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Master Equation and Molecular Dynamics Simulations of Excitability in a Model Chemical System

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We study the influence of internal fluctuations on a simple but realistic model of a chemical system in an excitable regime. Numerical simulations of the master equation are compared with results of molecular dynamics simulations. We show that internal fluctuations are able to excite the system, which is initially at a stable stationary state. The dependence of escape time on the system's volume is studied. We observe that correlations of fluctuations in concentrations do not depend on the volume and the results of both simulation methods are in excellent agreement.

I. Introduction

Nonlinear dynamical systems and in particular chemical ones in the so-called excitable regime are sensitive to internal fluctuations. In the simplest case an excitable system has one attracting stationary state, which is approached by all trajectories starting from any point of the phase space. However, trajectories initialized near the stationary state are attracted directly to it, whereas those beginning at a little greater distance initially evolve from the stationary state and later on they are attracted to it. The behavior of an excitable system changes qualitatively if one takes into account internal fluctuations, which are always present in any real, dynamical system. Fluctuations can influence the behavior of the system in such a way that trajectories starting from the area of the direct attraction are switched outside of it. In this case, the system may be spontaneously excited and, moreover, subsequent spontaneous excitations can lead to apparently oscillatory behavior.[1] Internal fluctuations may be described by introducing noise terms to phenomenological dynamics (Langevin approach).[2] The more rigorous approach is based on the master equation (ME),[2−4] but the most complete description can be achieved using molecular dynamics (MD) techniques.[5] At the moment there is no chance of describing any real, macroscopic excitable system using these two approaches because one needs to consider an enormous number of variables (of the order of 10^{23}). Nowadays, in studies of the influence of internal fluctuations on excitable systems, one must construct simple models that can be treated by numerical calculations.[6,7] Recently, we have presented the model of an open chemical system that allows direct simulations of an oscillatory regime by the master equation approach and by the molecular dynamics technique, which uses reactive hard spheres.[8] When the values of parameters are changed, the same model can also describe excitability.

In this paper we present results of ME and MD simulations of the influence of fluctuations on the behavior of the model chemical system in the excitable regime, which initially is at the stationary state or in the area of its direct attraction. In the ME approach the dynamics of the system is considered as a random walk along states determined by populations of molecules. Although the MD technique is much more demanding from a computational point of view, it provides the complete description of the dynamics of the system, i.e., positions and momenta of all molecules. The internal fluctuations appear in the MD simulations as consequence of the complex nature of motion in many-body systems and the stochastic character of reactive collisions. The chemical model considered includes binary reactions only, and therefore, we can apply a very efficient MD algorithm for reactive hard spheres.[9]

The paper is organized as follows. section II introduces the phenomenological model we use. In section III we describe the simulation schemes. Section IV presents results, and section V discusses them.

II. Phenomenological Model

The model consists of the following elementary (bimolecular) reactions:

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

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

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

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

$$\mathrm{V} + \mathrm{S} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{U} + \mathrm{S} \tag{5}$$

This scheme is a modification of the 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

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scheme) by the reactant V. Moreover, the reactant V is transformed directly to the product U in step 5. It is assumed, that S is a solvent, whose concentration is maintained constant. The system is open, owing to step 1, in which the reactant V is produced from the reagent R, whose concentration is also maintained constant. The model (eqs 1−5) has been recently used in our studies on microscopic and stochastic simulations of an oscillating chemical system. By a modification of its parameters, we can use it to simulate a system in an excitable regime.

The dynamics of the system is described by five kinetic equations for V, U, E, X, and Y, but it is easy to see that $E(t) + X(t) + Y(t) = E_0$ is the first integral of the system. Therefore, one of the variables E, X, or Y can be eliminated, and the behavior of the system is described by four kinetic equations only. These equations have the form

$$\frac{\mathrm{d}V}{\mathrm{d}t} = k_1RS - k_{-1}VS - k_2VE + k_{-2}XS - k_4VX + k_{-4}(E_0 - E - X)S - k_5VS + k_{-5}US \quad (6)$$

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -k_2VE + (k_{-2} + k_3)XS \quad (7)$$

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_2VE - (k_{-2} + k_3)XS - k_4VX + k_{-4}(E_0 - E - X)S \quad (8)$$

$$\frac{\mathrm{d}U}{\mathrm{d}t} = k_3XS + k_5VS - k_{-5}US \quad (9)$$

where, for convenience, the symbols of the reagents are used to denote their concentrations because this notation does not cause any misunderstandings.

