

Monte Carlo simulations for a Lotka-type model with reactant surface diffusion and interactions

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The standard Lotka-type model, which was introduced for the first time by Mai *et al.* [J. Phys. A **30**, 4171 (1997)] for a simplified description of autocatalytic surface reactions, is generalized here for a case of mobile and energetically interacting reactants. The mathematical formalism is proposed for determining the dependence of transition rates on the interaction energy (and temperature) for the general mathematical model, and the Lotka-type model, in particular. By means of Monte Carlo computer simulations, we have studied the impact of diffusion (with and without energetic interactions between reactants) on oscillatory properties of the $A + B \rightarrow 2B$ reaction. The diffusion leads to a desynchronization of oscillations and a subsequent decrease of oscillation amplitude. The energetic interaction between reactants has a dual effect depending on the type of mobile reactants. In the limiting case of mobile reactants B the repulsion results in a decrease of amplitudes. However, these amplitudes increase if reactants A are mobile and repulse each other. A simplified interpretation of the obtained results is given.

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I. INTRODUCTION

In the last decade along with studies of dissipative structures in homogeneous catalytic reactions of the Belousov-Zhabotinskii type, considerable attention was attracted to the heterogeneous catalytic reactions. They reveal a whole spectrum of synergetic effects, e.g., rate oscillations, concentration waves, spirals, and chaos [1]. The heterogeneous systems are simpler than the homogeneous ones. Therefore, one can use for their study a number of powerful experimental and theoretical methods, which allows one to determine the origin of spatiotemporal structures.

In particular, the oscillatory kinetics was observed in heterogeneous catalysis on many metal surfaces as well as on oxide catalysts [1]. The mechanism of oscillations is different for various catalysts [2]. The more so, for the same catalyst the origin of oscillations is different in the high and low gas pressure limits. However, independently on the type of a catalyst, the global synchronization of oscillations is observed [1]. This fact implies the existence of very universal rules in the behavior of oscillatory systems, which exist independently on both type of catalyst and mechanism of a particular catalytic reaction.

One of the theoretical methods used to attack the problem of catalysis is a Monte Carlo (MC) computer simulation (see Refs. [3,4], and references therein). Its role considerably increased during the last years due to increase of computational facilities. The idea of the MC method is to define a *mathematical model*, which accounts for basic experimentally detected reaction steps. The reactants are assumed to be classical particles (usually denoted as A , B , etc.), which can occupy sites on a discrete lattice. This allows easily to describe adsorption, desorption, diffusion, and reaction of reactants as one- or two-site processes with the corresponding rates. Both reconstructed and non-reconstructed surfaces can be modeled by assigning different sticking coefficients of reactants to lattice sites. Some models consist of more than ten-step reactions. A detailed mathematical model often

complicates an analysis of simulation results and thus prevents from the understanding of basic driving mechanisms, e.g., the origin of synchronization of oscillations.

To study the very basic properties of catalytic systems, mathematical models, which are less detailed, are of particular importance. One of such models is the Lotka-type model introduced for a simplified description of the autocatalytic surface reactions by Mai *et al.* [5] and further employed in Refs. [6–8]. This is a single-parameter model, with two kinds of reactants. It was shown that reactant concentrations exhibit here stable oscillations independently of lattice size. Self-sustained oscillations of the model allows one to apply standard methods used for a treatment of oscillatory systems. For example, the resonance properties of the Lotka-type model were analyzed recently [9] by periodically varying in time the control parameter. Another model which, however, show unstable oscillations is the Lotka-Volterra model. The effects of the spatial constraints on the dynamics of this model was studied recently [10].

Diffusion of reactants in real catalytic surface reactions is a very quick and important process, which can lead to a formation of aggregates, clusters and spatial structures. This is why of particular interest are those mathematical models which take into account diffusion of reactants. The studies of chemical reaction kinetics with mobile reactants have a long history [4]. The diffusion is implemented usually as random walks on the lattice with and without energetic interaction between reactants. For example, the coagulation effects as diffusion-controlled processes were studied for $A + B \rightarrow$ inert reactions by Silverberg and Ben-Shaul [11]. The Ziff-Gulary-Barshad (ZGB) model, which mimics the catalytic $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ reaction, had been also extended for diffusion of reactants on a regular surface [12–14], diffusion on a reconstructing surface [15], and for diffusion and energetic interaction between reactants on a regular surface [16]. Chemical reactions with mobile and energetically interacting reactants on a reconstructing catalytic surface were studied by Zhdanov (see Ref. [17], and references therein). However,

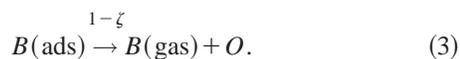
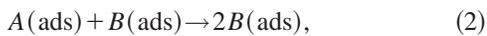
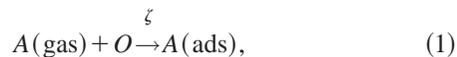
almost in all papers, which deal with reactant energetic interactions, the kinetic model is not defined uniquely. For the same system different authors use transition rates of elementary processes (e.g., adsorption, desorption, etc.), which could have or have not energetic (and temperature) dependence. It makes a comparison of the results practically impossible. The more so, the simulation algorithms are not always adequate to the problem. For example, in simulations of non-equilibrium processes in the kinetic model the method of Metropolis was used [17]. However, this method is defined only for equilibrium systems, where the kinetic aspects of the model are neglected.

In the present paper, we extend the standard Lotka-type model [5] via introduction of reactant diffusion. This step automatically leads to energetically dependent reaction rates. In particular, we are interested in determining and understanding the impact of mobile and interacting reactants on the temporal structures in the Lotka-type model.

The paper is organized in the following way. In Sec. II we introduce the standard Lotka-type model and generalize it by an incorporation of diffusion and energetic interaction of reactants. The algorithm and details of simulations is described in Sec. III. The simulation results and discussion are presented in Sec. IV. Lastly, conclusions are given in Sec. V. Taking into account the above-mentioned problems arising from incorporation of diffusion into the mathematical model, we give in Appendix A a detailed description of this procedure. The suggested *standard model* defines uniquely transition rates dependence on the interaction energy for all elementary process rates. The formalism can be applied to every kinetic lattice model. The relation between the ‘‘pair algorithm,’’ which is used in our MC simulations, and the master equation is given in Appendix B.

