

Oscillations and Waves in a Reactive Lattice-Gas Automaton

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A lattice-gas automaton model is constructed for multispecies, chemically reacting, spatially distributed systems and applied to a two-species reaction. The automaton simulations show monotone and oscillatory decay to the steady state as well as excitability and limit cycles. Chemical waves, such as rings and spiral waves, and Turing patterns that arise from the bifurcation of the homogeneous state are found. The model allows the exploration of nonequilibrium spatial structures at the mesoscopic level and goes beyond the usual reaction-diffusion equation descriptions.

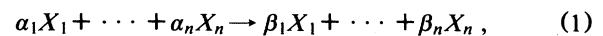
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Nonlinear far-from-equilibrium chemically reacting systems show many different kinds of dynamical behavior. Spatially homogeneous (well-stirred) systems can have one or many steady states, oscillate, or even exhibit chaos. If such reactions are allowed to occur under unstirred conditions then the nonlinear kinetics can combine with diffusion to display an even richer structure and one can observe rings, spiral waves, chemical turbulence, and Turing patterns.^{1,2} The details of these structures are being studied using new experimental probes.³ Usually, these phenomena are described by reaction-diffusion equations and this level of description suffices for most applications. However, it is interesting to inquire into the molecular nature of such macroscopic phenomena. How do chemical waves emerge from the molecular collision processes in the system? How do fluctuations, which arise from the molecular nature of the system, affect the spatiotemporal structures that are observed? How do fluctuations influence pattern formation processes and the behavior near bifurcation points where the system is very susceptible to small changes? These are just a few questions that can be answered if the system is viewed at a molecular level.

The most direct way to approach these questions is by molecular-dynamics (MD) simulations but this is still beyond even the most powerful computers due to the long distance and time scales that must be probed and the large numbers of molecules that are needed to simulate macroscopic phenomena. This has led to the development of approximate MD schemes; notable among these is the application of the Bird method to the study of chemical oscillations.⁴ Here we adopt a lattice-gas cellular automaton (LGCA) method where space, time, and particle velocities are taken to be discrete variables.⁵ This approach has proved to be very fruitful in the study of hydrodynamic problems⁶ and we demonstrate that such LGCA models can also be used to explore the rich phenomena of chemical systems. The potential usefulness of such an approach was presaged in a study of a

one-variable chemical reaction that shows phase separation.⁷ However, much of the most interesting phenomena like excitable chemical wave dynamics, oscillations, and Turing bifurcations occur only in systems with more than one chemical species. We present the formulation of the LGCA model for several species and show that it can be used to explore the varied phenomenology mentioned above.⁸

The system we consider is composed of n chemical species X_1, X_2, \dots, X_n whose reactive dynamics is of interest. The system may also contain solvent molecules as well as other chemical species that participate in chemical reactions but which are either in excess or have their average concentrations fixed by external constraints. The chemical intermediates X_τ undergo reactions of the general form



where we have not explicitly indicated species whose concentrations are fixed; their concentrations can be incorporated into the rate constants that determine the rates of (1).

In the LGCA model of such a reacting system, space is made discrete by requiring the particles to move on a lattice with coordination number m . Each node of the lattice is labeled by a vector \mathbf{r} and each particle has a discrete velocity c_i ($i=1, \dots, m$) pointing in one of the m possible directions on the lattice. To simplify the dynamics we impose an exclusion principle that prevents two particles of the same species to be at the same node with the same velocity. A conceptually attractive way to think of this is as a "stack" of n "species lattices" with identical labeling of the nodes. Each species then resides on its own lattice but the dynamics on these lattices is coupled by the chemical reactions.

