Multiscale modeling of colloidal dynamics in porous media including aggregation and deposition

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\textbf{Abstract}

We investigate the influence of aggregation and deposition on the colloidal dynamics in a saturated porous medium. On the pore scale, the aggregation of colloids is modeled by the Smoluchowski equation. Essentially, the colloidal mass splits into different size clusters and we treat clusters as different species involved in a diffusion–reaction mechanism. This modeling procedure allows for different material properties to be varied between the different species, specifically the diffusion rate, which changes due to size as described by the Stokes–Einstein relation, and the deposition rate. The periodic homogenization procedure is applied to obtain a macroscopic model. The resulting model is illustrated by numerical computations that capture the colloidal transport with and without aggregation.

\section{Introduction}

Colloids are particles with size from 1 to 1000 nanometers in at least one dimension. Colloidal particles play an important role in technological and biological applications, such as waste water treatment, the food industry, printing etc. The central topic of this paper is the treatment of aggregation that has been shown to be an important factor in contaminant transport \cite{34}.

A good discussion on aggregation can be found in \cite{28}. A thorough analysis of the aggregation in terms of ordinary differential equations can be found in \cite{6}.

Note that similar aggregation patterns emerge in pedestrian flows \cite{25}. Previous investigations into this topic that don't take aggregation into account can be found in \cite{17} and \cite{35}.

In this paper we study the influence of aggregation and deposition on the colloidal dynamics in a saturated porous medium. On the pore scale, we model the aggregation of colloids by means of the Smoluchowski equation. Following the Smoluchowski mechanism, the colloidal mass splits into different size clusters and we treat clusters as different species involved in a diffusion–reaction mechanism. This modeling procedure allows for different material properties to be varied between the different species, specifically the diffusion rate, which changes due to size as described by the Stokes–Einstein relation, and the deposition rate. Our main target is to upscale the overall system and detect the effect of aggregation on the effective transport coefficients. We proceed by applying the periodic homogenization asymptotics to obtain the structure of the macroscopic model and the calculation rules of all the effective coefficients. The resulting model is illustrated by numerical computations that capture the colloidal transport with and without aggregation.

The outline for the paper is as follows: In Section 2 a microscopic pore-scale model is set up for aggregation, diffusion and deposition of colloidal particles. In Section 3 the microscopic model is nondimensionalized. In Section 4 we use two-scale asymptotic expansion to obtain an equivalent macroscopic model. In Section 5 some numeric experiments are presented.

\section{Microscopic model}

The foundations of aggregation modeling were laid down in the classical work of Smoluchowski \cite{33}. A nice overview can be found in \cite{9}.

Here we assume that the colloidal population consists of identical particles, called primary particles, some of which form aggregate particles that are characterized by the number of primary particles that they contain – i.e. we have $u_i$ particles of size 1, $u_2$ particles of size 2, etc. We refer to each particle of size $i$ as a member of the $i$th species. The fundamental assumption is that aggregation is a second-order rate process, i.e. the rate of collision is proportional to concentrations of the colliding species. Thus $A_{ij}$ – the number of aggregates of size $i + j$ formed from the collision of particles of sizes $i$ and $j$ per unit
time and volume, equals:

$$A_{ij} := \gamma_{ij} u_i u_j, \quad \text{with}$$

$$\gamma_{ij} := \alpha_{ij} \beta_{ij}. \quad (1)$$

Here $\beta_{ij}$ is the collision kernel – rate constant determined by the transport mechanisms that bring the particles in close contact, while $\alpha_{ij} \in [0, 1]$ is the collision efficiency – fraction of collisions that finally form an aggregate. (Table 2)

The coefficients $\alpha_{ij}$ are determined by a combination of particle-particle interaction forces, both DLVO (i.e. double-layer repulsion and van der Waals attraction) and non-DLVO, e.g. steric interaction forces (see [8,12]).

A choice for $\alpha_{ij}$ and $\beta_{ij}$ can be found in [18]. The reaction rates, or population balances can be written as:

$$R_i(u) = \frac{1}{2} \sum_{i,j=1}^{N} \alpha_{ij} \beta_{ij} u_i u_j - u_i \sum_{i=1}^{\infty} \alpha_{ij} \beta_{ij} u_i,$$  

$$\quad (3)$$

where $u = (u_1, \ldots, u_N, \ldots)$ is the vector of concentrations for each size class.

