Master Equation and Molecular Dynamics Simulations of Spatiotemporal Effects in a Bistable Chemical System

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Received: March 4, 1998; In Final Form: November 16, 1998

A simple and realistic model of a bistable chemical system in which running fronts can be observed is studied. The stochastic dynamics of this model is described by the master equation for a spatially extended system. The results are compared with microscopic simulations of the system, performed using the molecular dynamics technique for reactive hard spheres. The velocity of the front and its shape obtained in both simulations agree well with the phenonenological description. For small volumes of the systems fluctuations grow locally and create pulses of concentrations.

I. Introduction

The dynamics of nonlinear chemical systems can be sensitive to fluctuations,[1−8] which appear as a consequence of the complex character of molecular motion and stochastic properties of reactive collisions. One can expect substantial differences in the influence of fluctuactions on homogeneous and inhomogeneous nonlinear chemical systems. Ideally stirred systems are of course homogeneous, but also unstirred systems can be treated as homogeneous ones if diffusion is sufficiently effective to disperse local inhomogeneities. Otherwise, the description of spatially extended systems has to include the dependence of concentrations on spatial coordinates. The phenomenological approach to dynamics of such systems is based on reaction−diffusion equations, in which internal fluctuations of concentrations are neglected. In spatially extended nonlinear systems, local fluctuations can qualitatively change evolution of the systems. The influence of fluctuations on the dynamics is particularly important if the system is close to a bifurcation. The simplest example in which such qualitative changes in the dynamical behavior can be expected is a bistable system close to a saddle-node bifurcation. In this case the stationary state very close to a saddle point is weakly stable, whereas the other stable stationary state is strongly attractive. For the homogeneous system, global fluctuations induce a "jump" of the whole system from a basin of attraction of the weakly stable state to the strongly attractive one. In the spatially extended system, a nucleation process can occur in which local fluctuations form small domains (nuclei) due to the similar jump in localized regions. These domains can next expand and cover a substantial part of the system.

There have been a number of investigations on fluctuations in both homogeneous and spatially extended bistable chemical systems. The simplified treatment of fluctuations in nonlinear systems can be based on the master equation (ME).[1,9,10] This method has been applied directly to simulate the propagation of the front in the Fisher−Kolmogorov model.[11] For large systems, the master equation can be further reduced to the corresponding Langevin equations, in which the deterministic reaction−diffusion equations are supplemented by the stochastic terms representing local fluctuations.[9,10] Such an approach has been used to describe the influence of fluctuations on the propagation of the Fisher−Kolmogorov-type front[12,13] as well as on the trigger fronts.[13,14] Many simulations of the effects of fluctuations on the fronts at the mesoscopic level use the lattice gas cellular automata methods.[15] In particular, the simulations were performed for the running front in the Schlögl model[16] and the fronts modeling chemical waves observed in heterogeneous catalytic reactions.[17]

The mesoscopic approach in numerical simulations is much less demanding from a computational point of view than any simulation at the molecular level. The most complete description of reaction−diffusion systems can be obtained using molecular dynamics (MD) techniques.[18] However, application of these methods to a real, macroscopic chemical system requires an enormous number of variables (of the order of 10^{23}). Moreover, chemical mechanisms of real systems exhibiting nonlinear phenomena are complex and involve processes ocurring at different time scales.[19−21] Therefore, microscopic simulations of such systems are not possible at present. To study the influence of internal fluctuations on nonlinear chemical systems it is necessary to construct simple models which can be adopted for numerical experiments. Such models should contain possibly a minimal number of elementary processes occurring on a similar time scale and involve reagents whose concentrations do not differ significantly. There are only a few papers dealing with simulations of nonlinear phenomena in spatially extended systems at the microscopic level.[22] In particular, investigations of fluctuations in a bistable system have been reported by Baras and Malek Mansour.[23]

The aim of our study is to compare the description obtained from ME with MD simulations for an inhomogeneous bistable system. While the influence of fluctuations on the velocity of chemical fronts has been studied previously by ME and Langevin approaches,[11−14] we mainly focus our attention on nucleaction, that is, spontaneous generation of pulses in regions ahead of the running front and in initially homogeneous systems. In the present paper, we apply the "hard-sphere chemistry"[24] as the simplest algorithm for MD simulations, which can be used provided a chemical model consists of bimolecular reactions only. Therefore, the simple models for the chemical trigger waves, like the Schlögl model, cannot be treated directly

10.1021/jp9813746 CCC: $18.00
Published on Web 04/08/1999

by MD because they contain trimolecular reactions, and comparison of the ME and MD approaches is not possible. Recently, we have presented the simple but realistic reaction scheme of a bistable system which consists of elementary processes only and does not include autocatalytic steps.[25] These properties allow us to perform for the first time direct simulations of the trigger front by the MD technique and ME method.

The paper is organized as follows. In section II, the model is described and its phenomenological dynamics in spatially extended systems is analyzed. The next section is concerned with the methods used in our simulations. In section IV, we present results for the inhomogeneous system as well as homogeneous one. The simulations are compared with results of a phenomenological description of the system.

II. Phenomenological Model

The model consists of seven elementary reactions:

$$\mathrm{R} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{V} + \mathrm{S} \tag{1}$$

$$\mathrm{V} + \mathrm{E} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{X} + \mathrm{S} \tag{2}$$

$$\mathrm{X} + \mathrm{S} \xrightarrow{k_3} \mathrm{E} + \mathrm{U} \tag{3}$$

$$\mathrm{X} + \mathrm{V} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{Y} + \mathrm{S} \tag{4}$$

It may be noticed that by substituting VE instead of X and V_2E instead of Y one obtains the well-known scheme for a catalytic (enzymatic) reaction inhibited by an excess of its reactant V. This scheme is a modification of the well-known model of an open chemical system with a catalytic (enzymatic) reaction, inhibited by an excess of its reactant V. The reactant V is transformed to the product U with E as the catalyst (steps 2 and 3). This part of the scheme is the well-known Langmuir−Hinshelwood mechanism of catalytic reactions (or the Michaelis−Menten kinetics for enzymatic reactions). Step 4 is the inhibition of the Langmuir−Hinshelwood mechanism (or the Michaelis−Menten scheme) by an excess of the reactant V. It is assumed that S is a solvent, whose concentration is held constant. The system is open, due to step 1, in which the reactant V is produced from the reagent R, whose concentration is also maintained constant. Step 1 can be replaced by a flow term which mimics a continuously strirred tank reactor (CSTR) open to the reactant V but closed to the catalyst E and its complexes X and Y, which can be immobilized inside the reactor.

In the sequel we are mainly interested in spatially extended systems. Therefore, we assume that the initial distributions of reagent concentrations depend on space coordinates. Such conditions can be achieved experimentally in a continuously fed unstirred reactor (CFUR) or a so-called "gel disc reactor". The local mass balance equations with reaction and diffusion terms for each reagent separately must be used to describe the dynamics of the system. According to the mass action law, the behavior of the system is described by four kinetic equations for V, E, X, and Y, where the symbols of the reagents are used to denote their concentrations for convenience, because this notation does not cause any misunderstandings. For simplicity, we restrict our considerations to one-dimensional systems. The kinetic equations have the form:

$$\frac{\partial V}{\partial t} - D_{\mathrm{V}}\frac{\partial^2 V}{\partial x^2} = k_1 RS - k_{-1}VS - k_2 VE + k_{-2}XS - k_4 VX + k_{-4}YS \tag{5}$$

$$\frac{\partial E}{\partial t} - D_{\mathrm{E}}\frac{\partial^2 E}{\partial x^2} = -k_2 VE + (k_{-2} + k_3)XS \tag{6}$$

$$\frac{\partial X}{\partial t} - D_{\mathrm{X}}\frac{\partial^2 X}{\partial x^2} = k_2 VE - (k_{-2} + k_3)XS - k_4 VX + k_{-4}YS \tag{7}$$

$$\frac{\partial Y}{\partial t} - D_{\mathrm{Y}}\frac{\partial^2 Y}{\partial x^2} = k_4 VX - k_{-4}YS \tag{8}$$

In the following, we assume that the diffusion coefficients of all reagents are identical and they are denoted by D. To simplify further considerations we also assume that initially the sum $E(x,0) + X(x,0) + Y(x,0) = E_0$ is constant in space. Then, summing up eqs 6−8 it is easy to see that $E(x,t) + X(x,t) + Y(x,t) = E_0$ for all times $t > 0$. Thus, one of the variables (for example Y) can be eliminated and the dynamics of the system is described by three reaction−diffusion equations only:

$$\frac{\partial V}{\partial t} - D\frac{\partial^2 V}{\partial x^2} = k_1 RS - k_{-1}VS - k_2 VE + k_{-2}XS - k_4 VX + k_{-4}(E_0 - E - X)S \tag{9}$$

$$\frac{\partial E}{\partial t} - D\frac{\partial^2 E}{\partial x^2} = -k_2 VE + (k_{-2} + k_3)XS \tag{10}$$

$$\frac{\partial X}{\partial t} - D\frac{\partial^2 X}{\partial x^2} = k_2 VE - (k_{-2} + k_3)XS - k_4 VX + k_{-4}(E_0 - E - X)S \tag{11}$$

The homogeneous system with reactions 1−4 and thus described by the above equations without the diffusion terms has been studied in our recent papers.[25] It may be shown that for a wide range of the parameters the model exhibits bistability with the stationary states, (V_1, E_1, X_1), (V_2, E_2, X_2), and (V_3, E_3, X_3). The state denoted as (V_1, E_1, X_1) is weakly attractive and (V_3, E_3, X_3) is strongly attractive, whereas (V_2, E_2, X_2) is repelling.

