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Reaction-diffusion master equation: A comparison with microscopic simulations

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Microscopic simulations are used to investigate the status of the stochastic theory of reaction-diffusion systems based on master equation. It is shown that the validity of this theory can only be guaranteed over length scales not smaller than the reactive mean free path. In this case, quantitative agreement is demonstrated in a variety of situations, including the vicinity of a pitchfork bifurcation point. [S1063-651X(96)08512-1]

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I. INTRODUCTION

The phenomenological theory of reaction-diffusion equations rests on the fundamental assumption of a clear-cut separation between macroscopic behavior, as described by the equations of chemical kinetics coupled to mass transfer, and dynamical processes at the microscopic level. Each event is considered to result from an average over all microscopic characteristics. This lumping of all but the macroscopic degrees of freedom ignores the spontaneous deviations from average behavior, the *fluctuations*. These deviations are always present in a macroscopic system that, because of the complexity of molecular motions, can be viewed as a spontaneous generator of noise.

The theoretical analysis of fluctuations requires an enlarged description in which information pertaining to microscopic behavior is incorporated. Such an enlarged description is traditionally based on the theory of stochastic processes [1,2]. The simplest approach is the Langevin formulation of reactive systems where Gaussian random white noise terms are added to the macroscopic evolution equations [3]. The amplitudes of these noise terms are directly related to the macroscopic path through a fluctuation-dissipation theorem, which guarantees that at equilibrium the resulting probability density becomes equivalent to one of the familiar Gibbs ensembles of equilibrium statistical physics [4–6]. The validity of this approach is thus directly related to the uniqueness of the solution of macroscopic equations. In particular, a Langevin description leads to a correct stationary distribution only if the corresponding macroscopic equations admit a single globally asymptotically stable attractor [7].

A more satisfactory approach is based on the master equation formulation of chemical systems, which gives a ''mechanistic'' point of view of what is going on at the molecular level [8,9]. Consider, for instance, an ideal isothermal chemical system at mechanical equilibrium. For the sake of clarity, we first focus on the description of chemical processes alone, postponing until the next section the discussion of the role of diffusion. The composition of the system can only change through reactive collisions, which, because of the existence of activation energies, are typically rare events as compared to nonreactive ones. This suggests that one can lump all the microscopic (position-momenta) degrees of freedom and view the dynamics as a succession of jumps corresponding to the change of composition through chemical reactions, interrupted by *waiting time* intervals. During these intervals the large number of nonreactive collisions will give rise to a randomization and a loss of memory. These remarks strongly suggest that the evolution of the system can be represented by a *jump Markov process* in an appropriate phase space. The probability distribution for the total number of particles U_i of species i obeys then the master equation [10]

$$\frac{d}{dt}P(\{U_i\};t)=\sum_{\{U_i'\}} W(\{U_i'\}|\{U_i\})P(\{U_i'\};t), \qquad (1)$$

where the W's are transition probabilities per unit time. They are proportional to the frequency of collisions between molecules of the constituents involved in each reaction and can thus easily be constructed through combinatorial arguments [1]. An important property of the transition probabilities is their extensivity, which expresses the physically obvious fact that the rate of a chemical process in a volume V must be proportional to V times a suitable function of *intensive* variables.

The master equation (1) is particularly well suited for describing the statistical properties of well stirred reactive systems. The main advantage of such a global description lies in its simplicity, which permits detailed analytical investigations. Its applicability to nonstirred media, however, remains questionable even if one limits oneself to macroscopically homogeneous systems. In fact, the global master equation selects the very limited class of exceptionally large fluctuations that appear at the level of the entire system, disregarding important nonequilibrium features originated by local fluctuations. A satisfactory approach must therefore include the effects of local fluctuations as well.

This paper is devoted to the study of the statistical properties of dilute isothermal reactive systems evolving in an unstirred medium. We shall tackle the subject from two complementary standpoints: microscopic simulations of reactive fluids and the master equation description of reaction-diffusion systems, the former being so far the only available method for testing the results of the latter.

The local formulation of the master equation will be laid down in the next section where we review the main assumptions at the basis of this description. Section III is devoted to the survey of the microscopic simulation of reactive fluids in the Boltzmann limit. We start our comparative analysis by considering in Sec. IV a simple chemical model that allows a detailed discussion of the limit of validity of the reaction-diffusion master equation. Section V is devoted to the study of a three variable model that can exhibit multiple steady state solutions. The main conclusions and perspectives are presented in Sec. VI.

II. REACTION-DIFFUSION MASTER EQUATION

The basic lines of the master equation formulation of reaction-diffusion systems can be summarized as follows [1,11–14]. We subdivide the reaction volume into spatial cells $\{\Delta V_{\mathbf{r}}\}$ and consider as variables the numbers of particles $\{U_{i\mathbf{r}}\}$ of species $i=1,2,\ldots$ in these cells. We assume as before that the set of variables $\{U_{i\mathbf{r}}\}$ defines a Markov process. The random variables $\{U_{i\mathbf{r}}\}$ change as a result of two processes: chemical reactions, which will be modeled as before by a jump Markov process, and diffusion whereby a particle may jump to an adjacent cell. The latter will be assimilated to a random walk. The resulting probability distribution $P(\{U_{i\mathbf{r}}\};t)$ obeys the so-called *multivariate master equation* :

$$\begin{aligned}\frac{d}{dt}P(\{U_{i\mathbf{r}}\};t)\\ &= \sum_{\mathbf{r},\{U'_{i\mathbf{r}}\}} W(\{U'_{i\mathbf{r}}\}|\{U_{i\mathbf{r}}\})P(\{U'_{i\mathbf{r}}\};t)\\ &\quad+\sum_i \frac{\widetilde{D}_i}{2d}\sum_{\mathbf{r},\ell}\{(U_{i\mathbf{r}}+1)P(\ldots,U_{i\mathbf{r}}+1,U_{i\mathbf{r}+\ell}-1,\ldots;t)\\ &\quad-U_{i\mathbf{r}}P(U_{i\mathbf{r}};t)\}. \qquad (2)\end{aligned}$$

The sum ℓ runs over the first nearest neighbors of the cell $\mathbf{r}$ and $\widetilde{D}_i$ represents the mean jump frequency of species i. It is related to Fick's diffusion coefficient of the species by

$$D_i=\frac{\ell^2}{2d}\widetilde{D}_i, \qquad (3)$$

where d represents the space dimension and ℓ is the characteristic length of a cell:

$$\Delta V=\ell^d. \qquad (4)$$

Note that again the transition probabilities are extensive quantities proportional to the volume ΔV of the cells.