The colloidal species $u_i$, defined in $\Omega$ (see Fig. 1), can deposit on the boundary of the solid matrix $\Gamma \subset \partial \Omega$, transforming into immobile species $v_i$, defined on $\Gamma$. This means that the colloids of different size can be present both in the bulk and on the boundary. The boundary condition for $\Gamma$ then looks like:

$$-d_i \nabla u_i \cdot n = f_i(x, u_i, v_i). \quad (4)$$

At this stage, we assume the deposition rate $f_i$ to be linear:

$$f_i(x, u_i, v_i) = a_i u_i - b_i v_i. \quad (5)$$

This resembles the structure of Henry’s law acting in the context of gas exchange at liquid interfaces [4]. The Eq. (5) closes the model, and the final system is then as follows:

$$\partial_t u_i + \nabla \cdot (-d_i \nabla u_i) = R_i(u) \quad \text{in} \ \Omega, $$

$$\partial_t v_i = a_i u_i - b_i v_i \quad \text{on} \ \Gamma, \quad (7)$$

with the boundary conditions

$$-d_i \nabla u_i \cdot n = a_i u_i - b_i v_i \quad \text{on} \ \Gamma, \quad (8)$$

$$-d_i \nabla u_i \cdot n = 0 \quad \text{on} \ \Gamma_{\nu}, \quad (9)$$

$$u_i = 0 \quad \text{on} \ \Gamma_{b}, \quad (10)$$

and the initial conditions

$$u_i(0, x) = u_{i0}(x) \quad \text{in} \ \Omega, \quad (11)$$

$$v_i(0, x) = v_{i0}(x) \quad \text{on} \ \Gamma. \quad (12)$$

2.1. Diffusivity coefficients for clusters

We take the diffusivity of the monomers $d_1$ as a baseline. All other diffusivities depend on $d_1$, in accordance with the Einstein–Stokes relation:

$$d_i = \frac{kT}{6\pi \eta r_i}. \quad (13)$$

$d_i$ in (13) are designed for diffusion of spherical particles through liquids of low Reynolds number. Note the following dependence of the aggregate radius $r_i$ on the number of monomers contained in the $i$-cluster:

$$r_i = \bar{r} r_i. \quad (14)$$

Here $d = 1/D_F$ and $D_F$ is a dimensionless parameter called the fractal dimension of the aggregate [23]. $D_F$ shows how porous the aggregate is. So a completely non-porous aggregate in three dimensions would have $D_F = 3$. Combining (13) and (14), we obtain:

$$d_i = \frac{1}{\bar{r}^2} d_1. \quad (15)$$

3. Non-dimensionalization

Let $t := \tau t$ and $x := Lx$, and $d_i := \bar{d} d_i$, and $u_i := u_0 \tilde{u}_i$, and $v_i := v_0 \tilde{v}_i$, and $a_i := a_0 \tilde{a}_i$, and $b_i := b_0 \tilde{b}_i$.

Note that we need to distinguish between $u_0$ and $v_0$ since they have different dimensions, i.e. volume and surface concentration, respectively. After substituting into (6) and (7), and dropping the tildes:

$$\partial_t \tilde{u}_i + \frac{\tau d}{2} \nabla \cdot (-d_i \nabla \tilde{u}_i) = \tau u_0 R_i(u), \quad (16)$$

$$-d_i \nabla \tilde{u}_i \cdot n = \frac{a_0 L}{d}(a_i \tilde{u}_i - b_i \tilde{v}_i), \quad (17)$$

$$\partial_t \tilde{v}_i = \tau a_i u_0 (a_i \tilde{u}_i - b_i \tilde{v}_i). \quad (18)$$

We denote $\tau \frac{d}{2}$ to be a small quantity $\varepsilon$, that is also related to the ratio of geometry scales. We choose to scale the system with $\tau := \frac{\bar{d}^2}{\bar{v}}$ – the characteristic time scale of diffusion. This leads to two other dimensionless numbers – the Thiele number $\Lambda := \frac{\bar{d}^2}{\bar{v}} \tau u_0$ and the Biot number $B_i := a_i \frac{\bar{d}^2}{\bar{v}} \frac{\nu_0}{\bar{v}_0}$. We should note that these numbers don’t have oscillations in them, i.e. they don’t depend on $\varepsilon$. The final system that we obtain is:

$$\partial_t \tilde{u}_i + \nabla \cdot (-d_i \nabla \tilde{u}_i) = \Lambda R_i(u),$$

$$-d_i \nabla \tilde{u}_i \cdot n = \varepsilon (a_i \tilde{u}_i - b_i \tilde{v}_i), \quad (19)$$

$$\partial_t \tilde{v}_i = B_i (a_i \tilde{u}_i - b_i \tilde{v}_i). \quad (20)$$
4. Derivation of the macroscopic model