It is well-known that a one-dimensional infinite system discribed by one reaction−diffusion equation for bistable dynamics has the running front as an asymptotic solution for properly chosen initial conditions.[26,27] If the total concentration of the catalyst (enzyme) E_0 is much smaller than the concentration of the reactant V then the dynamics of the homogeneous system can be reduced to one variable. In this case, one can separate scales of time in which the concentrations of the reagents change. The variables E and X are fast variables, whereas V is a slow one. On the basis of the Tikhonov theorem,[28] in slow time scale the fast variables remain equal to their quasistationary values, and then the behavior of the system can be described by one kinetic equation for V only.

$$\frac{\partial V}{\partial t} - D\frac{\partial^2 V}{\partial x^2} = k_1 RS - k_{-1}VS - \frac{k_3 E_0 VS}{K_{\mathrm{m}}S + V + V^2/(K_4 S)} = f(V) \tag{12}$$

where $K_{\mathrm{m}} = (k_{-2} + k_3)/k_2$ and $K_4 = k_{-4}/k_4$.

For appropriate values of the parameters, the variable V has three stationary states. The stationary states with the lowest and the highest concentrations are stable, whereas the middle one is unstable. Therefore, eq 12 with initial condition such that one part of the system is in a basin of attraction of one stable stationary state and the other one is in a basin of attraction of the other stable stationary state, has an asymptotic solution in the form of a running front $V(\xi)$, where $\xi = x \pm \rho t + x_0$. A velocity of the running front ρ is given by[27]

$$\rho = -\frac{\int_{V_1}^{V_3} f(V)\,\mathrm{d}V}{\int_{-\infty}^{+\infty}\left(\frac{\mathrm{d}V}{\mathrm{d}\xi}\right)^2 \mathrm{d}\xi} \tag{13}$$

For the particular form of the right-hand side of (12), the explicit form of solution is not known. However, a sign of ρ is determined by the sign of $\int_{V_1}^{V_3} f(V)\,\mathrm{d}V$. If this integral is positive, then the region with V close to V_3 expands, and for a negative value of the integral, the region with V close to V_1 expands. For uniform initial distributions of E_0, the distributions of E and X in a slow time scale are held at their quasistationary values which are determined by the asymptotic distribution of V.

It is a common belief and it has been confirmed by numerical calculations (but to our best knowleadge there is no proof) that also spatially extended infinite systems described by reaction−diffusion equations for many variables have asymptotic solutions in the form of the running front for properly chosen initial conditions. Similarly to the one-variable system, the kinetic equations without the diffusion terms should have three stationary states, two of them are stable and one is unstable. Therefore, on the basis of the results for the one-variable case, we expect that the three-variable system (9−11) has asymptotic solutions in the form of travelling fronts. Selecting values of the parameters and the diffusion coefficient for simulations, we are restricted mainly by the MD approach, in which a limited number of molecules is used. For efficient MD simulations, the numbers of molecules of the reagents should not differ by more than 3 orders of magnitude and, moreover, the rate constants should have values as close as possible. The diffusion coefficient is determined by microscopic parameters characterizing the system. In our MD simulations its value corresponds to a dense gas. MD simulations were performed for two sets of the rate constants and the diffusion coefficient: (A) $k_1 = 142.74$, $k_{-1} = 87.23$, $k_2 = 793.0$, $k_{-2} = 39.65$, $k_3 = 1546.35$, $k_4 = 793.0$, $k_{-4} = 396.5$ (all constants in $[10^{-8}$ s M$]^{-1}$) and $D = 1.175$ 10^{-3} μm$^2/10^{-8}$ s and (B) $k_1 = 137.52$, $k_{-1} = 84.04$, $k_2 = 764.0$, $k_{-2} = 38.2$, $k_3 = 1489.8$, $k_4 = 764.0$, $k_{-4} = 382.0$ (all constants in $[10^{-8}$ s M$]^{-1}$), and $D = 1.35$ 10^{-3} μm$^2/10^{-8}$ s.

We have carried out ME simulations and numerical solutions of eqs 9−11 for the same sets of the parameters. Moreover, some additional ME simulations were performed for (C) $k_1 = 144.0$, $k_{-1} = 88.0$, $k_2 = 800.0$, $k_{-2} = 40.0$, $k_3 = 1560.0$, $k_4 = 800.0$, $k_{-4} = 400.0$ (all constants in $[10^{-8}$ s M$]^{-1}$) and two values of the diffusion coefficient, 0.2 and 0.02 μm$^2/10^{-8}$s. In all simulations we used $R = 0.5$ M, $E_0 = 0.2$ M, and $S = 0.1$ M. For all sets of the rate constants the concentrations at the stationary states are identical and equal to $V_1 = 0.113816$, $E_1 = 0.069820$, $X_1 = 0.039733$; $V_2 = 0.139666$, $E_2 = 0.054810$, $X_2 = 0.038275$; $V_3 = 0.514699$, $E_3 = 0.006652$, $X_3 = 0.017120$.

We used two types of the boundary conditions, the periodic conditions in MD simulations and the zero-flux conditions for ME simulations. In all cases for appropriate initial conditions the system becomes uniform and approaches the strongly attractive stationary state V_3, E_3, X_3 after sufficiently long time. Numerical solutions can be treated as reasonable approximations of the running fronts in an infinite system if the "front's width" is small as compared with a size of the system. Moreover, the region occupied by the weakly stable stationary state should be sufficiently large that the front propagation can be observed.

III. Simulation Methods

Periodically Extended Molecular Dynamics. The periodically extended MD technique for reactive hard spheres[29] is applied to simulate the time evolution of an inhomogeneous system with reactions 1−4 at the microscopic level. The algorithm used in this paper is similar to the one applied in refs 25 and 30. All reactants (E, R, S, U, V, X, and Y) are represented by spheres with the same mass (m) and diameter (σ). The spheres are labeled by a chemical identity parameter which defines their "chemical" properties but does not have any influence on the mechanical motion. Both reactive and nonreactive collisions between spheres are considered. To control the rates of various chemical processes, the steric factors are introduced (they are denoted as s_i, s_{-i}; $i = 1, 4$). They describe a fraction of collisions between reactants of a given process which leads to a reaction. If a collision between spheres representing reagents of a given process occurs, then a random number generator is used and the collision is regarded as a reactive one if the obtained random number is smaller that the corresponding steric factor. After such a collision, the chemical identity parameters of the spheres involved are modified according to the assumed reaction scheme. Otherwise, the collision is a nonreactive one and the spheres retain their chemical identities.

If reactions 1−4 are thermoneutral, then all collisions between spheres are elastic. Within this assumption, the system of spheres as a whole is in thermal equilibrium with respect to the translational motion. Maintaining such equilibrium in a system with chemical reactions is very important from the computational point of view because it allows us to extend the size of the system using a prerecorded equilibrium trajectory.[29] Any trajectory which was calculated for a system of spheres with the periodic boundary conditions may be used as a database which allows one to enlarge the size of simulations. The periodic boundary conditions mean that positions and velocities of molecules are periodic in space with the period equal to the length of the box within which the simulations were performed. Therefore, the original small system may be periodically expanded in any of the directions by any integer number of the box lengths. Of course, if a chemical identity of molecules is neglected then such expansion does not bring us any new information. However, in a multicomponent chemical system, in which the translational motion is not related to chemical identity, the situation is different. First, different chemical composition may be initialized in various boxes by marking the equivalent (by periodicity) spheres in a different way. Second, steric factors (if they are not equal to unity) differentiate the time evolution in various boxes, as a collision between the same objects may be reactive in one box and nonreactive in another one. The periodic boundary conditions ensure free motion of molecules between boxes. The problems concerned with the influence of system size on the observed evolution may be studied in an effective way.

