Modeling Of Adsorption Isotherms from sc-CO_2 Using Cellular Automata

A. Kolnoochenko[a], P. Gurikov[a], I. Smirnova[b], N. Menshutina[a]

[a]Mendeleev University of Chemical Technology of Russia, Miusskay sq., 9 , Moscow, 125047, Russia
[b]Technical University of Hamburg - Harburg, Chair of Separation Science and Technology - V8 - Eiβendorferstr. 38, 21073 Hamburg, Germany

INTRODUCTION

Modern theoretical studies of physical adsorption and diffusion in porous media have been primarily focused on highly idealized pore geometries and ordered zeolite structures. However, little attention has been given to diffusion and adsorption of the relatively large molecules in complex inhomogeneous porous materials such as aerogels in supercritical solutions. Adsorption processes in supercritical fluids (SCF) have fundamental value and are important part of chromatographic determination and separation, porous materials impregnation and many other processes.

In general, mass transfer modeling in porous media can be divided into two interrelated parts. The first one is a realistic simulation of the structure of the porous body. Second one is simulation of intermolecular motions and adsorption, which provide the dynamics of the system.

SUBJECT

Aerogels seemed to be the lightest solid bodies. The density of some aerogel samples (they are often called “frozen smoke”) is only three times more that the density of air. Aerogels consist of spherical particles of nanometer sizes, which formed united three-dimensional structure. The space between particles forms pores with average size about 10-20 nm. Due to the variety of multi-sized pores specific surface area of aerogels reaches 1500 m^2/g.

The first aerogel based on SiO_2 was prepared by Kistler [1]. Today aerogels can be produced from several organic and inorganic substances. Modern conventional method of SiO_2 based aerogel production consists of two stages. The first stage is the hydrolysis of tetraalkylorthosilicates $Si(OR)_4$ with sol formation. Further sol becomes more and more viscous and reaction mixture turns to a gel filled with solvent. At the end the space particles joined in 3D structure. On the second stage supercritical drying of gel makes solvent evaporate and leave pores without 3D structure destruction.

Owing to many unique properties (extremely low density, low thermoconductivity, transparency) aerogels have many applications. According to the recent investigations attention is paid to using them as drug delivery systems. Aerogels based on SiO_2 are nontoxic, environmental friendly. No harmful substances are used in its production. Close physical and chemical similarity has Aerosil® (Evonik). This product successfully passed all clinical tests [2].

There are different ways to fill pores by drugs: in the sol solvent before drying stage or by adsorption from the solvent in supercritical CO_2. Depending on the aerogel surface (hydrophilous or hydrophobic) and drug chemical nature, aerogel-drug formulations show fast

or slow drug release. In [3] shown ketoprofen release from aerogel matrix is much faster than from crystalline state (50 min vs. 250 min), but the release of miconazole is vice versa (120 min vs. 60 min.). It is clear that the simulation of drug release from aerogel-drug formulations is actual task. Modeling of diffusion process with Fick law in porous media is rather arduous task with complicated boundary conditions. Moreover hygrophilous aerogels collapse in water solutions. That means that boundary conditions should also depend on time.

STRUCTURE MODELING

First of all, to simulate diffusion process of drugs modeling of internal aerogel structure is required. This model should correlate with experimental data about pore size distribution, specific surface area and porosity.

Generation process in overlapped spheres method (OSM) consists of two stages:

1. Creation of the set of equal-size spheres (size for SiO_2 particles d = 4 nm), overlapping each other not more than specific value (in our case 40% of particle diameter). Every new sphere with random center coordinates is added to the previously created. If new particle overlaps the neighbor one more than 40% of its diameter, this particle moves along the line between centers of the particles to reduce the overlapping. Process terminates when required porosity is reached (should be less than 50%), or in case of no possibility to add new sphere. Thus rather dense structure is generated (figure 1).

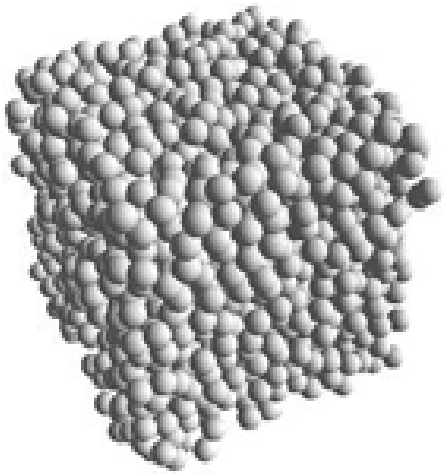


Figure 1. Close-pack configuration in OSM

2. Random spheres are removed from the structure. Spheres can be removed only if percolation cluster is kept. This condition was controlled by cluster labelling technique introduced by Hoshen and Kopelman [4].

