

**Catalytic reactions with bulk-mediated excursions: Mixing fails to restore chemical equilibrium**M. Coppey,<sup>1</sup> O. Bénichou,<sup>2</sup> J. Klafter,<sup>3</sup> M. Moreau,<sup>1</sup> and G. Oshanin<sup>1,4</sup><sup>1</sup>Laboratoire de Physique Théorique des Liquides, Université Paris 6, 4 Place Jussieu, 75252 Paris, France<sup>2</sup>Laboratoire de Physique de la Matière Condensée, Collège de France, 11 Place M. Berthelot, 75252 Paris Cedex 05, France<sup>3</sup>School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel<sup>4</sup>Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3, D-70569 Stuttgart, Germany  
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In this paper we analyze the effect of the bulk-mediated excursions (BME) of reactive species on the long-time behavior of the catalytic Langmuir-Hinshelwood-like  $A + B \rightarrow 0$  reactions in systems in which a catalytic plane (CP) is in contact with a *liquid* phase, containing concentrations of reactive particles. Such BME result from repeated particles desorption from the CP, subsequent diffusion in the liquid phase, and eventual readsorption on the CP away from the initial detachment point. This process leads to an effective superdiffusive transport along the CP. We consider both “batch” reactions, in which all particles of reactive species were initially adsorbed onto the CP, and reactions followed by a steady inflow of particles onto the CP. We show that for batch reactions the BME provide an effective mixing channel and here the mean-field-type behavior emerges. On the contrary, for reaction followed by a steady inflow of particles, we observe essential departures from the mean-field behavior and find that the mixing effect of the BME is insufficient to restore chemical equilibrium. We show that a steady state is established as  $t \rightarrow \infty$ , in which the limiting value of the mean coverage of the CP depends on the particles’ diffusion coefficient in the bulk liquid phase, and that the spatial distributions of adsorbed particles are strongly correlated. Moreover, we show that the relaxation to such a steady state is a power-law function of time, in contrast to the exponential time dependence describing the approach to equilibrium in perfectly stirred systems.

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**I. INTRODUCTION**

Catalytically activated reactions play an important role in various processes in chemistry, physics, and biology. Such reactions are involved, as well, in many industrial and technological processes, in which the design of desired chemicals requires the binding of chemically inactive molecules, which recombine only when some third substance—the catalytic substrate—is present [1–3].

One of the simplest examples of such catalytically activated reactions, which will be discussed here, is provided by the so-called Langmuir-Hinshelwood scheme [1–3]. This reaction scheme involves two types of reactive species—an  $A$  and a  $B$ , which are spread in a gaseous phase in contact with a solid surface; a catalyst may adsorb onto the surface at specific adsorption sites (at constant rates  $Q_{ads}^{(A,B)}$ ), desorb from them back to the gas phase (at constant rate  $Q^{(A,B)}$ ), and enter into the reaction



at a finite reaction rate  $K$ , as soon as any two of unlike species appear at neighboring adsorption sites. The reaction product  $P$  desorbs from the surface instantaneously and leaves the system.

Within the conventional mean-field approach [1–3] (in which one discards the correlations in particle’s distributions on the catalytic surface), one gets, in particular, in the simple limit  $Q_{ads}^{(A)} = Q_{ads}^{(B)} = Q_{ads}$ ,  $Q_{ads}^{(A)} \gg Q^{(A,B)}$  and at low particle’s densities in the gaseous phase, the following large- $t$  asymptotical behavior

$$C_A(t) = C_B(t) \approx \sqrt{\frac{Q_{ads}}{K}} \left[ 1 - \exp\left(-\frac{t}{T}\right) \right], \quad (2)$$

where  $C_{A,B}(t)$  denote mean surface coverage by the  $A$  and  $B$  species at time  $t$ , respectively, while  $T$  determines the characteristic time at which the value  $C_\infty = \sqrt{Q_{ads}/K}$  is approached. The expression in Eq. (2) can be readily generalized for arbitrary values of  $Q^{(A,B)}$ ,  $Q_{ads}^{(A,B)}$  and for arbitrary particle’s densities in the gas phase, which will result in a somewhat more complex expressions for  $C_\infty$  and for the characteristic relaxation time  $T$ . Note, however, that the long-time approach to  $C_\infty$  will be still described by an exponential function of time. It is also important to emphasize that the state approached as  $t \rightarrow \infty$  is believed to be a true *chemical equilibrium* state, in which the  $A$  and  $B$  particle’s distributions on the surface are  $\delta$  correlated and  $C_\infty$  is independent of the kinetic parameters.

Within the last two decades a considerable progress has been made in the theoretical analysis of the kinetics of *non-catalytic* reactions [4–19]. Here, a remarkable phenomenon of stochastic segregation has been discovered [4–19], and the effects of correlations and fluctuations in particle’s spatial distributions on the reaction course have been elucidated, which are in a striking contrast with the conventional mean-field picture [20]. These studies resulted in the inception of a novel interdisciplinary domain on the boundary between conventional chemistry and statistical physics—the fluctuation-dominated chemical kinetics.

Following the early works on the fluctuation phenomena in chemical reactions [4–8], Ziff and collaborators [21,22]

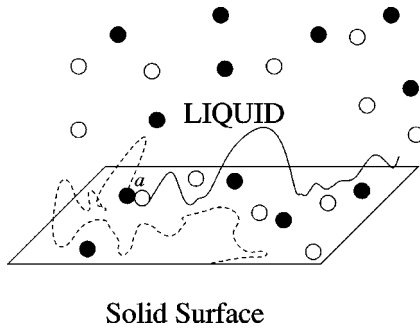


FIG. 1. A sketch of the reactive Langmuir-Hinshelwood-like system with bulk-mediated excursions. Black and white circles denote  $A$  and  $B$  particles, respectively. (a) denotes a particle configuration, in which reaction takes place. Solid and dashed curved lines depict effective trajectories of  $A$  and  $B$  particles, respectively.

have questioned the predictions of the mean-field approach in Eq. (2) for the *catalytic* Langmuir-Hinshelwood scheme. Focusing on the specific example of the oxidation process of the carbon monoxide on platinum surfaces,  $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ , Ziff *et al.* have observed a behavior which is by far richer and goes far beyond than the traditional mean-field predictions. In particular, they have discovered that as the CO gas pressure is lowered the system undergoes a first-order transition from a CO-saturated inactive phase (zero rate of  $\text{CO}_2$  production) into a reactive steady state (nonzero rate of  $\text{CO}_2$  production) followed by a continuous transition into an  $\text{O}_2$ -saturated inactive phase. This continuous transition was shown to belong to the same universality class as the directed percolation and the Reggeon field theory [23]. Different aspects of the kinetic and equilibrium behavior in this model have been scrutinized, revealing the importance of many-particle effects [24–42].

