

Chemical reaction simulations using Abstract Rewriting System on Multisets with Lattice Boltzmann Method

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Abstract

We have composed a simulation method for the reaction-diffusion-convection model of chemical reactions by synthesizing ARMS and the Lattice Boltzmann Method (LBM); LBM is a discrete expression of the Navier-Stokes Equation. **keywords:** Artificial Chemistries, Reaction diffusion and convection system, Lattice Boltzmann Method, Belousov Zhaboyinskii reaction, Abstract Rewriting System on Multisets (ARMS)

Abstract Rewriting System on Multisets, ARMS

ARMS proposed in 1996 [7], it relates to theoretical chemistry[2] and computational algebra [6], [5] An ARMS is a construct $\mathcal{A} = (A, w, R)$, where A is an alphabet, w is a multiset present in the initial configuration of the system, and R is the set of multiset rewriting rules.

Let A be an *alphabet* (a finite set of abstract symbols). A *multiset* over A is a mapping $M : A \mapsto \mathbf{N}$, where \mathbf{N} is the set of natural numbers; $0, 1, 2, \dots$. For each $a_i \in A$, $M(a_i)$ is the *multiplicity* of a_i in M , we also denote $M(a_i)$ as $[a_i]$. We denote by $A^\#$ the set of all multisets over A , with the empty multiset, \emptyset , defined by $\emptyset(a) = 0$ for all $a \in A$. A multiset $M : A \mapsto \mathbf{N}$, for $A = \{a_1, \dots, a_n\}$ is represented by the state vector $w = (M(a_1), M(a_2), \dots, M(a_n))$, w . The union of two multisets $M_1, M_2 : A \mapsto \mathbf{N}$ is the addition of vectors w_1 and w_2 that represent the multisets M_1, M_2 , respectively. If $M_1(a) \leq M_2(a)$ for all $a \in A$, then we say that multiset M_1 is included in multiset M_2 and we write $M_1 \subseteq M_2$. A *reaction rule* r over A can be defined as a couple of multisets, (s, u) , with $s, u \in A^\#$. A set of reaction rules is expressed as R . A rule $r = (s, u)$ is also represented as $r = s \rightarrow u$. Given a multiset $s \subseteq$, the application of a rule $r = s \rightarrow u$ to the multiset w produces a multiset w' such that $w' = w - s + u$. Note that s and u can also be zero vector (empty). The *reaction vector*, ν_{ji} denotes the change of the number of a_i molecules produced by one reaction of rule r_j .

f Algorithm of DARMS In Deterministic Abstract Rewriting System on multisets (DARMS), reaction rules are applied in maximally parallel and deterministic way. Hence, the DARMS accommodates P Systems, while it has background in theoretical chemistry [8].

Step 0(Initialization). The time t is set to 0 and the set of vectors $V = (\delta_1, \delta_2, \dots, \delta_N)$ ($j = 1, 2, \dots, m$), expressing the stoichiometric change of each species, are initialized. Then all inputs of the system are assigned to their respective variables, $X(a_1), X(a_2), \dots, X(a_N)$ are set to the initial quantities of species; k_1, \dots, k_m to set m rate constants corresponding to the m reactions; t_{stop} to the ending instant of simulation; set the value of Δt ; *Step 1(*Calculation of state change vector $\lambda(t)$). According to reaction rules, stoichiometric change of each specie λ_i is calculated as well as the state change vector; $\lambda(t) = (\lambda_1, \lambda_2, \dots, \lambda_N)$ is calculated, where $\lambda_i = \sum_{j=1}^m \nu_{ji} v_j \mathbf{x}(t)$.

Step 2(System update and branching). The quantity of each species and t is updated, by using $\lambda(t)$ and Δt : $\mathbf{x}(t) = \mathbf{x}(t - \Delta t) + \lambda(t - \Delta t)$, $t := t + \Delta t$. If $t \geq t_{stop}$ or if there are no reactions left in the reactor, the simulation is stopped and the results are sent to the output stream. Otherwise, the simulation returns to *Step 1*. In order to simulate pattern formation, we compose cellular automata by using the ARMS and call it Cellular Automata of Abstract Rewriting System on Multisets (CARMS)[8]. As for the calculation of diffusion, we use conventional explicit scheme

of difference method to solve partial differential equation of diffusion and for the calculation of convection, we use the Lattice Boltzmann Method [4].

