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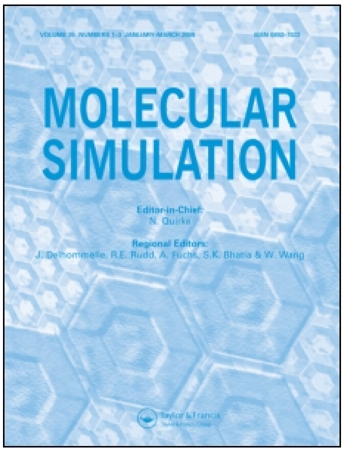

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LATTICE BOLTZMANN SIMULATION OF DIFFUSION-CONVECTION SYSTEMS WITH SURFACE CHEMICAL REACTION

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Chemical reactions on solid surfaces are ubiquitous in natural and industrial processes. In many situations, the reaction is complicated by diffusion and convection of reactants in the surrounding media. The system as a whole is usually highly nonlinear. Theoretical analysis for this complicated phenomenon is difficult if not entirely impossible. It is highly desired to develop efficient computational tools to simulate this process. The lattice Boltzmann method, based on mesoscopic description of fluid systems, is quite suitable for this purpose. This study will present a lattice Boltzmann scheme for simulating the diffusion-convection systems with surface chemical reactions.

Keywords: Lattice Boltzmann simulation; diffusion-convection; surface chemical reaction

1. INTRODUCTION

The chemical reactions on solid surfaces are ubiquitous in natural and industrial processes. The most noticeable example is the corrosion, which causes billions of economic loss each year. On the other hand, the chemical reaction on a solid surface is also an important process in various industrial applications. Examples can be found in electrochemical systems such as electrowining, electrorefining, and electroplating; batteries and fuel cells; and biologic interaction analysis devices. Needless to say, understanding and controlling this important process will help us to prevent the corrosion and to optimize the efficiency of current industrial devices.

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The chemical reaction on a solid surface is a complicated process. The reaction itself belongs to the non-equilibrium dynamics – a field that is still undergoing constant developments. In many situations, the chemical reaction on a solid surface occurs in a fluid environment which further complicates the process with the diffusion and convection of the reactants in the surrounding media. The system as a whole is usually highly nonlinear and may lead to elaborated phenomena such as the dendritic growth of the deposits. Theoretical analysis for this complicated system is difficult if not entirely impossible. This fact calls for alternative research approaches such as the numerical simulation. In this respect, the lattice Boltzmann method is quite suitable for this purpose.

The lattice Boltzmann method (LBM) is a numerical scheme which simulates transport phenomena based on mesoscopic description of fluid systems [1]. Rather than tracking individual molecules like the molecular dynamics, LBM simulates transport phenomena by following the evolution of ensembles of molecules. Because of this, the LBM simulations can be carried out with less computational cost than those based on molecular dynamics. In the mean time, using the ensemble averaged distribution function as the primary variable allows LBM to retain many of the microscopic physics. This feature gives LBM the advantage to study non-equilibrium dynamics over the conventional numerical methods that are based on solving macroscopic transport equations.

The lattice Boltzmann method has been applied to study a variety of transport phenomena such as porous media flow [2–4], multiphase flow [5–7], magneto-hydrodynamics [8], turbulence [9], and diffusions process [10, 11]. Compared to other applications, using the lattice Boltzmann method to study chemical reaction is relatively few. In saying so, we do not mean to ignore the numerous studies on diffusion-reaction problems using the lattice gas automaton (LGA). In fact, these work do provide us invaluable information on how to design reaction models on the mesoscopic level. However, as being pointed out in a review paper by Chen *et al.* [12], it is very difficult to incorporate the fluid convection in the LGA diffusion-reaction models. In addition, the intrinsic noise in the LGA prevents these models to become practical numerical simulation tools for engineering applications.

