Adapting particle methods to model the dynamics of concentration gradients and chemical reactivity under advective diffusive transport conditions

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ABSTRACT

Concentration organization and dynamics in heterogeneous porous media are key physical factors driving chemical reactivity. At equilibrium, reactivity depends not only on the concentration distribution but also on concentration gradients. As high and low values of concentration and concentration gradient do not superpose, we derive a transport equation for the concentration gradients and set up an adapted particle method to approach them numerically. Particles dynamically optimize their organization to provide highly accurate concentration gradients. The global strategy combining separate particle methods for the concentration and its gradient gives optimal predictions of reactivity.

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1. Introduction

Particle methods are frequently used to model transport processes in porous and fractured media [6,13,21,30]. When transport by advection largely dominates dispersion and diffusion processes, particle methods offer a relevant alternative to Eulerian methods [23,72,74]. Even though recent developments in Eulerian methods have reduced numerical diffusion issues [40,58], particle methods remain broadly appropriate to low dispersion conditions [18,59]. Particles efficiently adapt to flow structures and to local diffusive and dispersive conditions [8,49,68,69]. They can integrate exchanges between high and low flow zones with potentially sharp interfaces (e.g. fracture/matrix) [54,55] as well as chemical interactions with minerals and biofilms [5,33,64,65]. Because particles naturally resolve the multi-scale diversity of the transport conditions, they are frequently used to model flows with slight density variations processes that emerge from their collective behavior. It is the case of the upscaled dispersion also called macro-dispersion that results from the differential influence of deterministic velocity correlations and stochastic dispersive/diffusive processes [7,20,66].

Particle methods become more involved when the process of interest is driven by local interactions between particles as it is typically the case for reactions between solute species (homogeneous reactions). As reactivity is often nonlinearly sensitive to solute concentrations [3], particle methods have progressively evolved from random walk methods where independent particles are tracked following a Fokker–Planck equation [35,52,68] to meshfree methods with interacting particles carrying concentration properties [6,30,65]. Such methods provide continuous estimates of the concentration field that can be coupled numerically to chemical reactivity like any other Eulerian transport method [19,62,71]. Particle methods are

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relevant to model the chemical control of reactivity expressed in terms of concentrations but not the physical control expressed in terms of concentration gradients [23,57]. In fact, reactivity is physically controlled by the diffusive mixing of solutes of different chemical concentrations, as mixing two waters with equilibrated solute concentrations generally results in an out-of-equilibrium solution [41,60,61]. High concentration gradients thus promote diffusion, mixing and reactivity.

Particle methods are optimized to model concentration fields and not concentration gradients [23,57]. Whether independent or interacting, particles become sparser in the medium because of spreading and dilution following the overall decrease of concentrations. Particles move apart and, after some time, can no longer resolve the spatial variations of the velocity field, challenging any approximation of concentration gradients. While particle reseeding is commonly used for concentrations [6,13,21,30], we propose here a complementary strategy based on solving directly for concentration gradients instead of deriving concentration gradients from any approximation of the concentration field. Similar approaches have been studied for convective flows of slightly varying density [1].

We focus here on advection–diffusion processes in heterogeneous porous media. From the transport equation of concentrations, we derive the transport equation of concentration gradients and show how both differ (section 2). We propose adapted particle methods to solve the concentration gradients (section 3) and compare with finite difference approximations of concentration gradients (section 4). We finally show how these methods can be combined to compute reactivity rates when controlled both by concentrations and concentration gradients (section 5).

2. Transport equation of the concentration gradient

We focus here on advective and diffusive processes common in the transport of contaminants in porous media [4, 44]. In order to derive the transport equation of the concentration gradient, the gradient operator ∇ is applied to the advection–diffusion equation:

$$\nabla \left(\frac{\partial c}{\partial t} - \nabla \cdot (D\mathbf{g}) + \nabla \cdot (\mathbf{u}c) \right) = 0 \quad \text{with} \quad \mathbf{g} = \nabla c. \tag{1}$$

c is the concentration [$\mathrm{M\,L^{-3}}$], D is the diffusion coefficient [$\mathrm{L^2\,T^{-1}}$], $\mathbf{g}$ is the concentration gradient [$\mathrm{M\,L^{-4}}$] and $\mathbf{u}$ is the flow velocity [$\mathrm{L\,T^{-1}}$]. As $\nabla \wedge \mathbf{g}$ is zero and D is constant, the second term of equation (1) is given by:

$$\nabla(\nabla \cdot (D\mathbf{g})) = \nabla \cdot (\nabla(D\mathbf{g})) + \nabla \wedge (\nabla \wedge (D\mathbf{g})) = \nabla \cdot (\nabla(D\mathbf{g})). \tag{2}$$

Water flow being incompressible and irrotational in porous media, the third term of equation (1) is given by:

$$\begin{aligned} \nabla(\nabla \cdot (\mathbf{u}c)) &= \nabla((\nabla c) \cdot \mathbf{u} + (\nabla \cdot \mathbf{u})c) \\ &= (\mathbf{u} \cdot \nabla)\mathbf{g} + (\mathbf{g} \cdot \nabla)\mathbf{u} \\ &= \nabla \cdot (\mathbf{u} \otimes \mathbf{g}) + (\mathbf{g} \cdot \nabla)\mathbf{u} \end{aligned} \tag{3}$$

where $\otimes$ is the tensorial product. The substitution of the two simplifications (Eq. (2) and Eq. (3)) in equation (1) yields:

$$\frac{\partial \mathbf{g}}{\partial t} - \nabla \cdot (\nabla(D\mathbf{g})) + \nabla \cdot (\mathbf{u} \otimes \mathbf{g}) + (\mathbf{g} \cdot \nabla)\mathbf{u} = 0. \tag{4}$$

The second term of the previous equation describes the diffusion of the concentration gradient and the last two terms represent the transport of the concentration gradient by the velocity field. Three distinct effects are included. The first is the displacement of the gradient application point by the local velocity. This local velocity also induces a displacement and a distortion of concentration iso-contours. The variation of the distance between two such lines results in variations of the gradient intensity. These two effects are accounted for by the last term of equation (4). The last step consists in writing the diffusive term of equation (4) as an advective term by means of a diffusion velocity method [6,8,47,48,50]:

$$\frac{\partial \mathbf{g}}{\partial t} + \nabla \cdot ((\mathbf{u_d} + \mathbf{u}) \otimes \mathbf{g}) + (\mathbf{g} \cdot \nabla)\mathbf{u} = 0 \tag{5}$$

where $\mathbf{u_d}$ is the diffusion velocity [$\mathrm{L\,T^{-1}}$]. The transport equation of the concentration gradient (Eq. (4)) is then transformed in a purely advection equation with a source term (Eq. (5)). Particle methods are well suited to solve the pure advection equation [14,38,11]. It must be noticed that the gradient vector $\mathbf{g}$ is not affected by this transformation. Actually, the effect of the diffusion is to move the concentration iso-contours. The advection term is thus modified in order to transport the gradient application point accordingly. This operation ensures the consistency between the concentration and its gradient at any point. The expression of $\mathbf{u_d}$ is derived by means of a simple identification between equations (4) and (5):

$$\mathbf{u_d} \otimes \mathbf{g} = -\nabla(D\mathbf{g}). \tag{6}$$

It must be pointed out that the Particle Strength Exchange method can be considered as a valuable alternative to the Velocity Diffusion Method [17]. Both approaches have their advantages and drawbacks [74,6]. In our case, the main advantages of the velocity diffusion method is the straightforward inclusion of the heterogeneity of porous media in the formulation and