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

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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.

1. 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 [34].

A good discussion on aggregation can be found in [28]. A thorough analysis of the aggregation in terms of ordinary differential equations can be found in [6].

Note that similar aggregation patterns emerge in pedestrian flows [25]. Previous investigations into this topic that don't take aggregation into account can be found in [17] and [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.

2. Microscopic model

The foundations of aggregation modeling were laid down in the classical work of Smoluchowski [33]. A nice overview can be found in [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_1 particles of size 1, u_2 particles of size 2, etc. We refer to each particle of size i as a member of the ith 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

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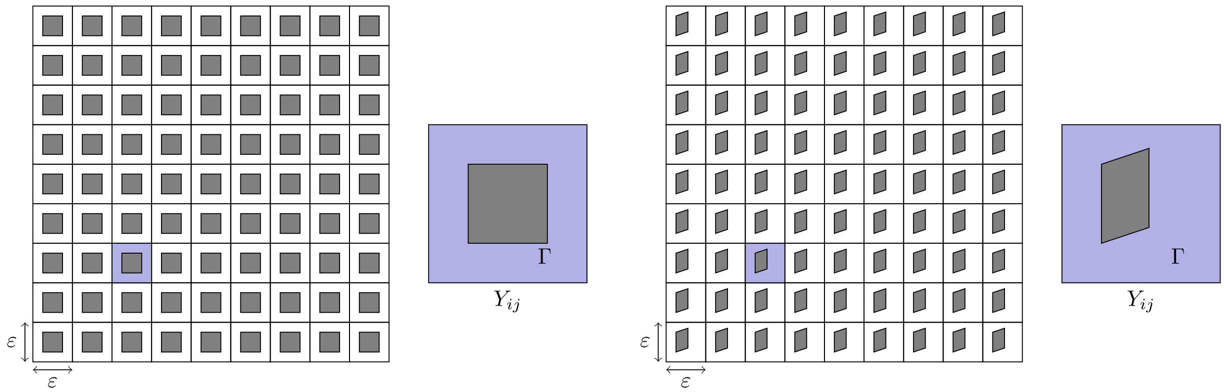

Fig. 1. Microstructure of Ω^ε (isotropic case on the left, anisotropic case on the right). Y_{ij} is the periodic cell.

time and volume, equals:

$$A_{ij} := \gamma_{ij} u_i u_j, \quad \text{with} \tag{1}$$

$$\gamma_{ij} := \alpha_{ij}\beta_{ij}. \tag{2}$$

Here β_{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 α_{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 α_{ij} and β_{ij} can be found in [18]. The reaction rates, or population balances can be written as:

$$R_i(u) = \frac{1}{2}\sum_{i+j=k} \alpha_{ij}\beta_{ij}u_i u_j - u_k \sum_{i=1}^{\infty} \alpha_{ki}\beta_{ki}u_i, \tag{3}$$

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

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

$$-d_i \nabla u_i \cdot n = F_i(x, u_i, v_i). \tag{4}$$

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

$$F_i(x, u_i, v_i) = a_i u_i - b_i v_i. \tag{5}$$

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:

$$\partial_t u_i + \nabla \cdot (-d_i \nabla u_i) = R_i(u) \quad \text{in } \Omega, \tag{6}$$

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

with the boundary conditions

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

$$-d_i \nabla u_i \cdot n = 0 \quad \text{on } \Gamma_N, \tag{9}$$

$$u_i = 0 \quad \text{on } \Gamma_D, \tag{10}$$

and the initial conditions

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

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

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:

$$d_i = \frac{kT}{6\pi\eta r_i}. \tag{13}$$

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:

$$r_i = i^d r_1. \tag{14}$$

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:

$$d_i = \frac{1}{i^d} d_1. \tag{15}$$

3. Nondimensionalization

Let $t := \tau\tilde{t}$, and $x := L\tilde{x}$, and $d_i := d\tilde{d}_i$, 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 $b_i := \frac{a_0 u_0}{v_0}\tilde{b}_i$.

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:

$$\partial_t u_i + \frac{\tau d}{L^2}\nabla \cdot (-d_i \nabla u_i) = \tau u_0 R_i(u), \tag{16}$$

$$-d_i \nabla u_i \cdot n = \frac{a_0 L}{d}(a_i u_i - b_i v_i), \tag{17}$$

$$\partial_t v_i = \frac{\tau a_0}{v_0} u_0 (a_i u_i - b_i v_i). \tag{18}$$

We denote $\frac{a_0 L}{d}$ to be a small quantity ε, that is also related to the ratio of geometry scales. We choose to scale the system with $\tau := \frac{L^2}{d}$ – the characteristic time scale of diffusion. This leads to two other dimensionless numbers – the Thiele number $\Lambda := \frac{L^2}{d}u_0$ and the Biot number $Bi := a_0\frac{L^2}{d}\frac{u_0}{v_0}$. We should note that these numbers don't have oscillations in them, i.e. they don't depend on ε. The final system that we obtain is:

$$\partial_t u_i + \nabla \cdot (-d_i \nabla u_i) = \Lambda R_i(u),$$
$$-d_i \nabla u_i \cdot n = \varepsilon(a_i u_i - b_i v_i),$$
$$\partial_t v_i = Bi(a_i u_i - b_i v_i).$$