The first lattice Boltzmann models for chemical reaction in a flow system were proposed by Kingdon and Schofield [13] and Dawson *et al.* [14] shortly after the appearance of the LBM hydrodynamic models. In these models, the chemical reaction was incorporated *via* proper source terms in the lattice Boltzmann equation. The reactants are assumed to be sufficiently dilute to not affect hydrodynamics of the solvent. The advection is primarily due to the solvent flow and the diffusions of solute are controlled by relaxations of the distribution functions to their corresponding equilibrium states. A similar model was used by Qian and Orszag [15] to study the diffusion-driven reactive system with an irreversible reaction. Weimar and Boon [16] also reported a similar LBM model for studying nonlinear reaction advected by a flow.

The aforementioned LBM reaction models have been proved to be useful tools for studying chemical reactions in bulk fluids [1]. Of particular interest to this study, however, is the chemical reaction on solid surfaces. The only relevant studies we found in the literature are those by Wells *et al.* [17] and Janekey *et al.* [18], who studied chemical reactions at mineral surfaces. In their studies, surface reactions involving dissolution and precipitation were simulated by allowing wall nodes to serve as sources or sinks for mass of a dissolved component. The mass transfer between fluid and surface depends on the disequilibrium between fluid and mineral. The present work aims to extend the above approach to incorporate explicitly the reaction kinetics into the LBM model. This is done by coupling the surface reaction with the diffusion between the wall and bulk fluid.

The rest of the paper is organized as follows. Section 2 describes the lattice Boltzmann scheme for simulating a convection-diffusion system with surface chemical reaction. The surface reaction is incorporated in the formulation *via* appropriate boundary conditions. Section 3 presents several benchmark studies to validate the proposed LBM scheme. Section 4 discusses and concludes the paper.

2. LATTICE BOLTZMANN MODEL FOR SURFACE REACTION IN FLOW SYSTEMS

2.1. Evolution Equations

At the macroscopic level, the transport of a soluble material in solvent simply takes place in the forms of convection and diffusion. The driven mechanisms at the microscopic level, however, could be quite complicated. The transport is usually a combined consequence of molecular collision, intermolecular interaction, external forces, *etc.* [11]. For simplicity, in this study, we only focus on the mass transport due to molecular collisions. In addition, the solute concentrations are assumed to be sufficiently low to not influence the solvent flow. The solute transport in such a system can be described by the following lattice Boltzmann equation [13, 14]:

$$g_\alpha^s(\mathbf{x}+\mathbf{e}_a\delta_t, t+\delta_t) - g_\alpha^s(\mathbf{x}, t) = -\frac{g_\alpha^s(\mathbf{x}, t) - g_\alpha^{s,\mathrm{eq}}(c^s, \mathbf{u})}{\tau_s + 0.5} + w_\alpha q^s \qquad (1)$$

where g_α^s is the distribution function; τ_s is the relaxation time; and q^s is the source term associated with chemical reaction in bulk fluids. The superscript stands for sth species. It should be noted that Eq. (1) has used the LBM model with second-order accuracy in time [19]. That is why the denominator of the relaxation term is $\tau_s + 0.5$ instead of τ_s as in conventional LBM models. $g_\alpha^{s,\mathrm{eq}}$ is the corresponding equilibrium distribution:

$$g_\alpha^{s,\mathrm{eq}}(c^s, \mathbf{u}) = w_\alpha c^s \left[1 + \frac{\mathbf{e}_a \cdot \mathbf{u}}{RT} + \frac{(\mathbf{e}_a \cdot \mathbf{u})^2}{2(RT)^2} - \frac{\mathbf{u}^2}{2RT}\right], \qquad (2)$$

where $\mathbf{u}$ is the solvent velocity, R is the gas constant, and T is the temperature. $\mathbf{e}_a$'s are the discrete velocities and w_α's are the associated weight coefficients. For the two-dimensional 9-speed LBM model, we have $RT = 1/3$ and,

$$\mathbf{e}_\alpha = \begin{cases} \mathbf{0}, & \alpha = 0, \\ (\cos[(\alpha-1)\pi/2], \sin[(\alpha-1)\pi/2]), & \alpha = 1,2,3,4, \\ \sqrt{2}(\cos[(\alpha-5)\pi/2+\pi/4], \sin[(\alpha-5)\pi/2+\pi/4]), & \alpha = 5,6,7,8, \end{cases} \qquad (3)$$

