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ON MODELING AND SIMULATION OF FLOCCULATION IN POROUS MEDIA

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Summary. Colloidal particles play an important role in technological and biological processes. The main issue which influences the colloidal dynamics within a porous medium, e.g., the soil, is the process of flocculation. Its accurate description in the context of advection-diffusion-reaction equations is not only of great impact since the microstructure of the porous medium depends on the attachment of flocculated particle clusters, but also because contaminant transport is strongly influenced by colloidal particles. Modern computational techniques are used to solve the aggregation-breakage equation. The solution is in turn used to estimate some parameters for the advection-diffusion equations, e.g. the diffusion coefficient.

1 INTRODUCTION

Colloids are particles with size in $[1, 1000]\, nm$ in at least one dimension. The materials that fall in this size range are fine clay particles, iron oxides, humic substances, bacteria and viruses. Natural colloids have been found in large concentrations in waters of diverse geological environments[7]. They are known to be mobile in groundwater and thus can play an important role in transport of contaminants that sorb to solid phases.

1.1 Population Balance Equations (PBE)

The foundations of aggregation modelling were laid down in the classical work of Smoluchowski[16]. 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 n_1 particles of size 1, n_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: aggregation is a second-order rate process[4], i.e. rate of collision is proportional to concentrations of the colliding species. Thus a_{ij} – the number of aggregates (of size $i+j$) formed from particles of sizes i and j per unit time and volume equals:

$$A_{ij} := \alpha_{ij}\beta_{ij}n_i n_j \tag{1}$$

Here β_{ij} is the *collision kernel* – a 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. α_{ij} are determined by *particle-particle interactions*.
$\alpha = 0$ – the particles are fully stable and no aggregation occurs.
$\alpha = 1$ – the particles are fully destabilized and every collision results in an aggregation.
α has been suggested to be of order $10^{-4} - 10^{-6}$ in natural groundwaters and $10^{-1} - 10^{0}$ in seawater[18].

From (1) it follows that the rate of change of concentration of k-sized aggregates is

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k}\alpha_{ij}\beta_{ij}n_i n_j - n_k\sum_{i=1}^{\infty}\alpha_{ij}\beta_{ki}n_i \tag{2}$$

The first term represents the gain in the k^{th} species by collisions of $i+j=k$. The second term represents the loss of k^{th} species due to collisions with others.

1.2 Transport mechanisms

The collision kernel β_{ij} is determined by a combination of three main transport mechanisms:

Perikinetic[16]:

$$\beta_{ij} := \frac{2kT}{3\mu}\frac{(d_i+d_j)^2}{d_i d_j} \tag{3}$$

Orthokinetic[16]:

$$\beta_{ij} := \frac{1}{6}G(d_i+d_j)^3 \tag{4}$$

Sedimentation[5]:

$$\beta_{ij} := \frac{\pi g}{72\mu}(\rho_s-\rho)(d_i+d_j)^3(d_i-d_j) \tag{5}$$

Here, d_i is the diameter of the i^{th} species, k is the Boltzmann constant, T is the absolute temperature, μ is the viscosity, G is the local shear rate, ρ is the density of fluid, ρ_s is the density of the aggregate, g is gravitation acceleration. Smoluchowski considered only the case of uniform laminar shear, i.e. $G = \mathrm{d}u/\mathrm{d}x$. Camp and Stein[2] have derived for a more general case a mean velocity gradient:

$$\overline{G} := \sqrt{\frac{\epsilon}{\nu}} \tag{6}$$

where ϵ is the power input per unit mass of fluid and ν is the kinematic viscosity. $\overline{G}$ can be inserted in place of G in (4).

1.3 Fractal dimension

Excepting the special case of of liquid droplets that coalesce on aggregation, forming a sphere of equivalent volume, aggregates generally have a porous structure – they take up much greater volume than the number of primary particles that constitute them.

