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Lagrangian modeling of reactive transport in heterogeneous porous media

Guillem Sole Mari

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Colophon
This thesis design is based on the *Clean Thesis* LaTeX 2_ε style developed by Ricardo Langner and inspired by user guide documents from Apple Inc.

> *“The Answer to the Great Question… Of Life, the Universe and Everything… Is… Forty-two”, said Deep Thought, with infinite majesty and calm.*
>
> *“Forty-two!” yelled Loonquawl. “Is that all you’ve got to show for seven and a half million years’ work?”*
>
> *“I checked it very thoroughly,” said the computer, “and that quite definitely is the answer. I think the problem, to be quite honest with you, is that you’ve never actually known what the question is.”*
>
> **— Douglas Adams,**
> ***The Hitchhiker’s Guide to the Galaxy***

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extranya per les equacions, els codis, les partícules i totes aquestes coses. També vull agrair el suport de la resta de família i amics, i dedicar-li aquesta tesi a la meva àvia Maria, que s'hauria sentit molt orgullosa.

Abstract

Fluid flow, solute transport, and chemical reactions in porous media are highly relevant for multiple applications and in several fields of knowledge. Aquifers are a typical example of porous media, but many others exist, like for instance biological tissues or wastewater treatment filters. Modeling and simulation of transport processes in porous media can be done through Lagrangian methods, which have certain advantages with respect to classical Eulerian methods. Among these advantages, a key one is that the solution of the advective transport term does not generate any numerical dispersion or instabilities, not even in those cases that are strongly dominated by advection, as opposed to what happens with classical Eulerian methods. However, the incorporation of chemical reaccions in the Lagrangian modeling context involves additional challenges and considerations with respect to conservative transport modeling. In this thesis, which is presented as a compendium of publications, new techniques are developed for modeling reactive transport of solutes in porous media from a Lagrangian perspective. Throghout the thesis, two different types of numerical particles are studied: mass-particles and fluid-particles. In both cases, continuum-scale dispersion (or at least part of it) is represented by random walks of numerical particles. Also in both cases, reactive transport simulations require interaction between nearby particles, either for directly computing reactions (when mass-particles are used) or for exchanging solutes (in the fluid-particle case). For this reason, a large part of this thesis revolves around the study of kernel functions, whose purpose is to mathematically represent the support volume of (and interaction between) particles. In this thesis it is shown that these functions, optimized using statistical theories of Kernel Density Estimation (KDE), may be used to simulate all kinds of nonlinear reactions with the mass-particle method known as Random Walk Particle Tracking (RWPT). Then, a new approach is developed for locally optimizing the particles' support volume (represented by the kernel bandwidth), such that it adapts its size and shape in time and space to minimize error. Thereafter, this technique is implemented in a hybrid manner in combination with a spatial discretization (binning) to improve its computational efficiency and to allow the incorporation of boundary conditions. Regarding fluid-particles, in this thesis it is shown that two methods that exist in the Lagrangian modeling literature (Smoothed Particle Hydrodynamics or SPH, and Mass Transfer Particle Tracking) are mathematically equivalent, and they only differ in the choice of kernel used for the solute exchange between particles, which simulates dispersive transport. Finally, a novel Lagrangian fluid-particle method is developed, with an algorithm based on Multi-Rate Interaction by Exchange with the Mean (MRIEM), which enables to account for local-scale concentration fluctuation effects, as well as their generation, transport and decay. The method is shown capable of reproducing experimental results of reactive transport in a porous medium with locally mixing-limited conditions.

Resumen

El flujo de fluidos, el transporte de solutos, y las reacciones químicas en medios porosos son procesos de gran relevancia en multitud de aplicaciones y ámbitos. Los acuíferos son un típico ejemplo de medios porosos, pero existen muchos más, como por ejemplo los tejidos biológicos, o los filtros para tratamiento de aguas residuales. La modelación y simuación de procesos de transporte de solutos en medios porosos puede ser llevada a cabo mediante métodos Lagrangianos, que presentan ciertas ventajas respecto a los clásicos métodos Eulerianos. Entre esas ventajas, una de las principales es que la solución del término advectivo del transporte no genera problemas de dispersión numérica o inestabilidades, ni siquiera en esos casos fuertemente dominados por la advección, a diferencia de lo que sucede con los métodos Eulerianos clásicos. Por otro lado, la incorporación de reacciones químicas en el contexto Lagrangiano conlleva retos y consideraciones adicionales en relación a las del transporte conservativo. En la presente tesis, presentada en formato de compendio de publicaciones, se desarrollan nuevas técnicas para modelar el transporte reactivo de solutos en medios porosos desde una perspectiva Lagrangiana. A lo largo de la tesis, se estudian dos tipos distintos de partículas numéricas: partículas de masa y partículas de fluido. En ambos casos, la dispersión a la escala de continuo (o almenos una parte de la misma) es representada mediante desplazamientos aleatorios de las partículas numéricas. También en ambos casos, las simulaciones de transporte reactivo requieren la interacción entre partículas cercanas, ya sea para computar directamente las reacciones (cuando se usan partículas de masa) o para intercanviar solutos (en el caso de partículas de fluido). Por esa razón, gran parte de la tesis se desarrolla entorno al estudio de las funciones kernel, las cuales tienen la finalidad de representar matemáticamente el volumen de soporte de (e interacción entre) las partículas. En la presente tesis se demuestra que estas funciones, optimizadas utilizando teorías estadísticas de estimación de densidad por kernels, pueden ser utilizadas para reproducir todo tipo de reacciones no lineales con el método basado en partículas de masa conocido como “Random Walk Particle Tracking”. A continuación, se desarrolla una nieva forma de optimizar localmente el volumen de soporte de las partículas (representado por el ancho de banda del kernel) de forma que se adapte en el tiempo y en el espacio para reducir el error. Posteriormente, esta técnica es implementada de manera híbrida en combinación con una discretización espacial para mejorar su eficiencia computacional y posibilitar la incorporación de condiciones de contorno. En cuanto al caso de partículas de fluido, en esta tesis se demuestra que dos métodos existentes en la literatura (“Smoothed Particle Hydrodynamics” o SPH, y “Mass Transfer Particle Tracking”) son matemáticamente equivalentes, y que se diferencian exclusivamente por el kernel que se usa en el intercanvio de solutos entre partículas, el cual simula el transporte dispersivo. Finalmente, se desarrolla un nuevo método Lagrangiano de partículas de fluido, con un algoritmo basado en la Interacción por Intercambio con la Media a Múltiples Velocidades (MRIEM, por sus siglas en inglés), que permite reproducir el efecto de las fluctuaciones de concentración a la escala local, así como la generación, transporte y destrucción de las mismas. Se demuestra que el método es capaz de reproducir resultados experimentales de transporte reactivo en un medio poroso en condiciones limitadas por la mezcla.

Resum

El flux de fluids, el transport de soluts, i les reaccions químiques en medis porosos són processos amb una gran rellevància en multitud d'aplicacions i àmbits. Els aqüífers són un típic exemple de medi porós, però n'existeixen molts d'altres, com per exemple els teixits biològics, o els filtres per tractament d'aigües residuals. La modelació i simulació de processos de transport de soluts en medis porosos pot ser duta a terme mitjançant mètodes Lagrangians, que presenten certs avantatges respecte als clàssics mètodes Eulerians. Entre aquests avantatges, un dels principals és que la solució del terme advectiu del transport no genera problemes de dispersió numèrica o inestabilitats, ni tan sols en aquells casos fortament dominats per l'advecció, a diferència del que passa amb els mètodes clàssics Eulerians. No obstant això, la incorporació de reaccions químiques en el context Lagrangià comporta reptes i consideracions addicionals respecte de les del transport conservatiu. En aquesta tesi, presentada en format de compendi de publicacions, es desenvolupen noves tècniques per a modelar el transport reactiu de soluts en medis porosos des d'una perspectiva Lagrangiana. Al llarg de la tesi, s'estudien dos tipus diferents de partícules numèriques: partícules de massa i partícules de fluid. En ambdós casos, la dispersió a l'escala de continuu (o almenys una part de la mateixa) és representada mitjançant desplaçaments aleatoris de les partícules numèriques. També en ambdós casos, les simulacions de transport reactiu requereixen la interacció entre partícules properes, ja sigui per a computar directament les reaccions (quan s'usen partícules de massa) o per a intercanviar soluts (en el cas de partícules de fluid). Per això, gran part de la tesi gira al voltant de l'estudi de les funcions kernel, les quals tenen la finalitat de representar matemàticament el volum de suport de (i interacció entre) les partícules. En aquesta tesi es demostra que aquestes funcions, optimitzades fent servir teories estadístiques d'estimació de densitat per kernels, poden ser utilitzades per a reproduir tot tipus de reaccions no lineals amb el mètode basat en partícules de massa conegut com a "Random Walk Particle Tracking". Seguidament, es desenvolupa una nova manera d'optimitzar localment el volum de suport de les partícules (representat per l'ample de banda del kernel), de manera que s'adapti en el temps i l'espai per reduir l'error. Posteriorment, aquesta tècnica és implementada de forma híbrida en combinació amb una discretització espaial per a millorar-ne l'eficiència computacional i possibilitar la incorporació de condicions de contorn. Pel que fa al cas de partícules de fluid, en aquesta tesi es demostra que dos mètodes existents a la literatura ("Smoothed Particle Hydrodynamics" o SPH, i "Mass Transfer Particle Tracking") són matemàticament equivalents, i que es diferencien únicament pel kernel que es fa servir en l'intercanvi de soluts entre partícules, que simula el transport dispersiu. Finalment, es desenvolupa un nou mètode Lagrangià de partícules de fluid, amb un algoritme basat en Interacció per Intercanvi amb la Mitja a Múltiples Velocitats (MRIEM, per les seves sigles en anglès), que permet reproduir l'efecte de les fluctuacions de concentració a l'escala local, així com la seva generació, transport i destrucció. Es demostra que el mètode és capaç de reproduir resultats experimentals de transport reactiu en un medi porós en condicions limitades per la mescla local.

Contents

Introduction

1

1.1 Background, motivation and goals

Advances in numerical modeling are subject, inevitably, to the available hardware technology. Because of this, modeling of flow and transport in porous media is a relatively young discipline that has experienced a profound renovation every decade since the beginning of the information age. The earliest hydrogeological models were based on low-resolution Eulerian grids on which flow and transport were simulated in a medium with homogenized (upscaled) properties (such as the early work of Pinder and Bredehoeft, 1968). Early research was thus placed on finding the values of lumped parameters that best could represent the system at some medium-large scales (see, e.g., Gelhar and Axness, 1983; Dagan, 1989), initially based on some assumptions regarding transport processes, such as Fickianity. It was soon established by the scientific community that the heterogeneous nature of porous media at multiple scales of observation could not be faithfully represented by such kind of approach. On the other hand, the need for fine discretizations in realistic models involving millions of nodes challenged the capability of early computers. Models of flow and transport in highly heterogeneous porous media started to gain importance, including high-resolution models of media with randomly distributed properties (see, e.g., Ababou et al., 1989; Tompson and Gelhar, 1990).

By dropping the assumption of macroscale Fickian behavior and replacing it with an explicit representation of the heterogeneous velocity field, transport models tend to become more advection-dominated, since dispersivity values are known to depend on the observation scale (Bear and Cheng, 2010). In these conditions, Eulerian approaches suffer from computational issues such as numerical dispersion and instabilities. These artifacts can strongly undermine the accuracy of reactive transport models, especially in the occurrence of strongly nonlinear reaction systems. The use of high-resolution schemes with a flux limiter can certainly mitigate these problems, but only up to moderate values of the grid-Péclet number (which quantifies the relative strength of advection with respect to diffusion within a computational cell). Thus, oftentimes, the only way to reach adequate stability and accuracy with Eulerian methods is to use extremely fine grids, increasing the computational demands up to challenging (or even unfeasible) levels (Sanchez-Vila and Fernàndez-Garcia, 2016). Besides these issues, the use of classical Eulerian approaches to reactive transport modeling involves ignoring the inherent multiscale nature of porous media and their heterogeneities (Dentz et al., 2011). Below the working scale and all the way down to the pore scale, irregular and complex flow patterns are found in natural porous media, producing local incomplete mixing effects that classical approaches are unable to capture (Valocchi et al., 2019). The characteristic manifestation of these effects is the segregation of reactants, which tends to reduce effective reaction rates (Chiogna and Bellin, 2013). This is exemplified by the fact that observed reaction rates in the field are often lower than predicted by controlled, well-mixed batch laboratory experiments (Raje and Kapoor, 2000; Gramling et al., 2002; Kang et al., 2019).

Lagrangian methods, which have gained popularity in the recent years, can be a convenient and efficient alternative to their Eulerian counterparts. By solving the transport using numerical elements (particles) that move along with advection, one avoids the aforementioned problems associated with the Eulerian solution of the advection term. As a consequence, Lagrangian approaches are virtually free of instabilities and numerical dispersion, and particularly well-suited for solving advection-dominated problems such as the strong-shear irregular flows that characterize heterogeneous porous media (Benson et al., 2017). Two big families of Lagrangian methods for transport simulation may be distinguished: mass-particle approaches, in which each individual particle represents some amount of solute mass (e.g, LaBolle et al., 1996); and fluid-particle approaches, in which a particle represents some amount of fluid with associated solute concentrations (e.g, Herrera et al., 2009). Each of these approaches has their own strengths and weaknesses: with mass-particles, advection-dispersion can be entirely simulated by means of the family of random walk methods, and no interaction between particles is required in the absence of nonlinear chemical reactions. Another advantage of the mass-particle approach is that different transport properties (for instance, different retardation or diffusion coefficients) can be straightforwardly assigned to each particle, depending on the chemical species they represent. For fluid-particles, on the other hand, simulating dispersion involves solute mass exchange (i.e., interaction) between particles. This implies, for instance, that “empty” particles need to be placed in all locations where solute mass can potentially exist during the simulation. On the other hand, a remarkable advantage of fluid-particle approaches is that, since concentrations are defined on particles, the implementation of chemical reactions is trivial (Benson and Bolster, 2016). Random Walk Particle Tracking (RWPT) methods (Salamon et al., 2006) belong to the mass-particle family of Lagrangian approaches. Although the previously mentioned advantages have made RWPT highly – and increasingly – popular among scientists and modelers, most well-established implementations are restricted to conservative (non-reactive) transport and linear reactions (e.g., Henri and Fernàndez-Garcia, 2014). Since solute concentrations (which drive chemical reactions) are not readily available in mass-particle methods, but come only from postprocessing of particle positions (Fernàndez-Garcia and Sanchez-Vila, 2011), the incorporation of nonlinear chemical reactions is non-trivial, and it involves some form of interaction between nearby particles (Benson and Meerschaert, 2008).

The purpose of this thesis is to improve our ability to model reactive transport of solutes in porous media from a Lagrangian perspective. Before this thesis work, only linear and bilinear reactions had been implemented in mass-particle (RWPT) transport models. More complex reaction systems had been simulated in a fluid-particle framework (Engdahl et al., 2017), an issue that is also explored within this thesis.