The corresponding weight coefficients are $w_0 = 4/9$, $w_\alpha = 1/9$ for $\alpha = 1, 2, 3, 4$, and $w_\alpha = 1/36$ for $\alpha = 5, 6, 7, 8$. The concentration of sth species is calculated using

$$c^s = \sum_\alpha g_\alpha^s. \qquad (4)$$

Using the Chapman-Enskog expansion technique, the above lattice Boltzmann equation can be proved to recover the following diffusion-reaction equation:

$$\frac{\partial c^s}{\partial t} + (\mathbf{u} \cdot \nabla) c^s = \nabla \cdot (D_s \nabla c^s) + q^s, \qquad (5)$$

where diffusion coefficient of sth component, D_s, is related to the corresponding relaxation time *via* $D_s = \tau_s RT$.

Since we have assumed that the mass transport of the solute has no effect on the movement of the bulk fluid, the solvent fluid can be simulated using an independent lattice Boltzmann equation:

$$f_\alpha(\mathbf{x}+\mathbf{e}_a\delta_t, t+\delta_t) - f_\alpha(\mathbf{x}, t) = -\frac{f_\alpha(\mathbf{x}, t) - f_\alpha^{\mathrm{eq}}(\rho, \mathbf{u})}{\tau + 0.5} \tag{6}$$

where f_α is the distribution function of the solvent, τ is the relaxation time which relates to the kinematic viscosity by $\nu = \tau RT$; and f_α^{eq} is the equilibrium distribution of f_α:

$$f_\alpha^{\mathrm{eq}}(\rho, \mathbf{u}) = w_\alpha \rho \left[1 + \frac{\mathbf{e}_a \cdot \mathbf{u}}{RT} + \frac{(\mathbf{e}_a \cdot \mathbf{u})^2}{2(RT)^2} - \frac{\mathbf{u}^2}{2RT}\right]. \tag{7}$$

The density and velocity of the bulk fluid are calculated using:

$$\rho = \sum_\alpha f_\alpha, \tag{8}$$

$$\rho\mathbf{u} = \sum_\alpha f_\alpha \mathbf{e}_a. \tag{9}$$

2.2. Boundary Condition

There are many similarities between the surface chemical reaction and that occurring in bulk fluids. Both of them can be described by the following reaction equation:

$$\alpha_1 X_1 + \alpha_2 X_2 + \cdots + \alpha_M X_M \rightleftharpoons \beta_1 Y_1 + \beta_2 Y_2 + \cdots + \beta_N Y_N. \tag{10}$$

The major difference between them is that not all components are free to move around in the surface reaction. Without losing generality, we consider in this paper a two-component synthetic reaction:

$$c + R \underset{k_\mathrm{d}}{\overset{k_\mathrm{a}}{\rightleftharpoons}} B, \tag{11}$$

where k_a and k_d are the association and dissociation rate constants, respectively. Both the reactant R and the product B are bound at the surface, and only the reactant c is soluble in the bulk fluid. Since the number of solute in the bulk fluid is reduced to one, we will neglect the superscript s in the following text.

For the bound species, mass conservation requires:

$$\frac{\partial B}{\partial t} = -\frac{\partial R}{\partial t} = k_\mathrm{a} c R - k_\mathrm{d} B. \tag{12}$$

For the soluble reactant, we assume its concentration in the wall is always in the saturation state. In another word, the soluble reactant consumed or produced in the reaction is purely supplied from or released to the bulk fluid through the diffusion:

$$D\frac{\partial c}{\partial n} = k_a cR - k_d B. \tag{13}$$

With the definitions of $h = k_a R$ and $c_\infty = k_d B / k_a R$, Eq. (13) can be also expressed in the form of the general boundary condition for diffusion problems:

$$D\frac{\partial c}{\partial n} = h(c - c_\infty). \tag{14}$$

Unlike in conventional diffusion problem, both h and c_∞ vary with time in our case because of the surface reaction.

