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A synchronous cellular automaton model of mass transport in porous media

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ABSTRACT

In this work we present a fully synchronous coarse grained cellular automaton model for large-scale simulations at molecular level. The model is based on Margolus partitioning scheme, which was generalized as to describe quantitatively diffusion, adsorption and directed flow in porous media. Our aim is to create conceptually simple and computationally efficient framework to model the mass transport in porous materials with large representative volume. This work focuses on the fundamental aspects of the generalized Margolus cellular automaton. We exemplify the model by solving several diffusion problems, studying the monolayer adsorption, chromatography on disordered porous structures and chemical transformation in a system with phase separation. The results indicate that the model reflects the essential features of these phenomena. Absence of round-off errors, fully synchronous way of implementation, autonomous physically meaningful time scale and ease-to-handle boundary conditions make this model a promising framework for study various transport phenomena in porous structures.

1. Introduction

Being extremely useful idealization, cellular automaton (CA) models grasp the essential of the dynamic systems and have provided deep insight into complex processes such as multiphase flows, chemical reaction, protein folding, drug release, neural activity, social segregation, music composing and many others (Ilachinski, 2001; Wolfram, 2002; Chopard and Droz, 2005). CA rely on an idealization of the physical system in which space and time are both discrete. One of the remarkable properties of CA approach is the representation of the entire system as a set of interacting cells. Each cell has a state from a finite set of possible ones. In practical implementations cells may be assigned with physical quantities, *e.g.* number of particles, temperature, velocity, *etc.* States are updated at each time step taking into account states of the neighbors and according to transition rules. In spite of locality and uniformity, CA models may demonstrate extremely complex behavior, while the transition rules can be very simple (Wolfram, 2002).

In the context of molecular modeling, one significant advantage of the CA models is that they can be constructed in a modular fashion by combining submodels, *e.g.* diffusion, stirring, chemical reaction, dissolution or swelling of a solid structure (Vanag, 1999). This modularity makes this class of the models conceptually simple and represents a certain advantage over differential equation based models as it reduces the complexity of model design, programming, debugging, simulation and analysis (Toffoli, 1984; D'Souza et al., 2002). Another advantage of CA models is that they are intrinsically coarse grained, *i.e.* internal molecular degrees of freedom and some intermolecular interactions are leaved out. Therefore, CA models can be formulated upon wide spatial and time scales ranging from angstroms to millimeters and from picoseconds to seconds. This results in a tremendous saving of computational effort and thus allows to model large systems and longer time scales (Lis et al., 2012).

A set of transition rules should reproduce experimentally observed behavior and allow for verifiable predictions. The main issue thereby is to establish reasonable transition rules for a given process (Richards et al., 1990). For some mass transfer problems such rules have been formulated to study drug release (Zygourakis and Markenscoff, 1996; Bertrand et al., 2007; Laaksonen et al., 2009), diffusion of ligands across the protein surface (Kier et al., 2003), transport through a chromatographic column (Kier et al., 2000), chemical etching and corrosion (Than and Büttgenbach, 1994; Córdoba-Torres et al., 2001). Ideally, the set of rules should not explicitly describe every possible response of the model, *i.e.* not be phemonological. The most famous example is the Game of Life wherein simple rules give rise to complex patterns and

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self-replication behavior (Wolfram, 2002). However, to match experimental results with modeling ones, it is often of necessity to introduce *ad hoc* transition rules into the model making it rather descriptive than explanatory (Toffoli and Margolus, 1990). The use of physically sound rules to study real life problems still remains challenging.

The great majority of the CA models developed so far can only be launched in the asynchronous mode. This means that transition rules are applied *one after another* to each cell on the lattice or to some of them. Even though the rules are local and all cells are updated uniformly, the parallel implementation becomes difficult, which in turn limits large-scale simulations. The most common example is the naive diffusion (Bandman, 1999), wherein a cell interchanges with its neighbor with a certain probability. Being applied to each cell on the lattice simultaneously, this rule leads to collisions, *i.e.* particles may vanish or multiply. Hence the asynchronous computation is only possible (Bandman, 1999).

In order to conciliate both realistic rules and as much synchronism as possible, some approaches have been developed. One class of deterministic models relies on microscopic gas dynamics in discretized space and time with discrete particle velocities, where particle collision and propagation rules determine the evolution of the system. This fully discrete and synchronous approach, so called lattice-gas automaton (LGA), has been extensively used to describe single and multiphase flow in porous media, chemically reacting flows and heat transfer (Wells et al., 1991; Biggs and Humby, 1998; Demontis et al., 2006). Although recent results indicate that LGA are merely a subset of CA and any LGA is immediately rewritable as a CA (Toffoli et al., 2008), it is perhaps useful to distinguish between LGA and CA. The reason lies in the fact that CA transition rules rather than LGA can embrace chemical intuition of how any given process proceeds.

