

Perturbation analysis for competing reactions with initially separated components

Inbal Hecht and Haim Taitelbaum

Department of Physics, Bar-Ilan University, Ramat-Gan 52900, Israel

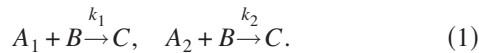
(Received 23 June 2005; revised manuscript received 23 January 2006; published 10 July 2006)

We study a competitive reaction-diffusion system with initially separated components. In this system, two similar species on one side of the system compete to react with the species on the other side. The competition is due to significant differences in the microscopic reaction constants and the initial densities of the two competing species. In the short-time limit, each of the competitive reactions is considered as perturbation with respect to the diffusion, the latter is essential for the effective mixing of the reactants. We identify the small parameters required for the perturbation analysis of the competitive scheme. The resulting perturbative expressions provide the rich spatiotemporal reaction front patterns, which were experimentally observed for $\text{Cr}^{3+} + \text{Xylenol Orange (XO)} \rightarrow \text{products}$, where the aggregated and nonaggregated forms of Cr^{3+} in aqueous solution compete to react with the XO.

DOI: [10.1103/PhysRevE.74.012101](https://doi.org/10.1103/PhysRevE.74.012101)

PACS number(s): 82.20.-w, 82.40.-g, 02.50.-r, 05.40.-a

Reaction-diffusion systems with initially separated components have attracted great interest in the last decade, following the pioneering work by Gálfi and Rácz [1]. The initial separation of reactants results in a dynamic reaction front, which exhibits rich spatiotemporal behavior and new dynamic exponents [1–9]. When competition between reactants is involved, the behavior becomes much more complex [10–12]. Competition arises when two *similar* species, A_1 and A_2 , on one side of the initially separated system, compete to react with the species on the other side of the system, B , (see Fig. 1), according to the scheme



These two processes are taking place simultaneously, each with a different microscopic reaction constant, k_1 and k_2 . The production of each reaction depends on the reaction constant, but also on the initial concentrations of A_1 and A_2 (a_{01} and a_{02}), and their diffusion constants (D_{A1} and D_{A2}), which are assumed to be equal to D_A for simplicity. We consider A_1 and A_2 to compete with each other for reacting with B , if $k_1 \gg k_2$, but $a_{01} \ll a_{02}$. This gives rise to a *fast* reaction involving few particles, which competes with a *slow* reaction involving most of the particles. Nontrivial spatiotemporal patterns are then produced, as has been shown experimentally and numerically [10,11]. The interesting feature of such a system is the existence of a second reaction center, due to the faster reaction, which is dominant in short times, but decays in longer times due to the smaller initial concentration. This reaction center is distinguished in space from the main front, as each front location strongly depends on the reactants concentrations [5–8] which are very different for the competing species. Following the simplest model of the $A+B \rightarrow C$ initially separated system [1], the following set of mean-field reaction-diffusion equations for the local concentrations ρ_{A1} , ρ_{A2} , ρ_B is assumed to describe the competitive system:

$$\begin{aligned} \dot{\rho}_{A1} &= D_A \nabla^2 \rho_{A1} - k_1 \rho_{A1} \rho_B, & \dot{\rho}_{A2} &= D_A \nabla^2 \rho_{A2} - k_2 \rho_{A2} \rho_B, \\ \dot{\rho}_B &= D_B \nabla^2 \rho_B - k_1 \rho_{A1} \rho_B - k_2 \rho_{A2} \rho_B. \end{aligned} \quad (2)$$

The initial separation along the x axis implies

$$\begin{aligned} \rho_{A1}(x, 0) &= a_{01}[1 - H(x)], & \rho_{A2}(x, 0) &= a_{02}[1 - H(x)], \\ \rho_B &= b_0 H(x), \end{aligned} \quad (3)$$

where a_{01} , a_{02} , b_0 are the initial densities and $H(x)$ is the Heaviside step function, so that the A 's are initially uniformly distributed on the left side ($x < 0$), and the B – on the right side ($x > 0$) of the initial boundary (see Fig. 1). The mean-field local production rate of C will be of the form

$$R(x, t) = k_1 \rho_{A1}(x, t) \rho_B(x, t) + k_2 \rho_{A2}(x, t) \rho_B(x, t). \quad (4)$$

The set of reaction-diffusion equations (2), (3) cannot be solved exactly. In Ref. [10], numerical calculations based on Eq. (4) were found to be in excellent agreement with experimental data. In this Brief Report we present perturbation analysis expressions for the profiles of the reacting species in the short-time limit, when the competition effects are relevant. These expressions lead to complex spatiotemporal patterns that agree very well with the experimental and numerical data presented in Ref. [10].

