Modeling and Simulation of High-Dimensional Stochastic Multiscale PDE Systems

G. Lin,[1] N. Zabaras,[2] Y. Kevrekidis,[3] D. Mei[4]

[1]Computational Sciences and Mathematics Division, Pacific Northwest National Laboratory, Richland, WA 99354, USA
[2]Mechanical and Aerospace Engineering, Cornell University, Ithaca, NY 14853-3801, USA
[3]Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544 USA
[4]Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99354, USA

Email: guang.lin@pnnl.gov

Abstract. In order to capture the small-scale heterogeneity, two computational multiscale algorithms are developed. The first approach is a stochastic multiscale method. This new method ensures both local and global mass conservation. Starting from a specified covariance function, the stochastic log-permeability is discretized in the stochastic space by using a truncated Karhunen-Loeve expansion with several random variables. Because of the small correlation length of the covariance function, a high stochastic dimensionality often results. Therefore, a newly developed adaptive high-dimensional model representation technique (HDMR) is used in the stochastic space. HDMR decomposes the high-dimensional problem into a set of low-dimensional stochastic subproblems, which are efficiently solved by using an adaptive sparse grid collocation method. Numerical examples are presented to show the accuracy and efficiency of the developed stochastic multiscale method. The second approach is a hybrid method by integrating first-principles kinetic Monte Carlo (KMC) simulation with a continuum model. We demonstrate this integrated computational framework by applying it to study the effects of heat and mass transfer on the heterogeneous reaction kinetics. The hybrid reaction model consists of a surface phase domain where catalytic surface reactions occur and a gas-phase boundary layer domain imposed on the catalyst surface where the temperature and pressure gradients exist. The surface phase is described by using site-explicit first-principles KMC simulations. The heat and mass transfer in the gas-phase boundary layer domain, which is represented by thermal and molecular diffusion, is characterized by using the continuum-based method. Simulation results indicate that heat and mass transfer in the gas-phase boundary layer could dramatically affect the observed reaction kinetics at nominal operating reaction condition.

1. Introduction

Flow through porous media is ubiquitous, occurring from large geological scales down to microscopic scales. Several critical engineering phenomena, such as contaminant spread, nuclear waste disposal, and oil recovery, rely on accurate analysis and prediction of these multiscale phenomena. Such analysis is complicated by heterogeneities at various length scales as well as inherent uncertainties. Thus, in order to predict the flow and transport in stochastic porous media, some type of stochastic upscaling or coarsening is needed for computational efficiency by solving these problems on a coarse grid. However, most of the existing multiscale methods are realization based; that is, they can solve a deterministic problem only for a single realization of the stochastic permeability field. This is not sufficient for uncertainty quantification since we are mostly interested in the statistics of the flow behavior, such as mean and standard deviation. In this paper, we propose a stochastic multiscale approach that resolves both uncertainties and subgrid scales. Our approach includes developing a new multiscale method and adopting a newly developed adaptive high-dimensional model representation (HDMR) [1]. The goal of the multiscale method is to coarsen the flow equations spatially, whereas HDMR is used to address the curse of dimensionality in high-dimensional stochastic spaces.

In simulating heterogeneous catalytic reactions, computational modeling plays an increasingly crucial role in the characterization and understanding of a broad range of elementary chemical transformations relevant to heterogeneous catalytic processes. It remains, however, a formidable challenge to computational models with a predictive capability that describe complex heterogeneous processes involving the intrinsic reaction kinetics and transport of momentum, mass and heat [2-3].

This paper is organized as follows. In Section 2, the mathematical framework of stochastic multiscale method and hybrid method are considered. In Section 3, various examples in porous media flow and catalytic reactions are given. In Section 4, concluding remarks are provided.