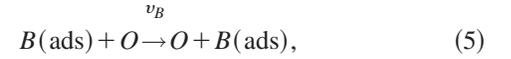
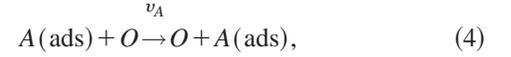
II. GENERALIZED LOTKA-TYPE MODEL

The Lotka-type model consists of two kinds of reactants labeled hereafter as $A(B)$, which are situated on a square discrete lattice. First, let us remind the definition of the standard Lotka-type model. The following rules are stated for reactants on the lattice: reactant A can be adsorbed from a gas phase in an empty site O with the adsorption rate ζ , Eq. (1):



If reactant A is located in the nearest neighbor (NN) position to an existing reactant B , an autocatalytic reproduction reaction takes place instantly, Eq. (2). It is assumed that this step takes no time. This leads to the state where reactants A and B never occupy NN positions. Reactant B can be desorbed with the rate $(1-\zeta)$, Eq. (3). It is sufficient to have these reactions for obtaining the temporal behavior—oscillations of reactant concentrations [5]. Secondly, the standard model can

be easily generalized by an incorporation of reactant diffusion. Reactant A (B) can jump to its NN site if it is empty:



with the jump rate v_J , where $J=A,B$. [The diffusion coefficient D_J is related to a jump rate by the following equation $D_J=(1/z)a^2v_J$, where z is a site coordination number and a is a lattice constant.] The jump rate for isolated reactant depends only on activation energy $e_{\text{act},J}$ (in the units of kT): $v_J=v_J^0=v_{0,J}\exp(-e_{\text{act},J})$, where $v_{0,J}$ is a pre-exponential factor and v_J^0 denotes the jump rate of noninteracting reactants. Lastly, we take into account an energetic interaction between reactants. To do it we introduce the energetic characteristics of the reactant configuration. If the two reactants are in the NN positions, their interaction energy equals to e_{AA} , e_{BB} , and e_{AB} (in the units of kT) depending on the type of reactants, AA , BB , AB , respectively. Since we are interested in determining the role of energetic interaction on temporal structures it is assumed that temperature T is constant, which allows us to consider energy terms $e_{JJ'}$ and $e_{\text{act},J}$ independently. The jump rate is weighted according to the reactant local configuration. The interaction energy at initial e_α and final e_β reactant state is calculated as

$$e_{\alpha,\beta}=e_{AA}n_A+e_{BB}n_B+e_{AB}n_{AB}, \quad (6)$$

where n_A (n_B) is the number of nearest reactants A (B) around the considered reactant and n_{AB} is the number of AB pairs, respectively. Finally, the jump rate for interacting reactants reads

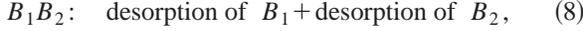
$$v_J=2v_J^0\frac{1}{1+\exp(e_\beta-e_\alpha)}, \quad (7)$$

see Appendix A for more details. If energetic interaction between reactants is neglected, then $e_\alpha=e_\beta=0$ and we obtain from Eq. (7) $v_J=v_J^0$.

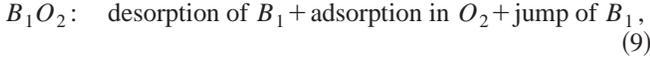
III. SIMULATION ALGORITHM

Unlike the standard MC, in our computer simulations we consider *pairs* of NN lattice sites. That makes a simulation procedure more transparent and its extension to two-site processes, such as diffusion, is straightforward. Relation between our simulation algorithm and a corresponding master equation is given in Appendix B. The considered algorithm has been used earlier (see, e.g., Refs. [18,19], and references therein). We want to stress here that on the basis of this algorithm it was proposed therein to use a very quick method of cellular automaton (CA) instead of usual MC. These methods coincide if the two conditions are fulfilled: The diffusion of reactants is very quick, and all transition rates are finite. Since these conditions are not fulfilled in the Lotka-type model, we have to use a standard MC procedure. Our simulation loop consists of the following steps.

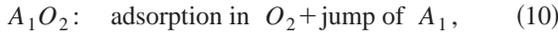
(1) The time update is determined as follows. All possible initial distributions i of reactants A (B) in the two lattice sites are considered. For each such a configuration all possible independent reactions Eqs. (1)–(5) are summed, which allows one to determine the transition rate p_i of changing the initial configuration:



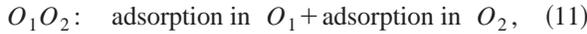
$$p_1 = 2(1 - \zeta),$$



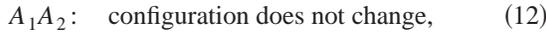
$$p_2 = 1 + 2v_B^0,$$



$$p_3 = \zeta + 2v_A^0,$$



$$p_4 = 2\zeta,$$



$$p_5 = 0,$$

where lower indices at X_1Y_2 denote the first and the second site of a pair. The step for an optimal time update is chosen to be proportional to an inverse of the maximal transition rate $dt = 1/\max(p_i)$. Time update cannot be chosen larger because the probabilities p_i are normalized to unity, i.e., $p_i dt < 1$ for all i . Time update can be chosen smaller, but then the computer code would not be very effective due to many empty loops.

(2) The simulation time is updated, $t \rightarrow t + 2dt/L^2$, where L is the lattice size.

(3) A random number (RN) is generated, in order to choose between horizontal or vertical orientations for a pair.

(4) Two RNs are generated to choose the coordinates of the pair.

(5) The state of chosen sites is determined. Depending on it, see Eqs. (8)–(12), one of independent reactions can be chosen randomly according to the standard MC simulation algorithm. For example, in the case of a pair A_1O_2 [Eq. (10)]: First, a RN is generated. Then reactant A adsorption step in O_2 is started if $\text{RN} < \zeta dt$, else if $\zeta dt \leq \text{RN} < p_3 dt$ the jump step of A_1 is started. Nothing happens if $\text{RN} \geq p_3 dt$.

(a) In a reactant A adsorption step, reactant A is created in the corresponding empty site. Then the system is checked for all AB pairs, which could be in the NN lattice sites. If such a pair is found, the autocatalytic reaction, Eq. (2), takes place instantly. The checking and autocatalytic steps are repeated until there are no AB pairs left in the lattice.

(b) In a reactant B desorption step, the corresponding B is removed from a lattice leaving empty site O .

(c) If the jump step is started, it does not necessarily mean that a reactant will really jump. The energy for initial and final configuration is calculated according to Eq. (6). A new

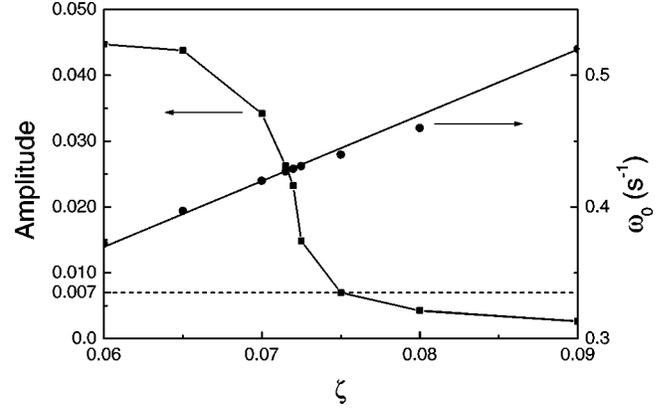


FIG. 1. The amplitude (squares) and frequency (circles) of oscillations vs the creation rate ζ of reactants A . The dashed line divides the oscillatory region (upper part) from the nonoscillation region (lower part).