1.2 Layout

This doctoral thesis is presented as a compendium of publications, all of them being related to Lagrangian modeling approaches. The compendium comprises the following four studies which are published in journals that lie within the category Water Resources in JCR, all being classified within the first quartile (Q1):

- Sole-Mari, G., Fernàndez-Garcia, D., Rodríguez-Escales, P., & Sanchez-Vila, X. (2017). *A KDE-based random walk method for modeling reactive transport with complex kinetics in porous media*. Water Resources Research, 53, 9019 9039.
  DOI:10.1002/2017WR021064

- Sole-Mari, G., & Fernàndez-Garcia, D. (2018). *Lagrangian modeling of reactive transport in heterogeneous porous media with an automatic locally adaptive particle support volume*. Water Resources Research, 54, 8309 8331. DOI:10.1029/2018WR023033

- Sole-Mari, G., Bolster, D., Fernàndez-Garcia, D., & Sanchez-Vila, X. (2019a). *Particle density estimation with grid-projected and boundary-corrected adaptive kernels*. Advances in Water Resources, 131, 103382. DOI:10.1016/j.advwatres.2019.103382

- Sole-Mari, G., Schmidt, M. J., Pankavich, S. D., & Benson, D. A. (2019b). *Numerical equivalence between SPH and probabilistic mass transfer methods for Lagrangian simulation of dispersion*. Advances in Water Resources, 126, 108115. DOI:10.1016/j.advwatres.2019.02.009

Additionally, a fifth research article is included as an Appendix. On the date of submission of this thesis, this fifth manuscript is under review at Water Resources Research and accessible with digital object identifier through the Earth and Space Science Open Archive:

- Sole-Mari, G., Fernàndez-Garcia, D., Sanchez-Vila, X., & Bolster, D. (2020). *Lagrangian modeling of mixing-limited reactive transport in porous media*. Water Resources Research (Under Review). DOI:10.1002/essoar.10501517.1

In the following, the motivation, scope and contents of each of the papers is summarized, and their contribution to the overall goal of this thesis is elucidated.

Since particle interaction is a key aspect of Lagrangian reactive transport simulation, a significant part of this thesis is dedicated to the study of kernel functions, which are used to model the aforementioned interactions. The first paper of the compendium (Sole-Mari et al., 2017) shows that the RWPT formulation for the (bilinear kinetic) reaction probability of a particle based on collocation probability is mathematically equivalent (notwithstanding a substantially different connotation for the interaction bandwidth parameter) to the Kernel Density Estimation (KDE) approach, in which each particle location is assigned a probability density function (pdf), instead of a fixed deterministic position, to deal with the problem of subsampling inherent to the numerical discretization. Then, the expression for the probability of reaction is extended to arbitrarily complex kinetics, showing for the first time that reactive random walks are not subjected to limitations for the reaction rate laws.

The kernel function used in the cited work follows the classical principles of KDE, which implies that the kernel size (bandwidth) is the same for all particles in the model. The accuracy of this approach may then be limited by the degree of spatial uniformity of the particle plume. This could be a limitation for modeling reactive transport in strongly heterogeneous porous media, characterized by marked spatial and temporal variations in transport behavior. Hence, in the second paper of the compendium (Sole-Mari and Fernàndez-Garcia, 2018), a novel approach is developed to incorporate spatial variations in the kernel size and shape, which are optimized to minimize the local KDE error. As a result, the local kernel functions adapt in space and time mimicking the current features of the nearby concentration field.

In the follow-up paper, the third of this compendium (Sole-Mari et al., 2019a), a hybrid implementation method is designed which allows the use of local kernels to reconstruct the concentrations with high efficiency while satisfying the boundary conditions. While the previous work (Sole-Mari and Fernàndez-Garcia, 2018) depended on some global optimal kernel for the estimation of the concentration curvatures, in this work a fixed-point iteration method is used, which means the previous size and shape of the kernel are the only inputs for the next optimization step. The developments and findings described up to this point allow the implementation of arbitrarily complex kinetic and equilibrium reactions on mass-particles (RWPT), efficiently, fully considering the impact upon reactions of the presence of boundaries of different types.

In order to explore alternatives, the use of fluid-particles is then investigated. In this case, since concentrations are defined on particles, the implementation of reactions is straightforward, and the interaction between particles occurs as a mass exchange in the dispersion step. In the fourth paper of this compendium (Sole-Mari et al., 2019b), two methods of the fluid-particle class (SPH and probabilistic mass transfer methods) are analyzed, showing that they are in fact numerically equivalent, the only difference (aside from the rationale for their derivation) being the type of criterion for the selection of the kernel function size. Motivated by this finding, a study of the influence of the kernel size on the simulation results (for a simple point diffusion problem), as well as the relation with particle density, disorder and time step length, is conducted.

A key observation is that a sufficiently fine discretization (including a large number of particles) always leads to the exact solution of the Advection Dispersion Equation (ADE). In the past, the latter has been found unable to properly upscale reactive transport in porous media with locally mixing-limited conditions. For this reason, in the Appendix and as an ending to this thesis, a novel fluid-particle Lagrangian approach (Sole-Mari et al., 2020) is developed to specifically account for the generation, transport and decay of local concentration fluctuations (and their impact on chemical reactions).

2

Discussion and Conclusions

In this thesis, Lagrangian approaches have been shown to offer a valid alternative for modeling reactive transport in porous media. It has been shown for the first time that stochastic reactive random walks could be applied to any type of kinetic reaction rate laws, instead of being limited to bimolecular reactions with second-order kinetics (Sole-Mari et al., 2017). Thanks to the use of optimal kernel functions, one-dimensional reactive transport simulations featuring complex kinetic reactions can converge to the exact solution for very small particle numbers. On the other hand, the cited work also exemplifies that reaction kinetics may not always be important, and that using previously existing Lagrangian techniques, which involve the assumption of second-order kinetics, may be a good proxy when the reaction process is mixing-limited.

The idea of extending the KDE approach to multidimensional heterogeneous aquifers motivated the development of a new optimal kernel methodology (Sole-Mari and Fernàndez-Garcia, 2018), in which the particle support volume, represented by the multi-dimensional kernel bandwidth, may locally modify its size and shape based on the neighboring particle distribution, adapting itself to the features of the nearby concentration field. Results revealed that simply allowing local adaptivity of the kernel size has a stronger impact on the accuracy of the results than allowing for additional degrees of freedom corresponding to the stretching and rotation of the local kernel. Most of the error reduction associated with the use of a local kernel function occurs in areas of relative low particle density, because the kernel is allowed to grow and reduce density estimation noise in those areas instead of being controlled by the features of high density / high curvature areas, in which a large kernel would cause over-smoothing. Tests exemplify how, for fixed initial and boundary conditions of the flow and transport problem, the distributions of local kernel sizes and elongations change when problem variables such as the Péclet number (through the dispersivity) or the log-conductivity variance are modified, mimicking the features of the solute plume deformation under the competition between advective compression and solute dispersion. This results in a more computationally efficient use of the particle number, i.e., less numerical particles are required in order to achieve the same degree of accuracy.

Despite the significant computational benefit of the adaptive kernel, large particle numbers may still result in long calculation times if the KDE algorithm needs to run on every particle. While this may be solved by sampling the density on pilot points (Sole-Mari and Fernàndez-Garcia, 2018), an even more efficient as well as mass-conserving strategy consists in implementing the KDE method on a pilot binning (Sole-Mari et al., 2019a). While unmodified KDE may produce unphysical artifacts near the domain boundaries, the hybridization between KDE and binning enables the introduction of corrections near the boundaries so that the relevant boundary conditions can be fulfilled. It has been shown that the local kernel optimization problem may be solved by fixed-point iteration, an approach which displayed robustness to reach the correct solution regardless of the starting value in an example implementation.

Lagrangian approaches other than RWPT have also been explored in this Thesis. The use of fluid-particle approaches instead of mass-particle ones is attractive for reactive transport simulations since no interpolation is required to access the solute concentration values, which are instead defined directly on particles. On the other hand, dispersion processes must involve solute-mass exchange between particles. An important finding included in this thesis is the equivalence between two major fluid-particle methods for transport simulation (Sole-Mari et al., 2019b), namely smoothed particle hydrodynamics (SPH) and probabilistic mass transfer methods, also known as collocation methods. It has been shown that besides the inherent differences in their derivation, these two approaches only differ in the selection criterion for the kernel size in the mass exchange algorithm. Analyses reveal that, in some cases, the classical principles of SPH kernel selection (which depends only on particle density) may apply. But for dense-enough particle populations, the collocation kernel (which is independent of particle density and instead controlled by Δt) becomes the better choice. This "sufficient" density value is significantly lower for random-walking particles than for static, randomly-placed particles.

Some authors have explored before the combined use of random walks and mass exchange between fluid-particles to emulate reactant segregation effects such as those characterizing transport in heterogeneous porous media. However, such approaches rely on the segregation effects associated to low particle numbers, that is, they converge towards a fully-mixed behavior as the particle number is increased. In this thesis, it has been shown that by using a more sophisticated mass exchange algorithm, denoted as Multi-Rate Interaction by Exchange with the Mean (MRIEM), one can simulate solute transport with incomplete mixing effects reproducing the main features of locally mixing-limited transport in actual porous media (Sole-Mari et al., 2020). The proposed approach constitutes a general mathematical modeling approach, in which features such as the particle number, smoothing operator, or time-step length are just numerical discretization aspects. The Eulerian description of the concentration fluctuations (local covariance) includes a source term, according to which the action of hydrodynamic dispersion on concentration gradients generates concentration covariance. On the other hand, covariance is destroyed at an effectively time-varying rate controlled by the MRIEM sub-model, which represents the local-scale diffusive mixing process. At the same time, the local covariance is transported at the coarse scale by advection-dispersion according to the same upscaled velocity and dispersion values experienced by the concentrations. A first implementation of the model has been successfully applied to reproduce data from laboratory experiments of mixing-limited reactive transport. It is found that the model's local-scale asymptotic mixing length matches the estimated typical pore size of the physical experiment, suggesting that the model parameter value is physically meaningful.

Overall, this thesis is a significant step forward in the applicability of Lagrangian methods to overcome some of the limitations that have been described in the literature for their application in the simulation of nonlinear reactive transport in complex heterogeneous media. With the new capabilities for solving complex reactions in an efficient manner, Lagrangian methods become a valid alternative over Eulerian methods to solve intricate problems, especially when considering their potential for improvement in terms of parallelization of the codes, and as computational capabilities of computers keep growing.

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Compendium

- Sole-Mari, G., Fernàndez-Garcia, D., Rodríguez-Escales, P., & Sanchez-Vila, X. (2017). *A KDE-based random walk method for modeling reactive transport with complex kinetics in porous media*. Water Resources Research, 53, 9019 9039. DOI:10.1002/2017WR021064
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AGU PUBLICATIONS

Water Resources Research

RESEARCH ARTICLE

10.1002/2017WR021064

A KDE-Based Random Walk Method for Modeling Reactive Transport With Complex Kinetics in Porous Media

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Abstract In recent years, a large body of the literature has been devoted to study reactive transport of solutes in porous media based on pure Lagrangian formulations. Such approaches have also been extended to accommodate second-order bimolecular reactions, in which the reaction rate is proportional to the concentrations of the reactants. Rather, in some cases, chemical reactions involving two reactants follow more complicated rate laws. Some examples are (1) reaction rate laws written in terms of powers of concentrations, (2) redox reactions incorporating a limiting term (e.g., Michaelis-Menten), or (3) any reaction where the activity coefficients vary with the concentration of the reactants, just to name a few. We provide a methodology to account for complex kinetic bimolecular reactions in a fully Lagrangian framework where each particle represents a fraction of the total mass of a specific solute. The method, built as an extension to the second-order case, is based on the concept of optimal Kernel Density Estimator, which allows the concentrations to be written in terms of particle locations, hence transferring the concept of reaction rate to that of particle location distribution. By doing so, we can update the probability of particles reacting without the need to fully reconstruct the concentration maps. The performance and convergence of the method is tested for several illustrative examples that simulate the Advection-Dispersion-Reaction Equation in a 1-D homogeneous column. Finally, a 2-D application example is presented evaluating the need of fully describing non-bilinear chemical kinetics in a randomly heterogeneous porous medium.

Key Points:

- A Random Walk Particle Tracking Method capable to simulate reactions with complex kinetics is presented
- Particles are equipped with optimal kernels to represent the uncertainty in the particle position driven by subsampling a large population
- The method is tested in several 1-D and 2-D synthetic reactive transport models

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1. Introduction

Random Walk Particle Tracking Methods (RWPTMs) offer a convenient Lagrangian numerical approach to simulate solute transport in porous media. RWPTMs have been demonstrated to be particularly efficient in dealing with aquifer heterogeneities and nonreactive transport involving a large variety of complex processes such as non-Fickian transport and multiple porosity systems (Benson & Meerschaert, 2009; Berkowitz et al., 2006; Cvetkovic & Haggerty, 2002; Delay & Bodin, 2001; Dentz & Castro, 2009; Henri & Fernández-Garcia, 2014, 2015; Huang et al., 2003; LaBolle et al., 1996; Riva et al., 2008; Salamon et al., 2006a, 2006b; Sánchez-Vila & Solís-Delfín, 1999; Tsang & Tsang, 2001; Wen & Gómez-Hernández, 1996; Willmann et al., 2013; Zhang & Benson, 2008). This family of methods essentially consists of discretizing the solute mass (existing initially or injected through the boundaries with time) into a finite number of particles, each representing a fraction of the total mass, and then moving such particles according to simple relationships that represent the transport mechanisms considered (e.g., advection, dispersion or diffusion into stagnant zones). RWPTMs are mass conservative by construction, and avoid some of the inherent numerical difficulties associated with Eulerian approaches, i.e., numerical dispersion and oscillations (Benson et al., 2017; Salamon et al., 2006a).

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Water Resources Research

RESEARCH ARTICLE
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Lagrangian Modeling of Reactive Transport in Heterogeneous Porous Media With an Automatic Locally Adaptive Particle Support Volume

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Key Points:

- We present a locally adaptive kernel density estimator for computation of chemical reactions in random walk models of solute transport
- The support volume adapts to the nearby particle distribution, adjusting its size and stretching along the direction of minimum curvature
- The local approach outperforms the existing methods when estimating concentrations and reaction rates in a heterogeneous porous medium

Abstract The particle support volume is crucial for simulating reactive transport with Lagrangian methods as it dictates the interaction among particles. Assuming that it is constant in space, the particle support volume can be selected by means of kernel density estimation theory, an approach that has been shown to provide accurate estimates in simple setups. However, the particle support volume should intuitively vary with the particle position and evolve with time so as to mimic the local behavior of the solute plume. In this paper, we present a new approach to select a locally optimal particle support volume in reactive transport simulations. We consider that each particle has a different support volume that can locally adapt its shape and size with time based on the nearby particle distribution. By introducing a new optimality criterion, closed-form expressions of the particle support volume are presented under certain assumptions. In advection-dominated transport, we propose to orient the support volume along the local velocities. Numerical simulations of solute transport in a randomly heterogeneous porous medium demonstrate that the new approach can substantially increase accuracy with a more rapid convergence to the true solution with the number of particles. The error reduction seen in local approaches is particularly important in regions with extreme (high and low) density of particles. The method is shown to be computationally efficient, displaying better results than traditional histogram or global kernel methods for the same computational effort.

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1. Introduction

Numerical models that deal with multiple species and chemical reactions are typically based on Eulerian approaches (e.g., Lichtner et al., 2015; Saaltink et al., 2004; Xu et al., 2014; Yeh et al., 2004). However, the incorporation of physical and biochemical heterogeneities into grid-based Eulerian codes that solve the multicomponent advection-dispersion equation coupled with reactions suffers from numerical problems stemming from the need to fulfill a small grid-Peclet number $\Delta x/\alpha$ to properly simulate reactions, being α the dispersivity and Δx the size of the numerical spatial discretization. Knowing that in porous media many chemical reactions are driven by mixing (De Simoni et al., 2005, 2007; Dentz et al., 2011; Gramling et al., 2002; Martinez-Landa et al., 2012) and controlled by very small values of transverse dispersivities (Cirpka et al., 1999, 2015), these numbers are seldom achieved in practical applications, and numerical simulations tend to overpredict the total amount of reaction produced (Benson et al., 2017; Sanchez-Vila & Fernàndez-Garcia, 2016). This renders reactive transport modeling a major challenge in hydrogeology nowadays.