As in the one-variable LGCA,⁷ the evolution consists of the product $R \circ C \circ P$ of three elementary operations: propagation P , chemical transformation C , and rotation R . In the propagation step each particle of a given

species moves on its own lattice from its node to a nearest-neighbor node in a direction determined by its velocity. The rotation operation can be described in the following way. At each node, independently of the others, the particle configuration is rotated through one of the possible angles $\theta_l = l2\pi/m$, $l = 1, \dots, m$, with probability p_l ; the probabilities may be different for each species. (The probabilities must satisfy certain relations to preserve isotropy.) The propagation and rotation steps simulate free streaming and elastic collisions whose net effect is to produce diffusion processes with different diffusion coefficients for the different species. The diffusion coefficients can also be modified by performing different numbers of propagation and rotation steps on each species lattice. At this level of description the n species lattices are uncoupled.

The chemical transformation C is at the heart of the LGCA model. In this step the reactions (1) that the intermediate chemical species undergo are modeled by probabilistic rules for the increase or decrease of the number of particles. The numbers of the different species in the reactant and product states can be specified by the vectors $\alpha = (\alpha_1, \dots, \alpha_n)$ and $\beta = (\beta_1, \dots, \beta_n)$, respectively, where $0 \leq \alpha_\tau, \beta_\tau \leq m$ for each $\tau = 1, \dots, n$. The configuration at node \mathbf{r} is examined and depending on the stoichiometric configuration α a transformation to configuration β is made with probability $P(\alpha\beta)$ regardless of the velocity states of the particles. This chemical-reaction step depends on the configurations of all species that reside at a node with label \mathbf{r} and thus couples the dynamics on the notional stack of species lattices. (Of course, a mathematical description of the au-

tomaton dynamics does not rely on this terminology using a stack of species lattices and can be formulated directly in terms of Boolean random fields.⁹⁾

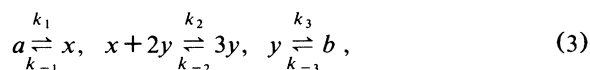
To summarize, for each time step we first propagate the particles one lattice unit in directions determined by their velocities (independently on each species lattice), then depending on the species numbers at a node on the entire stack of species lattices we effect a chemical transformation with probability $P(\alpha\beta)$, and finally we randomly rotate the configuration on each species lattice. The combination of the latter two operations simulates reactive and elastic collisions in the system yielding a mesoscopic model that mimics the molecular dynamics of the real reacting medium.

One aim of this work is to obtain a deeper understanding of the spatiotemporal structures that are known to exist for a given reaction-diffusion model or real chemical kinetics. Thus, it is important to establish a relation between the LGCA and a reaction-diffusion equation with specific (nonlinear) kinetics. The connection can be made by taking expectation values of the microdynamical equation for the automaton and deducing from these the chemical rate law and reaction-diffusion equation. This provides a "molecular-level" connection between the automaton parameters and the macroscopic rate constants and diffusion coefficients. This reduction was carried out for the multispecies automaton. We focus on the chemical rate law as an illustration. Taking the system to be spatially homogenous and assuming that the expectation value of products of random fields can be factored we obtain the following equation for the chemical concentrations:

$$\frac{d\rho_\tau(t)}{dt} = \sum'_{\alpha, \beta \in \mathcal{C}} (\beta_\tau - \alpha_\tau) P(\alpha\beta) \prod_{\kappa=1}^n \sum_{l=\alpha_\kappa}^m \binom{m}{\alpha_\kappa} \binom{m-\alpha_\kappa}{l-\alpha_\kappa} (-1)^{l-\alpha_\kappa} m^{-l} \rho_\kappa(t)^l. \quad (2)$$

Here ρ_τ is the particle density per node of species τ , \mathcal{C} is the set of all possible reactions that lead to β starting from α , and the prime on the sum means $\alpha \neq \beta$. This equation expresses the rate of change of the densities in terms of products of the densities and the chemical transformation probabilities. Equation (2) has the same form as the macroscopic rate law. By identifying the coefficients of equal powers of the densities in (2) with those in the phenomenological rate law we can establish relations between the $P(\alpha\beta)$ and the rate coefficients. This makes it possible to construct a whole family of LGCA rules that are consistent with a given macroscopic rate law.

