Effective mean field approach to kinetic Monte Carlo simulations in limit cycle dynamics with reactive and diffusive rewiring

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Abstract. The dynamics of stochastic nonlinear kinetic schemes is known to deviate from the mean field (MF) theory when restricted on low dimensional spatial supports. This failure has been attributed to (i) the influence of the support’s spatial extension which modifies the system’s dynamics and (ii) the influence of the noise. In the current study, we introduce effective parameters, which depend on the type of the support and which allow for an effective MF description. As working example the lattice limit cycle dynamics is used, restricted on a 2D square lattice with nearest neighbour interactions. We show that it is possible to describe the spatiotemporal average concentrations of the restricted dynamics using the MF model when the kinetic rates are replaced with their effective values. The same conclusion holds when reactive stochastic rewiring is introduced in the system via long distance coupling. Instead, when the stochastic coupling becomes diffusive the effective parameters no longer predict the steady state. This is attributed to the diffusion process which is an additional factor introduced into the dynamics and is not accounted for, in the kinetic MF scheme.

1 Introduction

The theory of nonlinear dynamics, as applied to reaction-diffusion processes, population dynamics, and social and economical systems, has for a long time mainly been restricted to studies of the macroscopic phenomenological, Mean Field (MF) equations. As a result, effects such as local interactions, spatial restrictions, defects, local stochastic effects, etc. were often ignored or added ad hoc. In the recent years, with the development of the kinetic (or dynamic) Monte Carlo methods, it is possible to include in detail these factors and to follow the system as it evolves dynamically from one state to another \cite{1–7}. By generating a state-to-state trajectory it is possible to explore the entire state space as the system is directed towards the steady state, while the dynamics and the steady state crucially depend on the dynamical history.

In models of chemical catalytic dynamics \cite{2,4,6–12}, ecological models \cite{13–15}, epidemiology \cite{16–19}, the existence of a spatial support is crucial and may modify considerably the MF approximation. In addition, diffusion of species may often modify the processes \cite{13,15}. In all these systems the supports present certain degrees of complexity. For example, in ecological systems the species live and interact in natural environments that present differences in their structure from a sub-area to another \cite{13,18,20}. As noted in reference \cite{20}, in the chemical, biological and ecological world, pattern formation is a very common phenomenon, that must be always taken into account in respective models, since they affect the dynamics between the species.

In a classic work \cite{9}, the NO + CO reaction on Pt surfaces was studied, without considering the corresponding spatial effects. The stability of the system was investigated and local kinetic oscillations were considered. In recent investigations of the same system \cite{10–12}, the dynamics leading to self-organization was shown to affect the “spatio-temporal organization” of the chemical catalytic reactions.

In reference \cite{13}, synchronization among populations of different species which are related to each other as predators-consumers-vegetation, was studied. The dynamics of such systems is of the limit cycle type. It was found that there is a strong relation between the populations synchronization and the spatio-temporal characteristics of the system. This phenomenon takes also into account the possible “diffusive migration” of some species to a neighbouring or distant areas.

In epidemiological models, the spatial characteristics of the systems are very important. In many studies (see, e.g., \cite{16–18}), the structures of social networks were shown
to affect the dynamics of spreading diseases [16]. In addition, targeted immunization to the individuals/sites of the network that are best connected can cause localization of the disease [17].

The impact of the support in many cases can be so influential that it can alter completely the dynamics. It has been shown that simple models which at the MF do not demonstrate oscillations, when a spatial support is introduced in combination with the kinetics may develop spatiotemporal patterns, and even regular and irregular (chaotic) oscillatory behaviour [21–26]. A particular application of this effect was shown for the dynamics of the CO + NO kinetics in reference [10].

The effects of a 2D square lattice support in a center dynamical system, the lattice Lotka-Voltera (LLV) system, was introduced in reference [27]. It was found that the conservative center dynamics reduces to local oscillations when the system is restricted on low dimensional supports. The attributes of the oscillations depend on the lattice size, the number of interacting neighbours and the general spatial restrictions. These oscillations are not of the limit cycle type, due to the nature of the interactions. Later on, long-distance diffusion [28] was added in the LLV system and as a result the out-of-phase local oscillations got phase synchronized and gave global oscillations which were stable. After a critical point, a Hopf-like bifurcation happens and the system enters into limit cycle-like dynamics.