In studies on chemical wave front propagation it is convenient to consider systems extended by a large number of cell lengths in the direction the wave propagates (the x direction) and by a few cell lengths in the transversal directions. The system is

initialized in such a way that a part of it is in one stationary state and the remaining part in another one. Let us consider a slice in the *x*th direction, which is one box wide. At the beginning of each MD simulation, the chemical identities within such a slice are assigned to spheres in a random way and all remaining spheres are marked as the reservoir particles. In simulations, the numbers of particles representing the reactants R and S are constant, which is achieved by assuming that the system contains nonrective particles which play the role of reservoirs of R and S molecules.[31] If a particle of S (R) vanishes in one of the reactions, then simultaneously a randomly selected particle of the reservoir, which belongs to the same slice, is transformed into S (R), respectively. On the other hand, if a particle of S (R) appears, then a randomly chosen particle of S (R), which belongs to the same slice, becomes a particle of the reservoir. However, the partices of S and R may migrate between slices and their numbers in different slices may change.

The applied technique forces the periodic boundary conditions for the mechanical motion of spheres in the extended system. For simplicity of the MD simulations, we considered a case in which both ends are in the weakly stable state and an interval in the middle corresponds to the strongly attractive state. For such a system, the boundary conditions in all directions were periodic.

The MD results discussed below have been obtained by a periodic extension of two trajectries. One of them describes $N = 500$ hard spheres placed in a cubic box with the side length $d = 14\sigma$ (and thus the packing fraction is $\eta \approx 0.095$). The trajectory contained 10 000 000 collisions (20 000 collision per sphere). The other one was recorded for $N = 400$ hard spheres placed in a cubic box with the side length $d = 12.5\sigma$ (and thus the packing fraction is $\eta \approx 0.11$). It contained 12 800 000 collisions (32 000 collision per sphere). For both trajectories, $\sigma = 5 \times 10^{-4}$ μm.

In both cases, the diffusion coefficients were calculated from the average square of the displacement of a sphere $r(t)$ as the function of time.

$$D = \frac{\langle r^2 \rangle(t)}{6t}$$

We obtained $D = 1.35 \times 10^{-3}$ $\mu m^2/10^{-8}$ s for $\eta \approx 0.095$ and $D = 1.175 \times 10^{-3}$ $\mu m^2/10^{-8}$ s for $\eta \approx 0.11$, and these values have been used in ME simulations and numerical solutions of (9−11) for comparison of the methods.

In MD simulations we assumed the following values of steric factors for reactions 1−4: $s_1 = 0.018$, $s_{-1} = 0.011$, $s_2 = 0.1$, $s_{-2} = 0.005$, $s_3 = 0.195$, $s_4 = 0.1$, $s_{-4} = 0.05$. These steric factors lead to sets A and B of the rate constants given in the previous Section.

Master Equation Approach. The ME approach determines the probability distribution of populations of molecules in a chemical system. To include the spatial dependence of concentrations (local populations), the (one-dimensional) system is divided into M cells along the spatial coordinate. The volume Ω and the length Δl of each cell are assumed identical. The state of our system (1−4) is described by the probability distribution $P(\{N_{V,i},N_{E,i},N_{X,i},N_{Y,i}\},t)$ of finding a set of populations $N_{Q,i}$ of species Q = V, E, X, Y in a cell $i = 1, ..., M$. (A number of molecules R, S in each cell is constant and equal to N_R and N_S.) A number of molecules $N_{V,i}$, $N_{E,i}$, $N_{X,i}$, $N_{Y,i}$ in the ith cell can be changed either by a chemical reaction between molecules within a cell or by a transfer of a molecule to or from adjacent cells. Both kind of these processes contribute independently to the time evolution of the distribution function, and the master equation for P can be presented in the following general form:

$$\frac{\partial}{\partial t}P(\{N_{V,i}\},\{N_{E,i}\},\{N_{X,i}\},\{N_{Y,i}\},t) = \left.\frac{\partial P}{\partial t}\right|_{chem} + \left.\frac{\partial P}{\partial t}\right|_{diff} \qquad (14)$$

The contribution due to the chemical processes describes isolated reactions in each single cell provided that populations in other cells remain unchanged; it is a straightforward extension of the corresponding term for the uniform system[25]

$$\begin{aligned}\left.\frac{\partial P}{\partial t}\right|_{chem} = \sum_{j=1}^{M}(&\kappa_1 N_R N_S P(..., N_{V,j} - 1, ..., t)\\ &+ \kappa_{-1}(N_{V,j} + 1)N_S P(..., N_{V,j} + 1, ..., t)\\ &+ \kappa_2(N_{V,j} + 1)(N_{E,j} + 1)P(..., N_{V,j} + 1, ..., N_{E,j} + 1, ..., t)\\ &+ \kappa_{-2}(N_{X,j} + 1)N_S P(..., N_{V,j} - 1, ..., N_{E,j} - 1, ..., N_{X,j} + 1, ..., t)\\ &+ \kappa_3(N_{X,j} + 1)N_S P(..., N_{E,j} - 1, ..., N_{X,j} + 1, ..., t)\\ &+ \kappa_4(N_{V,j} + 1)(N_{X,j} + 1)P(..., N_{V,j} + 1, ..., N_{X,j} + 1, ..., t)\\ &+ \kappa_{-4}(N_{Y,j} + 1)N_S P(..., N_{Y,j} + 1, ..., t))\\ &- \nu_{chem}P(\{N_{V,i}\},\{N_{E,i}\},\{N_{X,i}\},\{N_{Y,i}\},t)\end{aligned} \qquad (15)$$

The notation (..., $N_{Q,j}$, ...) means that except $N_{Q,j}$ all populations in the distribution function P remain unchanged. The right-hand side of (15) expresses the rate of change of a probability of a state $\{N_{V,i},N_{E,i},N_{X,i},N_{Y,i}\}$ as a balance of the "birth" and "death" processes. The "birth" term is formed by the positive components of (14), which describe creation of a given state, resulting from transitions from other states under particular chemical processes 1−4. Consequently, the last component of (14) is a "death" term, describing escape from this state to other points of the configuration space. The coefficient ν_{chem} provides the total rate of escape from the configuration ($\{N_{V,i},N_{E,i},N_{X,i},N_{Y,i}\}$), as a result of chemical reactions

$$\begin{aligned}\nu_{chem}(\{N_{V,i},N_{E,i},N_{X,i},N_{Y,i}\}) = \sum_{j=1}^{M}(&\kappa_1 N_R N_S + \kappa_{-1}N_{V,j}N_S +\\ &\kappa_2 N_{V,j}N_{E,j} + (\kappa_{-2} + \kappa_3)N_{X,j}N_S + \kappa_4 N_{X,j}N_{V,j} + \kappa_{-4}N_{Y,j}N_S)\end{aligned} \qquad (16)$$

The respective terms of sum (16) represent the rates of reactive collisions corresponding to reactions 1−4. The coefficients κ_i are related to the phenomenological rate constants of bimolecular reactions 1−4 by $\kappa_i = k_i/\Omega$. The units must be consistent so that the result is in (time unit)$^{-1}$. Due to this relation, the chemical terms in the phenomenological eqs 5−8 can be recovered from the master equation in the limit $\Omega \to \infty$, as the equations for the average number concentrations $\langle N_Q/\Omega \rangle$.

To account for the diffusion process it is assumed that every particle can jump with certain probability to a neighbor cell. These hoping rates are related to the diffusion coefficients and

in general can be specific for each species. The term of eq (14) describing diffusion has then the following form:

$$\begin{aligned}\left.\frac{\partial P}{\partial t}\right|_{\text{diff}} = &\sum_{j=1}^{M}(d_{\text{V}}(N_{\text{V},j-1}+1)P(...,N_{\text{V},j-1}+1,N_{\text{V},j}-1,...,t)\\ &+ d_{\text{V}}(N_{\text{V},j+1}+1)P(...,N_{\text{V},j}-1,N_{\text{V},j+1}+1,...,t)\\ &+ d_{\text{E}}(N_{\text{E},j-1}+1)P(...,N_{\text{E},j-1}+1,N_{\text{E},j}-1,...,t)\\ &+ d_{\text{E}}(N_{\text{E},j+1}+1)P(...,N_{\text{E},j}-1,N_{\text{E},j+1}+1,...,t)\\ &+ d_{\text{X}}(N_{\text{X},j-1}+1)P(...,N_{\text{X},j-1}+1,N_{\text{X},j}-1,...,t)\\ &+ d_{\text{X}}(N_{\text{X},j+1}+1)P(...,N_{\text{X},j}-1,N_{\text{X},j+1}+1,...,t)\\ &+ d_{\text{Y}}(N_{\text{Y},j-1}+1)P(...,N_{\text{Y},j-1}+1,N_{\text{Y},j}-1,...,t)\\ &+ d_{\text{Y}}(N_{\text{Y},j+1}+1)P(...,N_{\text{Y},j}-1,N_{\text{Y},j+1}+1,...,t))\\ &- \nu_{\text{diff}}P(\{N_{\text{V},i},N_{\text{E},i},N_{\text{X},i},N_{\text{Y},i}\},t) \end{aligned} \quad (17)$$

Let us notice that contrary to the phenomenological approach we cannot eliminate the species Y because the number of molecules in each cell fluctuates for all components due to diffusion.