Aggregates are recognized as *fractal objects*[14]. Due to the fractal structure of the aggregates the collision diameters are larger than that of volume-equivalent spheres. Self-similarity of the aggregate boils down to the fact that there's a power-law relationship between the size and mass of the aggregate. The collision diameter can thus be calculated as:

$$d_i = d_0 i^{\frac{1}{D_F}} \tag{7}$$

where D_F is called the fractal dimension $1 < D_F \leq 3$.
$D_F = 3$ corresponds to entirely compact aggregates, such as coalesced spheres. The lower D_F the more porous is the structure of the aggregate. Typical experimental values of D_F range from 1.8 to 2.1, depending on the transport mechanism and stability of particles.

1.4 Stability

The collision efficiency α_{ij} and its reciprocal – the stability ratio W_{ij} depend on the interaction potential $\varphi_{ij}(h)$ of particles i and j at distance h. The stability ratio was calculated by Fuchs[6]:

$$W_{ij} = 2 \int_0^\infty \frac{exp(\varphi_{ij}(h)/kT)}{(u+2)^2} du, \text{ where } \quad u = \frac{h}{d_i + d_j} \tag{8}$$

The theory of colloid stability of hydrophobic(lyophobic) colloid dispersions most commonly accepted is that proposed by Derjaguin and Landau[3] and Verway and Overbeek[20]. In this theory the total potential energy V of interaction for a two particle system is given by

$$\varphi = \varphi_R + \varphi_A, \tag{9}$$

where φ_R - the potential energy of repulsion, φ_A - the potential energy of attraction.

The potential energy of repulsion was calculated approximately by Reerink and Overbeek[15]:

$$\begin{aligned} V_R^{aa} &= 3.469 \times 10^{19} \varepsilon (kT)^2 (a\gamma^2/v^2) exp(-\tau u) \\ &= 4.62 \times 10^{-6} (a\gamma^2/v^2) exp(-\tau u) = C\, exp(-\tau u), \\ \gamma &= (e^z - 1)/(e^z + 1), \qquad z = ve\psi_\sigma/2kT, \\ \tau &= \kappa a \qquad u = H_0/a, \end{aligned} \tag{10}$$

where ε - dielectric constant, a - particle radius, v - valency,
κ - reciprocal Debye-Hückel double-layer thickness,
H_0 - particle separation, ψ_σ - Stern potential.

For repulsion between two unequal spheres of radii a and b, we take

$$V_R^{ab} = \frac{2b}{a+b} \times V_R^{aa}, \quad b > a \tag{11}$$

The potential energy of attraction for two spherical particles of equal size has been given by Hamaker[8 19]

$$V_A^{aa} = -\frac{A}{12}\left(\frac{1}{x^2+2x} + \frac{1}{x^2+2x+1} + 2ln\frac{x^2+2x}{x^2+2x+1}\right) \tag{12}$$

where $x = u/2$

A - Hamaker constant[1] which for particles of material 1 immersed in a liquid medium of material 2 is given by

$$A = (\sqrt{A_{11}} - \sqrt{A_{22}})^2 \tag{13}$$

V_A^{ab} for unequal spheres can be calculated as in (11)

Under condition $u \ll 1$, equation (12) reduces to

$$V_A^{aa} = -\frac{A}{12u} \tag{14}$$

1.5 Breakage mechanism

The discrete coagulation-fragmentation equation[17]:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum_{i+j=k} \beta_{ij} n_i n_j - n_k \sum_{i=1}^{max} \beta_{ki} n_i \tag{15}$$

$$- b_k n_k + \sum_{i=k}^{max} d_{ki} b_i n_i \tag{16}$$

where b_k - fragmentation rate of flocs of size k, d_{ki} - breakage distribution defining the volume fraction of the fragments of size k coming from i-sized particles.

[1] tabulated in[12] A9.1

2 SOLUTION OF PBE BY DISCRETIZATION

The fixed pivot approach[11] allows to use arbitrary grids, and to evaluate correctly two arbitrary moments of the distribution.
We give here a short description of this approach:
Consider the continuous aggregation-breakage PBE:

$$\begin{aligned}\frac{\partial n(v,t)}{\partial t} =& \frac{1}{2}\int_0^v \beta(v-u,u)n(v-u)n(u)du - \int_0^\infty \beta(u,v)n(u)n(v)du \\ & - b(v)n(v) + \int_v^\infty \gamma(v,u)b(u)n(u)du \end{aligned} \tag{17}$$