RN is generated. A reactant jumps to the empty site only if condition $\text{RN} < 1/[1 + \exp(e_\beta - e_\alpha)]$ is fulfilled.

(6) Loop returns to the step (2) if t is less than a given simulation time.

IV. SIMULATION RESULTS

The lattice size effect on oscillations amplitude in the Lotka-type model was analyzed by Mai *et al.* [5]. They found that there is a large noise level for small lattices. Only for 1024×1024 lattices and larger is the noise reduced to the level where oscillations are clearly seen. In our simulations we use a square discrete lattice of 1024×1024 sites with periodic boundary conditions.

There is certain relaxation time in our simulations, which depends on initial concentration and distribution of reactants B . The requirement for initial conditions is the following: reactants B should be present in the lattice and their concentration should be nonzero after the relaxation time. Reactants A initially are not required, but they can be added in free sites, which do not contain reactants B as NN. After the relaxation time simulation results are independent on initial conditions. The following initial conditions are used: There are no reactants A at the beginning and half of the lattice is randomly filled with reactants B .

From the MC computer simulations for every set of external parameters (adsorption rate ζ , jump rate v_j , and interaction energy $e_{jj'}$) we obtain the time dependence of concentrations of reactants A and B . The power spectral density (PSD) analysis is performed on concentration of reactants B as a function of time (see Refs. [9,20] for details). As a result, both oscillation frequency ω_0 and amplitude at this frequency are determined for various diffusion regimes.

(i) First, a standard Lotka-type model is analyzed in terms of the reactant A adsorption rate ζ . The oscillatory behavior is found for small ζ values, Fig. 1. It arises as an interplay between the two processes, which to a first approximation could be considered separately. First, reactants A are created in lattice and they form statistically a percolating cluster. Second, at the same time, reactants B are mainly desorbed

whereas the percolating cluster of A extends. At some moment the percolating A cluster meets one of survived reactants B and thus it is transformed from a cluster of A 's to a cluster of B 's. The cycle then repeats once again, reactants B desorb and reactants A form a new percolating cluster.

To distinguish between oscillatory and nonoscillatory behavior, we postulate that nonoscillatory region occurs, when visually one can see no longer oscillations. The corresponding PSD amplitude, which separates these two cases, is $\text{Amp}_{\text{crit}} = 0.007$ —see dashed line in Fig. 1. The amplitude in the nonoscillatory region (below the dashed line) is approximately seven times less than the maximal amplitude obtained in the oscillatory region. In addition to the shape of concentration oscillations has lost the clear sinusoidal behavior, which now is distorted by a large noise level. The PSD method is so sensitive that it can determine an oscillation frequency and amplitude even in the nonoscillatory region, since the peak at oscillation frequency is distinguishable from the background. The critical adsorption rate for a given lattice size, which separate oscillatory and nonoscillatory regions, can be found readily from Fig. 1 to be $\zeta_{\text{crit}} = 0.075$. The PSD amplitude's excess above Amp_{crit} observed for $\zeta < \zeta_{\text{crit}}$ reflects an increase of amplitude of concentration oscillations. Further decrease of ζ is accompanied by a catastrophe in the Lotka-type model: Reactants A are created so slowly that all existing reactants B are desorbed before any autocatalytic reaction begins to take place. Under these conditions the system is poisoned by reactants A .

To extend definition of oscillatory and nonoscillatory regions to other lattice sizes one should note, that postulated Amp_{crit} is used instead of signal-to-noise ratio (SNR). Since the noise level in our simulations (lattice size 1024×1024) turns out to be a constant, the Amp_{crit} is proportional to the critical SNR and we use only the PSD criterium. To relate this criterium to other lattice sizes it is necessary to introduce the critical SNR, which is independent of lattice size. The corresponding critical value ζ_{crit} depends on lattice size. For larger lattices ζ_{crit} value increases, if we use the SNR criterium. Both PSD amplitude and noise level decrease with respect to the results obtained for smaller lattices, but their ratio SNR increases, due to very effective noise level reduction for large lattices. Reactant A poisoning threshold shifts to smaller ζ values with an increase of lattice size.

(ii) Next, we considered A (B) diffusion without energetic interactions between reactants. In a general case of nonoscillating reactions, diffusion can lead to a segregation of reactants [21]. In case of oscillating reactions one of the important questions is synchronization of local oscillations [18,28]. In the Lotka-type model the synchronization of oscillations is possible even without diffusion of reactants, therefore the role of diffusion is not so obvious.

We have observed that diffusion of reactants decreases the PSD amplitude of oscillations. In addition, reactant B diffusion is more effective in suppressing concentration oscillations than that of reactants A , see Fig. 2. Mobile reactants A form clusters thus screening the inner reactants A and preventing them from moving. Only surface reactants can diffuse, which makes reactant A diffusion less effective in damping oscillations. The frequency of oscillations in this

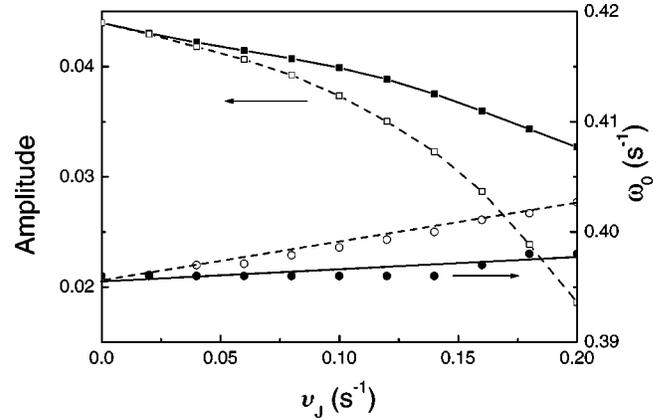


FIG. 2. The amplitude (squares) and frequency (circles) dependences on the jump rate ν_j of (i) reactants A , $J=A$ (solid interior) and (ii) reactants B , $J=B$ (open interior). Parameter $\zeta = 0.065$.

case is only slightly affected by mobile A , due to already discussed screening effect. In its turn, reactants B have more empty neighbor positions due to a random B desorption, Eq. (3). This makes reactant B diffusion more effective in the dumping oscillatory behavior. The frequency of oscillations increases with an increase of jump rate, Fig. 2. It reflects the fact, that, e.g., mobile reactants B find existing clusters of reactants A in a shorter time, which determines the higher oscillation frequency. Besides if some reactant B reaches a cluster of A quicker, the cluster of A does not have enough time to grow to a percolating size. As a result, we observe desynchronization of oscillations when the system splits into autonomously oscillating regions with different phases. This situation is similar to the case of the standard Lotka-type model without diffusion but at large parameter ζ values, Fig. 1.