Process is finished when real aerogel porosity is reached (5–15% for different types of aerogels and depends on production method).

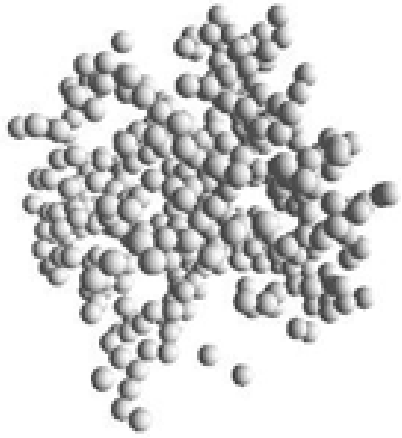


Figure 2. Final OSM configuration consists of one percolation cluster

On figure 2 shown the result of OSM. Diameter of silicon dioxide particle was chosen to 4 nm and volume to 50x50x50 nm^3. Iterations were performed until 90% free space has been achieved.

DIFFUSION SIMULATIONS

Cellular automaton with Margolus' neighborhood has been chosen for diffusion simulations in porous media. Cellular automata (CA) theory was developed in early 40s of 20^{th} century and nowadays it has become a reliable way for modeling a variety of real systems both discrete and continuous. CA is used as a simulating tool in many fields: from active hydrodynamics in chemical apparatus to road traffic simulating and from modeling of protein structures to neural systems' activities.

However, with the rise of task complexity the use of cellular automata approach requires large computing capacity to model significant time intervals in dynamic systems. That is why 3D cellular automata are used rather rarely, primarily, because of the necessity to store and process large amount of data. But from the other hand, application of 3D CA makes possible to come closer to detailed and precise modeling of real systems. This is why it is very important to look for new ways to increase calculation speed and computing capacity.

One of the remarkable properties of CA approach is the representation of the whole system as a set of independent cells, which are influenced only by neighbors. This allows us to use parallel computing algorithms.

Let's examine the Margolus cellular automaton for diffusion simulations [5]. Square lattice represents «space» and to each site of this lattice, or cell, there is associated a state variable, called the cell state ranging over a finite set, called state alphabet. In that case state alphabet consists of 2 values: $S_1 = 1$ (there is a particle in this cell) and $S_2 = 0$ (empty cell) (figure 3). All lattice is divided by blocks with 2x2 sites in each. There are two ways of this division: even (figure 4a) and odd (figure 4b). At each time step (computational iteration) there are two half-iterations – for even and odd divisions one provides right or left angle turn ($\pi/2$) to each block (figure 5). Thus transition rules for lattice size MxM (where M – even) consist in turning M/2 x M/2 blocks of even lattice and then in rotation M/2 x M/2 of the blocks in odd lattice.

Here we'll consider only such a "classical" automaton. It's able to simulate diffusion with specific diffusion coefficient (D = ¾). But in more advanced version one could take into account also interactions between different kinds of cells.

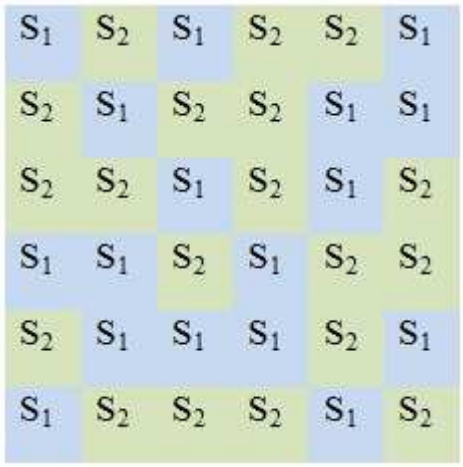
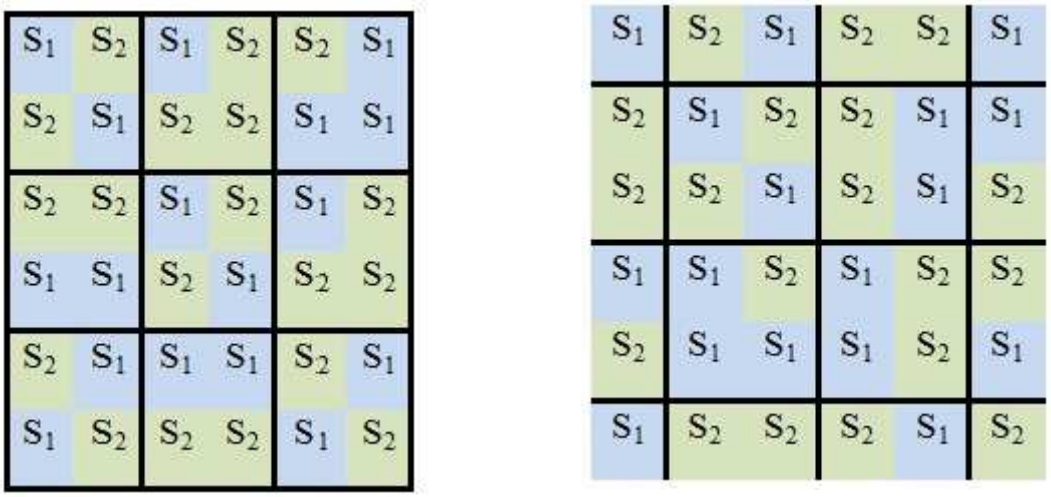


