Perturbation theory for the breakdown of mean-field kinetics in oscillatory reaction-diffusion systems

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(Received 14 October 1997; accepted 27 March 1998)

Spatially distributed, nonequilibrium chemical systems described by a Markov chain model are considered. The evolution of such systems arises from a combination of local birth-death reactive events and random walks executed by the particles on a lattice. The parameter γ, the ratio of characteristic time scales of reaction and diffusion, is used to gauge the relative contributions of these two processes to the overall dynamics. For the case of relatively fast diffusion, i.e., $\gamma \ll 1$, an approximate solution to the Markov chain in the form of a perturbation expansion in powers of γ is derived. Kinetic equations for the average concentrations that follow from the solution differ from the mass-action law and contain memory terms. For a reaction-diffusion system with Willamowski-Rössler reaction mechanism, we further derive the following two results: (a) in the limit of $\gamma \rightarrow 0$, these memory terms vanish and the mass-action law is recovered; (b) the memory kernel is found to assume a simple exponential form. A comparison with numerical results from lattice gas automaton simulations is also carried out. [S0021-9606(98)51225-1]

I. INTRODUCTION

The dynamics of chemical reactions in condensed media is commonly described by a set of reaction-diffusion equations[1] of the following general form:

$$\frac{\partial \overline{\mathbf{x}}(\mathbf{r},t)}{\partial t} = \mathbf{R}(\overline{\mathbf{x}}(\mathbf{r},t)) + \mathbf{D}\nabla^2 \overline{\mathbf{x}}(\mathbf{r},t), \tag{1}$$

where $\overline{\mathbf{x}}(\mathbf{r},t)$ is vector of concentrations, $\mathbf{r}$ position vector, t the time; $\mathbf{R}(\overline{\mathbf{x}}(\mathbf{r},t))$ denotes mass-action law terms, and $\mathbf{D}$ is the matrix of diffusion coefficients.

Such a description, while able to capture some of the features of the system's evolution, is not entirely free of shortcomings. For instance, as can be easily seen from (1), rescaling the diffusion coefficients by a constant factor is equivalent to rescaling of length. Contrary to this observation, the reaction dynamics in spatially distributed systems varies with diffusion in a much more complex way; thus, it has been shown that in the limit of slow diffusion, reaction dynamics has pronounced memory character,[2,3] while in the case of very fast diffusion it closely follows the mass-action law. Significant progress has been made in understanding the dynamics of simple diffusion-limited chemical reactions (e.g., $A+B \rightarrow \emptyset$) in low-dimensional systems.[4] Also, Chapman-Enskog methods have been applied to multivariate master equations to study reactive correlations in simple reaction-diffusion systems.[5] However, to date the dynamics of more complex reaction-diffusion systems whose mass-action laws exhibit periodic and chaotic oscillations has received much less attention. Recent numerical studies on such systems using lattice gas automaton models[6] and master equations[7,8] have indicated that there are interesting effects pertaining to modification of the structure of oscillatory and chaotic attractors with decreasing rate of diffusion.

The purpose of this paper is to develop a statistical mechanical theory that approximately accounts for the influence of finite diffusion and reactive correlations on the dynamics of nonequilibrium oscillatory chemical systems. We use a discrete-space, discrete-time probabilistic model defined on a set of sites, or nodes of a lattice. Its evolution is due to a combination of local reactive events and random walks which are executed by the particles of reactants on the lattice.

Our approach is based on a Chapman-Enskog-like development[9] applied to a Markov chain model. The expansion parameter γ is the ratio of characteristic time scales of diffusion and reaction processes, small for the diffusion-dominated regimes. We show that the corresponding kinetic equations for spatially averaged concentrations involve memory terms. As an example, we apply this theory to the Willamowski-Rössler reaction-diffusion system.[10] We find that the memory kernel for this system assumes simple exponential form. The memory kernel should have the same functional form for any reaction-diffusion system whose reaction mechanism involves mono- and bimolecular steps only. The dynamics predicted by the kinetic equations indicates that the influence of diffusion essentially amounts to a *backward shift* in the bifurcation cascade of the mass-action law. We compare these theoretical predictions with lattice gas automaton simulations of the Willamowski-Rössler model, and find that they are qualitatively in agreement.

The paper is organized as follows. In Sec. II we introduce the Markov chain model and construct its evolution operator. In Sec. III we present a perturbation expansion for the probability distribution function around the local binomial form and obtain equations that determine evolution of the terms of this expansion. The perturbed distribution function incorporates the local correlations between different species induced by the reactive events and thus cannot be factorized into a product of single-species distributions. The derivation of kinetic equations for global average concentrations (i.e., local concentrations averaged over the volume of the system) concludes this section. In Sec. IV we derive the memory kernel for the Willamowski-Rössler reaction-diffusion system and compare the predictions of the theory with the results of lattice gas automaton simulations. Finally, Sec. V contains discussion of our results.

II. MARKOV CHAIN DYNAMICS

The system under consideration consists of a number of chemical species diffusing and reacting in solution. We assume a discrete-space, discrete-time description of the system by partitioning the space into cells of volume V and time into intervals of arbitrary length. In the following, we view each cell as a node on a lattice and operate within this lattice representation. The solvent comprises a chemically inert species so that its only effect is to maintain the random walk dynamics of the solute particles. Furthermore, we associate N distinct ''channels'' with every cell; each channel can be occupied by no more than one particle of each solute species. Thus, if the number of solute species is ν, the number of solute particles in each cell cannot exceed νN — this is the so-called exclusion principle. At any given moment of time, the state of the system is fully specified by a set of state variables — the number and chemical nature of the particles occupying every cell. The system evolves by transition to one of the accessible states once every time interval with probability determined by the initial state. From the statistical point of view the system is described by the probability distribution function $P(\mathbf{s},t)$ defined on the space of discrete states of the system, whose time dependence is due to a Markov chain,[11] i.e.,

$$P(\mathbf{s},n+1)-P(\mathbf{s},n)=\sum_{\mathbf{s}'}\left[T_{\mathbf{ss}'}P(\mathbf{s}',n)-T_{\mathbf{s}'\mathbf{s}}P(\mathbf{s},n)\right], \tag{2}$$

where $\mathbf{s}$ is a set of state variables, n is the integer time variable, and the summation extends over all possible states. Clearly, due to discreteness of the state variables, Eq. (2) can be also written in matrix form,

$$P_{\mathbf{s}}(n+1)-P_{\mathbf{s}}(n)=\sum_{\mathbf{s}'} W_{\mathbf{ss}'}P_{\mathbf{s}'}(n), \tag{3}$$

where $W_{\mathbf{ss}'}$ are the matrix elements of the evolution operator, defined in terms of transition probabilities per unit time as follows:

$$W_{\mathbf{ss}'}=T_{\mathbf{ss}'}-\delta_{\mathbf{s}'\mathbf{s}}\sum_{\mathbf{s}''} T_{\mathbf{s}''\mathbf{s}}. \tag{4}$$

Here $\delta_{\mathbf{s}'\mathbf{s}}$ is a Kronecker delta.

Henceforth, all vector quantities, such as state variables or concentrations, are denoted by bold lowercase letters, while bold uppercase letters stand for matrix quantities. Components of vectors and matrices are specified where necessary by lower indices. We designate operators by a hat over corresponding symbols, and average quantities by an overbar. Angle brackets will often be used as a shorthand notation for summing over the ensemble of state variables.

For reaction-diffusion systems, transitions between different states occur due to two competing processes: passive transport of particles between cells and reactive collisions which change the nature of the particles within cells according to the reaction mechanism. Correspondingly, the evolution operator for the present model can be written as a sum of two terms, one for the diffusion process and the other for reactions. Below we derive the particular form of reaction and diffusion evolution operators to be used in our study.

A. Diffusion Markov chain

Let the particles at every node be randomly distributed among N channels. We pose a diffusion rule according to which the particles that have identical chemical nature and belong to the same channel propagate synchronously and in the same direction between neighboring nodes. The choice of a particular channel, direction of propagation, and species to be propagated is made at random each time the diffusion evolution operator is applied. We also impose periodic boundary conditions which, together with the above, completely characterize transport of matter within the system.

A similar diffusion model was recently used in simulations of the FitzHugh-Nagumo system.[12] It was shown that the occupancies of individual nodes become statistically independent of each other after a short period of relaxation. Hence, for long-time behavior, correlations between nodes are negligible, and the full probability distribution can be factorized into a product of single-site distributions. This reduction of description is readily extended to the present model; specifically, one has for nonvanishing reduced transition probabilities

$$\begin{aligned} T^{D}_{x_i(\mathbf{r})-1,x_i(\mathbf{r})}&=\frac{x_i(\mathbf{r})}{\nu N}\left(1-\frac{\chi_i(\mathbf{r},n)}{N}\right),\\ T^{D}_{x_i(\mathbf{r})+1,x_i(\mathbf{r})}&=\frac{\chi_i(\mathbf{r},n)}{\nu N}\left(1-\frac{x_i(\mathbf{r})}{N}\right), \end{aligned} \tag{5}$$

where

$$\begin{aligned}\chi_i(\mathbf{r},n)&=\frac{1}{m}\sum_{\mathbf{r}'\in\mathcal{N}(\mathbf{r})}\ \sum_{\mathbf{x}(\mathbf{r}')} x_i(\mathbf{r}')P(\mathbf{x}(\mathbf{r}'),n)\\ &=\frac{1}{m}\sum_{\mathbf{r}'\in\mathcal{N}(\mathbf{r})}\overline{x_i}(\mathbf{r}',n),\end{aligned}$$

m is the coordination number of the lattice and $\mathcal{N}(\mathbf{r})$ is neighborhood of $\mathbf{r}$. Thus, $\chi_i(\mathbf{r},n)$ is an average of the mean occupation number of the i-th species over the immediate neighborhood of node $\mathbf{r}$. The factors in the first expression in (5) simply reflect the fact that the probability of a diffusive hop of a particle of the i-th species from the node $\mathbf{r}$ to a neighboring node is given by a product of the probability that the i-th species is chosen for the hop, $1/\nu$, the probability that a chosen channel is occupied at the node $\mathbf{r}$, $x_i(\mathbf{r})/N$, and the probability that the same channel is empty at the neighboring node, $1-\chi_i(\mathbf{r},n)/N$. A similar interpretation can be also given to the second expression in (5).