An essential feature of the Langmuir-Hinshelwood model is that the phase confronting the catalytic surface and acting as a reservoir of particles is *gaseous*. This is not the case, however, in many instances. For many important applications, especially in biological and chemical systems, the catalytic substrate appears to be in contact with a *liquid* phase, which comprises concentrations of reactive species (see Fig. 1).

In such systems the reaction kinetic and equilibrium properties may be affected by yet another important process, not included in the previous models; namely, here the particles can perform long-range concerted excursions inside the bulk liquid phase. That is, as depicted in Fig. 1, the particles, adsorbed onto the surface being in contact with the bulk liquid phase, can desorb, diffuse rapidly (with the diffusion coefficient being several orders of magnitude larger than that for a surface diffusion) within the bulk phase, and then return to the surface at a new position far away from the detachment point.

Indeed, it has been shown both experimentally and theoretically (see, e.g., Refs. [43–47], and references therein) that such bulk-mediated excursions (hereafter abbreviated as the BME) can be the principal kind of motion for particles. In biological systems, such bulk-mediated excursions play a significant role since here most of the systems include mem-

branes surrounded by fluid environments [48]; as an example, one may consider the receptor-ligand reactions which take place on a membrane surface [49,50], or the catalytic efficiency of proteins, which cut the DNA molecules (one-dimensional substrates) at specific sequences [51]. More generally, BME may be involved in certain “searching” processes [52].

Several prominent features distinguish the situations with a liquid and with a gas phase in contact with a solid substrate. First, in the case when the solid surface is in contact with a liquid, the desorption of the adsorbed particles is generally much more pronounced than in the latter case; hence, one expects that the BME process will be more frequent here. Second, appearing in the liquid phase after the desorption event, a desorbed particle will move diffusively, being multiply scattered by the solvent molecules. In view of the geometry of the system, here the motion relative to the surface is effectively one dimensional, such that, after desorption and excursions in the bulk, any particle will be *certain* to return back to the surface, in contrast with the situation with the gaseous phase, in which the particle may travel away from the surface almost indefinitely [53].

Repeated many times, the adsorption/desorption events separated by the bulk-mediated excursions will result in an effective motion of any given particle along the surface. A most striking point here is that this motion is *superdiffusive*, such that with respect to its surface displacements, any given particle performs a “Lévy walk” (see Refs. [54,55] for ample physical discussion). Consequently, instead of a familiar Gaussian propagator, one finds [43–47] that here the distribution  $P(r,t)$  of particles’ displacements along the surface is that of a two-dimensional Cauchy process and is characterized by a long  $1/r^3$  tail [56]:

$$P(r,t) = \frac{1}{2\pi} \frac{ct}{[(ct)^2 + r^2]^{3/2}}, \quad (3)$$

where  $c = D/h$ ,  $D$  being the particles’ diffusion coefficient in the bulk liquid, while  $h = bQ_{ads}/Q$  stands for the “adsorption depth” and  $b$  is the “capture range”—the distance over which a particle can directly be adsorbed in a single displacement step [43–47]. This implies, in turn, that due to the BME, the distribution  $\phi(r)$  of particles’ displacements  $r$  along the surface obeys [43–47]

$$\phi(r) = \frac{r^*}{|r|^3}, \quad r > r^* = \sqrt{Dt^*}, \quad (4)$$

$t^*$  being the typical time between the reabsorption events,  $t^* = D/(Q_{ads}b)^2$  [43,44].

The impact of such a peculiar transport on the kinetics and equilibrium properties of the reaction process in Eq. (1) has not been elucidated theoretically up to the present time.

In this paper we analyze the effect of the bulk-mediated excursions of the reactive species on the long-time behavior of the catalytic Langmuir-Hinshelwood-like reactions, Eq. (1), in terms of a simplified model, which captures only some basic features of the physical system, but still allows to

draw several important conclusions. First of all, we concentrate here on a totally symmetric situation, in which the mean concentrations of the reactive particles in the liquid phase, as well as their adsorption and desorption rates, are equal to each other. Further on, in this model, we focus on the events taking place on the catalytic surface and incorporate a semi-infinite liquid phase containing concentrations of reactive species in an indirect fashion. That is, we assume that continuous inflow of  $A$  and  $B$  particles, dispersed in the semi-infinite liquid phase, to the catalytic surface can be modeled as a source, which creates  $A$  and  $B$  directly on the surface, independently of each other and at a constant production rate  $Q_{ads}$ . Furthermore, we suppose that the BME can be taken into account by letting the adsorbed particles to perform random, long-range hopping motion along the adsorption sites of the catalytic surface with suitably chosen hopping probabilities, determined by Eq. (4). Consequently, we propose here a two-dimensional model which includes two types of reactive species, which react upon encounters, perform long-range (Lévy or, more specifically, Gillis-Weiss [57,58]) walks on the lattice, and are continuously introduced onto the lattice from a reservoir maintained at a constant chemical potential.

We hasten to remark that this model serves only as a first approximation of the real physical system and there are several other important processes, which may influence the kinetic behavior of the reaction process in Eq. (1). First of all, an assumption that the “intensity” of particle’s creation on the lattice is not varying in time may be inadequate. As a matter of fact, here, in view of the effectively one-dimensional geometry and diffusive transport in the liquid phase, nonhomogenous particle density profiles in the direction perpendicular to the catalytic plane, characterized by a “depletion” zone, may emerge. In consequence, the actual intensity of particle’s production on the catalytic may vary with time. On the other hand, here we overestimate mixing effect of long-range BME, supposing that for any particle a jump on distance  $r$  along the lattice, once chosen with the probability distribution in Eq. (4), is executed *instantaneously*, while in reality the transport via BME on this distance takes some time, which is actually a random variable having a broad distribution. Consequent analysis of these effects requires much more complex approach, which is currently being carried out [59].

