

Influence of auto-organization and fluctuations on the kinetics of a monomer-monomer catalytic scheme

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We study analytically the kinetics of an elementary bimolecular reaction scheme of the Langmuir-Hinshelwood type taking place on a d -dimensional catalytic substrate. We propose a general approach that takes into account explicitly the influence of spatial correlations on the time evolution of the mean particle density. With this approach, we recover some known results concerning the time evolution of the mean particle density and establish others.

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I. INTRODUCTION

Catalytically activated processes play a significant role in numerous technologies as they serve to produce required products from species that are nonreactive under normal physical conditions. These chemically stable species may, however, enter into reaction in the presence of some third substance—the catalytic substrate [1–3]. Despite the widespread use of such processes, the knowledge of the underlying physics and chemistry still rests largely on phenomenological ideas and prescriptions, and thus remains a challenge for fundamental research [1–5].

At the simplest, mean-field level of description, reaction kinetics theory presumes that the reaction rate should be considered as the product of the reactant densities and the rate constant, which is dependent on the nature of the binding forces and on the particle dynamics. This rate constant is proportional to the hopping rate if the process is diffusion controlled, or to the reaction frequency, in case the reaction is kinetically controlled [6–9]. Hence, a clear cut separation is presumed to exist between the local variables that could be derived, say, from quantum mechanics, and collective variables, expressed in the most simple way as the product of mean densities of the particles involved.

One of the most significant recent developments in the field has been the recognition of the substantial importance of the multiparticle effects, spatial fluctuations, and self-organization, as opposed to conventional local energetic considerations, which emphasized the purely chemical constraints and focused on refined descriptions of the elementary reaction. Subsequently, statistical physics concepts were introduced in order to describe anomalous fluctuation-induced behaviors of noncatalytic chemical reactions [10–27] and simplest catalytic schemes [28–38], as well as to gain a better understanding of such collective phenomena as wave formation, presence of excitable media, or stochastic aggrega-

tion in chemical systems (see Refs. [30,34,35], and references therein). One conclusion that can be drawn from the statistical physics approach is that fluctuations, either spatial or temporal, may drive the reactive system into a set of new states that cannot be understood and described in terms of mean-field kinetic equations.

In this paper, we discuss in detail the influence of spatial fluctuations, statistical self-organization and random diffusive motion of reactants on the kinetics of catalytic reactions, using as a particular example the Langmuir-Hinshelwood-type reaction scheme. (See Fig. 1.) This reaction process, which is also often referred to as the monomer-monomer catalytic scheme, involves two different kinds of species, A and B , which are deposited (continuously in time with mean intensity I) onto the catalytic substrate by some external source; then, the particles start to diffuse along the substrate and react at encounters forming an inert reaction product O , $A + B \rightarrow O$, which is immediately removed from the system. Our aims here are twofold. First, we show that this seemingly simple catalytic reaction [which has, in fact, several practical applications (see, e.g., Refs. [28,29])] shows quite a rich behavior and represents an ideal illustrative example of

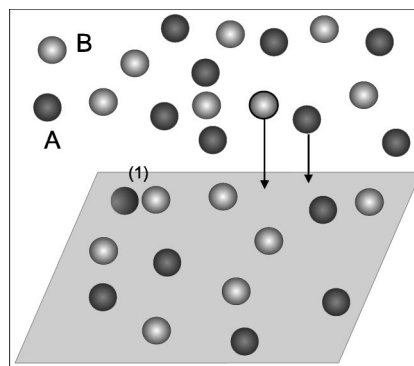


FIG. 1. Langmuir-Hinshelwood reaction on a two-dimensional catalytic substrate. Black and gray spheres denote particles of A and B species, respectively; (1) describes the situation in which an A and a B appear within the reactive distance from each other and may enter into reaction.

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the statistical effects in the reaction kinetics, which may be generic to more complicated schemes involved in real world catalytic processes. Second, we develop a unified analytical description that takes into account explicitly the influence of spatial correlations, dimensionality of space, and the way that the particles are introduced into the reaction bath on the time evolution of observables—mean particle densities. In terms of this approach, we recover some of previously known results and obtain others. We also note that our approach can be routinely generalized to describe the kinetics of more complex reaction schemes.

We focus here on several different aspects of the Langmuir-Hinshelwood reaction scheme. In particular, we address the question of how the kinetics depends on the dimensionality d of the reactive system. In addition to the standard Langmuir-Hinshelwood model in which the catalytic substrate is a two-dimensional flat surface, we analyze kinetics of $A+B\rightarrow O$ reactions followed by an external input of reactive species in one- and three-dimensional systems, i.e., the situations appropriate to reactions in capillary geometries [39] and annealing of the radiation damage in solids [14]. We show that the monomer-monomer catalytic reaction proceeds quite differently in low-dimensional ($d=1,2$) and three-dimensional systems. In addition, we examine how the method of introducing the particles into the system affects the properties of stationary states and also how these stationary states are approached in time. We consider here two different types of external inputs; in the first one (case I), the A and B particles are introduced independently of each other at random times and at random positions in space, while in the second case (case II), an A and a B species are introduced in correlated pairs of a fixed radius, the pairs being injected at random times and at random positions in space. We show that the way of input does matter significantly and may result in a completely different behavior.

The paper is structured as follows. In Sec. II we formulate the model, introduce a general analytic approach, and, in terms of this approach, derive closed-form equations describing the time evolution of the mean densities of the particle and pairwise correlation functions. In Sec. III we present solutions to these equations in one-, two-, and three-dimensional systems corresponding to different ways of particles injection to the reaction bath. Finally, we conclude in Sec. IV with a brief summary of our results and discussion.