The reduced probability distribution $P(\mathbf{x}(\mathbf{r}),t)$ evolves according to the following equation:

$$P(\mathbf{x}(\mathbf{r}),n+1)-P(\mathbf{x}(\mathbf{r}),n)$$
$$=\hat{W}^{D}P(\mathbf{x}(\mathbf{r}),n)$$
$$=\sum_{i}\hat{W}^{D^i}\left(\prod_{j\neq i}\delta_{x_j'(\mathbf{r}),x_j(\mathbf{r})}\right)P(\mathbf{x}(\mathbf{r}),n), \tag{6}$$

with matrix elements of $\hat{W}^{D^i}$ given by [cf. (5) and (4)]

$$\begin{aligned}W^{D^i}_{x_i(\mathbf{r}),x_i'(\mathbf{r})}=&\frac{\chi_i(\mathbf{r},n)}{\nu N}\left(1-\frac{x_i'(\mathbf{r})}{N}\right)\delta_{x_i'(\mathbf{r}),x_i(\mathbf{r})-1}\\&+\frac{x_i'(\mathbf{r})}{\nu N}\left(1-\frac{\chi_i(\mathbf{r},n)}{N}\right)\delta_{x_i'(\mathbf{r}),x_i(\mathbf{r})+1}\\&-\left[\frac{\chi_i(\mathbf{r},n)}{\nu N}\left(1-\frac{x_i'(\mathbf{r})}{N}\right)+\frac{x_i'(\mathbf{r})}{\nu N}\right.\\&\left.\times\left(1-\frac{\chi_i(\mathbf{r},n)}{N}\right)\right]\delta_{x_i'(\mathbf{r}),x_i(\mathbf{r})}.\end{aligned} \tag{7}$$

Thus, the structure of the diffusion Markov chain (6) arises naturally from the diffusion rule posed in the beginning, the existence of a maximum occupation number at any node (i.e., the exclusion principle), and the reduction of description to the level of single-node distribution functions.

Kinetic equations for average occupancies (concentrations) can be obtained in the standard way, by multiplying both sides of (6) by $x_i(\mathbf{r})$ and summing over all possible states. One finds, after a few simple transformations,

$$\begin{aligned}\overline{x_i}(\mathbf{r},n+1)-\overline{x_i}(\mathbf{r},n)=&\frac{1}{\nu mN}\sum_{\mathbf{r}'\in\mathcal{N}(\mathbf{r})}[\overline{x_i}(\mathbf{r}',n)\\&-\overline{x_i}(\mathbf{r},n)]=D\,\Delta\overline{x_i}(\mathbf{r},n),\end{aligned} \tag{8}$$

where Δ is the discrete Laplacian operator. This is just a discretized diffusion equation with diffusion coefficient $D=(\nu mN)^{-1}$ (the same for all species).

B. Reaction Markov chain

The probabilities of reactive transitions are defined similarly to those in lattice gas automaton models. The details of the derivation for the models with exclusion principle can be found in Ref. 13; here we only briefly summarize the general ideas and give the final results.

We consider reactions which are strictly local, i.e., they involve only particles occupying the same node. Let the overall reaction mechanism consist of r elementary steps of the form

$$\begin{aligned}&n^f_{i,1}X_1+n^f_{i,2}X_2+\cdots+n^f_{i,j}X_j+\cdots\\&\underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}}n^r_{i,1}X_1+n^r_{i,2}X_2+\cdots+n^r_{i,j}X_j+\cdots,\end{aligned}$$

where the indices $i=1,\ldots r$ and $j=1,\ldots,\nu$ label steps and species, respectively. The transitions due to the i-thh step in the mechanism are characterized by two sets of stoichiometric coefficients $\{n^f_{i,1},\ldots,n^f_{i,\nu}\}$ and $\{n^r_{i,1},\ldots,n^r_{i,\nu}\}$. Specifically, if we define the vector $\mathbf{m}^{(i)}$ with elements $m^{(i)}_j=n^r_{i,j}-n^f_{i,j}$, the forward reaction at node $\mathbf{r}$ can be represented in terms of occupancies by

$$\mathbf{x}(\mathbf{r})\rightarrow\mathbf{x}(\mathbf{r})+\mathbf{m}^{(i)}.$$

Similarly, for the reverse reaction,

$$\mathbf{x}(\mathbf{r})\rightarrow\mathbf{x}(\mathbf{r})-\mathbf{m}^{(i)}.$$

The transition probabilities of these birth-death reactive events can be derived using a simple combinatorial argument. That is, one expects that the probability of reaction must be proportional to the number of ways in which the particles of the reactants can be combined in order for that reaction to occur, given the present state of the node. Specifically, we put

$$\begin{aligned}T^R_{\mathbf{x}(\mathbf{r})+\mathbf{m}^{(i)},\mathbf{x}(\mathbf{r})}&=hk_i\prod_{j=1}^{\nu}N^{n^f_{i,j}}\frac{(N-n^f_{i,j})!}{N!}\frac{x_j(\mathbf{r})!}{(x_j(\mathbf{r})-n^f_{i,j})!},\\T^R_{\mathbf{x}(\mathbf{r})-\mathbf{m}^{(i)},\mathbf{x}(\mathbf{r})}&=hk_{-i}\prod_{j=1}^{\nu}N^{n^r_{i,j}}\frac{(N-n^r_{i,j})!}{N!}\frac{x_j(\mathbf{r})!}{(x_j(\mathbf{r})-n^r_{i,j})!}.\end{aligned} \tag{9}$$

The prefactors in (9) are chosen so that the mean-field kinetic equations can be written in a neat analytic form. The exclusion principle forbids those reactive events which produce particles of any species in excess of N. Therefore, we set

$$\begin{aligned}T^R_{\mathbf{x}(\mathbf{r})+\mathbf{m}^{(i)},\mathbf{x}(\mathbf{r})}&=0,\quad\text{if } x_j+m^{(i)}_j>N,\\T^R_{\mathbf{x}(\mathbf{r})-\mathbf{m}^{(i)},\mathbf{x}(\mathbf{r})}&=0,\quad\text{if } x_j-m^{(i)}_j>N,\end{aligned} \tag{10}$$

for any i,j. Substituting the transition probabilities (9), modified according to (10), into (4) yields the matrix elements of reaction evolution operator $\hat{W}^R$.

Let us consider the mean-field dynamics of the reaction Markov chain. To begin, we note that in the mean-field limit (i.e., in the limit of a well-stirred system where the rate of diffusion is infinite), the particles are redistributed among the nodes of the lattice instantaneously at every moment of time. Hence, the local correlations between different species are effectively destroyed at the same moment as the local reactive events create them. This implies that the particles populate every node independently of each other, and the local probability distribution is the time-dependent multivariate binomial

$$\begin{aligned}P(\mathbf{x}(\mathbf{r}),n)&=P_B(\mathbf{x}(\mathbf{r}),n)\\&=\prod_{j=1}^{\nu}\binom{N}{x_j(\mathbf{r})}\left(\frac{\overline{x_j}(n)}{N}\right)^{x_j(\mathbf{r})}\left(1-\frac{\overline{x_j}(n)}{N}\right)^{N-x_j(\mathbf{r})}.\end{aligned} \tag{11}$$

We have dropped the notation due to spatial coordinates in the average concentrations in (11) since the system is homogeneous in the mean-field picture. It is easy to show that the kinetic equations in this limit have the following form:

$$\begin{aligned}\overline{x_j}(n+1)-\overline{x_j}(n)&\\&=\sum_{\mathbf{x}} x_j\hat{W}^R P_B(\mathbf{x},n)\\&=h\sum_{i=1}^{r}(n^r_{i,j}-n^f_{i,j})\left[k_i\prod_{k=1}^{\nu}\overline{x_k}^{n^f_{i,k}}(n)\right.\\&\quad\left.-k_{-i}\prod_{k=1}^{\nu}\overline{x_k}^{n^r_{i,k}}(n)\right]+Q_j(\overline{\mathbf{x}}(n))=K_j(\overline{\mathbf{x}}(n)).\end{aligned}\tag{12}$$

One observes that the first term on the second line of (12) is the mass-action law (in the discrete-time notation) appropriate for the overall reaction mechanism. The additional term $\mathbf{Q}(\overline{\mathbf{x}}(n))$ describes the deviations of the mean-field dynamics from the mass-action law due to the exclusion corrections to the birth-death transition probabilities (9). Equation (12) is the exact mean-field rate law for our model. In the application to the Willamowski-Rössler reaction diffusion system in Sec. IV we shall consider conditions where $\mathbf{Q}(\overline{\mathbf{x}}(n))$ is negligible and Eq. (12) reduces to the mass-action law.

For a finite diffusion rate, neither (11) nor (12) will be valid. The nature of this breakdown of mean-field description forms the central point of the present study. Note also that the binomial distribution (11) depends on time only through its means $\overline{x_j}(n)$ which evolve according to (12). We will use this time-dependent binomial distribution as the zeroth-order approximation to the full distribution in the following section.