2. Methodology

Stochastic multiscale method for randomly heterogeneous porous media flow

In this work, a new multiscale methodology using the mixed finite-element method [4] is developed for the solution of elliptic equation arising from the heterogeneous porous media flow problem [5]. A novel boundary condition for the local cell problem is proposed that gives more realistic flow conditions across a coarse-element interface. In addition, a reconstruction method for the fine-scale velocity is proposed, which ensures the continuity of the mass at both local and global scales. The input uncertainty in the permeability considered in the current work is defined from an analytical KL expansion with known covariance, which represents only two-point statistics.

Additionally, we considered uncertainty quantification when the permeability field is modeled as a random field [6-7]. The newly developed multiscale method is used as a direct solver within the framework of ASGC [8] and HDMR [1]. The complete schematic of the developed stochastic multiscale method for porous media flow is illustrated in Fig.1, see details in [9].

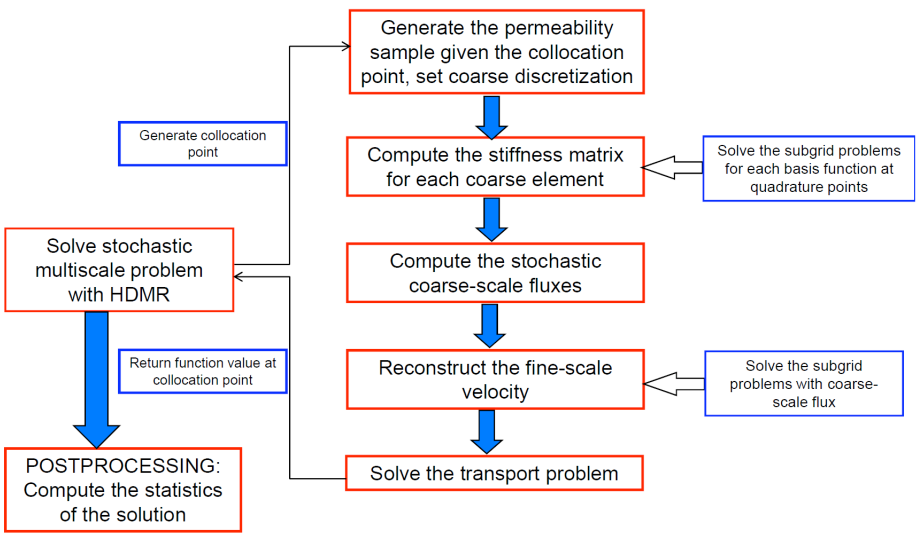

Fig. 1. Schematic of the developed stochastic multiscale method for porous media flow.

Hybrid method and its application to catalytic heterogeneous reactions

We developed a computational model that directly couples first-principles kinetic Monte Carlo (KMC) simulation with a finite difference continuum model in a real-time dynamical mode; see details in [10]. The effects of heat and mass transfer in gas phase on the catalytic reaction are considered before the steady-state reaction condition in entire catalytic system is reached. The in situ mass and heat transfer derived from surface reactions are directly used as the boundary condition for the continuum model. At the same time, the variations of the gas-phase pressure (or concentrations of reactant and products) and temperature adjacent to the catalyst surface that are calculated by the continuum model will implement in KMC simulation. In such a way, our model captures the inhomogeneous dynamical nature in both the gas

phase and the catalyst surface phase simultaneously. CO oxidation on $RuO_2(110)$ catalyst has been well studied both experimentally and theoretically [11-12]. Since the reaction kinetics of CO oxidation on RuO2(110) catalyst had thoroughly studied using first-principles KMC simulations [11,13], CO oxidation on RuO2(110) catalyst provides us a good benchmark reaction system for demonstrating our new model. In this work, we investigated the effects of heat and mass transfer on the reaction kinetics of CO oxidation on RuO2(110) catalysts with different thicknesses. Similar to the previous models [14,14], the entire heterogeneous catalytic reaction system is decomposed into the catalyst surface phase domain and the stagnant gas-phase boundary phase domain. As shown in Fig. 2, the nominal operating reaction condition such as temperature ($T^{(n)}$) and partial pressures ($P_{CO}^{(n)}$ and $P_{O_2}^{(n)}$) beyond the boundary layer are kept to be constant. For simplicity, the gas-phase boundary domain is treated as the stagnant phase without bulk flow. The first-principles KMC simulation and second-order finite difference Crank-Nicolson method are used for the surface phase and the gas-phase boundary layer domains, respectively.

