. \quad (2.5c,d) \]

Here \( D_{11} \) is the main Fickian diffusion coefficient of the host particles, while \( D_{12} \) is a cross-diffusion coefficient characterizing motion of the host particles caused by a gradient in tracer particle concentration \( \nabla n_2 \). Similarly, \( D_{22} \) is the Fickian tracer diffusivity, while \( D_{21} \) accounts for motion of the tracer particles caused by a gradient in \( n_1 \).

2.2. Batchelor’s theory

By calculating the bulk mobilities of spherical particles in a polydisperse suspension, Batchelor (1983, 1986) derived expressions for the phenomenological coefficients \( L_{ij} \) to
first order in the volume fractions \( \phi_i = \nu_i n_i \). For a bidisperse suspension in the dilute tracer limit \((\phi_2 \ll \phi_1 \ll 1)\) the \( L_{ij} \) are

\[
L_{11} = \frac{n_1}{6\pi \eta_0 R_1} \left( 1 + (K_{11} + K''_{11}) \phi_1 \right), \quad L_{12} = \frac{n_1}{6\pi \eta_0 R_1} \left( \lambda_{12}^{-3} K''_{12} \phi_2 \right), \quad (2.6a,b)
\]
\[
L_{21} = \frac{n_2}{6\pi \eta_0 R_2} \left( \lambda_{21}^{-3} K''_{21} \phi_1 \right), \quad L_{22} = \frac{n_2}{6\pi \eta_0 R_2} \left( 1 + K''_{21} \phi_1 \right), \quad (2.6c,d)
\]

where \( \eta_0 \) is the viscosity of the suspending fluid, \( \lambda_{ij} = R_j/R_i \), \( K'_{ij} = -2.5/(1 + 0.22\lambda_{ij}) \), and \( K''_{ij} = \lambda_{ij}^2/(1 + \lambda_{ij}^3) - (\lambda_{ij}^2 + 3\lambda_{ij} + 1) = \lambda_{ij}^2 K''_{ij} \).

In the dilute limit the binary hard-sphere gas chemical potentials are

\[
\mu_1 = \mu_1^0 + k_B T (\ln \phi_1 + n_{11} \phi_1 + b_{11} \phi_2), \quad \mu_2 = \mu_2^0 + k_B T (\ln \phi_2 + b_{22} \phi_2 + b_{12} \phi_1), \quad (2.7a)
\]

where \( k_B \) is Boltzmann’s constant, \( \mu_1^0 \) are constants (at constant \( T, P \)) and \( b_{ij} = (1 + \lambda_{ij}^3)^3 \) (Annunziata 2008; Santos & Rorhmann 2013). Differentiating (2.7) with respect to \( n_i \) gives

\[
\mu_{11} = k_B T (n_{1}^{-1} + \nu_1 b_{11}), \quad \mu_{12} = k_B T (n_{2}^{-1} + \nu_2 b_{22}). \quad (2.8a,b)
\]
\[
\mu_{21} = k_B T n_{1}^{-1}, \quad \mu_{22} = k_B T (n_{2}^{-1} + \nu_2 b_{22}). \quad (2.8c,d)
\]

Combining (2.8) and (2.6) with (2.5) leads to Batchelor’s expressions for the diffusion coefficients, in the limit \( \phi_2 \ll \phi_1 \ll 1 \), as

\[
D_{11} = D_1^0 (1 + 1.45 \phi_1), \quad D_{12} = D_1^0 (b_{12} + K''_{12}) \phi_1, \quad (2.9a,b)
\]
\[
D_{21} = D_2^0 (b_{21} + K''_{21}) \phi_2, \quad D_{22} = D_2^0 (1 + K''_{21} \phi_1), \quad (2.9c,d)
\]

where \( D_1^0 = k_B T/6\pi \eta_0 R_i \) is the Stokes-Einstein diffusivity of component \( i \).

3. Membrane transport formulation

Extending Batchelor’s theory to higher volume fractions of the host particles is challenging because of the difficulty of determining higher-order expressions for the phenomenological coefficients. However, progress can be made by rewriting the \( L_{ij} \) and \( \mu_{ij} \) in terms of the host-matrix permeability and osmotic pressure, for which experimental data and theoretical expressions are available.

3.1. Osmotic equilibrium

The chemical potentials can be replaced with osmotic pressures by considering the osmotic equilibrium system illustrated in figure 1. The suspension in compartment A at pressure \( P \) is in equilibrium across a semi-permeable partition with a reservoir at pressure \( p \) (compartment B) containing only the fluid and tracer particles. Compartment B is in turn in equilibrium with another reservoir (compartment C) that contains only the suspending fluid at pressure \( p_w \). At equilibrium the tracer chemical potential \( \mu_2 \) in the suspension is equal to the chemical potential \( \mu_2^w \) of the tracer particles in the reservoir, so that

\[
\mu_2 = \mu_2^w, \quad (3.1)
\]

The Gibbs-Duhem equation applied to the suspension in A is, at constant \( T \),

\[
n_1 d\mu_1 + n_2 d\mu_2 = d\Pi_T, \quad (3.2)
\]
where $\Pi_T \equiv P - p_w$ is the total osmotic pressure of the suspension. Equation (3.2) is a consequence of the analogy between hard-sphere fluids and hard-sphere suspensions, for which $\Pi_T$ plays the role of pressure (Batchelor 1983; Russel et al. 1989; Annunziata 2008). The Gibbs-Duhem equation applied to the reservoir compartment B is

$$n_r^2 \, d\mu^{\text{r}2} = d\pi,$$

(3.3)

where $\pi \equiv p - p_w$ is the tracer osmotic pressure. Combining (3.1)–(3.3) gives

$$n_1 \, d\mu^{\text{1}1} = \nabla \Pi + (1 - \alpha) \nabla \pi$$

and

$$n_2 \, d\mu^{\text{2}2} = \alpha \nabla \pi,$$

(3.5a,b)

Differentiating with respect to $n_i$ gives

$$\mu_{11} = n_1^{-1} (\Pi_1 + (1 - \alpha) \pi_1), \quad \mu_{12} = n_1^{-1} (\Pi_2 + (1 - \alpha) \pi_2),$$

$$\mu_{21} = n_2^{-1} \alpha \pi_1, \quad \mu_{22} = n_2^{-1} \alpha \pi_2,$$

(3.6a,b)

where $\Pi_1 = (\partial\Pi/\partial n_i)_{T,P,n_j \neq i}$ and $\pi_i = (\partial\pi/\partial n_i)_{T,P,n_j \neq i}$.