III. PERTURBATION THEORY

Suppose that the system is not completely homogeneous, i.e., diffusion occurs at a finite rate determined by the value of diffusion coefficient D. Such a regime can be characterized by two time scales, τ_D and τ_R, associated with diffusion and reaction processes, respectively. We consider finite systems so that long wavelength diffusion modes are suppressed and we may insure that $\tau_D \ll \tau_R$. In the context of our model, τ_D can be the mean time required for a particle to travel the distance between two neighboring nodes, and τ_R the inverse of the smallest eigenvalue of reaction evolution operator $\hat{W}^R$. The deviation from the mean-field limit is measured by the ratio τ_D/τ_R, which will be denoted as γ henceforth; γ is equal to zero in the mean-field limit, and increases away from it.

If γ is small, the local probability distribution $P(\mathbf{x}(\mathbf{r}),t)$ obeys

$$P(\mathbf{x}(\mathbf{r}),n+1)-P(\mathbf{x}(\mathbf{r}),n)=(\gamma\hat{W}^R+\hat{W}^D)P(\mathbf{x}(\mathbf{r}),n),\tag{13}$$

where $\hat{W}^R$ and $\hat{W}^D$ are the reaction and diffusion evolution operators constructed in the previous section. We expect that the solution of (13) monotonously approaches the local binomial distribution (11) of the mean-field limit as γ tends to zero. For a nonzero γ this mean-field result is not valid, and corrections to the local binomial distribution must be introduced. In view of this, for small γ reactions can be considered as a small perturbation to the pure diffusion process and perturbation theory can be applied to solve Eq. (13). Thus, we write the local probability distribution in the form of a perturbation series,

$$P(\mathbf{x}(\mathbf{r}),n)=P_B(\mathbf{x}(\mathbf{r}),n)+\gamma P_1(\mathbf{x}(\mathbf{r}),n)+\gamma^2P_2(\mathbf{x}(\mathbf{r}),n)+\cdots,\tag{14}$$

with the local binomial distribution as the zeroth-order term. Substituting (14) into evolution Eq. (13) gives

$$\begin{aligned}&P_B(\mathbf{x}(\mathbf{r}),n+1)-P_B(\mathbf{x}(\mathbf{r}),n)\\&\quad+\sum_{k=1}^{\infty}\gamma^k\{P_k(\mathbf{x}(\mathbf{r}),n+1)-P_k(\mathbf{x}(\mathbf{r}),n)\}\\&\quad=(\gamma\hat{W}^R+\hat{W}^D)\left(P_B(\mathbf{x}(\mathbf{r}),n)+\sum_{k=1}^{\infty}\gamma^kP_k(\mathbf{x}(\mathbf{r}),n)\right).\end{aligned}\tag{15}$$

In order to extract the time dependence of each of the expansion terms from (15), we use a perturbation theoretic procedure similar to Chapman-Enskog development.[9,14] Specifically, we note that the first two terms in (15) are equivalent to a discrete derivative of the binomial distribution $P_B(\mathbf{x}(\mathbf{r}),n)$ with respect to time. Recalling that this distribution depends on time implicitly, through its means $\overline{\mathbf{x}}(\mathbf{r},n)$, one can rewrite the derivative as follows:

$$\begin{aligned}&P_B(\mathbf{x}(\mathbf{r}),n+1)-P_B(\mathbf{x}(\mathbf{r}),n)\\&\quad=[\overline{\mathbf{x}}(\mathbf{r},n+1)-\overline{\mathbf{x}}(\mathbf{r},n)]\ \frac{\partial}{\partial\overline{\mathrm{x}}}P_B(\mathbf{x}(\mathbf{r}),n).\end{aligned}\tag{16}$$

The quantity $\overline{\mathbf{x}}(\mathbf{r},n+1)-\overline{\mathbf{x}}(\mathbf{r},n)$ appearing in (16) is given by the kinetic equations corresponding to (15). The latter can be obtained in the standard way, i.e., multiplying both sides of (15) by $\mathbf{x}(\mathbf{r})$ and summing over all possible combinations of the occupation numbers. Using the properties of operators $\hat{W}^D$ and $\hat{W}^R$ introduced in Sec. II, we find

$$\begin{aligned}\overline{\mathbf{x}}(\mathbf{r},n+1)-\overline{\mathbf{x}}(\mathbf{r},n)&=D\ \Delta\overline{\mathbf{x}}(\mathbf{r},n)+\gamma\mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n))\\&\quad+\sum_{k=1}^{\infty}\gamma^{k+1}\ \langle\mathbf{x}(\mathbf{r})\hat{W}^RP_k(\mathbf{x}(\mathbf{r}),n)\rangle,\end{aligned}\tag{17}$$

where $\mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n))$ stands for mean-field dynamics [cf. Eq. (12)], and

$$\langle\mathbf{x}(\mathbf{r})\hat{W}^RP_k(\mathbf{x}(\mathbf{r}),n)\rangle=\sum_{\mathbf{x}(\mathbf{r})}\mathbf{x}(\mathbf{r})\hat{W}^RP_k(\mathbf{x}(\mathbf{r}),n).\tag{18}$$

Before we proceed with the development of the solution to the evolution Eq. (15), one important question must be addressed: specifically, that of the validity of the regular perturbation expansion (14) for the case of far-from-equilibrium chemical systems. It is well known that the dynamics of such systems may be of relaxational character, i.e., it exhibits well-defined fast and slow parts. This is manifested by the significant jumps in reaction rates, as well as the higher derivatives of concentrations with respect to time which are observed as the system switches from fast to slow dynamics, or vice versa. In principle, it is quite possible that such jumps can cause a similar singular behavior in the probability distribution $P(\mathbf{x}(\mathbf{r}),n)$, thereby making the description in terms of a regular perturbation series invalid. In order to avoid such breakdown, we require that γ be small enough for the following relations to hold at all $\mathbf{r}$ and n:

$$\begin{aligned} &P_i(\mathbf{x}(\mathbf{r}),n)\ll\gamma^{-1},\\ &\langle \mathbf{x}(\mathbf{r})\hat{W}^R P_i(\mathbf{x}(\mathbf{r}),n)\rangle\ll\gamma^{-1},\quad i=1,2,3,\ldots\ . \end{aligned}\tag{19}$$

With this requirement satisfied, the regular perturbation method remains valid, at least on the level of description provided by Eqs. (15) and (17).

Now, suppose that we want to determine the probability distribution up to the k-th order term. For that purpose, it is sufficient to retain in (17) terms up to the order γ^k. Then, with the use of (17) and (16), we can separate (15) into a set of k equations, each describing evolution of one of the expansion terms $P_1(\mathbf{x}(\mathbf{r}),n),\ldots,P_k(\mathbf{x}(\mathbf{r}),n)$. Thus, the equation for $P_1(\mathbf{x}(\mathbf{r}),n)$ reads

$$\begin{aligned} &\gamma P_1(\mathbf{x}(\mathbf{r}),n+1)-\gamma P_1(\mathbf{x}(\mathbf{r}),n)\\ &\quad=\left[\hat{W}^D-\ D\ \Delta\overline{\mathrm{x}}(\mathbf{r},n)\ \frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n)\\ &\qquad+\gamma\left[\hat{W}^R-\ \mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n))\ \frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n)\\ &\qquad+\gamma\hat{W}^D P_1(\mathbf{x}(\mathbf{r}),n), \end{aligned}\tag{20}$$

and for $P_i(\mathbf{x}(\mathbf{r}),n)$, $1<i\leq k$ (cancelling out the factor γ^i),

$$\begin{aligned} &P_i(\mathbf{x}(\mathbf{r}),n+1)-P_i(\mathbf{x}(\mathbf{r}),n)\\ &\quad=\hat{W}^R P_{i-1}(\mathbf{x}(\mathbf{r}),n)+\hat{W}^D P_i(\mathbf{x}(\mathbf{r}),n)\\ &\qquad-\langle\mathbf{x}(\mathbf{r})\hat{W}^R P_i(\mathbf{x}(\mathbf{r}),n)\rangle\frac{\partial}{\partial\overline{\mathrm{x}}}P_B(\mathbf{x}(\mathbf{r}),n). \end{aligned}\tag{21}$$

The solution of this system of inhomogeneous linear equations will be unique if we require

$$\begin{aligned} &\langle P_i(\mathbf{x}(\mathbf{r}),n)\rangle=0,\\ &\langle\mathbf{x}(\mathbf{r})P_i(\mathbf{x}(\mathbf{r}),n)\rangle=0,\quad i=1,\ldots,k. \end{aligned}\tag{22}$$

Together with the solvability conditions (22), (20) and (21) form a closed hierarchy from which one may evaluate the terms of the perturbation expansion (14) to any desired order.

In the remainder of this paper our attention will be limited to the first two terms of the series (14). Therefore, we need only solve the lowest-order equation of the above hierarchy, i.e., (20). By direct computation of $\hat{W}^D P_B(\mathbf{x}(\mathbf{r}),n)$ we may show that the first term on the right-hand-side (rhs) of (20) is zero and, consequently, that $P_1(\mathbf{x}(\mathbf{r}),n+1)-P_1(\mathbf{x}(\mathbf{r}),n)$ does not contain contributions of order unity. For simplicity, we assume that the system consists of a single species. Using the definition of the diffusion evolution operator $\hat{W}^D$ [cf. (6) and (7)] we can write this term as

$$\begin{aligned} &\frac{\chi(\mathbf{r},n)}{N}\left[\left(1-\frac{x(\mathbf{r})-1}{N}\right)P_B(x(\mathbf{r})-1,n)\right.\\ &\quad\left.-\left(1-\frac{x(\mathbf{r})}{N}\right)P_B(x(\mathbf{r}),n)\right]+\left(1-\frac{\chi(\mathbf{r},n)}{N}\right)\\ &\quad\times\left[\frac{x(\mathbf{r})+1}{N}P_B(x(\mathbf{r})+1,n)-\frac{x(\mathbf{r})}{N}P_B(x(\mathbf{r}),n)\right]\\ &\quad-\frac{\chi(\mathbf{r},n)-\overline{x}(\mathbf{r},n)}{N}\ \frac{\partial}{\partial\overline{x}}P_B(x(\mathbf{r},n). \end{aligned}\tag{23}$$

Taking advantage of two easily proven results,

$$\begin{aligned} &\left(1-\frac{x-1}{N}\right)P_B(x-1,n)=\frac{x(N-\overline{x}(n))}{N\overline{x}(n)}P_B(x,n),\\ &\frac{\partial}{\partial\overline{x}}P_B(x,n)=\frac{xP_B(x,n)-(x+1)P_B(x+1,n)}{\overline{x}(n)}, \end{aligned}\tag{24}$$

we can show that (23) vanishes. Generalization of this result for a many-species system is straightforward due to the properties of the diffusion evolution operator [cf. (6)].