In the above equation, the terms for boundary cells, $j = 1$ and M, can formally include populations $\{N_{\text{Q},j\pm1}\}$ outside the system, that is, for $j = 0$ and $M + 1$. The interpretation of these values depends on boundary conditions. In the application of ME, we assumed that the boundaries of the system were impermeable walls (corresponding to zero-flux boundary conditions in the phenomenological description), and then transitions of molecules outside the system were forbidden. Consequently, the terms involving $j = 0$ and $M + 1$ are disregarded. The coefficient ν_{diff}, describing the total rate of diffusive jumps for all cells, for that system can be written as

$$\begin{aligned}\nu_{\text{diff}}(\{N_{\text{V},i},N_{\text{E},i},N_{\text{X},i},N_{\text{Y},i}\}) = &\, d_{\text{V}}N_{\text{V},1} + d_{\text{E}}N_{\text{E},1} + d_{\text{X}}N_{\text{X},1} +\\ &d_{\text{Y}}N_{\text{Y},1} + 2\sum_{j=2}^{M-1}(d_{V}N_{\text{V},j} + d_{\text{E}}N_{\text{E},j} + d_{\text{X}}N_{\text{X},j} + d_{\text{Y}}N_{\text{Y},j}) +\\ &d_{\text{V}}N_{\text{V},M} + d_{\text{E}}N_{\text{E},M} + d_{\text{X}}N_{\text{X},M} + d_{\text{Y}}N_{\text{Y},M} \end{aligned} \quad (18)$$

The relation between the transition rates d_{Q} and the diffusion coefficients D_{Q} is obtained from the condition that the usual diffusion terms are recovered from equation (17) in the limit of large volume, $\Omega \rightarrow \infty$, and fine division, $\Delta l \rightarrow 0$. This yields the relation $d_{\text{Q}} = D_{\text{Q}}/(\Delta l)^2$, which shows that for a given value of the diffusion coefficient the hopping rates d_{Q} increase for finer divisions.

The master equation describes the stochastic system in terms of the probability distribution function. Alternatively, a stochastic dynamics of a chemical system can be considered as a random walk in a discrete space, in which coordinates of each point give populations $\{N_{\text{Q},i}\}$ of molecules in each cell. We have performed Monte Carlo (MC) simulations of this (continuous time) random walk applying the method of Gillespie,[32] which generates a stochastic trajectory according to the following algorithm. Let us assume that the system at an instant t is in a state which is given by the point $(\{N_{\text{V},i},N_{\text{E},i},N_{\text{X},i},N_{\text{Y},i}\})$. The total rate of escape of the system from this point due to any reaction or diffusion process is equal to $\nu = \nu_{\text{chem}} + \nu_{\text{diff}}$. According to this, in the first step of the algorithm, a waiting time τ for the transition is sampled from the exponential distribution

$$\Theta(\tau) = \nu\exp(-\nu\tau) \quad (19)$$

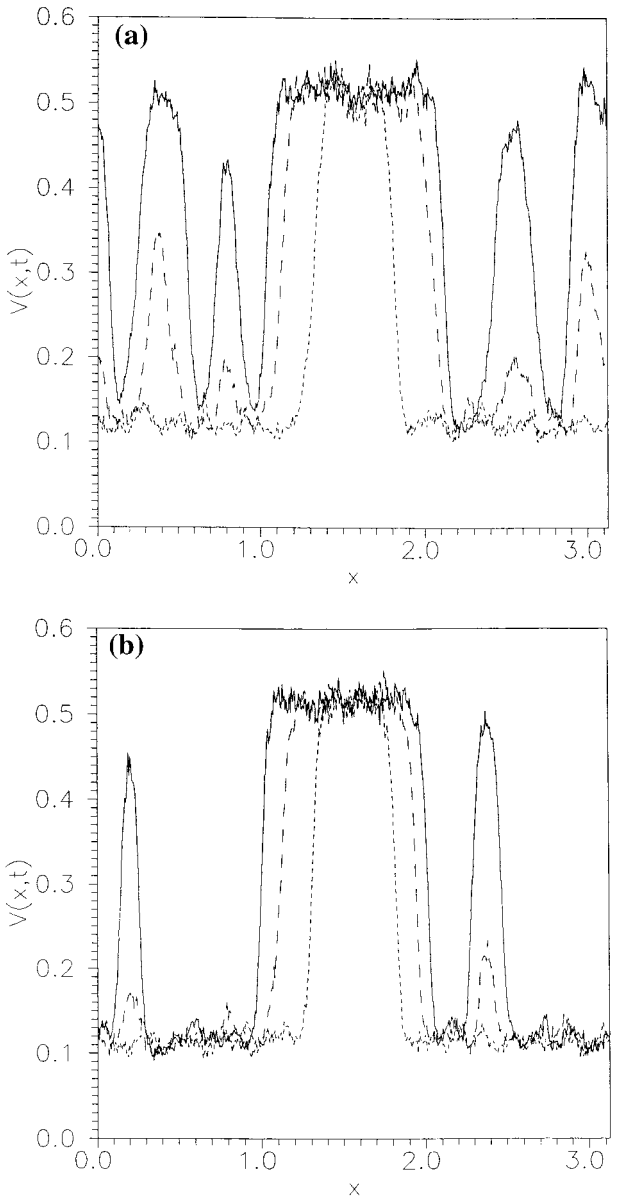

Figure 1. Spatial distributions of concentration of V. The values of the parameters from set A were used for MD and ME simulations. The cell volume $\Omega = 1.042 \times 10^{-5}\ \mu\text{m}^3$. (a) MD results for times t: 1.6696, the short dashed line; 4.4515, the dashed line; 5.842, the solid line. (b) ME results for times t: 1.6358, the short dashed line; 4.4399, the dashed line; 5.842, the solid line.

The next step consists of choosing a particular reaction or diffusion process, which causes a transfer of the system to another point. The probability $p(\alpha)$ of selection of process α is proportional to its contribution to the total rate of escape ν. For chemical reaction ρ in a cell j, that means

$$p_{\text{chem}}(\rho,j) = \nu^{-1}\kappa_{\rho}\text{N}_{1\rho,j}\text{N}_{2\rho,j} \quad (20)$$

where $N_{1\rho,j}$ and $N_{2\rho,j}$ denote populations of molecules of the corresponding two species involved in the bimolecular reaction ρ. Similarly, for the probability of a diffusive jump (to the left or right) of a molecule Q in a cell j one obtains

$$p_{\text{diff}}(\text{Q},j) = \nu^{-1}d_{\text{Q}}N_{\text{Q},j} \quad (21)$$

Next, the populations $\{N_{\text{V},j},N_{\text{E},j},N_{\text{X},j},N_{\text{Y},j}\}$ are updated as they result from the chosen process α; in terms of the random walk,

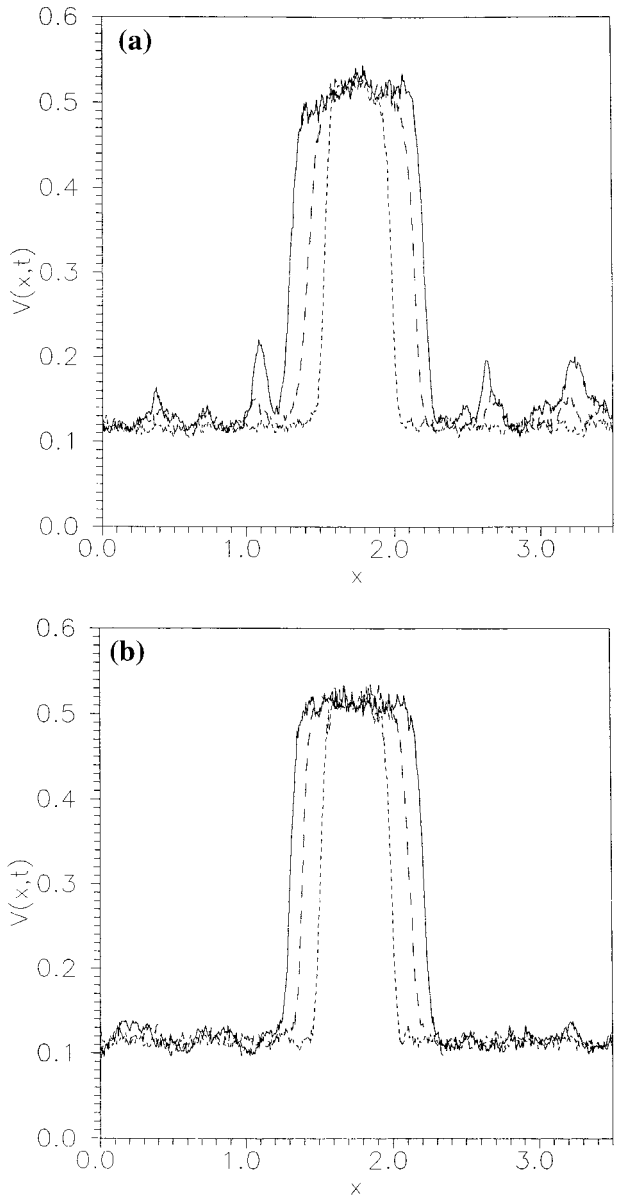

Figure 2. Same as in Figure 1, but for the parameters from set B. The cell volume $\Omega = 1.875 \times 10^{-5}\ \mu m^3$. (a) MD results for times *t*: 0.863, the short dashed line; 3.017, the dashed line; 4.309, the solid line. (b) ME results for times *t*: 0.862, the short dashed line; 3.017, the dashed line; 4.310, the solid line.