### 3.2. Membrane transport equations

The phenomenological coefficients $L_{ij}$ in (2.1) can be replaced with membrane transport quantities such as the host matrix permeability $k$ by making a change of independent variables from $\{n_1, n_2\}$ to the reservoir parameters $(p, n_r^2)$. Assuming $P$ is constant and that $\pi$ depends only on $n_r^2$ (isothermal incompressible fluid),

$$\nabla \Pi = -\nabla p \quad \text{and} \quad \nabla \pi = \pi_r \nabla n_r^2,$$

(3.7a,b)
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Kedem 1966),

\[ q = -\frac{k}{\eta_0} (\nabla p - \sigma \nabla \pi), \quad (3.8a) \]

\[ J = n_2^T (1 - \sigma) q - \alpha D_t \nabla n_2^T, \quad (3.8b) \]

where \( q = -J_1/n_1 = \mathbf{u} - \mathbf{u}_1 \) is the volume flux relative to the host particles and \( J = J_2 - n_2 J_1/n_1 = \alpha n_2^T (\mathbf{u}_2 - \mathbf{u}_1) \) is the tracer diffusive flux. The host matrix permeability \( k \), reflection coefficient \( \sigma \) and tracer diffusivity \( D_t \) are defined by the equations

\[ \frac{k}{\eta_0} \equiv -\left( \frac{q}{\nabla p} \right) \nabla \pi = 0, \quad \sigma \equiv \left( \frac{\nabla p}{\nabla \pi} \right) q = 0, \quad D_t \equiv \frac{\alpha}{\pi} \left( \frac{J/\alpha}{\nabla n_2^T} \right) q = 0, \quad (3.9a,b,c) \]

or, in terms of the phenomenological coefficients \( L_{ij} \),

\[ \frac{k}{\eta_0} = \frac{L_{11}}{n_1^T}, \quad \sigma = 1 - \alpha \left( 1 - \frac{L_{12} n_2}{L_{11} n_1} \right), \quad D_t = \frac{\pi}{n_2} \left( L_{22} - \frac{L_{12}^2}{L_{11}} \right). \quad (3.10a,b,c) \]

3.3. Diffusion coefficients

Inserting (3.10), (3.6) and (2.2) into (2.5) leads to

\[ D_{11} = n_1 \frac{k}{\eta_0} (\Pi_1 + \sigma \pi_1), \quad D_{12} = n_1 \frac{k}{\eta_0} (\Pi_2 + \sigma \pi_2), \quad (3.11a,b) \]

\[ D_{21} = \ell n_2 D_{11} - \gamma D_t, \quad D_{22} = \ell n_2 D_{12} + D_t, \quad (3.11c,d) \]

where \( \ell = (\sigma + \alpha - 1)/\alpha \) is a cross-diffusion factor and \( \gamma = -\pi_1/\pi_2 \) is a preferential interaction coefficient. Equations (3.11) are written in terms of the experimental quantities \( \{\Pi, \pi, k, \sigma, \alpha, D_t\} \), which replace the phenomenological coefficients and chemical potentials in (2.5). In Section 4, theoretical and semi-empirical expressions for these quantities are obtained as functions of the host-particle volume fraction \( \phi_1 \).

4. Volume fraction dependence

4.1. Host matrix permeability

In the tracer limit \( (\phi_2 \to 0) \), the permeability of the host particle matrix depends only on the volume fraction \( \phi_1 \) of the host particles (Thies-Weesie & Philipse 1994). The permeability can then be written in the form

\[ k = \frac{K}{6\pi R_1 n_1} = \frac{2R_2^2}{9\phi_1} K, \quad (4.1) \]

where \( K(\phi_1) \) is the dimensionless bulk mobility coefficient (sedimentation coefficient) of the host particle matrix (Russel et al. 1989; Peppin et al. 2005). Gilleland et al. (2011) and Fiore et al. (2018) suggest using a modified Richardson-Zaki equation

\[ K = \frac{(1 - \phi_1)^m}{1 + (6.55 - m)\phi_1}, \quad (4.2) \]

which agrees with Batchelor’s result \( K = 1 - 6.55 \phi_1 \) in the dilute limit \( \phi_1 \to 0 \) (Batchelor 1976). Choosing \( m = 3.9 \) yields a good fit to data and gives similar predictions to the Kozeny-Carman equation near close-packing (figure 2a). For spherical particles the Kozeny-Carman equation is \( k = R_1^2 (1 - \phi_1)^3/45\phi_1^2 \) (Carman 1939), so that (4.1) gives

\[ K = \frac{(1 - \phi_1)^3}{10\phi_1} \quad (4.3) \]
Figure 2. Plots of (a) the mobility function $K(\phi_1)$ and (b) the compressibility factor $Z(\phi_1)$. In (a) the data are from the sedimentation experiments of Xue et al. (1992) (circles) and Buzzacaro et al. (2008) (squares); from the numerical simulations of Ladd (1990) (stars); and from the permeation experiments of Carman (1939) (triangles). The curves in (a) are from equation (4.2) (solid) and from the Kozeny-Carman equation (4.3) (dash-dot). In (b) the data are from the sedimentation experiments of Buzzacaro et al. (2007) (stars) and the molecular dynamics simulations of Wu & Sadus (2005) (circles) and Rintoul & Torquato (1996) (diamonds). The curves are from equation (4.6) (solid), from the Carnahan-Starling equation of state (4.5) (dash-dot) and the Woodcock equation of state (dash).

as the Kozeny-Carman sedimentation coefficient (Philipse & Pathmamanoharan 1993). Equation (4.3) is plotted on figure 2a as the dash-dot curve.