With the first term on the rhs of (20) eliminated, we can obtain $P_1(\mathbf{x}(\mathbf{r}),n)$ by solving a simple initial-value problem. Suppose that at $n=0$ the local probability distribution is purely binomial, i.e., $P_1(\mathbf{x}(\mathbf{r}),0)=0$. Then, one finds from (20)

$$\begin{aligned} P_1(\mathbf{x}(\mathbf{r}),n)=&\sum_{n'=0}^{n-1}(\hat{I}+\hat{W}^D)^{n-n'-1}\\ &\times\left[\hat{W}^R-\mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n'))\frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n'), \end{aligned}\tag{25}$$

where $\hat{I}$ is the identity operator ($I_{\mathbf{x}'\mathbf{x}}=\delta_{\mathbf{x}'\mathbf{x}}$), and $(\hat{I}+\hat{W}^D)^{n-n'-1}$ is to be understood as a time-ordered product of $n-n'-1$ terms $(\hat{I}+\hat{W}^D)$, with the leftmost term taken at the moment of time $n-1$ and the rightmost at $n'+1$. In Appendix A we prove that (25) does satisfy the solvability conditions (22).

The quantities whose dynamics will be of interest to us are the global concentrations $\overline{\mathbf{x}}(t)$, i.e., the local concentrations $\overline{\mathbf{x}}(\mathbf{r},t)$ averaged over all nodes of the lattice. (Henceforth, whenever we omit $\mathbf{r}$ in the arguments of the concentrations, the global concentrations are meant.) The kinetic equations for the local concentrations are given by (17); at the level of present approximation we can truncate the infinite series on the rhs of (17) after the term of order γ^2. To obtain kinetic equations for the global concentrations we substitute $P_1(\mathbf{x}(\mathbf{r}),n)$ from (25) into (17), sum both sides over all $\mathbf{r}$, and divide by the total number of nodes M. Since diffusion conserves the total number of particles in the system, the pure diffusion term in (17) yields zero on summation and we obtain for the global concentration of the i-th species

$$\overline{x_i}(n+1)-\overline{x_i}(n)=\frac{\gamma}{M}\sum_{\mathbf{r}} K_i(\overline{\mathbf{x}}(\mathbf{r},n)) + \frac{\gamma^2}{M}\sum_{\mathbf{r}}\sum_{n'=0}^{n-1}\langle x_i(\mathbf{r})\hat{W}^R(\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x}(\mathbf{r}),n')\rangle, \quad (26)$$

where $\hat{S}=\hat{W}^R-\mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n'))\,\partial/\partial\overline{\mathbf{x}}$, and $\overline{\mathbf{x}}(n)$ is the vector of global concentrations.

If diffusion is sufficiently fast ($\gamma \ll 1$), the system remains nearly homogeneous at all times, i.e., $\overline{x_i}(\mathbf{r},n)$ are slowly varying functions of $\mathbf{r}$ which do not deviate significantly from their spatial averages $\overline{x_i}(n)$. Hence, if we put

$$\overline{x_i}(\mathbf{r},n)\approx\overline{x_i}(n) \quad (27)$$

for all $\mathbf{r}$ and n, the summation over $\mathbf{r}$ in (26) becomes trivial, and we find,

$$\overline{x_i}(n+1)-\overline{x_i}(n) =\gamma K_i(\overline{\mathbf{x}}(n))+\gamma^2 \times\sum_{n'=0}^{n-1}\langle x_i(\mathbf{r})\hat{W}^R(\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x},n')\rangle, \quad (28)$$

where the local concentrations appearing implicitly in $\hat{W}^D$, $\hat{S}$, and $P_B(\mathbf{x},n)$ in the last term are replaced by global concentrations $\overline{\mathbf{x}}(n)$.

The kinetic equations (28) do not readily offer a deeper insight into dynamics of the model since the memory function in the last term cannot be easily evaluated for general reaction mechanisms. However, as we will show in the following section, for specific reaction mechanisms it is possible to write these equations in a tidy analytic form which allows clear physical interpretation.

IV. APPLICATION TO WILLAMOWSKI-RÖSSLER MODEL

We now apply the above formalism to a reaction-diffusion system with the Willamowski-Rössler reaction mechanism.[10] This mechanism consists of the following elementary steps:

$$A_1+X\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}2X, \quad X+Y\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}2Y,$$

$$A_5+Y\underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}A_2, \quad X+Z\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}}A_3,$$

$$A_4+Z\underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}}2Z\ .$$

Here A_1, A_4, A_5 are initiators, and A_2, A_3 are final products; concentrations of all these species are held constant by external fluxes. The intermediates whose dynamics is followed are X, Y, and Z. The mass-action law for this model has the following form (indices 1,2,3 refer to X, Y, and Z species, respectively):

$$\frac{d\overline{x_1}}{dt}=\kappa_1\overline{x_1}(t)-\kappa_{-1}\overline{x_1^2}(t)-\kappa_2\overline{x_1}(t)\overline{x_2}(t)+\kappa_{-2}\overline{x_2^2}(t) -\kappa_4\overline{x_1}(t)\overline{x_3}(t)+\kappa_{-4}=R_1(\overline{x_1}(t),\overline{x_2}(t),\overline{x_3}(t)),$$

$$\frac{d\overline{x_2}}{dt}=\kappa_2\overline{x_1}(t)\overline{x_2}(t)-\kappa_{-2}\overline{x_2^2}(t)-\kappa_3\overline{x_2}(t)+\kappa_{-3} =R_2(\overline{x_1}(t),\overline{x_2}(t)), \quad (29)$$

$$\frac{d\overline{x_3}}{dt}=-\kappa_4\overline{x_1}(t)\overline{x_3}(t)+\kappa_5\overline{x_3}(t)-\kappa_{-5}\overline{x_3^2}(t)+\kappa_{-4} =R_3(\overline{x_1}(t),\overline{x_3}(t)),$$

where the concentrations of initiators and products are incorporated in the values of rate constants κ_i, $i=1,\ldots,5$. Equations (29) have been considered in earlier studies and are known to give rise to a period-doubling cascade leading to a chaotic attractor.[6,15,16]

We begin our analysis by calculating the contributions that the reactive steps of the Willamowski-Rössler mechanism make to the memory function in (28). Below, the contributions from mono- and bimolecular steps are considered in turn.

A. Monomolecular steps

All monomolecular steps in the Willamowski-Rössler model have the following form:

$$A_i\overset{k}{\rightarrow}n_jX_j+n_lX_l+n_mA_m, \quad n_j,n_l,n_m=0,1.$$

The matrix elements of the reaction evolution operator corresponding to such steps can be obtained from the general expression for reactive transition probabilities (9). We find

$$W^R_{\mathbf{x}\mathbf{x}'}=\begin{cases}-h\kappa(1-m_j\delta_{x_j,N})(1-m_l\delta_{x_l,N}), & \text{if } \mathbf{x}'=\mathbf{x},\\ h\kappa, & \text{if } \mathbf{x}'=\mathbf{x}-\mathbf{m},\\ 0, & \text{for all other } \mathbf{x}',\end{cases}$$

where the Kronecker deltas account for the exclusion principle, the concentration of species A_i is incorporated in the value of κ, and vector $\mathbf{m}$ is defined through the stoichiometric coefficients as outlined in Sec. II.

At this point, in order to facilitate further calculations, we neglect the terms in the memory function that arise from the exclusion principle. Such approximation is justified for the Willamowski-Rössler model, since those terms can always be made arbitrarily small by a simple rescaling of concentrations. As an example, suppose that $N=10$ and the concentrations are scaled so that they practically never exceed 1.5 particles per node. Given that the reactive transition probabilities are of the order of 10^{-3}–10^{-4}, numerical estimates show that the terms due to the exclusion principle are 2–3 orders of magnitude smaller than all the other terms in (28). (The concentration scaling and the value of N used in the lattice gas automaton simulations of the Willamowski-Rössler model below are the same as considered here.)

The contribution to the memory function can now be evaluated in a fairly straightforward way. We substitute the evolution operator from above in place of the leftmost $\hat{W}^R$ in the last term of (28), and calculate the average. After a few transformations, we arrive at

$$\gamma^2 h\kappa \sum_{n'=0}^{n-1} \langle (\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x},n')\rangle. \tag{30}$$

One immediately recognizes in (30) one of the two quantities (to within a constant multiplier) that we have dealt with in a different context in Appendix A [cf. (A1)]. Using the results obtained in Appendix A we find that (30) vanishes. Therefore, we conclude that monomolecular reactive steps in the Willamowski-Rössler mechanism do not contribute to the memory function in (28).