Finally, we would like to note that, apart from its relevance to the reaction process in Eq. (1) for a catalytic surface in contact with a liquid phase, our analysis sheds the light on the conceptually important question of the effect of mixing on the fluctuation-induced kinetics. As we have already remarked, for batch  $A + B \rightarrow 0$  reactions, i.e., reactions in which the particles of the reactive species are all initially introduced into the system, in case of equal mean particle’s densities and diffusive transport, diffusion appears to be a nonefficient mixing channel and the like species tend to segregate spontaneously in the reaction course, which causes deviations from the textbook kinetic behavior [4–19]. In presence of a steady inflow of reactive species, this effect gets dramatically increased and the deviations from the conventionally expected behavior [20] are getting even more

pronounced [11–13,15–17,39]. On the other hand, it has been shown recently in Refs. [60–62], which analyzed kinetics of the batch  $A + B \rightarrow 0$  reactions, involving particles which execute Lévy walks, that in this case, under certain conditions, accelerated diffusion destroys effectively the particle-particle segregation and the mean-field behavior prevails. One may now pose quite a legitimate question whether in situations with a steady inflow of reactive species the Lévy walks would provide a sufficiently fast mixing channel and overcome the strong tendency for segregation of like species in the course of the process in Eq. (1). Our answer is negative. We show that in the situation under study (despite the fact that we strongly enhanced mixing supposing that the BME are executed instantaneously), the state reached by the process in Eq. (1) as  $t \rightarrow \infty$  is not a true chemical equilibrium but only a steady state. As a matter of fact, we proceed to show that coverages  $C_\infty$  appear to depend on the kinetic parameters, such as, e.g., particle’s diffusion coefficient in the bulk, and moreover, particle’s distributions on the lattice are very strongly (algebraically) correlated and that the long-time approach to such a steady state is essentially delayed, as compared to the exponential dependence in Eq. (2)—it is described by a power-law function of time.

The paper is structured as follows. In Sec. II we introduce the model and basic notations. In Sec. III, focusing on the case of batch reactions, we present our analytical approach and reproduce several known results. In Sec. IV we analyze the steady-state behavior in models with steady particle’s input, which mimics Langmuir-Hinshelwood scheme with bulk-mediated excursions, and discuss the long-time approach to such a steady state. Finally, we conclude in Sec. V with a summary of our results and discussion.

## II. MODEL

Consider a two-dimensional regular lattice which is brought in contact with a reservoir of particles of two types—an  $A$  and a  $B$ , maintained at constant chemical potentials  $\mu_A$  and  $\mu_B$ . Here we restrict our analysis to the special case  $\mu_A \equiv \mu_B$ . The particles of both species may adsorb onto the lattice at constant rate  $Q_{ads}$ , desorb from the lattice at rate  $Q$ , an event followed by a long-range instantaneous jump of distance  $r$  with probability  $\phi(r)$  and an immediate re-adsorption. The particles then react at a constant rate  $K$  according to the scheme in Eq. (1) as soon as any two of unlike species appear on the same lattice site. In most of our analysis we will focus on the limit  $K \rightarrow \infty$ , which will allow us to emphasize the “statistical physics,” rather than purely “chemical” effects. We will discard the hard-core exclusion between like and unlike species, assuming that the particles’ coverage are sufficiently small.

Now, the long-range jumps performed by the particles of reactive species will be described here within the framework of the Gillis-Weiss random walks [57] (also referred to sometimes as the Riemann walks [58]), which represent the lattice version of Lévy flights [63] in the limit  $|\mathbf{r}| \gg 1$ . We will use here a bit more general definition of  $\phi(r)$ , than that in Eq. (4), and suppose that  $\phi(r)$  is given by

$$\phi(r) = \frac{\xi}{|\mathbf{r}|^{\mu+d}}. \quad (5)$$

Note that the distribution in Eq. (5) reduces to the one in Eq. (4) in the particular case when  $d=2$  and  $\mu=1$ . In this case, the parameter  $\xi=r^*$ . Note also that with this definition of the elementary jump probability, the mean square displacement per step  $\overline{\mathbf{r}^2}$  is infinite for all  $\mu < 2$ , which implies that such a random walk has an infinite variance [63,64]. The long-tailed distribution of the jump probabilities permits long-range jumps and generates a superdiffusive regime. Gillis-Weiss walks lead to anomalous diffusion, associated to the dynamic exponent  $2/\mu$  for  $\mu < 2$ ,  $|\mathbf{r}|^2 \sim t^{2/\mu}$ , and to conventional diffusion for  $\mu \geq 2$ , corresponding to Gaussian random walks,  $\overline{\mathbf{r}^2} \sim t$ . In the case of interest here, i.e., for  $\mu = 1$  and  $d=2$ , the case which mimics the reaction in Eq. (1) mediated by rapid excursions in the bulk, one has that in regard to surface displacements, the particles execute random ballistic-type (with an infinite velocity) motion with  $|\mathbf{r}| \sim t$ .

Let now  $C_A(\mathbf{r},t)$  and  $C_B(\mathbf{r},t)$  denote the local (at point with vector  $\mathbf{r}$ ), time-dependent coverage of  $A$  and  $B$  particles, respectively. Evolution of these properties is governed by the following rate equations:

$$\begin{aligned} \dot{C}_A(\mathbf{r}) = & -KC_A(\mathbf{r})C_B(\mathbf{r}) - \frac{1}{\tau_d} \sum_{\mathbf{r}'} \phi(\mathbf{r}'-\mathbf{r})C_A(\mathbf{r}) \\ & + \frac{1}{\tau_d} \sum_{\mathbf{r}'} \phi(\mathbf{r}-\mathbf{r}')C_A(\mathbf{r}') + Q_{ads}^{(A)}(\mathbf{r},t), \end{aligned} \quad (6)$$