The above formulation describes a boundary condition for surface reaction at the macroscopic level. To implement this into an LBM model, we have to formulate a boundary condition for the distribution functions. In this respect, we found the boundary condition for the thermal LBM model proposed by He *et al.* [19] is heuristic. This approach is based on the observation that, at a stationary wall, the non-equilibrium portion of the distribution function is proportional to the dot product of its microscopic velocity and the concentration gradient. Consequently, the non-equilibrium portion in opposite directions takes opposite sign. Taking a wall node in the bottom surface as an example (Fig. 1), the above consideration leads to the following boundary conditions:

$$g_2 = \frac{1-\lambda}{1+\lambda} g_4 + \lambda \left[g_2^{\mathrm{eq}}(c_\infty, \mathbf{u}) + \frac{1-\lambda}{1+\lambda} g_4^{\mathrm{eq}}(c_\infty, \mathbf{u}) \right], \tag{15}$$

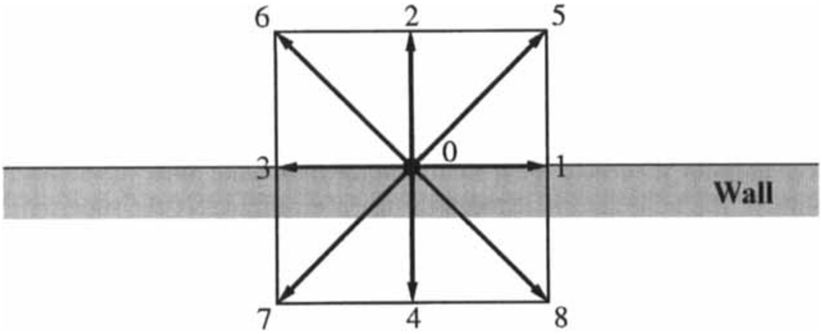


FIGURE 1 A wall node at the bottom surface.

$$g_5 = \frac{1-\lambda}{1+\lambda} g_7 + \lambda \left[g_5^{\mathrm{eq}}(c_\infty, \mathbf{u}) + \frac{1-\lambda}{1+\lambda} g_7^{\mathrm{eq}}(c_\infty, \mathbf{u}) \right], \tag{16}$$

$$g_6 = \frac{1-\lambda}{1+\lambda} g_8 + \lambda \left[g_6^{\mathrm{eq}}(c_\infty, \mathbf{u}) + \frac{1-\lambda}{1+\lambda} g_8^{\mathrm{eq}}(c_\infty, \mathbf{u}) \right], \tag{17}$$

where

$$\lambda = \frac{h}{RT} \left(1 + \frac{1}{2\tau_1} \right). \tag{18}$$

The above rules can be used as general boundary conditions for diffusion problems. In the limit of $h \to \infty$, they recover the fixed concentration condition of $c = c_\infty$. While in the limit of $h \to 0$ and $hc_\infty \to q_w$, they recover the fixed flux condition of $D\partial c/\partial n = q_w$.

3. SIMULATION RESULTS

In this section, we present simulation results of a convection-diffusion system with surface reaction. Figure 2 shows a schematic plot of the reaction chamber. Solvent flows in the channel at left and flows out at right. The reaction occurs at the bottom surface and the upper surface is insulated. For simplicity, we only focus on the fully developed laminar flow in which the horizontal velocity profile takes a parabolic shape and the vertical velocity is zero. This avoids the simulation of the solvent flow. The channel height is L and the solvent velocity at the centerline is U_c. For simplicity, we neglect the chemical reaction in the bulk fluid.

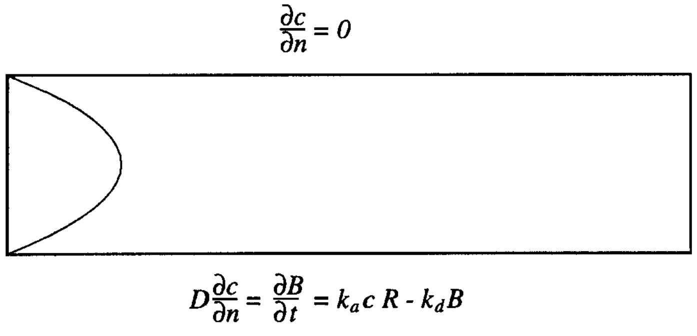


FIGURE 2 A schematic plot of the reaction chamber.