4.2. Osmotic pressures

4.2.1. Host particles

Similarly to $k$, in the dilute tracer limit $\phi_2 \to 0$, the host osmotic pressure $\Pi$ depends only on $\phi_1$ (Lekkerkerker & Stroobants 1993). The osmotic pressure can then be written as

$$\Pi = n_1 k_B T Z,$$

where $Z(\phi_1)$ is the hard-sphere compressibility factor (Russel et al. 1989). Over the range $(0 < \phi_1 < 0.55)$, $Z$ is given approximately by the Carnahan-Starling equation

$$Z = \frac{1 + \phi_1 + \phi_2^2 - \phi_3^2}{(1 - \phi_1)^3},$$

(Carnahan & Starling 1969), while at higher volume fractions $Z$ diverges according to Woodcock’s equation $Z \sim (1 - \phi_1/\phi_p)^{-1}$, where $\phi_p = 0.64$ is the volume fraction at random close packing (Woodcock 1981; Russel et al. 1989; O’Hern et al. 2003). The following combined expression,

$$Z(\phi_1) = \frac{1 + 2.45\phi_1 + 2.2\phi_2^2 + 20\phi_3^3 - 41\phi_4^4}{1 - \phi_1/\phi_p},$$

agrees with the Carnahan-Starling equation as $\phi_1 \to 0$ and with the Woodcock equation as $\phi_1 \to \phi_p$. Equation (4.6) is plotted on figure 2b along with data from sedimentation experiments (Buzzacaro et al. 2007) and molecular dynamics simulations (Rintoul &...
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Torquato 1996; Wu & Sadus 2005). The first two coefficients in the numerator of equation (4.6) were determined by requiring that $Z \rightarrow 1 + 4 \phi_1$ as $\phi_1 \rightarrow 0$ (Carnahan & Starling 1969); the remaining three coefficients were treated as adjustable parameters to achieve a best fit to the data. While more exact and complex equations of state have been developed (Liu 2006; Tian et al. 2010), equation (4.6) has a relatively simple form while maintaining accuracy near $\phi_p$.

Differentiating (4.4) with respect to $n_i$ gives

$$\Pi_1 = k_B T \frac{d(\phi_1 Z)}{d\phi_1} \quad \text{and} \quad \Pi_2 = 0. \quad (4.7)$$

4.2.2. Tracer particles

Assuming the tracer concentration in the reservoir compartment B is dilute the osmotic pressure $\pi$ is

$$\pi = n_r^2 k_B T. \quad (4.8)$$

Differentiating $\pi$ with respect to $n_i$ gives, bearing in mind that $n_r^2 = n_2^2/\alpha$ and assuming $\alpha = \alpha(n_1)$ (Lekkerkerker & Stroobants 1993),

$$\pi_1 = \frac{-n_2 \alpha_1 \pi_r}{\alpha^2} \quad \text{and} \quad \pi_2 = \frac{\pi_r}{\alpha}, \quad (4.9)$$

where $\alpha_1 = (\partial \alpha/\partial n_1)_{T,P,n_2}$ and $\pi_r = (\partial \pi/\partial n_r^2)_{T,p} = k_B T$.

4.3. Equilibrium partition coefficient

The partition coefficient $\alpha$ can be obtained by equating the chemical potential of the tracer particles in the suspension and reservoir of figure 1. In the dilute limit ($\phi_2 \ll \phi_1 \ll 1$), equation (2.7b) gives the chemical potential of the tracer particles in the suspension (compartment A) as

$$\mu_2 = \mu^0_2 + k_B T (\ln \phi_2 + b_{12}\phi_1). \quad (4.10)$$

When $\phi_2^* \ll 1$ the chemical potential of the tracer particles in the reservoir is

$$\mu_r = \mu^0_2 + k_B T \ln \phi_2^*, \quad (4.11)$$

where $\phi_2^* = v_2 \phi_2$ is the tracer volume fraction in the reservoir. Equating the chemical potentials at equilibrium, $\mu_2 = \mu_r^*$, gives the partition coefficient as

$$\alpha = \frac{\phi_2}{\phi_2^*} = e^{-b_{12}\phi_1}. \quad (4.12)$$

As $\phi_1 \rightarrow 0$, (4.12) becomes

$$\alpha = 1 - b_{12}\phi_1 = 1 - v_{ex} n_1, \quad (4.13)$$

where $v_{ex} = b_{12} v_1 = \frac{4}{3} \pi (R_1 + R_2)^3$ is the volume excluded to the center of a tracer particle by a host particle. Thus in the dilute limit $\alpha$ is a measure of the free volume fraction available to the tracer particles (Lekkerkerker & Stroobants 1993; Annunziata 2008). When $R_2 \ll R_1$, $\alpha$ is equal to the void fraction $1 - \phi_1$.

4.4. Preferential interaction coefficient

The preferential interaction coefficient appearing in equation (3.11c) is

$$\gamma = -\frac{\mu_{21}}{\mu_{22}} = -\frac{\pi_1}{\pi_2} = \left( \frac{\partial n_2}{\partial n_1} \right)_{T,P,\pi}, \quad (4.14)$$

and measures the number of tracer particles that must be added to compartment A of figure 1 per added host particle, in order to maintain $\pi(n_r^2)$ constant in compartment.
For charged proteins and adsorbing colloids, $\gamma$ can be positive or negative (Schneider & Trout 2009); however, for hard-sphere systems involving only volume exclusion $\gamma$ is negative (the host particles exclude tracer particles). With equations (4.9) and (4.12) the preferential interaction coefficient $\gamma$ is

$$\gamma = n_2 \frac{\alpha_1}{\alpha} = -n_2 v_{12} = -n_2 v_{ex}. \quad (4.15)$$

Thus, for each additional host particle added to compartment A of figure 1, $n_2 v_{ex}$ tracer particles must be removed in the dilute limit to maintain osmotic equilibrium with compartment B.

