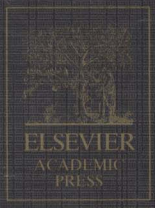

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Multiscale Analysis

Edited by

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PREFACE

The present volume being the first one I have been editing, I would like to take the opportunity to comment briefly on the needs and criteria a series such as "*Advances in Chemical Engineering*" should meet today.

In the first preface of this series, almost 50 years ago, the founding editors raised the issue of "the flood of information" created by "the practioners of the chemical engineering art". Communication both within and among scientific communities defines the borders of such a community and constitutes a major activity of any scientist, next to research as such of course. Complementary to the very important oral presentations and discussions at seminars or conferences, the scientific press has from the very beginning of print as medium been very instrumental in this: verba volent, scripta manent. The emergence of Information and Communication Technology (ICT) in general and Internet in particular has led to a tremendous increase of the amount of information that is available and the frequency at which it is exchanged. I am convinced that this does not decrease the added value of the so-called archival publications, on the contrary. This holds even more so for a series offering a stage to scholars who, upon invitation, are capable and willing to spend time to report in a broader context on their personal contributions to a field. Any paper in "*Advances in Chemical Engineering*" should allow to assess the state-of-the-art in a particular domain and to develop a feeling of its further evolution without claiming to be exhaustive. Going beyond the limits imposed by the "regular" scientific journals while not imposing those typical of a text book is part of the success recipe I have in mind.

The subjects covered are not limited to the classical chemical engineering disciplines. Contributions connecting chemical engineering to related scientific fields, either providing a fundamental basis or introducing new concepts and tools, are encouraged.

Of course applications of chemical engineering receive special attention. A balance between well-developed areas such as process industry, transformation of materials, energy and environmental issues and areas where applications of chemical engineering are more recent or emerging is aimed at.

The theme of the present volume "Multiscale Analysis" has been introduced about a decade ago and is now reaching a stage where a first balance can be made and further research directions should be decided. Which are the dominant and most successful concepts or methodologies? How do these relate to our "classics"? How and where should they be applied next?

The selection of the contributions was among others guided by the concern not to make the gap between the different scales too large. The reader will not be confronted with quantum mechanics at one side of the spectrum nor with chemical plants or even the environment on the other side. Bridging the gap

between the phenomena occurring on the scale of a catalytic site and those on the scale of a reactor or, even smaller, that of a polymer is sufficiently challenging and allows, if not to answer, at least to address the above questions. Maintaining a strong connection with reality, i.e. experimental data was another selection criterion. Experimental validation remains the corner stone of any theoretical development and very powerful experimental techniques are emerging.

First, a broad overview is provided by Dion Vlachos of the University of Delaware. An important example of experimental techniques is discussed in depth by Lynn Gladden and coworkers from the University of Cambridge. Coming from the medical world, Magnetic Resonance techniques can now provide even quantitative answers to problems our community is faced with. The modeling issue is discussed further in the paper coming from the Prague Institute of Chemical Technology and Imperial College, London. Finally, the limitations of the classic reactor engineering models are outlined in a paper from the University of Houston by contrasting the intuitive averaging over length and timescales they are based upon with the rigorous Liapunov–Schmidt method. The authors have made an effort to provide examples when appropriate. References to "a jar containing soup and meat balls" or to "the wall of a champagne glass" provocatively illustrate the broadness of the applications of chemical engineering.

This makes me return to the first preface of this series and even to the very first sentences of it. The danger of fragmentation of our field, some of us are so afraid of, was presented as an opportunity: "The chemical engineer ministers to an industry of far-flung interests. Its products range from soap to plutonium, from gasoline to paper, from antibiotics to cement. It flourishes on change: new products, processes, methods, and applications; new needs are created and foreseen. Versatile men with breath of interest in science and commerce have been demanded and the challenge of the field has found for it such men." I leave it up to the reader to appreciate the flavor of the "old" American, the list of applications, the used gender. Most striking and still very much a topic of the day, however, is the frontier spirit expressed by these lines. A spirit which can be summarized by the device of a 16th century scholar, Pieter de Zuttere, who lived and preached in the Low Countries and in particular in the city of Ghent:

"Cesse le vieux, s'il appert mieux" in old French, or in his and his contemporary Lowys Elsevier's native tongue:

"Als beter can blycken, dat oude sal wijcken".

