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SPONTANEOUS NUCLEATION IN A REACTIVE LATTICE GAS AUTOMATON

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1. Introduction

Nucleation in reaction-diffusion systems with bistability or excitability is the triggering process of phase transformation phenomena of importance in metallurgical, crystalline, chemical, and biological systems. Most models of nucleations deal either with homogeneous systems or with chemical inhomogeneties. Here we are interested in the influence of purely geometrical constraints (or inhomogeneties) on nucleations. As a typical bistable chemical system we consider the Schlögl model. We use the reactive lattice gas automata approach [1,2,3] to simulate this model including the intrinsic noise [5] generated by the discrete reactive events. This simulation technique allows an easy implementation of complex boundary conditions.

2. Bistability and Movement of Interfaces

The chemical reaction model devised by F. Schlögl [4] is a simple reaction scheme that exhibits bistability:

$$\begin{aligned} A + 2X &\leftrightarrow 3X \\ B + X &\leftrightarrow C \end{aligned} \tag{1}$$

In this model the concentrations of chemical A, B, and C are assumed to be held constant in space and time, so that the only variable of interest is the concentration of the "autocatalytic" variable X. By rescaling the dynamical equations take the form

$$\dot{x} = D\nabla^2 x + f(x)$$

with the rate function

$$f(x) = -a_3 x^3 + a_2 x^2 - a_1 x + a_0. \tag{2}$$

For certain parameter ranges this cubic rate function has three roots, $x_1 \leq x_3 \leq x_2$, which correspond to two stable steady states (x_1 and x_2) and one unstable steady state (x_3) of the reaction, such that $f(x) = -k(x - x_1)(x - x_2)(x - x_3)$. Schlögl [4] showed that in a spatially extended system, two phases can coexist, with the interface moving with speed $N = c - DK$, where D is the diffusion coefficient, K the curvature of the front and c the propagation speed of a planar front, $c = (2x_3 - x_1 - x_2)\sqrt{Dk/2}$. In one dimension the travelling front solution is

$$x(r,t) = \frac{x_2 - x_1}{2} \tanh\left(\frac{x_2 - x_1}{\sqrt{8D/k}}(r - ct)\right). \tag{3}$$

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3. Reactive Lattice Gas Model

The reactive LGA procedure [1,2,3] realizes a mapping of a reaction-diffusion (R-D) equation onto a probabilistic cellular automaton. R-D equations have the form $\dot{x} = f(x) + D\nabla^2 x$, where $f(x)$ describes a polynomial rate law of degree n. Reactive lattice gas automata can easily be constructed for multispecies systems [1], but for the sake of simplicity, only single species systems are described here.

The evolution of the automaton can be described in terms of three operations: propagation, inelastic collisions, and reactive collisions. Discrete particles move on a discrete lattice with discrete velocities, i.e., particles hop at discrete time steps from a node to one of its neighboring nodes, as dictated by the particle velocity. This is the propagation step (governed by the operator P), during which the number of particles and their momentum is conserved. In addition, particles at rest are allowed to reside on a node. An exclusion principle states that at most one particle can exist on each node with each velocity, of which there are b. Thus the state of the automaton is coded by an array of $N \times b$-bit words, where N is the number of nodes and each node has 2^b possible states.

Elastic collisions between the solvent and the reactive species (combined with propagation) give rise to diffusive behavior of the reactive species; here the solvent is virtual and its effect is modeled by a mixing operator R which redistributes the particle velocities in much the same way as repeated collisions with the solvent molecules would do. R operates simultaneously and independently on each node of the lattice. On each node, each particle is assigned a new velocity randomly, restricted by the exclusion principle. Note that the mixing operation conserves the number of particles but not their momentum. It can be shown [3] that the repeated application of $R \circ P$ makes particles perform random walks on the lattice and yields correct diffusive behavior in the continuous limit. The diffusion coefficient is $\frac{1}{b}$ in lattice space and time units for cubic or square lattices (all quantities are understood to be measured in these units).

Reactive processes are modeled with an operator C which also acts independently and simultaneously at each node and transforms a configuration of α particles into a configuration of β particles with transition probability $P_{\alpha\beta}$ $(\alpha, \beta = 0, \cdots, b)$. During the reaction operation particles are created $(\alpha < \beta)$ or annihilated $(\alpha > \beta)$. So the operator C conserves neither particle number nor momentum. It has been shown [2,3] that under the assumption of strong diffusion, i.e., when the ratio of reactive collisions to elastic collisions is sufficiently low that reactions occur at local diffusive equilibrium, the application of the operator C yields the reaction rate law for the rescaled particle density x

$$\frac{dx}{dt} = f(x) = \frac{1}{b} \sum_{\alpha=0}^{b} \binom{b}{\alpha} x^\alpha (1-x)^{b-\alpha} \sum_{\beta=0}^{b} (\beta - \alpha) P_{\alpha\beta}, \tag{4}$$

with $x = \rho/b$ (ρ is the average number of particles present at a node and x is the density per channel). This rate law is polynomial with maximum degree b. The repeated application of the three operators $(C \circ R \circ P)$ constitutes the complete automaton dynamics which models the R-D process in the limit of strong diffusion (or, equivalently, of unfrequent reactive collisions). The probabilities $P_{\alpha\beta}$ can be chosen such that most polynomial rate laws with degree less than b can be realized by Eqn. (4)[5].

4. Nucleation in the Lattice Gas Model

A two-dimensional model of the Schlögl reaction including the intrinsic noise from the reaction and from the diffusion is simulated by this reactive lattice gas automaton.