B. Bimolecular steps

The bimolecular steps in the Willamowski-Rössler model fall into three classes; these are listed below, along with the corresponding matrix elements of the $\hat{W}^R$ operator,

(1) $2X_i \xrightarrow{k} X_i + n_j X_j + n_l A_l, \quad n_j, n_l = 0,1,$

$$W^R_{\mathbf{xx}'} = \begin{cases} -\dfrac{N}{N-1} hkx_i(x_i-1)(1-m_j\delta_{x_j,N}), & \text{if } \mathbf{x}'=\mathbf{x}, \\ \dfrac{N}{N-1} hk(x_i-m_i)(x_i-m_i-1), & \text{if } \mathbf{x}'=\mathbf{x}-\mathbf{m}, \\ 0, & \text{for all other } \mathbf{x}', \end{cases}$$

(2) $X_i + X_j \xrightarrow{k} n_i X_i + n_j A_j, \quad n_i = 0,2; n_j = 0,1,$

$$W^R_{\mathbf{xx}'} = \begin{cases} -hkx_ix_j\left(1-\dfrac{m_i+1}{2}\delta_{x_i,N}\right), & \text{if } \mathbf{x}'=\mathbf{x}, \\ hk(x_i-m_i)(x_j-m_j), & \text{if } \mathbf{x}'=\mathbf{x}-\mathbf{m}, \\ 0, & \text{for all other } \mathbf{x}', \end{cases}$$

(3) $A_i + X_j \xrightarrow{k} 2X_j,$

$$W^R_{\mathbf{xx}'} = \begin{cases} -h\kappa x_j(1-\delta_{x_j,N}), & \text{if } \mathbf{x}'=\mathbf{x}, \\ h\kappa(x_j-m_j), & \text{if } \mathbf{x}'=\mathbf{x}-\mathbf{m}, \\ 0, & \text{for all other } \mathbf{x}', \end{cases}$$

where $m_j = 1$ and the concentration of A_i is incorporated into the value of κ.

We neglect the terms arising from the exclusion principle on the basis of the rescaling argument given above, and calculate the contributions to the memory function due to these reactive steps. We find

$$\begin{aligned} &(1) \quad \frac{N}{N-1} \gamma^2 hk \sum_{n'=0}^{n-1} \langle x_i(x_i-1) \\ &\qquad \times (\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x},n')\rangle, \\ &(2) \quad \gamma^2 hk \sum_{n'=0}^{n-1} \langle x_ix_j(\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x},n')\rangle. \\ &(3) \quad \gamma^2 h\kappa \sum_{n'=0}^{n-1} \langle x_j(\hat{I}+\hat{W}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x},n')\rangle. \end{aligned} \tag{31}$$

Note that the last contribution in (31) is identical (to within a constant multiplier) to one of the quantities considered in Appendix A [cf. (A9)]. From the results of Appendix A we infer that this contribution vanishes. Also, using the method of Appendix A one can show that the first two contributions in (31) can be reduced to the following memory terms with a simple exponential kernel:

$$\begin{aligned} &(1) \quad \frac{N}{N-1} \gamma^2 hk \sum_{n'=0}^{n-1} \left(1-\frac{2}{\nu N}\right)^{n-n'-1} \langle x_i^2 \hat{S}P_B(\mathbf{x},n'h)\rangle, \\ &(2) \quad \gamma^2 hk \sum_{n'=0}^{n-1} \left(1-\frac{2}{\nu N}\right)^{n-n'-1} \langle x_ix_j \hat{S}P_B(\mathbf{x},n'h)\rangle. \end{aligned} \tag{32}$$

Summarizing the results obtained above, we conclude that the only reactive steps that contribute to the memory function in (28) are those involving reactions between the particles of intermediate species. The contribution is given by the first term in (32) if the reacting particles are of the same chemical nature, and by the second term otherwise.

By inspection of the mechanism, we find four contributing steps for the X species

$$\begin{aligned} 2X &\xrightarrow{k_{-1}} A_1 + X, \\ 2Y &\xrightarrow{k_{-2}} X + Y, \\ X+Y &\xrightarrow{k_2} 2Y, \\ X+Z &\xrightarrow{k_4} A_3, \end{aligned}$$

two for the Y species

$$\begin{aligned} 2Y &\xrightarrow{k_{-2}} X + Y, \\ X+Y &\xrightarrow{k_2} 2Y, \end{aligned}$$

and two for the Z species

$$\begin{aligned} 2Z &\xrightarrow{k_{-5}} A_4 + Z, \\ X+Z &\xrightarrow{k_4} A_3, \end{aligned}$$

To obtain the kinetic equations for the global concentrations of each species, one simply adds contributions appropriate for the steps in each of the three groups above and substitutes the result in place of the memory term in (28). Proceeding in this way, we arrive at

$$\begin{aligned} &\overline{x_1}(n+1) - \overline{\mathbf{x}_1}(n) \\ &\quad = \gamma h R_1(\overline{\mathbf{x}}(n)) - \gamma^2 h \frac{N}{N-1} \sum_{n'=0}^{n-1} (1-\lambda)^{n-n'-1} \\ &\qquad \times [\kappa_{-1} C_{x_1,x_1}(n') - \kappa_{-2} C_{x_2,x_2}(n')] \\ &\qquad - \gamma^2 h \sum_{n'=0}^{n-1} (1-\lambda)^{n-n'-1} [\kappa_2 C_{x_1,x_2}(n') \\ &\qquad + \kappa_4 C_{x_1,x_3}(n')], \end{aligned} \tag{33}$$

$$\overline{x_2}(n+1)-\overline{x_2}(n) = \gamma h R_2(\overline{\mathbf{x}}(n)) - \gamma^2 h \sum_{n'=0}^{n-1} (1-\lambda)^{n-n'-1} \times\left[\frac{N\kappa_{-2}}{N-1} C_{x_2,x_2}(n') - \kappa_2 C_{x_1,x_2}(n')\right], \tag{34}$$

$$\overline{x_3}(n+1)-\overline{x_3}(n) = \gamma h R_3(\overline{\mathbf{x}}(n)) - \gamma^2 h \sum_{n'=0}^{n-1} (1-\lambda)^{n-n'-1} \times\left[\frac{N\kappa_{-5}}{N-1} C_{x_3,x_3}(n') + \kappa_4 C_{x_1,x_3}(n')\right], \tag{35}$$

where

$$C_{x_i,x_j}(t) = \langle x_i x_j \hat{S} P_B(\mathbf{x},n)\rangle, \quad \hat{S} = \hat{W}^R - h\mathbf{R}(\overline{\mathbf{x}}(n)) \frac{\partial}{\partial \overline{\mathbf{x}}}, \tag{36}$$

and $R_i(\overline{\mathbf{x}}(n))$, $i=1,2,3$ are the mass-action law terms from (29), $\lambda = 2/\nu N = 2/3N$ for the Willamowski-Rössler model. The procedure which we used above to evaluate the memory terms in (28) by neglecting terms due to the exclusion principle can be extended to any reaction mechanism involving only mono- and bimolecular steps. Note that in the scaling limit where the terms due to the exclusion principle can be omitted in evaluating all average quantities, the mean-field reaction dynamics is entirely due to the mass-action law, i.e., $\mathbf{K}(\overline{\mathbf{x}}(n)) = h\mathbf{R}(\overline{\mathbf{x}}(n))$ [cf. (12)]. The continuous-time form of Eqs. (33)–(35) is derived in Appendix B.

In order to evaluate the averages appearing in the Eqs. (33)–(35) one needs to know the matrix elements of the full reaction evolution operator $\hat{W}^R$. The latter are defined through the reactive transition probabilities which, for the Willamowski-Rössler model, are as follows:

$$\begin{aligned}
&T^R_{x_1+1,x_2,x_3;\mathbf{x}} = h\kappa_1 x_1(1-\delta_{x_1,N}), && T^R_{x_1-1,x_2,x_3;\mathbf{x}} = \frac{N}{N-1} h\kappa_{-1} x_1(x_1-1),\\
&T^R_{x_1-1,x_2+1,x_3;\mathbf{x}} = h\kappa_2 x_1 x_2(1-\delta_{x_2,N}), && T^R_{x_1+1,x_2-1,x_3;\mathbf{x}} = \frac{N}{N-1} h\kappa_{-2} x_2(x_2-1)(1-\delta_{x_1,N}),\\
&T^R_{x_1,x_2-1,x_3;\mathbf{x}} = h\kappa_3 x_2, && T^R_{x_1,x_2+1,x_3;\mathbf{x}} = h\kappa_{-3}(1-\delta_{x_2,N}),\\
&T^R_{x_1-1,x_2,x_3-1;\mathbf{x}} = h\kappa_4 x_1 x_3, && T^R_{x_1+1,x_2,x_3+1;\mathbf{x}} = h\kappa_{-4}(1-\delta_{x_1,N})(1-\delta_{x_3,N}),\\
&T^R_{x_1,x_2,x_3+1;\mathbf{x}} = h\kappa_5 x_3(1-\delta_{x_3,N}), && T^R_{x_1,x_2,x_3-1;\mathbf{x}} = \frac{N}{N-1} h\kappa_{-5} x_3(x_3-1).
\end{aligned} \tag{37}$$

Here $\mathbf{x} \equiv (x_1,x_2,x_3)$. Using the transition probabilities (37) to compute C_{x_i,x_j}, we obtain

$$\begin{aligned}
C_{x_1,x_1}(t) &= 2h\left[\kappa_1\overline{x_1}(t) - \kappa_{-1}\overline{x_1^2}(t)\left(1-\frac{\overline{x_1}(t)}{N}\right) + \frac{\kappa_{-2}}{N}\overline{x_1}(t)\overline{x_2^2}(t) + \frac{\kappa_{-4}}{N}\overline{x_1}(t)\right],\\
C_{x_2,x_2}(t) &= 2h\left[\kappa_2\overline{x_1}(t)\overline{x_2}(t) - \kappa_{-2}\overline{x_2^2}(t)\left(1-\frac{\overline{x_2}(t)}{N}\right) + \frac{\kappa_{-3}}{N}\overline{x_2}(t)\right],\\
C_{x_3,x_3}(t) &= 2h\left[\kappa_5\overline{x_3}(t) - \kappa_{-5}\overline{x_3^2}(t)\left(1-\frac{\overline{x_3}(t)}{N}\right) + \frac{\kappa_{-4}}{N}\overline{x_3}(t)\right],\\
C_{x_1,x_2}(t) &= h\left[\kappa_{-2}\overline{x_2^2}(t)\left(1-\frac{2\overline{x_2}(t)}{N}\right) - \kappa_2\overline{x_1}(t)\overline{x_2}(t) \times\left(1-\frac{\overline{x_2}(t)-\overline{x_1}(t)}{N}\right)\right],\\
C_{x_1,x_3}(t) &= h\left[\kappa_{-4} - \kappa_4\overline{x_1}(t)\overline{x_3}(t)\left(1-\frac{\overline{x_1}(t)+\overline{x_3}(t)}{N}\right)\right].
\end{aligned} \tag{38}$$

Equations (33)–(35), together with (38), describe the dynamics of the global concentrations within terms of order γ^2 for the Willamowski-Rössler reaction-diffusion system.