Before discussing the general properties of the master equation (2), it is appropriate to review the conditions under which it is expected to describe correctly realistic reaction-diffusion systems. Beside the Markovian hypothesis, the very basics of any stochastic theory of reactive fluids relies on the fundamental assumption that the state of the system can be completely specified in terms of a limited number of macroscopic variables. For isothermal systems, these are just the composition variables. The lumping of all microscopic degrees of freedom except the composition variables can only be justified in systems remaining permanently in a local thermal equilibrium state, which in turn requires a ''large'' number of molecules per cell. Detailed numerical studies show that a few hundred molecules are enough in most practical situations. The local equilibrium assumption is also a necessary condition that allows one to approximate the extremely complex motion of molecules by a simple random walk. This is a reasonable approximation provided the linear dimensions of a cell remain at least of the order of the mean free path, since otherwise the microscopic characteristics of individual molecules, such as their velocity distribution function, must also be incorporated into the theory [15]. The cell size, however, cannot be chosen arbitrarily large, even for macroscopically homogeneous systems. In fact, the reaction-diffusion master equation considers each cell as a perfectly coherent entity, which in turn implies that the linear dimensions of a cell must be smaller than the correlation length. Now, the correlation length is at least equal to the reactive mean free path, defined as the average distance traveled by a particle before it undergoes a reactive collision. We therefore arrive at the conclusion that the linear dimensions of a cell should be typically of the order of the reactive mean free path. We will have the opportunity to check the above intuitive arguments in Sec. IV devoted to microscopic simulations of a simple isothermal chemical systems.

The master equation (2) provides an elegant and simple generalization of reaction-diffusion equations. From a theoretical point of view, it has been shown that in the close vicinity of a pitchfork bifurcation point its solution can be cast into the exponential of a ''stochastic potential,'' which turns out to be the Landau-Ginzburg potential familiar in equilibrium critical phenomena [7]. Away from the bifurcation point, it leads to the Langevin reaction-diffusion equations with the correct fluctuation spectrum. In more complex situations, it can easily be studied numerically. Here, the evolution of the system is viewed as a random walk in a discrete phase space (space of ''numbers of particles'' of different species) for which transitions occur at randomly spaced time intervals. The process being Markovian leads to an exponential distribution of waiting times [16]. From this distribution and the transition probabilities associated to each elementary chemical step, explicit realizations of the process can be constructed, along the lines of a Monte Carlo type of simulation first developed by Gillespie [17,18]. Similar techniques are described in Refs. [19,20].

In view of the above results, one is tempted to consider the reaction-diffusion master equation as the starting point of a statistical mechanics of reactive systems. The validity of this equation, however, rests mainly on arguments that, although highly plausible, are nevertheless heuristic and need to be carefully tested. Sufficiently precise experimental data to clarify the situation do not exist, to our knowledge. Microscopic simulations remain therefore the most promising tool to shed some light on this important issue.

III. MICROSCOPIC SIMULATION OF REACTIVE FLUIDS

In this paper, we shall be mainly concerned with the microscopic simulation of reactive fluids capable of exhibiting nonequilibrium transitions. In this respect, we have to face some basic difficulties that are directly related to the very nature of chemical dynamics. A first problem arises in connection with the validity of the macroscopic rate equations describing the time evolution of the composition variables in dilute (ideal) mixtures. This implies that one needs to have ''enough'' elastic collisions between consecutive reactive collisions in order to ensure mechanical and thermal equilibrium. As a consequence, only a fraction of the computing time will contribute effectively to the evolution of the system, which results in much wasted bookkeeping with a corresponding waste of CPU time. A second problem is related to the fact that chemical time scales τ_c, such as, for example, the period of a limit cycle in an oscillating system, are frequently in the macroscopic range. To get reliable statistics, one needs to run the corresponding microscopic simulation over an amount of time several times larger than τ_c. This again implies an extremely large amount of running time.

To cope with these difficulties, one is forced to simplify as much as possible both the Newtonian and the chemical dynamics. This can be done by limiting the simulation to hard sphere dynamics and by considering dilute mixtures in the Boltzmann limit. In this respect, a legitimate question is whether it is possible to set up a simple algorithm, specially designed for Boltzmann dynamics, instead of using the exact Newtonian dynamics. This question was answered positively by Bird [21], who proposed an algorithm known as *direct simulation Monte Carlo method* (DSMC). The original purpose of the method was to deal with problems where the use of the standard hydrodynamic descriptions becomes questionable, such as the computation of high Knudsen number flows of a rarefied gas past an object (e.g., high altitude flight). Bird's method has become popular since it is in excellent agreement with experimental and molecular dynamic data. Its basic steps can be summarized as follows [22].

As with usual molecular dynamic methods, the state of the system is the set of particle positions and velocities, $\{\mathbf{r}_i, \mathbf{v}_i\}$, $i=1,\ldots,N$ where N is the total number of particles. The evolution is decomposed in time steps Δt, typically a fraction of the mean collision time for a particle. Within a time step, the free flight motion and the particle interactions (collisions) are assumed to be decoupled. The free flight motion for each particle i is computed as $\mathbf{r}_i(t+\Delta t)=\mathbf{r}_i(t)+\mathbf{v}_i(t)\Delta t$, along with the appropriate boundary conditions. After all the particles have been moved, they are sorted into spatial cells, typically a fraction of a mean free path in length. A set of representative collisions, for the time step Δt, is chosen in each cell. For each selected pair a random impact parameter is generated and the collision is performed. After the collision process has been completed in all cells, the particles are moved according to their updated velocities and the procedure is repeated as before. Note that very recently Bird proposed several modifications to DSMC that improve the performance and the flexibility of his original algorithm [23].

The major hypothesis in Bird's algorithm is that the cells are assumed to be perfectly homogeneous; i.e., all particles within a cell are considered to be potential collision partners, regardless of their exact positions. This assumption simplifies considerably the dynamics and allows the algorithm to be up to three orders of magnitude faster than the corresponding exact hard sphere dynamics. On the other hand, it also raises questions as to the reliability of the algorithm.