A different model, involving a limit cycle MF dynamics on lattice was introduced in 2002, the Lattice Limit Cycle (LLC) model [29,30]. For this model the behaviour in the MF level and in the Kinetic Monte Carlo (KMC) simulations level are different. In the MF level, the concentrations oscillate with constant amplitude, independent of the initial conditions (limit cycle dynamics). When the simulations are performed on a 2D square lattice, local, out of phase oscillations, are observed between different-distant subregions of the lattice. Again, the spatial restrictions of the system, the lattice size, etc., are strong parameters that affect the dynamical behaviour of the concentrations.

In the current study, the addition of long-distance reaction (LDR) and long-distance diffusion (LDD) processes is attempted on the LLC model. The aim of the study is twofold: on the one hand, it extends earlier works, by taking into account the spatial and stochastic coupling among the species involved in this highly nonlinear interaction scheme and it examines how the diffusion would alter the behaviour of the species and the dynamics of their concentrations. On the other hand, it proposes a posteriori effective parameters in the simulations to investigate possible restoration of the MF regime. Our numerical results show that the KMC average properties are well described by the effective MF approach in the case of LDR. In the case of LDD the MF results differ from KMC results even when the effective parameters are taken into account. This is attributed to the difference in the nature of the mixing process (diffusion), which is not accounted for, into the ordinary MF approach. In both cases, LDR and LDD, the use of the a posteriori effective parameters to predict the limit cycle dynamics around the steady state is a much harder problem and lies outside the scope of the current study.

Since kinetic models, such as the LLC, can be applied to a variety of physical systems, in this study we use a “neutral” notation in the description of the interacting units and refer to them as “species”. The species can diffuse on lattice and can interact (react) with their neighbours or other distant species in the system.

In the next section, the LLC model is presented where three different species interact in a circular chain, and the corresponding MF equations are recapitulated. To implement the model, KMC simulations are performed on a square lattice and the results are presented in Section 2. Differences between the MF and the KMC approaches are pointed out. In Section 3, effective reactive parameters \( p_1, p_2, p_3 \) are calculated a posteriori and the MF dynamics with effective parameters are compared successfully with the KMC results. In the next two sections, two different mechanisms and their consequences are studied. In Section 4, long distance reactions are added to the system, while in Section 5 long distance diffusion is implemented. In both cases, the species concentration is studied using the a posteriori effective values in the MF equations. The control parameters in these steps are the probability of long distance reaction and the probability of long distance diffusion. The main conclusions together with suggestions for future studies are presented in the concluding section.

### 2 The lattice limit cycle model: mean field and kinetic Monte Carlo approaches

The LLC model is a nonlinear model which describes the interactions among three competing species, in a circular chain [29]. With \( X_1, X_2 \) the two interacting species are denoted, whereas \( S \) is considered to be a fictitious – virtual species, representing the empty sites. In the model, the species live on a 2D square lattice and each site can be occupied by an \( X_1 \) or \( X_2 \) or it can be empty. Single occupancy of all sites is only allowed at all times. The species \( S \) represents the empty sites – vacuum states of the lattice, which “interact” with occupied lattice sites as it will be seen in the next paragraph.

Initially, the species are randomly distributed onto the lattice under given initial conditions. Each site can interact with its closest neighbours with given rates. The way that the species interact is described in the following scheme:

\[
2X_1 + 2X_2 \xrightarrow{p_1} 3X_2 + S \quad (1a)
\]
\[
X_1 + S \xrightarrow{p_3} 2X_1 \quad (1b)
\]
\[
X_2 + S \xrightarrow{p_3} 2S. \quad (1c)
\]

The reaction step (1a) describes the main interaction between the species \( X_1 \) and \( X_2 \) in the presence of empty lattice sites \( S \). It is a 4th order nonlinear process, which conserves the total number of species (real + virtual). In
all steps of scheme (1), the total number of species (reactants) on the left hand side is equal to the total number of species (products) on the right hand sides. This property makes the scheme (1) lattice compatible. This means that for simple lattice occupancy, the total number of species (real + virtual) is always conserved in time and is equal to the total number of available lattice sites.