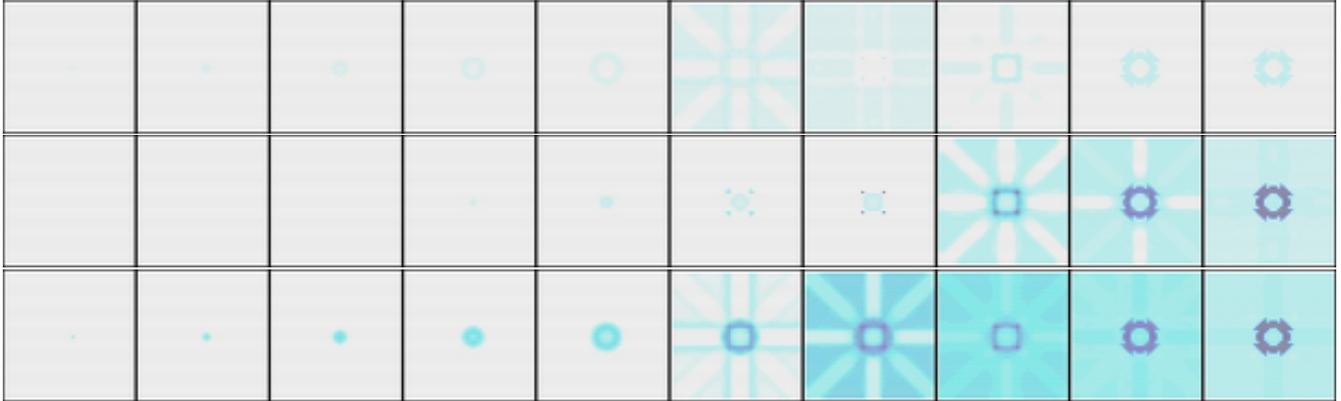


Figure 1: **Time evolution of chemicals:** Each line composed of the difference of the time evolution of concentration of X (top), Y (middle) and Z (bottom) in the CARMS, where, time evolution starts from right toward left. Blue illustrates that the concentration is high, while white, low and $\tau = 1.0 \times 10^4$

Lattice Boltzmann Method (LBM)

The lattice Boltzmann equation (LBE) method is emerging as a physically accurate and computationally viable tool for simulating laminar and turbulent flows. On the theoretical front, rigorous mathematical proof now exists demonstrating that the lattice Boltzmann method (LBM) is a special finite difference scheme of the Boltzmann equation that governs all fluid flows (the Navier-Stokes equation also has its basis in the Boltzmann equation).

The basic LBE for a single-component medium consists of two basic steps: collision and advection. The particle distribution function is thermalized locally through collision processes and advection to the closest neighboring sites occurs according to a small set of discrete particle velocities. The LBE proposed here is the lattice Boltzmann scheme with BGK approximation [8]; $n_\alpha(\mathbf{x} + e_\alpha \delta_t, t + \delta_t) = n_\alpha(\mathbf{x}, t) - \frac{1}{\tau}[n_\alpha(\mathbf{x}, t) - n_\alpha^{(eq)}(\mathbf{x}, t)]$ where n_α is the number density distribution function with discrete velocity e_α , $n_\alpha^{(eq)}$ is the equilibrium distribution function and τ is the relaxation time (towards equilibrium) which determines the viscosity. The time-step size is δ_t , which is the time taken for the advection process to be completed. For the sake of simplicity without losing generality, we adopt the nine-velocity model. Then the equilibrium distribution function for isothermal field is given as $n_\alpha^{(eq)} = w_\alpha n [1 + \frac{1}{c_s^2}(e_\alpha \cdot \mathbf{u}) + \frac{1}{2c_s^4}(e_\alpha \cdot \mathbf{u})^2 - \frac{1}{c_s^2}u^2]$ in which the discrete particle velocities e_α and the weighting factor w_α ($\alpha = 0, 1, 2, \dots, 8$) are