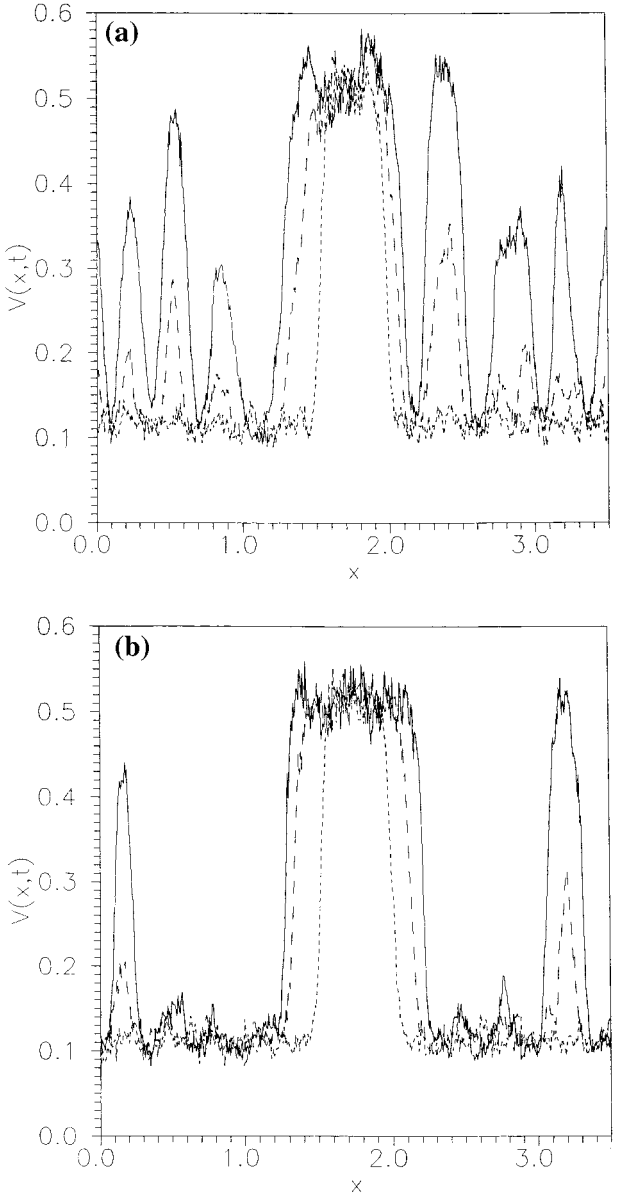

Figure 3. Same as in Figure 2, but the cell volume $\Omega = 0.469 \times 10^{-5}\ \mu m^3$.

the system moves to the new point. Given this new state, generation of the random trajectory proceeds beginning from the first step, and so on. The coarse-grained description provided by the master equation, which is based on a division of space in finite size cells, is valid when concentrations in each single cell can be regarded as uniform. This condition can be satisfied if the length of a cell is sufficiently small. The results of the phenomenological approach can be used as a first approximation for variation of concentration within a cell; on this basis a size of a cell can be roughly evaluated. Therefore, the master equation is applicable if the division is fine enough to describe inhomogenities relevant for a given problem. On the other hand, the transport between neighbor cells can be described by diffusion only if a single cell is longer than the mean free path of molecules. Also, the number of molecules in a cell must be sufficiently large to provide enough accurate statistics for populations, even for the reactant of the smallest concentration.

IV. Results

The simulations for initially inhomogeneous as well as homogeneous spatially extended systems were performed. We compare the results obtained by MD and ME approaches for the systems with the same rate constants, diffusion coeficients, and number of molecules. The only difference was that the boundary conditions used in MD were periodic, whereas for ME simulations the zero-flux conditions were assumed.

Let us recall that in simulations of ideally stirred systems with the same reaction scheme[25] we observed transitions from the basin of attraction of the weakly stable stationary state to the other one. It was found that the mean first passage time strongly increases with the volume of the system. On the basis of this dependence we were able roughly estimate a volume of the cell for simulations of spatially extended systems. For the nonuniform initial conditions described in section II, the region occupied by the strongly stable stationary state expands due to the running front mechanism. Moreover, one can expect that spontaneous transitions from the weakly to the strongly stable stationary state can occur locally in a finite time long before

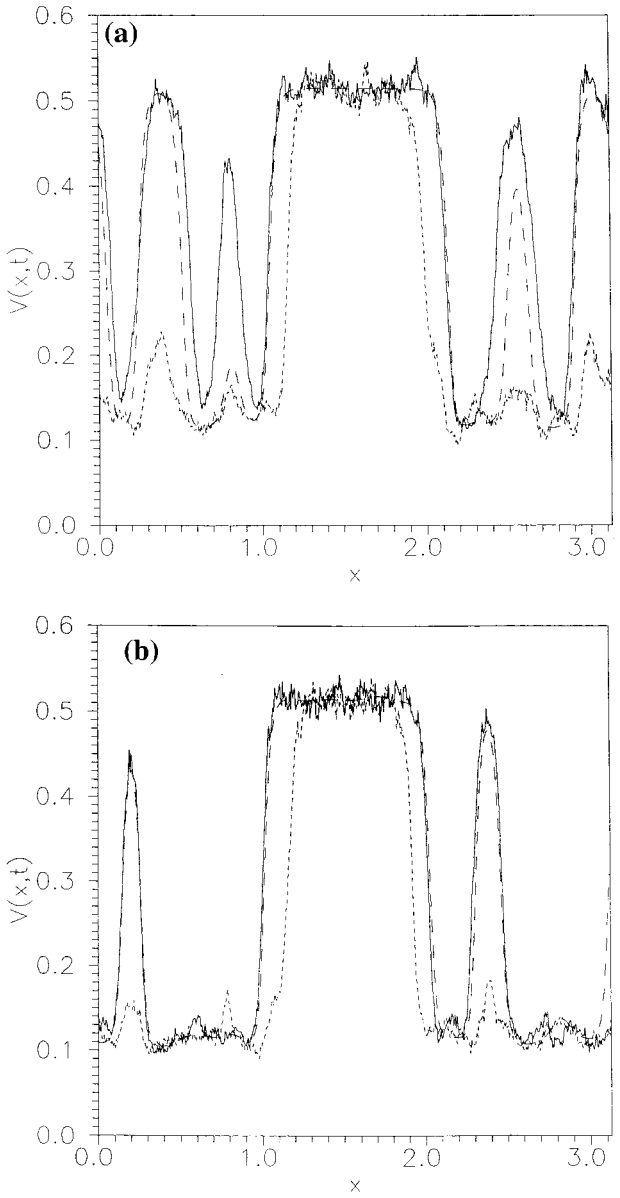

Figure 4. Comparison between numerical solutions of eqs 9−11 with MD simulations (a) and with ME simulations (b) for the system presented in Figure 1. The initial conditions in phenomenological calculations were defined by the concentration distributions obtained in simulations at $t = 4.17$ (MD) and $t = 3.97$ (ME). They are denoted by the short dashed line. The dashed line and the solid line show the results of simulations and phenomenological calculations for $t = 5.842$.