As it was shown, the reactant diffusion modifies the amplitude of oscillations, which in turn affects the critical adsorption rate ζ_{crit} dividing oscillatory and nonoscillatory regions. The diffusion of B suppresses the oscillations and thereby decreases the ζ_{crit} value in a larger extent than diffusion of A , Fig. 3, due to already discussed reactant A screening effect. The dependence of critical adsorption rate on diffusion is nonlinear, e.g., in order to decrease the ζ_{crit} by $\approx 20\%$ one needs to increase the jump rate ν_A from 0 to 1 s^{-1} . Further to get the same decrease, one needs to change ν_A from 1 to 3 s^{-1} . The reactant A poisoning region below the dashed lines, see Fig. 3, is defined as follows: The system is poisoned at a value ζ if the poisoning occurs during the relaxation time, which for the considered cases is $\approx 100 \text{ s}$. This definition does not include cases when poisoning may occur at a later time due to statistical fluctuations of reactant B concentration. Thus the oscillatory behavior takes place for ζ values between the lines with solid (open) squares and solid (open) circles in case of reactant A (B) diffusion, see Fig. 3, respectively. Above the lines with squares (solid and open) the amplitude of oscillations is less than Amp_{crit} and it is nonoscillatory region according to our postulate. Below the lines with circles (solid and open) the reactant A poisoning occurs.

(iii) Lastly, the energetic interaction of reactants can con-

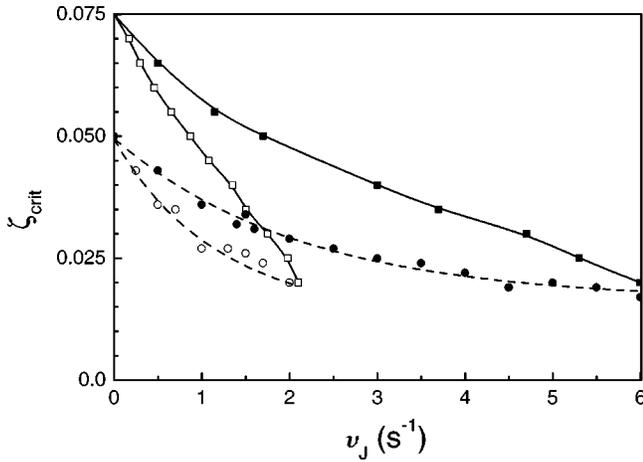


FIG. 3. The critical adsorption rate dependence on the jump rate v_J of (i) reactants A, $J=A$ (solid squares) and (ii) reactants B, $J=B$ (open squares), respectively. The border of the poisoning region is depicted as dashed line with solid (open) circles in the case of reactant A (B) diffusion.

siderably affect the oscillatory behavior. For example, an attraction between reactants promotes the formation of larger clusters. We consider the interaction between reactants only in NN sites, which determines the finite impact of interaction. For example, one could choose the interaction energy very large, but due to a short-range interaction, the effect will be still limited.

Let us now consider several limiting cases of *energetic interactions*. In a standard model the energetic interaction of reactants is taken into account only through diffusion of reactants, which is governed by three NN interaction energies e_{AA} , e_{AB} , and e_{BB} . In the limiting case, when one type of reactants is immobile, e.g., reactants A, the energetic parameter e_{AA} plays no role. Thus, we obtain a two-parameter model, where diffusion is governed only by e_{AB} and e_{BB} . Further, one can study separately the impact of each of these energetic parameters. In more complex situations when both energetic parameters are nonzero, usually some interference of corresponding limiting cases occurs.

First, let us consider the interaction effects in the case of mobile reactants B and immobile A. *Attraction* between similar reactants B ($e_{BB} < 0$) increases the amplitude of oscillations, see Fig. 4. This leads to a formation of clusters of B's, which reduces the reactivity of a single reactant B. This allows more reactants A to be accumulated in the system during an oscillation period and results in an increase of amplitude in Fig. 4. *Repulsion* between reactants B ($e_{BB} > 0$) promotes dissolving of clusters of B's. It makes every single reactant B to be even more effective in autocatalysis, Eq. (3). The frequency of oscillations decreases/increases slightly for $e_{BB} < 0$ and $e_{BB} > 0$, respectively. This reflects the fact, that for attracting/repelling reactants B it takes longer/shorter time to find a percolating cluster of A. The variation of amplitude with the energetic interaction saturates already for $|e_{BB}| > 2$, due to a short-range interaction nature used in our model.

Second, let us consider now the case of mobile reactants B with interaction between dissimilar reactants A and B. Re-

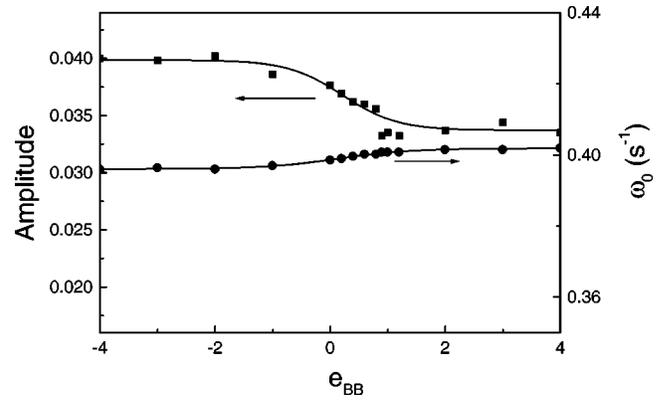


FIG. 4. The amplitude (squares) and frequency (circles) dependences on the dimensionless energetic interaction e_{BB} between similar reactants BB. The jump rate $v_B = 0.10 \text{ s}^{-1}$, $\zeta = 0.065$. No interaction, $e_{AA} = e_{AB} = 0$.

pulsion between reactants A and B, $e_{AB} > 0$, makes it harder for B to make a jump to an empty position, which has a reactant A in its nearest neighborhood. It promotes formation of large clusters of A's, which is reflected in an increase of PSD amplitude, Fig. 5. Oscillation frequency decreases slightly thus indicating that the time needed for a creation of percolating cluster of A has increased too. Contrary, an attraction between reactants A and B, $e_{AB} < 0$, leads to a decrease of the PSD amplitude, see Fig. 5. The period of oscillations is slightly decreased, which implies that mobile B finds quicker clusters of A. This prevents a creation of large clusters of A's and thus the PSD amplitude decreases.

