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FLUCTUATION CORRELATIONS IN REACTION-DIFFUSION SYSTEMS: REACTIVE LATTICE GAS AUTOMATA APPROACH

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Abstract

We model reaction-diffusion systems with reactive lattice gas automata, which possess intrinsic microscopic fluctuations. We show that, within the limits of linear theory, the commonly accepted Landau equation describes correctly the measured effects of the fluctuations, as evidenced by the density autocorrelation function. We suggest that the reactive lattice gas automata constitute a powerful method for investigating reaction-diffusion systems where intrinsic fluctuations play an important role.

Microscopic fluctuations in constrained systems can produce correlations which extend over distances large compared to the range of the molecular processes. These correlations play a crucial role at the mesoscopic and macroscopic levels in various situations, in particular when symmetry breaking is triggered by the destabilization of a homogeneous steady state. Space- and time-dependent structures, such as regular or irregular patterns, may then form spontaneously. It is particularly fascinating that such patterns can occur in unconfined reaction-diffusion systems where no boundary conditions are set to impose a (or a series of) preferential wavelength(s) (e.g. recently observed Turing patterns [1]). How such phenomena are induced by the enhancement of microscopic fluctuations cannot be investigated without a microscopic approach. In our work we are addressing this question with lattice gas automata (LGA) [2].

In recent years the LGA method [3] has been applied successfully to a variety of problems such as 2-d and 3-d weak turbulence [4] and basic statistical mechanics [5] as well as reactive phenomena [6]. Similarly as in molecular dynamics simulations [7], a LGA fluid system is constructed from an explicit description of the microscopic degrees of freedom of the system considered. However there is an essential paradigmatic difference between the two approaches: whereas in molecular dynamics the basic interactions are modeled according to a possibly realistic description of the intermolecular forces, the LGA microscopic dynamics is drastically oversimplified and fully discretized [3]. Yet the LGA models are constructed in such a way that the schematic simplifications introduced at the microscopic level should become unimportant and undetectable in the macroscopic limit where the realistic behavior of the fluid system is recovered. Besides the operational efficiency of the LGA method, a remarkable feature of the approach resides in the microscopic nature of the LGA which by construction possesses intrinsically spontaneous fluctuations [8].

Consequently the LGA approach provides *in principle* a powerful method to investigate the role of fluctuations on the macroscopic dynamics of complex systems. Emphasis should be put on the expression *in principle* because such a program can only be conducted with the guarantee that the LGA fluctuations capture the relevant aspects of actual fluctuations.* Therefore it is crucial that the simplifications introduced at the microscopic level manifest neither at macroscopic scales nor at smaller (mesoscopic) scales where the fluctuations can play an important role. So when the microscopic dynamics which is constructed for reaction-diffusion systems is severely simplified [2,6], the degree of confidence that one can invest in the LGA density fluctuations correlation function must be established before the model can be put to work for studying phenomena where density fluctuations are determinant. The purpose of this

* Note that the LGA model described in Ref. 8 is shown to exhibit spontaneous fluctuations whose correlation function is in excellent agreement with the dynamic structure factor as measured in real fluids.

paper is to discuss and clarify this important problem for a class of reactive LGA's. First we describe the reactive automaton; next we recall the Landau approach to fluctuations for reaction-diffusion (R-D) systems, which we then apply to the automaton. We show how to construct automata for given rate laws and given noise levels, and we conclude with a comparative analysis of the theoretical results and simulation data.

The reactive LGA procedure realizes a mapping of a reaction-diffusion (R-D) equation onto a d-dimensional probabilistic cellular automaton. R-D equations have the form $\dot{\mathbf{x}} = \mathbf{\Phi}(\mathbf{x}) + \mathbf{D}\Delta\mathbf{x}$, with $\mathbf{x}$ real, where $\mathbf{\Phi}(\mathbf{x})$ is a vector of polynomial rate laws of degree n and the second term on the rhs is the diffusion term. Reactive lattice gas automata can easily be constructed for multispecies systems [6], but for the sake of simplicity, only single species systems are described here, reducing the R-D equation to $\dot{x} = \phi(x) + D\nabla^2 x$.