### 4.5. Tortuosity and reflection coefficient

#### 4.5.1. Definition and dilute limit

The diffusive tortuosity factor $\tau$ is defined as the ratio of the tracer diffusivity $D_t$ in the suspension to the Stokes-Einstein diffusivity $D_0^2 = k_B T/6\pi R^2 \eta_0$ of a tracer particle in the pure suspending fluid:

$$\tau \equiv \frac{D_t}{D_0^2}. \quad (4.16)$$

In the dilute limit an expression for $\tau$ can be obtained using Batchelor’s equations (2.6). Equation (3.10c) combined with (2.6) and (4.8) gives in the limit $\phi_2 \ll \phi_1 \ll 1$ as

$$\tau = 1 - \tau_1 \phi_1, \quad (4.17)$$

where $\tau_1 = -K_{21}' = 2.5\lambda_{12}/(\lambda_{12} + 0.22)$. Similarly, equation (3.10b) can be combined with (4.13) and (2.6a,b) in the limit $\phi_2 \ll \phi_1 \ll 1$ to obtain

$$\sigma = \sigma_1 \phi_1, \quad (4.18)$$

where $\sigma_1 = b_{12} + K_{12}''$. Equation (4.18) shows that, because of excluded volume and long-range viscous effects, the host particles have a ‘membrane separation’ effect ($\sigma > 0$) on the tracer particles even in the dilute limit. Only when the tracer particles have negligible volume ($\lambda_{12} = R_2/R_1 \rightarrow 0$) does $\sigma$ reduce to zero. In concentrated suspensions, $\tau(\phi_1)$ and $\sigma(\phi_1)$ can be obtained using results of hindered diffusion models of tracer particles in cylindrical pores, as detailed below.

#### 4.5.2. Cylindrical pores

Expressions for $\tau$ and $\sigma$ of spherical tracer particles in cylindrical pores have been derived by Anderson & Quinn (1974) in the form

$$\tau = (1 - \lambda)^2 K_d, \quad (4.19)$$

and

$$\sigma = 1 - (1 - \lambda)^2 K_c, \quad (4.20)$$

where $K_c(\lambda)$ and $K_d(\lambda)$ are hydrodynamic factors and $\lambda = R_2/R_1$ is the ratio of tracer particle radius $R_2$ to the pore radius $R_p$. Equations (4.20) and (4.19) assume the tracer particles are equal to or smaller than the pore radius ($\lambda \leq 1$). When $\lambda > 1$, $\sigma = 1$ and $\tau = 0$ since the tracer particles in this case cannot enter the pores.

For $\lambda \leq 0.4$, Anderson & Quinn (1974) obtained $K_c = (1 + 2\lambda - \lambda^2)(1 - 2\lambda^2 - 0.163\lambda^4)$ and $K_d = 1 - 2.1\lambda + 2.09\lambda^3 - 0.95\lambda^5$. Recent finite element simulations (Oatley-Radcliffe et al. 2015), valid over the range $0 \leq \lambda \leq .98$, can be fit by the empirical equations

$$K_c = (1 + 2\lambda - \lambda^2)(1 - 0.81\lambda^2 + 0.31\lambda^4) \quad (4.21)$$
Figure 3. (a) Convective and diffusive hydrodynamic factors $K_c$ (top) and $K_d$ (bottom), respectively, plotted versus the tracer/cylindrical-pore size ratio $\lambda = R_2 / R_p$. The circles are data from finite element simulations (Oatley-Radcliffe et al. 2015); the dash-dot curves are from the theory of Anderson & Quinn (1974) (valid for $\lambda \leq 0.4$); and the solid curves are from equations (4.21) and (4.22). (b) Trapping volume fraction $\phi_1^c(\lambda_{12})$ for tracer diffusion in porous media (lower curve) and suspensions (upper curve), plotted versus the tracer/host particle size ratio $\lambda_{12} = R_2 / R_1$. The data are from Kim & Torquato (1992) (crosses), Gimel & Taco (2011) (triangles), Sung & Yethiraj (2008) (circle), Lockett & Al-Habooobly (1974) (squares) and Zaccarelli et al. (2015) (stars). (c) Porous media tortuosity factor $\tau(\phi_1)$ calculated from equation (4.25) for different values of $\lambda_{12}$. The dashed curves are from (4.25) with $K_d = 1$. The data are from Neale & Nader (1973) (circles), Kim & Torquato (1992) (crosses) Sung & Yethiraj (2008) (stars) and Gimel & Taco (2011) (triangles). (d) Porous media reflection coefficient $\sigma(\phi_1)$ for the same size ratios as in figure (c), calculated from equation (4.26). (e) Suspension tortuosity factor $\tau(\phi_1)$ calculated from equation (4.28) for several values of $\lambda_{12}$, with data from Segrè et al. (1995) (stars) and Guan et al. (2014) (circles). (f) Suspension reflection coefficient $\sigma(\phi_1)$ for the same size ratios as in figure (e), calculated from equation (4.29). The numbers next to the curves in (c-f) are the values of $\lambda_{12}$.

and

$$K_d = (1 - \lambda)^{2.2 + 0.55\lambda},$$

(4.22)
as shown on figure 3a.
4.5.3. **Porous media**

Equations (4.20)–(4.22) can be applied to porous media by noting that the approximate physical pore radius is $R_p = \epsilon / S_p (1 - \epsilon)$, where $\epsilon = 1 - \phi_1$ is the void fraction and $S_p$ is the specific surface area of the porous matrix (Carman 1939). For a matrix composed of spherical particles $S_p = 4\pi R^2_1 / 3\pi R^3_1 = 3/R_1$ (Bird et al. 2002), giving

$$\lambda_p = \frac{R_2}{R_p} = \frac{3\lambda_1 \phi_1}{(1 - \phi_1)},$$

(4.23)

In porous media there is in addition a geometric tortuosity $\tau_g$ related to the increased length of the meandering pathways tracer particles take through the pore space relative to straight cylindrical pores (Malusis et al. 2012; Ghanbarian et al. 2013). For spherical matrix particles Delgado (2006) obtains

$$\tau_g = (1 - \phi_1)^{0.4}.$$  

(4.24)