We have applied the above formalism to a two-variable reaction-diffusion system: the Selkov model.¹⁰ The chemical mechanism is



with rate law

$$\begin{aligned} \frac{d\rho_x}{dt} &= k_1\rho_a - k_{-1}\rho_x - k_2\rho_x\rho_y^2 + k_{-2}\rho_y^3, \\ \frac{d\rho_y}{dt} &= k_{-3}\rho_b - k_3\rho_y + k_2\rho_x\rho_y^2 - k_{-2}\rho_y^3. \end{aligned} \quad (4)$$

This system is known¹⁰ to possess a very rich bifurcation structure consisting of steady states which are either nodes or foci and which may have excitability properties. In addition the system can undergo a Hopf bifurcation to a limit-cycle state. The system also possesses regions where there is bistability between two fixed points or between a fixed point and a limit cycle. In the spatial domain the corresponding reaction-diffusion equation can support a variety of chemical waves and spatiotemporal and steady bifurcation structures.

In the Selkov LGCA model the elements of the 25×25

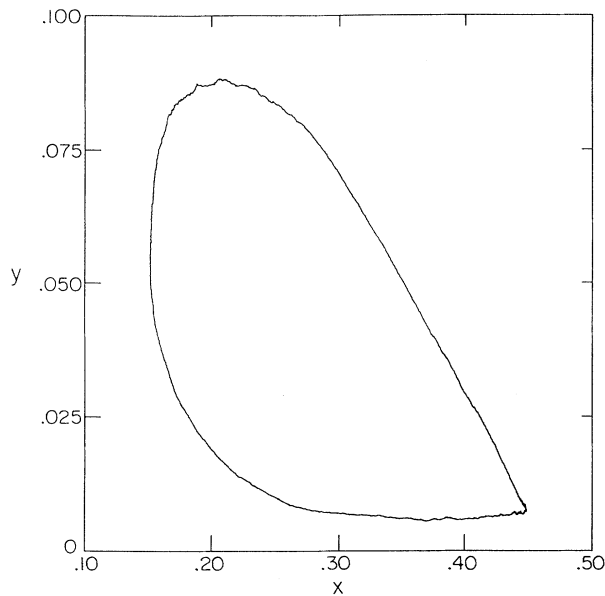


FIG. 1. Phase-plane representation of the limit cycle: $k_1\rho_a=0.0001897$, $k_3=0.001$, $k_{-1}=0.1k_3$, $k_2=k_{-2}=0.01$, $k_{-3}\rho_b=0.00002530$. The rotation probabilities are $\frac{1}{4}$ (diffusion coefficients $D_x=D_y=D$) and concentration units of x and y are particles per velocity direction. Lattice size 256×256 .

reaction probability matrix $P(ij, i'j')$, where $\alpha=(i, j)$ and $\beta=(i', j')$, were determined by restricting reactive particle changes to increases or decreases by one particle in accord with the Selkov kinetics and requiring the remaining nonzero elements to satisfy the constraints imposed by the relation between (2) and the phenomenological rate law (4). The model was simulated on a square lattice with periodic boundary conditions but, as

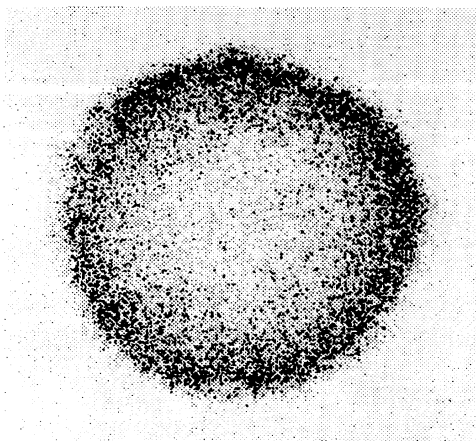


FIG. 2. Ring of excitation in the excitable region: $k_1\rho_a=0.00023717$, $k_3=0.001$, $k_{-1}=0.1k_3$, $k_2=k_{-2}=0.01$, $k_{-3}\rho_b=0.000006324$. Lattice size 512×512 ; and $D_x=D_y=D/3$.

is clear from the above, generalization is straightforward (and necessary if reactive flows are to be considered¹¹). Here we focus on the reaction-diffusion aspects of the problem.