GUY B. MARIN
GHENT, BELGIUM
March 2005

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Abstract

Multiscale simulation is an emerging scientific field that spans many disciplines, including physics, chemistry, mathematics, statistics, chemical engineering, mechanical engineering, and materials science. This review paper first defines this new scientific field and outlines its objectives. An overview of deterministic, continuum models and discrete, particle models is then given. Among discrete, particle models, emphasis is placed on Monte Carlo stochastic simulation methods in well-mixed and spatially distributed systems. Next, a classification of multiscale methods is carried out based on separation of length and time scales and the computational and mathematical approach taken. Broadly speaking, hybrid simulation and coarse graining or mesoscopic modeling are identified as two general and complementary approaches of multiscale modeling. The former is further classified into onion- and multigrid-type simulation depending on length scales and the presence or not of gradients. Several approaches, such as the net event, the probability weighted, the Poisson and binomial τ-leap, and the hybrid, are discussed for acceleration of stochastic simulation. In order to demonstrate the unifying principles of multiscale simulation, examples from different areas are discussed, including systems biology, materials growth and other reacting systems, fluids, and statistical mechanics. While the classification is general and examples from other scales and tools are touched upon, in this review emphasis is placed on stochastic models, their coarse graining, and their integration with continuum deterministic models, i.e., on the coupling of mesoscopic and macroscopic scales. The concept of hierarchical multiscale modeling is discussed in some length. Finally, the importance of systems-level tools such as sensitivity analysis, parameter estimation, optimization, control, model reduction, and bifurcation in multiscale analysis is underscored.

I. Introduction

A decadal report recently issued by the National Research Council (NRC), entitled *Beyond the Molecular Frontier: Challenges for Chemistry and Chemical*

Engineering (NRC, 2003a), advances 13 "Grand Challenges" for the field. "Advancing Chemical Theory and Modeling" is viewed as one of the critical, enabling technologies. Quoting from the report: "Chemistry covers an enormous span of time and space from atoms and molecules to industrial-scale processing. Advances in computing and modeling could help us connect phenomena at the electronic and molecular scale to the commercial processing." In the information and communications NRC report and in recent roadmaps, multiscale analysis is repeatedly identified as the emerging computational and mathematical science that could enable design and control of complex engineering systems (Thompson, 1999; NRC, 2003b).

The foundations of transport phenomena, reaction engineering, thermodynamics, and nonlinear analysis, along with significant advances in numerical analysis of differential equations at the continuum level and the increase in computational power, have shaped for the most part the **first engineering process modeling paradigm** of chemical sciences of the 20th century (the BSL paradigm of continuum conservation equations and continuum constitutive relations (Bird *et al.*, 1960)). An outcome of this long-time effort has been the widespread use of computational fluid dynamics (CFD) simulation that nowadays routinely assists the design of many industrial processes.

The rapid growth in computational speed over the past decades has enabled a *molecular-based* approach to product and process engineering. Molecular simulations such as molecular dynamics (MD) and Monte Carlo (MC) algorithms have emerged as preeminent computational tools for science and engineering research. Additional discrete particle simulations, such as Brownian dynamics (BD), lattice Boltzmann (LB), direct simulation Monte Carlo (DSMC), and dissipative particle dynamics (DPD), have attempted to bridge information from the molecular to the mesoscopic scale, but often in a phenomenological manner, as the rules of coarse graining are not fully established. At the other end of the modeling spectrum, quantum mechanical (QM) calculations, such as *ab initio* and density functional theory (DFT), in conjunction with transition state theory (TST), have extended the realm of simulation to smaller scales by providing electronic structure information such as potential energy surfaces (PESs) and activation energies that are used in molecular simulations. The advances in molecular and quantum mechanics theory and simulation have established the **second modeling paradigm** (the molecular and quantum modeling paradigm).

Multiscale simulation is emerging and will unquestionably become the **third modeling paradigm**. The idea of multiscale modeling is straightforward: one computes information at a smaller (finer) scale and passes it to a model at a larger (coarser) scale (see Fig. 1) by leaving out degrees of freedom as one moves from finer to coarser scales. Within this context, the most common goal of multiscale modeling is to predict the macroscopic behavior of an engineering process from first principles (*upscaling or bottom-up approach*). This approach has its roots in the work of Newton, Hooke, Bernoulli, Einstein, Bodenstein,

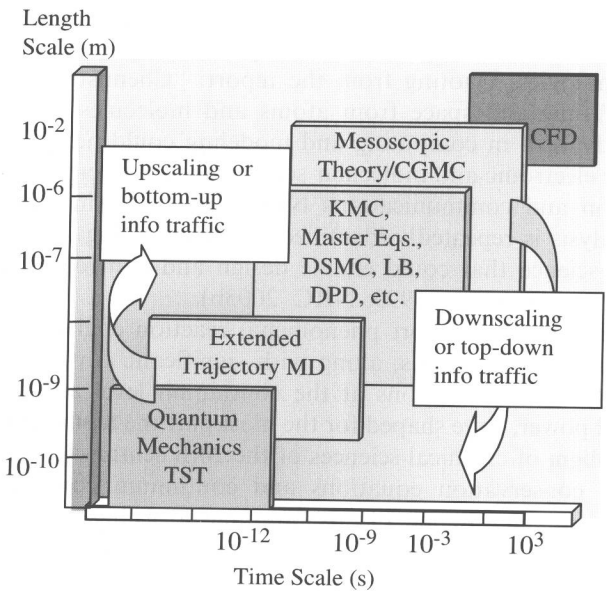

FIG. 1. Schematic representation depicting scales and various simulators. Most multiscale work has focused on the simplest, one-way information passing, usually from the finest to the coarsest scale model. On the other hand, most processes exhibit strong coupling between scales or lack separation of scales.