The rationale of the perturbation analysis in the short-time limit follows Ref. [5]. Due to the initial separation of the reactants, the reaction mechanism does not “work” in full strength at $t=0$, as the reactants have to diffuse into one another in order to encounter and react. This gradual mixing occurs in the short-time regime. It should be pointed out that

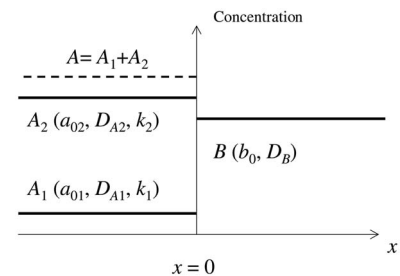


FIG. 1. A schematic sketch of the competitive initially separated system at $t=0$, where two species, A_1 and A_2 compete to react with B , with reaction constants k_1 , k_2 , respectively. Diffusivities and initial concentrations of A_1 , A_2 , B are D_{A1} , D_{A2} , D_B , and a_{01} , a_{02} , b_0 , respectively. In the competitive scheme $k_1 \gg k_2$, and $a_{01} \ll a_{02}$. The dashed line shows the total A ($=A_1+A_2$) concentration.

in many experimental cases (see, e.g., Refs. [3,4]) the reactions are relatively fast, and the system exhibits quite immediately its asymptotic, scaling behavior, which was studied by Gálfi and Rácz [1]. However, when the reaction constants are small enough [7,10,11], one observes a rich short-time behavior prior to the asymptotic time regime described in Ref. [1]. In such cases, reaction effects in short time are small compared to diffusion effects, and can be treated as a small perturbation. The unperturbed system, which is a pure diffusion system, can be solved exactly. This rationale is valid, independently, for both reactions in Eq. (1).

Therefore, in the competitive scheme, we consider each of the competitive reactions as perturbation with respect to the corresponding diffusion, assuming that each of these reactions is slow enough. This generalized scheme will allow us to identify the small parameters in the problem, i.e., the conditions for which one obtains the rich spatiotemporal patterns that were obtained experimentally and numerically [10,11]. The dimensionless variables and parameters needed for the perturbation analysis can be defined in several ways. For example, one can use different space and time scales for each reaction, based on its intrinsic space and time scales [13]. However, the following perturbation analysis is based on defining all dimensionless quantities in terms of parameters of the second, *slower*, reaction A_2+B , which lasts asymptotically. We first define a “velocity” scale, equal to $\sqrt{a_{02}b_0D_AD_B}$, based on the slower reaction, which allows us to define the dimensionless reaction parameters as

$$\varepsilon_1 = k_1/\sqrt{a_{02}b_0D_AD_B}, \quad \varepsilon_2 = k_2/\sqrt{a_{02}b_0D_AD_B}. \quad (5)$$

The dimensionless concentrations are

$$\alpha_1(x,t) = a_{01}^{-1}\rho_{A_1}(x,t), \quad \alpha_2(x,t) = a_{02}^{-1}\rho_{A_2}(x,t),$$

$$\beta(x,t) = b_0^{-1}\rho_B(x,t) \quad (6)$$

and the length and time scales defined in terms of the slower reaction scales are

$$\xi = x\sqrt{a_{02}b_0}, \quad (7)$$

$$\tau = ta_{02}b_0\sqrt{D_AD_B}. \quad (8)$$

We finally define the following ratio parameters D and r , assuming they are $O(1)$:

$$D = \sqrt{D_A/D_B}, \quad r = \sqrt{a_{01}/a_{02}}. \quad (9)$$

Equation (2) will now have the dimensionless form

$$\partial\alpha_1/\partial\tau = D\partial^2\alpha_1/\partial\xi^2 - (\varepsilon_1/r)\alpha_1\beta,$$

$$\partial\alpha_2/\partial\tau = D\partial^2\alpha_2/\partial\xi^2 - (\varepsilon_2/r)\alpha_2\beta,$$

$$\partial\beta/\partial\tau = (1/D)\partial^2\beta/\partial\xi^2 - [\varepsilon_1(a_{01}/a_{02})r\alpha_1 + \varepsilon_2r\alpha_2]\beta. \quad (10)$$

The structure of these equations demonstrates the essential similarity between the two reactions. The only difference is the concentration ratio, a_{01}/a_{02} , which appears as a prefactor in the third equation. This ratio, which is much smaller than

1 in the competitive scheme, compensates for the different intrinsic scales of the two reactions [see Eqs. (7) and (8)]. This is a key factor which should be taken into account when both reactions occur simultaneously.

On the assumption $\varepsilon_1, \varepsilon_2 \ll 1$, we can apply perturbation theory to solve Eq. (10). This assumption implies that both reaction constants k_1 and k_2 should be smaller than the characteristic velocity in order for the perturbation analysis to be valid in the competitive scheme. Indeed, both reactions have an early-time regime, exhibited by an early rise in their production rate, as will be shown later. Therefore we can expand α_1 , α_2 , and β in the series

$$\alpha_1 = \alpha_1^{(0)} + \sum_{j=1}^{\infty} \varepsilon_1^j \alpha_1^{(j)}, \quad \alpha_2 = \alpha_2^{(0)} + \sum_{j=1}^{\infty} \varepsilon_2^j \alpha_2^{(j)},$$

$$\beta = \beta^{(0)} + \sum_{j=1}^{\infty} (\varepsilon_1^j \beta_1^{(j)} + \varepsilon_2^j \beta_2^{(j)}), \quad (11)$$

where $\alpha_1^{(0)}$, $\alpha_2^{(0)}$, and $\beta^{(0)}$ are the zero-order terms in the unperturbed, diffusive stage, $\alpha_1^{(j)}$, $\alpha_2^{(j)}$ are the j th order approximation ($j \geq 1$) for the reaction of A_1 and A_2 with B , and $\beta_1^{(j)}$, $\beta_2^{(j)}$ are the corresponding, decomposed portions of B . We assume that the influence on the B species is combined of two *independent* contributions, one due to the reaction with A_1 and the other due to the reaction with A_2 . This assumption is valid only in short times, as will be discussed below.

In the zero order there is no reaction, as the species must first diffuse into one another to allow for reaction. Therefore $\alpha_1^{(0)}$, $\alpha_2^{(0)}$, and $\beta^{(0)}$ satisfy ordinary diffusion equation under the initial separation condition written in terms of dimensionless Heaviside step functions. The solution of Eq. (10) for the zeroth order is

$$\alpha_1^{(0)}(\xi, \tau) = \frac{1}{2}[1 - \text{erf}(\xi/2\sqrt{D\tau})],$$

$$\alpha_2^{(0)}(\xi, \tau) = \frac{1}{2}[1 - \text{erf}(\xi/2\sqrt{D\tau})],$$

$$\beta^{(0)}(\xi, \tau) = \frac{1}{2}[1 + \text{erf}(\xi\sqrt{D}/2\sqrt{\tau})], \quad (12)$$

where $\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$ is the error function. It should be noted that all expressions at this order are functions of the diffusion scaling variable $\xi/\sqrt{\tau}$ only.