The LGCA is able to reproduce the above-mentioned phenomena and, in addition, provides a means to study spatiotemporal dynamics at a nearly microscopic level. We have observed both monotone and oscillatory decay to a fixed point in the LGCA simulations. We have also selected system parameters to correspond to oscillatory kinetics in the Selkov model and an example of an LGCA limit cycle is shown in Fig. 1. Note the relaxation character of the limit cycle; harmonic-type oscillations have also been observed near a Hopf bifurcation.

Next we consider some illustrations of spatiotemporal dynamics in the LGCA. An especially interesting case to study is excitability where a stable fixed point exists and a perturbation of sufficiently large magnitude causes the system to make a long excursion in phase space before return to the fixed point. In the spatial domain this phenomenon gives rise to chemical waves like rings and spirals which have been the subject of intense experimental and theoretical activity.^{1,3} To simulate the formation of a ring of excitation we allowed the system to relax to the stable state starting from a random initial condition. A disk-shaped perturbation with average concentration greater than the threshold was then introduced. Figure 2 is a snapshot of the evolution of the y concentration showing a growing ring of excitation. If such a ring is sheared, spiral waves can develop by curling of the free ends. To simulate this, one-half of the ring was removed and that half of the lattice was seeded with particles at the steady-state concentration. This creates two free ends which curl to form a counterrotating pair of spiral waves (Fig. 3).

We have studied bifurcations of the homogeneous

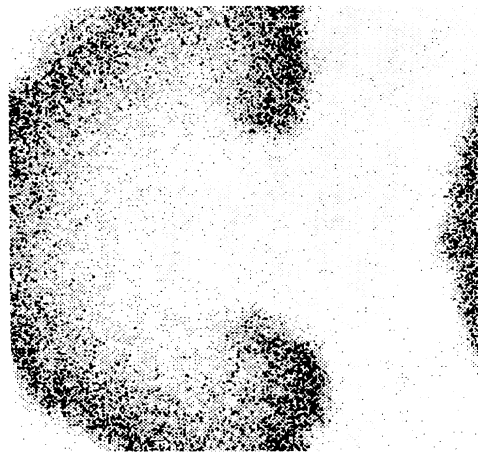


FIG. 3. Formation of a counterrotating spiral wave pair. parameters are the same as Fig. 2.

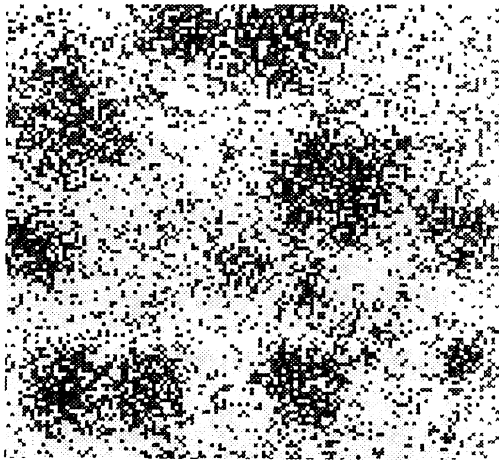


FIG. 4. Turing pattern formed from random initial conditions: $k_1\rho_a=0.0001897$, $k_3=0.001$, $k_{-1}=0.1k_3$, $k_2=k_{-2}=0.01$, $k_{-3}\rho_b=0.00003795$. Lattice size: 256×256 ; and $D_x=D$, $D_y=D/10$.

state induced by unequal diffusion coefficients. The diffusion coefficients were changed by performing different numbers of propagation and rotation steps on the two species lattices. Figure 4 shows an example of a spatial structure that is obtained when the Selkov parameters are chosen to lie in the vicinity of a Turing bifurcation. The characteristic length of the spot pattern is in accord with that predicted from a linear stability analysis. Simulations with smaller diffusion ratios do not show patterns providing evidence for a Turing bifurcation in the LGCA.

The LGCA model presented here can be used to study the varied phenomena that are found in far-from-equilibrium reacting systems and models of this type open up a new way of investigating these systems.

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