



A numerical framework for diffusion-controlled bimolecular-reactive systems to enforce maximum principles and the non-negative constraint



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ARTICLE INFO

Article history:

Received 18 October 2012

Received in revised form 11 June 2013

Accepted 8 July 2013

Available online 22 July 2013

Keywords:

Fast bimolecular reactions

Theory of interacting continua

Anisotropic diffusion

Rigid porous media

Non-negative constraint

Maximum principles

Convex programming

Semilinear partial differential equations

ABSTRACT

We present a novel computational framework for diffusive–reactive systems that satisfies the non-negative constraint and maximum principles on general computational grids. The governing equations for the concentration of reactants and product are written in terms of tensorial diffusion–reaction equations. We restrict our studies to fast irreversible bimolecular reactions. If one assumes that the reaction is diffusion-limited and all chemical species have the same diffusion coefficient, one can employ a linear transformation to rewrite the governing equations in terms of *invariants*, which are unaffected by the reaction. This results in two uncoupled tensorial diffusion equations in terms of these invariants, which are solved using a novel non-negative solver for tensorial diffusion-type equations. The concentrations of the reactants and the product are then calculated from invariants using algebraic manipulations. The novel aspect of the proposed computational framework is that it will always produce physically meaningful non-negative values for the concentrations of all chemical species. Several representative numerical examples are presented to illustrate the robustness, convergence, and the numerical performance of the proposed computational framework. We will also compare the proposed framework with other popular formulations. In particular, we will show that the Galerkin formulation (which is the standard single-field formulation) does not produce reliable solutions, and the reason can be attributed to the fact that the single-field formulation does not guarantee non-negative solutions. We will also show that the clipping procedure (which produces non-negative solutions but is considered as a variational crime) does not give accurate results when compared with the proposed computational framework.

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1. Introduction and motivation

Mixing of chemical species across plume boundaries has a major influence on the fate of reactive pollutants in subsurface flows. In many practical cases, the intrinsic rate of reaction is fast compared with other relevant time scales and hence the reaction may be assumed instantaneous (e.g., see Refs. [1,2]). Mixing is commonly modeled as an anisotropic Fickian diffusion process, with the effective diffusion coefficient aligned with the flow velocity (termed the longitudinal hydrodynamic dispersion coefficient) being much larger than the transverse components. Moreover, the small-scale spatial variability of

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permeability in real aquifers leads to highly heterogeneous velocity fields, which means that the principal directions of the diffusion tensor will vary in space and will not be aligned with the numerical grid. It has also been demonstrated that accurate treatment of dispersive mixing is crucial for computing the large-time spatial extent of the contaminant plume, which is a very important measure of the contaminant risk and thus of great interest to government regulators and the general public (e.g., see Ref. [3]). It is well-known that heterogeneity and anisotropy lead to irregular plume boundaries, which enhance mixing-controlled reactions through increasing the interfacial area of the plume. It is, therefore, crucial to capture heterogeneity and anisotropy in order to properly model reactive transport in hydrogeological systems.

One can capture heterogeneity computationally through adequate mesh refinement or by employing multiscale methods (for example, see Refs. [4–7]). Although simulating flow and transport in highly heterogeneous porous media is still an active area of research, we shall not address this aspect in this paper. We shall employ meshes that are fine enough to be able to resolve heterogeneity. This paper focuses on resolving anisotropy to be able to accurately predict the fate of chemical species. We shall model the spatial and temporal variation of chemical species through diffusion–reaction equations.

Diffusive–reactive equations arise naturally in modeling biological [8,9], chemical [10,11], and physical [12] systems. The areas of application of diffusion–reaction systems range from contaminant transport [13], semiconductors [14], combustion theory [15] to biological population dynamics [16]. It is well-known that these types of equations can exhibit complex and well-ordered structures/patterns [12,17]. A lot of effort has also been put into the mathematical analysis of diffusive–reactive systems. Many qualitative mathematical properties (e.g., comparison principles, maximum principles, the non-negative constraint) have been obtained for these systems [18–20]. A detailed discussion on mathematical aspects of diffusive–reactive systems is beyond the scope of this paper and is not central to the present study.

1.1. Fast bimolecular reactions

The main aim of this paper is to present a robust computation framework to obtain physically meaningful numerical solutions for diffusive–reactive systems. We shall restrict to bimolecular fast reactions for which the rate of reaction is controlled by diffusion of the two chemical species. Fast irreversible bimolecular diffusion–reaction equations come under the class of diffusion-controlled reactions [21,22]. Examples of such systems include ionic reactions occurring in aqueous solutions such as acid–base reactions [23,24], polymer chain growth kinetics [25], catalytic reactions [26] and enzymatic reactions [27]. In such systems the formation of the product is much faster than the diffusion of the reactants. In this paper we are only concerned about homogeneous reactions (i.e., the reactants are all in the same phase). Modeling diffusive–reactive systems in which reactions are heterogeneous (i.e., the reactants are in different phases) by incorporating the surface effects of the reactants (for example, see Refs. [28–34]) is beyond the scope of the present paper but will be considered in our future works.

Some main challenges in solving a system of diffusion–reaction equations are as follows:

- (a) *Anisotropy*: Developing robust computational frameworks for highly anisotropic diffusive–reactive systems is certainly gaining prominence. However, caution needs to be exercised in selecting numerical formulations to avoid negative values for the concentration of the chemical species. Many popular numerical schemes such as the standard single-field formulation [35], the lowest order Raviart–Thomas formulation [36], and the variational multiscale mixed formulation [37,38] give unphysical negative values for the concentration even for pure diffusion equations [39]. Furthermore, mesh refinement (either h -refinement [40] or p -refinement [41]) will not overcome the problem of negative values for the concentration. Keeping in mind about these concerns and developing a robust framework for diffusive–reactive systems is a challenging task.
- (b) *Nonlinearity*: The equations governing for these systems are coupled and nonlinear (see Eqs. (2.2a)–(2.2d), which are presented in a subsequent section). The solutions to these diffusive–reactive systems can exhibit steep gradients [42], and a robust numerical solution procedure should be able to handle such features.
- (c) *Scale dependence*: These types of systems can exhibit multiple spatial and temporal scales. For example, the diffusion process can be much slower than the chemical reactions. Therefore, the numerical techniques should be able to resolve these multiple scales. Compared to fast reactions, different solution strategies are required for moderate and slow reactions, which are typically easier to solve due to smaller gradients. Construction of adaptive numerical techniques that take the advantage of specific reaction kinetics and simultaneously satisfying the underlying mathematical properties is still in its infancy.
- (d) *Bifurcations, physical instabilities and pattern formations*: These systems are capable of exhibiting physical instabilities, and even chaos [18].

We shall overcome the first challenge by employing a novel non-negative solver that ensures physically meaningful non-negative values for the concentration of chemical species. We employ a transformation of variables, which will overcome the second and third challenges. We solve problems that do not exhibit physical instabilities and chaos. Although considerable progress has been made in developing numerical solutions of diffusive–reactive systems [43,44], none of these studies addressed the difficulties in obtaining non-negative solutions especially under strong anisotropy, which is the main focus of this paper. The following systematic approach has been employed to achieve the desired goal. The reactions are assumed to be fast and bimolecular. The concentration of reactants and product are governed by tensorial diffusion–reaction equations, and by an appropriate stoichiometric relationship. The three coupled tensorial diffusion–reaction equations are rewritten in

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