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Hierarchical multiscale model-based design of experiments, catalysts, and reactors for fuel processing

D.G. Vlachos *, A.B. Mhadeshwar, N.S. Kaisare

Department of Chemical Engineering and Center for Catalytic Science and Technology (CCST), University of Delaware, Newark, DE 19716, United States

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Abstract

In this paper a hierarchical multiscale simulation framework is outlined and experimental data injection into this framework is discussed. Specifically, we discuss multiscale model-based design of experiments to optimize the chemical information content of a detailed reaction mechanism in order to improve the fidelity and accuracy of reaction models. Extension of this framework to product (catalyst) design is briefly touched upon. Furthermore, we illustrate the use of such detailed and reduced kinetic models in reactor optimization as an example toward more conventional process design. It is proposed that hierarchical multiscale modeling offers a systematic framework for identification of the important scale(s) and model(s) where one should focus research efforts on. The ammonia decomposition on ruthenium to produce hydrogen and the water–gas shift reactions on platinum for converting syngas to hydrogen serve as illustrative fuel processing examples of various topics. The former is used to illustrate hierarchical multiscale model development and model-based parameter estimation as well as product engineering. The latter is employed to demonstrate model reduction and process optimization. Finally, opportunities for process design and control in portable microchemical devices (lab-on-a chip) for power generation are discussed.

Keywords: Multiscale; Process engineering; Product engineering; Model-based design of experiments; Parameter estimation; Reactor optimization; NH_3; Hydrogen; Microreactors; Water–gas shift

1. Introduction

Multiscale modeling is the enabling science that seamlessly and dynamically links models and phenomena across multiple length and time scales, spanning from quantum scales to macroscopic scales, in a two-way information traffic manner (see Fig. 1) (Braatz et al., 2004; Christofides, 2001; Kevrekidis, Gear, & Hummer, 2004; Maroudas, 2003; Vlachos, 2005). Macroscopic scales may include a process or even an entire plant. Macroscopic scale models involve detailed process simulators, such as computational fluid dynamics (CFD) with multicomponent mass and heat transfer and eventually plant simulators such as ASPEN. Such models often suffer from lack of thermodynamic and transport properties, use of approximate or inaccurate constitutive equations and/or approximate boundary conditions at interfaces. Quantum mechanical simulators, at the other extreme of the spectrum of scales, provide activation energies and pre-exponentials needed for reaction models and/or potential energy surfaces needed for atomistic simulators, such as molecular dynamics (MD) and Monte Carlo (MC) techniques. Atomistic simulators, in turn, take input from quantum mechanics and provide detailed atomistic information of the system. It is typically some suitable ensemble average property of atomistic simulators, which is needed for practical purposes, rather than atomic positions and momenta of individual atoms. Depending on the ensemble chosen, computed properties may involve thermodynamic or transport properties along with their corresponding constitutive equations. This information is fed to macroscopic models. An overview of atomistic simulators is given in (Vlachos, 2006) and references therein. Scales beyond the realm of atomistic simulation in terms of CPU, which still require discrete, atomistic treatment, are termed mesoscopic (Chatterjee, Snyder, & Vlachos, 2004a).

* Corresponding author. Tel.: +1 302 831 2830; fax: +1 302 831 1048.
E-mail address: vlachos@udel.edu (D.G. Vlachos).

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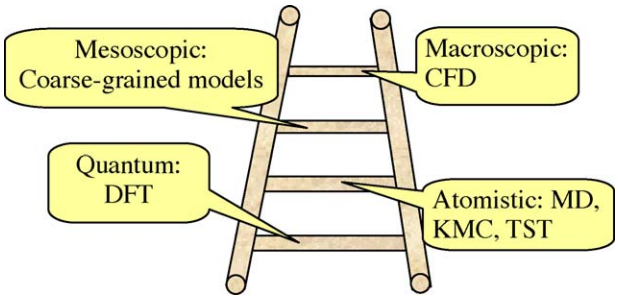

Fig. 1. Schematic of multiscale simulation ladder with main scales and typical tools. Information flows up (bottom-up) and down (top-down) the ladder. The step narrowing indicates the loss or coarse graining of information as one moves from lower to upper scales. For more discussion, see (Vlachos, 2005). DFT, density function theory; CFD, computational fluid dynamics; MD, molecular dynamics; KMC, kinetic Monte Carlo; TST, transition state theory.