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Pages 40 to 62 of the thesis are available at the editor’s web
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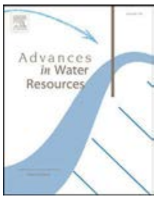

Particle density estimation with grid-projected and boundary-corrected adaptive kernels☆

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article info

Keywords:
Particle density
Adaptive kernels
Random walk particle tracking
Concentration estimation
Reactive transport

abstract

The reconstruction of smooth density fields from scattered data points is a procedure that has multiple applications in a variety of disciplines, including Lagrangian (particle-based) models of solute transport in fluids. In random walk particle tracking (RWPT) simulations, particle density is directly linked to solute concentrations, which is normally the main variable of interest, not just for visualization and post-processing of the results, but also for the computation of non-linear processes, such as chemical reactions. Previous works have shown the improved nature of kernel density estimation (KDE) over other methods such as binning, in terms of its ability to accurately estimate the "true" particle density relying on a limited amount of information. Here, we develop a grid-projected KDE methodology to determine particle densities by applying kernel smoothing on a pilot binning; this may be seen as a "hybrid" approach between binning and KDE. The kernel bandwidth is optimized locally. Through simple implementation examples, we elucidate several appealing aspects of the proposed approach, including its computational efficiency and the possibility to account for typical boundary conditions, which would otherwise be cumbersome in conventional KDE.

1. Introduction

Random Walk Particle Tracking (RWPT) methods are a family of methods commonly used in the hydrologic sciences to simulate transport. They are appealing as they can accurately emulate many different physical processes that occur in natural media such as diffusion, hydrodynamic dispersion, mass transfer across multiple porosity systems and linear sorption (Salamon et al., 2006a; 2006b). They are also conducive to simulating anomalous non-Fickian transport that arises due to medium heterogeneities below the scale of resolution (e.g., Berkowitz et al., 2006). With RWPTs, the solute mass is discretized into a large number of discrete particles that move across the medium following deterministic and probabilistic rules, which account for the processes of advection, dispersion, matrix diffusion, etc. Lagrangian methods for simulating scalar transport, among which RWPTs are some of the most common, have been shown to be particularly useful when modeling transport in advection-dominated systems, where Eulerian methods can suffer from numerical dispersion and instabilities (Salamon et al., 2006a; Benson et al., 2017).

However, the main shortcoming of RWPT methods is that, without modification, they may result in very noisy concentration fields due to subsampling effects associated with the finite number of particles in the system. This can be particularly troublesome when simulating solute transport in systems where processes are governed by nonlinearities or tight coupling and interactions between different solute concentrations, of which nonlinear chemical reactions are a prime example. Linear processes such as simple degradation, slow sorption or chain reactions can efficiently be incorporated to RWPT algorithms by means of additional probabilistic rules with little additional computational cost. On the other hand, nonlinear reactions involve interactions between neighboring particles, which adds complexity to the problemsince particles need to know both their location and the other particles' locations, which can result in an $\mathcal{O}(\square^2)$ numerical cost in naive implementations. Even with more optimized approaches that use better search algorithms (e.g., Engdahl et al., 2019), the additional numerical cost can become significant for high particle numbers.

A problem that clearly highlights these issues and has received considerable recent attention in the literature is the simulation of bimolecular reactions of the type $A + B \rightarrow C$ via RWPT (Benson and Meerschaert,

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Pages 64 to 76 of the thesis are availables at the editor's web
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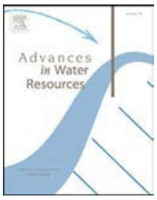

Numerical equivalence between SPH and probabilistic mass transfer methods for Lagrangian simulation of dispersion☆

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article info

Keywords:
Lagrangian modeling
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Smoothed particle hydrodynamics
Mass transfer particle tracking
Kernel bandwidth

abstract

Several Lagrangian methodologies have been proposed in recent years to simulate advection-dispersion of solutes in fluids as a mass exchange between numerical particles carrying the fluid. In this paper, we unify these methodologies, showing that mass transfer particle tracking (MTPT) algorithms can be framed within the context of smoothed particle hydrodynamics (SPH), provided the choice of a Gaussian smoothing kernel whose bandwidth depends on the dispersion and the time discretization. Numerical simulations are performed for a simple dispersion problem, and they are compared to an analytical solution. Based on the results, we advocate for the use of a kernel bandwidth of the size of the characteristic dispersion length □ = 2□Δ□, at least given a "dense enough" distribution of particles, for in this case the mass transfer operation is not just an approximation, but in fact the exact solution, of the solute's displacement by dispersion in a time step.

1. Introduction

In recent years, a number of Lagrangian numerical schemes have been proposed to simulate advection-dispersion processes in fluids. Some of these approaches rely exclusively on traditional random walks to simulate dispersion (Benson and Meerschaert, 20008; Benson et al., 2017; Bolster et al., 2016a; Bolster et al., 2016b; Ding et al., 2012; Ding and Benson, 2015; Ding et al., 2017; Paster et al., 2013; Paster et al., 2014; Schmidt et al., 2017; Sole-Mari et al., 2017, Sole-Mari and Fernàndez-Garcia, 2018), whereas a second class represents dispersion through mass transfer between particles that carry a given amount of fluid (Herrera et al., 2009,Herrera and Beckie,Benson and Bolster, 2016; Schmidt et al., 2018a). Other authors have hybridized random walks with mass transfer (Engdahl et al., 2017; Herrera et al.) in an approach that allows partitioning of total dispersion between mixing (simulated by mass transfer) and non-mixed spreading (simulated via random walks). Mass-transfer algorithms can be further subdivided into two groups. The first group (Herrera et al., 2009,Herrera and Beckie) derives the mass exchange rates from the well-established smoothed particle hydrodynamics (SPH) method (Gingold and Monaghan, 1977), which, besides solute transport, has been used in a variety of applications (Monaghan, 2012) such as astrophysics, fluid dynamics, and solid mechanics. A second group of approaches, often referred to as mass transfer particle tracking (MTPT) algorithms (Benson and Bolster, 2016; Schmidt et al., 2018a), derive the mass-exchange rate from stochastic rules governing the co-location probability of particles moving via dispersion. To date, a relationship between these two methodologies for mass transfer has not been established. In this paper we analytically derive the connection between the SPH and MTPT conventions and show that, for specific kernel choices and provided that equivalent normalization and averaging conventions are used, the SPH and MTPT approaches are numerically equivalent. Additionally, for the fixed choice of a Gaussian kernel, we investigate the effect of differing bandwidth choices on deviations from the analytical, well-mixed solution.

2. The link between SPH and MTPT

The SPH approach to approximating dispersion can be summarized by following (Herrera et al., 2009, Herrera and Beckie). Therein, the following equation describes the time evolution of the concentration, $C_i(t)$, carried by a numerical particle labeled □ = 1, .., □, assuming that

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Appendix

- Sole-Mari, G., Fernàndez-Garcia, D., Sanchez-Vila, X., & Bolster, D. (2020). *Lagrangian modeling of mixing-limited reactive transport in porous media*. Water Resources Research (Under Review). DOI:10.1002/essoar.10501517.1

Lagrangian modeling of mixing-limited reactive transport in porous media

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Key Points:

- Development of a new approach to reactive transport modeling that accounts for the dynamics of small-scale concentration fluctuations
- The temporal evolution of integrated mixing metrics agrees with the characteristic trends of fully-resolved systems
- Experimental observations of mixing-limited reactive transport are successfully reproduced

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Abstract

The presence of solute concentration fluctuations at spatial scales much below the working scale is a major challenge for modeling reactive transport in porous media. Overlooking small-scale fluctuations, which is the usual procedure, often results in strong disagreements between field observations and model predictions, including, but not limited to, the overestimation of effective reaction rates. Existing innovative approaches that account for local reactant segregation do not provide a general mathematical formulation for the generation, transport and decay of these fluctuations and their impact on chemical reactions. We propose a Lagrangian formulation based on the random motion of fluid particles whose departure from the local mean concentration is relaxed through multi-rate interaction by exchange with the mean (MRIEM). We derive and analyze the macroscopic description of the local concentration covariance that emerges from the model and show that mixing-limited processes can be properly simulated. The action of hydrodynamic dispersion on coarse-scale concentration gradients is responsible for the production of local concentration covariance, whereas covariance destruction stems from the local mixing process represented by the MRIEM formulation. The temporal evolution of integrated mixing metrics in two simple scenarios shows the trends that characterize fully-resolved physical systems, such as a late-time power-law decay of the relative importance of incomplete mixing with respect to the total mixing. Experimental observations of mixing-limited reactive transport are successfully reproduced by the model.

1 Introduction

The inherent difficulty of properly representing the interaction of reactive chemicals occurring over multiple spatio-temporal scales in complex hydrodynamic settings renders reactive transport modeling in porous media a major challenge in subsurface hydrology [*Dentz et al.*, 2011; *Sanchez-Vila and Fernàndez-Garcia*, 2016; *Benson et al.*, 2017; *Valocchi et al.*, 2019]. With the exception of highly idealized settings or incredibly small samples, generally in porous media it is unfeasible to obtain a completely resolved flow field within real porous media geometries based on the complete microscopic equations (e.g. Navier-Stokes). This in turn limits the resolution at which a transport model can be applied. Instead one typically describes the system with macroscopic equations in an equivalent continuum [*Icardi et al.*, 2019, and references therein]. By doing so, one essentially ignores detailed resolution of local velocity and concentration fluctuations occurring at the pore-scale, below the scale of the equivalent continuum. The system is represented by macroscopic variables and properties, which aim to represent subscale fluctuations in an effective manner, obtained for instance by volume averaging [*Quintard and Whitaker*, 1994; *Whitaker*, 1999; *Wood et al.*, 2003]. However, these effective parameters really only aim to capture mean behaviors and processes that depend nonlinearly on subscale fluctuations may often not be well described. Similarly, since macroscopic properties such as the hydraulic conductivity can vary substantially in space within real aquifers, one may further upscale flow and transport in heterogeneous media with a new set of effective parameters [*Dagan*, 1989; *Gelhar*, 1993; *Rubin*, 2003]. This step further reduces the apparent complexity of the system, but again does not contain potentially important information below the scale of the effective model.

Among available macroscopic models, the upscaled advection-dispersion-reaction equation (ADRE) is the most widely used for modeling reactive transport at all practical spatial scales. It is embedded as the standard in most popular reactive transport codes [e.g., *Cederberg et al.*, 1985; *Mangold and Tsang*, 1991; *Yeh and Tripathi*, 1991; *Steefel and Lasaga*, 1994; *Walter et al.*, 1994; *Saaltink et al.*, 2004; *De Simoni et al.*, 2005; *Bea et al.*, 2009; *Steefel et al.*, 2015, and references therein]. However, field and laboratory observations, numerical simulations and theoretical developments have demonstrated time and time again that the upscaled ADRE fails to adequately represent mixing and chemical reactions at all scales [*Rashidi et al.*, 1996; *Cao and Kitanidis*, 1998; *Gramling et al.*, 2002; *Palanichamy et al.*, 2009; *Tartakovsky et al.*, 2008; *Fernàndez-Garcia et al.*, 2008; *Edery et al.*, 2009; *Sanchez-Vila et al.*, 2010; *de Anna et al.*, 2014a,b; *Porta et al.*, 2016], because of its disregard for the local concentration fluctuations and the use of scale-averaged concentrations to compute reactions. In fact, the main reason why reaction rates observed in the field tend to be much lower than those measured in laboratory experiments is the presence of anti-correlated local fluctuations of reactant concentrations [*Chiogna and Bellin*, 2013; *Ding et al.*, 2017].

Hence, in order to obtain better predictions, effective transport models should somehow incorporate the sub-scale mixing limitation effects. Several such approaches have been proposed in recent years, both from the Eulerian and from the Lagrangian perspective (see *Porta et al.* [2016] and references therein). The Eulerian approaches are typically restricted to very specific initial and boundary conditions, corresponding to the mixing of two reactants moving across a column-shaped porous medium, forming a sharp interface at $t = 0$, as in the famous laboratory experiments of *Gramling et al.* [2002]. As such, existing effective solutions typically contain a time-decaying term controlling either an apparent kinetic reaction rate [*Sanchez-Vila et al.*, 2010], a pre-defined concentration covariance function [*Chiogna and Bellin*, 2013], or a mobile-mobile mass exchange rate coefficient [*Ginn*, 2018]. *Hochstetler and Kitanidis* [2013] consider a constant, Damkohler-dependent efficiency term multiplying the reaction rate, which accounts for the effect of reactant segregation. While all the above-mentioned approaches provide interesting simplified interpretations of the physical process, they do not provide general differential equations governing the transport of local concentration fluctuations, and hence they might not be applicable to broader sets of initial and boundary conditions. On the other hand, Lagrangian approaches that have been proposed to reproduce mixing-limited reactive transport [*Edery et al.*, 2009; *Ding et al.*, 2013; *Benson et al.*, 2019a] rely on finite particle number effects to emulate the segregation of reactants. While such approaches are equivalent to assuming a noisy initial condition [*Paster et al.*, 2013, 2014], it is difficult to formalize and generalize them in a rigorous manner [*Bolster et al.*, 2016].

Here we present a novel Lagrangian approach to simultaneously account for (*i*) coarse-scale advective-dispersive behavior as well as (*ii*) the generation, transport and decay of local concentration fluctuations. The model aims to offer not just a solution specific to one setting, but rather a mathematical framework to potentially represent a broad array of settings and transport problems. Unlike the aforementioned Lagrangian approaches, the proposed model does not rely on low particle numbers to represent reactant segregation, but in fact converges to the desired solution with sufficient particles (i.e., the particle number is only a numerical discretization). In fact, Eulerian implementations of the proposed model are possible, but Lagrangian implementation is currently more natural and straightforward.

The paper is structured as follows. In §2 we develop the conceptual and mathematical model leading to the differential equation describing the local concentration fluctuations perceived by a random-walking Lagrangian particle. In §3 we derive the resulting Eulerian differential equation describing the transport, generation and decay of concentration point-covariance; we also provide the temporal evolution of the spatial integral of the former (or *mixing state*) in two simple cases of initial and boundary conditions with pseudo-analytical solution. In §4 we implement the proposed model to reproduce the reaction product concentration data corresponding to the laboratory experiments of *Gramling et al.* [2002]. Finally, in §5 we summarize our main conclusions.