In order for (1a) to take place, two species species are needed. When they are found in the proximity of one another (closest neighbours) then with rate $p_1$, one of the two $X_1$ becomes an $X_2$ while the second $X_1$ desorbs (or dies) leaving its site empty ($S$). The step (1b) describes how the species $X_1$ is born. The vacuum state interacts directly with neighbour states $X_1$ and $X_2$. In particular, when an empty site $S$ is found close to a site containing $X_1$ then another $X_1$ is born and replaces $S$ with rate proportional to $p_2$, $S \rightarrow X_1$. Step (1c) describes how the species $X_2$ dies. When an $X_2$ is found close to an empty site $S$ then with rate $p_3$, $X_2$ dies leaving its site empty, $X_2 \rightarrow S$. The interactions rates, which are given by the parameters $p_1$, $p_2$, $p_3$, will be later translated into probabilities when the simulation algorithm will be introduced.

### 2.1 The classical mean field theory

In this subsection, we briefly recapitulate the main attributes of the classical MF theory describing the LLC scheme [29,31]. The nonlinear kinetic equations for the species concentrations have the form:

\[
\begin{align*}
\frac{dx_1}{dt} &= -2p_1x_1^2x_2^2 + p_2x_1s \\
\frac{dx_2}{dt} &= p_1x_1^2x_2^2 - p_3x_2s \\
\frac{ds}{dt} &= p_1x_1^2x_2^2 - p_2x_1s + p_3x_2s,
\end{align*}
\]

where the small letters $x_1$, $x_2$ and $s$ represent the global MF concentrations. The space conservation condition

\[x_1 + x_2 + s = \text{const}.,\]

is automatically satisfied. As usual, the constant is chosen equal to unity, leading to the interpretation of $x_1$, $x_2$ and $s$ as partial concentrations of species $X_1$, $X_2$ and empty sites. Using the conservation condition equation (3), it is straightforward to reduce the system by eliminating the $s (\text{=} 1 - x_1 - x_2)$ variable:

\[
\begin{align*}
\frac{dx_1}{dt} &= -2p_1x_1^2x_2^2 + p_2x_1(1 - x_1 - x_2), \\
\frac{dx_2}{dt} &= p_1x_1^2x_2^2 - p_3x_2(1 - x_1 - x_2).
\end{align*}
\]

This reduced system admits four steady state solutions, three of which are trivial and correspond to full occupation of the lattice by one of the three species. The three trivial solutions can be represented as state vectors in the reduced ($x_1$ and $x_2$) dimensions, namely $Q_1 = (0, 0)$ (empty lattice), $Q_2 = (0, 1)$ (lattice poisoned by $X_2$) and $Q_3 = (1, 0)$ (lattice poisoned by $X_1$). In addition, the system (2) admits a fourth nontrivial solution with coexistence of all species in the steady state:

\[
Q_4 = \left(\sqrt{\frac{p_3^2}{p_3p_1} [1 + K]} \pm \sqrt{\frac{p_3^2}{p_3p_1} [1 - K]}\right),
\]

where the constant $K$ is only a function of the three interaction rates,

\[K = \sqrt{1 + (2p_3 + p_2)^2 / (27p_1p_2p_3)}.
\]

Standard linear stability analysis indicates that the first three trivial fixed points are saddles, while the stability of $Q_4$ depends on the parameter values. For certain parameter values $Q_4$ undergoes a supercritical Hopf bifurcation, becomes an unstable focus and in its vicinity a stable limit cycle appears. In this regime the concentrations $x_1$ and $x_2$ oscillate periodically, while the amplitude of the oscillations depends also on the system parameters.

Note that although the MF description is appropriate for describing the main long time tendencies of the system, it is not a suitable approach when fluctuations, spatial restrictions and stochastic effects are considered.