We now proceed to calculate the next-order terms. According to perturbation theory for a single reaction [5], the equation that needs to be solved for the next-order term, e.g., $\alpha_1^{(1)}$, is

$$\partial\alpha_1^{(1)}/\partial\tau = D\partial^2\alpha_1^{(1)}/\partial\xi^2 - (1/r)\alpha_1^{(0)}(\xi, \tau)\beta^{(0)}(\xi, \tau). \quad (13)$$

The solution, based on the Green function for the diffusion equation, can be expressed as the double integral

$$\alpha_1^{(1)}(\xi, \tau) = -\frac{1}{r\sqrt{D}} \frac{1}{\sqrt{4\pi}} \int_{-\infty}^{\infty} d\lambda \int_0^{\tau} \frac{d\tau'}{\sqrt{\tau-\tau'}}$$

$$\times \alpha_1^{(0)}(\xi, \tau') \beta^{(0)}(\xi, \tau') \exp\{-\frac{1}{4D}(\xi-\lambda)^2(\tau-\tau')\} \quad (14)$$

which, after an appropriate change of variables ($u = \lambda/\sqrt{\tau'}$, $\Delta = \tau'/\tau$) becomes [5]

$$\alpha_1^{(1)}(\xi, \tau) = -\frac{1}{r\sqrt{D}} \frac{\tau}{\sqrt{4\pi}} \int_{-\infty}^{\infty} du \int_0^1 \frac{d\Delta}{\sqrt{1-\Delta}} f(u) \times \exp\left\{-\frac{(\rho - u\sqrt{\Delta})^2}{4D(1-\Delta)}\right\}, \quad (15)$$

where $\rho = \xi/\sqrt{\tau}$, and $f(\xi, \tau) = f(\xi/\sqrt{\tau}) = \alpha_1^{(0)}(\xi, \tau)\beta^{(0)}(\xi, \tau)$. The solution for $\alpha_2^{(1)}$ is similar. The solutions for $\beta_1^{(1)}$ and $\beta_2^{(1)}$ have the same form, but with D and r replaced by $1/D$ and $1/r$, respectively, and with the prefactor a_{01}/a_{02} for $\beta_1^{(1)}$.

We next denote the double integral in Eq. (15) by $I_{\alpha_1}(\rho, D)$ and similarly $I_{\beta_1}(\rho, D)$ for the corresponding β_1 integral. A numerical evaluation of these integrals [6] shows that they are well approximated by a Gaussian shape with respect to ρ , with maxima at $\rho_{\alpha_1}^*(D)$ and $\rho_{\beta_1}^*(D)$. In addition, they satisfy the following properties:

$$I_{\alpha_1}(0, D) = I_{\beta_1}(0, 1/D), \quad I'_{\alpha_1}(0, D) = -I'_{\beta_1}(0, 1/D),$$

$$I_{\alpha_1}(\rho_{\alpha_1}^*, D) = I_{\beta_1}(\rho_{\beta_1}^*, 1/D), \quad \rho_{\alpha_1}^*(D) = -\rho_{\beta_1}^*(1/D). \quad (16)$$

The following functions have been found [6] to obey these relations:

$$I_{\alpha_1}(\rho, D) \approx \exp\left\{-\frac{1}{4}[\xi/\sqrt{D}\tau - (1/\sqrt{D} - \sqrt{D})]^2 - 1/4D\right\},$$

$$I_{\beta_1}(\rho, D) \approx \exp\left\{-\frac{1}{4}[\xi\sqrt{D}/\sqrt{\tau} - (1/\sqrt{D} - \sqrt{D})]^2 - D/4\right\}. \quad (17)$$

These approximated forms have been successfully used to predict the exotic nonmonotonic motion of the reaction front center [7,8]. Generalizing these results for the system of competing reactions, one obtains

$$\alpha_1^{(1)}(\xi, \tau) \approx -\frac{1}{r\sqrt{D}} \frac{\tau}{\sqrt{4\pi}} \times \exp\left\{-\frac{1}{4}[\xi/\sqrt{D}\tau - (1/\sqrt{D} - \sqrt{D})]^2 - 1/4D\right\},$$

$$\alpha_2^{(1)}(\xi, \tau) \approx -\frac{1}{r\sqrt{D}} \frac{\tau}{\sqrt{4\pi}} \times \exp\left\{-\frac{1}{4}[\xi/\sqrt{D}\tau - (1/\sqrt{D} - \sqrt{D})]^2 - 1/4D\right\},$$