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

and

$$w_\alpha = \begin{cases} 4/9 & \alpha = 0 \\ 1/9 & \alpha = 1, 2, 3, 4 \\ 1/36 & \alpha = 5, 6, 7, 8 \end{cases} \quad (2)$$

respectively. The sound speed is $w_\alpha = 1/\sqrt{3}(\delta_x/\delta_t)$ with δ_x being the lattice constant of the underlying square lattice. The macroscopic quantities, such as particle density n , mass density ρ and mass velocity \mathbf{u} are given by $n = \sum_\alpha n_\alpha$, $\rho = mn$, $\rho \mathbf{u} = m \sum_\alpha n_\alpha e_\alpha$ where m is the molecular weight (for more detail of the LBM, refer [4]).

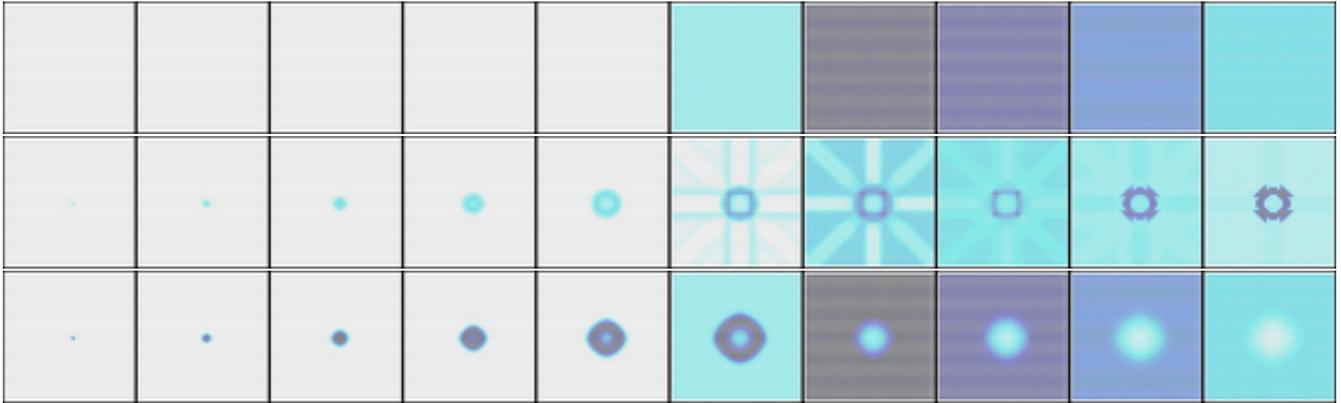


Figure 2: **Effectiveness of the convection** The difference of the time evolution of concentration of Z in the CARMS, where time evolution starts from right toward left. Blue illustrates that the concentration is high, while white, low. The effect of convection is changed; the value of τ denotes the degree of effectiveness of the convection, as the τ is getting large, the effectiveness becomes large. Each line illustrates when $\tau = 10$ (top), $\tau = 1.0 \times 10^4$ (middle), $\tau = 1.0 \times 10^7$ (bottom), respectively

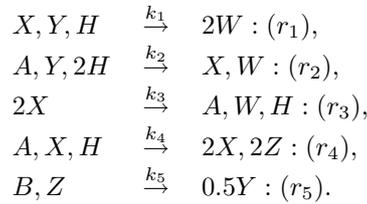


Table 1: Oregonator

Lattice Boltzman Equations for Reaction flow In a reacting flow, the state of the fluid at any given point in space and time can be completely specified in terms of fluid velocity, composition vector (either in terms of mass fraction or concentration). We will need to develop the LBE for all these variables. For generating a background flow, the conventional LBM sub-steps of collision (relaxation) and streaming (convection) are used. However for the concentration fields, there is an extra sub-step between collision and streaming sub-steps to account for reaction-diffusion and convection. This is identical to the time-splitting approach used in continuum methods for chemically reacting flows.