$$\begin{aligned} \dot{C}_B(\mathbf{r}) = & -KC_A(\mathbf{r})C_B(\mathbf{r}) - \frac{1}{\tau_d} \sum_{\mathbf{r}'} \phi(\mathbf{r}'-\mathbf{r})C_B(\mathbf{r}) \\ & + \frac{1}{\tau_d} \sum_{\mathbf{r}'} \phi(\mathbf{r}-\mathbf{r}')C_B(\mathbf{r}') + Q_{ads}^{(B)}(\mathbf{r},t), \end{aligned} \quad (7)$$

where the dot denotes the time derivative, the first term on the right-hand side (rhs) describes the decrease in particles' coverage due to the reaction events, the second and the third terms describe departures and arrivals of the particles at the site  $\mathbf{r}$  at time  $t$  due to long-range jumps, respectively. Note that the summation in the second and the third terms on the rhs of Eqs. (6) and (7) extends over all lattice sites, which signifies the long-range character of particles' migration, while  $\tau_d$  denotes the time each particle typically spends on each lattice site between the desorption events,  $\tau_d = Q^{-1}$ . In turn, the fourth terms on the rhs of Eqs. (6) and (7) describe the (random) contributions to particles' coverage due to adsorption of particles from the reservoir, which mimics, in our model, the presence of particles in the bulk liquid phase. In the usual fashion, we admit the following statistical properties of these "source" terms:

$$\langle Q_{ads}^{(A)}(\mathbf{r},t) \rangle = \langle Q_{ads}^{(B)}(\mathbf{r},t) \rangle = Q_{ads}, \quad (8)$$

$$\langle Q_{ads}^{(A)}(\mathbf{r},t) Q_{ads}^{(A)}(\mathbf{r}+\lambda, t+\tau) \rangle = Q_{ads}^2 + Q_{ads} \delta(\lambda) \delta(\tau), \quad (9)$$

$$\langle Q_{ads}^{(B)}(\mathbf{r},t) Q_{ads}^{(B)}(\mathbf{r}+\lambda, t+\tau) \rangle = Q_{ads}^2 + Q_{ads} \delta(\lambda) \delta(\tau), \quad (10)$$

and

$$\langle Q_{ads}^{(A)}(\mathbf{r},t) Q_{ads}^{(B)}(\mathbf{r}+\lambda, t+\tau) \rangle = 0, \quad (11)$$

where  $\delta(\lambda)$  is the delta function,  $\lambda$  is the correlation parameter, and the angle brackets  $\langle \dots \rangle$ , here and henceforth, denote the volume averages. Consequently, we stipulate that creation of particles on the catalytic surface proceeds completely at random (in space and in time), and at a constant rate, which describes arrivals of the particles, located initially in the bulk liquid phase, at progressively longer distances in the direction perpendicular to the catalytic surface.

In what follows, we discuss the behavior of the solutions of the dynamic rate equations, Eqs. (6) and (7), under different physical conditions.

### III. BATCH REACTIONS

To set up the scene, we discuss first the effect of the BME on the kinetics of  $A+B \rightarrow 0$  in the "batch" reaction case; namely, in situations in which all particles of the reactive species which were dispersed initially in the bulk liquid phase were absorbed onto the surface by some "rapid quench;" steady inflow of reactants by the external source is supposed to be absent here,  $Q_{ads}^{(A)}(\mathbf{r},t) = Q_{ads}^{(B)}(\mathbf{r},t) \equiv 0$ . We suppose, however, that at  $t > 0$  particles' desorption from the catalytic surface, and consequently, the BME, are allowed.

In this case, we assume that the initial particles' distributions on the lattice are random Gaussian,  $\delta$  correlated with mean coverage  $C_0$ ; that is,  $C_A(\mathbf{r},0)$  and  $C_B(\mathbf{r},0)$  obey

$$\langle C_A(\mathbf{r},0) \rangle = \langle C_B(\mathbf{r},0) \rangle = C_0, \quad (12)$$

$$\langle C_A(\mathbf{r},0) C_A(\mathbf{r}+\lambda,0) \rangle = C_0^2 + C_0 \delta(\lambda), \quad (13)$$

$$\langle C_B(\mathbf{r},0) C_B(\mathbf{r}+\lambda,0) \rangle = C_0^2 + C_0 \delta(\lambda), \quad (14)$$

and

$$\langle C_A(\mathbf{r},0) C_B(\mathbf{r}+\lambda,0) \rangle = C_0^2. \quad (15)$$

Now, to analyze the time evolution of the mean particles' coverage, we make use of the analytical approach first proposed in Ref. [5] for the description of the fluctuation-induced kinetics of irreversible diffusion-limited  $A+B \rightarrow 0$  reactions. In this approach the hierarchy of the reaction-diffusion equations for the higher-order correlation functions has been truncated at the level of third-order correlations. Subsequent works (see, e.g., Refs. [12,17,39]) generalized the approach to more complex reaction schemes, e.g., to reversible reactions or reactions involving interacting particles, and also showed that such a truncation is tantamount to the assumption that fluctuations in the fields  $C_{A,B}(\mathbf{r},t)$ , which are initially Gaussian and  $\delta$  correlated, remain Gaussian  $\delta$  correlated at all times; this implies that the fourth-order correlations decouple automatically into the product of the pairwise correlations, which ensures, in turn, that the third-order

correlations vanish. On physical grounds, it means that particles' diffusion is supposed to mix effectively inhomogeneities created locally due to reaction events, preserving the initial  $\delta$ -correlated particles' distributions. On the other hand, Lévy walks are known to mix the system even more effectively than conventional diffusion [60,62]. Consequently, we believe that truncation of the hierarchy at the level of third-order correlations is appropriate for the system under study. We also note that this procedure allows us to reproduce the results obtained within a different analytical approach [60,62].

Following Ref. [5], we write first the local coverage  $C_{A,B}(\mathbf{r},t)$  in the form

$$C_{A,B}(\mathbf{r},t) = C(t) + \delta C_{A,B}(\mathbf{r},t), \quad (16)$$

where  $\delta C_{A,B}(\mathbf{r},t)$  denote *local* deviations from the mean coverage  $C(t)$ . By definition,  $\langle \delta C_{A,B}(\mathbf{r},t) \rangle = 0$ .