$$\beta_1^{(1)}(\xi, \tau) \approx -\frac{a_{01}/a_{02}}{r\sqrt{D}} \frac{\tau}{\sqrt{4\pi}} \times \exp\left\{-\frac{1}{4}[\xi\sqrt{D}/\sqrt{\tau} - (1/\sqrt{D} - \sqrt{D})]^2 - D/4\right\},$$

$$\beta_2^{(1)}(\xi, \tau) \approx -\frac{r\sqrt{D}}{r\sqrt{D}} \frac{\tau}{\sqrt{4\pi}} \times \exp\left\{-\frac{1}{4}[\xi\sqrt{D}/\sqrt{\tau} - (1/\sqrt{D} - \sqrt{D})]^2 - D/4\right\}, \quad (18)$$

where all the prefactors, including the key factor a_{01}/a_{02} for $\beta_1^{(1)}(\xi, \tau)$, follow the corresponding terms in Eq. (10). These first-order terms, which are all negative, describe the correction to the reactants' densities due to the reaction (i.e., the densities decrease as the species react).

In order to use these approximated expressions to calculate the production rate $R(x, t)$ [Eq. (4)], we need to revert to the original quantities, using the inverse transformations of Eqs. (5)–(9). Figure 2 shows the perturbation analysis results up to the first order, for the temporal evolution of $R(x, t)$, as

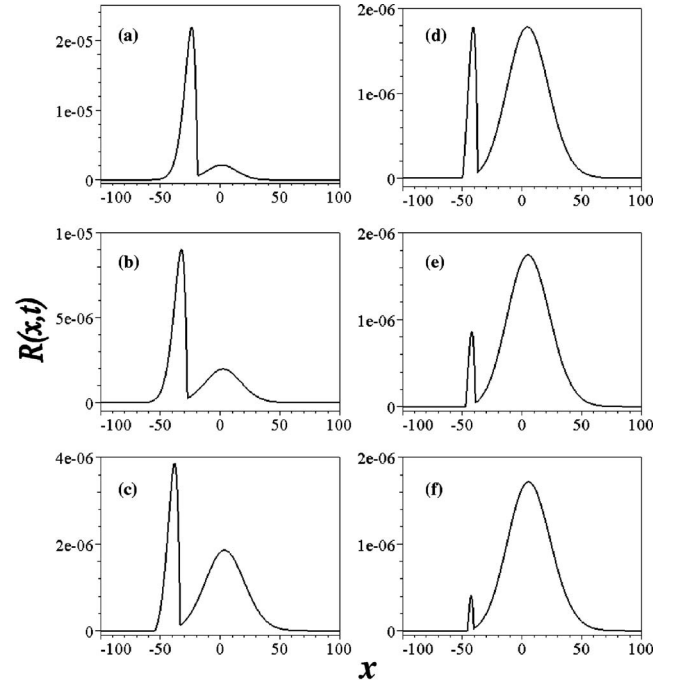


FIG. 2. Perturbation analysis results for $R(x, t)$, for $a_{01}=3\%$, $a_{02}=97\%$ of the total A density ($a_0 \equiv a_{01} + a_{02} = 1$), $b_0=1$, reaction constants $k_1=10^{-2}$, $k_2=10^{-5}$, and diffusivities $D_A=D_B=0.1$. The dimensionless parameters are $D=1$, $r=0.985$, $\varepsilon_1=0.102$, $\varepsilon_2=0.000102$. The times t (in arbitrary units) are (a) 1000, (b) 1500, (c) 1900, (d) 2150, (e) 2300, (f) 2400.