2 Conceptual and mathematical model

2.1 Conservative transport and mixing

By definition, all continuum-scale models of transport in porous media assume or solve a flow field with some degree of coarse-graining; that is, the velocity variability below some threshold resolution is removed and replaced by an upscaled dispersion tensor. We distinguish two spatial scales, above and below this aforementioned threshold, which hereafter we refer to as *coarse scale* and *local scale*, respectively. Coarse-scale concentrations of species A at position $\mathbf{x}$ and time t, $\overline{c}_\mathrm{A}(\mathbf{x}, t)$, are often assumed to obey the upscaled advection-dispersion equation,

$$\frac{\partial \overline{c}_\mathrm{A}}{\partial t} = \mathcal{L}(\overline{c}_\mathrm{A}; \mathbf{v}, \mathbf{D}), \qquad \mathcal{L}(u; \mathbf{v}, \mathbf{D}) := \nabla \cdot (-\mathbf{v}u + \mathbf{D}\nabla u) \tag{1}$$

where $\mathbf{v}$ is the coarse-scale velocity, and $\mathbf{D}$ is the dispersion tensor, which represents the combined effect of velocity fluctuations at the local scale (around $\mathbf{v}$) and molecular diffusion. (1) assumes that

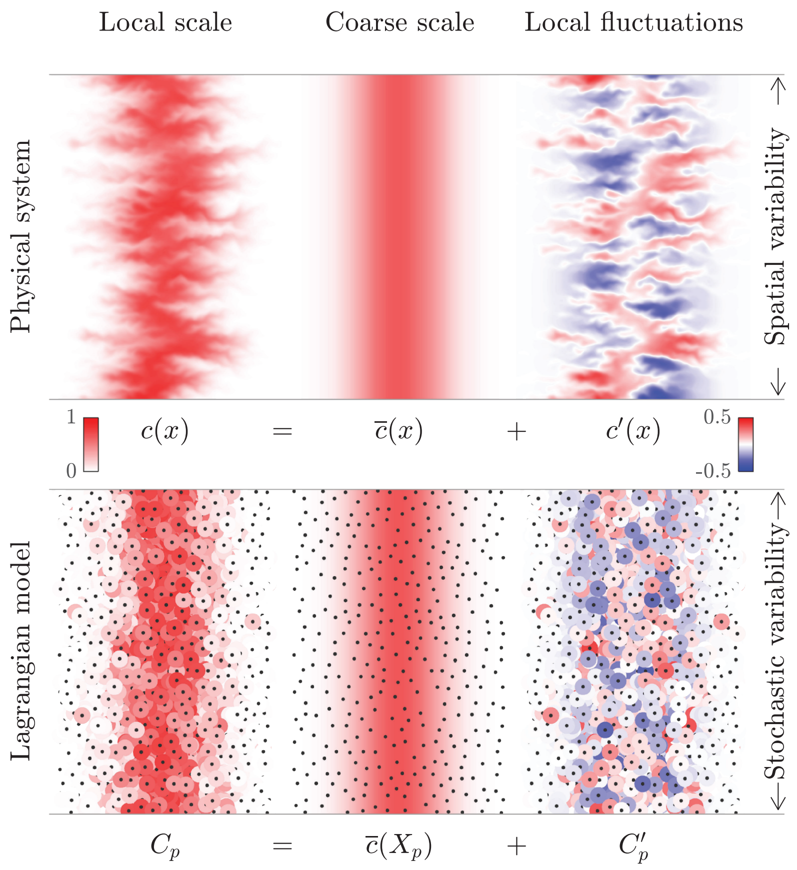

Figure 1. Local concentration variability within a true physical system and its conceptual representation in the proposed Lagrangian model, in which the coarse-scale concentrations are defined on the Eulerian space whereas the local concentrations are defined on the Lagrangian particles. Particles are represented by dark dots, and the colored circles around them show the corresponding local concentrations.

the porosity (volume of fluid per unit volume of medium) is constant. Hereafter, we also assume that $\mathbf{v}$ and $\mathbf{D}$ are spatially and temporally constant. These assumptions simplify the presentation and analysis of the model, but generalization should be readily possible.

One manner for solving equation (1) is via Random Walk Particle Tracking (RWPT) [e.g., *Salamon et al.*, 2006], a Lagrangian approach in which particles $p = 1, \ldots, N$ carry solute mass of one or several chemical species, and their trajectory over small time intervals $[t, t + \Delta t]$ is defined as a combination of deterministic advective displacements and a Wiener random process emulating dispersion,

$$\mathbf{X}_p\,(t + \Delta t) = \mathbf{X}_p\,(t) + \mathbf{v}\Delta t + \mathbf{B}\boldsymbol{\xi}\sqrt{\Delta t}, \tag{2}$$

where $\mathbf{X}_p$ is the position of particle p, $\mathbf{B}$ is a matrix such that $\mathbf{B}\mathbf{B}^{\mathrm{T}} = \mathbf{D}$, and $\boldsymbol{\xi}$ is a vector of random numbers drawn independently from a standard normal distribution. Here, similar to *Benson and Bolster* [2016a] and *Engdahl et al.* [2017], each particle p is assigned a static mass of solvent, m_p, and a variable concentration of solute A, $C_{\mathrm{A},p}$; therefore the mass of A carried by p is $m_p C_{\mathrm{A},p}$.

Given any particle attribute Ψ_p, one may define its interpolation onto the Eulerian space [*Monaghan*, 2005], here referred to as *local average* (since the interpolation removes any localized

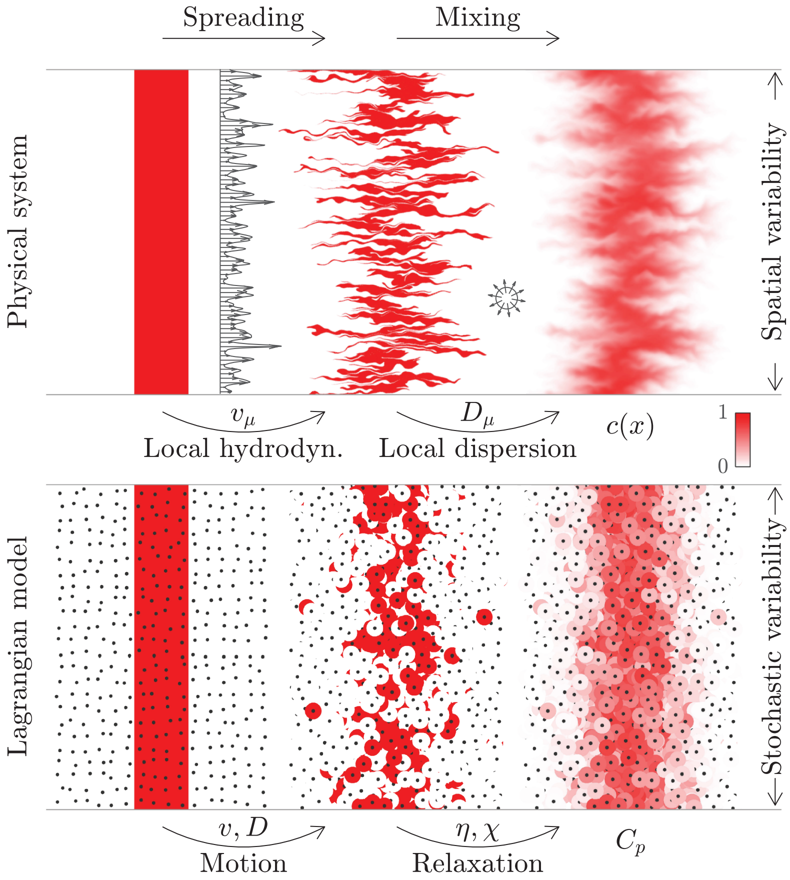

Figure 2. Spreading and mixing within a true physical system and their conceptual representation in the proposed Lagrangian model, in which the coarse-scale transport is simulated by the random motion of particles (2), and the local concentration is updated through multi-rate interaction by exchange with the mean (9). Particles are represented by dark dots, and the colored circles around them show the corresponding local concentrations or fluctuations.

variability), at any point $\mathbf{x}$ in model domain Ω^d, where d is the number of spatial dimensions,

$$\langle \Psi \rangle(\mathbf{x}) := \sum_p \frac{m_p}{\rho(\mathbf{X}_p)} \Psi_p \delta(\mathbf{x} - \mathbf{X}_p), \tag{3}$$

$$\rho(\mathbf{x}) := \sum_p m_p \delta(\mathbf{x} - \mathbf{X}_p), \tag{4}$$

where summation is implied over all particles $p = 1, \ldots, N$, and $\delta(\mathbf{x})$ is the d-dimensional Dirac delta function. Expression (3) is simply a weighted average of Ψ_p over particles p located at $\mathbf{X}_p = \mathbf{x}$; however, this interpretation of the interpolated concentrations is not smooth, other than in the limit of $N \to \infty$, and in practice it must be replaced by some form of small-volume average, for instance by replacing δ in (3) by a kernel function W with nonzero support volume. More details are given in Appendix A. For

$$\overline{c}_{\mathrm{A}}(\mathbf{x}, t) := \langle C_{\mathrm{A}}(t) \rangle(\mathbf{x}), \tag{5}$$

given particle motion equation (2) and in the limit $N \to \infty$, $\Delta t \to 0$, the *averaged concentrations* $\overline{c}_{\mathrm{A}}(\mathbf{x}, t)$ converge to being governed by the Fokker-Planck equation [*Risken*, 1989], which is equivalent to the ADE (1) when $\mathbf{D}$ is spatially constant; otherwise a correction can be applied to the drift term, see *LaBolle et al.* [1996].

To summarize, in the proposed Lagrangian model, each numerical particle represents a discrete amount of a chemical solution traveling through a porous medium, moving by displacements representing the scale-averaged advection (deterministic) and upscaled dispersion (normal random). Consequently, at the coarse scale, the concentration field obeys the advection-dispersion equation (ADE). This type of Lagrangian model is widely used by researchers and practitioners in hydrology to simulate nonreactive transport of solutes.

While coarse-scale concentrations of non-reactive chemicals may agree reasonably well with the ADE under certain conditions [*Dagan*, 1984], concentration fluctuations may still occur at the local scale. These local-scale fluctuations, which are not explicitly accounted for in classical formulations, may drive the outcome of nonlinear processes, such as chemical reactions, far from what would be predicted by the ADE [*Kang et al.*, 2019]. Note that by using equation (2) (or similar stochastic formulations), where each particle follows its own unique random path, it is implied that at any given time each particle is only sampling a portion of the local-scale fluid velocity field. Analogously, in the proposed model, particle concentrations $C_{\mathrm{A},p}(t)$ are assumed to represent the local-scale concentrations, and may therefore be at disequilibrium with the averaged $\overline{c}_\mathrm{A}(\mathbf{x}, t)$. Hence, hereafter we refer to $C_{\mathrm{A},p}(t)$ as *local concentrations*. Figure 1 is a schematic representation that illustrates our proposed conceptual model. The local-scale structured spatial variability of concentrations in the physical system is emulated by the stochastic variability of local concentrations experienced by overlapping Lagrangian particles in the model. Because it is defined by interpolation (see Appendix A), the coarse-scale concentration is a smooth function in the Eulerian space, whereas local departures from the well-mixed equilibrium or *local fluctuations* are only defined on the Lagrangian particles. In order to represent the evolution of these local fluctuations we need to define a *mixing model*.

A simple representation of the local mixing as seen by a particle p could be to assume a Fickian process driven by a local diffusion D_μ within a fluctuation structure of dimension d_μ and characteristic mixing length ℓ_μ,

$$\frac{\mathrm{d}C_{\mathrm{A},p}}{\mathrm{d}t} = -\frac{\chi}{2}[C_{\mathrm{A},p}(t) - \overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)], \tag{6}$$

where

$$\chi := 2d_\mu D_\mu/\ell_\mu^2 \tag{7}$$

is the mixing rate, which is equal to the inverse time scale for which a typical diffusive displacement matches the characteristic mixing length ℓ_μ. The notation d/dt in (6) indicates a *Lagrangian* time-derivative, defined as the temporal variation experienced by a moving fluid particle. This definition is similar to the classical concept of *material* derivative, with the difference that here particles follow stochastic paths instead of pure deterministic advection. The simple model embedded in (6) was originally suggested for mixing in turbulent flows, and it is known as *Interaction by Exchange with the Mean* (IEM) [*Villermaux*, 1972; *Pope*, 2000]. Its practical numerical implementation requires some careful consideration, related to features such as mass conservation. Implementation aspects, including small-volume approximations of the averaging operator, are discussed in Appendix A. An appealing advantage of this kind of mixing model is that a local value's variation in time depends only on its current degree of departure from the mean, potentially avoiding direct particle-particle interaction. Importantly in our context, the process is Markovian, i.e., the time-derivative (6) depends only on the current state. We note, however, that equation (6) is overly simplistic. Previous attempts to apply the IEM model (from an Eulerian perspective) to laminar flow and transport in heterogeneous porous media have concluded that, at the beginning of new contact between solutions with different chemical composition, one should account for a growing stage of ℓ_μ before it reaches a stable asymptotic value [*Kapoor and Kitanidis*, 1998; *de Dreuzy et al.*, 2012]. That is, a single constant value of χ cannot reproduce the distinct stages of the mixing process, and one should consider not only a slow linear mixing, but also a fast stretching-enhanced mixing stage. Moreover, fluctuations may occur across multiple overlapping length scales. As acknowledged by *Villermaux* [1983] in the context of IEM applied to turbulent mixing, "several stages for mixing, each with their own time constants should be considered, possibly in series or in parallel". Here, we propose a parallel multi-rate interaction by exchange with the mean (MRIEM), based on representing the mixing process as occurring within different virtual *mixing zones* $i = 1, \ldots, N_\mathrm{Z}$, each being sampled by a fraction η_i of the particle ($\sum_i \eta_i = 1$). Within each mixing zone i, each particle p sees a local concentration $C_{\mathrm{A},p,i}(t)$ of each species A, possibly at disequilibrium with $\overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)$, such that

$$C_{\mathrm{A},p}(t) = \sum_i \eta_i C_{\mathrm{A},p,i}(t), \tag{8}$$

and

$$\frac{\mathrm{d}C_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\chi_i}{2}\left[C_{\mathrm{A},p,i}(t) - \overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)\right]. \tag{9}$$

The values of η_i and χ_i are assumed to depend on local-scale flow and transport conditions. The zone-concentration values $C_{\mathrm{A},p,i}(t)$ do not necessarily have a physical meaning individually, but are instead intended to emulate the complex transient nature of the mixing process. In principle, parameter sets η_i and χ_i can be different for each species to account, for instance, for different values of the local-scale diffusion coefficient.

Given any Lagrangian-defined attribute Ψ_p and its average across the particle space $\langle \Psi \rangle$, it can be shown (see Appendix B) that, if particles move according to (2), the following relation holds between the Eulerian and the Lagrangian time-derivatives of Ψ:

$$\frac{\partial \langle \Psi \rangle}{\partial t} = \mathcal{L}\left(\langle \Psi \rangle; \mathbf{v}, \mathbf{D}\right) + \left\langle \frac{\mathrm{d}\Psi}{\mathrm{d}t} \right\rangle. \tag{10}$$

Then, by combining (10) with (8) and (9) we see that

$$\frac{\partial \overline{c}_\mathrm{A}}{\partial t} \equiv \frac{\partial \langle C_\mathrm{A} \rangle}{\partial t} = \mathcal{L}\left(\overline{c}_\mathrm{A}; \mathbf{v}, \mathbf{D}\right). \tag{11}$$

That is, the local mixing process described by (9) does not modify the coarse-scale description of non-reactive transport, driven by the particle displacements in (2).

One of the simplest implementations would comprise only two zones, one of them with an *instantaneous* mixing rate (i.e., very fast in relation to the time scale of interest),

$$1 - \eta_1 = \eta_2 \equiv \eta, \qquad \chi_1 \approx \infty, \qquad \chi_2 \equiv \chi. \tag{12}$$

Hereafter, we refer to this particular case as *dual-rate*, to η as the *slow mixing fraction*, and to χ as the *slow mixing rate*. In this case the local concentration in zone 1 is always at equilibrium with the coarse-scale concentration. Combining equations (8), (9) and (12) we may write:

$$\frac{\mathrm{d}C_{\mathrm{A},p}}{\mathrm{d}t} = (1-\eta)\frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t} - \frac{\chi}{2}\left[C_{\mathrm{A},p}(t) - \overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)\right], \tag{13}$$

where for conciseness from here on, inside the derivative we use the notation $\overline{c}_{\mathrm{A},p}(t) \equiv \overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)$. In the dual-rate model (12), equation (13) can be interpreted as such: While following its random path described by (2), fluid-particle p may experience variations in the perceived coarse-scale concentration of A. Conceptually, these changes correspond to the particle seeing itself involved in new *mixing events*, that is, in the formation of new fluctuation structures. Only a portion $1 - \eta$ of these variations, corresponding to the pre-asymptotic or deformation-related mixing fraction, equilibrates instantaneously with the new coarse-scale concentration. Hence, a local disequilibrium of the opposite sign corresponding to the remaining unmixed fraction η is generated, and it will decay over time following a stationary Fickian mixing process at rate χ.