### 2.2 The kinetic Monte Carlo approach

When a detailed description of the system’s dynamics is needed, where fluctuations, spatial restrictions and stochastic effects are considered, the ultimate description is the probabilistic master equation approach. It describes the temporal evolution of the system from one state to another in detail. In particular, if the system is found in a finite number of states $i = 1, 2, \ldots, N$ then the probability $P(j, t)$ to find the system in state $j$, at time $t$, is described by the master equation as:

\[
P(j, t) = \sum_{k=1}^{N} w_{kj} P(k, t - 1) - \sum_{l=1}^{N} w_{lj} P(j, t - 1),
\]

where the matrix element $w_{jk}$ represents the transition probability from state $j$ to state $k$. The matrix $W$ with elements $w_{jk}$, $j, k = 1, \ldots, N$ is called the transition probability matrix. The solution of the master equation is easy when the number of states $N$ is small, but in the case of systems with a large number of states, as the LLC lattice model, it becomes intractable. An alternative method, where the system samples its state space stochastically and thus for relatively large times gives a good approximating solution to the master equation, is the KMC method, which is used in the current study.
The KMC method is a discrete time method starting from an initial random configuration of species $X_1$, $X_2$, and $S$ residing on lattice and the update is random and sequential, following the LLC reactive scheme (1). The substrate is a 2D square lattice of size $L \times L$ and each species interacts only locally with its nearest neighbours. Later, in Sections 4 and 5, stochastic long distance couplings will be allowed with other, distant sites. Each lattice site, whose coordinates are denoted as $(i,j)$, contains only one species ($X_1$ or $X_2$) or is empty ($S$). Originally, the three species are randomly distributed on the lattice with given initial concentrations. Each elementary time step (ETS) of the KMC algorithm contains five stages.

1. One site, $(i,j)$, is randomly chosen throughout the lattice.
2. If the site $(i,j)$ contains an $X_2$ species and amongst the four nearest neighbours one species of type $S$ is found then the site $(i,j)$ changes its state from $X_2$ to $S$ with probability $p_3$. This is the realisation of kinetic step (1c).
3. If the site $(i,j)$ contains an $S$ species and amongst the nearest neighbours a species of type $X_1$ is found then the site $(i,j)$ changes its state from $S$ to $X_1$ with probability $p_2$. This is the realisation of kinetic step (1b).
4. If the site $(i,j)$ contains $X_1$, and its immediate neighbourhood contains one $X_1$ and two $X_2$ species, then the original and the neighbour $X_1$ change simultaneously to $S$ and $X_2$, with probability $p_1$. This is the lattice realisation of kinetic step (1a).
5. If none of the three kinetic steps is realised, the lattice remains unchanged.
6. One ETS is completed. The algorithm returns to stage (1) for a new ETS to start.

The indicative Monte Carlo time step (MCS) consists of a number of elementary steps equal to the lattice size $L^2$, namely $1 \text{MCS} = L^2 \text{ETS}$. In one MCS step each lattice site has reacted once, on average. The above KMC algorithm is a slight variance of the original one, proposed in reference [29], in order to establish consistency between the short distance interactions introduced in reference [29] and the long distance ones which will be introduced in the next two sections.

As working parameter set the values $p_1 = 0.9585$, $p_2 = 0.016$ and $p_3 = 0.026$ will be used which are located well inside the Hopf bifurcation region and give rise to periodic oscillations with large amplitudes [29]. In addition the working parameter values were chosen to be $p_i \leq 1$, so that they can directly be interpreted as reaction probabilities in the KMC scheme. In cases where the rates $p_i$ are greater than unity they can be transformed into probabilities in two ways: (i) either by dividing each one of them by the sum of all $p_i$ (i.e., $p_i \rightarrow p_i/\sum p_j$, $i, j = 1, 2, 3$) or (ii) by dividing each $p_i$ by the maximum of the reactive rates (i.e., $p_i \rightarrow p_i/p_{max}$, $i = 1, 2, 3$). In both cases, this rate rescaling is equivalent to a time rescaling of the system [29]. Note that the large gap in the working set value of $p_1$ in relation to $p_2$ and $p_3$ balances the highly selective, nonlinear structure of kinetic step (1a).

![Fig. 1. Time series of average $x_1$ density for different lattice sizes shows intermittent oscillations. The parameter values are: $p_1 = 0.9585$, $p_2 = 0.016$ and $p_3 = 0.026$. The dotted black line denotes the MF steady state solution (Eq. (5)).](image)

In Figure 1 the average concentration of species $X_1$ over all the lattice is depicted as a function of time for two different lattice sizes, $L = 2^8$ (red dashed line) and $L = 2^{10}$ (blue solid line). As was also noted in reference [29] the restriction of the reactive dynamics on a support, the effects of spatial species distribution and the stochastic noise induce the following modifications to the MF behaviour: (i) the oscillations loose their regularity and become intermittent (stochastic effects), (ii) the amplitude of the intermittent oscillations shrinks as the size grows $L$ increases, and this is attributed to the stochastic effects which randomise the phases of the local limit cycle oscillators and (iii) a small shift is observed in the center of the KMC cycles with respect to the MF solution. For comparison the dotted black line denotes the MF position of the center of the limit cycle.