The porous medium that we consider, $\Omega^\varepsilon$ is modeled as a composite
periodic structure with $\varepsilon > 0$ as a small scale parameter, which relates the
pore length scale to the domain length scale. $\Omega^\varepsilon$ is depicted in
Fig. 1. Note a periodic array of cells, where each cell is the standard cell, say $Y$, scaled by $\varepsilon$, and translated in space to cover the porous
medium. (Table 1)

For simplicity, assume that $\Omega$ is rectangular and with dimensions
such that the boundary of $\Omega$ is contained within $\Gamma^\varepsilon$. Then we can de
define:

We introduce the fast variable $y := x / \varepsilon$ and let the unknowns be represented by the following expansions:

\[
\begin{align*}
\bar{u}^\varepsilon(X) &:= u^\varepsilon_0(x, y) + \varepsilon^2 u^\varepsilon_2(x, y) + O(\varepsilon^3), \\
\hat{u}^\varepsilon(X) &:= \hat{u}_0(x, y) + \varepsilon^2 \hat{u}_2(x, y) + O(\varepsilon^3).
\end{align*}
\]

Ansatz (19) can be justified by means of the concept of two-scale convergence of Nguetseng and
alalair [1,26]. Taking into account the chain rule $\bar{\nabla} := \nabla + \varepsilon \hat{\nabla}$, we get:

\[
\nabla^\varepsilon u^\varepsilon = -\varepsilon \bar{\nabla} u^\varepsilon_0 + \varepsilon^2 \nabla^\varepsilon u^\varepsilon_2 + \varepsilon^2 \nabla^\varepsilon u^\varepsilon_0 + \varepsilon^2 \nabla^\varepsilon u^\varepsilon_2 + O(\varepsilon^3),
\]

This gives us the following diffusion term:

\[
\begin{align*}
\bar{d}^\varepsilon_y \nabla^\varepsilon u^\varepsilon &:= \varepsilon^2 \bar{d}_y \nabla^\varepsilon u^\varepsilon_0 + \varepsilon^2 \bar{d}_y \nabla^\varepsilon u^\varepsilon_1 + \varepsilon^2 \bar{d}_y \nabla^\varepsilon u^\varepsilon_2 + \varepsilon^2 \bar{d}_y \nabla^\varepsilon u^\varepsilon_3 + O(\varepsilon^3),
\end{align*}
\]

Collecting the terms with $\varepsilon^{-2}$ gives:

\[
\begin{align*}
\bar{d}_y \nabla^\varepsilon u^\varepsilon_0 &= 0.
\end{align*}
\]

Recalling that this system with periodic boundary conditions has a solution unique up to a constant, we get $u^\varepsilon_0 = u^\varepsilon_0(x)$. This means that
$\nabla^\varepsilon u^\varepsilon_0 = 0$.

The terms with $\varepsilon^{-1}$ give:

\[
\begin{align*}
\bar{d}_y \nabla^\varepsilon u^\varepsilon_1 &= -\nabla^\varepsilon d^\varepsilon_y (\bar{u}_y) \cdot \nabla^\varepsilon u^\varepsilon_0.
\end{align*}
\]

Let $w_j(y)$ solve the following cell problem:

\[
\begin{align*}
\nabla^\varepsilon \bar{d}^\varepsilon_y (\bar{u}^\varepsilon_0) w^0_j + \bar{d}^\varepsilon_y j = 0, \\
\nabla^\varepsilon \bar{d}^\varepsilon_y (\bar{u}^\varepsilon_0) w^1_j = -\nabla^\varepsilon d^\varepsilon_y (\bar{u}_y) \cdot \nabla^\varepsilon u^\varepsilon_0.
\end{align*}
\]