Further on, we introduce the pair-correlation functions

$$G_{AB}(\lambda,t) = \langle \delta C_A(\mathbf{r},t) \delta C_B(\mathbf{r}+\lambda,t) \rangle, \quad (17)$$

$$G_{AA}(\lambda,t) = \langle \delta C_A(\mathbf{r},t) \delta C_A(\mathbf{r}+\lambda,t) \rangle, \quad (18)$$

and

$$G_{BB}(\lambda,t) = \langle \delta C_B(\mathbf{r},t) \delta C_B(\mathbf{r}+\lambda,t) \rangle, \quad (19)$$

$\lambda$  being the correlation parameter. Note that since we have assumed a totally symmetric situation with regard to the adsorption/desorption rates, the correlation functions  $G_{AA}(\lambda,t)$  and  $G_{BB}(\lambda,t)$  are obviously equal to each other at any time moment,  $G_{AA}(\lambda,t) = G_{BB}(\lambda,t)$ .

Next, averaging Eqs. (6) and (7), we obtain

$$\dot{C}(t) = -K[C^2(t) + G_{AB}(t)], \quad (20)$$

where we have used the notation  $G_{AB}(t) = G_{AB}(\mathbf{0},t)$ , i.e.,  $G_{AB}(t)$  is the value of the particle-particle pairwise correlations at distance  $\lambda$  which is equal to the reaction radius  $R$  (here, in the lattice version of the model, we assumed that reaction takes place when two particles of unlike species appear at the same site, i.e.,  $R=0$ ).

Note now that Eq. (20) shows that the time evolution of the mean coverage is *ostensibly* coupled to the evolution of the pairwise correlation function. Note also that if the correlations are supposed to be insignificant,  $G_{AB}(t)=0$ , as one generally takes for the mean-field approach, one obtains from Eq. (20) that  $\dot{C}(t) = -KC^2(t)$ , i.e., the conventional "law of mass action." This law yields  $C(t) \sim 1/Kt$  for systems of any spatial dimension and regardless of the way how the particles move in the system. On the other hand, assuming perfect, instantaneous reaction with  $K \equiv \infty$ , one gets that

$$C(t) = \sqrt{-G_{AB}(t)}, \quad (21)$$

which represents the mathematical formulation of the segregation effect; as a matter of fact, Eq. (21) shows that the time evolution of the observable—the mean coverage—is guided at any time  $t$  by the time evolution of the pairwise correlations in the system. In case when both species move diffu-

sively, Eq. (21) entails an unusual kinetic law  $C(t) \sim 1/t^{d/4}$  [4–8,10], which thus predicts for  $d < 4$  a *slower* time evolution of the mean coverage than that defined within the mean-field approach. Note also that for finite  $K$  Eq. (21) holds for times  $t$  sufficiently large such that the fluctuation-induced law  $C(t) \sim 1/t^{d/4}$  determines the long-time asymptotic behavior.

Now, to determine analytically the time evolution of the mean coverage in our case with BME, we have to evaluate the time dependence of  $G_{AB}(t)$  which embodies all necessary information on the initial fluctuation spectra and particle's dynamics. Making use of Eqs. (6)–(20), neglecting the third-order correlations, and employing an evident symmetry condition between the  $AA$  and  $BB$  correlation functions [ $G_{AA}(\lambda,t) \equiv G_{BB}(\lambda,t)$ ], we find that  $G_{AB}(\lambda,t)$  and  $G_{AA}(\lambda,t)$  obey the following system of reaction/transport equations:

$$\begin{aligned} \dot{G}_{AB}(\lambda,t) = & -2KC(t)[G_{AB}(\lambda,t) + G_{AA}(\lambda,t)] \\ & + \frac{1}{\tau_d} \sum_{\mathbf{y}} \phi(\mathbf{y}) \hat{\mathcal{L}}_{\lambda} G_{AB}(\lambda,t), \end{aligned} \quad (22)$$

and

$$\begin{aligned} \dot{G}_{AA}(\lambda,t) = & -2KC(t)[G_{AB}(\lambda,t) + G_{AA}(\lambda,t)] \\ & + \frac{1}{\tau_d} \sum_{\mathbf{y}} \phi(\mathbf{y}) \hat{\mathcal{L}}_{\lambda} G_{AA}(\lambda,t), \end{aligned} \quad (23)$$

where

$$\hat{\mathcal{L}}_{\lambda} G_{AB}(\lambda,t) = G_{AB}(\lambda + \mathbf{y},t) + G_{AB}(\lambda - \mathbf{y},t) - 2G_{AB}(\lambda,t). \quad (24)$$

Note that Eqs. (22) and (23) together with Eq. (20) are *closed* with respect to the mean coverage and pairwise correlations, and permits the evaluation of these quantities.

In order to solve the system of Eqs. (22), (23), and (20), it is expedient to introduce a pair of discrete Fourier transforms:

$$\tilde{F}(\mathbf{k},t) = \sum_{\mathbf{r}} F(\mathbf{r},t) e^{i(\mathbf{k} \cdot \mathbf{r})}$$

and

$$F(\mathbf{r},t) = \frac{1}{(2\pi)^d} \int_{\mathcal{B}} \tilde{F}(\mathbf{k},t) e^{-i(\mathbf{k} \cdot \mathbf{r})} d^d k,$$

where  $\mathcal{B}$  denotes the first Brillouin zone.

Transforming Eqs. (22) and (23), we get

$$\begin{aligned} \dot{\tilde{G}}_{AB}(\mathbf{k},t) = & -2KC(t)[\tilde{G}_{AB}(\mathbf{k},t) + \tilde{G}_{AA}(\mathbf{k},t)] \\ & + \frac{2}{\tau_d} [\tilde{\phi}(\mathbf{k}) - \tilde{\phi}(\mathbf{0})] \tilde{G}_{AB}(\mathbf{k},t) \end{aligned} \quad (25)$$

and

$$\begin{aligned} \tilde{G}_{AA}(\mathbf{k}, t) = & -2KC(t)[\tilde{G}_{AB}(\mathbf{k}, t) + \tilde{G}_{AA}(\mathbf{k}, t)] \\ & + \frac{2}{\tau_d}[\tilde{\phi}(\mathbf{k}) - \tilde{\phi}(\mathbf{0})]\tilde{G}_{AA}(\mathbf{k}, t), \end{aligned} \quad (26)$$

in which equations we have made use of the condition  $\tilde{\phi}(-\mathbf{k}) = \tilde{\phi}(\mathbf{k})$ , since random jump process under consideration is symmetric. Equations (25) and (26) are accompanied by the initial conditions, which follow from the ones in Eqs. (12)–(15),

$$\tilde{G}_{AA}(\mathbf{k}, 0) = \tilde{G}_{BB}(\mathbf{k}, 0) = C_0, \quad \tilde{G}_{AB}(\mathbf{k}, 0) = 0. \quad (27)$$