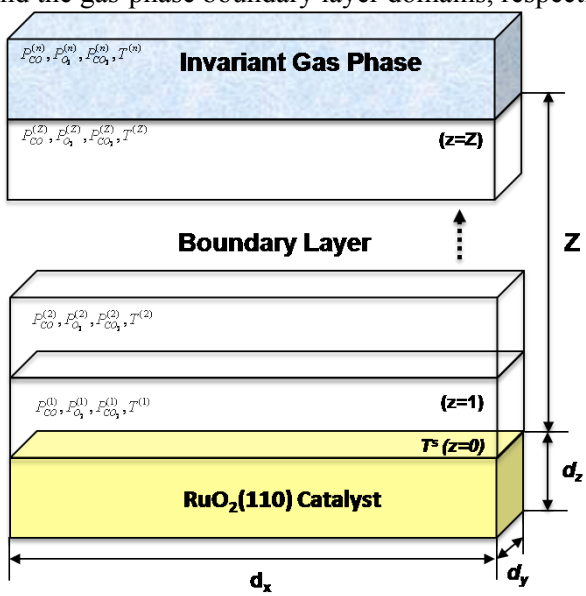

Fig. 2. Schematic diagram of the multiscale model.

3. Numerical Results

In this section, we consider only a sample realization from a random permeability field, which can be considered as a deterministic run at a collocation point in a stochastic simulation. The permeability is defined on a 100 $\times$ 100 fine-scale grid. Flow is induced from left-to-right with Dirichlet boundary conditions p = 100 on $\{x_1 = 0\}$, p = 0 on $\{x_1 = 100\}$ and no-flow homogeneous Neumann boundary conditions on the other two edges. We also impose zero initial condition for saturation S(x, 0) = 0 and boundary condition S(x, t) = 1 on the inflow boundary $\{x_1 = 0\}$. The reference solution is again taken from the single-scale, mixed finite-element method on the fine-scale grid directly.

In Fig. 3, we compare the mean and standard deviation at 0.2 PVI. We note that although the permeability field shows heterogeneity for different realizations, the mean saturation is the same as the solution with homogeneous mean permeability field. This behavior is called “heterogeneity induced dispersion” where the heterogeneity smoothes the water saturation profile in the ensemble sense. Our results again confirm this phenomenon. The figure also indicates that higher water saturation variations are concentrated near displacement fronts, which are areas of steep saturation gradients. Therefore, the comparisons between the MC and HDMR results are only shown around the displacement fronts on the bottom two plots in Fig. 3. One can see that the solutions from HDMR compare well with the Monte Carlo results.