In this paper we are intended to draw attention to another class of fully synchronous models, namely, partitioning CA, proposed by Margolus. The key idea of the partitioning cellular automata is the discretization of space to get uniform and separate blocks, which can evolve independently (Toffoli and Margolus, 1987). The lattice is divided into 2×2 blocks in two ways, even and odd (Fig. 1). Any cell is either occupied with molecule or empty (cells are of molecular size). As molecular diffusion can be simulated through the random walking of molecules along the lattice, the transition rule can be expressed as follows: rotate each block by $\pi/2$ either clockwise or counter clockwise with certain probabilities. Keeping alternating between even and odd scheme, and applying rotations to each block, global evolution of the system can be deduced. It is noteworthy to highlight here that the evolution of each block is independent of each other and thus computations can be performed in a parallel manner.

Advantages of the Margolus scheme revealed in the past works can be summarized as follows. First, the scheme is conceptually simple and has been proved to be reliable framework to simulate diffusion transport. Second, it is intrinsically synchronous and thus allows for parallel implementation (see Section 2.4). Third, not only diffusion but also chemical reactions can be built into the model in a modular fashion. Several attempts have been made to apply the partitioning CA to transport problems and heterogeneous chemical kinetics. Bandman (2007) has modeled diffusion and convection by rotations with subsequent drift along the direction of the applied force. Di Maio et al. (2000) have utilized the Margolus partitioning scheme to simulate both diffusion and heterogeneous reaction of coal combustion. Roussel and Lim (1995) have developed a discrete dynamic model of lignin growth, where influx, diffusion and chemical bonding of the monomer were all realized within 2×2 blocks in a parallel manner. Application of the Margolus CA to the modeling of heterogeneous chemical reaction started from pioneering works of Berryman and Franceschetti (1989) and further developed by Mai and von Niessen (1992) with recent application to chaotic chemical dynamics (Lemos and Córdoba, 2010).

To the best of our knowledge, no attempt has been made to develop a consistent approach to transport phenomena in porous media using Margolus scheme. Neither inter-particle nor particle–wall interactions have explicitly been considered in previous works. Particles are treated as an ideal gas with excluded volume (they are not allowed to overlap). Therefore we are attempted to elaborate a framework wherein the rotation probabilities are related to corresponding free energy changes so that each block tends to the local equilibrium. Since adsorption and convective mass transfer are essential processes for great majority of the molecular systems we address the question whether synchronous Margolus scheme can be extended to embrace these phenomena *via* proper selection of rotation probabilities. Besides, it is advantageous to retain parallelizability of the original scheme to utilize the high degree of parallelism of modern computers. Our long-term aim is to create conceptually simple and computationally efficient framework to model mass transport in disordered porous media such as aerogels. This class of materials has a large representative volume and disordered mesoporous structure (Pohl et al., 1995; Salazar and Gelb, 2007) and thus can hardly be simulated with existing methods like MD and MC.

Current study is a first step toward this aim and presents the extended CA model wherein diffusion, adsorption, directed flow in porous media and chemical transformations are all described in a unified manner using Margolus partitioning scheme. The central focus of the paper is to demonstrate reliability of this model by solving simplified mass transport problems with known analytical solution such as diffusion in cylindrical, conical and parabolic pores, monolayer adsorption on random porous structure and chromatography. Incorporation of chemical transformations into the model is exemplified by a system with spinodal decomposition with simultaneous chemical reaction. Chemical engineering processes where the information provided by these simulations has significant relevance are outlined.

2. The cellular automaton model

2.1. Cell states and transitions

In this work, the CA model is composed as a set of cells forming 2D rectangular lattice. A set $S = \{E, M, S\}$ contains possible states of each cell: E (empty or solvent), M (occupied with a molecule), S (solid phase). At each discrete time step 2×2 blocks are singled out from the lattice following even and odd division patterns, as in the classical Margolus scheme (Fig. 1). Molecular motion is modeled for each block independently by its rotation. In that, only M-cells are able to diffuse on the lattice, whereas S-cells are fixed by initial conditions. Thus S-cells are treated as immutable porous media.

If one or more S-cells fall into a block, it can be rotated if and only if there is no overlapping between S- and M-cells. To generalize the Margolus model, besides clockwise (cw) and counter clockwise (ccw) rotations, a block is allowed to remain unmoved (um). A set of possible transitions T is defined as

$$T = \{\text{um} \rightarrow \text{cw}; \text{um} \rightarrow \text{ccw}; \text{um} \rightarrow \text{um}\}.$$

A transition $tr \in T$ transforms one configuration inside the block into another keeping the positions of S-cells unchanged. When all blocks have undergone rotations, even and odd partitioning changes over to ensure the isotropy of space (Toffoli and Margolus, 1990).

As mentioned in Introduction, some transport problems have been solved using the Margolus CA. The essential extension that we propose in this work is to bring together ability of the classical