II. DEFINITIONS AND BASIC EQUATIONS

In this section we present a kinetic description of the monomer-monomer catalytic scheme involving diffusive particles in terms of a certain analytical approach, which takes explicitly into account the influence of pairwise correlations on the time evolution of mean densities; such a description was first proposed in Ref. [11], which analyzed the effects of fluctuations on the kinetics of $A+B\rightarrow O$ reactions and yielded the celebrated $t^{-d/4}$ law for the decrease of the mean particle density. Subsequent works [24,26,27,40–48] extended this approach to more general reaction schemes (e.g., reversible and coagulation reactions), three-body and catalytic reactions, and also included the possibility of mu-

tual long-ranged interparticle interactions.

Here we will focus on the application of the approach to the analytical description of the $A+B\rightarrow O$ reaction kinetics in systems with a continuous, random external input of the reactive species. We will recover some previously known results obtained for the monomer-monomer catalytic scheme involving diffusive monomers and will establish other results concerning primarily the long-time relaxation of mean particles density to their steady-state values and the dependence of this steady-state densities and pairwise correlations on the system parameters.

We start with the formulation of the model. Consider a d -dimensional reaction bath of volume V [we suppose that V is sufficiently large such that we can discard different finite-size effects, e.g., hard-core exclusion between particles, the termination of reaction within a finite time interval or saturation (poisoning)] in which A and B particles are continuously introduced by an external random source. The statistical properties of the source will be defined below. After injection into the system, the A and B particles begin to diffuse. For simplicity, we assume that their diffusion constants are equal, i.e., $D_A=D_B=D$. It will be made clear below that such a description is also appropriate to the case of nonequal diffusivities; the calculations in this case are only essentially more lengthy even in absence of external particle input [49]. Now, the reaction event is defined as follows: When any two A and B particles approach each other at a fixed separation R (the reaction radius), they may enter into reaction, forming (an inert with respect to the reaction) reaction product O . The recombination upon an encounter of A and B happens with a finite probability p (with probability $q=1-p$, the particles can be reflected) that defines the constant of an elementary reaction, K . This constant describes the intrinsic chemical activities of A and B molecules and is dependent on the nature of the intramolecular and intermolecular binding forces. In the following we will suppose that this purely “chemical” constant is known *a priori*. Furthermore, we will assume that K is large (i.e., the probability of reflection is low) and thus will emphasize the “statistical physics” effects on the reaction kinetics, rather than the effects of chemical constraints. Consequently, all the factors that are exponentially small in K will be neglected here.

We now define the statistical properties of the particle injection more precisely. Let $I_A(r,t)$ and $I_B(r,t)$ be the local, at the point with the vector r , intensities of the production rates of A and B particles. We assume that the volume-averaged values of the production rates obey

$$\frac{1}{V} \int_V dr I_A(r,t) = \frac{1}{V} \int_V dr I_B(r,t) = I, \quad (1)$$

which means that particle generation is steady in time and the mean production rates I of A and B particles are equal.

To define the correlations in the production rates $I_{A,B}(r,t)$ we consider two different situations. In the first one (case I), we suppose that A and B particles are introduced into the reaction bath statistically independent of each other [16–24]; that is, the fluctuations of the sources are correlated neither in space nor in time. In this case, we have

$$\frac{1}{V} \int_V dr I_A(r,t) I_A(r+\lambda, t+\tau) - I^2 = I \delta(\lambda) \delta(\tau), \quad (2a)$$

$$\frac{1}{V} \int_V dr I_B(r,t) I_B(r+\lambda, t+\tau) - I^2 = I \delta(\lambda) \delta(\tau), \quad (2b)$$

$$\frac{1}{V} \int_V dr I_B(r,t) I_A(r+\lambda, t+\tau) = 0. \quad (2c)$$

In the second case we suppose that A and B particles are introduced as correlated A - B pairs,¹ separated by a fixed distance λ_g [17,22–24]. This type of external generation may arise in chemical systems in which a complex reaction product O is continuously forced to break up by external radiation (say, laser pulses) into correlated pairs of the component molecules. Here the radius of pair λ_g will be mainly determined by the difference of energy “attributed” to O and the energy required to dissociate the reaction product. Another example in which such pairs are produced is the annealing of radiation damage in solids. When the solid is irradiated, atoms are knocked out of their places in the lattice to become interstitials, leaving behind a vacancy; then the vacancies and interstitials diffuse and recombine. In case II, different A - B pairs are statistically uncorrelated, and occur, with an average intensity I , at random positions in the reaction bath. Then, the fluctuations of the sources obey [17,41]

$$\frac{1}{V} \int_V dr I_A(r,t) I_A(r+\lambda, t+\tau) - I^2 = I \delta(\lambda) \delta(\tau), \quad (3a)$$

$$\frac{1}{V} \int_V dr I_B(r,t) I_B(r+\lambda, t+\tau) - I^2 = I \delta(\lambda) \delta(\tau), \quad (3b)$$

$$\frac{1}{V} \int_V dr I_B(r,t) I_A(r+\lambda, t+\tau) = \gamma_d(\lambda_g) I \delta(|\lambda| - \lambda_g). \quad (3c)$$

In Eq. (3c), the parameter $\gamma_d(\lambda_g)$ is the normalization factor that arises because of different possible angular orientations of a given A - B pair in a d -dimensional continuum; the value of $\gamma_d(\lambda_g)$ depends on the dimensionality of the reaction bath and for $d=1, 2$, and 3 equals 1 , $(2\pi\lambda_g)^{-1}$, and $(4\pi\lambda_g^2)^{-1}$, respectively.