The first case we studied is a limiting case in which the bottom surface acts as a sink. The bound reactant at surface is abundant so that it consumes all soluble reactant coming from the solution. Consequently, the concentration of the soluble reactant is always zero at the bottom surface. The soluble reactant flows in the channel with a concentration of c_0. For large Peclet number, $\mathrm{Pe} = U_c L/D$, this problem has an analytic solution – the Lévêque solution [21] – at the steady state. Figure 3 compares the calculated flux of the solute with the Lévêque solution:

$$\frac{L}{c_0}\frac{\partial c}{\partial n} = \frac{1}{\Gamma(4/3)9^{1/3}}\left(\frac{4\mathrm{Pe}}{x/L}\right)^{1/3}. \tag{19}$$

The agreement is very good except around the inlet corner where the theoretical concentration gradient possess a singularity.

The second case we studied is the surface reaction with the parameters listed in Table I. The simulation starts from the initial conditions of $c = 0$,

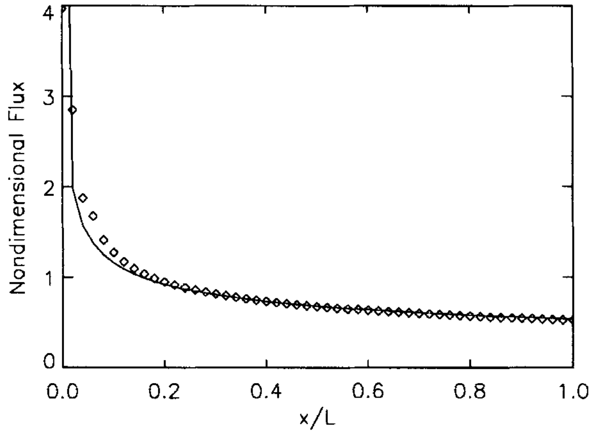


FIGURE 3 Comparison of the calculated solute flux at the surface (symbols) with the Lévêque solution (solid line).

TABLE I Simulation parameters for biologic interactive analysis system

Symbols	*Values*
c_0	25 nM
R_0	1.25 nM cm
U_c	5 cm/s
k_a	0.008 l/nM l/s
k_d	0.2 l/s

$R = R_0$, and $B = 0$. In the first 50 seconds, the soluble reactant flows in the channel with a concentration of c_0 and the association is dominant in the surface reaction. After this association phase, the species supply is cut off and the inlet concentration of the soluble reactant goes back to zero. Dissociation becomes the dominant reaction in this period. Figure 4 plots the time histories of the concentrations of the bound complex and the soluble reactant at the bottom surface. Several meshes were used in the simulation to check the convergence of the results. The convergence is shown to be satisfactory. Also plotted in (Fig. 4) is the simulation result using the finite element method [20]. As shown, the results from both methods agree with each other well.