From a macroscopic point of view, extensive use of DSMC by Bird and others, in a variety of problems dealing with nonequilibrium gas dynamics, has always shown perfect agreement with experimental data [21,24,25]. For example, it correctly yields the density profile of a relatively high Mach number (>2) shock wave [26]. It also reproduces correctly the data obtained through hard sphere molecular dynamics in extremely strong shock wave conditions (Mach number >100), a domain far beyond the validity of Navier-Stokes equations [27].

At the microscopic level, DSMC have also been used to study the behavior of fluctuation spectra in dilute gas subjected to strong nonequilibrium constraints, both for systems under temperature gradient [28,29] and velocity gradient [30] (shear). The results were shown to be in very good agreement with those obtained by the Landau-Lifshitz fluctuating hydrodynamics [31], whose validity is now well established [32–34]. We can therefore conclude that the Bird algorithm reproduces perfectly both the macroscopic behavior and the fluctuation spectrum of dilute gases, even under severe nonequilibrium regimes.

Note finally that there are other techniques, such as the lattice gas cellular automata (LGCA) or the lattice Boltzmann method, that allow the simulation of reactive fluids [35,36]. So far, however, it is not clear whether these methods contain more information than the macroscopic equations, at least in nonequilibrium systems. It has only recently been shown that LGCA reproduces correctly the fluctuation spectrum in equilibrium systems [37,38].

We next define what we mean by ''reactive hard sphere collisions'' [39,40]. We assign to each species a ''color.'' A reactive collision occurs if the colliding particles have ''enough'' energy, i.e., if their relative kinetic energy exceeds some threshold related to the activation energy of the reaction. If this is the case, then the colors of the particles are changed, according to the chemical step under consideration. This procedure, however, leads to a continuous energy transfer from reactants to products that induce a deformation of the Maxwell-Boltzmann distribution and can thus modify significantly the values of the rate constants [41,42]. To avoid these nonequilibrium effects, the frequency of reactive collisions must be significantly smaller than the frequency of elastic collisions, entailing important waste of CPU time. One way to overcome this difficulty is to further simplify the reactive collision rules by the following procedure. Let us consider a typical bimolecular chemical step:

$$A+B\xrightarrow{k}C+D \tag{5}$$

with

$$k=\nu\ \exp\left\{-\frac{E}{k_BT}\right\}\equiv\nu k_A, \tag{6}$$

where ν is the collision frequency. After a collision between two particles A and B has occurred, we choose randomly k_A% of the collisions to be reactive, where k_A stands for the Arrhenius factor defined in Eq. (6). Obviously, this procedure avoids the deformation of the Maxwell-Boltzmann distribution, since it does not involve any systematic energy transfer between reactants and products. It is, however, restricted to isothermal chemical systems.

IV. MICROSCOPIC SIMULATION OF AN EXACTLY SOLUBLE MODEL

Our main objective in this paper is to check the validity of the reaction-diffusion master equation in the vicinity of a bifurcation point, through a microscopic simulation of a representative chemical model. Testing phenomenological theories through microscopic simulations is not always easy, as it involves a number of pitfalls one should be aware of before drawing any definitive conclusions. This is especially true for reactive systems so that it is instructive to concentrate first on the following simple model, which can be solved exactly [43,44]:

$$S+U\xrightarrow{k_1}U+U, \tag{7a}$$

$$S+U\underset{k_3}{\overset{k_2}{\rightleftharpoons}}S+S, \tag{7b}$$

where the concentration of S particles (hereafter referred to as ‘‘solvent’’ particles) is supposed to remain constant. This can be achieved by introducing one more participant, say molecules A. Every time an S particle is created (destroyed) in a collision, an S (A) particle is chosen at random in the same collisional cell and replaced by an A (S) particle. Since the A molecules do not participate in any reaction, they merely constitute a reservoir of particles maintaining the solvent concentration fixed [40]. We further restrict ourselves to a one-dimensional system with periodic boundary conditions, i.e., a long thin torus.

We first consider the master equation formulation. Dividing the system length L into N_c cells and following the arguments developed in Sec. II, one can write

$$\begin{aligned}\frac{d}{dt}P(\{U_i\};t)={}&\sum_{i=1}^{N_c}\,[\,\upsilon(U_i-1)P(\,\ldots,U_i-1,\ldots;t)-\upsilon(U_i)P(\{U_i\};t)+\mu(U_i+1)P(\,\ldots,U_i+1,\ldots;t)-\mu(U_i)P(\{U_i\};t)]\\&+\frac{\widetilde{D}}{2}\sum_{i=1}^{N_c}\sum_{\ell=\pm1}[(U_i+1)P(\,\ldots,U_i+1,U_{i+\ell}-1,\ldots;t)-(U_i)P(\{U_i\};t)]\end{aligned} \tag{8a}$$

with

$$\upsilon(U_i)=k_1sU_i+k_3\frac{s(S-1)}{2},\qquad \mu(U_i)=k_2sU_i, \tag{8b}$$

where s and S represent the mole fraction and the number of solvent particles per cell, respectively, and the factor 1/2 in Eq. (8b) takes into account the fact that the S-S reaction involves a pair of the same particles. Owing to the periodic boundary conditions,

$$U_{N_c+1}=U_1,\qquad U_0=U_{N_c}. \tag{9}$$

The master equation (8) admits a stationary solution provided $k_2>k_1$ since otherwise the random variables $\{U_i\}$ become unboundedly large as $t\rightarrow\infty$. In this case, the stationary probability distribution possesses translational symmetry, i.e., $P_{\mathrm{st}}(U_i=a,U_{i+k}=b)=P_{\mathrm{st}}(U_j=a,U_{j+k}=b)$, $\forall i,j,k$. For instance, the average number of U particles per cell reads

$$\langle U_i\rangle=\frac{k_3(S-1)}{2(k_2-k_1)}\equiv\langle U\rangle,\quad \forall i \tag{10}$$

The static spatial correlation function is readily found to obey

$$\frac{\widetilde{D}}{2}(g_{i+1,j}+g_{i-1,j}-2gi,j)-s(k_2-k_1)g_{i,j}=-k_1s\langle U\rangle\delta_{i,j}^{Kr},$$

$$i,j=1,2\ldots,N_c, \tag{11}$$

where we have defined

$$g_{i,j}\equiv\langle\delta U_i\delta U_j\rangle-\langle U\rangle\delta_{i;j}^{Kr}. \tag{12}$$