The tortuosity and reflection coefficient can then be written as

$$\tau = \begin{cases} 
\tau_g (1 - \lambda_p)^2 K_d(\lambda_p) & \text{if } 0 \leq \lambda_p \leq 1 \\
1 & \text{if } \lambda_p > 1
\end{cases}$$

(4.25)

and

$$\sigma = \begin{cases} 
1 - (1 - \lambda_p)^2 K_c(\lambda_p) & \text{if } 0 \leq \lambda_p \leq 1 \\
1 & \text{if } \lambda_p > 1
\end{cases}.$$ 

(4.26)

Figures 3c and d show $\tau$ and $\sigma$ plotted versus $\phi_1$ for several values of $\lambda_{12}$, along with experimental data for $\tau$ from Neale & Nader (1973) and numerical data from Kim & Torquato (1992), Sung & Yethiraj (2008) and Gimel & Taco (2011). As the numerical simulations did not include viscous effects, also shown on figure 3c are results from (4.25) with the hydrodynamic factor $K_d$ set to 1 (dashed curves).

In the dilute host limit ($\phi_1 \ll 1$), the pore size is large ($R_p \gg R_2$) and the host particles have little effect on the tracer diffusion, so that $\tau \to 1$ and $\sigma \to 0$. At higher matrix concentrations the pore radius $R_p$ approaches the tracer radius $R_2$ and the tracer diffusion is strongly hindered ($\tau < 1$). At a critical host volume fraction $\phi_{c1}$, $R_p = R_2$ and the particles are trapped within the pores, so that $\tau = 0$ and $\sigma = 1$. Setting $\lambda_p = 1$ in equation (4.23) gives

$$\phi_{c1} = (1 + 3\lambda_{12})^{-1},$$

(4.27)

so that $\phi_{c1} = 0.25$ when $\lambda_{12} = 1$. Figure 3b (lower curve) shows $\phi_{c1}$ plotted versus $\lambda_{12}$ along with experimental and numerical data from Kim & Torquato (1992), Sung & Yethiraj (2008) and Gimel & Taco (2011). In the case of small tracer particles ($\lambda_{12} \ll .11$ in figure 3c) the particles are hindered by the host matrix as $\phi_1$ increases, but can still diffuse throughout the pore space even up to the close-packed limit $\phi_p = 0.64$.

4.5.4. **Suspensions**

In contrast to porous media where the matrix is fixed in place, in suspensions the host particles are able to move in response to viscous and Brownian forces (Wang & Brady 2015; Bruna & Chapman 2015; Sentjabrskaja et al. 2016). Tracer particles in suspensions therefore can diffuse even when the tracer radius $R_2$ is larger than the pore size $R_p$; the host particles can adjust their positions, opening dynamic heterogeneities through which the tracer particles can pass (Rallison 1988; Kumar et al. 2006; Wang et al. 2012; Guan et al. 2014). Previously, this effect has been modelled phenomenologically by assuming the host suspension is composed of fast and slow domains having different viscosities
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(Hodgdon & Stillinger 1993; Xia & Wolynes 2001; Fan et al. 2007) or by introducing a scaling factor for the tracer radius (Kalwarczyk et al. 2014). A similar method used here is to assume the tracer particles in suspensions experience an effective diffusive pore size $R_d = c_d R_p$, where $c_d > 1$ is an empirical scaling factor to be determined. Assuming power laws for $\tau$ and $\sigma$ of the form

$$
\tau = \begin{cases} (1 - \lambda_d)^a \tau & \text{if } 0 \leq \lambda_d \leq 1 \\ 1 & \text{if } \lambda_d > 1 \end{cases} \tag{4.28}
$$

and

$$
\sigma = \begin{cases} 1 - (1 - \lambda_d)^a \sigma & \text{if } 0 \leq \lambda_d \leq 1 \\ 1 & \text{if } \lambda_d > 1 \end{cases} \tag{4.29}
$$

where

$$
\lambda_d = \frac{3 \lambda_{12} \phi_1}{c_d (1 - \phi_1)}, \tag{4.30}
$$

the exponents $a_\tau$ and $a_\sigma$ can be obtained by requiring (4.28) and (4.29) to match (4.17) and (4.18) in the limit $\phi_1 \to 0$. In this limit (4.28) and (4.29) become $\tau = 1 - 3 \lambda_{12} a_\tau \phi_1 / c_d$ and $\sigma = 3 \lambda_{12} a_\sigma \phi_1 / c_d$ giving

$$
a_\tau = \frac{\tau_1 c_d}{3 \lambda_{12}} \quad \text{and} \quad a_\sigma = \frac{\sigma_1 c_d}{3 \lambda_{12}}. \tag{4.31}
$$

A fit of (4.28) to data for the viscosity of a hard-sphere suspension (Section 6.1) gives

$$
c_d = 3 \frac{\phi_g}{(1 - \phi_g) (1 + \lambda_{12})}, \tag{4.32}
$$

where $\phi_g = 0.58$ is the volume fraction at the hard-sphere glass transition (Hunter & Weeks 2012).

The tortuosity $\tau(\phi_1)$ and reflection coefficient $\sigma(\phi_1)$ calculated from equations (4.28)–(4.32) are plotted on figure 3e,f for several values of the particle size ratio $\lambda_{12} = R_2 / R_1$, along with experimental data from Segrè et al. (1995) and Guan et al. (2014). The critical trapping volume fraction $\phi^*_c$ at which $\tau = 0$ in suspensions can be obtained by setting $\lambda_d = 1$ in (4.30) giving

$$
\phi^*_c = (1 + 3 \lambda_{12} / c_d)^{-1}. \tag{4.33}
$$

Equation (4.33) is plotted as the upper curve in figure 3b, along with estimates of $\phi^*_c$ from the data of Zaccarelli et al. (2015). In suspensions the tracer diffusion is significantly less hindered than in porous media – in the self-diffusion case $\lambda_{12} = 1$, tracer diffusion ceases at the glass transition $\phi^*_1 = 0.58$, while for porous media $\phi^*_1 = 0.25$.