In this paper, we first present an overview on multiscale simulation focusing on a new idea of hierarchical multiscale modeling of chemical reactors that has recently been proposed for model development and/or parameter estimation (Mhadeshwar & Vlachos, 2005b; Snyder & Vlachos, 2004). We propose that this new branch of multiscale modeling is a systematic framework to address the important question of which scales and models should one focus on. Then we introduce new ideas and examples of using these models for model-based design of experiments with the objectives of (1) maximizing the information content of a reaction model, (2) reduction of model complexity, (3) carry out catalyst design, and (4) optimal reactor design. These are some of the first demonstrations toward the direction of multiscale model-based product and process engineering in the area of fuel processing for H_2 production, which could, in conjunction with fuel cells, be used for portable power generation. We start with an abstract discussion of the development and the role of hierarchical multiscale modeling in product and process engineering followed by an example of such a model.

2. Multiscale modeling: process versus product engineering

The typical objective of multiscale modeling is to predict macroscopic behavior, such as selectivity, conversion, pollutant levels, hot spots, etc. from first principles. Multiscale modeling involves computing information at smaller scales and moving towards the top of the "simulation ladder" by coarsening degrees of freedom as one goes from finer to coarser scales. Prediction of large-scale process performance based on small-scale information is termed bottom-up approach or upscaling. Since it can be easily assimilated with process alternatives, it is congruent with the traditional objective of *process engineering*. Recent reviews on multiscale modeling of chemical reactors, systems biology, and materials highlighting this view are given by Raimondeau, Aghalayam, Vlachos, and Katsoulakis (2001), Raimondeau and Vlachos (2002), Vlachos (2005) and references therein.

A probably more important but relatively unexplored role of multiscale modeling is in *product engineering*. Coupling of models between scales provides a 'descriptor' or a 'ladder' (see Fig. 1) linking atomistic scale information of materials with macroscopic scale processing. Such a descriptor provides a unique opportunity for product engineering. In the context of multiscale simulation, product engineering can be viewed as the possibility to define desirable performance (objective functions) at the macroscopic scale and then come up with better materials of suitable atomistic structure and possible synthesis protocols via the use of multiscale modeling. Examples can entail the identification of better (cheaper, more stable, more active and selective, etc.) catalysts, of optimal pore size distribution, of templates that produce a desirable zeolite, etc.

Combined process–product engineering is obviously also very important. In particular one is often interested in manipulating variables at the macroscopic scale, e.g., change flow rates and composition, but achieve control at the nanoscopic length scale either by optimum design or model-based on-line control (Lou & Christofides 2003, 2004; Raimondeau & Vlachos, 2000). An example is the ability to control the particle size distribution, the particle shape, and the atomistic packing of materials in crystallization of proteins. Atomistic details of intermolecular forces and templating effects along with more traditional variables, such as local pH and supersaturation, significantly impact polymorphism and thus whether one gets the right material. Yet, macroscopically manipulated variables control the local (i.e., at the nanoparticle scale) supersaturation, concentration of templates, and pH, and therefore the local gradient in chemical potential that in turn affects growth rate and packing.

Multiscale model-based control is currently plagued by the tremendous computational cost of multiscale simulation and the difficulty of having numerous nanoscopic sensors and actuators distributed in a system. The former can be handled using suitable reduced models. Model reduction of complex multiscale models is an important research direction (Vlachos, 2005) that will only be discussed briefly later in this paper. The prospect of using a small number of *mobile sensors and actuators* that can collect information from 'optimal' spatial and temporal locations is a promising avenue to overcome the latter and enable product–process system engineering.

2.1. Hierarchical multiscale simulation: which scale and which model?

The above multiscale science vision, while stimulating, is currently too ambitious to be of practical value for the design and control of complex systems, such as those encountered in microchemical systems for portable fuel processors. There are numerous reasons rationalizing this fact. Consider the example of quantum mechanics at the smallest scale. Density functional theory (DFT) is breaking new grounds in the parameter estimation front. Recent work sets a paradigm for DFT-based parameter estimation on single crystals (Gokhale, Kandoi, Greeley, Mavrikakis, & Dumesic, 2004; Hansen & Neurock, 2000; Jacobsen et al., 2002; Kandoi, Gokhale, Grabow, Dumesic, & Mavrikakis, 2004; Linic & Barteau, 2003; Liu, Hu, & Lee, 2003; Norskov et al., 2002). While DFT is the only truly founded theoretical technique of practical interest for catalysis that has great