Figure 2 illustrates the conceptual decoupling of transport as a combination of spreading and mixing, in the true physical system as well as in the proposed Lagrangian model in one coarse-scale dimension. In the physical system, spreading represents the growth of the width (variance) of a solute plume due to velocity variability, which, alone, does not generate new contact between otherwise segregated solute molecules. Mixing, on the other hand, is precisely the generation of new contact between formerly segregated solutes, and is the result of local dispersion applied to the structure generated by spreading (see upper-right part of Figure 2). This decoupled picture is a simplification, because there is a continuous interplay between the two processes. The rate of spreading is influenced non-linearly by local dispersion [e.g., *van Milligen and Bons*, 2012]. Similarly, mixing is influenced by the growth of contact surfaces, which is controlled by local advection [e.g., *Villermaux*, 2012]. In the proposed Lagrangian model, spreading is represented by particle motion (2), which controls the coarse-scale behavior of concentrations; mixing is represented by the relaxation equation (9), which mitigates local departures from equilibrium experienced by individual particles, arising due to the aforementioned random motion.

2.2 Reactive transport

The proposed Lagrangian model can be extended to reactive transport applications by following the premise that chemical reactions occur at the local scale and thus are controlled exclusively by local concentrations defined on Lagrangian particles. We provide a brief summary on the incorporation of kinetic transformation (§2.2.1) and equilibrium speciation (§2.2.2). Naturally, the two may be integrated together, such as in *Molins et al.* [2004].

2.2.1 Kinetic reactions

Consider multiple kinetic reactions labeled $k = 1, \dots, N_\mathrm{R}$, with reaction rate laws that model reactions as a function of solute concentrations, $r_k(\mathbf{C})$, where $\mathbf{C} \equiv [C_\mathrm{A}, C_\mathrm{B}, \dots]^\mathrm{T}$; and stoichiometric coefficients $\nu_{\mathrm{A},k}, \nu_{\mathrm{B},k}, \dots$, which indicate the generation/consumption of concentration per unit extent of reaction. Equation (9) is then extended to:

$$\frac{\mathrm{d}C_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\chi_i}{2}[C_{\mathrm{A},p,i}(t) - \overline{c}_\mathrm{A}(\mathbf{X}_p(t), t)] + \mathcal{R}_\mathrm{A}(\mathbf{C}_p(t)) \tag{14}$$

where

$$\mathcal{R}_\mathrm{A}(\mathbf{C}) \coloneqq \sum_k \nu_{\mathrm{A},k} r_k(C_\mathrm{A}, C_\mathrm{B}, \dots). \tag{15}$$

By combining (14) with (10) we obtain the coarse-scale Eulerian description

$$\frac{\partial \overline{c}_\mathrm{A}}{\partial t} = \mathcal{L}(\overline{c}_\mathrm{A}; \mathbf{v}, \mathbf{D}) + \langle \mathcal{R}_\mathrm{A}(\mathbf{C}) \rangle. \tag{16}$$

Equation (16) elucidates that, for nonlinear reaction systems, i.e., $\langle \mathcal{R}_\mathrm{A}(\mathbf{C}) \rangle \neq \mathcal{R}_\mathrm{A}(\overline{\mathbf{c}})$, the Eulerian description of reactive transport does not obey the classical form of the advection-dispersion-reaction equation (ADRE) where reactions are computed directly from averaged concentrations. This is in contrast with the conservative transport case, where as shown by equation (11), coarse-scale concentrations do follow the classical ADE.

2.2.2 Equilibrium reactions

In the case of equilibrium reactions, a common approach is to compute the transport of chemically conservative components [e.g., *Saaltink et al.*, 1998; *Molins et al.*, 2004; *De Simoni et al.*, 2005], and then speciation is provided by solving equilibrium system,

$$C_{\mathrm{A},p}(t) = \mathcal{E}_\mathrm{A}(\mathbf{U}_p(t)). \tag{17}$$

where $\mathcal{E}_\mathrm{A}(\mathbf{U})$ combines the law of mass action and the different stoichiometries to find the equilibrium concentrations, from components $\mathbf{U} \equiv \{U_\mathrm{A}, U_\mathrm{B}, \dots\}$. In (17), $\mathbf{U}_p$ follow the conservative transport and mixing model presented in §2.1. By taking the particle average on both sides of (17), we obtain the coarse-scale description of the equilibrium reaction system

$$\overline{c}_\mathrm{A} = \langle \mathcal{E}_\mathrm{A}(\mathbf{U}) \rangle. \tag{18}$$

We note from (18) that, similar to the kinetic reaction example, $\overline{c}_\mathrm{A} \neq \mathcal{E}_\mathrm{A}(\overline{\mathbf{u}})$, as opposed to classical well-mixed reactive transport approaches.

3 Covariance of fluctuations

Here we study the behavior of the local concentration fluctuations, in terms of the local concentration co-variance of two chemically conservative compounds A and B (where the particular single-compound case is implicitly included as $\mathrm{A} \equiv \mathrm{B}$). First, in §3.1, we derive the partial differential equation describing covariance generation, transport and destruction. Then, in §3.2, we study integrated mixing metrics for two specific cases with closed form solutions.

3.1 Governing equation

By defining the local fluctuation as the departure from well-mixed equilibrium on particles,

$$C'_{\mathrm{A},p}(t) \coloneqq C_{\mathrm{A},p}(t) - \overline{c}_{\mathrm{A}}(\mathbf{X}_p(t), t) = \sum_i \eta_i C'_{\mathrm{A},p,i}(t), \tag{19}$$

$$C'_{\mathrm{A},p,i}(t) \coloneqq C_{\mathrm{A},p,i}(t) - \overline{c}_{\mathrm{A}}(\mathbf{X}_p(t), t), \tag{20}$$

one may rewrite equation (9) as

$$\frac{\mathrm{d}C'_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\mathrm{d}\overline{c}_{\mathrm{A},p}}{\mathrm{d}t} - \frac{\chi_i}{2} C'_{\mathrm{A},p,i}(t). \tag{21}$$

By definition, $\langle C'_{\mathrm{A}} \rangle(\mathbf{x}, t) = 0$. We study the concentration covariance of species A and B, which we denote as $\mathit{\Sigma}_{\mathrm{AB}}(\mathbf{x}, t)$,

$$\mathit{\Sigma}_{\mathrm{AB}} \coloneqq \langle C'_{\mathrm{A}} C'_{\mathrm{B}} \rangle = \sum_{i,j} \hat{\eta}_{ij} \langle C'_{\mathrm{A},i} C'_{\mathrm{B},j} \rangle \equiv \sum_{i,j} \hat{\eta}_{ij} \mathit{\Sigma}_{\mathrm{AB},ij}, \qquad \hat{\eta}_{ij} \coloneqq \eta_i \eta_j. \tag{22}$$

As noted in §2.1, the assumption that the mixing dynamics of A and B can be described by the same sets of parameters $\{\eta_1, \ldots, \eta_{N_{\mathrm{Z}}}\}$, $\{\chi_1, \ldots, \chi_{N_{\mathrm{Z}}}\}$, is made here only for the sake of simplicity, and this assumption could be relaxed.

For a particle p, following a first-order integration of equation (21) over a small time step $[t, t + \Delta t]$, we have

$$\begin{aligned} C'_{\mathrm{A},p,i}(t+\Delta t)\, C'_{\mathrm{B},p,j}(t+\Delta t) = {} & \left(C'_{\mathrm{A},p,i}(t) - \left[\overline{c}_{\mathrm{A},p}(t+\Delta t) - \overline{c}_{\mathrm{A},p}(t) \right] - \frac{\chi_i}{2} \Delta t\, C'_{\mathrm{A},p,i}(t) \right) \\ & \times \left(C'_{\mathrm{B},p,j}(t) - \left[\overline{c}_{\mathrm{B},p}(t+\Delta t) - \overline{c}_{\mathrm{B},p}(t) \right] - \frac{\chi_j}{2} \Delta t\, C'_{\mathrm{B},p,j}(t) \right). \end{aligned} \tag{23}$$

For $\chi \Delta t \ll 1$, this can be rewritten as

$$\Delta(C'_{\mathrm{A},p,i} C'_{\mathrm{B},p,j}) = \Delta\overline{c}_{\mathrm{A},p} \Delta\overline{c}_{\mathrm{B},p} - \hat{\chi}_{ij} \Delta t C'_{\mathrm{A},p,i} C'_{\mathrm{B},p,j} - \left(C'_{\mathrm{A},p,i} \Delta\overline{c}_{\mathrm{B},p} + C'_{\mathrm{B},p,j} \Delta\overline{c}_{\mathrm{A},p} \right), \tag{24}$$

with ΔU denoting the variaton of U in time step Δt, and

$$\hat{\chi}_{ij} \coloneqq \frac{\chi_i + \chi_j}{2}. \tag{25}$$

The first-order Taylor expansion of $\Delta\overline{c}_{\mathrm{A},p}$ is

$$\begin{aligned} \Delta\overline{c}_{\mathrm{A},p} &\approx \Delta\mathbf{X}_p^{\mathrm{T}} \nabla\overline{c}_{\mathrm{A}} + \Delta t \frac{\partial \overline{c}_{\mathrm{A}}}{\partial t} = \sqrt{2\Delta t}\, \boldsymbol{\xi}^{\mathrm{T}} \mathbf{B}^{\mathrm{T}} \nabla\overline{c}_{\mathrm{A}} + \Delta t \left[\mathbf{v}^{\mathrm{T}} \nabla\overline{c}_{\mathrm{A}} + \mathcal{L}(\overline{c}_{\mathrm{A}}; \mathbf{v}, \mathbf{D}) \right] \\ &= \sqrt{2\Delta t}\, \boldsymbol{\xi}^{\mathrm{T}} \mathbf{B}^{\mathrm{T}} \nabla\overline{c}_{\mathrm{A}} + \Delta t\, \nabla \cdot (\mathbf{D} \nabla c_{\mathrm{A}}) \approx \sqrt{2\Delta t}\, \boldsymbol{\xi}^{\mathrm{T}} \mathbf{B}^{\mathrm{T}} \nabla\overline{c}_{\mathrm{A}}. \end{aligned} \tag{26}$$

Note that in the last step of (26) we keep the lower-order term only. Considering the analogous expression for $\Delta\overline{c}_{\mathrm{B},p}$, we may rewrite (24) as

$$\Delta(C'_{\mathrm{A},p,i} C'_{\mathrm{B},p,j}) = 2\Delta t \nabla\overline{c}_{\mathrm{A}}^{\mathrm{T}} \mathbf{B} \boldsymbol{\xi} \boldsymbol{\xi}^{\mathrm{T}} \mathbf{B}^{\mathrm{T}} \nabla\overline{c}_{\mathrm{B}} - \hat{\chi}_{ij} \Delta t C'_{\mathrm{A},p,i} C'_{\mathrm{B},p,j} - \left(C'_{\mathrm{A},p,i} \Delta\overline{c}_{\mathrm{B},p} + C'_{\mathrm{B},p,j} \Delta\overline{c}_{\mathrm{A},p} \right). \tag{27}$$

Dividing both sides of (27) by Δt, taking the limit of $\Delta t \to 0$, and taking the expected value, we obtain:

$$\left\langle \frac{\mathrm{d}(C'_{\mathrm{A},i} C'_{\mathrm{B},j})}{\mathrm{d}t} \right\rangle = 2 \nabla \bar{c}_{\mathrm{A}}^{\mathrm{T}} \mathbf{D} \nabla \bar{c}_{\mathrm{B}} - \hat{\chi}_{ij} \langle C'_{\mathrm{A},i} C'_{\mathrm{B},j} \rangle. \tag{28}$$

Finally, substituting into equation (10),

$$\frac{\partial \Sigma_{\mathrm{AB},ij}}{\partial t} = 2 \nabla \bar{c}_{\mathrm{A}}^{\mathrm{T}} \mathbf{D} \nabla \bar{c}_{\mathrm{B}} - \hat{\chi}_{ij} \Sigma_{\mathrm{AB},ij} + \mathcal{L}(\Sigma_{\mathrm{AB},ij}; \mathbf{v}, \mathbf{D}). \tag{29}$$

We have obtained the partial differential equation describing the spatio-temporal evolution of the "ij" entry of the local concentration covariance of A and B in the absence of reactions. The total local concentration covariance can be then obtained as the sum of all entries, as indicated by (22). Let us consider, once again, the specific case represented by (12). Then, one may write:

$$\frac{\partial \Sigma_{\mathrm{AB}}}{\partial t} = 2\eta^2 \nabla \bar{c}_{\mathrm{A}}^{\mathrm{T}} \mathbf{D} \nabla \bar{c}_{\mathrm{B}} - \chi \Sigma_{\mathrm{AB}} + \mathcal{L}(\Sigma_{\mathrm{AB}}; \mathbf{v}, \mathbf{D}). \tag{30}$$

It is worth remarking that, for B = A, expression (30) is mathematically equivalent to the *concentration variance conservation equation* introduced by *Kapoor and Gelhar* [1994, equation 56], provided a scalar proportionality in their proposed dual-dispersivity system such that η fulfills $\mathbf{A} = \eta^2(\boldsymbol{\alpha} + \mathbf{A})$, where $\boldsymbol{\alpha}$ and $\mathbf{A}$ are the microdispersivity and macrodispersivity tensors, respectively. Hence, the two conceptual models have clear similarities since in our case η is the fraction of non-instantaneous mixing, and in *Kapoor and Gelhar* [1994], by analogy, it is the square root of the fraction of total dispersivity that is attributed to the macrodispersivity, i.e., to the non-mixed spreading. Nevertheless, there are important nuances that distinguish the models, as will be discussed in §4.2.

In any case, determining concentration variance/covariance is not the main, or at least not the only, purpose of our model. As outlined in §2.2, the distribution of local concentrations represented by the particles affects local processes such as chemical reactions. Nevertheless, the concentration covariance is a powerful tool to assess contact between solutions, and therefore a good proxy for the potential magnitude of incomplete mixing effects on chemical reactions.