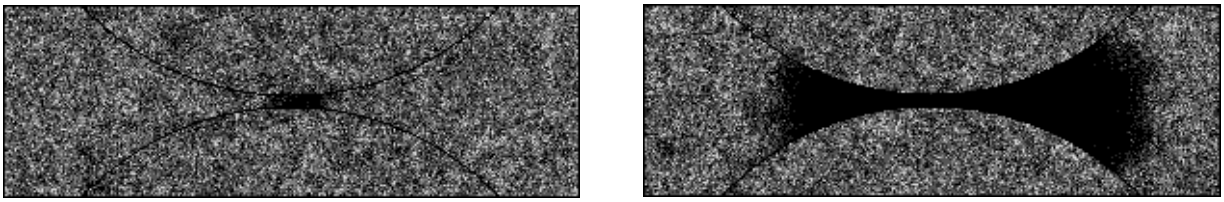

Figure 1: *State of the system at t=3000 and t=13000. Two black circular segments define the reflecting boundary, while the system is periodic in both x- and y-direction.*

Here, the parameters for the rate law are $x_1 = 0.0$, $x_3 = 0.25$ and $x_2 = 0.45$. Thus a region in state x_1 will invade regions in state x_2. With a diffusion coefficient of 0.2 and a rate $f(x) = -0.2(x)(x - 0.25)(x - 0.45)$ a planar front moves with speed $c = 0.00707$. A front with high curvature moves slower and at the critical radius $R_c = 28.28$ the speed N becomes zero. Since this critical radius is larger than the typical correlation length in the less stable phase ($x = x_2$), 3.33, a spontaneous transition from a uniform state $x = x_2$ is only possible with high noise amplitudes. On the other hand, in one-dimensional systems, curvature does not play a role and spontaneous transition is much more likely.

These considerations lead to the idea to place a region of constrained geometry (e.g. a narrow channel) into a two-dimensional system. Since in 1-d systems (or regions in space which are nearly 1-d), transitions are much more likely, one is able to observe that nucleation starts at the center of the channel and spreads outward (Figure 1). Without such a constrained channel, no nucleation was observed even after very long time.

5. Geometric Considerations

Geometrical constraints are particularly favorable to nucleation if the following conditions are met: (i) There exists a constrained area with an opening to the bulk area. This opening must be such that a circular wave propagating out has a radius larger than the critical radius. (ii) There exists a region in this constrained area where the width of the channel is of the order of the correlation length in the system at the initial stable state (call this the breeding area). (iii) The geometry is such that a circular wave propagating out from the breeding area, and having a front that intersects at a right angles with the boundaries at all times (boundary condition), has a radius always above the critical radius.

These conditions lead us to consider the limiting case where the propagating wave has always the same curvature. In the case symmetric to the x-axis, this curve can be described by the differential equation

$$r^2 = y^2(x) + \left(\frac{y(x)}{y'(x)}\right)^2,$$

the solution of which is given by

$$\frac{x}{r} + C = \sqrt{1 - \left(\frac{y}{r}\right)^2} - \ln \frac{r + \sqrt{1 - \left(\frac{y}{r}\right)^2}}{\left(\frac{y}{r}\right)}.$$

This curve is known as the "tractrix". Figure 2 shows this curve ($r = 1$) along with the circles that show the position of an emerging front at equal time intervals. The normal speed of a front emerging from this structure would be $N = c - D/r$. If the size of the curve is smaller than the critical radius for the propagation of a curved interface,

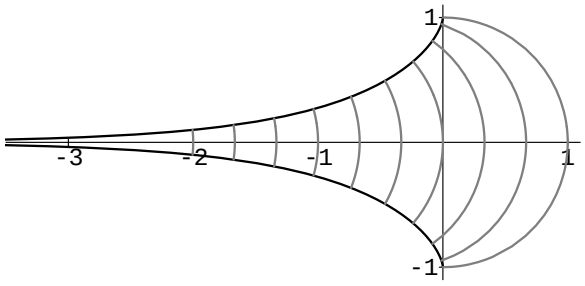

Figure 2: *Critical curve (black) for which an emerging wave has constant radius $r = 1$, together with 7 positions of the wave at equal time intervals (gray).*

$r < R_c$, then nucleation will be unlikely. This curve serves thus as a comparison to other geometrical curves.

In the experiment shown in Figure 1, the area is constrained by two quarter-circles with radius 150 (cells) and shortest distance 6. In this case the radius of an outward propagating wave would be infinite at the center. Going outward, the radius decreases to 42.8 when the wave is a section of a circle around the center with radius 42.8 and then increases to 150 at the opening. We see that the minimal radius (42.8) is well above the critical radius (28.28) and that the smallest channel width (6) is comparable to the correlation length (3.33) in the initial state.

Another experiment uses a long narrow "tube". In this case the nucleation starts much quicker, since the constrained area is longer. But once the tube is filled, the nucleation cannot proceed, because the openings of the tube are smaller than the critical radius and thus the wave cannot leave the constrained area.

6. Conclusions

Reactive lattice gas automata are a powerful method to investigate phenomena in reaction-diffusion systems where intrinsic noise plays a role. Lattice gas automata are especially suited for problems with complex geometries. Here we investigated the influence of geometric constraints on nucleation phenomena in bistable reactions. We demonstrated that a narrow channel with a gradual opening is an ideal geometry to facilitate nucleations. In the narrow part of the channel the boundaries enhance the intrinsic fluctuations, which can lead to nucleations. The gradual opening then allows the nucleation to grow beyond the critical radius, so that growth can continue in the open medium. This is viewed as one mechanism for nucleation in bistable and excitable media in the absence of chemical inhomogeneties.

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