We conclude this discussion by proving that the dynamics predicted by Eqs. (33)–(35) is consistent with the initial assumptions of the theory, i.e., that it converges to mass-action law dynamics in the well-stirred regime (i.e., $\gamma \to 0$). Because h is arbitrary, we observe that assigning a smaller value to γ simply amounts to following the dynamics due to (33)–(35) on a smaller time scale. This implies

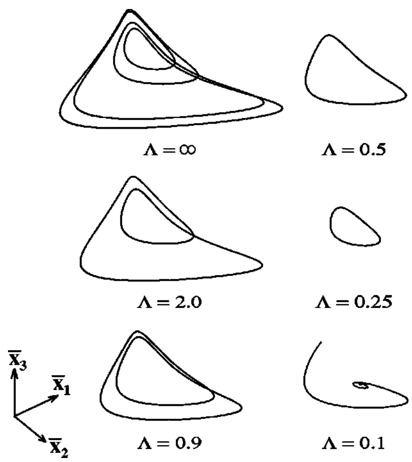

FIG. 1. Phase-space trajectories obtained from Eqs. (33)–(35) for different values of Λ. Mass-action law trajectory ($\Lambda=\infty$) is period-4. Indices 1, 2, and 3 in the coordinate labels correspond to X, Y, Z species, respectively. All trajectories are drawn to the same scale. The values of Λ are given in units of $1/h$ ($h=5\cdot 10^{-4}$).

that under a rescaling of time $h'=\gamma h$, the limit $\gamma\to 0$ is formally equivalent to the limit $h'\to 0$ with γ fixed. Defining a new discrete (real-valued) time variable $t_n=(n/\gamma)\,h'$, we can recast (33)–(35) in the following form [we put $\gamma=1$ and consider only Eq. (34), for simplicity]:

$$\begin{aligned}\overline{x_2}(t_n+h')-\overline{x_2}(t_n)\\ &=h'R_2(\overline{\mathbf{x}}(t_n))-h'^2\sum_{n'=0}^{n-1}(1-\lambda)^{\frac{t_n-t_{n'}-h'}{h'}}\\ &\times\left[\frac{N}{N-1}\,\frac{\kappa_{-2}C_{x_2,x_2}(t_{n'})}{h'}-\frac{\kappa_2 C_{x_1,x_2}(t_{n'})}{h'}\right].\end{aligned} \tag{39}$$

Keeping t_n and $t_{n'}$ constant as we let h' tend to zero, we obtain

$$\begin{aligned}\frac{d\overline{x_2}(t)}{dt}&=R_2(\overline{\mathbf{x}}(t))-\lim_{h'\to 0}\int_0^{t-h'}e^{-\frac{\lambda(t-t'-h')}{h'}}\\ &\times\left[\frac{N}{N-1}\,\frac{\kappa_{-2}C_{x_2,x_2}(t')}{h'}-\frac{\kappa_2 C_{x_1,x_2}(t')}{h'}\right]dt'\\ &=R_2(\overline{\mathbf{x}}(t)).\end{aligned} \tag{40}$$

The result on the last line follows since the kernel of the integral term vanishes exponentially for all $t-t'$. Similar results hold for Eqs. (33) and (35) as well.

C. Numerical results

We have solved numerically the continuous-time form of the Eqs. (33)–(35) (cf. Appendix B) using Euler's algorithm; the integral terms were evaluated at every time step by Simpson's method. In Fig. 1 we present the phase-space trajectories obtained for different values of the diffusion coefficient (as measured by the exponent of the memory kernel Λ) as well as for the mean-field regime ($\Lambda=\infty$). The values of rate constants used in these calculations are as follows: $\kappa_1=31.2, \kappa_{-1}=0.2, \kappa_2=1.533, \kappa_{-2}=0.1, \kappa_3=10.8, \kappa_{-3}\kappa_1=31.2$, $\kappa_{-1}=0.2, \kappa_2=1.533$, $\kappa_{-2}=0.1, \kappa_3=10.8, \kappa_{-3}=0.12, \kappa_4=1.02, \kappa_{-4}=0.01, \kappa_5=16.5, \kappa_{-5}=0.5$; this choice corresponds to the period-4 regime in the mass-action dynamics. The integration time step h was equal to $5\cdot 10^{-4}$.

It is evident from Fig. 1 that, as the diffusion becomes slower (i.e., the value of Λ becomes smaller), the trajectories are monotonously transformed so that they traverse the period-doubling cascade of the mass-action law (29) in the backward direction: the smaller the value of the diffusion coefficient (with rate constants unchanged), the less the dynamics of the global concentrations corresponds to the mass-action law. Furthermore, this breakdown of mass-action description can be modeled by a parametric shift in the mass-action law (along with rescaling of time and, possibly, concentrations) such that the dynamics proceeds from the period-4 regime (corresponding to the mean-field regime in Fig. 1) to period-2, period-1, and finally to stable focus.

We now turn to the comparison of the numerical solutions of Eqs. (33)–(35) and the dynamics observed in the lattice gas automaton simulations of the Willamowski-Rössler model. The lattice gas automaton used in these simulations was implemented in essentially the same way as in the earlier studies;[6,13] the only difference is in the nature of the diffusion rule, which we modify so that it corresponds to the diffusion evolution operator (7). The simulations were performed for a triangular lattice of size 200×200 nodes, with time step $h=5\cdot 10^{-4}$. The exclusion parameter N was equal to 10 (i.e., no more than 10 particles of each species were allowed to occupy any node at any time). All concentrations were scaled by a factor of 40 so that they do not exceed 1.5 particles per node throughout the simulations.

In a lattice gas automaton simulation, the local probability distribution evolves in time according to the following equation:

$$P(\mathbf{x}(\mathbf{r}),n+1)=(\hat{I}+\hat{W}^R)^{m_R}(\hat{I}+\hat{W}^D)^{m_D}P(\mathbf{x}(\mathbf{r}),n), \tag{41}$$

where m_R, m_D are positive integers, and $\hat{I}$ is the identity operator. Equation (41) is approximately equivalent to the reaction-diffusion evolution Eq. (13), with parameter γ given, to the leading order, by the ratio (m_R/m_D). This fact, along with definition of the parameter Λ [$\Lambda=2/3N\gamma h$ for the Willamowski-Rössler model], allows us to approximately relate the results of an automaton simulation with a certain value of (m_R/m_D) to a solution of the kinetic Eqs. (33)–(35) with an appropriate value of Λ.

In Fig. 2 we present phase-space trajectories from typical lattice gas automaton simulations for the parametric regimes where the mass-action law dynamics is period-1 and period-2. All rate constants except κ_2 are the same as in Fig. 1; κ_2 is equal to 1.4 and 1.5, respectively. For each regime, Λ was equal to 0.667, 13.333, and ∞, the latter corresponding to the limit of a well-stirred system. The simulations of a well-stirred system were performed by reseeding the nodes of the lattice according to binomial distribution at every time step.

We observe that the trajectories from these simulations exhibit the same general trend as those computed using kinetic Eqs. (33)–(35) in Fig. 1. Namely, note that for the regime where the mass-action law dynamics is period-2, the

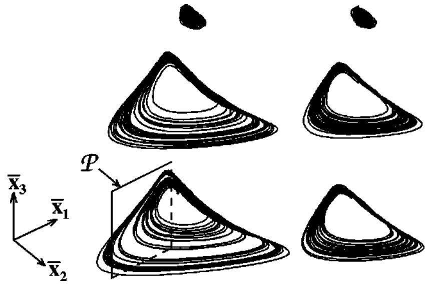

FIG. 2. Phase-space trajectories from lattice gas automaton simulations for $\kappa_2=1.5$ (left) and $\kappa_2=1.4$ (right). The mass-action law dynamics is period-2 and period-1, respectively. For each parametric regime, the values of Λ (in units of $1/h$) are: 0.667 (top panel), 13.333 (middle panel), and ∞ (bottom panel). All trajectories are drawn to the same scale. Concentration scaling parameter is 40.

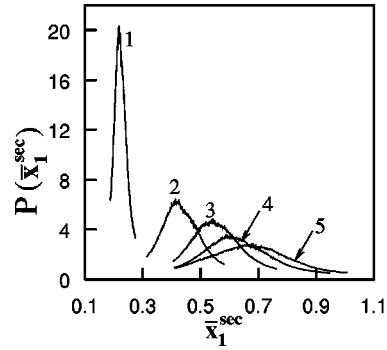

FIG. 4. Distribution of concentration of X species on Poincaré section $\mathcal{P}$ for different values of Λ. The mass-action law dynamics is period-2 ($\kappa_2=1.5$). The graphs are numbered according to the value of Λ as in Fig. 3. Each distribution is computed from a set of 2000 data points.

trajectory is gradually transformed from noisy period-2 ($\Lambda=\infty$) to noisy period-1 ($\Lambda=13.333$), and finally to the stable focus ($\Lambda=0.667$). In order to investigate this effect in more detail, we construct a Poincaré section for the trajectories from automaton simulation. The half-plane of the section (denoted by $\mathcal{P}$) is shown in Fig. 2, bottom left panel, and defined as follows: $\{\mathcal{P}:\overline{x}_1\geqslant 0.3;\overline{x}_2=0.25;\overline{x}_3\geqslant 0\}$.