obtained using Eqs. (11), (12), and (18). Results are presented for rate constants $k_1=10^{-2}$ and $k_2=10^{-5}$ ($k_1 \gg k_2$) and initial densities $a_{01}=3\%$ and $a_{02}=97\%$ ($a_{01} \ll a_{02}$) of the total A density, which reflect the competition between A_1 and A_2 . The small parameters [Eq. (5)] are then $\varepsilon_1=0.102$ and $\varepsilon_2=0.000102$. At relatively early times [Fig. 2(a)] two reaction centers appear. The sharper left peak is a result of the reaction of B with the faster reacting, lower density species A_1 , while the right peak is due to the reaction of B with the slower reacting, higher density species A_2 . As time increases, the faster reaction peak decreases, since the A_1 density is lower, and the slower reaction peak increases. At some intermediate time [Fig. 2(d)], the two centers' heights are equal, thereafter the front resulting from the slow reaction with the higher density species A_2 (right-hand-side peak), becomes dominant over the front of the fast reaction (left-hand-side peak). In Fig. 3 we show another set of calculations, performed with higher values of both reaction constants, which are similar to the values appear in Ref. [10]. The small parameters are $\varepsilon_1=0.68$ and $\varepsilon_2=0.000068$ and the competitive patterns are recovered as well.

These results agree very well with the experimental two-peak pattern found in Ref. [10], for the reaction of Cr^{3+} (A) with Xylenol Orange (B). At early times, the primary contribution derives from the relatively faster reacting *non-aggregated* form of Cr^{3+} in aqueous solution ($A_1=3\%$ A), while at later times the main contribution is from the much slower reacting Cr^{3+} *aggregate* ions ($A_2=97\%$ A), which diffuses farther right into the reaction zone before reacting. The

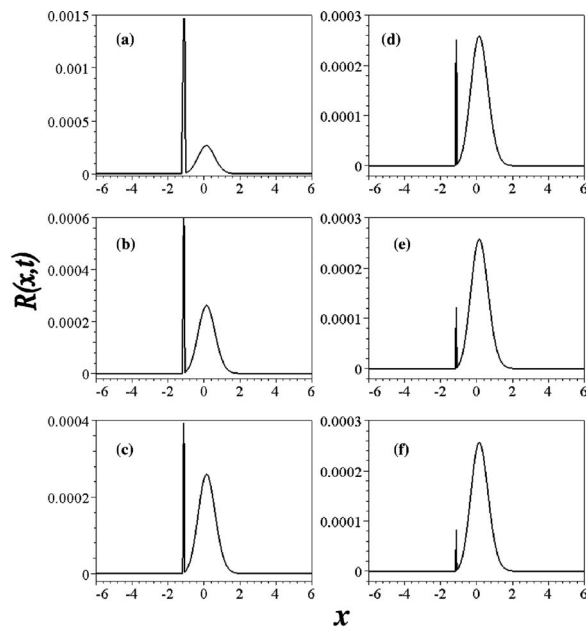


FIG. 3. Perturbation analysis results for $R(x,t)$, for $a_{01}=3\%$, $a_{02}=97\%$ of the total A density ($a_0=15$), $b_0=15$, reaction constants $k_1=1$, $k_2=10^{-4}$, and diffusivities $D_A=D_B=0.1$. The dimensionless parameters are $D=1$, $r=0.985$, $\varepsilon_1=0.68$, $\varepsilon_2=0.000\,068$. The times t (in arbitrary units) are (a) 1.55, (b) 1.635, (c) 1.662, (d) 1.684, (e) 1.71, (f) 1.72.

reaction constants, satisfying $k_1 \gg k_2$, could not be measured directly and were estimated using the fact that the process took several *hours*. This implies that both reaction constants are small. These experimental facts motivated the choice of the parameters in Figs. 2 and 3, and the experimental spatiotemporal patterns were indeed reproduced.

The validity limit of the perturbation expressions can be inferred from the time dependence of the global reaction rate $R(t)=\int_{-\infty}^{+\infty}R(x,t)dx$ for a *single* reaction. This is plotted in Fig. 4 using a set of approximated expressions for a single reaction (say α_1 and β_1), based on Eqs. (11), (12), and (18). It exhibits an initial increase due to the mixing, followed by a decrease starting at time $t^* \sim k_1^{-1}$, due to the segregation between the species [5]. This implies that the absolute values of the first-order terms, $\alpha_1^{(1)}$ and $\beta_1^{(1)}$, which represent the concentrations *change* due to the reaction, should *decrease* around t^* . However, the result for $\beta_1^{(1)}$ of the single reaction approximation (based on Eq. (18)) shows that its value is continuously *increasing* in time (Fig. 4). This means that