4.6. Cross-diffusion factor

The cross-diffusion factor in (3.11c) is

$$
\ell = \left( \frac{\sigma + \alpha - 1}{\alpha} \right) = \frac{n_1 L_{12}}{n_2 L_{11}}, \tag{4.34}
$$

and is a measure of fluid-mediated friction interactions between the tracer and host particles. In the dilute limit ($\phi_2 \ll \phi_1 \ll 1$), equations (4.13) and (4.18) give

$$
\ell = K''_{12} \phi_1. \tag{4.35}
$$

At higher host volume fractions $\ell$ can be obtained using (4.34) with (4.29) for $\sigma(\phi_1)$ and (4.12) for $\alpha(\phi_1)$. At host volume fractions above $\phi^*_1$ where $\sigma = 1$, equation (4.34) gives $\ell = 1$. 
5. Diffusion and cross-diffusion coefficients

With the results of Section 4, equations (3.11) can be used to calculate the diffusion coefficients $D_{ij}$ as functions of $\phi_1$. In terms of dimensionless quantities, equations (3.11) can be written as

$$\hat{D}_{11} = K(\hat{\Pi}_1 + \sigma \hat{\pi}_1), \quad \hat{D}_{12} = K(\hat{\Pi}_2 + \sigma \hat{\pi}_2), \quad (5.1a,b)$$

$$\hat{D}_{21} = \hat{\ell}\hat{D}_{11} - \gamma\tau, \quad \hat{D}_{22} = \hat{\ell}\hat{D}_{12} + \tau, \quad (5.1c,d)$$

where $\hat{D}_{ij} = D_{ij}/D_0^0$, $\hat{\Pi}_i = \Pi_i/k_BT$, $\hat{\pi}_i = \pi_i/k_BT$ and $\hat{\ell} = \phi_2\ell/\phi_1\lambda_{12}$. The $\hat{D}_{ij}$ are plotted on figure 4 as functions of $\phi_1$ for the case $\phi_2 = 10^{-5}$ and $\lambda_{12} = 1$, along with experimental data and Batchelor’s equations (2.9) (dashed lines). When the tracer particles are sufficiently dilute that $\phi_2 \ll \alpha$ (corresponding via equation (4.12) to $\phi_2^* \ll 1$), then several terms involving $\phi_2$ in (3.11) can be neglected, yielding the simpler equations

$$\hat{D}_{11} = K\hat{\Pi}_1, \quad \hat{D}_{12} = K\sigma\hat{\pi}_2, \quad (5.2a,b)$$

$$\hat{D}_{21} = \hat{\ell}\hat{D}_{11} - \gamma\tau, \quad \hat{D}_{22} = \tau, \quad (5.2c,d)$$

Equations (5.2) are plotted on figure 4 as the dash-dot curves; for the case $\phi_2 = 10^{-5}$ they are nearly indistinguishable from the solid curves. If in addition $\tau \ll 1$ (crowded
host matrix), then the $\gamma\tau$ term in (5.2c) can also be neglected, so that

$$\hat{D}_{21} = \hat{\ell} \hat{D}_{11}. \quad (5.3)$$

Equation (5.3) is plotted on figure 4c as the dotted curve, which agrees with (5.2c) when $\phi_1 \gtrsim 0.5$.

The behaviour of $\hat{D}_{11}$ (figure 4a) is similar to that observed in previous works on diffusion in hard-sphere suspensions (Auzeiras et al. 1988; Peppin et al. 2006). The slope of the diffusivity curve is reduced, relative to the dilute case, at intermediate $\phi_1$ because of viscous drag, but eventually diverges as $\phi_1 \to \phi_p$ owing to the infinite repulsion between hard-sphere particles at contact (Auzeiras et al. 1988). The host particle cross-diffusion coefficient $\hat{D}_{12}$, being proportional to $\sigma$, increases with $\phi_1$ (figure 4b); viscous drag, accounted for by the mobility $K(\phi_1)$, works to reduce the value of $\hat{D}_{12}$ as $\phi_1$ approaches $\phi_p$. The tracer cross diffusion coefficient $\hat{D}_{21}$ (figure 4c) is predicted to at first decrease with $\phi_1$, even dipping below 0, owing to the cross-diffusion factor $\ell$, which is negative at low $\phi_1$ (equation (4.35)). While negative cross-diffusion coefficients have been observed experimentally (Annunziata et al. 2000), the results for $\hat{D}_{21}$ must be viewed with caution as they depend strongly on $\sigma(\phi_1)$, and without experimental data it is difficult to make firm conclusions. $\hat{D}_{21}$ is predicted to diverge as $\phi_1 \to \phi_p$, owing to the fact that $\ell \to 1$ and $\hat{D}_{11} \to \infty$ as $\phi_1 \to \phi_p$. The main Fickian tracer diffusivity $\hat{D}_{22}$ approaches zero in this limit (figure 4d), suggesting that the transport of tracer particles at concentrations near to and above the glass transition could be strongly affected by cross diffusion. The tracer diffusivity $\hat{D}_{22}(\phi_1)$ (figure 4d) decreases with $\phi_1$ because of the reduced pore space available for diffusion. For $\lambda_{12} = 1$, $\hat{D}_{22}$ approaches zero at the glass transition $\phi_1 = \phi_g$, while for $\lambda_{12} = 0.125$ $\hat{D}_{22}$ remains above zero at all volume fractions including the close packing limit $\phi_1 = \phi_p$.

Batchelor’s equations (2.9) are in good agreement with the data for $\hat{D}_{11}$ and $\hat{D}_{22}$, well beyond the dilute limit up to $\phi_1 \approx 0.45$. As $\phi_1$ approaches the glass transition $\phi_g = 0.58$ the data for $\hat{D}_{22}$ departs from Batchelor’s solution and agrees more closely with (5.1d), as shown in the inset to figure 4d. Unfortunately, no data is available for $\hat{D}_{11}$ near the glass transition, nor is any data available for the cross-diffusion coefficients in hard-sphere suspensions with which to compare equations (5.1b,c). Data for all four diffusion coefficients have been obtained for a range of polymer and protein solutions (Vergara et al. 2004; Annunziata et al. 2009). It is possible the results obtained here could be adapted to such systems by using an effective hard sphere model (Minton 2007), though this is beyond the scope of the present work.

