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Wavelet-based surrogate time series for multiscale simulation of heterogeneous catalysis ☆

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HIGHLIGHTS

- An efficient wavelet-based surrogate algorithm is proposed for multiscale coupling.
- Generated surrogates replicate stochastic features from complex surface reactions.
- Catalytic reactions modeled by KMC are demonstrated for upscaling using surrogates.
- Computational overhead can be significantly reduced by the multiscale coupling.

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ABSTRACT

We propose a wavelet-based scheme that encodes the essential dynamics of discrete microscale surface reactions in a form that can be coupled with continuum macroscale flow simulations with high computational efficiency. This makes it possible to simulate the dynamic behavior of reactor-scale heterogeneous catalysis without requiring detailed concurrent simulations at both the surface and continuum scales using different models. Our scheme is based on the application of wavelet-based surrogate time series that encodes the essential temporal and/or spatial fine-scale dynamics at the catalyst surface. The encoded dynamics are then used to generate statistically equivalent, randomized surrogate time series, which can be linked to the continuum scale simulation. We illustrate an application of this approach using two different kinetic Monte Carlo simulations with different characteristic behaviors typical for heterogeneous chemical reactions.

1. Introduction and background

Accounting for dynamic, multiscale, spatiotemporal interactions is a major concern in computational simulation of chemical reactions (Mishra et al., 2008a). This is especially true for heterogeneous catalysis (Salciccioli et al., 2011; Stamatakis, 2015), where molecular and mesoscale chemical reactions at the catalyst surface must ultimately be linked to continuum-scale hydrodynamic processes in a fluid phase. This is especially important when the rate controlling processes involved at either or both scales are significantly nonlinear and thus sensitive to the effects of external inputs. However, such inter-scale coupling poses major challenges that are frequently beyond current computational capabilities. Thus, we are motivated to seek approaches that can reduce the need for running detailed concurrent simulations at all the scales, while still preserving the important dynamics associated with scale-to-scale interactions. Specifically, we are concerned with simulating the basic reaction system summarized in Fig. 1. The key features of this system include: 1) a fluid that contains both

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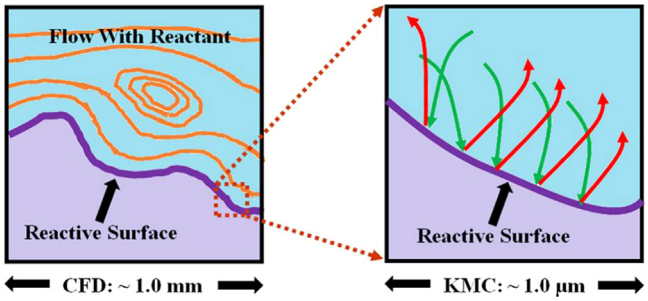

Fig. 1. Illustration of the basic reaction system of interest. The fluid phase behaves according to continuum hydrodynamics (orange lines) with relatively large spatial (e.g., $>10^{-3}$ m) and temporal (e.g., $>10^{-3}$ s) scales. Reactant (green arrows) and product (red arrows) molecules transport between the fluid and surface phases. Surface reactions occurring on discrete catalytic sites can span ranges that include much smaller spatial and temporal scales (e.g., $<10^{-6}$ m and $<10^{-6}$ s). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reactant and product species moving past a solid catalytic surface (the coarsest scale); 2) interphase transport between the fluid and solid surface; 3) adsorption/desorption of reactant and product molecules onto catalytic sites on the surface; and 4) reactions at the surface on the catalytic sites (the finest scale). For the fluid phase, we assume that the dynamics can be simulated with a continuum model, such as those used for computational fluid dynamics (CFD). For the surface, we assume that the dynamics should be simulated with a model that accounts for discrete physics, such as molecular dynamics or kinetic Monte Carlo (kMC) to account for molecular-scale and surface topological effects such as facet specific selectivity, etc. The main issue then becomes how to accurately account for the dynamical interactions between these two types of models across these widely different spatio-temporal scales. We expect this to be especially relevant to situations where the goal is to design catalysts with surface properties that improve expected global reaction performance (e.g., higher conversion, improved selectivity, lower operating temperature, improved durability).