As this equation is subjected to periodic boundary conditions, Eq. (9), it can be solved through lattice Fourier transform. After some calculation, one finds

$$g_{i,j}=\frac{2k_1s\langle U\rangle\alpha}{\widetilde{D}(\alpha^2-1)(\alpha^{N_c}-1)}[\alpha^{|i-j|}+\alpha^{N_c-|i-j|}],$$

$$|i-j|=0,1\ldots,N_c-1, \tag{13}$$

where we have set

$$\alpha=(1+\beta/\widetilde{D})+\sqrt{(1+\beta/\widetilde{D})^2-1} \tag{14a}$$

with

$$\beta=s(k_2-k_1). \tag{14b}$$

For the microscopic simulation, we consider a system made of an assembly of $N=42\,000$ hard spheres of diameter d confined in a rectangular box of $L=3780\,d$ long with a number density $n=5\times10^{-3}$ particles per d^3 (the mean free path λ is about $45\,d$). All the particles have the same mass and diameter, regardless of their chemical (color) identity. For practical convenience, lengths and masses are scaled by the sphere diameter d and the particle mass m, respectively; i.e., we take $d=m=1$. Similarly, by an appropriate scaling of time and velocities, the temperature and thermal velocity are set to unity. In these units, the diffusion coefficient $D=29.92$ and the collision frequency $\nu=0.025$. The system is divided into 84 collisional cells of $45d$ long, each containing an average of 500 particles (the cell volume is of about $1.1\lambda^3$). The other parameters are chosen as follows:

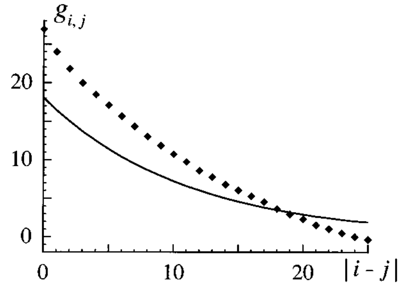

FIG. 1. Spatial correlation function g_{ij}, Eq. (12), as a function of $|i-j|$. The solid curve corresponds to the solution of the master equation, Eq. (13), whereas the squares are obtained through a microscopic simulation based on Bird's algorithm. The estimated statistical errors are less than 4%. The parameters are given in Eq. (15).

$$k_1=0.1\nu, \quad k_2=0.15\nu, \quad k_3=0.4\nu, \quad s=0.1. \tag{15}$$

A time average over 10^6 collisions per particle (CPP) was performed to measure the spatial static correlation function, after the stationary state had been reached (about 10^5 CPP). The result is presented in Fig. 1, together with that obtained from the master equation, Eq. (13). The agreement is definitely not good. Note that traditional hard-disk and hard-sphere molecular dynamics (MD) simulations have led in the past to basically the same type of results [45].

Detailed analysis shows that the origin of the observed discrepancy is closely related to the way the solvent concentration is kept constant in the microscopic simulation. As already underlined, each time a solvent particle S is created (destroyed) in a collision with the other species an S (A) particle is chosen at random in the same collisional cell and replaced by an A (S) particle. This procedure ensures the conservation of solvent particles in reactive collisions, but does not prevent them from moving freely from cell to cell. In other words, the number of solvent particles in a cell fluctuates, but the fluctuations arise only because of diffusion. The effect is negligibly small in macroscopic systems, but not in microscopic simulations where the number of particles per cell is generally quite small. For instance, in our case the average number of solvent particles per cell is only 50.

To check the validity of the above arguments, we consider once more the model Eq. (7), but now we allow the solvent particles to diffuse as well. The corresponding master equation proves to be much more difficult to handle analytically, mainly because the transition probabilities are now nonlinear functions of the state variables $\{U_i, S_i\}$. It can nevertheless be solved numerically and the results are shown in Fig. 2, where a much better agreement with the microscopic results is observed. Still, the agreement is not totally satisfactory. In particular, near the origin the discrepancy is about 9%, well above the expected statistical errors (4%). We note that such a relatively small discrepancy would be quite difficult to detect through hard sphere molecular dynamic simulations, since here the statistical errors associated with the measurement of fluctuations can hardly be lowered below 8% within a reasonable CPU time of present day computers.

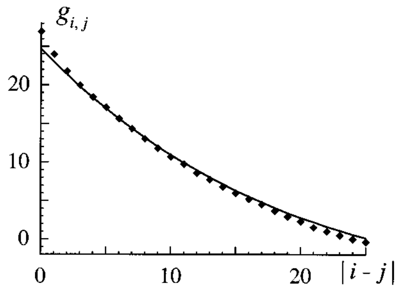

FIG. 2. Spatial correlation function g_{ij}, Eq. (12), as a function of $|i-j|$. The solid curve corresponds to the numerical solution of the master equation, Eq. (8), where the diffusion of solvent particles have has been included, whereas the squares are obtained through a microscopic simulation based on Bird's algorithm. The parameters are given in Eq. (15).

The origin of this last discrepancy is deeper and, in a way, more difficult to understand than the previous one. Nevertheless, the simplicity of the model together with the flexibility of the Bird algorithm leads to a complete clarification of the problem. As already stated in Sec. II, the linear dimensions of a cell in the reaction-diffusion master equation cannot be chosen arbitrarily. Too large a cell size violates the cell statistical homogeneity assumptions, whereas too small a cell size may compromise the separability of reaction and diffusion viewed as elementary processes. Intuitive arguments, developed in Section II, lead to the conclusion that the cell sizes should be typically of the order of the reactive mean free path. In other words, the reaction-diffusion master equation cannot probe correctly processes arising on a scale smaller than the reactive mean free path. For the parameter values we have chosen, the largest kinetic constant $k_3=0.4$, so that the reactive mean free path exceeds necessarily 2.5λ, where λ denotes the usual ''elastic'' mean free path.