3.2 Mixing state evolution

This section focuses on the dual-rate (fast/slow) local mixing parametrization (12). The results are elementary building blocks for other more complex cases. The differential equation (30) is linked with the solution of (1) through the source term

$$S(\mathbf{x}, t) := 2\eta^2 \nabla \bar{c}_{\mathrm{A}}^{\mathrm{T}} \mathbf{D} \nabla \bar{c}_{\mathrm{B}}. \tag{31}$$

The other terms are exponential decay, advection, and dispersion. Therefore, if $S(\mathbf{x}, t)$ is known, $\Sigma_{\mathrm{AB}}(\mathbf{x}, 0) = 0$, and the domain is unbounded, the solution for the point-covariance evolution can be obtained through the space-time convolution of the Greens function with the source term, i.e.:

$$\Sigma_{\mathrm{AB}}(\mathbf{x}, t) = \int_0^t \int_{\mathbb{R}^d} G\left(\mathbf{x} - \boldsymbol{\kappa}, t - \tau\right) S\left(\boldsymbol{\kappa}, \tau\right) d\boldsymbol{\kappa} \mathrm{d}\tau, \tag{32}$$

with

$$G(\mathbf{x}, t) := \left([2\pi]^d 2 |\mathbf{D}| t\right)^{-\frac{1}{2}} \exp\left(-\frac{[\mathbf{x} - \mathbf{v}t]^{\mathrm{T}} \mathbf{D}^{-1} [\mathbf{x} - \mathbf{v}t]}{4t} - \chi t\right), \tag{33}$$

where the operator $|\ |$ applied to a tensor is its determinant. A metric that is commonly used to characterize spatial fluctuations of solute concentrations is the so-called mixing state [*Bolster et al.*, 2011; *de Dreuzy et al.*, 2012], which is defined as the spatial integral of the squared concentrations. Here we extend this definition, for any two solutes, A and B, as the spatial integral of the product of the two concentrations. In the present two-scale context, this may be written as

$$M_{\mathrm{AB}}(t) := \int_{\Omega^d} \langle C_{\mathrm{A}} C_{\mathrm{B}} \rangle \, \mathrm{d}\mathbf{x} = M_{\mathrm{AB}}^{\bar{\mathrm{c}}}(t) + M_{\mathrm{AB}}^{\Sigma}(t), \tag{34}$$

where Ω^d is the model domain, M_{AB} is the mixing state, $M^{\overline{c}}_{\mathrm{AB}}$ is the *ideal* mixing when sub-scale fluctuations are not considered, and M^{Σ}_{AB} is the contribution of the local fluctuations to the mixing state (which may be either positive or negative):

$$M^{\overline{c}}_{\mathrm{AB}}(t) := \int_{\Omega^d} \overline{c}_{\mathrm{A}}(\mathbf{x},t)\overline{c}_{\mathrm{B}}(\mathbf{x},t)\,\mathrm{d}\mathbf{x}, \qquad M^{\Sigma}_{\mathrm{AB}}(t) := \int_{\Omega^d} \mathit{\Sigma}_{\mathrm{AB}}(\mathbf{x},t)\,\mathrm{d}\mathbf{x}. \tag{35}$$

In the particular case A = B one recovers the classical definition. Additionally, we also quantify the relative deviation from the ideal *well-mixed* behavior:

$$\gamma_{\mathrm{AB}}(t) := \frac{M_{\mathrm{AB}} - M^{\overline{c}}_{\mathrm{AB}}}{M^{\overline{c}}_{\mathrm{AB}}} = \frac{M^{\Sigma}_{\mathrm{AB}}}{M^{\overline{c}}_{\mathrm{AB}}}. \tag{36}$$

Here, quantity $\gamma_{\mathrm{AB}}(t)$ is analogous to the $\gamma(t)$ from *de Dreuzy et al.* [2012] for a single species.

In some cases with simple boundary and initial conditions, closed-form solutions exist for the integrals in (35). Below, we provide and discuss two such simple but representative cases.

3.2.1 Continuous injection

Consider a mean-uniform stationary flow in an infinitely long domain, which at the coarse scale can be considered as one-dimensional. At $t = 0$, the concentrations of two solutes A and B are represented by Heaviside-step functions, forming a sharp interface at $x = 0$:

$$\overline{c}_{\mathrm{A}}(x,0) = c_{\mathrm{o}}\mathcal{H}(-x), \qquad \overline{c}_{\mathrm{B}}(x,0) = c_{\mathrm{o}}\mathcal{H}(x), \tag{37}$$

where $\mathcal{H}(x)$ is the Heaviside step function. Additionally, $\mathit{\Sigma}_{\mathrm{AB}}(x,0) = 0$.

The solution of the ADE (1) in this case is

$$\overline{c}_{\mathrm{A}}(x,t) = c_{\mathrm{o}} - \overline{c}_{\mathrm{B}}(x,t) = \frac{c_{\mathrm{o}}}{2}\mathrm{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right). \tag{38}$$

Then, the ideal mixing term is

$$M^{\overline{c}}_{\mathrm{AB}}(t) = \int_{-\infty}^{\infty} \overline{c}_{\mathrm{A}}(x,t)\overline{c}_{\mathrm{B}}(x,t)\,\mathrm{d}x = \pi^{-\frac{1}{2}} c_{\mathrm{o}}^2 \sqrt{2Dt} \equiv \pi^{-\frac{1}{2}} c_{\mathrm{o}}^2 \ell \sqrt{\chi t}, \tag{39}$$

with the characteristic *coarse-scale mixing length* ℓ, defined as

$$\ell := \sqrt{2D/\chi}, \tag{40}$$

which is the typical distance traveled by the solute by dispersion within one characteristic mixing time.

For this case, the source term of the covariance (eq. (31)) is:

$$S(x,t) = -\frac{\eta^2 c_{\mathrm{o}}^2\, \mathrm{e}^{-\frac{(x-vt)^2}{2Dt}}}{2\pi t}, \tag{41}$$

and then the covariance, obtained through equation (32), is

$$\mathit{\Sigma}_{\mathrm{AB}}(x,t) = -\frac{\eta^2 c_{\mathrm{o}}^2}{2\pi} \int_0^t [\tau(2t-\tau)]^{-\frac{1}{2}} \exp\left(-\frac{(x-vt)^2}{2D(2t-\tau)} - \chi(t-\tau)\right)\mathrm{d}\tau. \tag{42}$$

To our knowledge, the resulting time-integral in (42) does not have an exact analytical solution. Nevertheless, a (pseudo-)closed form does exist for its integral in space (i.e., the local mixing term):

$$M^{\Sigma}_{\mathrm{AB}}(t) = \int_{-\infty}^{\infty} \mathit{\Sigma}_{\mathrm{AB}}(x,t)\,\mathrm{d}x = -\pi^{-\frac{1}{2}} \eta^2 c_{\mathrm{o}}^2 \sqrt{\frac{2D}{\chi}}\, F\left(\sqrt{\chi t}\right) \equiv -\pi^{-\frac{1}{2}} \eta^2 c_{\mathrm{o}}^2 \ell\, F\left(\sqrt{\chi t}\right), \tag{43}$$

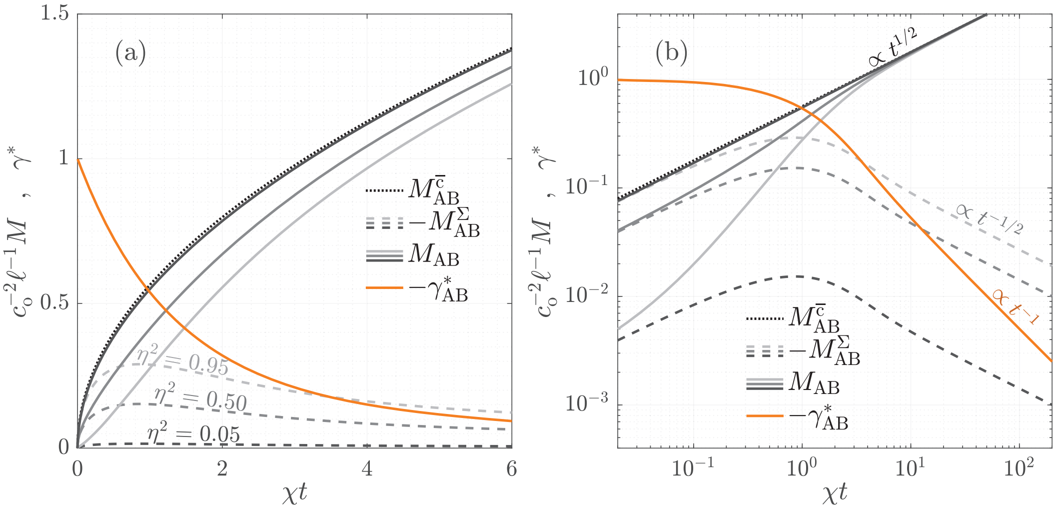

Figure 3. Temporal evolution of various mixing metrics for the dual-rate model (12), according to the solution of equations (1) and (30), for two solutes A and B initially forming a sharp interface perpendicular to the flow direction, shown in (a) linear and (b) logarithmic scale.

where $F(u)$ is the Dawson integral:

$$F(u) := \mathrm{e}^{-u^2}\int_0^u \mathrm{e}^{r^2}\mathrm{d}r \approx \begin{cases} u, & \text{for } u \ll 1, \\ \frac{1}{2}u^{-1}, & \text{for } u \gg 1. \end{cases} \tag{44}$$

From (43) and (44), we see that there is an early-time regime where concentration covariance generation dominates ($M_{\mathrm{AB}}^{\Sigma} \propto t^{1/2}$) followed by a late-time regime where concentration covariance destruction dominates ($M_{\mathrm{AB}}^{\Sigma} \propto t^{-1/2}$). M_{AB}^{Σ} is negative meaning that the local covariance reduces the contact between A and B with respect to the ideal value $M_{\mathrm{AB}}^{\bar{c}}$. The maximum negative magnitude of $M_{\mathrm{AB}}^{\Sigma}(t)$ is achieved for $t = 0.854\chi^{-1}$.

We study the relative deviation from ideal "well-mixed" behavior through γ_{AB} (eq. (36)). From (39) and (43)

$$\gamma_{\mathrm{AB}}(t) = \eta^2\gamma_{\mathrm{AB}}^*(\chi t), \tag{45}$$

$$\gamma_{\mathrm{AB}}^*(t^*) := -\frac{1}{\sqrt{t^*}}F\left(\sqrt{t^*}\right), \tag{46}$$

where $t^* := \chi t$ is a dimensionless time.

Figure 3 shows the evolution in time of the mixing metrics. Higher values of the slow-mixing fraction η in the dual-rate model accentuate the departure of the actual mixing state (continuous lines) from the ideal well-mixed case (dotted line). The relative difference between these two quantities, quantified by $\gamma_{\mathrm{AB}} = \eta^2\gamma_{\mathrm{AB}}^*$, is highest at the beginning, and decays for $\chi t \gg 1$ as t^{-1}, as can be observed on the log-log scale plot. The actual mixing scales with $t^{1/2}$ for $\chi t \gg 1$. Taking the modeled mixing state M_{AB}, depicted in Figure 3(b), as a proxy for the amount of reaction, we see that it does reproduce trends observed in mixing-limited systems such as simple Poiseuille flows [e.g., *Perez et al.*, 2019, Figure 7].

As outlined at the beginning of §3.2, the summation in (22) allows us generalize the solution for any choice of mixing parameters as a summation of elementary solutions given by (46):

$$\gamma_{\mathrm{AB}}(t) = \sum_{i,j}\hat{\eta}_{ij}\gamma_{\mathrm{AB}}^*(\hat{\chi}_{ij}t). \tag{47}$$

3.2.2 Pulse injection

Now let us consider the same simple uniform flow in an infinite-length medium, but with a different initial condition. In this case, there is only one solute A, of which a mass (per cross-section unit area) m_o is injected over a small region around the origin with a Gaussian distribution characterized by a length λ_o:

$$\bar{c}_\mathrm{A}(x,0) = \frac{m_\mathrm{o}}{\sqrt{2\pi}\lambda_\mathrm{o}} \mathrm{e}^{-\frac{x^2}{2\lambda_\mathrm{o}^2}}. \tag{48}$$

Here we study the mixing state of A, $M_\mathrm{AA}(t)$. Note that it has the opposite intuitive meaning than the $M_\mathrm{AB}(t)$ analyzed in §3.2.1: A more advanced mixing process will be characterized by lower values of $M_\mathrm{AA}(t)$, and viceversa. Once again, we assume that the initial condition for the fluctuations is $\Sigma_\mathrm{AA}(x,0) = 0$.

The resulting time-dependent mean-concentration profile is also a Gaussian:

$$\bar{c}_\mathrm{A}(x,t) = \frac{m_\mathrm{o}}{2\sqrt{\pi D(t+t_\mathrm{o})}} \mathrm{e}^{-\frac{(x-vt)^2}{4D(t+t_\mathrm{o})}}, \tag{49}$$

with $t_\mathrm{o} := \lambda_\mathrm{o}^2/2D$. Then, the ideal mixing term is

$$M_\mathrm{AA}^{\bar{c}}(t) = \int_{-\infty}^{\infty} \bar{c}_\mathrm{A}^2(x,t)\,\mathrm{d}x = \frac{m_\mathrm{o}^2}{\sqrt{8\pi D(t+t_\mathrm{o})}} \equiv \frac{m_\mathrm{o}^2}{2\ell\sqrt{\pi\chi(t+t_\mathrm{o})}}. \tag{50}$$

Here, the source term of the variance (eq. (31) with B = A) is:

$$S(x,t) = 2\eta^2 D \left(\frac{\partial \bar{c}_\mathrm{A}}{\partial x}\right)^2 = \frac{\eta^2 m_\mathrm{o}^2 (x-vt)^2}{8\pi D^2 (t+t_\mathrm{o})^3} \mathrm{e}^{-\frac{(x-vt)^2}{2D(t+t_\mathrm{o})}}, \tag{51}$$

and expression (32) gives the evolution of the variance:

$$\begin{aligned}\Sigma_\mathrm{AA}(x,t) = \frac{\eta^2 m_\mathrm{o}^2}{8\pi D^2} \int_0^t & \frac{2D(t-\tau)(2t-\tau+t_\mathrm{o}) + (x-vt)^2(\tau+t_\mathrm{o})}{(2t-\tau+t_\mathrm{o})^{2.5}(\tau+t_\mathrm{o})^{1.5}} \\ & \times \exp\left(-\frac{(x-vt)^2}{2D(2t-\tau+t_\mathrm{o})} - \chi(t-\tau)\right) \mathrm{d}\tau.\end{aligned} \tag{52}$$

Like in the continuous injection case (42), we could not find a closed-form solution to the time-integral in (52). But again, its spatial integral (the local mixing term) can be expressed in terms of the Dawson function (or more precisely, its derivative):

$$\begin{aligned}M_\mathrm{AA}^{\Sigma}(t) = \int_{-\infty}^{\infty} \Sigma_\mathrm{AA}(x,t)\,\mathrm{d}x &= \frac{\eta^2 m_\mathrm{o}^2}{\sqrt{8\pi D(t+t_\mathrm{o})}} \left[f\left(\sqrt{\chi t_\mathrm{o}}\right)\left(\sqrt{1+t/t_\mathrm{o}}\right)\mathrm{e}^{-\chi t} - f\left(\sqrt{\chi(t+t_\mathrm{o})}\right)\right] \\ &\equiv \frac{\eta^2 m_\mathrm{o}^2}{2\ell\sqrt{\pi\chi(t+t_\mathrm{o})}} \left[f\left(\sqrt{\chi t_\mathrm{o}}\right)\left(\sqrt{1+t/t_\mathrm{o}}\right)\mathrm{e}^{-\chi t} - f\left(\sqrt{\chi(t+t_\mathrm{o})}\right)\right],\end{aligned} \tag{53}$$

with $f(u)$ defined as the derivative of $F(u)$,

$$f(u) := \frac{\mathrm{d}F}{\mathrm{d}u} = 1 - 2u\,F(u) \approx \begin{cases} 1, & \text{for } u \ll 1, \\ -\frac{1}{2}u^{-2}, & \text{for } u \gg 1. \end{cases} \tag{54}$$

Once again, we characterize the relative deviation from the well-mixed behavior:

$$\gamma_\mathrm{AA}(t) := \frac{M_\mathrm{AA}^{\Sigma}}{M_\mathrm{AA}^{\bar{c}}} = \eta^2 \gamma_\mathrm{AA}^*(\chi t; \chi t_\mathrm{o}), \tag{55}$$

$$\gamma_\mathrm{AA}^*(t^*; t_\mathrm{o}^*) := f\left(\sqrt{t_\mathrm{o}^*}\right)\left(\sqrt{1+t^*/t_\mathrm{o}^*}\right)\mathrm{e}^{-t^*} - f\left(\sqrt{t^*+t_\mathrm{o}^*}\right), \tag{56}$$

with $t_\mathrm{o}^* := \chi t_\mathrm{o}$.