6. Discussion

The development in Section 4 contains several approximations leading to the expressions for $\sigma$, $\tau$ and for the $D_{ij}$. While agreement with experiment for $D_{11}$ and $D_{22}$ is good, the results for $D_{12}$ and $D_{21}$ are less certain and there is a need for experimental data. Nevertheless, the expressions (3.11) for the $D_{ij}$ should hold quite generally, and the development in Section 4 can be updated as new data and theories become available. In this section the results are applied to study the breakdown of the Stokes-Einstein equation near the glass transition, to sedimentation in binary suspensions, and to the physical interpretation and measurement of the reflection coefficient $\sigma$. 
6.1. Viscosity and the Stokes-Einstein equation

When \( R_2 \gg R_1 \) (very large tracer particles) the host suspension behaves like an effective continuum within which the tracer particles diffuse. The diffusivity of a tracer particle is then given by the Stokes-Einstein equation

\[
D_t = D_{SE} = \frac{k_B T}{6 \pi R_2 \eta}, \tag{6.1}
\]

where \( \eta(\phi_1) \) is the viscosity of the host particle suspension (Sutherland 1905; Einstein 1956; Kalwarczyk et al. 2014). Equations (6.1), (4.16), (4.28) and (4.30)–(4.32) can be combined in the limit \( \lambda_{12} \to \infty \) to give

\[
\eta = \lim_{\lambda_{12} \to \infty} \frac{\eta_0}{\tau} = \eta_0 \left( 1 - \frac{\phi_1 (1 - \phi_g)}{\phi_g (1 - \phi_1)} \right)^{-\frac{2.5}{\phi_g}} \frac{\phi_g}{\phi_1}. \tag{6.2}
\]

Equation (6.2) is similar to an equation for \( \eta \) derived by Faroughi & Huber (2015), and is plotted on figure 5a along with experimental data from Segrè et al. (1995) and Russel et al. (2013). The fit is quite good, supporting equation (4.32) for the scaling factor \( c_d \).

In studies of the breakdown of the Stokes-Einstein relation the tracer diffusivity is often written in the form

\[
D_t = C \frac{k_B T}{6 \pi R_2 \eta}, \tag{6.3}
\]

where \( C = D_{SE}/D_t \) is a factor such that when \( C \neq 1 \) there is a deviation of the tracer diffusivity from the Stokes-Einstein equation (6.1) (Edward 1970; Segrè et al. 1995; Mackowiak et al. 2011). Comparing with equation (4.16) gives

\[
C = \frac{\eta_0}{\eta \tau}. \tag{6.4}
\]

Equation (6.4), with (6.2) for \( \eta \) and (4.28) for \( \tau \), is plotted on figure 5b versus \( \phi_1 \) for several values of the particle size ratio \( \lambda_{12} \), along with data from Segrè et al. (1995) for the self-diffusion case \( \lambda_{12} = 1 \). The agreement is good for \( \phi_1 < 0.4 \), providing additional support for (4.32). In the self-diffusion case \( C \) is less than 1, implying that self-diffusion is enhanced compared to Stokes-Einstein diffusion. There is a clear breakdown of the Stokes-Einstein equation (\( C \to 0 \)) as the glass transition is approached (Kumar et al. 2006; Mackowiak et al. 2011). Near the glass transition, however, the value of \( C \) is very
sensitive to the value of $\lambda_{12}$. For very small tracers ($\lambda_{12} \leq 0.01$), $\tau \approx 1$ and $C = \eta_0/\eta$ so that $D_t$ is equal to the Stokes-Einstein diffusivity of a tracer in the pure solvent, $D_t = k_B T/6\pi R_2 \eta_0$. For large tracers ($\lambda_{12} \geq 100$), $C = 1$ over nearly the whole range in $\phi_1$, failing only as $\phi_1 \to \phi_g$; equation (6.4) suggests that diffusion is reduced ($C > 1$) for large tracers near the glass transition (Mackowiak et al. 2011).

6.2. Physical interpretation of $\tau$ and $\sigma$

In general the tracer diffusivity can be written in the form

$$D_t = \frac{k_B T}{6\pi R^2 \eta_{\text{eff}}},$$

(6.5)

where $\eta_{\text{eff}} = C \eta = \eta_0/\tau$ is an effective viscosity that depends on the tracer radius and the pore size of the host matrix (Fan et al. 2007; Holyst et al. 2009; Kalwarczyk et al. 2014). Physically, $\tau = \eta_0/\eta_{\text{eff}}$ represents a dimensionless viscous drag force experienced by the tracer particles within the host matrix. For $\lambda_{12} \to 0$ (vanishingly small tracer particles or infinitely large pores) the effective viscosity is equal to the pure fluid viscosity $\eta_0$ and $\tau = 1$. As $R_2$ increases in a given host matrix the effective viscosity $\eta_{\text{eff}}$ experienced by the tracer particles also increases until, in the limit $R_2 \to \infty$, $\eta_{\text{eff}}$ is equal to the macroscopic viscosity $\eta$ of the host suspension (Kalwarczyk et al. 2014).