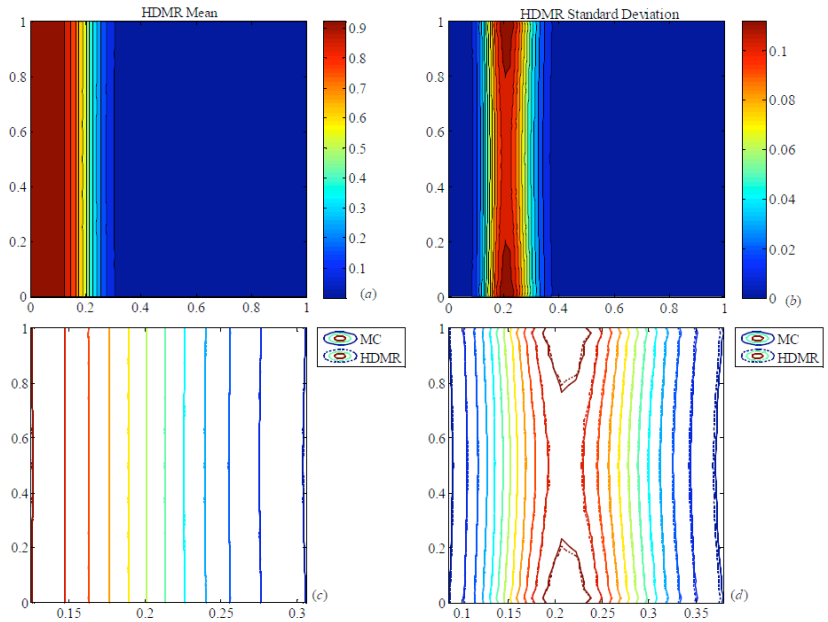

Fig. 3. Mean and standard deviation of saturation at 0.2 PVI for isotropic random field. Top: Mean (a) and standard deviation (b) form HDMR. Bottom: Comparison of mean (c) and standard deviation (d) between MC and HDMR near the saturation front.

The reaction kinetics of CO oxidation over the RuO2(110) catalyst surface under invariant gas-phase reaction conditions had been investigated by using first-principles KMC simulations. Figure 2 shows the normalized turnover frequencies (TOFs) of CO2 as a function of CO partial pressure at $T^{(n)}$ =350 K and $P_{O_2}^{(n)}$ = 1.0×10-10 atm. The normalized TOF of CO2 is the total number of CO2 molecules desorbed from the surface per site per second. As CO partial pressure $P_{CO}^{(n)}$ increases from 3.0×10-10 to 1.2×10-9 atm, the maximum CO2 TOF, which indicates the most active reaction condition occurs at $P_{CO}^{(n)}$ = 4.0×10-10 atm.

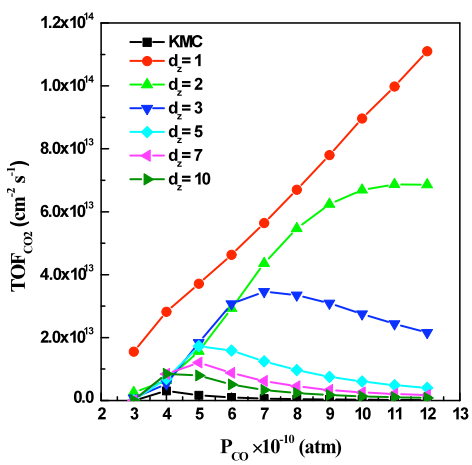

Fig. 4. Simulated CO_2 TOFs as a fucntion of $P_{CO}^{(n)}$ at the nominal reaction condition of $T^{(n)}$ = 350 K and $P_{O_2}^{(n)} = 1.0 \times 10^{-10}$ atm.

4. Summary

A new stochastic multiscale method using a mixed finite-element method is developed for the solution of elliptic equation arising from the heterogeneous porous media flow problem. The newly developed multiscale method is used as a direct solver within the framework of ASGC and HDMR to quantify the uncertainty when the permeability field is modeled as a random field. The new method is demonstrated on a randomly heterogeneous porous media flow. Numerical results validate the new approach by comparing with Monte Carlo simulations. In this work, we also presented a multiscale model that integrates first-principles KMC simulations with a simple continuum model. The developed new hybrid model directly connects two phase domains: a reaction phase where catalytic surface reaction occurs and a boundary gas-phase layer above the catalyst surface where the temperature and pressure gradients exist. The surface reaction phase is modeled by using site-explicit, first-principles KMC simulations. The heat and mass transfer via thermal and molecular diffusions of reactants and products in the gas-phase boundary layer is characterized by using grid-based continuum model. With CO oxidation on the RuO2(110) catalyst as our benchmark reaction system, we demonstrate that the heat and mass transfer in the gas-phase boundary layer, which is induced by the catalyst's thickness could dramatically alter the observed surface reaction kinetics.

Acknowledgments

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