Using (21), we can express the first order term in (19) as:

\[
\begin{align*}
u^\varepsilon_1 (x, y) &= \nu(y) \cdot \nabla^\varepsilon u^\varepsilon_0(x) + u^\varepsilon_1(x),
\end{align*}
\]

where $u^\varepsilon_0(x)$ does not depend on $y$. Note that

\[
\begin{align*}
\nabla^\varepsilon \bar{u}^\varepsilon_1(x, y) = \nu(y) \cdot \nabla^\varepsilon u^\varepsilon_0(x).
\end{align*}
\]

The terms with $\varepsilon^0$ give:

\[
\begin{align*}
\partial_t u^\varepsilon_0 &= \bar{d}^\varepsilon_y (\nu) \Delta u^\varepsilon_0 + d^\varepsilon_y (\nu) \nabla \nu(y) \cdot \nabla^\varepsilon u^\varepsilon_0
\end{align*}
\]

Integrating over $Y$, we note that $|Y| = 1$:

\[
\begin{align*}
\partial_t u^\varepsilon_0 &= \bar{D}_y : \nabla^\varepsilon u^\varepsilon_0 - \int_\Omega d^\varepsilon_y (\nabla^\varepsilon u^\varepsilon_0 + \nabla^\varepsilon u^\varepsilon_0) \cdot n d\sigma(y) + R_0(u^\varepsilon_0).
\end{align*}
\]

The upscaled diffusion tensor read:

\[
\partial_t u^\varepsilon_0 = \bar{D}_y : \nabla^\varepsilon u^\varepsilon_0 - \int_\Omega d^\varepsilon_y (\nabla^\varepsilon u^\varepsilon_0 + \nabla^\varepsilon u^\varepsilon_0) \cdot n d\sigma(y) + R_0(u^\varepsilon_0).
\]

The boundary term in (28) can be expressed recalling the corresponsing deposition boundary condition:

\[
\begin{align*}
d^\varepsilon_y \nabla^\varepsilon u^\varepsilon_0 \cdot n &= \bar{a}^\varepsilon_0 (\nu^e) \cdot \nabla \nu(y).
\end{align*}
\]

Finally, we get that:

\[
\begin{align*}
\partial_t u^\varepsilon_0 &= \partial_x (\nabla^\varepsilon u^\varepsilon_0 + \nabla^\varepsilon u^\varepsilon_0) \cdot n = \bar{a}^\varepsilon_0 (\nu^e) \nabla \nu(y) + \bar{a}^\varepsilon_0 (\nu^e) \nabla \nu(y).
\end{align*}
\]

This means that the final upscaled equation for $u$ is:

\[
\partial_t u^\varepsilon_0 = \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_\Omega \partial_x (\bar{D}_y \nabla u^\varepsilon_0).
\]

Note that the microscopic surface exchange term leads to a macroscopic bulk term. Also, the upscaled equation for $v_j$ is:

\[
\partial_t v_j = A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0).
\]

To summarize, the macroscopic system of partial differential equations reads:

\[
\begin{align*}
\partial_t u^\varepsilon_0 &= \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_\Omega \partial_x (\bar{D}_y \nabla u^\varepsilon_0),
\end{align*}
\]

\[
\begin{align*}
\partial_t v_j &= A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0),
\end{align*}
\]

\[
\begin{align*}
\partial_t w_j &= A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0),
\end{align*}
\]

\[
\begin{align*}
\partial_t w_j &= A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0) + A_j \partial_x (\bar{D}_y \nabla u^\varepsilon_0).
\end{align*}
\]

Remark 1. If the microstructures would have been disposed in a locally periodic fashion, then the upscaled system of partial differential equations would have kept the structure obtained in the periodic

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td>Macroscopic mode notations.</td>
</tr>
<tr>
<td>$(0, T)$</td>
</tr>
<tr>
<td>$\Omega$</td>
</tr>
<tr>
<td>$\partial \Omega$</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
</tr>
<tr>
<td>$Y$</td>
</tr>
<tr>
<td>$Y_0$</td>
</tr>
<tr>
<td>$Y_1$</td>
</tr>
<tr>
<td>$\Gamma^\varepsilon$</td>
</tr>
<tr>
<td>$X^\varepsilon$</td>
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</table>

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroscopic mode notations.</td>
</tr>
<tr>
<td>$\Omega^\varepsilon_0$</td>
</tr>
<tr>
<td>$\Omega^\varepsilon$</td>
</tr>
<tr>
<td>$\Gamma^\varepsilon$</td>
</tr>
</tbody>
</table>

Fig. 2. Solutions to the cell problems that correspond to isotropic periodic geometry (Fig. 1, left). See Table 3 for the resulting effective diffusion tensor.