A physical interpretation of the colloidal reflection coefficient $\sigma$ can be obtained from equation (3.11b), which with (4.7b) can be written as

$$\sigma = \frac{D_{12}}{n_1 \pi_2 \kappa / \eta_0} = \frac{\alpha}{K} \hat{D}_{12},$$

(6.6)

so that $\sigma = \hat{D}_{12}$ in the dilute limit $\phi_2 \ll \phi_1 \ll 1$. The cross-diffusion coefficient $D_{12}$ quantifies diffusiophoresis—the flux of host particles induced by a gradient in tracer concentration (Anderson 1989; Annunziata et al. 2012). Therefore, $\sigma$ is a measure of the diffusiophoretic force exerted on the host matrix by the tracer particles in the pore space. Furthermore, combining equations (3.7a) and (3.9b) shows that

$$\sigma = -\frac{\nabla \Pi}{\nabla \pi} \bigg|_{q=0} = 0.$$  

(6.7)

Given a tracer osmotic pressure gradient $\nabla \pi$ in compartment B of figure 6, when $\sigma = 0$ the tracer particles exert no force on the host matrix and $\nabla \Pi = 0$. Conversely, when $\sigma = 1$ the entire tracer thermodynamic force $\nabla \pi$ is transferred via diffusiophoresis to the host matrix, generating an equal and opposite force $\nabla \Pi$.

6.3. Experimental measurement of $\sigma$

The reflection coefficient $\sigma(\phi_1)$ can in principle be measured using the setup illustrated in figure 6, which is similar to that studied numerically by Ariza & Puertas (2009) and used by Smit et al. (1975) for porous media. Two reservoirs, A and C, having different pressures and tracer concentrations, are placed in contact with the suspension in B across semi-permeable partitions. The tracer concentration difference $\Delta n_2$ between the reservoirs leads to a diffusive flux $J$. The pressure difference $\Delta p$ between the reservoirs is adjusted to ensure no volume flow ($q = 0$). For sufficiently small $\Delta n_2$, at steady state, $\sigma$ is then determined from equation (3.9) as $\sigma = \Delta p/\Delta \pi = \Delta p/\Delta n_2 \kappa T$. Repeating the experiment for different initial values of $\phi_1$ yields the function $\sigma(\phi_1)$.

An alternative method to obtain $\sigma$ is to measure $D_{12}$ via diffusiophoresis experiments (Annunziata et al. 2012; Anderson 1989) and use equation (6.6). It may also be possible
Figure 6. Illustration of a system for measuring the reflection coefficient $\sigma$ of a colloidal suspension. The central compartment B contains a bidisperse suspension at pressure $P$ and average host matrix volume fraction $\phi_1 = n_1 v_1$. The partition on either side of the central compartment is permeable to the fluid and tracer particles, but impermeable to the host particles. A tracer particle concentration difference $\Delta n_r^2$ is maintained between compartments A and C, causing a tracer diffusive flux $J$. A pressure difference $\Delta p$ between compartments A and C is adjusted to ensure that the volume flux $q$ is zero. Measurements of $\Delta n_r^2$ and $\Delta p$ then yield $\sigma$ via equation (3.9).

to obtain $\sigma(\phi_1)$ from tracer sedimentation experiments. As shown by Batchelor (1986), the particle fluxes in the homogeneous region of a sedimentation column are

$$n_1 u_1 = L_{11} F_1 + L_{12} F_2,$$

$$n_2 u_2 = L_{21} F_1 + L_{22} F_2,$$

where $F_i = v_i (\rho_p - \rho_f) g$ is the buoyancy force acting on particle $i$, with $\rho_p$ the particle density and $\rho_f$ the fluid density. With equations (3.10), (4.1), (4.8) and (4.16) equations (6.8) can be written in the tracer limit $\phi_2 \to 0$ as

$$u_1 = K u_1^0,$$

$$u_2 = \ell u_1 + \tau u_2^0,$$

where $u_i^0 = F_i / 6 \pi R_i \eta_0$ is the Stokes velocity of particle $i$ in the fluid. Given $\tau(\phi_1)$, measurements of $u_i$ can therefore be used to determine the cross-diffusion factor $\ell$; given $\alpha(\phi_1)$, the reflection coefficient can then be obtained from (4.34) as $\sigma = 1 - \alpha(1 - \ell)$.

It is interesting to consider the case $\phi_1 \geq \phi_1^c$, where $\tau = 0$, $\sigma = 1$ and the tracer particles are trapped in the pores (Section 4.5). Equation (4.34) gives $\ell = 1$ and (6.9b) becomes $u_2 = u_1$, so that the tracer particles are constrained to sediment at the same speed as the host particles (Kaye & Davies 1972; Lockett & Al-Habbooby 1974; Snabre et al. 2009). Figure 3b shows data for the critical trapping volume fraction at which $u_2 = u_1$ in the sedimentation experiments of Lockett & Al-Habbooby (1974) (squares). The data lie close to the lower curve in figure 3b, suggesting that the expressions for $\sigma$ and $\tau$ developed for porous media, equations (4.25) and (4.26), may be appropriate in this case rather than the suspension equations (4.28) and (4.29). This can be explained by the Peclet number, $Pe = u_1 R_1 / D_0^1$, which was approximately $10^8$ in their system (Lockett & Al-Habbooby 1974). The timescale for sedimentation of the particles was therefore much faster than the timescale for diffusive heterogeneities to appear, and the host matrix may have behaved effectively like a porous medium. It would be interesting to compare with tracer sedimentation experiments at smaller $Pe \sim 1$ to see if $\phi_1^c$ shifts toward the upper curve in figure 3b.
7. Conclusion

Equations for the diffusion and cross-diffusion coefficients $D_{ij}$ of tracer particles in hard-sphere suspensions have been obtained as functions of the host particle volume fraction $\phi_1$ and particle size ratio $\lambda_{12} = R_2/R_1$. By transforming the chemical potentials and phenomenological coefficients into more experimentally-convenient quantities such as the permeability $k$ and osmotic pressure $\Pi$, expressions have been obtained for the diffusion coefficients at volume fractions up to the close-packing limit. These expressions contain the reflection coefficient $\sigma$; a brief discussion of the physical interpretation and experimental measurement of $\sigma$ in suspensions has been included. Tracer Fickian diffusion, and segregation during sedimentation, cease at a critical trapping volume fraction $\phi_{1c}$, which depends on the effective pore size in the suspension. Cross diffusion of the tracer particles may become increasingly important relative to Fickian diffusion at volume fractions near to and above $\phi_{1c}$.


REFERENCES


Tracer diffusion


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