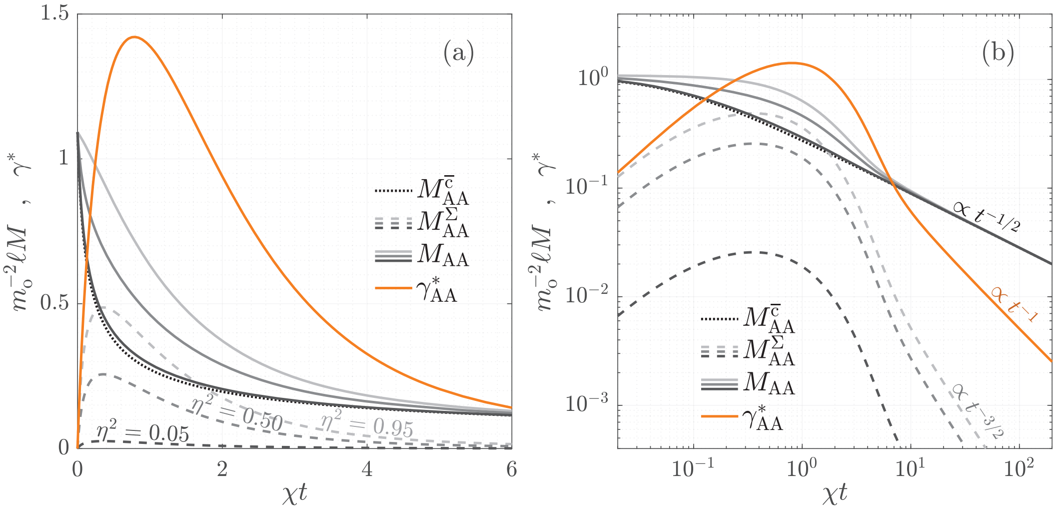

Figure 4. Temporal evolution of various mixing metrics for the dual-rate model (12), according to the solution of equations (1) and (30), for one solute A initially placed as a Gaussian pulse of longitudinal standard deviation 0.26ℓ, shown in (a) linear and (b) logarithmic scale.

Figure 4 depicts the evolution of the mixing metrics in dimensionless time, for a small value of initial pulse size, with $t_o = (15\chi)^{-1}$. Similar to the case in §3.2.1, higher values of η result in reduced mixing, as exhibited here by higher values of the actual mixing state (continuous lines) compared to the ideal mixing state (dotted line). The ratio between these two quantities, $\gamma_{AA} = \eta^2\gamma^*_{AA}$, is zero at $t = 0$, since there is no incomplete mixing, and it starts to grow as the spreading process generates local concentration fluctuations. This increasing trend peaks at $\chi t \approx 0.785$ (for the specific value of $\chi t_o = 1/15$). After that, fluctuation destruction dominates and γ_{AA} decreases as t^{-1} for $\chi t \gg 1$. At these long times, the actual mixing tends to approach the $\propto t^{-1/2}$ trend of ideal mixing. These features agree with semi-analytical [*Bolster et al.*, 2011] and numerical [*de Dreuzy et al.*, 2012] calculations of the mixing state evolution in fully-resolved porous media flows for a pulse injection of solute.

As in §3.2.1, elementary solution (56) is a building block for generalizing (55) to more complex mixing parametrizations than the dual-rate form:

$$\gamma_{AA}(t) = \sum_{i,j} \hat{\eta}_{ij}\gamma^*_{AA}(\hat{\chi}_{ij}t; \hat{\chi}_{ij}t_o). \tag{57}$$

4 Reproducing results of a reactive transport experiment

4.1 Experimental setup and background

In this Section we use the proposed model to reproduce results from the now well known experiments of *Gramling et al.* [2002]. In these experiments, performed in a column with a saturated granular material, a solution of EDTA^{4-}, initially occupying all the pore space with concentration c_o, was displaced longitudinally by an invading solution of CuSO$_4$ with the same molar concentration c_o. As these two solutes moved through the porous medium, the combination of hydrodynamic dispersion and molecular diffusion allowed them to mix and react forming CuEDTA^{2-}, among other reaction products. Hereafter, for simplicity and consistency with the original work, we refer to the three cited compounds as A, B, and AB, respectively. The reaction can be expressed as

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{AB}, \tag{58}$$

with equilibrium equation,

$$k_{\mathrm{eq}} \coloneqq \frac{c_{\mathrm{A}}c_{\mathrm{B}}}{c_{\mathrm{AB}}} \ll 1, \tag{59}$$

and a reaction rate that can be assumed instantaneous given the time scales of the experiment. Because equilibrium constant k_{eq} is very small (practically zero), c_{A} and c_{B} will always be instantaneously consumed when in contact, until one of them is exhausted locally (i.e., they cannot coexist). Hence, if we define the following conservative components,

$$u_{\mathrm{A}} \coloneqq c_{\mathrm{A}} + c_{\mathrm{AB}}, \qquad u_{\mathrm{B}} \coloneqq c_{\mathrm{B}} + c_{\mathrm{AB}}, \tag{60}$$

then the reaction product concentration will be given by

$$c_{\mathrm{AB}} = \mathcal{E}_{\mathrm{AB}}(u_{\mathrm{A}}, u_{\mathrm{B}}) = \min\left(u_{\mathrm{A}}, u_{\mathrm{B}}\right). \tag{61}$$

The fully-resolved (pore-scale) transport of u_{A} and u_{B} follows the conservative form of the advection-diffusion equation,

$$\frac{\partial u_{\mathrm{A}}}{\partial t} = \mathcal{L}(u_{\mathrm{A}}; \mathbf{v}_\mu, D_\mu), \tag{62}$$

with operator $\mathcal{L}$ defined as in (1), $\mathbf{v}_\mu$ being the heterogeneous velocity field within the saturated pore geometry, and D_μ being the molecular diffusion coefficient. The analogous of (62) applies to u_{B}; however, in this particular case, because of the initial condition, $u_{\mathrm{A}}(\mathbf{x}, t) + u_{\mathrm{B}}(\mathbf{x}, t) = c_{\mathrm{o}}$, hence we have that $u_{\mathrm{B}}(\mathbf{x}, t) = c_{\mathrm{o}} - u_{\mathrm{A}}(\mathbf{x}, t)$ and the transport is fully described by just one of the two equilibrium components.

However, in practice, a simple and complete solution is rarely obtainable, because of (*i*) the lack of detailed information on the pore geometry and (*ii*) high computational demands, which is why this problem requires an upscaled approach. As an approximation, we ignore the boundary effect at the inlet, i.e., we assume an infinite medium. Then, the upscaled one-dimensional description of the transport of $\overline{u}_{\mathrm{A}}$ and $\overline{u}_{\mathrm{B}}$, under the assumption of Fickian hydrodynamic dispersion, is identical to (38),

$$\overline{u}_{\mathrm{A}}(x, t) = c_{\mathrm{o}} - \overline{u}_{\mathrm{B}}(x, t) = \frac{c_{\mathrm{o}}}{2}\mathrm{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right), \tag{63}$$

where the constants v and D are the cross-section averaged vertical velocity and the upscaled longitudinal hydrodynamic dispersion coefficient, respectively. These constants were quantified by the authors of the cited experiment as $v = 1.21 \times 10^{-2}$ cm/s and $D = 1.75 \times 10^{-3}$ cm^2/s. In the classical well-mixed upscaled ADRE approach, in which coarse-scale concentrations govern the chemical reactions, the combination of (63) with (61) would lead to the following equation for the concentration of AB:

$$\overline{c}_{\mathrm{AB}}(x, t) = \frac{c_{\mathrm{o}}}{2}\mathrm{erfc}\left(\frac{|x - vt|}{2\sqrt{Dt}}\right). \tag{64}$$

However, the experimental observations of *Gramling et al.* [2002] do not agree with (64). Instead, the latter tends to overestimate the amount of reaction product generation, because of the incorrectness of the underlying assumption of full local mixing.

4.2 Model implementation and results

The proposed Lagrangian model is implemented as follows. Particles carry local concentrations of just one of the two conservative components, $U_{\mathrm{A},p}(t)$, because the other is defined by $U_{\mathrm{B},p}(t) = 1 - U_{\mathrm{A},p}(t)$. Equal volumes (weights) are assigned to $N = 10^6$ particles, which are initially distributed in space uniformly over an interval $[-L/2, L/2]$, with $L = 15$ cm, and

$$U_{\mathrm{A},p}(0) = \mathcal{H}(-X_p(0)). \tag{65}$$

As detailed in §2.1, transport and mixing of $U_{\mathrm{A},p}(t)$ are decoupled and reproduced by equations (2) and (9), respectively. In the latter, the local averaging operator is implemented through *binning* (see Appendix A), with a bin size $L/300$. We use a simple dual-rate mixing model like (12), parameterized by a slow mixing fraction η and a slow mixing rate χ. Note that one does not need to

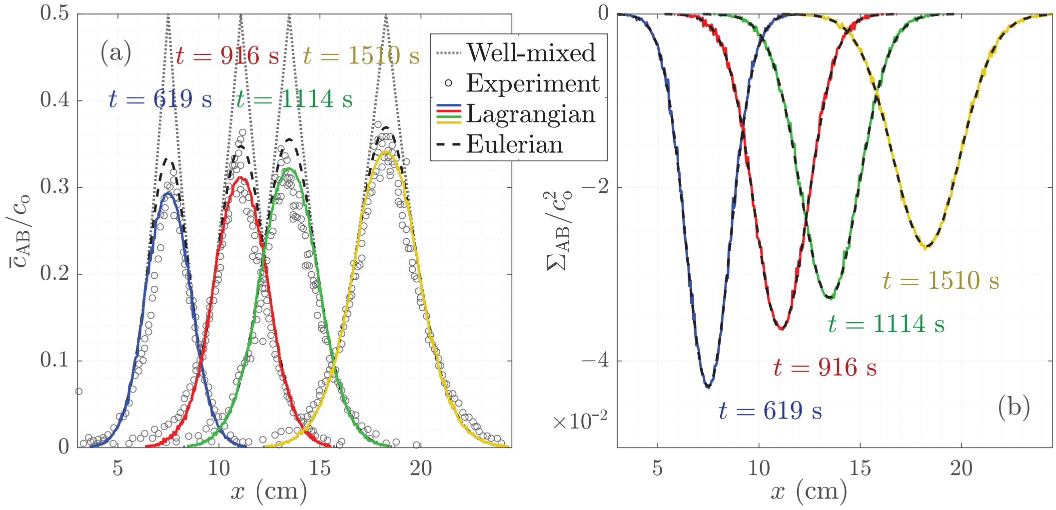

Figure 5. (a) Comparison of various models' predictions of reaction product coarse-scale concentration, $\overline{c}_{\mathrm{AB}}$, to the experimental observations of *Gramling et al.* [2002], at four different times, and (b) corresponding point-covariance of U_{A} and U_{B}, Σ_{AB}. The local mixing model is given by (9) and (12), with $\eta = 0.5$ and $\chi = 10^{-3}$ s^{-1}. The curves labeled as *Lagrangian* correspond to small-volume average (66) performed on particles in a Lagrangian simulation, whereas the curves labeled as *Eulerian* are drawn using equations (42), (63) and (67). The curves labeled as *Well-mixed* correspond to equation (64).

explicitly simulate the evolution of the local concentration fraction corresponding to the fast mixing zone, $U_{\mathrm{A},p,1}(t)$, which is always in equilibrium with the average at $X_p(t)$. The coarse-scale reaction product concentration is given by the combination of (61) and (18),

$$\overline{c}_{\mathrm{AB}}(x,t) = \langle \min(U_{\mathrm{A}}(t), U_{\mathrm{B}}(t)) \rangle (x) = \frac{c_{\mathrm{o}}}{2} + \left\langle \left| \frac{c_{\mathrm{o}}}{2} - U_{\mathrm{A}}(t) \right| \right\rangle (x). \tag{66}$$

The code implementing this is written in Matlab (version 2016b) and the simulation runs in less than 5 minutes on a conventional laptop computer (Intel® Core™ i7-6700HQ, 2.60GHz).

An alternative approach to implement the proposed model is also tested, which we refer to as the Eulerian approach since it does not require to explicitly simulate the Lagrangian particles. In this specific case, we have an analytical solution for $\overline{u}_{\mathrm{A}}(x,t) = 1 - \overline{u}_{\mathrm{B}}(x,t)$, given by (63), as well as a semi-analytical solution for $\Sigma_{\mathrm{AB}}(x,t) = -\Sigma_{\mathrm{AA}}(x,t) = -\Sigma_{\mathrm{BB}}(x,t)$, given by (42). These quantities are, in fact, entries of the mean and the covariance matrix of a bivariate distribution (i.e., probability density function) of local concentrations of components A and B at any (coarse-scale) position and time, $\mathcal{F}(U_{\mathrm{A}}, U_{\mathrm{B}}, x, t)$. By assuming that $\mathcal{F}$ is multiGaussian, it is then fully defined by its mean and covariance matrix, and the local average (66) becomes

$$\begin{aligned} \overline{c}_{\mathrm{AB}}(x,t) &= \int_0^{c_{\mathrm{o}}} \int_0^{c_{\mathrm{o}}} \min(U_{\mathrm{A}}, U_{\mathrm{B}}) \mathcal{F}(U_{\mathrm{A}}, U_{\mathrm{B}}, x, t) \mathrm{d}U_{\mathrm{A}} \mathrm{d}U_{\mathrm{B}} \\ &= \frac{c_{\mathrm{o}}}{2} - \sqrt{\frac{2\Sigma_{\mathrm{AA}}}{\pi}} \exp\left(-\frac{(c_{\mathrm{o}}/2 - \overline{u}_{\mathrm{A}})^2}{2\Sigma_{\mathrm{AA}}} \right) - (c_{\mathrm{o}}/2 - \overline{u}_{\mathrm{A}}) \,\mathrm{erf}\left(\frac{c_{\mathrm{o}}/2 - \overline{u}_{\mathrm{A}}}{\sqrt{2\Sigma_{\mathrm{AA}}}} \right), \end{aligned} \tag{67}$$

where we use equation (63) for $\overline{u}_{\mathrm{A}}$ and the numerical time-integration of (42) for $\Sigma_{\mathrm{AA}} = -\Sigma_{\mathrm{AB}}$. Note that the multiGaussianity assumption may introduce inaccuracies, including the fact that a portion of $\mathcal{F}$ may fall outside the physically meaningful interval $[0, c_{\mathrm{o}}]$.

Similar to *Sanchez-Vila et al.* [2010], the dispersion coefficient is set to $D = 1.3 \times 10^{-3}$ cm^2/s, slightly lower than the value of $D = 1.75 \times 10^{-3}$ cm^2/s estimated by *Gramling et al.* [2002] from the results of non-reactive experiments. The results of the Lagrangian approach display close agreement with the experimental observations, as shown in Figure 5(a), for manually-adjusted values $\eta = 0.5$ and $\chi = 10^{-3}$ s^{-1}. A possible interpretation is that in the pore-scale flow and transport conditions of the experiment, pre-asymptotic fast mixing controlled about half of the mixing process, whereas diffusive mixing across stable fluctuation structures was responsible for the other half. Assuming that the latter is essentially two-dimensional (dominated by transverse diffusion between concentration filaments), and approximating both reactants' bulk diffusion coefficients as the value for AB reported by the authors of the experiment, $D_\mu = 7.02 \times 10^{-7}$ cm/s, then according to (7),

$$\ell_\mu = \sqrt{4D_\mu/\chi} = 0.53 \text{ cm} \approx 0.4b, \tag{68}$$

where $b = 0.13$ cm is the mean grain size of the granular medium. That is, ℓ_μ is approximately the typical size of a pore, considering the reported porosity of 0.36. This suggests that the slow mixing process captured by the model corresponds indeed to the diffusive relaxation of pore-scale concentration fluctuations. The inferred value of $\eta = 0.5$ shows that a single-rate local mixing model (i.e, $\eta = 1$) would not be able to reproduce the experimental results. Neither would the high value of $\eta = \sqrt{1 - D_\mu/D} \approx 1$ that would render our model's local covariance behavior equivalent to *Kapoor and Gelhar* [1994] (see discussion below equation (30)). This is consistent with previous studies on mixing in porous media, both at pore and Darcy scales [e.g., *Kapoor and Kitanidis*, 1998; *de Anna et al.*, 2014b; *Le Borgne et al.*, 2013, 2015], which show that, after first encounter between two solutions with different composition, the mixing rate is higher at the beginning and decreases with time. In other words, the dynamics of mixing are subjected to aging, a feature which is effectively reproduced in our model by a parallel multi-rate process (9), without introducing any time-dependent parameters. Although the dual-rate simplification appears to capture the general behavior for this case-study, allowing us to reproduce the experimental results, more complicated forms may be needed depending on the characteristics of the flow field, especially for highly heterogeneous porous media. This should be the subject of future research and as future experimental datasets in such settings become available.