Let $C_A(r,t)$ and $C_B(r,t)$ denote the local densities of A and B particles at a point with vector r at time t . The time evolution of local densities due to the diffusion of species, their reaction, and an external production can be described by the following reaction-diffusion equations [16,21,22]:

$$\begin{aligned} \dot{C}_A(r,t) = & -\gamma_d(R)K \int_V dr' \delta(|r-r'| - R) C_A(r,t) C_B(r',t) \\ & + D \Delta_r C_A(r,t) + I_A(r,t), \end{aligned} \quad (4)$$

$$\begin{aligned} \dot{C}_B(r,t) = & -\gamma_d(R)K \int_V dr' \delta(|r-r'| - R) C_B(r,t) C_A(r',t) \\ & + D \Delta_r C_B(r,t) + I_B(r,t), \end{aligned} \quad (5)$$

where the symbol Δ_r denotes the d -dimensional Laplace operator acting on the spatial variable r , and the integration with the delta function $\delta(|r-r'| - R)$ accounts for all possible orientations of an A - B pair, at which an elementary reaction act can take place.

Now, the experimentally accessible property is not, however, the local density, but rather its volume-averaged value

$$C(t) = \frac{1}{V} \int_V dr C_{A,B}(r,t). \quad (6)$$

To find an equation that governs the time evolution of $C(t)$, let us first represent the local densities in the form

$$C_{A,B}(r,t) = C(t) + \delta C_{A,B}(r,t), \quad (7)$$

where $\delta C_{A,B}(r,t)$ denote local deviations of the densities from their mean values. By definition,

$$\frac{1}{V} \int_V dr \delta C_{A,B}(r,t) = 0. \quad (8)$$

Then, substituting Eq. (7) into Eqs. (4) and (5) and taking the volume average, we get the following equation:

$$\dot{C}(t) = -K[C^2(t) + G_{AB}(|\lambda|=R, t)] + I, \quad (9)$$

in which $G_{AB}(\lambda, t)$ stands for the pairwise, central correlation function of the form

$$G_{AB}(\lambda, t) = \frac{1}{V} \int_V \int_V dr dr' \delta(r-r'-\lambda) \delta C_A(r,t) \delta C_B(r',t), \quad (10)$$

the variable λ being a d -dimensional correlation parameter.

Therefore, Eq. (9) shows that the time evolution of the mean particle density is coupled to the evolution of the pairwise correlations in the reactive system. Neglecting these correlations, i.e., setting $G_{AB}(\lambda, t) = 0$, which is equivalent to the traditional, “mean-field” assumption that the spatial distribution of particles is uniform, we obtain the customary, textbook “law of mass action.” Such an approximation predicts a linear growth of the mean density at relatively short times, i.e.,

$$C(t) \propto It, \quad (11)$$

and, in the large- t limit, an exponentially fast relaxation to the equilibrium density $C(t \rightarrow \infty) = (I/K)^{1/2}$, i.e.,

$$C(t) \propto \left(\frac{I}{K}\right)^{1/2} [1 - \exp\{-2(IK)^{1/2}t\} + \dots]. \quad (12)$$

The short-time behavior of Eq. (11) is quite reasonable and describes the regime in which the particles are merely added into the (initially empty) system by the external source and the reaction between them is negligible, i.e., the regime in which particle density remains very small. As for the analytical prediction in Eq. (12), one may question its validity

¹The particles in the pair can, of course, diffuse apart after injection.

on intuitive grounds. First, diffusion is the only mechanism to bring particles together and let them react. This motion is essentially d dependent, whilst Eq. (12) is independent of the dimensionality of the reaction bath. Second, it shows that with an increase of the chemical reaction constant K the equilibrium density tends to zero, which is apparently an artificial behavior. Below we will show that the actual behavior of $C(t)$ as $t \rightarrow \infty$ is very different, depending essentially on the dimensionality of the reactive system and also on the way that the particles are injected into the system.

We turn now to Eq. (9) and continue our analysis of the binary reaction kinetics taking into account the influence of pairwise correlations on the time evolution of $C(t)$. From Eqs. (4), (5), and (7), we find that the system of equations for the time evolution of the pairwise correlation functions reads

$$\begin{aligned} \dot{G}_{AB}(\lambda, t) = & -KC(t)[2G_{AB}(\lambda, t) + G_{AA}(\lambda, t) + G_{BB}(\lambda, t)] \\ & + 2D\Delta_\lambda G_{AB}(\lambda, t) + I_{AB}(\lambda) + T_{AB}(\lambda), \end{aligned} \quad (13)$$

$$\begin{aligned} \dot{G}_{AA}(\lambda, t) = & -2KC(t)[G_{AB}(\lambda, t) + G_{AA}(\lambda, t)] \\ & + 2D\Delta_\lambda G_{AA}(\lambda, t) + I\delta(\lambda) + T_{AA}(\lambda), \end{aligned} \quad (14)$$

$$\begin{aligned} \dot{G}_{BB}(\lambda, t) = & -2KC(t)[G_{AB}(\lambda, t) + G_{BB}(\lambda, t)] \\ & + 2D\Delta_\lambda G_{BB}(\lambda, t) + I\delta(\lambda) + T_{BB}(\lambda), \end{aligned} \quad (15)$$

where Δ_λ denotes the Laplace operator acting on the d -dimensional variable λ , the symbol $I_{AB}(\lambda)$ in Eq. (13) describes the correlations in the production rates of A and B particles; it is equal to zero in case I (uncorrelated generation of particles) and to

$$I_{AB}(\lambda) = \gamma_d(\lambda_g)I\delta(|\lambda| - \lambda_g) \quad (16)$$

in case II, when the particles are introduced into the system in correlated A - B pairs. Finally, in Eqs. (13)–(15) the terms T_{ij} denote the third-order correlation functions.