The large amplitude dispersion observed in Fig. 5 is due to the following reasons. To reduce the simulation time, we have assumed that concentration oscillations have no memory effect. Thus, we used a single long simulation run, i.e., we neglected the relaxation time only once. We considered various parts from a simulation as independent simulations, in order to get an average of PSD amplitude. This method works fine in many cases. However, for the case of attraction between AB the system obviously has memory effects. We choose this method as a compromise between the

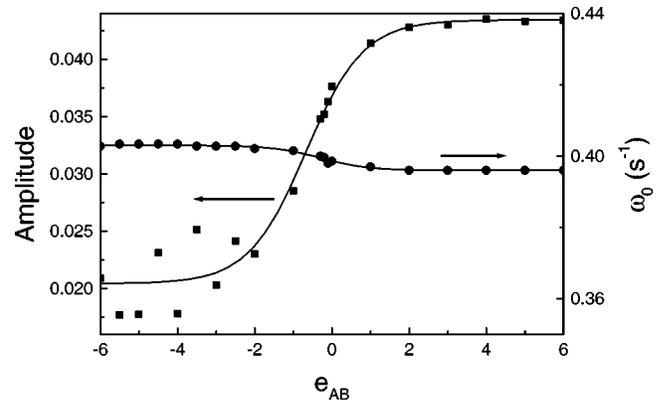


FIG. 5. The amplitude (squares) and frequency (circles) dependences on the dimensionless energetic interaction e_{AB} between dissimilar reactants AB. The jump rate $v_B = 0.10 \text{ s}^{-1}$, $\zeta = 0.065$. No interaction between similar reactants, $e_{AA} = e_{BB} = 0$.

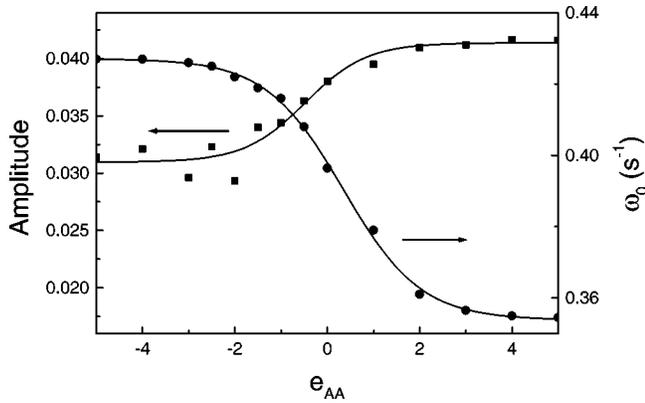


FIG. 6. The amplitude (squares) and frequency (circles) dependences on the dimensionless energetic interaction e_{AA} between similar reactants AA . The jump rate $\nu_A = 0.14 \text{ s}^{-1}$, $\zeta = 0.065$ and $e_{AB} = e_{BB} = 0$.

accuracy of the results and large simulation time.

Third, we consider now the case when reactants A are mobile but B 's do not move. An incorporation of interaction between reactants A and B gives results similar to the case of mobile reactants B : Repulsion between reactants A and B allows accumulation of more reactants A per period, which increases the amplitude. Contrary to the mobile B case, the frequency of oscillations is not changed at all.

Fourth, an interesting case occurs if only reactants A are mobile and we consider the energetic interaction only between AA , Fig. 6. Since the Lotka-type model is asymmetric with respect to A and B reactants, this behavior differs from the case of interacting and mobile reactants B . Now, if we consider an attraction between reactants AA ($e_{AA} < 0$), the percolating cluster of A 's is created quicker (the critical concentration of reactants A is less than that in the noninteracting case). This process takes shorter time and, as a result, the amplitude and the period of oscillations decrease (the frequency increases), as observed from simulations in Fig. 6. In the case of repulsion between reactants AA , the critical concentration of reactants A should be larger, in order to create a percolating cluster of A 's. Reactants A , which sit on the surfaces of clusters, repel from reactants A in their NN positions. Thus, a loose structure is formed, which can accumulate additional reactants A . This process is more time consuming which is well seen from a decrease of the frequency for $e_{AA} > 0$, see Fig. 6.

V. CONCLUSIONS

It is well known that the standard Lotka-type model has a self-sustained oscillatory behavior [5]. Therefore, we were able to expand this standard model by an incorporation of diffusion of reactants and to analyze the impact of diffusion on the temporal structures. Since diffusion is a reversible process, which leads the system to equilibrium, we introduced the energetic (and temperature) dependence into the model. In Appendix A a detailed description of this procedure is given, which however is not unique, unless we introduce the standard model.

Usually diffusion can give rise to the spatiotemporal structures, such as running waves or spirals. In our computer simulations the spatial structures were not found, because of a peculiarity of the Lotka-type model. Namely, an infinite reaction rate $A + B \rightarrow 2B$ determines, that configurations with reactants A and B in the NN sites do not exist. In other words, the front of reaction goes with an infinite speed and all clusters of A 's are transformed into clusters of B 's instantly, without any reaction front.

We have observed that diffusion results only in desynchronization of concentration oscillations. The amplitude of oscillations decreases with an increase of diffusion. Particularly, diffusion of reactants A is less effective in destroying the oscillatory behavior, because reactants A form clusters and only a portion of reactants at cluster surfaces can diffuse, whereas most of inner reactants A are screened. In contrast, clusters of reactants B are more loose due to reactant B desorption. Thus, reactants B turn out to be more mobile, which results in more pronounced mobility effects.

Lastly, a nontrivial behavior has been observed in the case of mobile and interacting reactants A . For example, repulsion between reactants AA leads to such a reactant distribution, which accumulates more reactants A before the percolation cluster of reactants A occurs. This results in an increase of the amplitude and decrease of the oscillation frequency.

To understand the impact of diffusion, we used here a simple mathematical model. More detailed models could better reproduce experimentally observed structures. However, the understanding of the mechanisms of these phenomena is often problematic or even impossible. Therefore, models such as the Lotka-type are of great importance, since they allow one to study and understand individual processes, e.g., diffusion or energetic interaction, independently of other factors.

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APPENDIX A: DEFINITIONS OF TRANSITION RATES

The kinetic model is uniquely defined by a set of possible states of a stochastic system and the transition rates between these states. To extend the mathematical model by an incorporation of the energetic interaction between reactants, one has to define the transition rate dependence on the energy and temperature. However, this procedure is not unique.

Let us consider for the illustration an elementary transition of a system from the state α to the state β . Examples are (i) process of diffusion, considered as a jump from one lattice site to another; (ii) adsorption/desorption of a reactant from a gas phase on a randomly chosen empty lattice site. In the first case the system is closed and a number of reactants is preserved (a single mobile reactant), but the total systems energy changes after diffusion jump due to different configurations of surrounding reactants. In the second case, the sys-

tem is open. The state α corresponds to an absent reactant (empty site), whereas the state β corresponds to an adsorbed reactant (occupied site), which interacts with its neighborhood.