Solution of Eqs. (25)–(27) can be readily obtained explicitly and reads

$$\begin{aligned} \tilde{G}_{AB}(\mathbf{k}, t) = & -\frac{C_0}{2} \exp\left[-2[\tilde{\phi}(\mathbf{0}) - \tilde{\phi}(\mathbf{k})]\frac{t}{\tau_d}\right] \\ & \times \left[1 - \exp\left(-4K \int_0^t C(t') dt'\right)\right]. \end{aligned} \quad (28)$$

We focus first on the case of so-called “perfect” reactions, when  $P$  is formed with probability 1 at any encounter of  $A$  and  $B$  and hence, when  $K \equiv \infty$ . Here,  $\tilde{G}_{AB}(\mathbf{k}, t)$  in Eq. (28) simplifies

$$\tilde{G}_{AB}(\mathbf{k}, t) = -\frac{C_0}{2} \exp\left[-2[\tilde{\phi}(\mathbf{0}) - \tilde{\phi}(\mathbf{k})]\frac{t}{\tau_d}\right], \quad (29)$$

and  $G_{AB}(t)$ , which enters Eq. (21) and governs evolution of the mean coverage, is given by

$$G_{AB}(t) = \frac{1}{(2\pi)^d} \int_B \tilde{G}_{AB}(\mathbf{k}, t) d\mathbf{k}. \quad (30)$$

Now, it is well known (see, e.g., Refs. [58,60]) that the leading in the small- $k$  limit behavior of structure function  $\tilde{\phi}(\mathbf{k}) = \xi \sum_{\mathbf{r}} |\mathbf{r}|^{-\mu-d} \exp(-i\mathbf{r} \cdot \mathbf{k})$  follows for all values of  $\mu \leq 2$ :

$$\tilde{\phi}(\mathbf{0}) - \tilde{\phi}(\mathbf{k}) \sim A |\mathbf{k}|^\mu, \quad (31)$$

where  $A$  is a constant,  $A = \pi \xi / \Gamma(d + \mu) \sin(\pi\mu/2)$ ,  $\Gamma(x)$  being the Gamma function. Consequently, for  $d=2$  the long-time behavior of the correlation function  $G_{AB}(t)$  obeys

$$\begin{aligned} G_{AB}(t) = & -\frac{C_0}{2(2\pi)^2} \int_B \exp\left[-\frac{2At}{\tau_d} |\mathbf{k}|^\mu\right] d\mathbf{k} \\ \sim & -\frac{C_0}{2(2\pi)^2} \int_0^\infty \exp\left[-\frac{2At}{\tau_d} k^\mu\right] k dk \\ = & -\alpha_\mu C_0 \left(\frac{\xi t}{\tau_d}\right)^{-2/\mu}, \end{aligned} \quad (32)$$

where  $\alpha_\mu$  is a dimensionless constant,  $\alpha_\mu = \Gamma(2/\mu) \Gamma^{2/\mu}(2 + \mu) \sin^{2/\mu}(\pi\mu/2) / 4^{1+1/\mu} \mu \pi^{1+2/\mu}$ . Hence, the long-time decay of the mean coverage  $C(t)$  is given by

$$C(t) \simeq \alpha_\mu^{1/2} C_0^{1/2} \left(\frac{\tau_d}{\xi t}\right)^{1/\mu} \sim t^{-1/\mu}. \quad (33)$$

Generalization of the result in Eq. (33) for arbitrary  $d$  is straightforward and yields

$$C(t) \sim t^{-d/2\mu}, \quad (34)$$

which is precisely the result obtained for batch  $A+B \rightarrow 0$  reactions involving particles performing Lévy walks using a different theoretical approach in Refs. [60,62]. Note also that for  $\mu=2$ , which corresponds to the case of a standard random walk, we recover from Eq. (34) the celebrated fluctuation-induced law  $C(t) \sim t^{-d/4}$  [4–8,10]. On the other hand, for sufficiently small values of  $\mu$ , such as  $\mu < d/2$ , Eq. (33) predicts a decay which is faster than the usual mean-field  $1/t$  law. We hasten to remark that such a behavior is specific for the *perfect* reaction limit, when  $K \equiv \infty$ . Actually, for systems with a *finite* reaction rate  $K$ , the fact that  $G_{AB}(t)$  decays at a *faster* rate than  $1/t^2$  means that correlations become *unimportant* and the actual long-time decay of particles’ coverages follows the standard textbook prediction  $1/Kt$ . Similar effect has been also obtained for reactions in inhomogeneous systems in Ref. [65].

We turn now to the borderline case  $d=2$  and  $\mu=1$ , which is of special interest here, since it corresponds to the reactions mediated by bulk excursions. Here, Eq. (33) entails the behavior  $C(t) \sim t^{-1}$ , i.e., the decay of the mean coverage mediated by the Cauchy walks proceeds exactly in the same fashion, as the decay obtained within the conventional mean-field approach [20]. This circumstance has prompted the authors of Refs. [60,62] to conclude that such a long-range transport may serve as an effective mixing channel which suppresses effectively the “undesired” segregation effect. In the following section, we will examine whether this conclusion remains valid in case of reactions followed by a steady inflow of reactive species.

Finally, we note that this special case, in which the “mean-field,” purely chemical component, and the decay of correlations contribute to the overall kinetics at the same rate, can be viewed from a different perspective. Following the celebrated Collins-Kimball treatment of imperfect ( $K < \infty$ ) diffusion-limited reactions [66], one may stipulate that here the time evolution of the mean coverage obeys effectively the second-order rate equation of the form

$$\dot{C}(t) = -K_{app} C^2(t), \quad (35)$$

where  $K_{app}$  is the apparent or effective rate constant, dependent both on  $K$  and on the parameters of the Cauchy process.