The time evolution of the pairwise correlations is coupled to the evolution of the third-order correlations, which, in turn, depends on the correlations of the fourth order. This infinite hierarchy of equations coupled with the nonlinear reaction-diffusion Eqs. (4) and (5) requires one to resort to some approximate methods [51].

The most commonly used method of truncating the hierarchy is to approximate the third-order correlation functions in terms of $C(t)$ and $G_{ij}(\lambda, t)$ [50]. Such an approach, as was first noticed in Ref. [14], results in the Smoluchowski-type approximate results with improved numerical coefficients and is appropriate for the description of the single-species reactions $A + A \rightarrow O$, but not for the description of reactions involving two different types of particles. The problem is that such an approximation misses an important conservation law, which is specific for $A + B \rightarrow O$ reactions. Namely, the reaction conserves the difference $Z(r, t)$ of local densities, $Z(r, t) = C_A(r, t) - C_B(r, t)$, which changes only as the result of the diffusion of particles and thus is a pure diffusive mode of the system. Conservation of $Z(r, t)$ entails, in turn, the conservation of the combination of pairwise cor-

relation functions, $S_-(\lambda, t) = G_{AA}(\lambda, t) + G_{BB}(\lambda, t) - 2G_{AB}(\lambda, t)$, which is also a pure diffusive mode.² Consequently, only truncation schemes that do not violate the conservation law can correctly describe the behavior of the binary reaction [14].

The simplest nontrivial truncation scheme, which preserves the conservation laws, was first proposed in Ref. [11]. In this scheme the third-order correlation functions, i.e., T_{ij} , were set equal to zero. This truncation, as shown in Refs. [24] and [40–42], is equivalent to the assumption that fields $\delta C_{A,B}(\lambda, t)$ have a Gaussian distribution. Then, the fourth-order correlation functions automatically decouple into the product of pairwise correlation functions and the third-order correlations are equal to zero. Such an approach leads to, for instance, the correct long-time decay law of the densities, i.e., the $t^{-d/4}$ law, but fails to reproduce correctly the intermediate time behavior; at intermediate times, this approach predicts essentially the same behavior as the formal kinetic “law of mass action” and thus disregards the effects of diffusion at intermediate times.

This shortcoming has been revisited and improved in Refs. [40–42], where it was shown that correlation functions of the third order are small only in the limit $|\lambda| > R$, while in the domain $|\lambda| \approx R$, they are singular and this singularity has an impact on the behavior of the pairwise correlation at the intermediate times. In a discrete-space picture, essential at scales $|\lambda| \approx R$, the third-order correlation functions have been computed explicitly [41,51],

$$T_{AA} \approx T_{BB} \approx T_{AB} \approx \gamma_d(R)\dot{C}(t)\delta(|\lambda| - R). \quad (17)$$

Substituting Eq. (17) into Eqs. (13)–(15) yields a closed, with respect to $C(t)$ and $G_{ij}(\lambda, t)$, system of equations. To solve it, it is expedient to represent the pairwise correlations in the form

$$G_{ij}(\lambda, t) = \hat{G}_{ij}(\lambda, t) + g_{ij}(\lambda, t), \quad (18)$$

where $\hat{G}_{ij}(\lambda, t)$ denotes a “singular” part, which accounts merely for the behavior of the third-order correlations, and $g_{ij}(\lambda, t)$ —the “fluctuational” part, which accounts for the fluctuation spectrum of the external source and fluctuations stemming from reaction and diffusion.

The “singular” part of the pairwise correlation functions was determined in Ref. [41]. In particular, at sufficiently large times the leading behavior of $\hat{G}_{ij}(|\lambda| = R, t)$ is

$$\hat{G}_{ij}(R, t) \approx \dot{C}(t)(\pi t/8D)^{1/2}, \quad (19)$$

in one-dimensional systems,

$$\hat{G}_{ij}(R, t) \approx \dot{C}(t) \frac{\ln(Dt/R^2)}{8\pi D} \quad (20)$$

and

$$\hat{G}_{ij}(R, t) \approx \dot{C}(t)8\pi DR \quad (21)$$

²One may readily verify that $T_{AA} + T_{BB} - 2T_{AB}$ is exactly equal to zero.

in two- and three-dimensional systems, respectively.