The evolution of the automaton can be described in terms of three operations: propagation, inelastic collisions, and reactive collisions. 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. Consequently we denote by b the total number of *channels* per node which can be occupied simultaneously: for d-dimensional cubic lattices, $b = 2md + b_0$, where m is the number of channels for each non-zero velocity, and b_0 is the number of zero-velocity channels. We have here implicitly introduced a somewhat relaxed exclusion principle without loss of computational efficiency (the state of a node is given by a b-bit word). Thus the state of the automaton is coded by a d-dimensional matrix 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. A possible realization is to rotate the particle configuration at a node by a randomly chosen angle (within the lattice geometry) [2,6]. A more general procedure (used here as it extends to any dimensionality and can incorporate resting particles) is to randomly select a configuration from the set of all configurations compatible with the input configuration. Note that the mixing operation conserves the number of particles but not their momentum. It can be shown 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 $\frac{m}{b}$ in lattice space and time units for d-dimensional cubic lattices.

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] 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

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

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. A systematic procedure has been developed [2,6] to determine suitable values $P_{\alpha\beta}$ for a prescribed phenomenological rate law $\phi(x)$.

The repeated application of the three operators $(C \circ R \circ P)$ constitutes the complete automaton dynamics which models a R-D process in the limit of strong diffusion (or, equivalently, of unfrequent reactive collisions).

As discussed above, LGA's develop their own intrinsic microscopic noise which, for stochastic automata as considered here, is produced by the discreteness of the microscopic density field and the probabilistic nature of the microdynamics. Here we are primarily interested in the mesoscopic manifestation of these fluctuations at the level of the density correlations. A standard method to evaluate the correlation functions in non-equilibrium steady states (far from a bifurcation point) is the Landau approach where a process independent noise is added to the phenomenological equation, linearized around a steady state x_0 $(x = x_0 + \hat{x})$, i.e., here

$$\frac{d\hat{x}}{dt} = -K\hat{x} + D\nabla^2 \hat{x} + f_D + f_R, \tag{2}$$

with K, the linearized reaction rate coefficient, and where the diffusive noise f_D and the reactive noise f_R are assumed to be additive and characterized by

$$\begin{aligned} \langle f_R(\mathbf{r},t)\ \hat{x}\rangle = \langle f_D(\mathbf{r},t)\ \hat{x}\rangle = \langle f_R(\mathbf{r},t)\ f_D(\mathbf{r}',t')\rangle = 0 \\ \langle f_R(\mathbf{r},t)\ f_R(\mathbf{r}',t')\rangle = A_R \delta(t'-t)\delta(\mathbf{r}'-\mathbf{r}) \\ \langle f_D(\mathbf{r},t)\ f_D(\mathbf{r}',t')\rangle = -A_D \delta(t'-t)\nabla^2\delta(\mathbf{r}'-\mathbf{r}). \end{aligned} \tag{3}$$

† Except for the non-reactive events corresponding to the diagonal elements $P_{\alpha\alpha}$ which leave the state of the node unchanged.

The Landau approach is justified in the linear case where it is known to be equivalent to the more general master equation approach describing the rate of change of the reacting species density as a Markov process [9].

The amplitude factors A_R and A_D are usually evaluated from thermodynamic relations using the local equilibrium hypothesis. They can also be obtained by direct consideration of the microscopic processes governing the particle dynamics. The latter method is quite legitimate within the LGA approach, subject to the underlying hypotheses that (i) the fluctuation dynamics is validly described by the R-D dynamics, and (ii) the fluctuations amplitude is weak so that the linearized R-D equation is a valid approximation.