It is easy to check that eqs 6−9 have only one stationary state with the coordinates:

$$V_s = \frac{R}{K_1} \quad (10)$$

$$U_s = \frac{k_3E_0SR}{k_2k_{-5}(k_2(R^2/(K_1K_4) + RS) + K_1S^2(k_{-2} + k_3)} + \frac{R}{K_1K_5} \quad (11)$$

$$E_s = \frac{E_0S^2(k_{-2} + k_3)}{(R^2/(K_1^2K_4) + RS/K_1)k_2 + S^2(k_{-2} + k_3)} \quad (12)$$

$$X_s = \frac{E_0SRk_2}{(R^2/(K_1K_4) + RS)k_2 + K_1S^2(k_{-2} + k_3)} \quad (13)$$

where $K_i = k_{-i}/k_i$ for $i = 1$, 4, and 5.

For an appropriate choice of the rate constants and the concentrations of S, R, and E_0, eqs 6−9 describe an excitable system. The simulations can performed in an efficient way if the rate constants are not very different, which means that all reactions occur on a similar time scale. For the same reason ratios of the concentrations of all reagents must remain within 3 orders of magnitude of unity. In particular, in simulations described below we have used $S = 0.1$, $R = 0.2$, $E_0 = 0.2$ and $k_1 = 0.01$, $k_{-1} = 0.012$, $k_2 = 8.0$, $k_{-2} = 0.1$, $k_3 = 3.9$, $k_4 = 1.0$, $k_{-4} = 4.0$, $k_5 = 0.1$, $k_{-5} = 0.1$. For the chosen values of the parameters the concentrations at the stationary state are equal to

$$V_s = 0.16666, \quad U_s = 4.71035, \quad E_s = 0.03495, \quad X_s = 0.11650$$

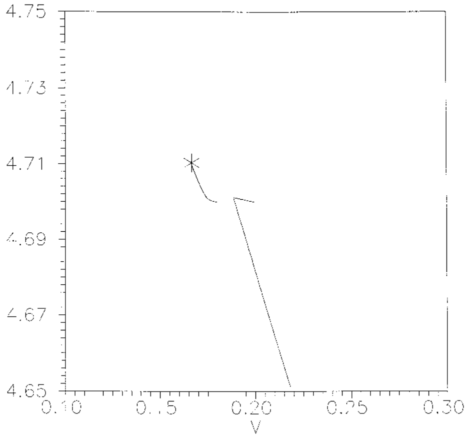

Figure 1. Projections of two trajectories obtained from numerical solutions of eqs 6−9 on the V × U plane. The evolutions substantially depend on initial conditions. The trajectory starting from $V = 0.18$, $U = 4.70$, $E = 0.03495$, $X = 0.1165$ directly approaches the stationary state (the large star), whereas other one beginning at $V = 0.20$, $U = 4.70$, $E = 0.03495$, $X = 0.1165$ initially goes away from the attracting point (only the initial fragment of this trajectory is shown).

and the characteristic equation for the linearized case, which describes the evolution of infinitesimal perturbations of the stationary state, has two negative and two complex eigenvalues equal to

$$\lambda_1 = -1.96316, \quad \lambda_2 = -0.75350, \quad \lambda_3 = -0.00573 + 0.00644\mathrm{i}, \quad \lambda_4 = -0.00573 - 0.00644\mathrm{i}$$

Trajectories beginning sufficiently close to the stable stationary state are attracted to it with decreasing amplitude. It is sufficient to change the initial condition a little. The variable U initially decreases to small values accompanied by a corresponding increase in V (see Figure 1). Next, V rapidly falls (U grows) below the value at the stationary state, and later on, we see a long time interval in which V approaches its asymptotic value.

III. Simulation Methods

In the mesoscopic treatment,[2−4] a state of the system is described by the probability distribution $P(N_V,N_U,N_E,N_X,t)$ of finding a given number of reagent molecules at time t (by assumption, populations N_S and N_R are kept constant). Let us consider a system that contains N_V,N_U,N_E, and N_X molecules of the respective species. The system “escapes” from the state described by this set of molecular populations when any of reactions 1−5 is performed. Thus, the total rate of “death” of this state is given by the total frequency of reactive collisions in the system

$$v(N_V,N_U,N_E,N_X) = \kappa_1N_RN_S + \kappa_{-1}N_VN_S + \kappa_2N_VN_E + (\kappa_{-2} + \kappa_3)N_XN_S + \kappa_4N_XN_V + \kappa_{-4}(N_{E_0} - N_E - N_X)N_S + \kappa_5N_VN_S + \kappa_{-5}N_UN_S \quad (14)$$