Integrating (17) over a discrete size interval $[v_i, v_{i+1}]$:

$$\begin{aligned}\frac{dN_i(t)}{dt} =& \frac{1}{2}\int_{v_i}^{v_{i+1}} dv \int_0^v \beta(v-u,u)n(v-u)n(u)du \\ & - \int_{v_i}^{v_{i+1}} n(v)dv \int_v^\infty \beta(u,v)n(u)n(v)du \\ & + \int_{v_i}^{v_{i+1}} dv \int_v^\infty \gamma(v,u)b(u)n(u)du - \int_{v_i}^{v_{i+1}} b(v)n(v)dv, \end{aligned} \tag{18}$$

where

$$N_i(t) = \int_{v_i}^{v_{i+1}} n(v,t)dv \tag{19}$$

A closed set of equations can be obtained by representing the r.h.s. of (18) in terms of N_i.

The resulting equations are:

$$\frac{dN_i(t)}{dt} = \sum_{\substack{k=1}}^{max}\sum_{\substack{j=k \\ x_{i-1}\leq(x_j+x_k)\leq x_{i+1}}}^{max} (1-\frac{1}{2}\delta_{jk})\phi_i^{jk}A_{jk}$$
$$-\sum_{k=1}^{max} A_{ik} + \sum_{k=i}^{max}\psi_{i,k}b_kN_k(t) - b_iN_i(t)$$
$$\phi_i^{jk} = \begin{cases} \frac{x_{i+1}-v}{x_{i+1}-x_i}, & x_i \leq (v=x_j+x_k) \leq x_{i+1} \\ \frac{v-x_{i-1}}{x_i-x_{i-1}}, & x_{i-1} \leq (v=x_j+x_k) \leq x_i \end{cases}$$
$$\psi_{i,k} = \frac{B_{i,k}^{(\xi)}x_{i+1}^{\eta} - B_{i,k}^{(\eta)}x_{i+1}^{\xi}}{x_i^{\xi}x_{i+1}^{\eta} - x_i^{\eta}x_{i+1}^{\xi}} + \frac{B_{i-1,k}^{(\xi)}x_{i-1}^{\eta} - B_{i-1,k}^{(\eta)}x_{i-1}^{\xi}}{x_i^{\xi}x_{i-1}^{\eta} - x_i^{\eta}x_{i-1}^{\xi}}$$
$$B_{i,k}^{(\xi)} = \int_{x_i}^{x_{i+1}} v^{\xi}\gamma(v,x_k)dv$$

The parameters of the method are ξ and η which determine the two moments to be preserved. In the case that we choose to preserve the zeroth and first order moments(i.e. mass and number of particles) and $x_{i+1} = 2x_i$, the method reduces to[10] that has a simpler notation that we use next.

2.1 The advection-diffusion-reaction equations

Different aggregates have varying size, which allows us to prescribe different diffusion coefficients to the species according to Einstein-Stokes relation.

The transport equation:

$$\frac{\partial u_i}{dt} = \nabla\cdot(D_i\nabla u_i - cu_i) + \sum_{j=1}^{i-2} 2^{j-i+1}\beta_{i-1,j}u_{i-1}u_j + \frac{1}{2}\beta_{i-1,i-1}u_{i-1}^2$$
$$- u_i\sum_{j=1}^{i-1} 2^{j-i}\beta_{i,j}u_j - u_i\sum_{j=i}^{i\,max}\beta_{i,j}u_j - b_iu_i + \sum_{j=i}^{i\,max} d_{i,j}b_ju_j$$

2.2 Implementation

Although the code offers the possibility to solve the fully coupled problem, the computation time can be significantly reduced by using operator splitting. Simple noniterative operator splitting method is used[13]. The spatial discretization was implemented using DUNE[1] – a numeric library for parallel computations in the field of PDEs. The code is implemented for 2-D/3-D problems and uses conformal finite elements on unstructured

grids. The aggregation-breakage ODE system is solved using CVODE library from the SUNDIALS package[9]. CVODE includes the Adams-Moulton formulas for nonstiff problems, and the Backward Differentiation Formulas (BDFs) for stiff problems.

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