Obviously the solution to the R-D equation (2) without the noise terms is a fixed point (steady state) and the effect of the noise is clearly evidenced by the explicit expression for the density correlation function $G(r,t) = \langle \hat{x}(\mathbf{r}',t')\hat{x}(\mathbf{r}'+\mathbf{r},t'+t)\rangle_{\mathbf{r}',t'}$ where $r = |\mathbf{r}|$, since the diffusion is isotropic. Eqs. (2), (3) can be solved exactly (for example by Fourier transformation) and the solution gives the following result for the static correlation function ($G(r,t=0) \equiv G(r)$)

$$G(r) = \frac{A_D}{2D}\delta(r) + \frac{1}{4\pi r_0^2}\left(\frac{A_R}{K} - \frac{A_D}{D}\right) H\left(\frac{r}{r_0}\right) \tag{4}$$

with $r_0 = \sqrt{\frac{D}{K}}$ and where the function $H(z)$ depends on the space dimension:

$$\begin{aligned} 1-d: &\quad H(z) = \pi r_0 e^{-z}; \\ 2-d: &\quad H(z) = K_0(z) \quad \text{(modified Bessel function)}; \\ 3-d: &\quad H(z) = \frac{1}{2}\frac{e^{-z}}{r_0 z}. \end{aligned} \tag{5}$$

In order to apply the Landau theory to the lattice gas model, the noise amplitudes A_D and A_R must be determined. The diffusive noise amplitude A_D is found by identifying the variance of the rescaled particle number on a node in the automaton ($var(x_0) = x_0(1-x_0)/b$) with the variance in the Landau theory, $A_D/2D$, obtained by integrating $G(r)$ over a unit volume in the strong diffusion limit. The amplitude of the reactive noise $A_R = A_R(x_0)$ can be controlled through the construction of the transition probability matrix for a given macroscopic rate law. Analog to the reaction rate (Eq. (1)), which is given by the *average* change in the number of particles induced by the action of operator C (weighted by the probability of occurrence of an initial configuration with α particles $P_\alpha(x_0) = \binom{b}{\alpha} x_0^\alpha (1-x_0)^{b-\alpha}$), the noise amplitude is given

by the *variance* ‡ of the change in the number of particles§:

$$A_R(x_0) = \sum_{\alpha=0}^{b} P_\alpha(x_0) \sum_{\beta=0}^{b} \left(\frac{\beta - \alpha}{b} - \phi(x_0) \right)^2 P_{\alpha\beta}, \tag{6}$$

where $\phi(x_0)$ is given by Eq.(1).

It is possible to realize a given rate law $\phi(x)$ and noise function $A_R(x)$ within some limits: If $\phi(0) \geq 0$ and $\phi(1) \leq 0$, then all trajectories for x remain inside the interval $[0,1]$ and it is possible to select a scaling factor such that the matrix $(P_{\alpha\beta})$ can be constructed [2]. Here we merely sketch the construction procedure. The given polynomials $\phi(x)$ and $A_R(x)$ are expressed in the polynomial basis functions $P_\alpha(x)$. This gives a set of coefficients c_α and m_α associated with $\phi(x)$ and $A_R(x)$, which for each row α in the matrix $P_{\alpha\beta}$ give the average (c_α) and variance (m_α) of the distribution of the change in particle number $(\beta - \alpha)$. One then constructs a discrete distribution with this given average and variance for each α. This can be done in a variety of ways, but for small enough c_α and m_α three entries suffice. For $\alpha = 0$ these are given by $P_{0,1} = c_0 - \epsilon/(i-1)$, $P_{0,i} = \epsilon/(i^2 - i)$, and $P_{0,0} = 1 - P_{0,1} - P_{0,i}$ with $\epsilon = m_0 - c_0 + c_0^2$ and a suitably chosen i (e.g. $i = \lceil \epsilon/c_0 \rceil + 1$). The case of $\alpha = b$ is dual to $\alpha = 0$, while for $0 < \alpha < b$, $P_{\alpha,\alpha\pm1} = (m_\alpha \pm c_\alpha + c_\alpha^2)/2$. From the positivity condition for the probabilities it follows that the lower bound for the noise term is $m_\alpha \geq |c_\alpha| - |c_\alpha|^2$. Upper bounds on $\phi(x)$ and $A_R(x)$ can always be removed by rescaling of time and space scales.