The coefficients κ_i are determined from the condition that this expression must agree with the rates of reactions in the phenomenological eqs 6−9. This requirement yields the relation $\kappa_i = k_i/\Omega$ between κ_i and the phenomenological rate constants k_i, where Ω is the volume of the system. Similarly, the rate of creation of a given state is a result of transitions from other states, associated with one of the reactions from the eqs 1−5. In this “birth” process, the final state is fixed but the initial state depends on what particular chemical reaction is performed. A balance of the “birth” and “death” rates yields the master equation, which describes the dynamics of the probability distribution function $P(N_V,N_U,N_E,N_X,t)$:

$$\frac{\partial P}{\partial t} = \kappa_1 N_R N_S P(N_V-1,N_U,N_E,N_X,t) + \kappa_{-1}(N_V+1)N_S P(N_V+1,N_U,N_E,N_X,t) + \kappa_2(N_V+1)(N_E+1)P(N_V+1,N_U,N_E+1,N_X-1,t) + \kappa_{-2}(N_X+1)N_S P(N_V-1,N_U,N_E-1,N_X+1,t) + \kappa_3(N_X+1)N_S P(N_V,N_U-1,N_E-1,N_X+1,t) + \kappa_4(N_V+1)(N_X+1)P(N_V+1,N_U,N_E,N_X+1,t) + \kappa_{-4}(N_{E_0}-N_E-N_X+1)N_S P(N_V-1,N_U,N_E,N_X-1,t) + \kappa_5(N_V+1)N_S P(N_V+1,N_U-1,N_E,N_X,t) + \kappa_{-5}(N_U+1)N_S P(N_V-1,N_U+1,N_E,N_X,t) - v(N_V,N_U,N_E,N_X)P(N_V,N_U,N_E,N_X,t) \quad (15)$$

The positive components of the right-hand side of the master equation describe the gain term corresponding to “creation” processes. The phenomenological eqs 6−9 can be recovered from the ME in the limit $\Omega \rightarrow \infty$ as the equations for the average concentrations $\langle N_i/\Omega\rangle$. Equation 15 applies to a homogeneous system, so it does not take into account local fluctuations.

From another point of view, the dynamics of a single chemical system can be regarded as a random walk in the configuration space, in which the coordinates are given by populations of molecules. The form eq 15 of the ME, involving discrete numbers N_α for populations of the species, is convenient for numerical simulations of this random motion. We have applied the method of Gillespie[10] to generate a random trajectory according to the following algorithm. Let us assume that the system at an instant t is in a state $\{N_V,N_U,N_E,N_X\}$. In the first step, a waiting time τ for escape of the system from this configuration point is sampled from the exponential distribution

$$\Theta(\tau) = v\exp(-v\tau) \quad (16)$$

in which v is given by eq 14. The next step consists of choosing a particular reaction, which causes a transition of the system to another point. The probability p_α of selection of a chemical process α from the scheme denoted by eqs 1−5 is proportional to the contribution of this reaction to the total rate v of reactive collisions. That means

$$p_\alpha = v_{-1}\kappa_\alpha \mathrm{N}_{\alpha 1}\mathrm{N}_{\alpha 2} \quad (17)$$

where $N_{\alpha 1}$ and $N_{\alpha 2}$ denote populations of molecules of the corresponding two species involved in the bimolecular reaction α. After the reactive collision, the populations $\{N_V,N_U,N_E,N_X\}$ are updated because they result from the chosen reaction α. Given this new state, the generation of the dynamics proceeds from the first step and so on.

The periodically extended MD technique for reactive hard spheres[11] is applied to simulate the time evolution of the system with reactions 1−5 at the microscopic level. The algorithm used in this paper is exactly the same as described in refs 7 and 8. All reactants E, R, S, U, V, X, and Y are represented by hard spheres with the same mass (m) and diameter (d). We assume that there are no thermal effects in reactions 1−5, so no kinetic energy is released or consumed when a reaction occurs. The spheres are labeled by a chemical identity parameter that defines their “chemical” properties but does not have any influence on the mechanical motion. In simulations all collisions between spheres are elastic. The rates of chemical processes are controlled by the steric factors (theyare denoted as s_i, s_{-i}, $i = 1, 5$). If a collision between spheres representing reagents of a particular process occurs, then a random number generator is called by the program, and if the resulting random number is smaller than the corresponding steric factor, then the collision is regarded as a reactive one. After such a collision the chemical identity parameters of the spheres involved are modified according to the reaction scheme depicted by eqs 1−5. Otherwise, the collision is nonreactive and the spheres retain their chemical identities.