and others (Phillips, 2002; Raimondeau and Vlachos, 2002a) who left out many degrees of freedom to propose continuum-based constitutive equations and simple models for obtaining answers of interest. In recent times, this goal has been served well, for example, by equilibrium statistical mechanics with QM-based potentials and associated molecular (MD and MC) models. I envision an equally important second goal of multiscale analysis, stemming from the emerging areas of biotechnology, nanotechnology, and device miniaturization. This goal is the ability to predict and control phenomena and devices with resolution approaching nanoscopic scale while manipulating macroscopic (engineering) scale variables such as flow rates, pressures, and temperature (*downscaling or top-down approach*). This manipulation may not happen with active model-based control but instead by properly designing a system, using multiscale model-based information, to function desirably at the molecular level. This issue is further discussed in the section on systems tasks. *Reverse engineering* is yet a third potential goal of top-down information flow: given a desirable property, it is desirable to predict suitable candidate materials (e.g., multicomponent, multifunctional catalysts) and develop rational ways to synthesize them. This last goal addresses product-driven engineering that is believed by many to be the future of chemical sciences (Cussler and Wei, 2003). For the most part, the last two goals have so far remained elusive but are the ones on which

multiscale modeling and simulation would have the most impact in the next decade.

Advances in analytical methods, such as scanning probe and high-resolution transmission electron microscopy, now enable experiments with molecular-level resolution. Furthermore, data from small ensembles of molecules or single entities (e.g., a living cell) become more common. Effectively utilizing these and related emerging tools and data to develop new products and processes will be greatly facilitated by a complementary development in multiscale modeling that can not only model experimentally observed phenomena, but also aid in the *prediction* of new, as of yet, unproven products and processes.

Multiscale simulation is growing so rapidly that it emerges as a new multidisciplinary scientific field. Figure 2 summarizes the number of publications over the past decade using the term "multiscale" and "multi-scale" in their title only or in all title, abstract, and keywords. While the term multiscale means different things in various fields, the explosion is clear. Two new journals, Multiscale Modeling and Simulation, A SIAM Interdisciplinary Journal, and the International Journal on Multiscale Computational Engineering (Begell House Publishers, NY) started in 2003, point to the rapid evolution of this new field. There have been many activities that speak to the same fact. Examples include the recent issues 8 and 9 of the 59th volume of Chemical Engineering

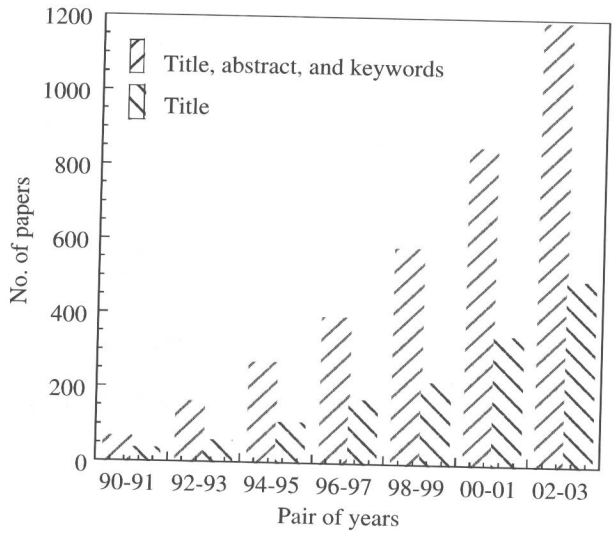

FIG. 2. Sum of the number of publications over periods of two years containing the word "multiscale" and "multi-scale" in the title only or in the title, abstract, and keywords (found through the Web of Science). An explosion in the number of publications is observed. However, this search is just a measure since many of these papers do not really adhere with the definition of multiscale modeling used here, and others, while truly multiscale, are not accounted for because "multiscale" or "multi-scale" is not present in their title, abstract, and keywords.

Science in 2004 that have been dedicated to Complex Systems and Multi-scale Methodology, the forth issue of the 29th volume in Computers in Chemical Engineering on Multiscale Simulation published in 2005, the Springer-Verlag IMA edited book on Dispersive Transport Equations and Multiscale Models resulting from a related workshop, numerous workshops, and a topical conference on Multiscale Analysis in the 2005 AIChE meeting, just to mention a few.