To determine  $K_{app}$ , we proceed as follows: We notice first that for finite  $K$  the mean coverage defined by Eq. (20) cannot decrease faster than the  $t^{-1}$  law expected from the mean-field kinetics. This implies that the integral  $\int_0^t C(t') dt'$  is divergent for  $t \rightarrow \infty$ , and hence, at sufficiently large times

$$\exp\left[-4K \int_0^t C(t') dt'\right] \ll 1, \quad (36)$$

and Eq. (32) describes correctly the long-time evolution of the pairwise correlation function for finite values of  $K$ . Now, from Eq. (32) we have that in this case

$$G_{AB}(t) \sim -\frac{C_0 \tau_d^2}{4\pi^3 \xi^2} t^{-2}. \quad (37)$$

Substituting this expression into Eq. (20) and searching for the solution of the resulting equation in the form  $C(t) = 1/K_{app}t$ , we obtain

$$K_{app} = \frac{2\pi^3 \xi^2}{C_0 \tau_d^2 K} \left( \sqrt{1 + \frac{C_0 \tau_d^2 K^2}{\pi^3 \xi^2}} - 1 \right). \quad (38)$$

Recollecting next that  $\tau_d = Q^{-1}$  and  $\xi = r^* = \sqrt{Dt^*}$ , where  $t^* = D/Q_{ads}^2 b^2$ , we may rewrite  $K_{app}$  as

$$K_{app} = \frac{2\pi^3}{C_0 K} \left( \frac{DQ}{bQ_{ads}} \right)^2 \left( \sqrt{1 + \frac{C_0 b^2}{\pi^3} \left( \frac{KQ_{ads}}{DQ} \right)^2} - 1 \right), \quad (39)$$

which relates the kinetic behavior of the batch reactions with the BME to the physical parameters describing our model. The expression in Eq. (39) is thus an extension of the celebrated Collins and Kimball result for the apparent reaction rate constant for catalytic reactions with bulk-mediated excursions.

#### IV. REACTIONS WITH STEADY INFLOW OF SPECIES

Let us now consider the case when the reaction process in Eq. (1) is accompanied by a steady inflow of particles onto the lattice, which mimics in our model of reactions with bulk-mediated excursions arrivals onto the surface of particles (initially dispersed in the liquid phase) from progressively larger and larger distances in the direction perpendicular to the surface. The statistical properties of external sources are defined in Sec. II, Eqs. (8)–(11).

Averaging Eqs. (6) and (7), we find that in this case the time evolution of the mean coverage is governed by

$$\dot{C}(t) = -K[C(t)^2 + G_{AB}(t)] + Q_{ads}. \quad (40)$$

On the other hand, we find that the pairwise correlation function  $G_{AB}(\lambda, t)$  is still determined by Eq. (22), while  $G_{AA}(\lambda, t)$  obeys (see, e.g., Refs. [17,39] for the details of the derivation in the diffusion-controlled case)

$$\begin{aligned} \dot{G}_{AA}(\lambda, t) = & -2KC(t)[G_{AB}(\lambda, t) + G_{AA}(\lambda, t)] \\ & + \frac{1}{\tau_d} \sum_y \phi(y) \hat{\mathcal{L}}_\lambda G_{AA}(\lambda, t) + Q_{ads}. \end{aligned} \quad (41)$$

We note, parenthetically, that discarding correlations, i.e., setting in Eq. (40) formally  $G_{AB}(t) \equiv 0$ , we recover the mean-field result in Eq. (2), which claims that (i) the state approached as  $t \rightarrow \infty$  is a true chemical equilibrium, (ii)  $C_\infty = \sqrt{Q_{ads}/K}$ , and (iii)  $C_\infty$  is approached exponentially fast. On the other hand, there is an ample evidence that all three

of these statements are wrong because of the segregation effects in the case when reactive particles perform conventional diffusive motion on a two-dimensional surface in presence of a steady inflow [17,39]. However, as demonstrated in Refs. [60,62] and in Sec. III of the present paper, for batch reactions with the BME, which ultimately result in random ballisticlike motion along the surface, the segregation effect is suppressed and, apart from some renormalization of the reaction constant  $K$ , kinetic behavior follows an essentially mean-field-type dependence  $C(t) \sim 1/t$ . Consequently, it is not *a priori* clear whether  $G_{AB}(t)$  governs (or even contributes to) the long-time evolution of the system in the case  $d = 2$  and  $\mu = 1$ .

To answer this question, we turn to the time evolution of  $G_{AB}(\lambda, t)$ , defined by Eqs. (22) and (41). Applying the Fourier transformation, we find, after elementary calculations, that in the long-time limit [in which the asymptotic behavior in Eq. (31) holds] the Fourier image of the pairwise correlation function  $G_{AB}(\lambda, t)$  reads:

$$\begin{aligned} \tilde{G}_{AB}(\mathbf{k}, t) \sim & -\frac{Q_{ads} \tau_d}{4A |\mathbf{k}|^\mu} \left( 1 - \exp \left[ -2A |\mathbf{k}|^\mu \frac{t}{\tau_d} \right] \right) \\ & + \frac{Q_{ads}}{2} \int_0^t \exp \left[ -2A |\mathbf{k}|^\mu \frac{t-t'}{\tau_d} \right] \\ & - 4K \int_{t'}^t C(t'') dt'' \Big] dt'. \end{aligned} \quad (42)$$

Now, some analysis shows that due to the presence of the function  $4K \int_{t'}^t C(t'') dt''$  in the exponential, the second term on the rhs of Eq. (42) is negligibly small compared to the first one. Consequently, we focus on the behavior of the dominant contribution.