In simulations the numbers of particles representing the reactants R and S are constant, which is achieved by assuming that the system contains nonreactive particles that play the role of a reservoir of R and S molecules.[12] If a particle of S (R) vanishes in one of the reactions, then simultaneously a randomly selected particle of reservoir 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) becomes a particle of reservoir. These processes have no influence on the dynamics of the system because they do not participate in eqs 1−5.

To make simulations efficient, we use a prerecorded trajectory representing a small system of spheres at thermal equilibrium as the database on the sequence of collisions.[11] Here, we study periodic expansions of a system of $N = 400$ hard spheres placed in a cubic box with a side of length $l = 12.5d$ (and thus, the packing fraction is $\eta \approx 0.11$). The prerecorded trajectory contained information on 12 800 000 collisions (over 30 000 collision per sphere). We assume that the density of the system is 8 [mol/L], which corresponds to the volume of the original box equal to $83.(3) \times 10^{-21}$ cm^3. We rescale the unit of volume used in the simulations to 10^3 cm^3/N_A = $1.6(6) \times 10^{-21}$ cm^3 where N_A is Avogadro’s number. The volume of the original box is equal to 50 in these units. In the new units the number concentrations of reagents are numerically equal to the concentrations in mol/L in the phenomenological equations.

The values of steric factors for MD simulations were obtained by scaling the phenomenological rate constants by 0.02, which leads to $s_1 = 0.0002$, $s_{-1} = 0.00024$, $s_{-2} = 0.002$, $s_2 = 0.16$, $s_3 = 0.074$, $s_4 = 0.02$, $s_{-4} = 0.08$, $s_5 = 0.002$, and $s_{-5} = 0.002$ for reactions 1−5, respectively. To adjust the frequencies of reactive collisions to the rate constants k_i appearing in the kinetic equations, the real time of the MD simulations t_{MD} is rescaled to the phenomenological time t according to

$$t = \frac{1}{8}d^2 g\sqrt{\frac{\pi k_B T}{m}}\frac{s_1}{k_1}t_{MD} \quad (18)$$

where $g = 1.35$ is the value of the radial distribution function at the sphere diameter d for the system of spheres characterized by the assumed density, k_B is the Boltzmann constant, and $T = 300$ K is the temperature of our system. The results of all simulations are presented using the phenomenological time scale. The prerecorded trajectory describes the time evolution within $t_e = 160$ time units. At the beginning of each MD simulation, the chemical identities are assigned to spheres in a random way and all remaining spheres are marked as the reservoir particles.

IV. Results

Figure 2 compares the results obtained in ME and MD simulations for a system with $\Omega = 17\,150$ with the numerical solution of eqs 6−9. Let us mention that the escape from the stationary state and its return require a much longer time than $t_e = 160$, which is reached in a single run of MD simulation.