To check the above intuitive arguments, we consider our microscopic simulation, with the same number of collisional cells as before, but now we divide the system into 28 ''statistical'' cells; i.e., we group the cells three by three and measure the statistical properties of the system over these enlarged cells. Similarly, we solve numerically the master equation divided also into 28 cells. The results are depicted in Fig. 3, which now shows perfect agreement. Furthermore, a careful comparison of Fig. 2 with Fig. 3 reveals that the correlation functions corresponding to the master equation are the same for both cases. In other words, the system remains statistically homogeneous over length scales smaller than the reactive mean free path. Obviously, this behavior holds only at the level of the master equation formulation and breaks down in a more refined description where the velocity distribution of the chemicals is taken into account as well.

V. MICROSCOPIC SIMULATION OF A MODEL CONTAINING A PITCHFORK BIFURCATION

Simple chemical models exhibiting complex behavior, such as the Brusselator or the Schlögl model, involve trimolecular collisions [1,2]. The Bird algorithm, however, is restricted to binary collisions only, i.e., to second-order chemi-

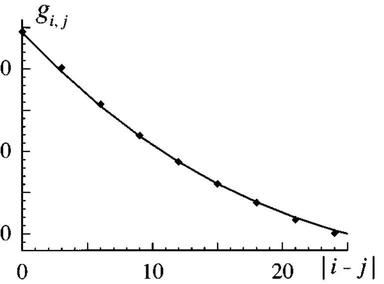

FIG. 3. Same as in Fig. 2, except that here the statistics is taken over enlarged cells of about 3 mean free paths long.

cal reactions [46]. It has been shown that the trimolecular step can be approximated by a pair of bimolecular steps involving different time scales, so that an adiabatic elimination of a fast variable leads to an effective trimolecular step [47]. Nevertheless, such a scheme is inappropriate for microscopic simulation because the species represented by the slow variables undergo far fewer reactive collisions per unit time than those represented by fast variables. We thus look here for a chemical model satisfying the following three constraints: (i) it consists of binary collisions only; (ii) it has no significant separation of time scales; (iii) it involves as few reactants as possible. As was shown in Ref. [48], the above requirements are fully satisfied by the following chemical model:

$$U+W\xrightarrow{k_1}V+W, \tag{16a}$$

$$V+V\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}W+S, \tag{16b}$$

$$V+S\xrightarrow{k_3}S+S, \tag{16c}$$

where the concentration of the S particles is supposed to remain constant. The reactants are confined in a long thin tube, laterally in contact with a ‘‘reservoir’’ with which it can exchange particles through a semipermeable membrane. The reactor thus operates effectively as a one-dimensional system. Note that laboratory reactors dealing with unstirred systems are quite similar to the one we just described [49,50].

The macroscopic rate equations corresponding to the model (16) read

$$\frac{du}{dt}=-k_1uw+\alpha_u(u_f-u),+D_u\frac{\partial^2}{\partial x^2}u, \tag{17a}$$

$$\frac{dv}{dt}=k_1uw-2(k_2v^2-k_{-2}ws)-k_3vs+\alpha_v(v_f-v)+D_v\frac{\partial^2}{\partial x^2}v, \tag{17b}$$

$$\frac{dw}{dt}=k_2v^2-k_{-2}ws+D_w\frac{\partial^2}{\partial x^2}w, \tag{17c}$$

where u, v, w, and s are the mole fractions of U, V, W, and S, respectively; $k_{\pm i}$ are the rate constants of the ith reaction; α_u and α_v are the transfer coefficients (feed rate) of U and V with the reservoir; D_u, D_v, and D_w are the diffusion coefficients; and u_f, v_f are the mole fractions of U and V in the reservoir (feed mole fractions), respectively. The system is assumed impermeable to W.

The transfer coefficient of a species depends on the diffusion coefficient of that species as well as on the property of the membrane separating the system with the reservoir. For simplicity, in our microscopic simulation we shall assign to all of the particles the same mass and sphere diameter, regardless of their chemical identity. This implies that the diffusion coefficients, and consequently the transfer coefficients, are equal:

$$D_u=D_v=D_w\equiv D, \tag{18a}$$

$$\alpha_u=\alpha_v\equiv\alpha. \tag{18b}$$

For certain ranges of parameter values, the macroscopic equations (17) can admit multiple steady states and limit-cycle oscillations. In this paper we concentrate on a possible occurrence of a pitchfork bifurcation. We first note that the stationary state mole fractions obey the following relations:

$$w_s=\frac{k_2}{sk_m}v_s^2,\quad u_s=\frac{\alpha}{k_1w_s+\alpha}u_f, \tag{19a}$$

$$k_1k_2(k+\alpha)v_s^3-\alpha k_1k_2(u_f+v_f)v_s^2+\alpha k_m(k+\alpha)v_s-\alpha^2k_mv_f=0, \tag{19b}$$

where we have used the condition (18) and set

$$k=k_3s,\quad k_m=k_{-2}s. \tag{20}$$

As is well known, the general solution of the cubic equation (19b) can be entirely described in terms of two parameters only (see, for example, [51]). Thus, without loss of generality, we are allowed to impose a certain number of suitable relations among the various parameters of the problem. One guideline stems from the fact that at a pitchfork bifurcation point the cubic equation (19b) must admit a triple root. On the other hand, the stationary state mole fractions of the chemically active components, and that of solvent molecules, should not be significantly different from each other for, otherwise, the microscopic simulation of the model will become highly inefficient.

Keeping the above comments in mind, we find after some algebra that if we set

$$k=\frac{1}{3}(u_f+v_f)\sqrt{2\alpha\frac{k_1k_2}{k_m}\frac{(u_f+v_f)}{(u_f-2v_f)}}-\alpha \tag{21}$$

then Eq. (19b) reduces to the following simple form:

$$(v_s-v_s^{(1)})^3+\frac{4\alpha}{(u_f+v_f)}\frac{k_m}{k_1k_2}(v_f-u_f/8)(v_s-v_s^{(1)})=0, \tag{22}$$

where we have introduced the ‘‘reference’’ stationary state

$$v_s^{(1)}=\frac{1}{3}(u_f+v_f)\frac{\alpha}{k+\alpha}. \tag{23}$$

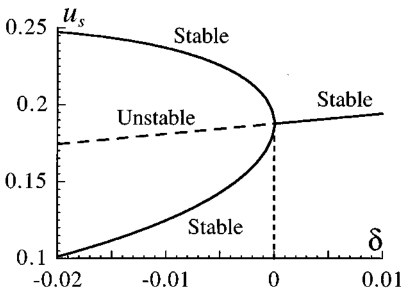

FIG. 4. Stability diagram for the model (16). δ is defined in Eq. (24) and the parameters are given in Eq. (25).