3 Calculating the effective parameter values

As shown in Section 2, the stochastic and spatial effects modify the reactive dynamics with respect to the MF behaviour. Apart from the stochasticity in the amplitude of the oscillations, the position of the center, one of the most essential characteristics of the MF, is displaced. Because the position of the center is solely defined by the parameters $p_1$, $p_2$ and $p_3$, we need to explore whether the spatial and stochastic effects influence these parameters.

To this purpose, we calculate, a posteriori, the “effective” reactive parameters, which realistically occur during the KMC simulations. In many cases, when a species/site is selected to interact with favorable rate, the event might not take place due to inappropriate environment (nearest neighbouring species) or to stochastic choice. This way the original rates are modified and new, “effective” rates govern the dynamics of the system. These rates are computed, a posteriori, within the algorithm provided in Section 2.2.

During the application of the algorithm we introduce three event counters $N_1$, $N_2$ and $N_3$, which increase by...
Fig. 2. Average effective interaction probabilities $p'_i$ as functions of the imposed reactive rate $p_1$. The other parameter values are: $p_2 = 0.016$ and $p_3 = 0.026$ and the system size is $L = 2^9$. Averages are taken over 10 runs. The error bars on the $p'_i$ values are of the order of $4 \times 10^{-4}$.

one unit when the kinetic steps (1a), (1b) and (1c) take place, respectively. The “effective” parameters, $p'_i$, $i = 1, 2, 3$, are calculated as [32]:

$$p'_1 = \frac{N_1}{\langle x_1 \rangle} \langle x_2 \rangle^2,$$

$$p'_2 = \frac{N_2}{\langle x_1 \rangle} \langle s \rangle,$$

$$p'_3 = \frac{N_3}{\langle s \rangle \langle x_2 \rangle}.$$

As an example, in Figure 2, the effective values $p'_1$ is plotted for various values of $p_1$ when the other parameters $p_2$ and $p_3$ are kept constant. From the figure it is clear that as the reaction probability increases the effective reaction probability, which averages out all the local effects, also increases proportionally.

Using the effective parameters $p'_i$, the effective MF steady state values $x'_1$, $x'_2$ and $s'$ are calculated using equation (5), where the kinetic parameters are replaced with the effective ones (Eqs. (7a)–(7c)). The results are plotted in Figure 3 for various values of the original parameter $p_1$ and keeping the other two fixed ($p_2 = 0.016$ and $p_3 = 0.026$). In particular, in Figure 3 the three curves represent: (i) the averaged values $\langle x_1 \rangle$ taken directly from the KMC simulations, average taken over 10 runs (black line with circles), (ii) the average (over 10 configurations) MF calculated effective partial density $\langle x'_1 \rangle$ of species $X_1$, using the effective probabilities $p'_i$ in the MF equation (5), (red line with crosses) and (iii) the original MF partial density $x_1$, using the original probabilities $p_i$ in the MF equation (5) (green line with diamonds). The simple MF clearly underestimate the average partial densities, while the effective MF gives a very close approximation to the KMC simulations. These results indicate that, as far as the steady state properties of the LLC model are concerned, the restriction of the system on the substrate together with the stochastic character of the reactions lead to new effective parameter values, while the MF steady state is achieved for these shifted parameter values.

4 Kinetic lattice Monte Carlo with stochastic reactive rewiring

Stochastic rewiring usually takes place in networks where species interact with far away “neighbours”. An illustrative example is the opinion exchange through the Internet or through the telephone network. Opinions are discussed and exchanged without actual displacement of the individuals. In such interaction environments the individuals are exposed both to the local environment (family, workplace) where the interactions are governed by rates $p_i$, and to the long distance environment where the interactions are governed by rates $p_{i,\text{long}}$ which, in general, are different from the local rates $p_i$. The long distance interactions/reactions introduce a type of reactive mixing in the system and drive the system towards its MF behaviour. In some cases the distant interactions are considered using delays, but in the current study both distant and local interactions are assumed to take place simultaneously.