Fig. 3. Solutions to the cell problems that correspond to anisotropic periodic geometry (Fig. 1, right). See Table 3 for the resulting effective diffusion tensor.

Table 3
Examples of effective diffusive tensors corresponding to the first colloidal species (the monomer population) for the two choices of microstructures.

<table>
<thead>
<tr>
<th></th>
<th>Isotropic</th>
<th>Anisotropic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bar{D}_1$</td>
<td>$\begin{bmatrix} 0.75 &amp; 0.71476 \ 0.71476 &amp; 0.75 \end{bmatrix}$</td>
<td>$\begin{bmatrix} 0.817467 &amp; 0.0786338 \ 0.214942 &amp; 0.817467 \end{bmatrix}$</td>
</tr>
</tbody>
</table>

The main difference lies now in the computability of the effective coefficients.

Figs. 2 and 3 show the solutions to the cell problems (21) for the isotropic and anisotropic geometry case, respectively. The 2D solver for elliptic PDE with periodic boundary conditions needed for these periodic cell problems was implemented in C++ using deal. I1 Numerics library; see [2] for details on this platform.

Controlling the cell functions allows us also to approximate the tortuosity tensor in a direct manner, avoiding complex analytical calculations hard to justify theoretically or experimentally; compare e.g. with Ref. [11]. An example in this sense is shown in Table 3. To obtain it, we use the relation

$$\bar{D}_1 = d_1 \phi \bar{T}^*,$$

where $d_1$ is a scalar diffusion coefficient, $\phi$ is the porosity, and $\bar{T}^*$ is the tortuosity (see [5], e.g.) and the fact that for the microstructures shown in Fig. 1 we know that the porosity for the isotropic case is 0.75, while the porosity for the anisotropic case amounts to 0.85. We refer the reader to [14] for more numerical examples of multiscale investigations of anisotropy effects on transport in periodically perforated media.

As soon as the covering with microstructures lacks ergodicity and/or stationarity, such evaluations are often replaced by efforts to calculate accurate upper bounds on the prominent effective coefficients; see Ref. [24], for instance, for details in this direction.

Eq. (27) is used to calculate the corresponding tensors shown in Table 3. For more information on the upscaling of diffusion–reaction systems, we refer the reader for instance to [10] and [30]. See also [19] for an analysis of a similar diffusion–reaction system featuring an advection term based on thermal flux.

5. Simulation studies

In this section, we study how aggregation affects deposition during the transport of colloids in porous media. Within this frame we work with a reference parameter regime pointing out to the fast aggregation – slow deposition regime, that is high $\Lambda$ and low $\text{Bi}$.

We take the model from [16] as the starting point of this discussion and aim at recovering their results. We interpret all coefficients from [16] in terms of our effective coefficients obtained by the asymptotic homogenization performed in Section 4. As main task, we search for new effects coming into play due to colloids aggregation.

The model for the evolution of the single mobile colloid species $n(x, t)$ and the surface coverage of the porous matrix by the immobile colloids $\theta(x, t)$ (that corresponds to the amount of mass deposited) is as follows: Find the pair $(n, \theta)$ satisfying the balance equations

$$\partial_t n = -\nu_p \cdot \nabla n + D_h \Delta n - \frac{f}{\pi \alpha_p^2} \partial_t \theta,$$

(38)
\[ \frac{\partial}{\partial t} \theta = \pi a_c^3 \beta n B(\theta), \]  
\[ n(t, 0) = \begin{cases} n_0 & t \leq t_0, \\ 0 & t > t_0. \end{cases} \]  
\[ \frac{\partial n}{\partial y} (t, L) = 0. \]  
with the switch boundary conditions
\[ n(0, x) = 0, \]
\[ \theta(0, x) = 0, \quad x \in [0, L]. \]  
\]  
The dynamic blocking function \( B(\theta) \) in (39) accounts for the transient rate of particle deposition. As the colloids accumulate on the surface of the porous matrix, they exclude a part of the surface, limiting the amount of sites for further particle attachment.