Now, let us fix the configuration of reactants and allow one of the following events: in the case of (i) reactant either can jump to the NN empty site thus leaving the initial configuration, or jump from NN occupied site to empty site (two-site process). In the case (ii) reactant can be adsorbed/desorbed on a single site (one-site process). The kinetics of these extremely simplified processes is described by the kinetic equation

$$\begin{aligned} \frac{dW(\beta)}{dt} &= - \frac{dW(\alpha)}{dt} \\ &= K(\alpha \rightarrow \beta)W(\alpha) - K(\beta \rightarrow \alpha)W(\beta). \end{aligned} \quad (\text{A1})$$

Here $W(\alpha)$ and $W(\beta)$, $W(\alpha) + W(\beta) = 1$, are probabilities to find the system in the state α and β , $K(\alpha \rightarrow \beta)$ and $K(\beta \rightarrow \alpha)$ are transition rates from one state to another, respectively. As a result of such processes, the local equilibrium should be reached in the limit $t \rightarrow \infty$

$$W^{\text{eq}}(\beta) = f(\varepsilon, \mu), \quad W^{\text{eq}}(\alpha) = 1 - f(\varepsilon, \mu), \quad (\text{A2})$$

where $\mu = 0$ in the case (i) and $\mu \neq 0$ in the case (ii). The function

$$f(\varepsilon, \mu) = \frac{1}{1 + \exp[(\varepsilon - \mu)/k_B T]}, \quad (\text{A3})$$

where μ denotes chemical potential and $\varepsilon = E_\beta - E_\alpha$. Equation (A3) might look similar to the Fermi-Dirac distribution. However, this is not a case. The fermionic shape of distribution is determined by the following fact: We have considered one reactant in the two possible states. If one would like to consider the adsorption-desorption of not a monomer but a dimer (still two possible states, but now for a pair of reactants) Eq. (A3) should be correspondingly modified, see Ref. [22] for details. The unknown chemical potential μ is usually determined from the given average number of particles in a system. Quite different assumption is used in the kinetic models: The chemical potential is determined by the corresponding direct and backward transition rates from an initial state to a final one, see below for details. The unique definition of the transition rates is impossible, because the equilibrium condition of Eq. (A1) gives only the ratio of transition rates but not the rates themselves:

$$\frac{K(\alpha \rightarrow \beta)}{K(\beta \rightarrow \alpha)} = \frac{W^{\text{eq}}(\beta)}{W^{\text{eq}}(\alpha)}. \quad (\text{A4})$$

In other words, the kinetic model with reactant energetic interaction is not defined uniquely by the analysis of the limiting case, where one can use the Gibbs statistics. The same equilibrium distribution (if it takes place) could be reached with different transition rates.

To solve this problem, it was suggested [22] to use a so-called standard model for describing the chemical reac-

tions. We note that ideas of the standard model applied for simpler systems such as the kinetic Ising model, gives already known definition of individual transition rates suggested by Glauber [23] (see also Refs. [24–27]).

It is defined in the standard model that

$$K(\alpha \rightarrow \beta) = QW^{\text{eq}}(\beta), \quad K(\beta \rightarrow \alpha) = QW^{\text{eq}}(\alpha), \quad (\text{A5})$$

where Q is a cofactor independent of α and β , which value is defined by the procedure described below. This ansatz, Eq. (A5), fulfils the requirements of Eq. (A4).

To find the cofactor Q , let us consider the limiting case of a surface, where there are no other reactants in the neighborhood of a given reactant. Formally this limit corresponds to the value $\varepsilon = 0$ in Eq. (A5). So, in the case of diffusion, the parameter $\mu = 0$ and $f(0, 0) = 1/2$, then the right hand sides of Eq. (A5) in this limit give $Q/2$. These relations determine the jump rate on an empty surface. If we denote it by v^0 then we arrive at the relation $Q = 2v^0$.

Now we consider the case when the number of reactants changes. According to our interpretation, in case (ii), the limit $\varepsilon = 0$ for the transition rate $K(\alpha \rightarrow \beta)$ should give an adsorption rate p on an empty surface $Qf(0, \mu) = p$. For the reverse process (desorption from an empty surface k) we get $Q[1 - f(0, \mu)] = k$, correspondingly. As a result, we have two equations for two unknown values Q and μ . This allows us to determine uniquely the transition rates in the general case. We arrive at the relations

$$Q = p + k, \quad \frac{p}{k} = \frac{f(0, \mu)}{1 - f(0, \mu)}. \quad (\text{A6})$$

The last equations establish an important property of the standard model. Namely, they allow one to define the energetic dependence for the transition rates.

For example, let us consider the irreversible adsorption in the Lotka-type model: Reactant A could be adsorbed with $p \neq 0$, but the desorption is forbidden $k = 0$. The irreversible process then is defined as a limiting case, when the transition rate k tends to zero. It follows from Eq. (A6) that $Q = p$ and $f(0, \mu) = 1$ (or $\mu \rightarrow \infty$). Taking this into account and considering the case $\varepsilon \neq 0$, we obtain the adsorption rate to follow $pf(\varepsilon, \mu) = p$ for every neighboring configuration of reactants. In other words, we have to use a constant transition rate, which is independent of energetic interactions. The described methodology applied to other irreversible processes leads to energetically independent transition rates.

In summary, we wish to note, that three irreversible processes in the Lotka-type model are adsorption of A , desorption of B , and the reaction $A + B \rightarrow 2B$. It means that energetic interactions in these processes are trivial by definition, i.e., transition rates are energetically independent constants. We should take energetic interaction into account in the only reversible process, namely diffusion.

The standard model defines uniquely the energetic dependence of every transition rate. The formulation of the standard model eliminates the ambiguity in the previous definitions of mathematical models, when energetic dependence could be freely attributed to some parameters.

APPENDIX B: THE BASIS OF THE PAIR ALGORITHM

Below we give the formal foundations of our algorithm. It was already used without detailed description in a series of papers [18,28–31], where it was applied to different problems of the surface reaction kinetics. The main advantages of the proposed algorithm are (i) its universality (adding of a new process does not demand rewriting a whole code) and (ii) it is very quick (the code mainly generates random numbers and compares these numbers with predefined limits of processes). We do not consider here the energetic interaction between particles, in order to keep the explanation transparent. The corresponding generalization can be easily done.