To realise the long distance rewiring process, a rewiring rate $r$ is introduced which denotes the relative rate of long distance versus local interactions. For the local (short distance) interactions the rates are denoted as $p_i$, $i = 1, 2, 3$, as previously, while for the long distance ones the parameters are denoted as $p_{i,\text{long}}$, $i = 1, 2, 3$.

Having chosen the values of $r$, $p_i$ and $p_{i,\text{long}}, i = 1, 2, 3$ the modifications to the KMC algorithm are straightforward. With probability $1 - r$ the classical KMC is realised, as described in Section 2.2. With probability $r$ the same algorithm holds, but now the neighbours are randomly chosen between all species in the system and the reactions are realised with rates $p_{i,\text{long}}$. In one ETS either
effective MF partial densities always close to the nontrivial deviation on the average values as a function is that the addition of a rewiring process introduces the nearest neighbours” are drawn with equal probability within the entire system.

To find out how the rewiring process modulates the local properties dominate, while the long distance interactions dominate, for all values of $r$ the long distance interactions dominate. $r_c$ stands for the specific rewiring value where the global properties take over. For clarity, in Figure 4 we add a dotted horizontal line which denotes the original center fixed point $x_1 = 0.36$, calculated from equation (5) with $(p_1, p_2, p_3) = (0.95, 0.016, 0.026)$. The corresponding mean value of the $x_1$ variable, calculated from the numerical integration of the kinetic scheme, equations (4), is $\langle x_1 \rangle_{MF} = 0.524$ (not shown). None of them relates to the nontrivial shape of KMC partial density curve. Note, that the effective parameters $(p'_1, p'_2, p'_3)$, drive the average effective MF partial densities always close to the nontrivial fixed point $Q_3$ ($x_1 = 1.0$), for all values of $r$. Similar effects are also observed in the behaviour of the other two variables $x_2$ and $s$.

In the same plot the average $x_1$ densities are computed using the effective parameters $p'_i$, via equation (5). With the use of the effective parameters the average KMC densities are very well predicted by the MF model. This comes as no surprise, after the successful results of the previous section, where the effective MF theory predicted well the local steady state concentrations. Here, the introduction of the long distance KMC rewiring drives the system towards the MF and thus the effective MF approximation has a higher advantage in the description of the system over the previous, purely local, KMC approach. It is possible to obtain the minimum of the partial concentration curves in Figure 4 if we assume that the overall collective effects due to the stochastic KMC process and to the long distance reactions is a multiplicative factor $a$, which facilitates the $p_1$ rate as $a^3p_1$, the $p_2$ rate as $a^1p_2$ and the $p_3$ rate as $a^2p_3$. Then the critical value $a_c$ could be obtained from the calculation of the minimum with respect to $a$ of equation (5) (with the $a$-modified rates). The $a$-modified fixed point $Q_{4mod}^\prime$ is given as:

$$
Q_{4mod}^\prime = \frac{3}{a^2p_3} \left[ 1 + K_{mod}^\prime \right] + \frac{3}{a^2p_1p_2} \left[ 1 - K_{mod}^\prime \right],
$$

where $K_{mod}^\prime = \sqrt{1 + (2p_1 + p_2)^2/(27a^2p_1p_2p_3)}$. The most important qualitative characteristic of Figure 4, that should be reflected in the MF approximating equation (8), is the single minimum in the concentration. Extreme values of equation (8) can be obtained by taking its derivative with respect to $a$ and calculating the number of times it crosses the $y = 0$-axis. For the working parameter set, the derivative $dx_{1mod}^\prime/da$ with respect to $a$ is shown in Figure 5. It is observed that $dx_{1mod}^\prime/da$ crosses the $y = 0$-axis at a single value $a_c \approx 0.48$, which corresponds to the single minimum $r_e$ in Figure 4. Thus, the approximation equation (8) presents, qualitatively, this main feature of the KMC simulated average concentrations.
5 Kinetic lattice Monte Carlo with stochastic diffusive rewiring

Long distance, stochastic motion (or long distance diffusion) usually takes place in networks with mobile species [28]. A common example is the long distance migration in ecology, especially in bird motion. In such systems species migrate in variable distances and they react locally wherever they land. There are many systems in which long distance reaction and long distance diffusion are both possible. For example, in opinion dynamics the individuals can interact with other distant individuals (over the phone or via the Internet) and can also relocate and then interact locally. Another such network is the sales network where potential clients can be contacted either by Internet (long distance reaction) or by salesmen (long distance motion-diffusion).