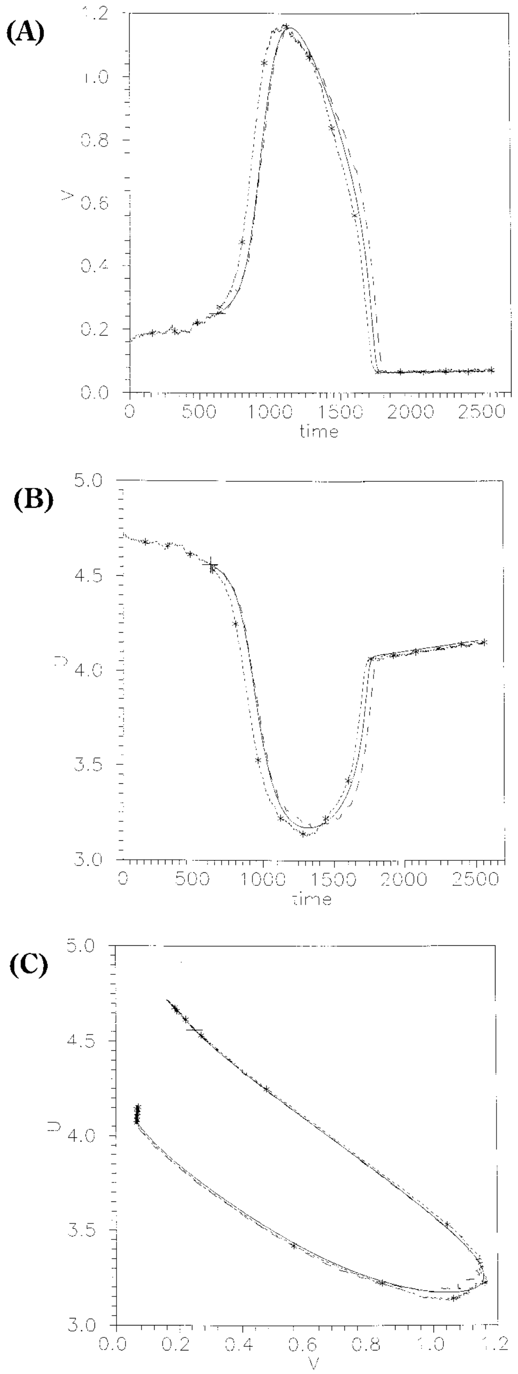

Figure 2. Concentrations of V (A) and of U (B) obtained in phenomenology (solid line), MD (the short dashed line) and ME (the long dashed line) simulations for $\Omega = 17\,150$ as functions of time. Stars mark the ends of intervals t_e long which correspond to the individual simulation MD programs. (C) Projections of the MD (dashed line) and phenomenological trajectory (solid line) for the initial condition $V(0) = 0.1666$, $U(0) = 4.710$, $E(0) = 0.0349$ and $X(0) = 0.1165$ on the $V \times$ U plane.

Therefore, to study a longer time behavior of the system by the MD technique, we have performed a single simulation in which the concentrations obtained at the end of one run were used as the initial conditions for the next one. This procedure introduces some stirring into our system after each t_e interval, and it destroys possible spatial correlations, which may appear between particles representing different reactants. The single long MD simulation drawn by the short dashed line is composed of several (16) individual MD programs. The ends of the individual MD programs are marked by stars in Figure 2. The solutions of the phenomenological equations (the solid line) and ME simulations (long dashed line) start from an arbitrary chosen initial condition belonging to the MD trajectory (the initial point is marked by a big cross). This initial condition belongs to the region of space in which the system's behavior is controlled by the phenomenological dynamics, and the agreement between phenomenology and both simulation methods is very good indeed. The projection of the ME and MD trajectories on the plane $V \times U$ is shown in Figure 2C, and also here, the results of both methods agree very well with phenomenology.

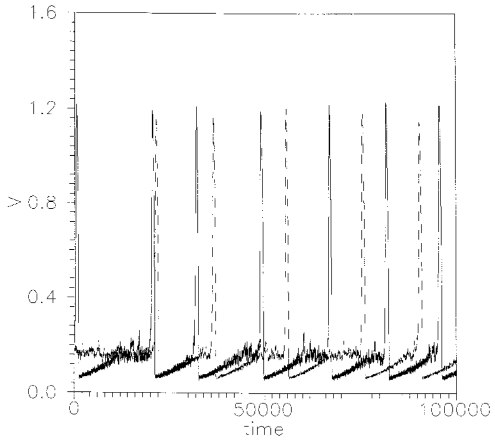

Figure 3. Concentration of V obtained in ME simulations as a function of time for a long interval $0 < t < 100\,000$. Results for $\Omega = 6250$ are plotted as a solid line and for $\Omega = 10\,800$ as a dashed line.

Figure 3 shows the concentration of V obtained in ME simulations for a time interval much longer than that in Figure 2 for systems with the volume $\Omega = 6250$ and 17 150. In all simulations presented below, the initial concentrations of reagents are equal to their values at the stationary state V_s, U_s, E_s, and X_s . The dependence of V on t (as well as other variables) exhibits apparently oscillatory character, with a random time interval separating the subsequent peaks. The peaks appear more frequently for the system with $\Omega = 6250$ because the smaller system more easily escapes from the region of direct attraction of the stationary state. This conclusion is confirmed in simulations of a still larger system with $\Omega = 50\,000$, for which we have observed only a single peak in the time interval $0 < t < 100\,000$. We can define the escape time from the stationary state as the time in which the concentration of V reaches 0.7 which is approximately half the height of the peaks in Figure 3. Using ME simulations, we have been able to calculate the distribution function of this escape time for our system with relatively small volumes $\Omega = 6250$ (from the sample of 26 000 trajectories) and $\Omega = 10\,800$ (from 11 000 runs). These results are shown in Figure 4. The distributions exhibit sharp maxima and long time tails. As expected, the most probable value of the escape time is greater for the larger system.