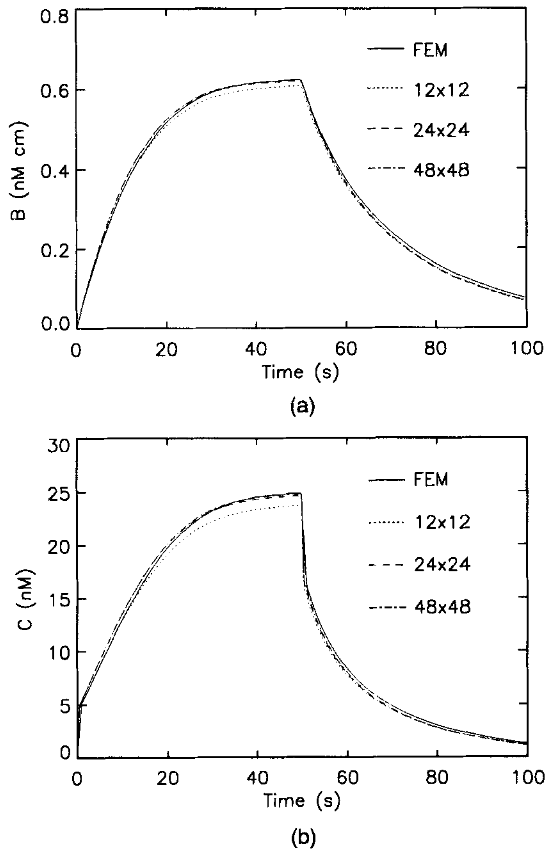
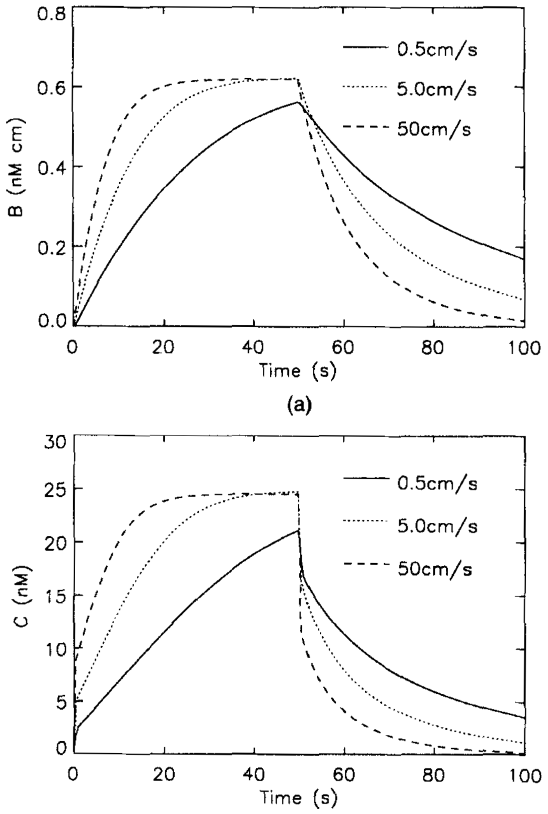


FIGURE 4 Mesh convergence study and comparison of the LBM simulation with the finite element simulation; (a) the time history of the binding complex concentration and (b) the time history of the surface receptor concentration. Simulation parameters are listed in Table I.

The above experimental setup is widely used in the biologic interactive analysis system to measure the rate constants [22]. The concentration of the synthesis or binding complex can be continuously measured based on the optical phenomenon of surface plasmon resonance. The time-history of the binding complex is then used to estimate the association and dissociation rate constants. In this application, it is important to know the response time of the surface receptor. A significant error could be incurred if the response time of the surface receptor is comparable to that of the binding complex. This is exactly what happens in the aforementioned case.

The response of the surface receptor can be expedited by a variety of means. One of them is to increase the solvent flow in the reaction chamber.



(a)

(b)

FIGURE 5 Effects of the flow rate on the response time of, (a) the binding complex concentration and (b) the surface receptor concentration.

To study the effect of the flow rate on the response of the receptor on surface, we carried out simulations at three different flow rates, 0.5 cm/s, 5.0 cm/s, and 50 cm/s. Figure 5 shows the time histories of concentrations of the binding complex and the surface receptor. Increase of flow rate helps to reduce the response time of the surface receptor. In the cases studied here, at the flow rate of 0.5 cm/s, the surface receptor is not even close to the concentration in bulk fluid at end of the 50-seconds association phase. While at the flow rate of 50 cm/s, the surface receptor reaches the bulk fluid level at about 20 seconds. Nevertheless, it has not yet completely eliminated the response time of the surface receptor.

4. CONCLUSIONS

In conclusion, we have proposed a lattice Boltzmann model for simulation of diffusion-convection systems with surface chemical reactions. The focus is on how to incorporate the surface reaction into the lattice Boltzmann model. The surface reaction is modeled by treating wall nodes as sinks or sources of the dissolved components. By assuming the soluble reactant is always in the saturation state, we connected the surface reaction equation to the diffusion of the soluble reactant between the bulk fluid and the wall. The boundary condition is further expressed in the form of distribution functions. Simulations were carried out to benchmark the proposed model for surface reaction. The results agree well with both the analytic solution and finite element simulations.

The present work is only the first step of further studies of more complicated diffusion-reaction phenomena. For example, although we have considered the mass transfer between the solid surface and bulk fluid, the wall displacement due to the chemical reaction is neglected. Including the wall displacement will reveal more complicated processes such as dendritic growth. Another future challenge will be how to incorporate the electric potential into the LBM model. This is essential for simulation of electrochemical process.

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