As can be seen, for $v_f > u_f/8$ the stationary solution is unique, i.e., $v_s = v_s^{(1)}$, whereas for $v_f < u_f/8$ one has three stationary solutions, showing clearly that the system undergoes a bifurcation at $v_f = u_f/8$. More detailed analysis shows that the latter corresponds to a pitchfork bifurcation point. This is illustrated in Fig. 4, where the stability diagram for the variable u is depicted. The parameter δ in this figure represents the ''distance'' from the bifurcation point, defined as

$$v_f = \frac{u_f}{8} + \delta. \tag{24}$$

The other parameters are set to

$$k_1 = \nu, \quad k_2 = \nu/2, \quad k_m = \nu/26, \quad u_f = 1/4, \quad \alpha = 0.28\nu, \tag{25}$$

where ν represents the collision frequency. Note that in writing the relation (21) we have implicitly assumed that $u_f - 2v_f > 0$, which is clearly satisfied beyond ($\delta < 0$) and in the vicinity of the bifurcation point, $\delta \approx 0$.

We first consider the stochastic simulation of the model (16), for which we can write a reaction-diffusion master equation similar to Eq. (8), with periodic boundary conditions allowing the S particles to diffuse as well. We use δ, defined in Eq. (24), as the control parameter and set the values of the other parameters according to Eq. (25). Long before the bifurcation point, the dynamics can be linearized around the reference state so that the behavior of the system is basically the same as in the case of the model (7). As we move towards the bifurcation point, $\delta \to 0$, we observe a dramatic increase in the fluctuation lifetime, with a corresponding increase of their amplitude. Detailed analysis shows that the local fluctuations exhibit markedly non-Gaussian behavior for values of δ ranging from about 10^{-2} to -10^{-2}. The associated probability distribution, however, remains always unimodal, regardless of the value of δ. This behavior seems to indicate that the nonequilibrium transition associated to pitchfork bifurcations is probably destroyed in a one-dimensional system. The full discussion of this problem, however, is beyond the scope of the present paper and will be reported elsewhere.

We next concentrate on the microscopic simulation of the model (16). In order to carry out a microscopic modeling of the transfer process with the reservoir, we introduce two more pairs of reactions:

$$S + S \underset{a_-}{\overset{a_+}{\rightleftharpoons}} S + U, \tag{26a}$$

$$S + S \underset{b_-}{\overset{b_+}{\rightleftharpoons}} S + V. \tag{26b}$$

The forward reaction corresponds to inflow and the reverse reaction to outflow; $a_\pm$ and $b_\pm$ are the fractions of reactive collisions for these two reactions. Furthermore, an S-S reaction can result in the production of either U or V molecules. The fraction of ''reactive'' S-S collisions resulting in the production of a U molecule is $u_f/(u_f + v_f)$ and the fraction of ''reactive'' collisions resulting in the production of a V molecule is then just $v_f/(u_f + v_f)$. It can be easily checked that the reactions (26) lead indeed to the correct macroscopic transfer terms, provided we set

$$a_+ = \frac{2\alpha u_f}{s^2}, \quad b_+ = \frac{2\alpha v_f}{s^2}, \quad a_- = b_- = \frac{\alpha}{s}. \tag{27}$$

Note that the factor 2 in the above relations for a_+ and b_+ is related to the fact that the forward reactions (26) involve a pair of the same molecules.

One last problem remains, which arises whenever the concentration of some of the species has to be kept constant all along the simulation. For the model (16), this is the case of the S particles that undergo reactive collisions with the other species and participate, in addition, in reactions designed to mimic the exchange of particles with the reservoir. As already discussed in the previous section, this can be achieved by introducing one more participant, say molecules A. Every time an S particle is created (destroyed) in a collision, an $S(A)$ particle is chosen at random in the same collisional cell and replaced by an $A(S)$ particle. Since the A molecules do not participate in any reaction, they merely constitute a reservoir of particles maintaining the S mole fraction fixed. We note that the simulation procedure is completely specified in terms of kinetic constants, transfer rate and the mole fraction of S particles.

For the microscopic simulation, we consider the same basic parameters as those chosen for the simple model Eq. (7), i.e., $N = 42\,000$ hard spheres of diameter d, $L = 3780\,d$, and $n = 5 \times 10^{-3}$ particles per d^3. We also use the same scaling as before, so that the diffusion coefficient $D = 29.92$ and the collision frequency $\nu = 0.025$, in system units. The system is divided into 84 collisional cells, of about 1 mean free path long, and statistics are collected over each such cell as well as over groups of 2, 4, and 7 cells.

We first consider positive values of δ, i.e., before the bifurcation point and run the simulation for two different values of the bifurcation parameter: $\delta = 10^{-2}$ and $\delta = 3 \times 10^{-3}$. In both cases, the system exhibits significant long life fluctuations so that to lower the statistical errors below 8% in the evaluation of the correlation functions, we had to run the simulation about 5 times longer than in the case of model (7). With the parameter values (25), the reactive mean free path is close to 2λ. According to our previous analysis (cf. Sec. IV), the cell size in the master equation formulation must also be set to about 2λ. On the other hand, given the close vicinity of the bifurcation point, the system exhibits long range spatial correlation so that larger cell sizes should also be allowed. This is demonstrated in Fig. 5 where

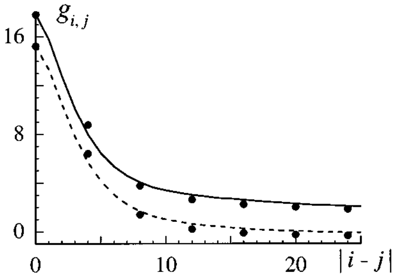

FIG. 5. Spatial correlation function g_{ij}, Eq. (12), as a function of $|i-j|$ for the model (16). The solid and the dashed curves correspond to the numerical solution of the master equation for $\delta=3\times10^{-3}$ and $\delta=10^{-2}$, respectively. The circles are obtained through the corresponding microscopic simulation based on Bird's algorithm. The statistics is taken over enlarged cells of about 4 mean free paths long. The parameters are given in Eq. (25).