The results presented in Figure 2 indicate that the escape from the stationary state and the return to it require too long a time to be modeled by molecular dynamics. However, the influence of fluctuations is most important at the initial stage of the escape process because the evolution after the escape can be satisfactorily described by the phenomenology, as seen in Figure 2. For the initial parts of trajectories we have been able to obtain average behavior from MD simulations. We considered two sizes of the system: $\Omega = 6250$ and $\Omega = 10\,800$. The averages have been calculated from 36 reaction paths for $\Omega = 6250$ and 34 reaction paths for $\Omega = 10\,800$. For the same volumes of our system, the corresponding averages using the ME approach

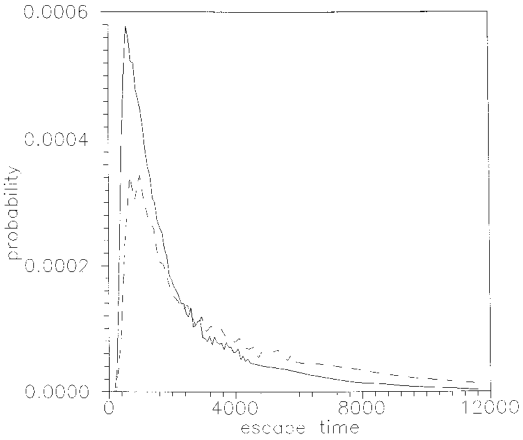

Figure 4. Distribution of escape times from the stationary state: results for Ω = 6250 (solid line); results for Ω = 10 800 (dashed line).

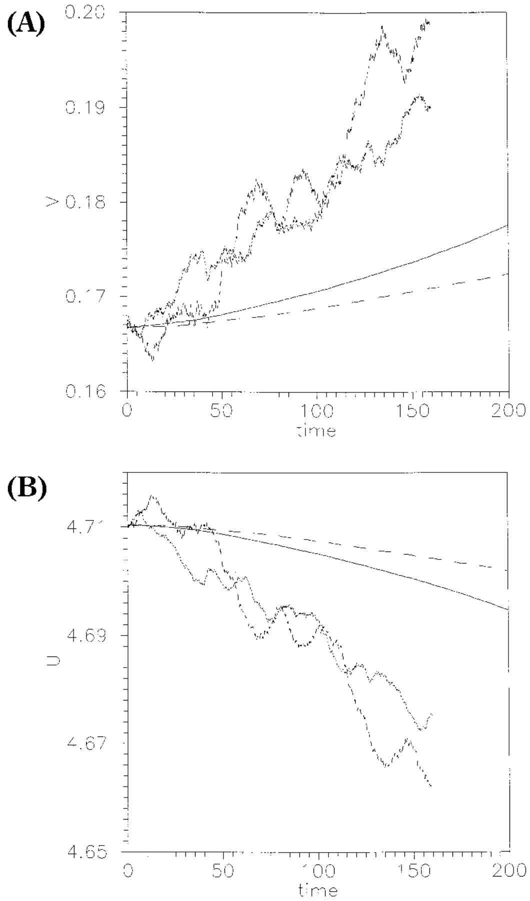

Figure 5. Average concentrations of V (A) and of U (B) obtained in MD and ME simulations for Ω = 6250 (short dashed line for MD and long dashed line for MD) and Ω = 10 800 (points for MD and solid line for ME) as functions of time.

have been obtained from 40 000 and 30 000 runs, respectively. We compare the mean concentrations, their dispersions, and cross correlations between fluctuations of concentrations calculated from these two approaches. The results are shown in Figures 5−7, in which the following notation is used. The solid and the long dashed lines represent the outcome of ME ensembles for Ω = 6250 and Ω = 10800, respectively. The dotted line and the short dashed line are obtained by averaging over MD samples. The escape of V and U concentrations from the stationary state is shown in Figure 5. The escape rates decrease with the system volume as internal fluctuations are reduced.