Flow Field The background flow-field is obtained using the following stencil for partial pressure $p_\alpha(\mathbf{x} + \mathbf{e}_\alpha, t + 1) = p_\alpha(\mathbf{x}, t) - \frac{1}{\tau_p} [p_\alpha(\mathbf{x}, t) - p_\alpha^{(eq)}(\mathbf{x}, t)]$ where $p_\alpha^{(eq)} = w_\alpha p [1 + 3(\mathbf{e}_\alpha \cdot \mathbf{u}) + \frac{9}{2}(\mathbf{e}_\alpha \cdot \mathbf{u})^2 - \frac{3}{2}u^2]$ The total pressure $p (= \rho c_s^2)$ and the fluid velocity are calculated using $p = \sum_\alpha p_\alpha u = \frac{1}{p} \sum_\alpha e_{\alpha} p_\alpha$ This is the velocity used for determining the equilibrium distribution functions in temperature and concentration fields.

Concentration fields For concentration field, there is an extra computational sub-step, reaction and diffusion by using the DARMS and CARMS besides conventional computational sub-steps of collision and advection. **Collision of chemical specie i** $Y_\alpha^i(\mathbf{x}, t) = Y_\alpha^i(\mathbf{x}, t) - \frac{1}{\tau_i} [Y_\alpha^i(\mathbf{x}, t) - Y_\alpha^{i(eq)}(\mathbf{x}, t)]$ where Y^i denotes the concentration of chemical specie i , $Y_\alpha^{i(eq)} = w_\alpha Y^i [1 + 3(\mathbf{e}_\alpha \cdot \mathbf{u}) + \frac{9}{2}(\mathbf{e}_\alpha \cdot \mathbf{u})^2 - \frac{3}{2}u^2]$ and $Y^i = \sum_\alpha Y_\alpha^i$, Relaxation time-constant τ is determined by thermal diffusivity and τ_i 's are determined by the diffusivity of corresponding species.

Simulation of the Oregonator

The Oregonator scheme is outlined in Table 1: In this paper, a combination of Tyson's "Lo" and Field-Försterling values (TFF parameter) are used [8]: $k_1 : 10^6 M^{-2} S^{-1}$, $k_2 : 2 M^{-3} S^{-1}$, $k_3 : 2 \times 10^3 M^{-1} S^{-1}$, $k_4 : 10 M^{-2} S^{-1}$, $k_5 : B \times 2 \times 10^{-2} S^{-1}$, where M stands for one molar, and S stands for a second.

Results of the simulation We take the non-slip boundary condition (the velocities of particles which hit the wall are inverted after the collision). The condition of the simulation is described as follows; the amount of computation steps is 20,000, $\Delta t = 0.01$, $\tau = 10, 1.0 \times 10^4, 1.0 \times 10^7$, the diffusion constants D obtained by chemical experiments [8]; ($\text{cm}^2 / \text{sec.}$) of X, D_X and Z, D_Z are 1.5×10^{-5} and $D_X = 0.9 \times 10^{-5}$.

It is assumed that the size of reactor in the CARMS is a $6\text{cm} \times 6\text{cm}$ square, where 50×50 DARMSES are placed. So, the distance between DARMSES is $x = \frac{6}{50}\text{cm}$. In the chemical experiment of BZ reaction, usually a excitation point is generated by stinging a sliver stick, which evokes oxidation reaction. In order to express the generation of the excitation point, we change the concentration of X and Y are smaller, while that of Z is 100 times larger.

The results of simulation of the Oregonator illustrate that the CARMS with reaction, diffusion and convection exhibits typical chemical wave spatial pattern of the Oregonator on every chemical specie X, Y and Z .

Next, we change effectiveness of the convection. Since the value of τ denotes the effectiveness, we change $\tau = 10$ (the effectiveness is strong), $\tau = 1.0 \times 10^4$ (middle) and $\tau = 1.0 \times 10^7$ (weak). And we confirmed that the effectiveness of the convection change the spatio-temporal pattern of chemical reaction (figure 2). When the effectiveness is strong (the top line in the figure 2), since the convection was strong, the reactor was well stirred and spatial patterns were excluded, but temporal patterns were preserved. And when the effectiveness is middle (the middle line in the figure), there emerged spatio-temporal pattern, however, its pattern was different from the case when the effectiveness is weak. When the effectiveness of convection is weak, it is almost same to the system only with reaction and diffusion. We confirmed that when the effectiveness of convection is weak, its pattern (the bottom line in the figure) is similar to the ARMS with reaction-diffusion.

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