Computation of the actual correlations in one-, two- and three-dimensional lattice gases was performed for a wide variety of values of x_0 and K. A few examples are presented here. Figure 1 shows the density correlation function for three different microdynamics corresponding to the same linear macroscopic rate law. The system exhibits negative spatial correlations when A_R is minimized: $A_D/D > A_R/K$, and positive correlations* in the opposite case: $A_R/K > A_D/D$. When reactive detailed balance is preserved in the transition probability matrix ($\binom{b}{\alpha} P_{\alpha\beta} = \binom{b}{\beta} P_{\beta\alpha}$), there are no spatial correlations (see data in Fig. 1). The effect of dimensionality is illustrated in Fig. 2: clearly the range of spatial correlations decays with the dimension of the system, as intuitively expected. In all cases we obtain excellent agreement with the theoretical predictions from Eqs. (4) and (5) (see Figs. 1 and 2)†.

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‡ The variance is calculated with respect to the grand canonical ensemble distribution. The microcanonical distribution gives the same result in the strong diffusion limit.

§ In the master equation approach, A_R is taken to be the second moment of the transition probability [10]

* The effect of strong positive correlations can also be observed from snapshots of the universe (not shown), where large scale fluctuations are clearly visible.

† For small values of r, some deviations occur due to the inevitable short-range anisotropy of lattices

The main features of the present work can be summarized as follows: (i) we show that the steady state fluctuations in reactive LGA's behave (for linear models) exactly as predicted by the stochastic partial differential equation with process independent white noise (Landau equation); (ii) we compute the noise amplitude from the parameters defining the reaction-diffusion system (the matrix $P_{\alpha\beta}$ and the diffusion coefficient D); (iii) we show how to construct the transition probability matrix $P_{\alpha\beta}$ to realize a given rate law $\phi(x)$ and a given noise amplitude function; (iv) we measure the effect of fluctuations through the density correlation function $G(r)$; (v) we find that the measured $G(r)$ is in excellent agreement with the theoretical prediction, Eqs. (4) and (5). In conclusion, reactive lattice gas automata can be considered as a powerful alternative to established methods to investigate reaction-diffusion systems where intrinsic noise plays an important role. We are now investigating the LGA method in the nonlinear regime and the effects of the details of the noise function on the fluctuation correlations.

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References

[1] Castets V., Dulos E., Boissonade J.and DeKepper P., *Phys. Rev. Lett.* **64** (1990) 2953; DeKepper P., Castets V., Dulos E.,and Boissonade J., *Physica* **49D** (1991) 161; Ouyang Q. and Swinney H. L., *Nature* **352** (1991) 610, and *Chaos* **1** (1991) 411.

[2] Dab D., Lawniczak A., Boon J.P., and R. Kapral, *Phys. Rev. Lett.* **64** (1990) 2462; Lawniczak A., Dab D., Kapral R., and Boon J.P., *Physica* **47D** (1991) 132.

[3] Frisch U., d'Humières D., Hasslacher B., Lallemand P., and Rivet J.-P., *Complex Systems* **1** (1987) 649; J.P. Boon, *Physica* **47D** (1991) 1.

[4] Rivet J. P., Hénon M., Frisch U., and d'Humières D., *Europhys. Lett.***7** (1988) 231; Rivet J. P., *C. R. Acad. Sci. Paris* **313** (1991) 151; Succi S., Santangelo P., and Benzi R., *Phys. Rev. Lett.* **60** (1988) 26.

[5] van den Hoef M. A. and Frenkel D., *Phys. Rev. Lett.* **66** (1991) 2535; Frenkel D. and Ernst M. H., *Phys. Rev. Lett.* **63** (1989) 2165.