In Fig. 3 we show the normalized distribution of concentration of X species on Poincaré section $\mathcal{P}$ for different values Λ. The value of κ_2 is 1.4; corresponding mass-action law dynamics is period-1. One observes that the peak of the distribution shifts toward lower concentrations as Λ decreases, indicating that the trajectory shrinks as the rate diffusion is decreased. That this shrinking is due to a parametric shift and not to simple rescaling of volume can be seen from the fact that the shift of the peak vanishes as the diffusion becomes faster and the automaton trajectory approaches that of the mass-action law. Note that the width of the distribution does not vanish as the rate of diffusion increases, but instead approaches a nonzero limiting value. This effect arises as a result of fluctuations which the global average concentrations experience due to the finite number of particles involved in the simulations.

Figure 4 presents similar distributions computed for $\kappa_2=1.5$ (the mass-action law dynamics is period-2). The values of Λ used in these calculations are the same as in Fig. 3.

Note that for the highest value of Λ (i.e., the fastest diffusion) the width of distribution in Fig. 4 is considerably greater than in Fig. 3. The additional spreading comes from the fact that the dynamics is already beyond the period-doubling bifurcation at this value of Λ. However, the concentration fluctuations destroy the bimodality in distribution, and we are unable to distinguish the loops of period-2 trajectory even for relatively fast diffusion. Larger system sizes are necessary in order to resolve this structure.

Finally, in Fig. 5 we show the average oscillation amplitude for the concentration of Y species for a series of lattice gas automaton simulations. The values of the rate constants correspond to period-1 regime in the mass-action law dynamics and are the same for all simulations, while Λ is varied from 0.667 to 13.333. The results obtained from the kinetic Eqs. (33)–(35) are shown by the solid line. The oscillation amplitude $\overline{x}_i^{amp}$ is defined as the difference between the maximum and the minimum of $\overline{x}_i$ over one full cycle of trajectory around the unstable focus. Since the present theory is approximate, our primary aim here is to present a qualitative, rather than quantitative, comparison of theoretical data and simulations. Therefore, the exponent Λ is given in Fig. 5 in rescaled form, $\Lambda_{resc}=(\Lambda-\Lambda_{ref})/\Lambda_{ref}$. Here Λ_{ref} is the reference value of Λ, which is equal to 0.667 for the automaton simulations, and 0.128 for the theoretical

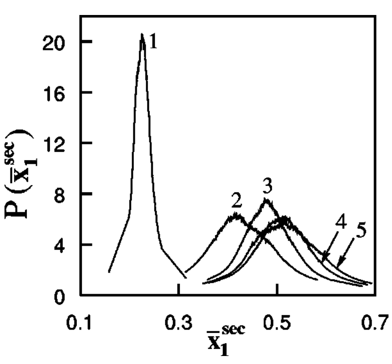

FIG. 3. Distribution of concentration of X species on Poincaré section $\mathcal{P}$ for different values of Λ. The mass-action law dynamics is period-1 ($\kappa_2=1.4$). The graphs are numbered according to the value of Λ (in units of $1/h$) as follows: 1,$\Lambda=0.667$; 2,$\Lambda=3.333$; 3,$\Lambda=6.667$; 4,$\Lambda=10.0$; 5,$\Lambda=13.333$. Each distribution is computed from a set of 2000 data points.

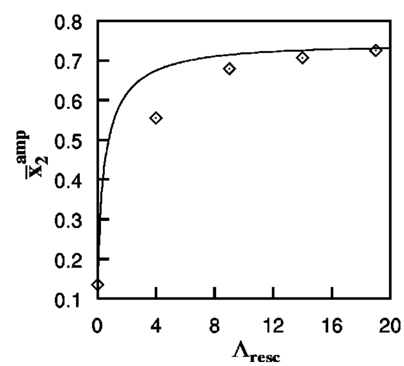

FIG. 5. Oscillation amplitude for the concentration of Y species in period-1 regime for different values of Λ obtained from the kinetic Eqs. (33)–(35) (solid line) and from lattice gas automaton simulations (open diamonds).

data; at these values of Λ the amplitude obtained from simulations and predicted theoretically match exactly. One sees that, qualitatively, kinetic Eqs. (33)–(35) correctly describe the breakdown of the mass-action law description for the dynamics of global concentrations as the diffusion coefficient is decreased.

V. CONCLUSIONS

In this paper, the breakdown of the mean-field dynamics in nonequilibrium reaction-diffusion systems is studied by the means of a Chapman-Enskog type expansion using a probabilistic discrete-space, discrete-time model. It is shown that this breakdown is related to the memory effects in the evolution of average concentrations that emerge for finite values of the diffusion coefficient. The memory kernel, although quite complicated in the general case, was simplified for the case of the Willamowski-Rössler reaction-diffusion system to a simple exponential $e^{-\Lambda(t-t')}$, where the exponent Λ is determined by the diffusion coefficient and t is the (continuous) time variable.

A numerical analysis of theoretically derived kinetic equations with memory led to a further insight into the nature of the breakdown of mean-field dynamics. Namely, the effect of a decreasing diffusion coefficient on the reaction dynamics can be described by a backward shift in the bifurcation cascade of the mass-action law, i.e., the breakdown is essentially a parametric phenomenon. This conclusion is further supported by a comparison to the results of lattice gas automaton simulations of the Willamowski-Rössler model.

The breakdown of the mean-field description for the dynamics of reaction-diffusion systems has been considered in a number of earlier studies. Thus, simulations of the reaction-diffusion master equation for the Brusselator model showed that the deterministic limit cycle is gradually destroyed as the rate of diffusion is decreased and the inhomogeneous dynamic modes become excited.[7] Recently, Bussemaker and Brito used ring kinetic theory to explain shrinking of the limit cycle for the Maginu model with attenuation in the rate of diffusion.[17] These authors were able to qualitatively reproduce the effect of the breakdown of the mean-field kinetics observed in lattice gas automaton simulations by accounting for the reactive correlations in a phenomenological way. Because the probabilistic model used in these studies is similar to that which we used here, it may be interesting to consider the relation among these approaches.

There are a number of important questions which were not considered in this work. For instance, development of an analytic means for estimating the effective parametric shift exhibited by the solutions of kinetic Eqs. (33)–(35) as a function of diffusion coefficient would be useful. A different, no less challenging question concerns the extension of this theory to the level of local concentrations and the incorporation of long wavelength diffusion modes into the description of the dynamics. Such an extension would clearly be expedient for studies of stability and evolution of spatio-temporal structures in reaction-diffusion systems.

ACKNOWLEDGMENTS

This work was partially supported by the Natural Sciences and Engineering Research Council of Canada. M.V. also benefits from a Connaught Scholarship. Computing resources for this study were provided in part by the University of Toronto Information Commons.

APPENDIX A

Substituting $P_1(\mathbf{x}(\mathbf{r}),n)$ from (25) into the rhs of the first of the solvability conditions (22) gives

$$\langle P_1(\mathbf{x}(\mathbf{r}),n)\rangle = \sum_{n'=0}^{n-1}\left\langle (\hat{I}+\hat{W}^D)^{n-n'-1}\left[\hat{W}^R - \mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n'))\frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n')\right\rangle. \tag{A1}$$

To simplify this expression, note that by definition

$$(\hat{I}+\hat{W}^D)^p \equiv \hat{I} + \sum_{p'=1}^{p}\sum_{\boldsymbol{\pi}(p')}(\hat{W}^D)^{p'}, \tag{A2}$$

where p is any positive integer and $\Sigma_{\boldsymbol{\pi}(p')}(\hat{W}^D)^{p'}$ denotes sum over all possible time-ordered products of p' operators $\hat{W}^D$ selected from the full set of p such operators.

Given (A2), we can write (A1) as

$$\begin{aligned}\langle P_1(\mathbf{x}(\mathbf{r}),n)\rangle &= \sum_{n'=0}^{n-1}\left\{\left\langle\left[\hat{W}^R - \mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n'))\frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n')\right\rangle\right.\\ &\quad + \sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\left\langle(\hat{W}^D)^l\left[\hat{W}^R\right.\right.\\ &\quad \left.\left.\left. - \mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n'))\frac{\partial}{\partial\overline{\mathbf{x}}}\right]P_B(\mathbf{x}(\mathbf{r}),n')\right\rangle\right\}.\end{aligned} \tag{A3}$$

The first summand in (A3) vanishes, since for all n we have

$$\begin{aligned}&\langle \hat{W}^R P_B(\mathbf{x}(\mathbf{r}),n)\rangle = 0,\\ &\langle P_B(\mathbf{x}(\mathbf{r}),n)\rangle = 1.\end{aligned} \tag{A4}$$

The remainder of our analysis is easier to carry out in matrix form. We define

$$B_{\mathbf{x}(\mathbf{r})}^{(l)}(n) = (\hat{W}^D)^l \hat{S} P_B(\mathbf{x}(\mathbf{r}),n), \tag{A5}$$

where

$$\begin{aligned}&\hat{S} = \hat{W}^R - \mathbf{K}(\overline{\mathbf{x}}(\mathbf{r},n))\frac{\partial}{\partial\overline{\mathbf{x}}},\\ &(\hat{W}^D)^0 \equiv \hat{I},\end{aligned} \tag{A6}$$

and rewrite (A3) in terms of vector elements $B_{\mathbf{x}(\mathbf{r})}^{(l)}(n)$ as follows:

$$\langle P_1(\mathbf{x}(\mathbf{r}),n)\rangle = \sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle \hat{W}^D B_{\mathbf{x}(\mathbf{r})}^{(l-1)}(n')\rangle. \tag{A7}$$