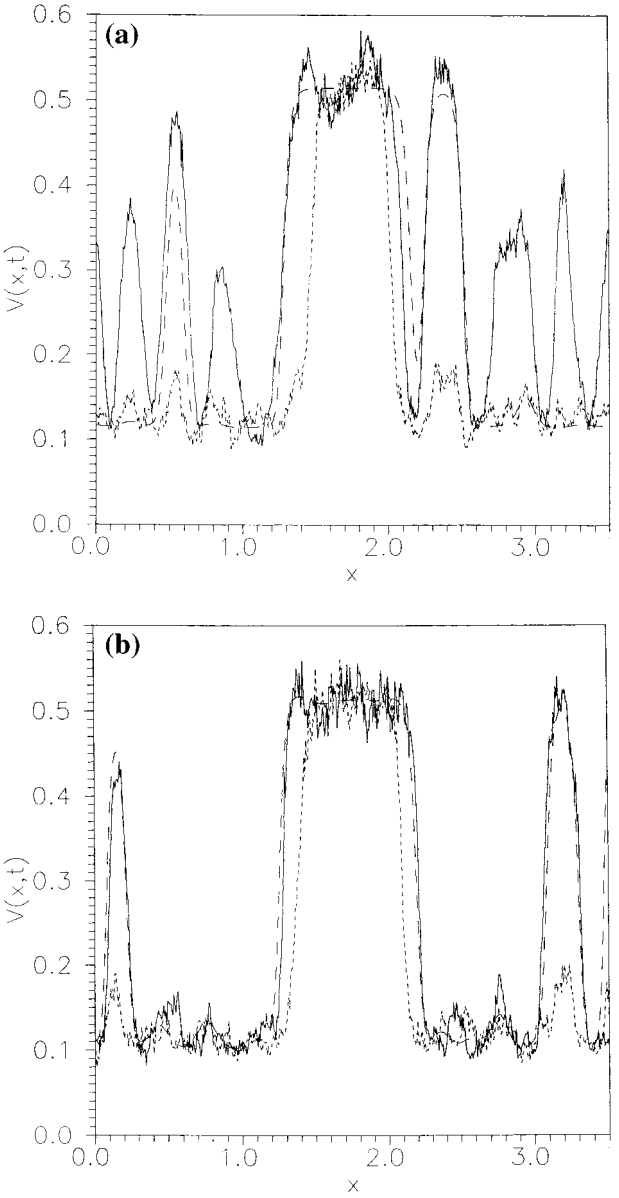

Figure 5. Same as in Figure 4 but for the system presented in Figure 3. The initial conditions in phenomenological calculations were defined by the concentration distributions obtained in simulations at $t = 2.154$ (MD) and $t = 2.586$ (ME). The dashed line and the solid line show the results of simulations and phenomenological calculations for $t = 4.310$.

the running front arrives. The appearing domains spread out like the running front too. For the selected values of the parameters, we can clearly observe both the propagation of the running front and spontaneous creations of pulses.

In Figures 1−3, we present a comparison between results obtained for initially inhomogeneous systems by (a) MD and (b) ME methods at selected times. In these simulations our system consists of 500 cells. At the beginning, the concentrations of the reagents in cells numbered from 220 to 280 corresponded to the strongly attracting stable stationary state, whereas in all other cells, the weakly stable stationary state was assumed. Figure 1 shows the evolution of V for the system characterized by the volume of a single cell, 1.042×10^{-5} μm^3, and the parameters from set A. The length of the system is 3.125 μm. Expansion of the pulse initialized in the middle zone of the system is seen. It can be treated as propagation of two fronts in the opposite directions. The agreement between MD and ME results is very good for times less than 1.7. For longer times, the results of the two methods coincide for the front progating to the left. In MD simulation the front propagating to the right moves faster than the one obtained in ME simulation. The evolution of the system for times longer than 1.7 is strongly affected by spontaneous generation of new pulses which originate due to transitions from the weakly to the strongly stable state induced by local fluctuations. These transitions occur more frequently in MD simulations than in ME ones.

Figure 2 presents snapshots of V for the system characterized by the volume of single cell 1.875×10^{-5} μm^3 and the parameters from set B. This is the largest volume we considered in our MD simulations. The length of the system is 3.5 μm. The profiles of the expanding pulse obtained from the two simulation methods agree perfectly for this system. The main difference in comparison with the previous case is that for such large volume the spontaneous generation of new pulses is much more difficult. Local fluctuations are smaller because the volume

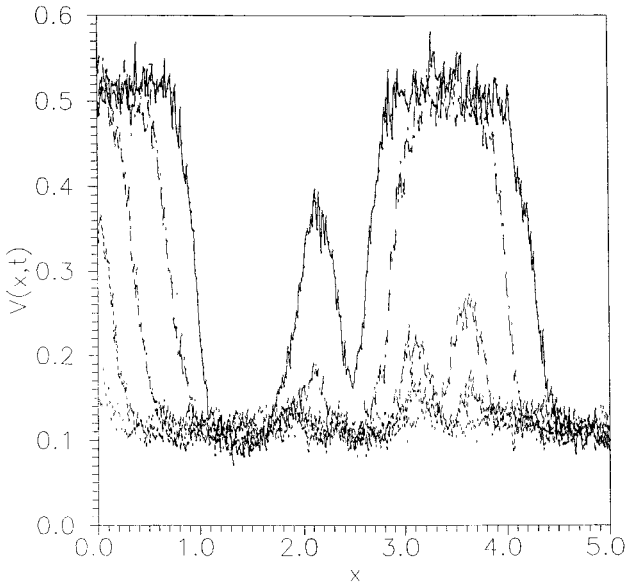

Figure 6. Spatial distributions of concentration of V obtained in ME simulations of an initially homogeneous system at V_1, E_1, X_1 for set C and the diffusion coefficient $D = 0.02\ \mu m^2/10^{-8}$ s. The division in $M = 400$ cells with $\Omega = 2.5 \times 10^{-6}\ \mu m^3$ was used. Snapshots for times t: 1.25, the short dashed line; 2.50, the dashed line; 3.75, the long dashed line; 4.0, the solid line.

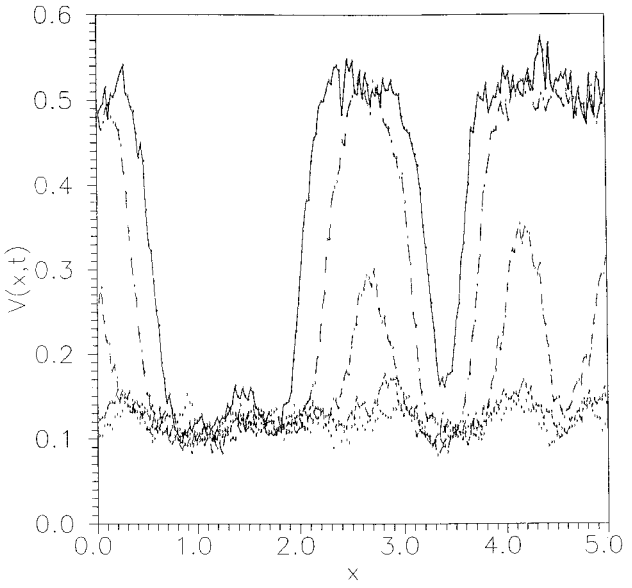

Figure 7. Same as in Figure 6 but for $M = 200$ and $\Omega = 5 \times 10^{-6}\ \mu m^3$.

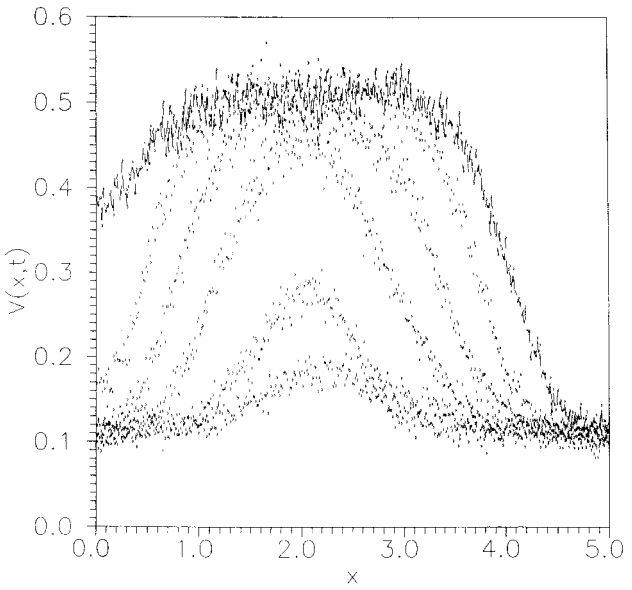

Figure 8. Same as in Figure 6 but for $D = 0.2\ \mu m^2/10^{-8}$ s at times t: 9.25, 10.00, 10.75, 11.25, 11.75, 12.25.

of a cell is much larger. It is expected that the evolution of the system with parameter set B is qualitatively similar to that seen in Figure 1 if the cell volume is smaller. Figure 3 shows snapshots of V for the system with the same values of the parameters as in Figure 2, but the volume of a single cell is reduced to $0.469 \times 10^{-5}\ \mu m^3$. Many new pulses appear in this system at the same time. Also, in this case both simulation methods give similar rates of expansion of the initial pulse. Similarly to in Figure 1, for the system with parametr set B the spontaneous generation of pulses is easier in MD as compared with ME simulations.