Now, inserting Eqs. (19)–(21) into Eq. (9), we obtain the following equation for the time evolution of the density:

$$\dot{C}(t) = -\frac{KK_S(d)}{K+K_S(d)}[C^2(t) + g_{AB}(|\lambda|=R, t)] + \frac{I}{1+K/K_S(d)}, \quad (22)$$

where $K_S(d)$ obeys, as $t \rightarrow \infty$,

$$K_S(d=1) \approx \left(\frac{8D}{\pi t}\right)^{1/2}, \quad (23)$$

$$K_S(d=2) \approx \frac{8\pi D}{\ln(Dt/R^2)}, \quad (24)$$

and

$$K_S(d=3) \approx 8\pi DR. \quad (25)$$

One may readily notice that in three dimensions the $K_S(d)$, Eq. (25), coincides exactly with the so-called ‘‘diffusive’’ Smoluchowski constant; a reaction constant that was first calculated by von Smoluchowski [6] in his approximate description of the effects of diffusion on the chemical reactions kinetics. This constant accounts for, heuristically, the ‘‘resistivity’’ of random, diffusive transport of particles with respect to the reaction [51]. Employing the Smoluchowski method, the analogues of such a constant have been obtained in Ref. [52] for one- and two-dimensional systems. Remarkably, our results in Eqs. (23) and (24) coincide with those obtained in Refs. [9] and [52]. We note also that the prefactor before the brackets in Eq. (22), i.e., the ratio $K_{app} = KK_S(d)/[K+K_S(d)]$, is the so-called effective or apparent reaction constant, which was first derived for three-dimensional systems in Ref. [7]. Therefore, accounting for the ‘‘singular’’ part of the third-order correlation function and subsequent extraction of the ‘‘singular’’ part in the pairwise correlators leads us to results equivalent to those obtained with the Smoluchowski approach.

Hence, Eq. (12), in which one sets $g_{AB}(|\lambda|=R, t) = 0$ and $K_S(d) = \infty$, reduces to the formal kinetic ‘‘law of mass action,’’ while setting $g_{AB}(|\lambda|=R, t) = 0$ and using $K_S(d)$ as in Eqs. (23)–(25), one obtains the effective kinetic equation of the Smoluchowski-type approach. Below, we proceed to show that by taking into account the time evolution of the pairwise correlations, i.e., the term $g_{AB}(|\lambda|=R, t)$, one arrives at completely different physical behavior compared with that predicted by the formal kinetic and Smoluchowski approaches.

Finally, we obtain the following system of equations, obeyed by the ‘‘fluctuational’’ part of the pairwise correlation functions:

$$\dot{g}_{AB}(\lambda, t) = -KC(t)[2g_{AB}(\lambda, t) + g_{AA}(\lambda, t) + g_{BB}(\lambda, t)] + 2D\Delta_\lambda g_{AB}(\lambda, t) + I_{AB}(\lambda), \quad (26)$$

$$\dot{g}_{AA}(\lambda, t) = -2KC(t)[g_{AB}(\lambda, t) + g_{AA}(\lambda, t)] + 2D\Delta_\lambda g_{AA}(\lambda, t) + I\delta(\lambda), \quad (27)$$

$$\dot{g}_{BB}(\lambda, t) = -2KC(t)[g_{AB}(\lambda, t) + g_{BB}(\lambda, t)] + 2D\Delta_\lambda g_{BB}(\lambda, t) + I\delta(\lambda). \quad (28)$$

Equations (26)–(28), accompanied by Eq. (22), are now closed with respect to the mean densities and pairwise correlations, and allow the computation of the time evolution of the monomer-monomer reaction scheme.

III. KINETICS OF THE MONOMER-MONOMER REACTION SCHEME

Below we will analyze solutions of Eqs. (22)–(28) in systems of different dimensionalities and with different types of external particle generation. The derivation of results in case of one-dimensional systems will be presented in detail. The steps involved for such a derivation in higher dimensions are essentially the same and here we will merely discuss the results.

A. Low-dimensional systems

Let us start with the case of one-dimensional systems in which an external source produces uncorrelated A and B particles.

We note first that the system of Eqs. (26)–(28) possesses two integrable combinations

$$S_-(\lambda, t) = 2g_{AB}(\lambda, t) - g_{AA}(\lambda, t) - g_{BB}(\lambda, t), \quad (29)$$

which is related to the conserved property $Z(r, t)$, and

$$S_+(\lambda, t) = 2g_{AB}(\lambda, t) + g_{AA}(\lambda, t) + g_{BB}(\lambda, t). \quad (30)$$

These integrable combinations obey

$$\dot{S}_-(\lambda, t) = 2D\Delta_\lambda S_-(\lambda, t) - 2I\delta(\lambda), \quad (31)$$

which is thus the pure diffusive mode of the system, not affected by the reaction, and

$$\dot{S}_+(\lambda, t) = 2D\Delta_\lambda S_+(\lambda, t) - 4KC(t)S_+(\lambda, t) + 2I\delta(\lambda). \quad (32)$$

The desired property, i.e., the correlation function $g_{AB}(\lambda, t)$ that enters Eq. (22), may then be expressed in terms of these integrable combinations as

$$g_{AB}(\lambda, t) = \frac{1}{4}[S_-(\lambda, t) + S_+(\lambda, t)]. \quad (33)$$

Consider now the solutions to Eqs. (31) and (32) in one-dimensional systems. Applying the Fourier transformation over the variable λ ,

$$S_\pm(\omega, t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\lambda \exp(i\omega\lambda) S_\pm(\lambda, t) \quad (34)$$

to Eqs. (31) and (32), and assuming that at $t=0$, no A and B particles were present in the system, one readily gets that the Fourier images of the integrable combinations as follows:

$$\begin{aligned}
 S_-(\omega, t) &= -I \sqrt{\frac{2}{\pi}} \int_0^t d\tau \exp(-2D\tau\omega^2) \\
 &= -\frac{I}{D\omega^2 \sqrt{2\pi}} [1 - \exp(-2Dt\omega^2)] \quad (35)
 \end{aligned}$$

and

$$S_+(\omega, t) = -I \sqrt{\frac{2}{\pi}} \int_0^t d\tau \exp\left[-2D\tau\omega^2 - 4K \int_\tau^t d\tau' C(\tau')\right]. \quad (36)$$