Figure 3. Cellular automaton's lattice



a) Blocks in even division b) Blocks in odd division

Figure 4. Two ways of lattice's division

a) b)

Figure 5. Right and left angle block turns

Some modifications are used to apply this algorithm to diffusion simulations. State alphabet is expanded by adding a new value: $S_3 = 2$ (solid body). Transition rules stay the

same, with the exception of not turning the block if there is even a single cell is in the state S_3. In this case the particle can't replace the solid body and the latter become impermeable for the former.

A physical size of the cells is very important for exact simulation of real life physicochemical systems. E.g. maximum number of active substance particles in cell (cell capacity) depends on it.

It's also necessary to create accurate structure of porous body, that is a configuration of cells in S_3 state. Main parameters here are a number of such cells and cells' mutual distribution.

However during the solutions of these problems is also clear that he motion of particles is independent and there is no interactions between solvent, active substance particles and solid body. In this respect active substance particles can be considered as if it was ideal gas. That is the reason why there is no possibility to take into account chemical features of an active substance, porous media (i.e. hydrophilic or hydrophobic) and destruction of solid body dependent upon capillary forces.

Thus following actions are necessary for an accurate diffusion simulations using Margolus CA:

1. Specify cells' size
2. Create model of solid body structure considering experimental data (OSM)
3. Create model of aerogel-drug system taking into account experimental data
4. Consider interactions between drug, solid body and solvent.

POTENTIAL OF THE INTERMOLECULAR INTERACTION

For each pair of connected cells we introduce constant energies of interactions, which depends on the states of these cells only. The total energy of the block 2^X2 depends on the sum of pair interactions only:

$$E^S_{block} = \sum_{i\in\{D,E\}} \sum_{j\in\{A,D,E\}} K_{ij}E_{ij},$$

where K_{ij} – the number of contacts between the cells with the state S_i and the cells with the state S_j, E_{ij} – energy of the pair interaction. Summation in the equation provides only for the nearest adjacent neighbors, connected with the current block. The cells are supposed not to interact inside the block.

As the molecular motions depend on rotations of the block which take place with some relativities, thus it's natural to make a correlation between the rotation of the block and changing of total energy of the block when that rotation occur.

If to be more specific - before the rotation of the block should be calculated its energy in seven states: unmoved, after right angle turn and after left angle turn around each of three axes. In general case all three values of these energies will be different and turn with the lowest energy can be interpreted as the most possible one. The relation between energies and possibilities can be represented as an analogue of the partition function.

$$Q = \sum \exp\left(-E^{rotation}_{block}\right),$$

$$P_{rotation} = \frac{\exp\left(-E^{rotation}_{block}\right)}{Q},$$

where – energies of the block after turning it right and left angle around one of the axes, – possibilities of keeping the block unmoved, turning it right or turn it left.

RESULTS AND DISCUSSION

All diffusion simulation trials were performed for the structure with 4 nm particles diameters and volume to 50x50x50 nm^3. All pair interaction energies are equal zero excluding "aerogel – drug" interaction *E*(AD). In order to fit calculated isotherms to experimental values [6] few runs were implemented with different *E*(AD). It was shown that with proper selection of interaction energy values between solid body and diffuse molecules a good correspondence between experimental and calculated adsorption isotherms can be achieved with *E*(AD) = 1,47±0,04 (fig. 6). It should be noted that interaction energy is dimensionless and defined for isothermal adsorption process and constant aerogel density (0.10 g/cc). Calculations with the *E*(AD) = 1,47 were also performed to quantify experimental isotherms for the dense aerogel (0.19 g/cc). Important test to applicability of the proposed model is that the agreement between experimental and calculated adsorption in this case is also good (no more 5 % for the both densities).