To study the influence of fluctuations on the dynamics of the system, we compared the solutions of the deterministic eqs 9−11 with the MD and ME simulations. The initial conditions for eqs 9−11 were taken as the concentrations of the reagents obtained in simulations for selected times. Figure 4 shows the comparison between simulations (MD (a), ME (b)) and phenomenological equations for the system presented in Figure 1. The phenomenological calculations were initiated by the simulation results for $t = 4.17$ (MD) and $t = 3.97$ (ME). We have found a very good agreement for the expansion of the initial pulse, as well as for evolution of sufficiently developed spontaneous pulses. However, small fluctuations vanish in the deterministic evolution, whereas they may grow to macroscopic size in the simulations. A similar relation between the phenomenological description and the simulations is observed in Figure 5, in which the calculations for the system presented in Figure 3, initialized by the simulation results for $t = 2.15$ (MD (a)) and $t = 2.59$ (ME (b)) are shown.

To check the influence of division of the system into cells of various volumes on the ME results we have performed special simulations in which we used various system divisions.[25] These simulations were carried out for initially inhomogeneous as well as uniform systems. Set C of the parameters was used, and the length of the system was equal to 5 μm. The example results for initially homogeneous system are shown in Figures 6 and 7. In these two cases the total volumes of the systems were the same, but $M = 400$ and $\Omega = 2.5 \times 10^{-6}\ \mu m^3$ in Figure 6, whereas $M = 200$ and $\Omega = 5 \times 10^{-6}\ \mu m^3$ in Figure 7. The results presented in these figures (as well as those not shown here) indicate that general features of the dynamics do not depend on divisions used in our ME simulations (regardless the stochastic details).

Spontaneous creation of pulses is more difficult if diffusion is faster, and this effect is worth studing in more detail by simulations of systems which differ by diffusion coefficients only. In MD simulations we could not achieve wider variations of the diffusion coefficient. This restriction does not play major role in ME simulations. In Figure 8 we show the results of ME simulations for the initially homogeneous system and the same division and cell volume as in Figure 6, but with the diffusion coefficient one order larger, equal to 0.2. It can be noticed that in this case only the single pulse appears and at a much later time.

One can estimate a size of fluctuations which are able to switch the system from the basin of attraction of V_1, E_1, and X_1 to the basin of attraction of V_3, E_3, and X_3 on the basis of the

reduced system described by (12). The linear stability theory determines the behavior of infinitely small perturbations of the homogeneous stationary states V_1, V_2, and V_3 in the form of normal modes $\delta V_i(t,x) = \delta V_{0i} \exp(iqx + \sigma t)$ for which the dispersion relation is

$$\sigma = -Dq^2 + \frac{\mathrm{d}f(V_i)}{\mathrm{d}V} \tag{22}$$

It is easy to check that if

$$\frac{\mathrm{d}f(V_i)}{\mathrm{d}V} = -k_{-1}S - \frac{k_3E_0S[K_mS - V_i^2/(K_4S)]}{[K_mS + V_i + V_i^2/(K_4S)]^2} \leq 0 \tag{23}$$

then the perturbations with any wavenumbers q decay in time. Therefore, the homogeneous stationary states V_1 and V_3 are stable. It is not the case for V_2, for which $\mathrm{d}f(V_2)/dV \geq 0$. Thus, for $q \leq q_c = (1/D\mathrm{d}f(V_2)/\mathrm{d}V)^{1/2}$ the value of σ can be positive and the perturbations of the homogeneous state V_2 can grow in time. The size of the critical nucleus given by $\lambda = 2\pi/q_c$ is equal to 0.145 μm for $D = 0.02\ \mu\mathrm{m}^2/10^{-8}$ s and 0.46 μm for $D = 0.2\ \mu\mathrm{m}^2/10^{-8}$ s for the parameters used in Figures 6−8 (set C). These values are rough estimations, and they give approximate minimal sizes of fluctuations which can switch the system from the basin of attraction of the weakly stable stationary state to the strongly stable stationary one. The results shown in Figures 6−8 confirm these estimations, although the system is initialized as uniform at the stable state V_1, E_1, X_1, not in the unstable saddle point V_2, E_2, X_2.

Analysis of the Fourier spectrum of concentration of V in the region of space which remains close to the weakly stable stationary state can be used to evaluate a critical wavenumber below which spontaneous excitations grow in time. Figure 9 shows changes of the Fourier spectrum in time obtained from MD (Figure 9A) and ME (Figure 9B) simulations for the system with the parameters defined by set B. The results are in qualitative agreement with those obtained from the phenomenological descripition given above. In both MD and ME simulations, the Fourier components with small wavenumbers grow in time, whereas for large wavenumbers their amplitudes fluctuate at low level. The evolution of $V(q)$ obtained from both simulation methods is in quantitative agreement. MD and ME indicate that in the system studied $q_c \approx 50 \pm 10\ \mu\mathrm{m}^{-1}$, which gives the size of the critical nucleus $\lambda_c \approx 0.126\ \mu$m. λ_c calculated from eq 23 is equal to 0.154 μm which is in quite good agreement with the critical size nucleus evaluated above.

Similar analysis of the Fourier spectrum obtained from ME simulations for the system (set C) with a large diffusion coefficient $D = 0.2\ \mu\mathrm{m}^2/10^{-8}$ s initialized at the weakly stable stationary state is shown in Figure 10. In this case the critical wavenumber evaluated from eq 23 is $q_c \approx 14\ \mu\mathrm{m}^{-1}$, ($\lambda_c \approx 0.449$ μm) which is also in good agreement with the results of simulations. On the basis of the above observations, we can conclude that the criterion deduced from the linear stability applied to the saddle point gives a reasonable estimation of the size of the critical nucleus.

The approximate theoretical description of fluctuations in the reaction−diffusion system may be based on the Langevin approach in which additional terms corresponding to stochastic character of reaction and diffusion processes are added to eq 12. As the simplest approximation, one can consider that the stochastic terms are given by the white noise which is uncorrelated in time and space. Within this approximation, one can show that the square of the amplitude of the Fourier components

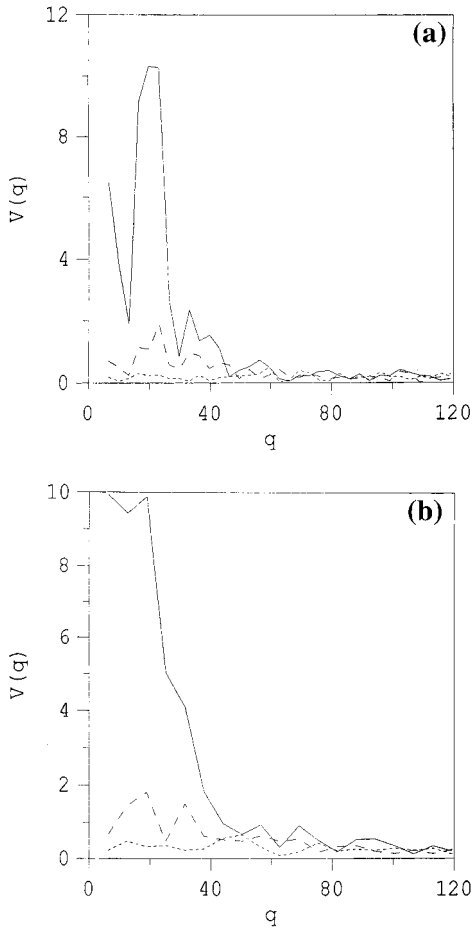

Figure 9. Time evolution of the modulus of the Fourier spectrum of the region remaining close to the weakly stable stationary state obtained from MD (a) and ME (b) simulations. Both simulations are performed for the same set of the parameters (set B) and $\Omega = 0.469 \times 10^{-5}\ \mu\mathrm{m}^3$. The curves show results for the following times: 0.431, the short dashed line; 2.155, the long dashed line; 4.31, the solid line.

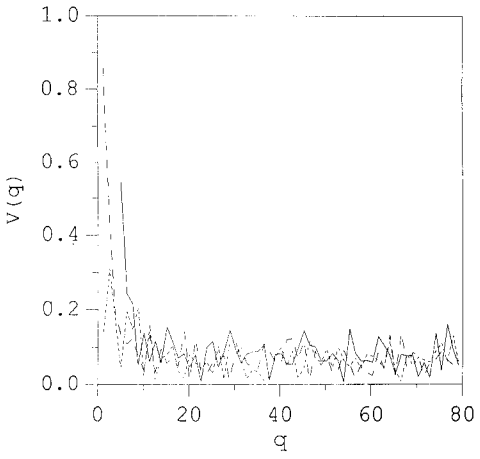

Figure 10. Fourier spectrum for the simulations presented in Figure 8 at the following times: 2.5, the short dashed line; 6.25, the long dashed line; 10.0, the solid line.

for $q > q_c$ should converge to $\epsilon/2(Dq^2 - \mathrm{d}f(V_2)/\mathrm{d}V)$ where ϵ is the noise amplitude.[10] We have calculated the average modulus of the Fourier components for $q > 80\ \mu\mathrm{m}^{-1}$ obtained from MD simulations of the system with set B for two volumes: $0.469 \times 10^{-5}\ \mu\mathrm{m}^3$ and $1.875 \times 10^{-5}\ \mu\mathrm{m}^3$. The average modulus of amplitude does not depend on time, and it equals approximately 0.18 and 0.11, respectively. The square of their ratio roughly corresponds to the inverse ratio of the system's sizes.