Now we notice that in the extreme situation, when reaction occurs at any encounter of any A and B particle (i.e., when $K = \infty$) the second integrable combination $S_+(\omega, t)$ vanishes since the integral $\int_\tau^t d\tau' C(\tau')$ is obviously positively defined. One can show, however, that even for the finite K s the influence of $S_+(\omega, t)$ on the pairwise correlation function, Eq. (33), is not essential at large times and the dominant contribution to g_{AB} comes from $S_-(\omega, t)$.

We note that setting $t = \infty$ in Eq. (35) we obtain that $S_-(\omega, \infty)$ has a steady-state spectrum of the form $S_-(\omega, \infty) \sim 1/\omega^2$, i.e., the spectrum that has a nonintegrable singularity in low dimensions when $\omega \rightarrow 0$. This singular behavior of the fluctuation spectrum of the pairwise correlations in systems with binary reactions followed by an external uncorrelated production of the reactive species was first predicted, using a different approach, in Refs. [16] and [17–19]. The authors concluded that the steady state of such a system is highly anomalous; since such a singularity is not integrable in low-dimensional systems, the steady-state values of the integrable combination $S_-(\lambda, t)$, and thus of the correlation function g_{AB} , are infinitely large, which means that as time evolves the system progressively coarsens into the domains containing particles of only one type.

Consider now how the integrable combination $S_-(\lambda, t)$ and the correlation function g_{AB} grow in time. Taking the inverse Fourier transformation of the first line in Eq. (35) we get

$$S_-(\lambda, t) = -\frac{I}{\sqrt{2\pi D}} \int_0^t \frac{d\tau}{\sqrt{\tau}} \exp(-\lambda^2/8D\tau). \quad (37)$$

The integrand in Eq. (37) is a bell-shaped function with a maximum at $\tau = \lambda^2/8D$. For bounded λ , the bulk contribution to the integral comes from the algebraic tail $1/\sqrt{\tau}$ and consequently, the leading behavior at $t \gg R^2/8D$ of the integrable combination follows

$$S_-(|\lambda| = R, t) = -I \sqrt{\frac{2t}{\pi D}}. \quad (38)$$

Accordingly, the absolute value of the ‘‘fluctuational’’ part of the pairwise correlation function grows in time as

$$g_{AB}(|\lambda| = R, t) = -I \sqrt{\frac{t}{8\pi D}}. \quad (39)$$

Inserting this in Eq. (22) we notice that the source term on the right-hand side of Eq. (22) vanishes as $t \rightarrow \infty$, as does the prefactor before the terms in the brackets—the apparent rate constant $KK_S(d)/[K + K_S(d)]$; hence, the leading large- t asymptotical behavior of the mean density in the Riccati-type Eq. (22) should be such that it compensates the negative pairwise correlations $g_{AB}(|\lambda| = R, t)$ that grow by absolute value. This implies that in the large- t limit

$$C(t) \approx \sqrt{-g_{AB}(|\lambda| = R, t)}, \quad (40)$$

which yields

$$C(t) = I^{1/2} \left(\frac{t}{8\pi D} \right)^{1/4}, \quad (41)$$

i.e., in one-dimensional systems with random uncorrelated generation of the reactive species the mean particle density grows sublinearly in time. Note that this result is consistent with the behavior observed numerically in Ref. [18].

Consider now how the situation will be changed in the case II, when A and B particles are introduced into the reactive bath as correlated pairs. In this case we get that the Fourier image of the integrable combination $S_-(\lambda, t)$ obeys the following equation:

$$\dot{S}_-(\omega, t) = -2D\omega^2 S_-(\omega, t) - 2I[1 - \cos(\omega\lambda_g)], \quad (42)$$

whose solution reads

$$S_-(\omega, t) = -\frac{I[1 - \cos(\omega\lambda_g)]}{D\omega^2 \sqrt{2\pi}} [1 - \exp(-2Dt\omega^2)]. \quad (43)$$

We note now a very important feature of Eq. (43); in striking contrast to case I, the steady-state spectrum is no longer singular in the limit $\omega \rightarrow 0$, but tends to a constant value,

$$S_-(\omega \rightarrow 0, t = \infty) = -\frac{I\lambda_g^2}{\sqrt{8\pi D}}, \quad (44)$$

which means that $S_-(\lambda, \infty)$ and hence, $g_{AB}(\lambda, \infty)$ are bounded in systems of any dimensionality, and thus the well-defined steady-state mean density $C(t = \infty)$ should exist. We notice, however, that the steady-state pairwise correlation function is proportional to λ_g^2 and thus may increase indefinitely with growth of λ_g . This unbounded growth is, of course, quite consistent with the result in Eq. (39), since the limit $\lambda_g \rightarrow \infty$ corresponds to the case of uncorrelated generation of particles.