[6] Dab D., Boon J.P., and Li Y.-X., *Phys. Rev. Lett.* **66** (1991) 2535; Kapral R., Lawniczak A., and Masiar P., *Phys. Rev. Lett.* **66** (1991) 2539.

[7] Boon J.P. and Yip S., *Molecular Hydrodynamics* (Dover, New York, 1991).

[8] Grosfils P., Boon J.P., and Lallemand P., *Phys. Rev. Lett.* **68** (1992) 1077 .

[9] Malek Mansour M., Van Den Broeck C., Nicolis G., and Turner J. W., *Annals of Physics* **131** (1981) 283.

[10] Nitzan A., Ortoleva P., Deutch J., and Ross J., *J. Chem. Phys.* **61** (1974) 1056.

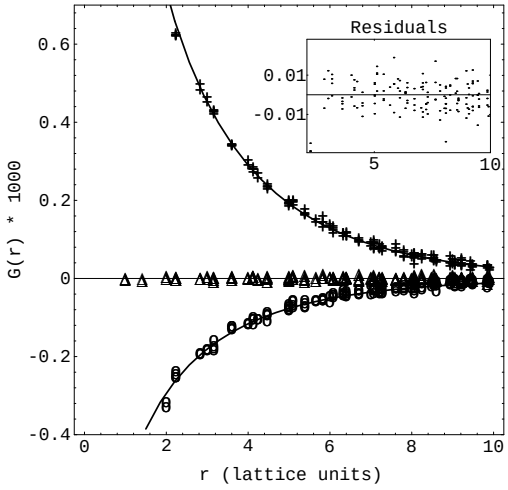

Figure 1: *The spatial fluctuations correlation function $G(r)$ (units l^{-2} with lattice spacing l) in a two-dimensional reactive lattice gas ($b = 5$, $b_0 = 1$, $x_0 = 0.5$ and $K = 0.02$): simulation data (symbols) and theoretical predictions, Eqs. (4) and (5) (solid curves). Parameters $A_D(x_0)/D = 0.1$ and $A_R(x_0)/K = 0.05, 0.1,$ and 0.225 (see text for explanation). The inset shows the absolute deviations for the upper curve. Error bars would be smaller than the size of the symbols.*

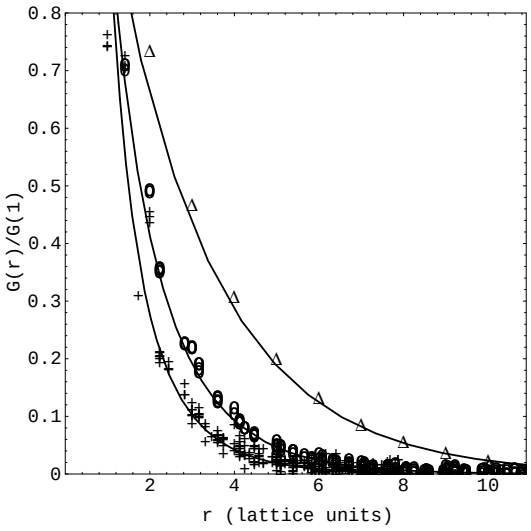

Figure 2: *The normalized correlation function $G(r)/G(1)$ in one- (triangles), two- (circles) and three- (crosses) dimensional lattice gases ($x_0 = 0.5$, $K = 0.05$, same $P_{\alpha\beta}$ for all three systems). Number of particles per node: $b = 7$, with $b_0 = 3$ (1-d and 2-d), $b_0 = 1$ (3-d), $m = 2$ (1-d), and $m = 1$ (2-d and 3-d). Diffusion coefficient: $D = 2/7$ (1-d) and $D = 1/7$ (2-d and 3-d). Symbols are simulation data and solid curves are obtained from Eqs. (4) and (5). Normalization values G(1)= 0.00202804 (1-d), 0.000647127 (2-d), and 0.000227087 (3-d) (theoretical values). Errors as in Fig. 1.*