Multiscale simulation builds on the foundations developed in the 20th century of continuum, deterministic and discrete, particle-type models. It attempts to seamlessly integrate models at various scales, extend existing tools to larger length and time scales, and develop theoretical connections between tools over multiple scales. It seems then appropriate to first provide a classification and an overview of models at various scales before multiscale simulation is more formally introduced and recent progress is reviewed. Since we have recently given a review on multiscale simulation in catalysis and reaction engineering (Raimondeau and Vlachos, 2002a), here a broader overview of multiscale simulation is given. The multidisciplinary nature of this emerging field makes this a daunting task. For this reason, I have chosen to mainly focus on the areas of systems biology and materials growth because these two fields are enticing an increasing number of chemical engineers. Furthermore, by choosing two areas one can clearly see unifying multiscale concepts that emerge across chemical engineering. Some rather introductory examples from statistical mechanics and reaction systems are also employed to illustrate key points and methods. Finally, I have tried to include references to some key mathematical pieces of work and multiscale references from the physics, materials, and hydrodynamics communities I am aware of with the hope of cross-fertilizing various disciplines without necessarily being exhaustive in coverage (these areas deserve their own review). For example, a recent, very good review from the mathematics community has just appeared after the submission of this manuscript that presents some of the mathematical underpinnings of the algorithms and methods touched upon below (Givon *et al.*, 2004). While the discussed multiscale approach and issues are generic and apply to various models and scales, I have judiciously chosen to mainly focus on the MC method, among other atomistic or mesoscopic models, and the integration of MC with deterministic, continuum models as an example of stochastic/continuum hybrid multiscale models. This naturally provides more coherence to the chapter. Some key references from other types of multiscale models are also given.

II. Deterministic, Continuum Models

Traditionally, modeling in chemical engineering has invoked continuum descriptions of momentum, mass, and energy conservation (Bird *et al.*, 1960)

where substantial mathematical and computational contributions have been made over the past decades. Here, the discussion is limited to a brief classification that introduces the necessary terminology used in the remainder of the chapter.

A. Hierarchy of Models

Continuum modeling has often been based on algebraic equations (AEs), ordinary differential equations (ODEs), partial differential equations (PDEs), and differential-algebraic equations (DAEs). PDEs provide the most general description at the continuum level. ODEs typically describe transient, well-mixed systems, such as the concentrations and temperature in a batch reactor or in a continuous stirred tank reactor (CSTR), or 1D steady state balances, such as a plug flow reactor (PFR) model or an axial dispersion model. A distinction of ODEs entails initial vs. boundary value problems depending on where the conditions are imposed, namely, only at the entrance or at the entrance and exit, respectively. The hierarchy of deterministic, continuum models is summarized in Fig. 3a. Using concepts of dimensional analysis and symmetry, models toward the bottom of the graph can be thought of as reductions or limits of higher dimensionality models (found toward the top of the graph).

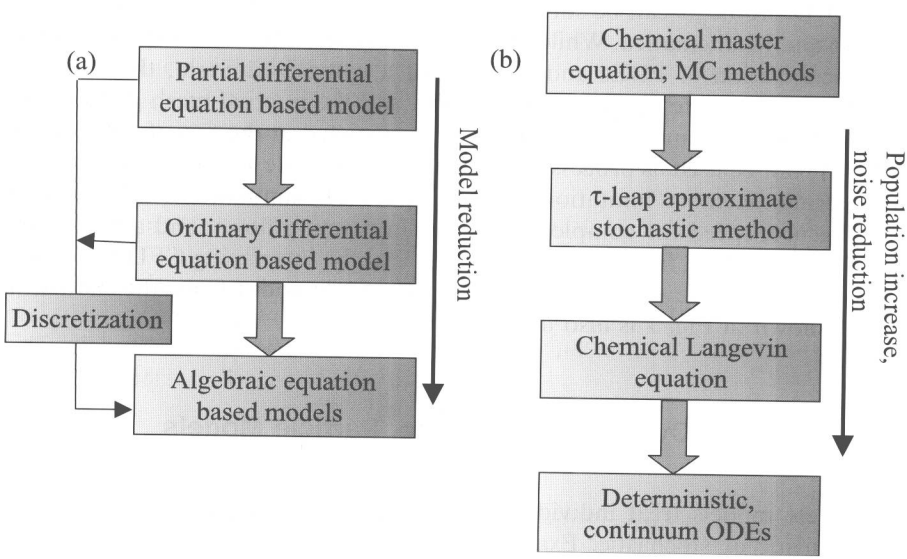

FIG. 3. (a) Hierarchy of deterministic, continuum models. Dimensional analysis and symmetry are powerful concepts in reducing the dimensionality of complex models. (b) Hierarchy of stochastic models for chemically reacting well-mixed systems.