Now, inverse Fourier transformation gives

$$\begin{aligned}
 S_-(\lambda, t) &= -\frac{I}{\sqrt{2\pi D}} \int_0^t \frac{d\tau}{\sqrt{\tau}} \left\{ \exp\left(-\frac{\lambda^2}{8D\tau}\right) \right. \\
 &\quad \left. - \frac{1}{2} \exp\left[-\frac{(\lambda-\lambda_g)^2}{8D\tau}\right] - \frac{1}{2} \exp\left[-\frac{(\lambda+\lambda_g)^2}{8D\tau}\right] \right\} \\
 &= -\frac{I\lambda}{4D\sqrt{\pi}} \left\{ \Gamma\left[-1/2, \frac{\lambda^2}{8Dt}\right] - \frac{1}{2} \Gamma\left[-1/2, \frac{(\lambda_g-\lambda)^2}{8Dt}\right] \right. \\
 &\quad \left. - \frac{1}{2} \Gamma\left[-1/2, \frac{(\lambda_g+\lambda)^2}{8Dt}\right] \right\}, \quad (45)
 \end{aligned}$$

where $\Gamma(\alpha, x)$ denotes the incomplete gamma function [53].

Consider now the asymptotic behavior of the pairwise correlation function, Eq. (33), for different values of parameters λ and λ_g at different values of time t .

We get from Eq. (45) that at sufficiently short times, when $\lambda \gg \lambda_g \gg 8Dt$, the pairwise correlation function obeys

$$g_{AB}(\lambda, \lambda_g, t) = -\frac{3I\lambda_g^2(8Dt)^{3/2}}{8\sqrt{\pi D}\lambda^4} \exp\left(-\frac{\lambda^2}{8Dt}\right), \quad (46)$$

which shows that correlations drop off as a Gaussian function at large scales.

Now, at short scales, such that $\lambda \ll \lambda_g$ and $\lambda \ll 8Dt$, and when λ_g is sufficiently large, $\lambda_g \gg 8Dt$, we obtain that $g_{AB}(\lambda, \lambda_g, t)$ obeys Eq. (39), which is not a surprising result since at such scales the correlations between injected particles should be irrelevant.

Within the opposite limit, when $8Dt \ll \lambda \ll \lambda_g$ the correlator follows

$$g_{AB}(\lambda, \lambda_g, t) \approx -\frac{I(8Dt)^{3/2}}{16\sqrt{\pi D}\lambda^2} \exp\left(-\frac{\lambda^2}{8Dt}\right), \quad (47)$$

which is reminiscent of the behavior in Eq. (46).

Finally, in the limit when both $\lambda \ll 8Dt$ and $\lambda_g \ll 8Dt$ (and $\lambda_g > \lambda$), i.e., in the limit of very long times, we find the following asymptotic expansion

$$\begin{aligned}
 g_{AB}(\lambda, \lambda_g, t) &\approx -\frac{I(\lambda_g - \lambda)}{16D} \\
 &\quad \times \left[1 - \frac{\lambda_g^2}{\lambda\sqrt{\pi Dt}} \exp\left(-\frac{\lambda^2}{8Dt}\right) + O(1/t) \right], \\
 &\quad \lambda_g \geq \lambda, \quad (48)
 \end{aligned}$$

where the symbol $O(1/t)$ signifies that the correction terms decay with time as $1/t$.

Equation (48) suffices to derive the large- t evolution of the mean particle density in the case of generation by correlated pairs, which reads

$$C(t) \approx \sqrt{\frac{I(\lambda_g - R)}{16D}} \left[1 - \frac{\lambda_g^2}{2R\sqrt{\pi Dt}} + O(1/t) \right], \quad \lambda_g \geq R. \quad (49)$$

Equations (49) reveals two surprising features; first, the steady-state density turns out to be dependent both on the diffusion constant and on the radius of pairs, generated by the source. Such an unusual dependence is, of course, inconsistent with the predictions of the formal kinetic approach, based on the textbook ‘‘law of mass action.’’ Second, the approach of particle densities to their steady-state values obeys a power-law dependence, in a striking contrast to the exponential one, predicted both by the formal kinetic and the Smoluchowski approach.

To close this subsection let us briefly consider the behavior of solutions of the reaction-diffusion equations (22) and (26)–(28) in two-dimensional systems.

In case I, we have from Eqs. (31) and (33) that as $t \rightarrow \infty$ the pairwise correlation function grows (by absolute value) as

$$g_{AB}(|\lambda|=R, t) \approx -I \ln(Dt/R^2), \quad Dt \gg R^2, \quad (50)$$

and consequently, we get from Eq. (40) that in this case at large times the mean particle density exhibits logarithmically slow growth,

$$C(t) \approx \sqrt{I \ln(Dt/R^2)}, \quad (51)$$

which is consistent with earlier predictions made in Refs. [16,17] and [19].

We turn next to analysis of case II. Here, we find that $g_{AB}(|\lambda|=R, \infty)$ behaves as

$$g_{AB}(|\lambda|=R, \infty) \approx -I \ln(\lambda_g), \quad (52)$$

which implies that the steady-state density exists and is a slowly growing function of the radius of the generated pairs,

$$C(t=\infty) \approx \sqrt{I \ln(\lambda_g)}. \quad (53)$$

Lastly, we find that the steady-state density is approached via an algebraic law

$$C(t) - C(t=\infty) \approx (Dt)^{-1}, \quad (54)$$

which should be contrasted to the exponential dependence predicted by mean-field descriptions.

B. Three-dimensional systems

As we have already mentioned, in case I, the steady-state fluctuation spectrum is characterized by an essential singularity of the type $1/\omega^2$ as $\omega \rightarrow 0$. In three-dimensional systems such a singularity is integrable, which ensures that the steady-state correlations exist and vanish as $\lambda \rightarrow \infty$. This circumstance allows us to claim [19] that segregation effects are absent in three and higher dimensions.