In this section, we attempt to compare how the long distance reaction and long distance diffusion mechanisms affect the output of the reactive dynamics. Both mechanisms cause a mixing in the system and one could assume that the two processes lead to very similar output results. Nonetheless, this is not the case and, as will be demonstrated later in this section; the two processes combined with the local reactions lead to very different overall dynamics.

To compare with the previous Section 4, we only consider here local interactions together with long distance diffusion mechanisms. The local processes are realised according to the KMC algorithm described in Section 2.2, and all the local reaction parameters are the same as in Sections 2.2 and 3. The local reactions are governed by rates $p_i$, while the long distance diffusion rates are denoted by $p_{i,\text{diff}}$. In general the rates $p_{i,\text{diff}}$ may be different for the different species. In the current study, in order to reduce the number of parameters, we assume that all species diffuse with the same rate $p_d$.

Having chosen the values of $p_d$ and $p_i$, $i = 1, 2, 3$, the modifications to the KMC algorithm of Section 2.2 are straightforward. Once a lattice site is selected the hosted species reacts according to the classical KMC as described in Section 2.2 with probability $1 - p_d$. Otherwise, with probability $p_d$ the hosted species exchanges position with another one, randomly selected on the lattice. In one ETS either a local reaction event or a long distance diffusion event may take place, thus the ratio of number of ETS where local interactions occur to the number of ETS where long distance events happen is $p_d/(1 - p_d)$, in direct similarity with the long distance reaction process presented in the previous section (Sect. 4). In addition, for comparison with previous results we choose to work with the same local reaction rates, i.e. $(p_1, p_2, p_3) = (0.95, 0.016, 0.026)$ and with variable $p_d$. The diffusion range $l_d$ for the simulations presented here is set to $l_d = L/2$, but similar results are obtained for all $l_d$ that are greater than the size of the local oscillators $R$ [29], which for the current working parameter set is $R \sim 10$.

As shown in Figure 6 there is a decrease in the rate of production of $X_1$ species, which takes place already for small values of diffusive mixing, while in the case of reactive mixing the decrease is more gradual (see Fig. 4). The use of “effective” rates, $p_i^\prime$, calculated as in equations (7), gives some of the curve tendencies, but overall the KMC partial densities are not well predicted. When $p_d = 1$ only diffusive mixing takes place, the effective reaction rates $p_i^\prime$ are 0 and the partial densities remain unaltered. That is, for $p_d = 1$, $(x_1) = (x_1(t = 0))$, $(x_2) = (x_2(t = 0))$, $(s) = (s(t = 0))$. For equiprobable initial conditions which are often used in the KMC process, the final state is $(x_1) = (x_2) = (s) = 1/3$ for $p_d = 1$. As in Figure 4, for clarity, we add in Figure 6 a dotted horizontal line which denotes the original center fixed point $x_1 = 0.36$, calculated from equation (5) with $(p_1, p_2, p_3) = (0.95, 0.016, 0.026)$. As before, this value does not relate to the nontrivial shape of KMC partial density curve.

In the same figure the red dashed line represents the predictions of the effective MF approach. Unlike in the case of reactive mixing the effective MF theory fails to predict quantitatively the KMC partial densities. This is because the introduced diffusion is a new process which is not taken into account by the effective MF model. And although long distance reaction and long distance diffusion both induce mixing effects, the details of each process lead to different outputs in the steady state production of the three species.

6 Conclusions

In this work we study the impact of long distance reaction and diffusion effects on the steady state of a process governed by local limit cycle dynamics. The process is realised on a square lattice using kinetic Monte Carlo simulations.
For the case where only local interactions are considered, we show that the calculation of a posteriori effective reaction rates, allows to get a good approximation of the system’s steady state average properties, using the MF effective rates. Furthermore, when long distance reactions together with local ones take place, the effective MF approximation still faithfully describes the steady state average properties of the system.