The suggested algorithm “translates” the master equations of the defined class of kinetic lattice models to the language of MC simulation. We consider the lattice with equivalent sites (the coordination number is z). The state of each site \mathbf{l} is determined by a variable σ_l , which can have different values: 0 (empty site), A (site occupied by a reactant A), etc. The kinetic model is characterized by a set of elementary events and transition rates. The change of elementary events determine the change of the state of a whole system $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \dots)$. In the development of algorithm, we have chosen one important class of lattice models: namely, we allow for only monomolecular and bimolecular processes (the terminology and abbreviation follows [18,19]). The bimolecular processes are allowed only for particles in the NN positions. The monomolecular processes are defined as processes, which result in a change of only one site of a lattice. Examples are adsorption ($0 \rightarrow A$) and desorption ($B \rightarrow 0$) of a monomer. The bimolecular processes describe diffusion ($A0 \rightarrow 0A$), ($B0 \rightarrow 0B$) and reaction (annihilation) of the nearest two reactants ($AB \rightarrow 00$). In this case the state of two sites changes simultaneously.

1. Master equation

The master equation for the model of a chosen class looks quite simple:

$$\frac{d}{dt}\rho(\boldsymbol{\sigma}) = \frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{in}} - \frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{out}}, \quad (\text{B1})$$

where

$$\begin{aligned} \frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{in}} = & \sum_{\mathbf{l}} \sum_{\sigma'_l} P(\sigma'_l \rightarrow \sigma_l) \rho(\boldsymbol{\sigma}'_l) \\ & + \frac{1}{z} \sum_{\sigma'_l, \sigma'_m} \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} Q(\sigma'_l \sigma'_m \rightarrow \sigma_l \sigma_m) \rho(\boldsymbol{\sigma}'_{lm}), \end{aligned} \quad (\text{B2})$$

$$\begin{aligned} \frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{out}} = & \sum_{\mathbf{l}} \sum_{\sigma'_l} P(\sigma_l \rightarrow \sigma'_l) \rho(\boldsymbol{\sigma}_l) \\ & + \frac{1}{z} \sum_{\sigma'_l, \sigma'_m} \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} Q(\sigma_l \sigma_m \rightarrow \sigma'_l \sigma'_m) \rho(\boldsymbol{\sigma}_{lm}). \end{aligned} \quad (\text{B3})$$

Here we use the following notations: $\boldsymbol{\sigma}_l = (\sigma_1, \dots, \sigma_l, \dots)$, $\boldsymbol{\sigma}'_l = (\sigma_1, \dots, \sigma'_l, \dots)$, $\boldsymbol{\sigma}_{lm} = (\sigma_1, \dots, \sigma_l, \sigma_m, \dots)$, $\boldsymbol{\sigma}'_{lm} = (\sigma_1, \dots, \sigma'_l, \sigma'_m, \dots)$. The transition rates of monomolecular processes are denoted as $P(\sigma_l \rightarrow \sigma'_l)$, those for bimolecular processes as $Q(\sigma_l \sigma_m \rightarrow \sigma'_l \sigma'_m)$. The symbol $\langle \mathbf{l}, \mathbf{m} \rangle$ stands for a summation of pairs, which are NNs. The cofactor $1/z$ has been used for the convenience in the further transformations (see Refs. [18,31]).

If transition rates for monomolecular and bimolecular processes are described using abbreviation

$$\begin{aligned} w(\lambda \mu \rightarrow \lambda' \mu') = & \frac{1}{z} [Q(\lambda \mu \rightarrow \lambda' \mu') + P(\lambda \rightarrow \lambda') \delta_{\mu \mu'} \\ & + P(\mu \rightarrow \mu') \delta_{\lambda \lambda'}], \end{aligned} \quad (\text{B4})$$

where $\delta_{\lambda \mu}$ stands for Kronecker delta symbol then Eqs. (B2) and (B3) obtain a very compact form

$$\frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{in}} = \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} \sum_{\sigma'_l, \sigma'_m} w(\sigma'_l \sigma'_m \rightarrow \sigma_l \sigma_m) \rho(\boldsymbol{\sigma}'_{lm}), \quad (\text{B5})$$

$$\frac{d}{dt}\rho(\boldsymbol{\sigma})\Big|_{\text{out}} = \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} \sum_{\sigma'_l, \sigma'_m} w(\sigma_l \sigma_m \rightarrow \sigma'_l \sigma'_m) \rho(\boldsymbol{\sigma}_{lm}). \quad (\text{B6})$$

The transition rates introduced in Eq. (B4) describe general pseudobimolecular transitions in two NN sites. The transition $\sigma_l \sigma_m \rightarrow \sigma'_l \sigma'_m$ is considered as both: a real bimolecular transition (the state of two sites changes instantly) and pseudotransition (the state of one of the sites does not change). The goal of the transformation is to demonstrate that the kinetics of the given class of problems formally can be described using only pair pseudoelementary processes.

2. Monte Carlo

Formally the MC simulations are equivalent to the problem of random walks in multidimensional space $\boldsymbol{\sigma}$ (the state of a whole system). For the given class of kinetic problems, in every step only two projections of the vector $\boldsymbol{\sigma}$ can be changed simultaneously.

The random walks are described by a set of equations

$$\rho_{n+1}(\boldsymbol{\sigma}) = \sum_{\boldsymbol{\sigma}'} U(\boldsymbol{\sigma}' \rightarrow \boldsymbol{\sigma}) \rho_n(\boldsymbol{\sigma}'), \quad (\text{B7})$$

which for the kinetic applications should be accompanied by an additional relation, which determines the time

$$t_{n+1} = t_n + \delta t_n. \quad (\text{B8})$$

Here $\rho_n(\boldsymbol{\sigma})$ is the probability to find the system in a state $\boldsymbol{\sigma}$ at the n th microscopical step, t_n the corresponding time, δt_n the time increment, $U(\boldsymbol{\sigma}' \rightarrow \boldsymbol{\sigma})$ the transition probability from state $(\boldsymbol{\sigma}')$ to state $(\boldsymbol{\sigma})$.

We use the following normalization condition for the transitions:

$$\sum_{\boldsymbol{\sigma}'} U(\boldsymbol{\sigma} \rightarrow \boldsymbol{\sigma}') = 1, \quad (\text{B9})$$

which determines the normalization of probabilities $\rho_n(\boldsymbol{\sigma})$ to

$$\sum_{\boldsymbol{\sigma}} \rho_n(\boldsymbol{\sigma}) = 1. \quad (\text{B10})$$

For the models of a given class with pseudobimolecular transitions

$$\rho_{n+1}(\boldsymbol{\sigma}) = \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} \frac{1}{M} \sum_{\sigma'_l, \sigma'_m} u(\sigma'_l \sigma'_m \rightarrow \sigma_l \sigma_m) \rho_n(\boldsymbol{\sigma}'_{lm}) \quad (\text{B11})$$

the transition probabilities in a random pair $u(\lambda \mu \rightarrow \lambda' \mu')$ are normalized to unity

$$\sum_{\lambda' \mu'} u(\lambda \mu \rightarrow \lambda' \mu') = 1. \quad (\text{B12})$$

Equation (B11) has a clear mathematical structure and corresponds to the following MC algorithm.