We used the Finite Element Numerics toolbox DUNE [3] to implement a solver for the model. We use Newton method to deal with the nonlinearities in the aggregation term and in the blocking function term.

The results of the simulation with parameters as above can be seen in Fig. 4. A single-species system (38)–(43) is compared to a two-species system with a square pulse going from one side of the domain for a fixed amount of time in the first species only. The resulting breakthrough curves are plotted. It is of interest to compare the breakthrough curves for the total amount of mass going through, no matter if it’s in the form of small or large particles. As we can see, there is a perceptible difference between the two curves, being the mass for the two-species case coming in slower. This due to larger particles having higher affinity for deposition. (Table 4)

### 5.1. Simulation for dynamic blocking functions

Let us focus now our attention on a specific aspect of the deposition process, namely on the effect of the dynamic blocking functions. The context is as follows: The rate of colloidal deposition is known to go down as more particles attach themselves the favorable deposition sites of the porous matrix; see, for instance, [22] and references cited therein.

One of the choices for the blocking function in (39) corresponds to Langmuir’s molecular adsorption model [21]. It is an affine function in terms of \( \theta \), reaching the maximum of 1 when the fraction of the surface covered is zero. In other words, \( B(\cdot) \) is defined as
\[ B(\theta) := 1 - \beta \theta. \]  
\[ \frac{\partial n}{\partial y} (t, L) = 0, \]  
and initial conditions
\[ n(0, x) = 0, \]
\[ \theta(0, x) = 0, \quad x \in [0, L]. \]

For the simulations, we used the value \( \beta = 2.9 \). This corresponds to the hard sphere jamming limit \( \theta_\infty = 0.345 \), which is specific to spherical collector geometry and the experimental conditions described in [15].

A simulation example of our balance Eqs. (38)–(43) with the Langmuirian blocking function is shown in Fig. 5.

Another choice is the RSA dynamic blocking function as developed in [32]. RSA stands for “random sequential adsorption”. The RSA blocking choice is based on a third order expansion of excluded area effects and can be used for low and moderate surface coverage. Here \( B(\theta) \) is defined as:
\[ B(\theta) := 1 - 4\theta_\infty \beta \theta + 3.308(\theta_\infty \beta \theta)^2 + 1.4069(\theta_\infty \beta \theta)^3. \]  

Here, \( \theta_\infty \) is the hard sphere jamming limit. A simulation example of the balance Eqs. (38)–(43) including the RSA blocking function is shown in Fig. 6.

### 5.2. Validation of the computational approach

We point out here the convergence of the \( L^2 \) errors \( e_i^p \) and \( e_i^f \) \((i = 1, 2)\) at the final time step of Fig. 6 versus the finely refined solution; see for instance [7] for a definition of the semi-discrete norms defined on fine and coarse meshes. For five consecutive refinement levels, we focus on the bulk errors for the species \( u_1 \) and \( u_2 \) and on the interface errors for the species \( v_1 \) and \( v_2 \). Using in the calculations the reference aggregation rate, we obtain:

Now, taking into consideration the double of the reference aggregation rate, we obtain the information from Table 6.

From Tables 5 and 6 we basically read that the size of the aggregation rate does not affect the convergence rate. Similar results can be obtained for all colloidal species.
Fig. 5. The effect of the Langmuirian dynamic blocking function on the deposition (right) versus no blocking function (left). $u_1$ and $u_2$ are the breakthrough curves, while $v_1$ and $v_2$ are the concentrations of the deposited species.

Fig. 6. The effect of the RSA dynamic blocking function on the deposition (right) versus no blocking function (left). $u_1$ and $u_2$ are the breakthrough curves, while $v_1$ and $v_2$ are the concentrations of the deposited species.

Table 5
$L_2$ error w.r.t. the fine scale solution of case 1 in Fig. 4.

<table>
<thead>
<tr>
<th>Ref. level</th>
<th>$e^*_1$</th>
<th>$e^*_2$</th>
<th>$e^*_1$</th>
<th>$e^*_2$</th>
</tr>
</thead>
<tbody>
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Table 6
$L_2$ error w.r.t. the fine scale solution of case 2 in Fig. 4.