When long distance diffusion on the local reactive dynamics are added the effective MF description is no more valid. This is because the diffusion is a new process, not taken into account by the original MF equations which include only reactive terms. Thus the effective MF, based only on the reactive terms, fails to describe the composite system. An extended MF model needs to be devised to include also diffusion effects. The extended LLC can serve as a better candidate on which to base an effective MF theory to describe the LLC dynamics enhanced with the long distance diffusion terms.

In the current study, we have only discussed the average properties of the steady state and not the dynamics around it. In future studies the influence of the long distance reactive and diffusive processes on the dynamics of the limit cycle, on synchronisation effects and on the position of the bifurcation point need to be addressed.

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References

1. A.P.J. Jansen, J.J. Lukkien, Catalysis Today 53, 259 (1999)
2. M. Nagasaka, H. Kondoh, I. Nakai, T. Ohta, J. Chem. Phys. 126, 044704 (2007)
3. N.V. Petrova, I.N. Yakovkin, Eur. Phys. J. B 58, 257 (2007)
4. Y. De Decker, F. Baras, Eur. Phys. J. B 78, 173 (2010)
5. L. Alvarez-Falcon, L. Vicente, Int. J. Quantum Chem. 112, 1803 (2012)
6. A. Farkas, F. Hess, H. Over, J. Phys. Chem. C 116, 581 (2012)
7. S.J. Alas, L. Vicente, Surf. Sci. 604, 957 (2010)
8. R. Imbihl, G. Ertl, Chem. Rev. 95, 697 (1995)
9. R. Imbihl, T. Fink, K. Krisher, J. Chem. Phys. 96, 6236 (1992)
10. O. Korthake, V.N. Kuzovkov, W. von Niessen, Phys. Rev. Lett. 81, 2164 (1998)
11. V.P. Zhdanov, Catalysis Lett. 93, 135 (2004)
12. R. Imbihl, Surf. Sci. 603, 1671 (2009)
13. B. Blasius, A. Huppert, L. Stone, Nature 399, 354 (1999)
14. J.L. Deneubourg, A. Lioni, C. Detrain, Biol. Bull. 202, 262 (2002)
15. N. Kouvaris, A. Provata, D. Kugiumtzis, Phys. Lett. A 374, 507 (2010)
16. M. Kuperman, G. Abramson, Phys. Rev. Lett. 86, 2909 (2001)
17. D.H. Zanette, M. Kuperman, Physica A 309, 445 (2002)
18. U. Naether, E.B. Postnikov, I.M. Sokolov, Eur. Phys. J. B 65, 353 (2008)
19. C.P. Ferreira, J.F. Fontanari, R.M.Z. dos Santos, Phys. Rev. E 64, 041903 (2001)
20. R.S. Baghel, J. Dhar, R. Jain, Electron. J. Diff. Equations 21, 1 (2012)
21. V.P. Zhdanov, Surf. Sci. 392, 185 (1997)
22. V.P. Zhdanov, Langmuir 17, 1793 (2001)
23. V. Kuzovkov, E. Kotomin, Rep. Prog. Phys. 51, 1479 (1988)
24. J.P. Hovi, A.P.J. Jansen, R.M. Nieminen, Phys. Rev. E 55, 4170 (1997)
25. E. Kotomin, V. Kuzovkov, Modern Aspects of Diffusion-Controlled Processes Cooperative Phenomena in Bimolecular Reactions (Elsevier Science B.V., Amsterdam, 1996), Vol. 34
26. V. Kashcheevs, V.N. Kuzovkov, Phys. Rev. E 63, 061107 (2001)
27. A. Provata, G. Nicolis, F. Baras, J. Chem. Phys. 110, 8361 (1999)
28. A. Efimov, A. Shabunin, A. Provata, Phys. Rev. E 78, 056201 (2008)
29. A.V. Shabunin, F. Baras, A. Provata, Phys. Rev. E 66, 036219 (2002)
30. A. Provata et al., Fluct. Noise Lett. 3, L241 (2003)
31. G.A. Tsekouras, A. Provata, Eur. Phys. J. B 52, 107 (2006)
32. J.-S. Wang, R.H. Swendsen, J. Stat. Phys. 106, 245 (2002)