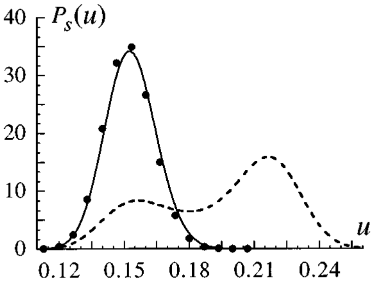

FIG. 7. Probability distribution of the U variable for the model (16) with $\delta=-3\times10^{-3}$. The solid curve corresponds to results of the master equation whereas the circles are obtained through a microscopic simulation over enlarged cells of about 4 mean free paths long. The dashed curve represents the probability distribution corresponding to the global master equation with 2000 particles. The other parameters are given in Eq. (25).

the spatial correlation function, evaluated for groups of 4 cells (about 4λ), is depicted, which indeed shows quantitative agreement with results obtained from the master equation. The agreement, however, becomes gradually less good as we consider larger cell sizes. Figure 6 illustrates this fact, where the master equation results, obtained for groups of 7 cells, are compared with the corresponding results of the microscopic simulations. The agreement is indeed less good, the discrepancy exceeding the estimate statistical errors (8%). Again this result seems to indicate the destruction of the pitchfork bifurcation in a one-dimensional system.

We next consider negative values of δ, i.e., above the bifurcation point. Here again, the static correlation functions show quantitative agreement with master equation predictions. Furthermore, the probability distribution associated to local composition variables remains unimodal. This is illustrated in Fig. 7 for $\delta=-3\times10^{-3}$, where the probability distributions of the U variable, sampled over enlarged cells of about 4 mean free paths long, are depicted. Besides the microscopic and the reaction-diffusion master equation results, we have also reported the probability distribution obtain from the ''global'' master equation. The latter reflects the behavior of a zero-dimensional system, containing the same number of particles as the sample cells we used in the microscopic simulations, i.e., 2000 particles. The probability distributions for both the reaction-diffusion master equation and the microscopic simulation remain unimodal, in perfect quantitative agreement with each other. On the contrary, the global master equation leads to a bimodal probability distribution, each of the maximum being centered around stable stationary solutions of the macroscopic equations. This major discrepancy is in part due to the pathological properties of one-dimensional systems. It nevertheless underlines the inadequacy of a global description of unstirred media.

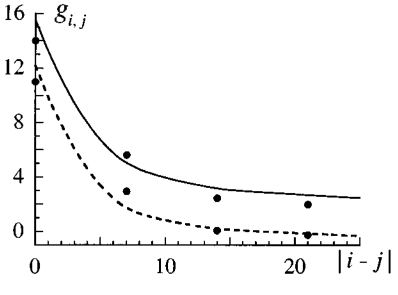

FIG. 6. Same as in the Fig. 5, except that here the statistics is taken over enlarged cells of about 7 mean free paths long.

VI. CONCLUDING REMARKS

The main purpose of this work was to use microscopic simulations of chemical systems to study the limit of validity of the stochastic formulation of reaction-diffusion systems based on the master equation. Contrary to the Langevin approach, the master equation formulation provides a mechanistic view of the dynamics at the molecular level. The state variables are the number of particles of chemical components, which are sampled in spatial cells whose linear dimension ℓ is considered as an adjustable parameter. Each cell is assumed to be perfectly homogeneous; i.e., all particles within it are considered to be candidate partners for a reactive collision, regardless of their exact positions. Within each cell, the dynamics is decomposed in two independent processes: reaction and diffusion, which are modeled as a birth and death process and random walk, respectively.

The validity of the above stochastic formulation rests upon an adequate choice of ℓ: Too large a cell size violates the cell statistical homogeneity assumptions, whereas too small a cell size may compromise the separability of reaction and diffusion viewed as independent elementary processes. In the absence of any further information as to the range of spatial correlations, the linear dimensions of a cell must remain of the order of the reactive mean free path, defined as the average distance traveled by a sample particle between two reactive collisions. In fact, expanding the reaction-diffusion master equation in the inverse power of ℓ, although mathematically correct, may lead to unphysical results contradicting the macroscopic reaction-diffusion equations [52].

After analyzing in detail the statistical properties of a simple model, we have next considered a more complex model that contains a pitchfork bifurcation. This model allows one to check the validity of the reaction-diffusion master equation in the immediate vicinity of the bifurcation point. Quantitative agreement was demonstrated both before and after the bifurcation point. We thus can conclude that the reaction-diffusion master equation can be considered as the starting point of a statistical mechanics of dilute reactive systems.