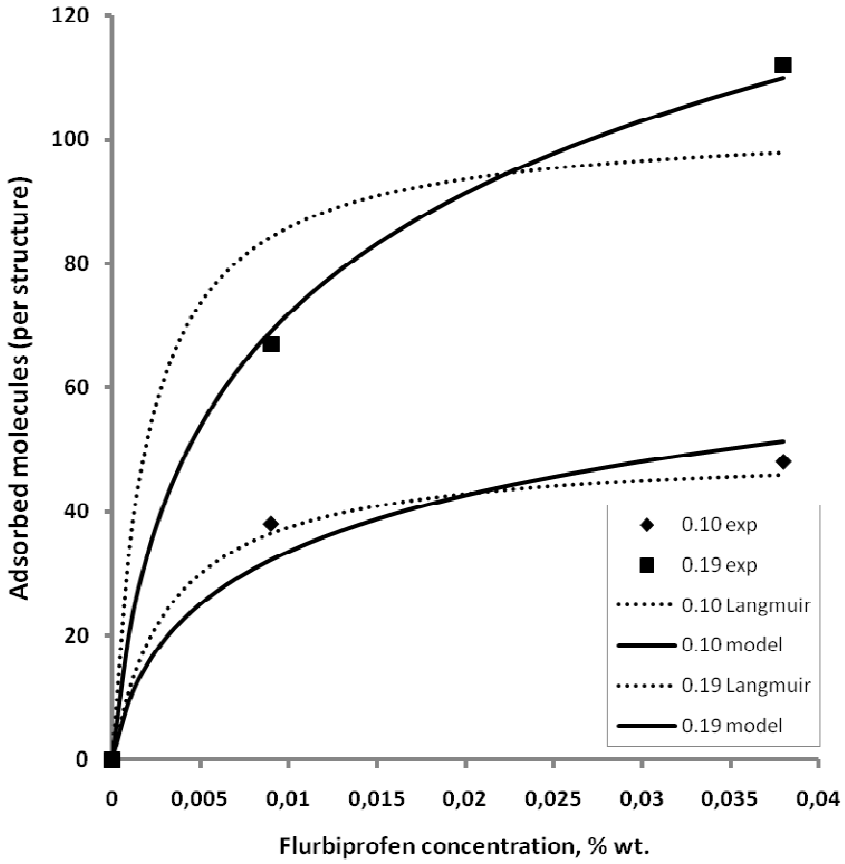


Figure 6. Flurbiprofen experimental isotherms (points) for different aerogel densities (g/cc) compared with Langmuir fiiting (dashed line) and derived from the model (solid line)

Model described above is suitable and flexible tool for the mesoscopic investigation mass transfer processes in the porous material like aerogel with respect to the diffusion and

adsorption phenomena. Adsorption kinetics calculations are also possible in the described model in contrast our previous work [7]. Detailed experimental kinetics investigations for aerogels microparticles are mostly not available. However, there are considerable data on the supercritical chromatography and we believe this model can provide a relatively simple method of calculation of chromatographic processes with an emphasis on the investigation of the role of the stationary phase nature and mixture composition in the separation process.

REFERENCES

1. S. Kistler, **1931**, Coherent Expanded Aerogels and Jellies, Nature, 127, 741.
2. Degussa, **2001**, Technical Bulletin Aerosil & Silanes, Company publication, Dusseldorf.
3. I. Smirnova, **2002**, PhD Thesis, Technical University of Berlin.
4. J. Hoshen, R. Kopelman, **1976**, Percolation and Cluster Distribution. I. Cluster Multiple Labelling Technique and Critical Concentration Algorithm, Phys. Rev. B, 14, 3438–3445.
5. T. Toffoli, N. Margolus, **1990**, Invertible cellular automata: A review, Physica D, 45, 229–253.
6. S. Suttiruengwong, **2005**, PhD Thesis, University of Erlangen Nuremberg, Germany.
7. P. A. Gurikov, A. V. Kolnoochenko, N. V. Menshutina, **2009**, 3D Reversible Cellular Automata for Simulation of the Drug Release from Aerogel-Drug Formulations, Computer Aided Chemical Engineering. 26, 943–947.