Looking closely at Figure 5, the main discrepancy between the data and the well-mixed solution (64) is the notable decrease in the peak of reaction product concentrations at the coarse-scale mixing interface. In the Lagrangian simulation, this reduction is caused by the anti-correlated fluctuations of $U_{\mathrm{A},p}$ and $U_{\mathrm{B},p}$ on particles with respect to the local average, which is also reflected by the negative values of Σ_{AB}, depicted in Figure 5(b). As expected, the spatiotemporal description of the covariance in the Eulerian and in the Lagrangian approach are identical, which ratifies the validity of the expressions given in §3.1. However, the reaction product concentration prediction is slightly different, because of the multiGaussian approximation used in the Eulerian approach.

5 Summary and conclusions

We have proposed a Lagrangian mathematical model to represent the transport and mixing of solutes in a dual-scale (coarse/local) framework. Local concentrations carried by individual particles evolve by relaxation towards the coarse-scale concentration values that they perceive along their random path (described by (2)). This relaxation or mixing process is characterized by (9) as a parallel multi-rate *interaction by exchange with the mean* (MRIEM). We derived the differential equation describing the corresponding evolution of the (Eulerian) concentration point-covariance (29), and found solutions corresponding to the mixing state evolution for two simple generic cases. Finally, the proposed model (in its dual-rate form) was successfully implemented to reproduce reaction product concentration data from a well-known laboratory experiment that displays incomplete mixing effects. Below, we enumerate additional findings and conclusions:

1. The partial differential equation describing the behavior of the local concentration covariance becomes nearly equivalent to the *concentration variance conservation equation* suggested by *Kapoor and Gelhar* [1994], given a dual-rate (fast/slow) parametrization of the mixing process.
2. The temporal evolution of the mixing state for a pulse injection shows similar trends to those observed in previous studies of mixing in porous media within fully-resolved systems [*Bolster*

et al., 2011; *de Dreuzy et al.*, 2012], suggesting that the model may be able to accurately upscale local mixing limitations. Both for a pulse and for a continuous injection, the ratio between the mixing state components corresponding to the fluctuating and the averaged concentration terms decays at late times as the inverse of time.

3. The *Gramling et al.* [2002] results would not be explicable, from our model's perspective, through a single-rate local mixing process. This agrees with previous knowledge on the complexity of mixing dynamics in porous media [*de Anna et al.*, 2014b; *Le Borgne et al.*, 2013], which establish the need to somehow include a temporal decrease of the mixing rate from the time of first coarse-scale contact between reactants.
4. Along the same vein, the $\eta = 0.5$ value for the dual-rate model that fits the cited experimental results does not agree with *Kapoor and Gelhar*'s model, that is, with the restriction $\eta^2 = 1 - D_\mu/D \approx 0.9995$, if D_μ is assumed to be the molecular diffusion. This discrepancy can be attributed to the pre-asymptotic stage where mixing is enhanced by fluid deformation dynamics, as noted by *Kapoor and Kitanidis* [1998].
5. Considering the characteristic local mixing distance $\ell_\mu = \sqrt{4D_\mu/\chi}$, the fitted value of $\chi = 10^{-3}$ s^{-1} yields $\ell_\mu \approx 0.05$ cm, which is approximately equal to the typical pore size. This consistency of scale suggests that the model is properly capturing the physics underlying the mixing process.

Several future avenues for research arise due to this work, including (*i*) identifying methods to readily estimate parameter values in (8) and (9) to upscale mixing within different local-scale heterogeneity patterns of velocity and dispersion, thus making the model scalable and translatable to the diverse range of hydrogeologic settings out there (*ii*) exploring the use of motion equations other than (2) [e.g. *Berkowitz et al.*, 2006; *Le Borgne et al.*, 2008], which are well-known to better describe coarse-scale transport in complex heterogeneous settings (*iii*) extending the model to incorporate heterogeneous reactions, and (*iv*) using the model to study the effects of local concentration fluctuations on realistic complex geochemical reaction systems.

A: Aspects of numerical implementation

A.1 Smooth local average

As outlined in §2.1, the numerical implementation of (9), as well as the reactive extensions described in §2.2, entails the definition of a smooth small-volume approximation for the local average operator $\langle\,\rangle(\mathbf{x})$ (equation (3)), which is used to compute the averaged concentrations $\overline{c}_\mathrm{A}(\mathbf{x}, t)$ from overlapping local concentrations defined on particles. Here we discuss two possible approaches, and their respective advantages and disadvantages.

A.1.1 Binning

A straightforward approach to compute the averaged concentrations is to discretize the spatial domain into a set of bins. The Dirac Delta $\delta(\mathbf{x} - \mathbf{X}_p)$ in (3) and (4) is then replaced by an indicator function $I(\mathbf{x}, \mathbf{X}_p)$ that has a value of 1 when $\mathbf{x}$ and $\mathbf{X}_p$ belong to the same bin, and a value of 0 otherwise. Compared to other smoothing techniques, this approach has very low computational demands. Another advantage is that it does not present any mass conservation issues. This is because the sum of all differences with respect to the mean within each individual bin is zero by definition, and therefore so is the sum of all exchanges with the mean given by (9). The main potential disadvantage of binning is that, compared to other smoothing techniques, it tends to require higher particle numbers (here, a finer Lagrangian discretization of the fluid mass) in order to converge to a smooth solution [*Fernàndez-Garcia and Sanchez-Vila*, 2011]. This approach is used in the Lagrangian implementation described in §4.2.

A.1.2 Kernel smoothing

An alternative to binning is to use kernel smoothing on particles, that is, to replace the Dirac Delta $\delta(\mathbf{x}-\mathbf{X}_p)$ in (3) and (4) with a radially symmetric kernel $W(\mathbf{x}-\mathbf{X}_p;h)$, where h is the smoothing bandwidth. This interpolation method is commonly used in smoothed particle hydrodynamics [*Monaghan*, 2005]. This approach may offer better convergence rates with particle number than binning. On the other hand, in this case, exact mass conservation for (9) is not guaranteed by default, and a correction strategy is required. One mass-conserving approach can be obtained by considering symmetric pair-wise particle interactions. Let us first define a smooth interpolator to approximate (3) that is pair-wise symmetric

$$\langle\Psi\rangle(\mathbf{x}) := \sum_p \frac{m_p}{\tilde{\rho}(\mathbf{x},\mathbf{X}_p)}\Psi_p W(\mathbf{x}-\mathbf{X}_p). \tag{A.1}$$

Here, $\tilde{\rho}(\mathbf{x},\mathbf{X}_p)$ is some average of $\rho(\mathbf{x})$ and $\rho(\mathbf{X}_p)$. We redefine (9) by inserting $C_{\mathrm{A},p,i}$ inside the local average operator

$$\frac{\mathrm{d}C_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\chi_i}{2}\langle C_{\mathrm{A},p,i}-C_{\mathrm{A},i}\rangle(\mathbf{X}_p) = -\frac{\chi_i}{2}\sum_q \frac{m_q}{\tilde{\rho}(\mathbf{X}_q,\mathbf{X}_p)}[C_{\mathrm{A},p,i}-C_{\mathrm{A},q,i}]W(\mathbf{X}_q-\mathbf{X}_p). \tag{A.2}$$

The right-hand side of (A.2) clearly shows that a symmetric and therefore consistent mass exchange between each pair of particles p, q, is imposed [*Herrera et al.*, 2009; *Sole-Mari et al.*, 2019]. This expression may also be rewritten as

$$\frac{\mathrm{d}C_{\mathrm{A},p,i}}{\mathrm{d}t} = -\frac{\chi_i}{2}[C_{\mathrm{A},p,i}\langle 1\rangle(\mathbf{X}_p) - \overline{c}_{\mathrm{A}}(\mathbf{X}_p)], \tag{A.3}$$

which elucidates that mass conservation can be achieved in the kernel-based MRIEM through multiplication of $C_{\mathrm{A},p,i}$ by a correcting factor $\langle 1\rangle(\mathbf{X}_p)$, which converges to 1 as $N\to\infty$ and $h\to 0$. However, this approach does come at higher computational cost than binning.

A.2 Numerical dispersion and relation with other formulations

Smoothing tends to artificially spread out particle masses, which may generate some numerical dispersion in the Lagrangian numerical implementation. This can be straightforwardly quantified by comparing the right-hand side of (A.2) to the SPH formulation used to simulate a diffusion D_{SPH} with a multiGaussian W [*Sole-Mari et al.*, 2019, eq. 8]. Both expressions become equivalent by setting

$$D_{\mathrm{SPH}} = \frac{1}{4}\chi_i h^2. \tag{A.4}$$

That is, the identity (A.4) quantifies the numerical diffusion involved in the numerical simulation of a MRIEM mixing with rate χ_i using a Gaussian smoothing kernel with bandwidth h for computing the averaged concentrations. The same quadratic scaling should be expected for the bin size when binning is the chosen smoothing approach. Fortunately, as explained in §4.2, the high or virtually instantaneous fraction of mixing rates in the MRIEM formulation do not need to be explicitly simulated, and therefore only the small values of χ_i may produce numerical dispersion, which can be controlled by choosing a small-enough smoothing bandwidth h, or by slightly reducing the value of D used in the particle motion such that the added total dispersion has the correct value. The latter strategy, in fact, is tightly related to previous works [*Benson and Bolster*, 2016b; *Herrera et al.*, 2017; *Sole-Mari et al.*, 2019; *Engdahl et al.*, 2019; *Benson et al.*, 2019a,b] in which the total dispersion results from the sum of (*i*) random walks and (*ii*) some form of exchange between particles. In particular, if we look at the approach suggested by *Benson and Bolster* [2016b, eq. 7], with mass transfers based on probabilities of collision between particles, we see that it is equivalent to the kernel form of the MRIEM as given by (A.2) for the specific case of a single mixing zone $i=1$ with mixing rate $\chi_1 = 1/\mathrm{d}t$, and a multiGaussian W with bandwidth $h^2 = 4D_{\mathrm{MT}}\mathrm{d}t$. That is, the mass transfer approach by *Benson and Bolster* [2016b] is equivalent to a Gaussian kernel-based single-rate IEM with instantaneous full mixing and "numerical" dispersion (see (A.4)) $D_{\mathrm{SPH}} = D_{\mathrm{MT}}$.

B: Relation between local averages of Eulerian and Lagrangian derivatives

In this Appendix we provide the derivation for expression (10) given in §2.1. We start from the definition of local average (3). Note that, for incompressible flow, the fluid density $\rho(\mathbf{X}_p)$ is proportional to the porosity – amount of fluid per unit volume of medium. Hence, maintaining the assumption of constant porosity, the particle estimate of fluid density given by (4) must converge to a constant value ρ as $N \longrightarrow \infty$, N being the number of particles. The time-derivative of expression (3) is then

$$\frac{\partial\langle\Psi\rangle}{\partial t} = \sum_p \frac{m_p}{\rho}\Psi_p \frac{\mathrm{d}\delta(\mathbf{x}-\mathbf{X}_p)}{\mathrm{d}t} + \sum_p \frac{m_p}{\rho}\frac{\mathrm{d}\Psi_p}{\mathrm{d}t}\delta(\mathbf{x}-\mathbf{X}_p) = \sum_p \frac{m_p}{\rho}\Psi_p\frac{\Delta\delta(\mathbf{x}-\mathbf{X}_p)}{\Delta t} + \Big\langle \frac{\mathrm{d}\Psi}{\mathrm{d}t}\Big\rangle. \qquad \text{(B.1)}$$

where the time-derivative of the Dirac delta function has been written as the variation $\Delta\delta(\mathbf{x}-\mathbf{X}_p)$ over Δt, where $\Delta t \longrightarrow 0$. A second-order Taylor expansion over the corresponding small particle displacement $\Delta\mathbf{X}_p$ writes:

$$\Delta\delta(\mathbf{x}-\mathbf{X}_p) \approx \Delta\mathbf{X}_p^{\mathrm{T}}\delta'(\mathbf{x}-\mathbf{X}_p) + \frac{1}{2}\Delta\mathbf{X}_p^{\mathrm{T}}\delta''(\mathbf{x}-\mathbf{X}_p)\Delta\mathbf{X}_p, \qquad \text{(B.2)}$$

where δ' and δ'' are, respectively, the gradient and the Hessian matrix of δ. Then, using expression (B.2), knowing that the weighted summation is equivalent (in the limit $N \longrightarrow \infty$) to an integral over the particle space, and given the evaluation properties of the Dirac delta distributional derivatives, we may rewrite the summation in (B.1) as

$$\begin{aligned}\sum_p \frac{m_p}{\rho}\Psi_p\frac{\Delta\delta(\mathbf{x}-\mathbf{X}_p)}{\Delta t} &\approx \sum_p \frac{m_p}{\rho}\left[-\nabla\cdot\left(\Psi_p\frac{\Delta\mathbf{X}_p}{\Delta t}\right) + \frac{1}{2}\nabla\nabla : \left(\Psi_p\frac{\Delta\mathbf{X}_p^{\mathrm{T}}\Delta\mathbf{X}_p}{\Delta t}\right)\right]\delta(\mathbf{x}-\mathbf{X}_p) \\ &= -\nabla\cdot\langle\Psi_p\frac{\Delta\mathbf{X}_p}{\Delta t}\rangle + \frac{1}{2}\nabla\nabla : \langle\Psi_p\frac{\Delta\mathbf{X}_p^{\mathrm{T}}\Delta\mathbf{X}_p}{\Delta t}\rangle \\ &= -\mathbf{v}\nabla\cdot\langle\Psi_p\rangle + \mathbf{D}\nabla\nabla : \langle\Psi_p\rangle = \mathcal{L}\left(\langle\Psi\rangle;\mathbf{v},\mathbf{D}\right),\end{aligned} \qquad \text{(B.3)}$$

where we applied well-known identities associated to (2) [*Risken*, 1989; *Salamon et al.*, 2006], $\langle\Delta\mathbf{X}_p\rangle = \mathbf{v}\Delta t$ and $\langle\Delta\mathbf{X}_p^{\mathrm{T}}\Delta\mathbf{X}_p\rangle = 2\mathbf{D}\Delta t$ (for $\Delta t \longrightarrow 0$), and assumed that $\mathbf{v}$ and $\mathbf{D}$ are spatially constant. Finally, introducing the result from (B.3) in (B.1), we obtain the expression given by (10),

$$\frac{\partial\langle\Psi\rangle}{\partial t} = \mathcal{L}\left(\langle\Psi\rangle;\mathbf{v},\mathbf{D}\right) + \Big\langle\frac{\mathrm{d}\Psi}{\mathrm{d}t}\Big\rangle, \qquad \text{(B.4)}$$

which states that the Eulerian temporal variation of $\langle\Psi\rangle$ comprises a contribution from the flux of particles (Fokker-Planck) plus a local contribution from variations on particles.

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