<table>
<thead>
<tr>
<th>Ref. level</th>
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<th>$e^*_2$</th>
<th>$e^*_1$</th>
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<td>5</td>
<td>0.00047736510</td>
<td>0.00128739870</td>
<td>0.00098408797</td>
<td>0.00001390174</td>
</tr>
</tbody>
</table>
Fig. 7. The effect of aggregation rates on the breakthrough curves. In the first case, the default rate of aggregation is used, in the second - it is doubled. A change of aggregation rate can be achieved by varying the concentration of salt in the suspension, according to the DLVO theory. Note the strong effect of aggregation on deposition.

Table 7

The homogenized diffusion coefficient for gradually refined mesh in Fig. 3.

<table>
<thead>
<tr>
<th>Cells</th>
<th>$d_{00}$</th>
<th>$d_{01}$</th>
<th>$d_{10}$</th>
<th>$d_{11}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2048</td>
<td>0.817467</td>
<td>0.0786338</td>
<td>0.214942</td>
<td>0.817467</td>
</tr>
<tr>
<td>8192</td>
<td>0.817209</td>
<td>0.0791351</td>
<td>0.216011</td>
<td>0.817209</td>
</tr>
<tr>
<td>32,768</td>
<td>0.817090</td>
<td>0.0793378</td>
<td>0.216440</td>
<td>0.817090</td>
</tr>
<tr>
<td>131,072</td>
<td>0.817036</td>
<td>0.0794198</td>
<td>0.216614</td>
<td>0.817036</td>
</tr>
<tr>
<td>524,288</td>
<td>0.817011</td>
<td>0.0794530</td>
<td>0.216685</td>
<td>0.817011</td>
</tr>
<tr>
<td>2,097,152</td>
<td>0.817001</td>
<td>0.0794665</td>
<td>0.216714</td>
<td>0.817001</td>
</tr>
</tbody>
</table>

We now consider the anisotropic geometry in computations with gradual grid refinement. We examine the sensitivity of the effective diffusion tensor $D_1$ corresponding to the species $u_1$. The results are shown in Table 7.

Looking at Table 7, we observe that the entries $d_{00}$, $d_{01}$, $d_{10}$ and $d_{11}$ in the effective diffusion tensor $D_1$ are rather insensitive to repeated refinements of the grid.

It is worth mentioning that the Thiele modulus corresponding to our modeling scenario is high, showing that the process is actually in its fast-reaction regime. To treat the stiffness of the problem is treated by a rescaled time stepping for the simulation is as follows: $t$ changes from 0 to 1.2 with a uniform time step 0.01. For the time stepping, DUNE’s built-in OneStepMethod class is used, that implements the method of lines, which is helpful in solving our stiff system.

6. Discussion

This paper sheds light on the transport, aggregation/flocculation, and deposition of colloidal particles in heterogeneous media. We succeeded to recover basic results obtained with previous models for (single class, single species) colloidal transport. Furthermore, our model includes information about the multi scale structure of the porous medium and demonstrates new effects attributed to flocculation, such as the occurrence of an overall decrease in the species mobility due to a higher affinity for deposition of the large size classes of colloidal species; see Fig. 7 for this effect. The simulations show that our model depends continuously on the initial data, the boundary data and the model parameters.

Extensions of this work can go at least in a threefold direction:

(i) Cf. [22], the extent of colloidal transport in groundwater is largely determined by the rate at which colloids deposit on stationary grain surfaces. The assumption of stationarity can be potentially relaxed, thus aiming to incorporate the interplay between biofilms growth and deposition and hence obtaining a better understanding of the clogging/blocking of the pores; see e.g. [27,31]. In a forthcoming publication, we will address the effect of the microscopic motion of the free interfaces on the effective transport properties of the medium using the averaging method by Lacey, cf. [20].

(ii) If repulsive forces between colloids are absent, then, under suitable chemical conditions, the deposition rate tends to increase as colloids accumulate on the grain surface. Based on [22], this enhancement of deposition kinetics is attributed to the retained particles and is generally referred to as ripening. Active repulsive forces seem to lead to a decline in the deposition kinetics. These effects could be investigated by our model, provided a suitable modifications of the fluxes responsible for the transport of colloidal species are taken into account [13].

(iii) The role of the electrolyte concentration (typically a salt, e.g. KCl) and the effect of the interplay between the electrostatic and van der Waals interactions on deposition kinetics can be studied by further developing the model. A few basic ideas on how to proceed in this case are collected, for instance, in [30].

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References