Let us analyze now the form of these correlations. Solving Eq. (31) in three dimensions we find (up to the correction terms that are exponentially small with K) that

$$g_{AB}(\lambda, t=\infty) \approx -\frac{I}{8\pi D\lambda}, \quad (55)$$

i.e., A - B correlations vanish with the distance between particles λ as $1/\lambda$, which shows that in the monomer-monomer catalytic scheme taking place in three-dimensional systems the correlations in the steady-state show a *quasi-long-range* order decaying only as the first inverse power of the interparticle distance. Straightforward calculations show that *quasi-long-range* order persists also in higher dimensions; here, the decay of correlations is also algebraic and obeys $g_{AB}(\lambda, t=\infty) \approx \lambda^{-(d-2)}$. Therefore, we conclude that despite the fact that segregation effects are absent in three- (and higher-) dimensional systems, the steady state is still characterized by significant correlations.

Now, substituting Eq. (55) into Eq. (22) we find the following expression for the steady-state density in three dimensions:

$$C(t=\infty) = \sqrt{\left(\frac{1}{8\pi DR} + \frac{1}{K}\right)I}, \quad (56)$$

which shows that A - B correlations lead here to an effective renormalization of the reaction constant in the steady state, i.e., $C(t=\infty)$ has the form $C(t=\infty) = \sqrt{I/K_{app}}$, where K_{app} is the above-mentioned apparent reaction constant [7].

Consider now how such a steady-state is approached at long times. Expanding the solution of Eq. (31) near the steady state, we find that pairwise correlations approach the steady state as a power law,

$$g_{AB}(|\lambda|=R, t) \approx \frac{I}{8\pi DR} \left[1 - \frac{R}{\sqrt{\pi Dt}} + O(1/t) \right], \quad (57)$$

which yields, in turn, a power-law relaxation of the mean particle density to the steady state

$$C(t) - C(t=\infty) \approx (Dt)^{-1/2}. \quad (58)$$

Therefore, in contrast to low-dimensional systems, in three-dimensional systems with random uncorrelated generation of the reactive species, the essential singularity in the fluctuation spectrum is integrable, correlations vanish with the distance between particles, and the steady-state mean particle density exists. However, the steady-state density is different from that predicted by the mean-field ‘‘law of mass action’’ and shows, in particular, dependence on the particle diffusivity D . In addition, Eq. (58) reveals that the approach to the steady state is described by a power law with the characteristic exponent $-1/2$, which is essentially non-mean-field behavior.

Finally, for case II, we find the following results for the correlation function and mean density. In the steady state the A - B correlations are equal to zero for $\lambda \geq \lambda_g$ (again, apart from the exponentially small with K terms). In the domain $\lambda < \lambda_g$, the correlations exist and are described by

$$g_{AB}(\lambda, t=\infty) \approx -\frac{I}{8\pi D\lambda} \left(1 - \frac{\lambda}{\lambda_g} \right), \quad (59)$$

which reduces to the result in Eq. (55) when $\lambda_g = \infty$. In contrast to the behavior as in Eq. (55), however, the correlations vanish at finite values of the correlation parameter λ .

Now, Eq. (59) yields for the steady-state mean-particle density

$$C(t=\infty) = \sqrt{I \left(\frac{1}{K} + \frac{1-R/\lambda_g}{8\pi DR} \right)}, \quad (60)$$

which is less than the steady-state density in case I, Eq. (56), due to the factor $1-R/\lambda_g$, which renormalizes the Smoluchowski constant. Consequently, for $\lambda_g > R$ the apparent rate constant takes the form

$$K_{app} = \frac{8\pi DRK}{8\pi DR + (1-R/\lambda_g)K}. \quad (61)$$

We finally find that such a steady state is approached via a power law,

$$C(t) - C(t=\infty) \approx (Dt)^{-3/2}, \quad (62)$$

which is faster than the approach described by Eq. (58), but still very different from the exponential behavior predicted by mean-field analysis.

IV. CONCLUSION

To summarize, we have shown that in both cases I and II, fluctuation effects dominate the kinetics of the monomer-monomer catalytic scheme involving diffusive particles and induce essential departures from the predictions of the mean-field approaches. In case I, the effects of fluctuation are especially pronounced in low-dimensional systems—the steady-state does not exist and mean particle density grows indefinitely in time, in absence of hard-core exclusion between particles. In three dimensions the steady state exists, but is characterized by very strong interparticle correlations, which, in turn, have a strong impact on the value of the steady-state mean particle density. The steady-state density is different from that predicted by the mean-field ‘‘law of mass action.’’ The approach to this steady state is described by an anomalous power law with the characteristic exponent $-1/2$, which stems from the presence of an essential singularity in the steady-state fluctuation spectrum. In case II, the steady-state fluctuation spectrum and the steady-state mean particle density exist in any dimension, but show an anomalous, non-mean-field dependence on the particles’ diffusivity and the radius of pairs, generated by the source. Approach to the steady state follows a universal power law with the characteristic exponent $-d/2$, which resembles, apart from the dependence of the prefactors on the system parameters (e.g., constant of the backward reaction), the long-time approach to the equilibrium in reversible chemical reactions [12,13,40–44]. The origin of this behavior is that the fluctuation spectrum in the steady state is flat at small values of the wave vector, i.e., the essential singularity in the steady-state spectrum of fluctuations is screened.

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