Previous approaches (Maestri and Cuoci, 2013; Matera et al., 2014) have been proposed for coupling the multiple scales involved in heterogeneous catalysis, i.e. to transfer the micro scale catalytic surface reaction kinetics information to the continuum (macroscale) fluid flow field. Matera et al. (2014) propose an efficient and stable method to integrate first-principles based kMC (1p-kMC) reaction microkinetics into computational fluid dynamics (CFD) by interpolating irregularly gridded 1p-kMC data using time-averages of approximate kMC steady-state reaction rates as source terms for the CFD conservation equations. The use of time averages would appear to exclude the detailed dynamic effects of short-time-scale concentration/rate fluctuations on the macro-scale behavior, but this issue does not appear to have been resolved as yet. One possible workaround to the time averaging issue may be to implement on-the-fly kMC simulations or pre-computed kMC simulations at selected intervals. However, such methods may be inefficient when millions to billions of kMC cases are needed to account for the non-uniform dynamic evolution of the system. Thus, to account more accurately for the dynamic consequences of the small-scale perturbations on the macro-scale dynamics, it is necessary to construct an efficient concurrent coupling strategy that is both suitable for large-scale CFD simulations and yet still upwardly communicates the essential dynamic information generated at the micro-scale to the larger system.

Other methods proposed for reducing the micro-scale computational burden in multi-scale simulations are reviewed by Vvedensky (2004). Some publications (Bi and Li, 2004; Dollet, 2004; Mishra et al., 2008b) specifically address reaction and surface problems related to the problem of interest here. Two widely utilized approaches for addressing the multiscale problem are the so-called gap tooth (Kevrekidis et al., 2002) and time stepping (Kevrekidis et al., 2002; Vasenkov et al., 2006) methods. Wavelet-based methods have also received much attention for addressing both spatial (Frantziskonis and Deymier, 2000; Frantziskonis, 2002a, 2002b; Frantziskonis et al., 2006; Mishra et al., 2008a) and temporal scaling (Frantziskonis and Deymier, 2003; Frantziskonis et al., 2006). In particular, one recent review paper (Hariharan and Kannan, 2014) describes the application of wavelet-based methods for simulating reaction-diffusion systems and cites almost 140 relevant publications. Other wavelet-based scaling methodologies include the dynamic compound wavelet matrix technique of Muralidharan et al. (2008) and the time-parallel compound wavelet matrix technique of Frantziskonis et al. (2009). Other wavelet applications to reaction-diffusion simulations are those by Bindal et al. (2003), Stundzia and Lumsden (1996), Burger and Ruiz-Baier (2009), Chen et al. (2010), Ewing et al. (2004), Hariharan and Kannan (2009, 2010a, 2010b), and Cai and Zhang (1998).

Wavelet-based techniques offer certain advantages over other multiscale methods because they provide scale-wise data fusion mechanisms that allow ready upscaling and downscaling of dynamic features (Frantziskonis et al., 2006). In addition, wavelet transformation has the advantage that it preserves non-stationary features in the dynamics that would be lost or significantly distorted by other types of infinite basis transforms (e.g., Fourier analysis). This becomes more important when the information generated by fine-scale models is limited in extent and includes non-stationary effects.

On the other hand, like Fourier transform, it is possible to use wavelet transform to generate 'surrogate' data series; that is, artificial data series that are equivalent dynamical replicates (but still individually unique), which retain the same key statistical and dynamical properties as the original data. Surrogate data methods have been widely used for several years in characterizing and testing null hypotheses with data from complex dynamical systems (Breakspear et al., 2003; Keylock, 2006; Rouyer et al., 2008), but our use of surrogates here is directed towards a different problem: the transfer of dynamic information across scales. Specifically, in this study we are concerned with the need to minimize the need for long time-scale simulations of the fine-scale dynamics that would consume large amounts of computational resources. Expressed in another way, we desire to use the results from relatively short simulations of the fine-scale dynamics to generate longer or wider equivalent data sequences that can be coupled with coarse-scale simulations. To minimize artifacts, our objective is to create surrogates that retain the most important dynamical features in the fine-scale data that could have significant impacts on the coarse scale by carrying moments (mean, variance, etc.) of the final scale statistics. The surrogates then can serve as substitutes for fine-scale information to 'fill in the gaps' between updated fine-scale simulations.

In the following sections, we describe our proposed surrogate generation methodology and illustrate its application to a simulated problem in heterogeneous catalysis where the surface reaction rates are modeled with a multistep kMC model. We then describe how we expect surrogates of this type can be used as a general "upscaling interface" to transfer the important dynamical information from the fine scale to the coarse scale.

2. Proposed approach for generating surrogates

As noted above, we propose a wavelet-based approach for encoding the fine-scale dynamic information from the catalyst