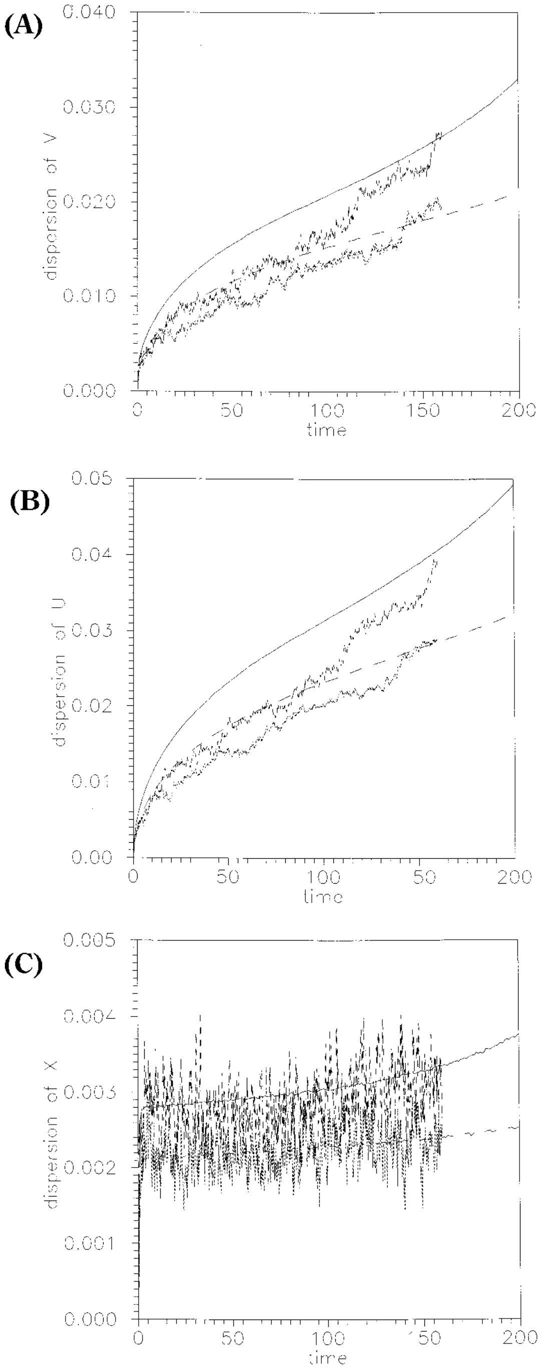

Figure 6. Dispersions of V (A), U (B), and X (C) obtained in MD and ME simulations for Ω = 6250 and Ω = 10 800 as functions of time. Notation is as in Figure 5.

Significant differences between ME and MD results are observed. The MD simulations give much faster escape compared with ME simulations. Figure 6 shows changes of dispersions of V, U, and X in time defined as

$$\sigma_A(t) = \sqrt{\langle (A(t) - \langle A(t)\rangle)^2 \rangle} \qquad (19)$$

where A = V, U, or X. The dispersions decrease with the system volumes, and the agreement between ME and MD is quite satisfactory.

In Figure 7 we show the correlations between fluctuations of concentrations as functions of time, which are calculated from