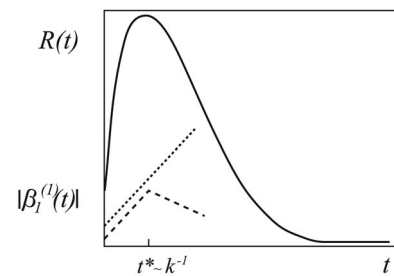


FIG. 4. *Single* reaction. A schematic draw of the global reaction rate $R(t)$ (solid line) and the absolute value of the first-order term $\beta_1^{(1)}(t)$ (dotted and dashed lines), both as a function of time. The calculated value (dotted) is compared with the *expected* behavior (dashed). The disagreement illustrates the validity limit of the first-order approximation of the perturbation analysis.

when the global reaction rate has significantly decreased, the first-order approximation breaks down. In our two species competing reaction system, the validity limit is determined by the faster reaction. By the time the slower reaction becomes significant, the faster reaction approximation (18) has already exceeded its validity limit, and one needs to consider higher-order terms. However, the spatiotemporal competitive patterns shown in Figs. 2 and 3, which are all short-time effects, are included within this limit.

Finally, we should mention the coupling between $\alpha_1^{(j)}$ and $\alpha_2^{(j)}$ as well as $\beta_1^{(j)}$ and $\beta_2^{(j)}$, as the two reactions [Eq. (1)] are coupled via the B reactant. However, this can be neglected as the correlation between A_1 and A_2 is only of second order. The assumption that the change in the concentration of B is combined of two independent contributions is similar to the multiplane method of Lipshtat and Biham [14]. They solved a set of master equations for chemical reactions on dust grains, neglecting second-order correlations, and showed that this coincides with the exact solution.

In summary, we presented an analytical scheme for the short-time behavior of a system of two competing reactions with initial separation in space. Our perturbation analysis produces the “competitive” spatiotemporal patterns, that were experimentally observed in the reaction of Cr^{3+} with XO , where Cr^{3+} aggregate and nonaggregate ions in aqueous solution compete to react with the XO . We identified the small parameters in the system and showed that this approximation is valid in the short-time regime, when the competition is relevant.

This research was supported by The Israel Science Foundation (Grant No. 1342/04).

[1] L. Gálfi and Z. Rácz, *Phys. Rev. A* **38**, R3151 (1988).
 [2] Z. Jiang and C. Ebner, *Phys. Rev. A* **42**, 7483 (1990).
 [3] Y-E. L. Koo and R. Kopelman, *J. Stat. Phys.* **65**, 893 (1991).
 [4] S. H. Park *et al.*, *Phys. Rev. E* **64**, 055102(R) (2001).
 [5] H. Taitelbaum *et al.*, *J. Stat. Phys.* **65**, 873 (1991).
 [6] H. Taitelbaum, Ph.D. thesis, Bar-Ilan University, Ramat-Gan, Israel, 1991.
 [7] H. Taitelbaum *et al.*, *Phys. Rev. A* **46**, 2151 (1992).
 [8] Z. Koza and H. Taitelbaum, *Phys. Rev. E* **54**, R1040 (1996).

[9] D. Ben-Avraham and S. Havlin, *Diffusion and Reactions in Fractals and Disordered Systems* (Cambridge University Press, Cambridge, 2000), Chap. 14, and references therein.
 [10] H. Taitelbaum *et al.*, *Phys. Rev. Lett.* **77**, 1640 (1996).
 [11] A. Yen *et al.*, *J. Phys. Chem. A* **101**, 2819 (1997).
 [12] M. Sinder *et al.*, *Phys. Rev. E* **68**, 022101 (2003).
 [13] I. Hecht, Ph.D. thesis, Bar-Ilan University, Ramat-Gan, Israel, 2004.
 [14] A. Lipshtat and O. Biham, *Phys. Rev. Lett.* **93**, 170601 (2004).