Using the definition of the matrix elements of the diffusion evolution operator given by (6) and (7), we expand the leftmost $\hat{W}^D$ in (A7), and obtain

$$\langle P_1(\mathbf{x}(\mathbf{r}),n)\rangle=\sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle\hat{W}^D B_{\mathbf{x}(\mathbf{r})}^{(l-1)}(n')\rangle=0. \tag{A8}$$

Proceeding in the similar manner with the other condition in (22), we find

$$\begin{aligned}\langle\mathbf{x}(\mathbf{r})P_1(\mathbf{x}(\mathbf{r}),n)\rangle&=\sum_{n'=0}^{n-1}\langle\mathbf{x}(\mathbf{r})(\hat{I}+\hat{\mathbf{W}}^D)^{n-n'-1}\hat{S}P_B(\mathbf{x}(\mathbf{r}),n')\rangle,\\&=\sum_{n'=0}^{n-1}\Big\{\langle\mathbf{x}(\mathbf{r})\hat{S}P_B(\mathbf{x}(\mathbf{r}),n')\rangle\\&\quad+\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle\mathbf{x}(\mathbf{r})(\hat{W}^D)^l\hat{S}P_B(\mathbf{x}(\mathbf{r}),n')\rangle\Big\}.\end{aligned} \tag{A9}$$

The summand on the second line of (A9) again vanishes because of the following relations:

$$\begin{aligned}&\langle x_i(\mathbf{r})\hat{W}^R P_B(\mathbf{x}(\mathbf{r}),n)\rangle=K_i(\overline{\mathbf{x}}(\mathbf{r},n)),\\&\langle x_i(\mathbf{r})P_B(\mathbf{x}(\mathbf{r}),n)\rangle=\overline{x}_i(\mathbf{r},n).\end{aligned} \tag{A10}$$

Hence, one can again expand the leftmost operator $\hat{W}^D$ and rewrite (A9) as follows:

$$\begin{aligned}\langle\mathbf{x}(\mathbf{r})P_1(\mathbf{x}(\mathbf{r}),n)\rangle&=\sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle\mathbf{x}(\mathbf{r})\hat{W}^D B_{\mathbf{x}(\mathbf{r})}^{(l-1)}(n')\rangle,\\&=\frac{1}{N}\sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle[\chi(\mathbf{r},n'')-x(\mathbf{r})]B_{x(\mathbf{r})}^{(l-1)}(n')\rangle,\end{aligned} \tag{A11}$$

where n'' is the moment of time at which the leftmost operator $\hat{W}^D$ was applied $(0\leqslant n''\leqslant n-n'-1)$, $B_{x(\mathbf{r})}^{(l)}(t)$ is defined by (A5).

One can now separate the leftmost operator $\hat{W}^D$ from vector elements $B_{x(\mathbf{r})}^{(l)}(n)$ where possible, and repeat the calculations in (A11). Taking advantage of the results in (A4) and (A10), we obtain

$$\begin{aligned}\langle\mathbf{x}(\mathbf{r})P_1(\mathbf{x}(\mathbf{r}),n)\rangle&=\frac{1}{N}\sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle[\chi(\mathbf{r},n'')-x(\mathbf{r})]B_{x(\mathbf{r})}^{(l-1)}(n')\rangle,\\&=-\frac{1}{N}\sum_{n'=0}^{n-1}\Big\{(n-n'-1)\langle x(\mathbf{r})B_{x(\mathbf{r})}^{(0)}(n')\rangle\\&\quad+\sum_{l=2}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle x(\mathbf{r})B_{\mathbf{x}(\mathbf{r})}^{(l-1)}(n')\rangle\Big\},\\&=-\frac{1}{N}\sum_{n'=0}^{n-1}\Big\{(n-n'-1)\langle x(\mathbf{r})B_{x(\mathbf{r})}^{(0)}(n')\rangle\\&\quad+\sum_{l=2}^{n-n'-1}\sum_{\boldsymbol{\pi}(l)}\langle x(\mathbf{r})\hat{W}^D B_{\mathbf{x}(\mathbf{r})}^{(l-2)}(n')\rangle\Big\},\\&\cdots\\&=\sum_{n'=0}^{n-1}\sum_{l=1}^{n-n'-1}\binom{n-n'-1}{l}\Big(-\frac{1}{N}\Big)^l\langle x(\mathbf{r})B_{x(\mathbf{r})}^{(0)}(n')\rangle,\\&=0.\end{aligned} \tag{A12}$$

APPENDIX B

It is convenient to consider the continuous-time limit of kinetic Eqs. (33)–(35) in rescaled time units, $h'=\gamma h$. Thus, we define a discrete, real-valued time variable $t_n=(n/\gamma)h'$, and recast (33)–(35) in the following form:

$$\begin{aligned}&\overline{x}_1\Big(t_n+\frac{h'}{\gamma}\Big)-\overline{x}_1(t_n)\\&=h'R_1(\overline{\mathbf{x}}(t_n))-h'^2\frac{N}{N-1}\sum_{n'=0}^{n-1}\Big[(1-\lambda)^{\frac{t_n-t_{n'}-h'/\gamma}{h'/\gamma}}\\&\quad\times\frac{\kappa_{-1}C_{x_1,x_1}(t_{n'})-\kappa_{-2}C_{x_2,x_2}(t_{n'})}{h'/\gamma}\Big]-h'^2\\&\quad\times\sum_{n'=0}^{n-1}\Big[(1-\lambda)^{\frac{t_n-t_{n'}-h'/\gamma}{h'/\gamma}}\\&\quad\times\frac{\kappa_2C_{x_1,x_2}(t_{n'})+\kappa_4C_{x_1,x_3}(t_{n'})}{h'/\gamma}\Big],\end{aligned} \tag{B1}$$

$$\begin{aligned}&\overline{x}_2\Big(t_n+\frac{h'}{\gamma}\Big)-\overline{x}_2(t_n)\\&=h'R_2(\overline{\mathrm{x}}(t_n))-h'^2\sum_{n'=0}^{n-1}(1-\lambda)^{\frac{t_n-t_{n'}-h'/\gamma}{h'/\gamma}}\\&\quad\times\Big[\frac{N}{N-1}\,\frac{\kappa_{-2}C_{x_2,x_2}(t_{n'})}{h'/\gamma}-\frac{\kappa_2C_{x_1,x_2}(t_{n'})}{h'/\gamma}\Big],\end{aligned} \tag{B2}$$

$$\begin{aligned}&\overline{x}_3\Big(t_n+\frac{h'}{\gamma}\Big)-\overline{x}_3(t_n)\\&=h'R_3(\overline{\mathbf{x}}(t_n))-h'^2\sum_{n'=0}^{n-1}(1-\lambda)^{\frac{t_n-t_{n'}-h'/\gamma}{h'/\gamma}}\\&\quad\times\Big[\frac{N}{N-1}\,\frac{\kappa_{-5}C_{x_3,x_3}(t_{n'})}{h'/\gamma}+\frac{\kappa_4C_{x_1,x_3}(t_{n'})}{h'/\gamma}\Big].\end{aligned} \tag{B3}$$

We now have to evaluate the limit of (B1)–(B3) as h' tends to 0 in such a way that the diffusion coefficient remains unchanged. Formally, we can do so by letting $\lambda=\Lambda h'=\gamma\Lambda h$, and keeping Λ constant as $h'\to0$. From the point of view of statistical theory, such an operation is equivalent to replacing the diffusion transition probabilities

(5) with appropriate transition rates (such that the resulting diffusion coefficient is identical in both cases) as the diffusion Markov chain (6) is replaced with a continuous-time Markov process. Proceeding in this manner, we obtain

$$\frac{sd\overline{x_1}(t)}{dt}=R_1(\overline{\mathbf{x}}(t))-\frac{N}{N-1}\int_0^t e^{-\Lambda(t-t')}[\kappa_{-1}\mathcal{C}_{x_1,x_1}(t') - \kappa_{-2}\mathcal{C}_{x_2,x_2}(t')]dt' - \int_0^t e^{-\Lambda(t-t')}[\kappa_2\mathcal{C}_{x_1,x_2}(t')+\kappa_4\mathcal{C}_{x_1,x_3}(t')]dt', \tag{B4}$$

$$\frac{d\overline{x_2}(t)}{dt}=R_2(\overline{\mathbf{x}}(t))-\int_0^t e^{-\Lambda(t-t')}\left[\frac{N\kappa_{-2}}{N-1}\mathcal{C}_{x_2,x_2}(t') - \kappa_2\mathcal{C}_{x_1,x_2}(t')\right]dt', \tag{B5}$$

$$\frac{d\overline{x_3}(t)}{dt}=R_3(\overline{\mathrm{x}}(t))-\int_0^t e^{-\Lambda(t-t')}\left[\frac{N\kappa_{-5}}{N-1}\mathcal{C}_{x_3,x_3}(t') + \kappa_4\mathcal{C}_{x_1,x_3}(t')\right]dt', \tag{B6}$$

where $\mathcal{C}_{x_i,x_j}(t)=C_{x_i,x_j}(t)/(h'/\gamma)=C_{x_i,x_j}(t)/h$, and $C_{x_i,x_j}(t)$ are defined by (36) and (38). Equations (B4)–(B6) represent the continuous-time form of the kinetic Eqs. (33)–(35). The parameter Λ is defined as $\Lambda=\lambda/h'=2/\nu N\gamma h$, where h is the time unit of diffusion Markov chain (6).

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