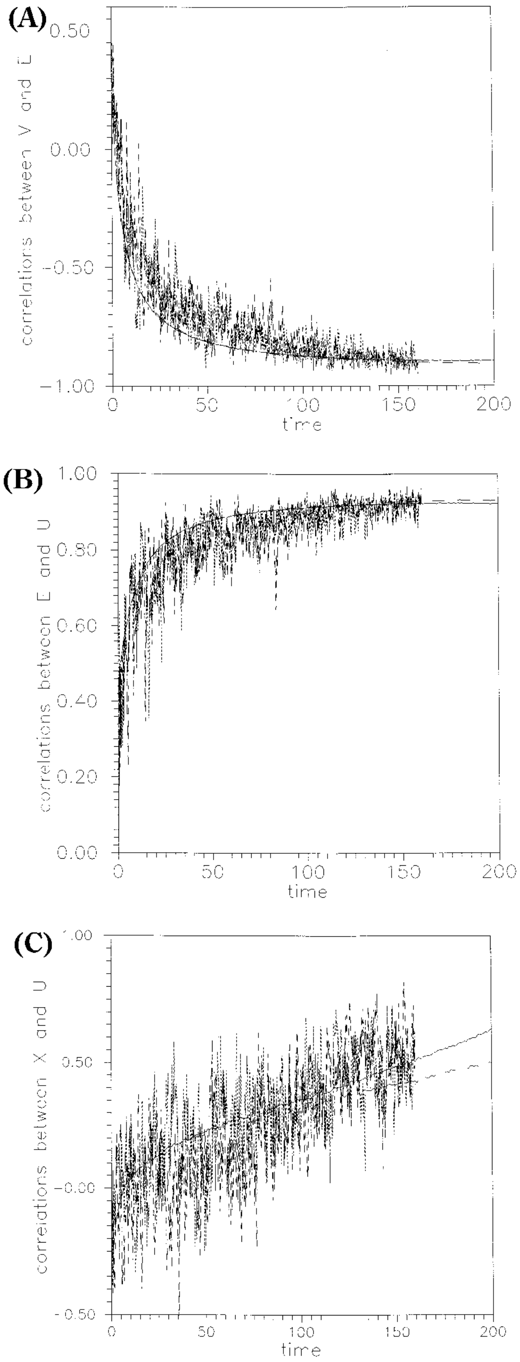

Figure 7. Correlations between V and E (A), E and U (B) and X and U (C) obtained in MD and ME simulations for $\Omega = 6250$ and $\Omega = 10\,800$ as functions of time. Notation is as in Figure 5.

$$\mathrm{Corr}(A,B,t) = \frac{\langle A(t)B(t)\rangle - \langle A(t)\rangle\langle B(t)\rangle}{\sigma_A(t)\sigma_B(t)} \tag{20}$$

The correlations decrease with the system volumes, and the agreement between ME and MD is excellent. As can be seen from Figure 7, the absolute values of the correlations Corr(V,E,t) and Corr(U,E,t) rapidly approach values close to 1. It means that the corresponding fluctuations become strongly correlated on a short time scale. These results can be understood because V and E as well as U and E participate directly in the elementary processes 2 and 3, respectively. The correlations Corr(U,X,t) are much smaller, and they develop on longer time scales than Corr(V,E,t) and Corr(U,E,t). It can be explained by the fact that U and X are not directly involved in any of reactions 1−5.

V. Discussion

In this paper we presented results of microscopic simulations for a chemical model of an excitable system. We have found that the internal fluctuations move the system out of the domain of direct attraction to the stationary state and that its further evolution is governed mainly by deterministic dynamics. Excitations exhibit stochastic character only in a small neighborhood of the stationary state, which is manifested by the randomness in times at which the subsequent peaks appear.

The model studied also describes limit cycle type oscillations.[8] By appropriate changes of the parameters, we can switch the system from an oscillatory regime to an excitable one and vice versa. There is an important difference in the apparently oscillatory behavior in the excitable system (see Figure 3) and in the system in the oscillatory regime. In the latter case we have observed that the period of oscillations does not depend on the volume of the system.[8] In the excitable system the apparent “period” of oscillations strongly increases with the volume. To explain this property, let us discuss in more detail the master equation. For large volumes, the discreteness of the ME becomes less important and eq 15 can be expressed in terms of continuum variables N_α/Ω, i.e., concentrations. This transformation yields the multivariable Fokker−Planck equation,[2,4] the form of which allows for a physical interpretation. Terms involving first derivatives with respect to concentrations are related to deterministic dynamics whereas terms with second derivatives describe dispersion of deterministic states, due to internal fluctuations in the system. The fluctuation terms are of the order of $1/\Omega$, and therefore, fluctuations play a more important role in systems with smaller volumes. As a result, the escape time from the stationary state increases with volume. Moreover, a large dispersion of apparent “periods” of oscillations increasing with the volume of the system should be observed in simulations of the excitable regime, whereas no such dependence has been found for the system in the oscillatory regime.[8] The conclusions on the role of fluctuations in the excitable system based on the ME are confirmed in the MD simulations. As can be seen in Figure 6, the dispersions as functions of time obtained in both simulations are in fair agreement, although the average values of the concentrations are different (see Figure 5). Moreover, the correlations between fluctuations agree very well (see Figure 7). Thus, we believe that the ME approach may be successfully applied to the study of the role of global fluctuations in nonlinear chemical systems.

We want to stress that the model presented in this paper does not contain any autocatalytic step and consists of bimolecular reactions only. The core of the model is commonly used in chemical and enzymatic kinetics. The inhibition of the Langmuir−Hinshelwood or Michaelis−Menten schemes described by step 4 is the simplest way to explain the decreasing rates of catalytic or enzymatic reactions observed for increasing concentration of a reactant in many reactions. Therefore, we believe that our model can be useful for looking at real systems, which can be tested experimentally for the influence of fluctuations.

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