Consider first the long-time evolution of  $G_{AB}(t)$ , which enters the rhs of Eq. (40) and hence, may affect the evolution of the observable—the mean coverage. Inverting the Fourier transform, we find then that in the long-time limit  $G_{AB}(t)$  obeys, in  $d$  dimensions and for arbitrary  $\mu$ ,

$$\begin{aligned} G_{AB}(t) = & -\frac{Q_{ads} \tau_d}{4A (2\pi)^d} \int_B \frac{d^d k}{|\mathbf{k}|^\mu} \left( 1 - \exp \left[ -2A |\mathbf{k}|^\mu \frac{t}{\tau_d} \right] \right) \\ \sim & -\frac{Q_{ads} \tau_d}{8\pi A} \int_0^{2\pi} \frac{dk}{k^{\mu-d+1}} \left( 1 - \exp \left[ -2A |k|^\mu \frac{t}{\tau_d} \right] \right). \end{aligned} \quad (43)$$

Analyzing the behavior of  $G_{AB}(t)$ , defined in Eq. (43), one notices first that  $G_{AB}(t \rightarrow \infty) = \infty$  for  $\mu \geq d$ , which signifies that in such situations  $G_{AB}(t)$  is a growing with  $t$  function [67]. This is precisely the case discussed in Refs. [17,39], which concerned with the behavior of two-dimensional  $A + B \rightarrow 0$  reactions involving diffusive species in presence of external uncorrelated input of particles. On the other hand, for  $\mu < d$  the stationary value  $G_{AB}(t \rightarrow \infty)$  is finite.

Consequently, in the case of interest here, i.e., for  $d = 2$  and  $\mu = 1$ , we find from Eq. (43) the following behavior:

$$G_{AB}(t) \sim -\frac{Q_{ads}\tau_d}{4A} + \frac{Q_{ads}\tau_d^2}{16\pi A^2 t}, \quad (44)$$

which predicts that the stationary value of  $G_{AB}(t)$ , i.e.,  $-Q_{ads}\tau_d/4A$  is approached as a power law, at a rate which is proportional to the first inverse power of time. Note also that  $G_{AB}(t) < 0$ , which means that pairwise correlation slows down the *forward* reaction.

Substituting the expression in Eq. (44) into Eq. (40) and solving the resulting equation in the limit  $t \rightarrow \infty$ , we find eventually that at sufficiently long times the mean coverage obeys

$$C(t) = \sqrt{\frac{Q_{ads}}{K} + \frac{bQ_{ads}^2}{2\pi DQ}} \left[ 1 - \frac{t_{char}}{t} + O\left(\frac{1}{t^2}\right) \right], \quad (45)$$

where we have made use of relations  $\xi = r^*$  and  $\tau_d = Q^{-1}$ , and the characteristic relaxation time  $t_{char}$  is given by

$$t_{char} = \frac{b^4 Q_{ads}^5}{4\pi^3 Q^2 D^3} \left( \frac{Q_{ads}}{K} + \frac{bQ_{ads}^2}{2\pi DQ} \right)^{-1}. \quad (46)$$

Now, several comments are in order. First of all, we notice that in contrast to the behavior in Eq. (2), predicted by the mean-field approach, the actual approach to the  $t = \infty$  state is algebraic, proportional to the first inverse power of time. This means that the long-time relaxation of the mean coverage to its  $t \rightarrow \infty$  value is *governed* entirely by the time evolution of the pairwise correlations. Second,  $C_\infty$  is generally different from the mean-field value ( $= \sqrt{Q_{ads}/K}$ ) and reduces to it only when the particle's diffusion coefficient in the bulk liquid phase  $D \rightarrow \infty$ . The fact that  $C_\infty$  depends on such a "kinetic" parameter as  $D$  is also quite a prominent feature - it shows unambiguously that in the reaction process under study there is no true *equilibrium* but rather a *steady state*.

To emphasize this point, we turn finally to the analysis of the particle-particle correlations on the surface in the limit  $t = \infty$ , embodied in the pairwise correlation function  $G_{AB}(\mathbf{r}) = G_{AB}(\mathbf{r}, t = \infty)$ . From Eq. (42) we find then that these stationary correlations obey for  $d=2$  and  $\mu=1$

$$G_{AB}(\mathbf{r}) = -\frac{Q_{ads}\tau_d}{16\pi^2 A} \int_0^{2\pi} d\theta \int_0^{2\pi} dk \exp[ikr\cos(\theta)], \quad (47)$$

which yields, in the limit  $|\mathbf{r}| \rightarrow \infty$ , the following behavior:

$$G_{AB}(\mathbf{r}) = -\frac{bQ_{ads}^2}{8\pi^3 QD} \frac{1}{|\mathbf{r}|} + O\left(\frac{1}{|\mathbf{r}|^{3/2}}\right). \quad (48)$$

Therefore, the decay of correlations in the particles' distributions on the surface is algebraic, i.e., the particles' distributions show a quasi-long-range order. As a consequence, despite the fact that the BME process effectively mixes the system in the case of batch reactions restoring the mean-field-type behavior and suppressing the segregation effects, in the case with a steady inflow of particles, which mimics the presence of particle's concentrations in the bulk liquid phase, the bulk-mediated excursions fail to establish chemical equilibrium.

## V. CONCLUSION

To conclude, in this paper we have analyzed the effect of the bulk-mediated excursions of reactive species on the long-time behavior of the catalytic Langmuir-Hinshelwood-like reactions in systems in which a catalytic surface confronts a *liquid* phase, containing concentrations of reactive particles. Such bulk-mediated excursions result from particle's desorption from the lattice, subsequent fast diffusion in the liquid phase, and eventual adsorption on the surface far away from the initial detachment point. Repeated many times, such BME yield an effectively long-range particle's transport along the catalytic surface with superdiffusive related properties. We have considered both batch reactions, i.e., reactions in which all particles of reactive species were initially adsorbed onto the surface, and reactions followed by a steady inflow of particles onto the catalytic surface. The latter situations, under certain assumptions, mimic the presence of particle's concentrations in the bulk liquid phase which act as a reservoir of particles. We have shown that for batch reactions, in accord with previous analysis [60,62], the BME provide a very effective mixing channel which suppresses the segregation effects, such that the mean-field-type behavior prevails. On contrary, for reactions followed by a steady inflow of particles, we observe essential departures from the mean-field behavior and find that the mixing effect of the BME is insufficient to restore chemical equilibrium. We show that here a steady state is established as  $t \rightarrow \infty$ , in which the limiting value of mean coverage of the catalytic surface depends on the particles' diffusion coefficient in the bulk liquid phase and the particles' distributions on the lattice are strongly, algebraically correlated. Moreover, the relaxation to such a steady state is described by a power-law function of time, in contrast to the exponential time dependence describing the approach to equilibrium in perfectly stirred systems.

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