Estimations of the size of the critical nucleus were derived by Nitzan et al.[33] from the Fokker−Planck equation approach for two- and three-dimensional systems in space with chemical kinetics described by a potential. However, we cannot apply these results to our model because the dynamics of the system given by eqs 9−11 cannot be described by any potential and moreover our system is treated as one-dimensional in space.

V. Conclusions

In the present paper we have demonstrated that both molecular dynamics and master equation can be successfully applied for the description of spatiotemporal wave phenomena in the multicomponent chemical systems for the appropriate constructed model. The numerical solutions of the reaction−diffusion equations are consistent with the simulations in the case that the stochastic character of processes is not very impotrant. In particular, the velocities of the expanding initial pulse obtained in the phenomenological description are in good agreement with the simulations. This happens if diffusion is sufficiently fast to disperse local fluctuations before they reach a macroscopic size. However, when fluctuations become comparable with macroscopic quantities, the stochastic effects give rise to the behavior which is not predicted by the phenomenological equations. We have observed spontaneous generation of pulses which subsequently expanded according to a chemical wave mechanism. The appearance of these pulses substantially changes the dynamics of the whole system. In our simulations, the system is switched to (V_3, E_3, X_3) long before the running front arrives. Therefore, the spontaneous generation of pulses decreases an interval of time necessary to complete the transition to the strongly stable stationary state in a finite system. However, it is worth stressing that if a fluctuation reaches sufficiently large magnitude, its subsequent evolution obtained in the simulations and in the phenomenological approach are consistent. The spontaneous generation of the pulses has been previously observed in simulations of bistable systems by cellular automata techniques,[16] but to our best knowledge, our paper presents the first study of this phenomenon using both ME and MD simulations. The rate constants and diffusion coefficients we used in the simulations have realistic values. The size of the simulated systems follows then from the above parameters and our computer facilities. We have found that the description of fluctuations in the spatially extended chemical systems given by the master equation agrees well with the molecular dynamics simulations. This conclusion is important because the numerical algorithm used for simulation of master equation are more efficient than those for MD, and they allow for simulations of larger systems at much longer time scales. However, the molecular dynamics methods give the insight into evolutions on the microscopic level, and therefore, they can be useful to describe nonequilibrium effects which are completely neglected in the ME approach.

Acknowledgment. This work was supported by Grant KBN 3T09A 120 08 provided by the Polish State Committee for Scientific Research.

References and Notes

(1) Nicolis, G.; Prigogine, I. *Self-Organization in Nonequilibrium Systems*; Wiley: New York, 1977.

(2) Ortoleva, P.; Yip, S. *J. Chem. Phys.* **1976**, *65*, 2045.

(3) Richter, P. H.; Procaccia, I.; Ross, J. *Adv. Chem. Phys.* **1980**, *43*, 217.

(4) *Stochastic Nonlinear Systems*; Arnold, L., Lefever, R., Eds.; Springer: Berlin, 1981.

(5) *Spatial Inhomogeneities and Transient Behaviour in Chemical Kinetics*; Gray, P., Nicolis, G., Baras, F., Borckmans, P., Scott, S. K., Eds.; Manchester University Press: Manchester, 1990.

(6) *Far-from-Equilibrium Dynamics of Chemical Systems*; Popielawski, J., Gorecki, J., Eds.; World Scientific: Singapore, 1991.

(7) Baras, F.; Malek Mansour, M. *Adv. Chem. Phys.* **1997**, *100*, 393.

(8) Gorecki, J.; Kawczyński, A. L. *J. Chem. Phys.* **1990**, *92*, 7546. Kawczyński, A. L.; Gorecki, J. *J. Phys. Chem.* **1992**, *96*, 1060. Kawczyński, A. L.; Gorecki, J. *J. Phys. Chem.* **1993**, *97*, 10358. Gorecki, J.; Kawczyński, A. L. *J. Phys. Chem.* **1996**, *100*, 19371.

(9) van Kampen, N. G. *Stochastic Processes in Physics and Chemistry*; North-Holland: Amsterdam, 1983.

(10) Gardiner, C. W. *Handbook of Stochastic Methods*; Springer-Verlag: Berlin, 1985.

(11) Breuer, H. P.; Huber, W.; Petrucione, F. *Physica D* **1994**, *73*, 257. Breuer, H. P.; Huber, W.; Petrucione, F. *Europhys. Lett.* **1995**, *30*, 69.

(12) Mazenko, G. F.; Valls, O. T.; Ruggiero, P. *Phys. Rev. B* **1989**, *40*, 384. Lemarchand, A.; Lesne, A.; Mareschal, M. *Phys. Rev. E* **1995**, *51*, 4457.

(13) de Pasquale, F.; Gorecki, J.; Popielawski, J. *J. Phys. A* **1992**, *25*, 433. Karzazi, M. A.; Lemarchand, A.; Mareschal, M. *Phys. Rev. E* **1996**, *54*, 4888.

(14) Mikhailov, A. S.; Schimansky-Geier, L.; Ebeling, W.; *Phys. Lett.* **1983**, *96A*, 453. Schimansky-Geier, L.; Mikhailov, A. S.; Ebeling, W. *Ann. Phys. (Leipzig)* **1983**, *40*, 277. Frankowicz, M.; Kawczyński, A. L. *J. Phys. Chem.* **1989**, *93*, 2755.

(15) Kapral, R. *J. Math. Chem.* **1991**, *6*, 113. Lawniczak, A.; Dab, D.; Kapral, R.; Boon, J. P. *Physica D* **1991**, *47*, 132. Kapral, R.; Lawniczak, A.; Masiar, P. *Phys. Rev. Lett.* **1991**, *66*, 2539.

(16) Gruner, D.; Kapral, R.; Lawniczak, A. *J. Chem. Phys.* **1993**, *99*, 3938.

(17) Goodman, R. H.; Graff, D. S.; Sander, L. M.; Leroux-Hugon, P.; Clement, E. *Phys. Rev. E* **1995**, *52*, 5904. Möller, P.; Wetzl, K.; Eiswirth, M.; Ertl, G.; *J. Chem. Phys.* **1986**, *85*, 5328. Schwankner, R. J.; Eiswirth, M.; Möller, P.; Wetzl, K.; Ertl, G. *J. Chem. Phys.* **1987**, *87*, 742.

(18) Allen M. P.; Tidesley D. J. *Computer Simulations of Liquids*; Clarendon Press: Oxford, 1987.

(19) *Oscillations and Traveling Waves in Chemical Systems*; Field, R. J., Burger, M., Eds.; Springer: Berlin, 1985.

(20) *Chaos in Chemistry and Biochemistry*; Field, R. J., György, L., Eds.; World Scientific: Singapore, 1993.

(21) Scheeline, A.; Olson, D. L.; Williksen, E. P.; Horras, G. A.; Klein, M. L.; Larter, R. *Chem. Rev.* **1997**, *97*, 739.

(22) Baras, F.; Malek Mansour, M. *Adv. Chem. Phys.* **1997**, *100*, 393.

(23) Baras, F.; Malek Mansour, M. *Phys. Rev. E* **1996**, *54*, 6139.

(24) Gorecki, J.; Gryko, J. *Comput. Phys. Commun.* **1989**, *54*, 245.

(25) Kawczyński, A. L.; Nowakowski, B. *Pol. J. Chem.* **1996**, *70*, 1468. Gorecki, J.; Kawczyński, A. L.; Nowakowski, B. *Pol. J. Chem.* **1997**, *71*, 244. Frankowicz, M.; Kawczyński, A. L. *Pol. J. Chem.* **1997**, *71*, 467. Nowakowski, B.; Kawczyński, A. L. *Acta Phys. Pol., B* **1997**, *28*, 2057.

(26) Kanel, Ya. I. *Mater. Sbor.* **1962**, *59*, 243 (in Russian).

(27) Fife, P. C. *Mathematical Aspects of Reacting and Diffusing Systems*; Springer, Berlin, 1979.

(28) Tikhonov, A. N. *Mater. Sbor.* **1952**, *31*, 575 (in Russian).

(29) Gorecki, J. *Mol. Phys. Rep.* **1995**, *10*, 48.

(30) Gorecki, J.; Kawczyński, A. L. *Pol. J. Chem.* **1997**, *71*, 1553.

(31) Boissonade, J. *Physica A* **1982**, *113A*, 607.

(32) Gillespie, D. T. *J. Phys. Chem.* **1977**, *81*, 2340.

(33) Nitzan, A.; Ortoleva, P.; Ross, J. *Faraday Symp. Chem. Soc.* **1974**, *9*, 241.