A pair of NN sites is chosen randomly from a number of pairs $M = (z/2)L^2$ available on a lattice of size L [the cofactor $1/M$ in Eq. (B11) stands for the probability to choose the corresponding pair].

One of the possible events in the pair is chosen randomly (with the help of a random number $\varsigma \in [0,1)$ according to the weight $u(\lambda' \mu' \rightarrow \lambda \mu)$). As a result, two variables of the state of sites are changed correspondingly, $\sigma'_l \sigma'_m \rightarrow \sigma_l \sigma_m$.

3. The transition scheme from the master equation to the Monte Carlo

Now we have to establish the relation between the master equation and the random walks (and MC). In other words, we have to relate the language of the transition rates (and time) and language of the transition probabilities (and MC steps). We use here the differential transition scheme, where we exploit the analogy between Eqs. (B1) and (B11) and we choose the algorithm with $\delta t_n = \text{const}$. Several transition schemes were suggested in Ref. [15], where the time step δt_n is a random variable and its value is determined from the corresponding distribution. The methods described in Ref. [15] are related to the previously considered algorithm in the same manner as continuous-time random walks (CTRW) introduced by Montroll and Weiss [32] is related to the problem of random walks. Both approaches are practically identical, if the average value $\langle \delta t_n \rangle$ in CTRW coincides with δt in the random walks problem. The CTRW schemes require more random numbers. A comparison of these two methods has revealed that our algorithm is a very economic one.

To connect the formalism of random walks and the master equation, let us first construct the differential analog of a derivative from Eq. (B7)

$$\frac{\rho_{n+1}(\boldsymbol{\sigma}) - \rho_n(\boldsymbol{\sigma})}{\delta t_n} = \frac{1}{\delta t_n} \left[\sum_{\boldsymbol{\sigma}'} U(\boldsymbol{\sigma}' \rightarrow \boldsymbol{\sigma}) \rho_n(\boldsymbol{\sigma}') - \sum_{\boldsymbol{\sigma}'} U(\boldsymbol{\sigma} \rightarrow \boldsymbol{\sigma}') \rho_n(\boldsymbol{\sigma}) \right], \quad (\text{B13})$$

where the normalization condition of Eq. (B9) is used on the right hand side. The differential equation is obtained using the correspondences

$$\frac{\rho_{n+1}(\boldsymbol{\sigma}) - \rho_n(\boldsymbol{\sigma})}{\delta t_n} \Rightarrow \frac{d}{dt} \rho(\boldsymbol{\sigma}), \quad \rho_n(\boldsymbol{\sigma}) \Rightarrow \rho(\boldsymbol{\sigma}), \quad (\text{B14})$$

with t instead of t_n , and $\rho(\boldsymbol{\sigma})$ instead of $\rho_n(\boldsymbol{\sigma})$. Secondly, the time increment can be chosen constant $\delta t_n = \delta t = \text{const}$ (the method is easily generalized to the problems, where the transition rates depend on time) in the simplest MC algorithm

$$\delta t = \frac{z\tau}{M}, \quad (\text{B15})$$

where parameter τ has a dimension of time. Then the master equation follows from the system of Eqs. (B11) and (B13)–(B15) with

$$\frac{d}{dt} \rho(\boldsymbol{\sigma})|_{\text{in}} = \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} \sum_{\sigma'_l, \sigma'_m} \frac{1}{z\tau} u(\sigma'_l \sigma'_m \rightarrow \sigma_l \sigma_m) \rho(\boldsymbol{\sigma}'_{lm}), \quad (\text{B16})$$

$$\frac{d}{dt} \rho(\boldsymbol{\sigma})|_{\text{out}} = \sum_{\langle \mathbf{l}, \mathbf{m} \rangle} \sum_{\sigma'_l, \sigma'_m} \frac{1}{z\tau} u(\sigma_l \sigma_m \rightarrow \sigma'_l \sigma'_m) \rho(\boldsymbol{\sigma}_{lm}). \quad (\text{B17})$$

The main difference lies in the terms of transition probabilities ($1/z\tau u(\lambda \mu \rightarrow \lambda' \mu')$ of Eqs. (B16) and (B17) instead of $w(\lambda \mu \rightarrow \lambda' \mu')$, see Eqs. (B5) and (B6). The transition rates $w(\lambda \mu \rightarrow \lambda' \mu')$ of the master equation as defined consider only nontrivial transitions $\lambda \mu \neq \lambda' \mu'$. In contrary, the transition probabilities $u(\lambda \mu \rightarrow \lambda' \mu')$ form a complete set due to the normalization Eq. (B12) and thus contain trivial (empty) transitions $\lambda \mu = \lambda' \mu'$. Additional terms in Eqs. (B16) and (B17) mutually vanish, since the trivial transitions do not change a state of a system.

Let us now define

$$W_{\lambda \mu} = z \sum_{\lambda' \neq \lambda} \sum_{\mu' \neq \mu} w(\lambda \mu \rightarrow \lambda' \mu'). \quad (\text{B18})$$

Using Eq. (B4) one arrives at

$$W_{\lambda \mu} = \sum_{\lambda' \mu'} Q(\lambda \mu \rightarrow \lambda' \mu') + \sum_{\lambda'} P(\lambda \rightarrow \lambda') + \sum_{\mu'} P(\mu \rightarrow \mu'). \quad (\text{B19})$$

If we choose $W_0 = \max[W_{\lambda \mu}]$ and define τ as $\tau = W_0^{-1}$ then transition probabilities read

$$u(\lambda \mu \rightarrow \lambda' \mu') = \frac{z}{W_0} w(\lambda \mu \rightarrow \lambda' \mu'). \quad (\text{B20})$$

Since a sum

$$\sum_{\lambda' \neq \lambda} \sum_{\mu' \neq \mu} u(\lambda\mu \rightarrow \lambda'\mu') \leq 1 \quad (\text{B21})$$

is always restricted, the trivial transitions obtain a unique definition as terms, which complement the sum to unity

$$\sum_{\lambda'} \sum_{\mu'} u(\lambda\mu \rightarrow \lambda'\mu') \equiv 1. \quad (\text{B22})$$

Thus, MC simulations become a uniquely defined problem,

which coincide with the initial kinetic problem described by the master equation. These relations could look rather formal, however, they allow us a very simple and effective realization in a computer code. We note, that the state of a pair of sites $\lambda\mu$ is denoted in the code by a single number, thus the transition probability $u(\lambda\mu \rightarrow \lambda'\mu')$ can be written as a two dimensional matrix. The elements of the matrix are pre-defined, therefore during MC simulations they are not calculated. The efficiency of the code is characterized by the fact that the speed is determined by the random number generator, which is not characteristic for other algorithms.

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