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[1] G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley-Interscience, New York, 1977).
[2] H. Haken, *Synergetics: An Introduction* (Springer-Verlag, Berlin, 1977).
[3] A. Nitzan, P. Ortoleva, R. Deutch, and J. Ross, J. Chem. Phys. **61**, 1056 (1974).
[4] S. Grossman, J. Chem. Phys. **65**, 2007 (1976).
[5] J. Keizer, J. Chem. Phys. **67**, 1473 (1977).
[6] K. Seki and K. Kitahara, J. Mol. Liq. (to be published).
[7] M. Malek Mansour, C. Van Den Broeck, G. Nicolis, and J. W. Turner, Ann. Phys. (N.Y.) **131**, 283 (1981).
[8] D. McQuarrie, in *Supplementary Review Series in Applied Probability*, edited by J. Gani (Methuen, London, 1967), Vol. 8, pp. 1–68.
[9] N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1983).
[10] W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, New York, 1967), Vol. 1.
[11] K. Kitahara, Ph.D. thesis, Université Libre de Bruxelles, 1974 (unpublished).
[12] H. Haken, Z. Phys. B **20**, 413 (1975).
[13] C. W. Gardiner, K. J. Macneil, D. F. Walls, and I. S. Matheson, J. Stat. Phys. **14**, 307 (1976).
[14] H. Lemarchand and G. Nicolis, Physica A **82**, 251 (1976).
[15] Such a ‘‘phase space’’ formulation of the master equation has been proposed by G. Nicolis and I. Prigogine, Proc. Natl. Acad. Sci. U.S.A. **68**, 2102 (1971).
[16] S. Karlin and H. Taylor, *A First Course in Stochastic Processes* (Academic Press, New York, 1975).
[17] D. T. Gillespie, J. Comput. Phys. **22**, 403 (1976); J. Chem. Phys. **81**, 2340 (1977).
[18] D.T. Gillespie, *Markov Processes: an Introduction of Physical Scientists* (Academic Press, New York, 1992).
[19] J. S. Turner, J. Phys. Chem. **81**, 237 (1977).
[20] P. Hanusse and A. Blanché, J. Chem. Phys. **74**, 6148 (1981).
[21] G. A. Bird, *Molecular Gas Dynamics* (Clarendon, Oxford, 1976).
[22] A. L. Garcia, *Numerical Methods for Physics* (Prentice-Hall, Englewood Cliffs, NJ, 1994).
[23] G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon, Oxford, 1994).
[24] D. R. Chenoweth and S. Paolucci, Phys. Fluids **28**, 2365 (1985); G. A. Bird, *ibid.* **30**, 364 (1987).
[25] E. P. Muntz, Annu. Rev. Mech. **21**, 387 (1989).
[26] R. E. Meyer, *Introduction to Mathematical Fluid Mechanics* (Dover, New York, 1971); G. A. Bird, Phys. Fluids **13**, 1172 (1970).
[27] E. Salomons and M. Mareschal, Phys. Rev. Lett. **69**, 269 (1992).
[28] M. Malek Mansour, A. Garcia, G. Lie, and E. Clementi, Phys. Rev. Lett. **58**, 874 (1987).
[29] M. Malek Mansour, M. Mareschal, G. Sonnino, and E. Kestemont, in *Microscopic Simulations of Complex Hyfrodynamic Phenomena*, Vol. 292 of *NATO Advanced Studies Institute Series B: Physics*, edited by M. Mareschal and B. Holian (Plenum Press, New York, 1992), p. 87.
[30] A. Garcia, M. Malek Mansour, G. Lie, and E. Clementi, Phys. Rev. A **36**, 4348 (1987).
[31] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1984).
[32] B. J. Bern and R. Pecora, *Dynamic Light Scattering with Applications to Chemistry, Biology, and Physics* (Wiley, New York, 1976).
[33] J. P. Boon and S. Yip, *Molecular Hydrodynamics* (McGraw-Hill, New York, 1980) (reprinted by Dover, New York, 1991).
[34] Some recent experimental results concerning systems under temperature gradient can be found in B. M. Law and J. V. Sengers, J. Stat. Phys. **57**, 531 (1989); B. M. Law, P. N. Segrè, R. W. Gammon, and J. V. Sengers, Phys. Rev. A **41**, 816 (1990); W. B. Li, J. V. Sengers, R. W. Gammon, and P. N. Segrè, Int. J. Thermophysics **16**, 23 (1995).
[35] G. X.-G. Wu and R. Kapral, Phys. Rev. Lett. **70**, 1940 (1993); J. Chem. Phys. **100**, 5936 (1994); A. Lemarchand, A. Lesne, A. Perera, M. Moreau, and M. Mareschal, Phys. Rev. E **48**, 1568 (1993)
[36] D. Dab, A. Lawniczak, J. P. Boon, and R. Kapral, Phys. Rev. Lett. **64**, 2462 (1990); D. Dab, J. P. Boon, and Y. Li, *ibid.* **66**, 2535 (1991); R. Kapral, A. Lawniczak, and P. Masiar, *ibid.* **66**, 2539 (1991).
[37] P. Grosfils, J. P. Boon, and P. Lallemand, Phys. Rev. Lett. **68**, 1077 (1992); P. Grosfils, J. P. Boon, R. Brito, and M. H. Ernst, Phys. Rev. E **48**, 2665 (1993); J. R. Weimar, D. Dab, J. P. Boon, and S. Succi, Europhys. Lett. **20**, 627 (1992).
[38] A lattice Boltzmann simulation with fluctuating stress tensor (Landau-Lifshitz) is presented in A.J.C. Ladd, Phys. Rev. Lett. **70**, 1339 (1993).
[39] P. Ortoleva and S. Yip, J. Chem. Phys. **65**, 2045 (1976).
[40] J. Boissonade, Phys. Lett. A **74**, 285 (1979); J. Boissonade, in *Nonlinear Phenomena in Chemical Dynamics*, edited by C. Vidal and A. Pacault (Springer-Verlag, Berlin, 1981); J. Boissonade, Physica A **113**, 607 (1982).
[41] I. Prigogine and E. Xhrouet, Physica **15**, 913 (1949); I. Prigogine and M. Mahieu, *ibid.* **16**, 51 (1950).
[42] F. Baras and M. Malek Mansour, Phys. Rev. Lett. **63**, 2429 (1989); M. Malek Mansour and F. Baras, Physica A **188**, 253 (1992).

[43] C. W. Gardiner, K. J. Macneil, and D. F. Walls, Phys. Lett. A **53**, 205 (1975).

[44] M. Malek Mansour and C. Van den Broeck, in *Instabilities, Bifurcations and Fluctuations in Chemical Systems*, edited by L. E. Reichl and W. C. Schieve (University of Texas Press, Austin, 1982).

[45] MD studies of this approach is reported in G. J. Nicolis, A. Amellal, G. Dupont, and M. Mareschal, J. Mol. Liq. **41**, 5 (1989); A. Amellal and M. Mareschal, *ibid.* **63**, 199 (1995).

[46] A microscopic simulation ''mimicking'' three-body collisions has been considered successfully by M. Mareschal and A. De Wit, J. Chem. Phys. **96**, 2000 (1992).

[47] S. K. Scott, *Chemical Chaos* (Oxford Science Publications, Oxford, 1993).

[48] F. Baras, J. E. Pearson, and M. Malek Mansour, J. Chem. Phys. **93**, 5747 (1990).

[49] V. Castel, E. Dulos, J. Boissonade, and P. De Kepper, Phys. Rev. Lett. **64**, 2953 (1990); Q. Quyang and H. L. Swinney, Nature (London) **352**, 610 (1991).

[50] *Chemical Waves and Patterns*, edited by R. Kapral and K. Showalter (Kluwer Academic Publishers, Amsterdam, 1994).

[51] G. Nicolis, *Introduction to Nonlinear Science* (Cambridge University Press, Cambridge, 1995).

[52] L. Arnold and M. Theodosopulu, Adv. Appl. Probab. **12**, 367 (1980).