

# Product desorption rate influence on catalytic reactivity of spatially inhomogeneous surfaces

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**Abstract** We investigate numerically a phenomenological mathematical model of unimolecular reactions proceeding on inhomogeneous planar surfaces in the two-dimensional space case taking into account: the bulk diffusion of the reactant from the bounded vessel toward the adsorbent and the product bulk one from the adsorbent into the same vessel, the adsorption and desorption of reactant particles, long-range surface diffusion of the adsorbate, and a slow product desorption from the adsorbent. Simulations were performed using the finite difference technique. The influence of the long-range surface diffusion and product desorption rate on the kinetics of processes catalysed by inhomogeneous surfaces with different arrangements of reactive and nonreactive adsorption sites are studied.

**Keywords** Heterogeneous reactions · Adsorption · Desorption · Surface diffusion

## 1 Introduction

In a heterogeneous catalytic process, molecules of reactants diffuse from a volume to the surface of the catalyst, adsorb onto the surface, diffuse on it, and react to form a product that diffuses into a volume. Diffusion of adsorbed particles on solid surfaces occurs in a number of modern technologies [1,2]. To describe the surface diffusion of the adsorbate, usually a discrete arrangement of the surface adsorption sites is considered, and the Monte Carlo technique based on jumps of adsorbed particles to nearest-neighbor vacant sites or phenomenological (mean-field) models based on

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Fick's diffusion law are used (see, e.g., [3–13]). However, models involving Fick's law are indirectly based on the particle jumps to nearest-neighbor vacant sites and cannot describe the long-range diffusion of adsorbed particles. In the case where the energy exchange between adsorbed particles and substrate is slow and corrugation of the adsorption potential is weak or the temperature is sufficiently high, the long-range jumps may be significant [14–16]. Experiments [16–19] also showed that long-range jumps of adsorbed particles may play a dominant role. The influence of long-range jumps on the diffusion coefficient was studied in [1, 8, 20–22] by using the Langevin equation. The influence of long-range jumps on the catalytic reactivity of spatially inhomogeneous surfaces was studied in [23] by using a phenomenological surface diffusion model based on the integral diffusion mechanism. In all these papers, the product desorption is considered as a rapid phenomenon, and the assumption of immediate desorption is used. Generally, product particles before their desorption can stay or diffuse on the surface and poison the catalyst [12]. In [9], three models of unimolecular surface reactions are studied taking into account the surface diffusion of the adsorbate, product surface diffusion before its desorption from the surface, or both. In these models, the surface diffusion is based on Fick's law, and the product desorption is considered as a slow phenomenon. The adsorbate surface diffusion role on poisoning of catalytic sites of uniform surfaces in monomer–dimer reactions is studied in [6, 7] by using models based on Fick's law. The influence of photocatalytic processes on the product desorption rate is studied in [24].

The goal of this paper is a qualitative study of the influence of product desorption rate on the catalytic reactivity of spatially inhomogeneous surfaces. To study this influence, we involve the slow product desorption from the surfaces into the phenomenological unimolecular surface reactions model [23], which describes the surface reactions coupled with the reactant and product bulk diffusion and the long-range diffusion of adsorbed particles on spatially inhomogeneous planar surfaces. We also use generalized transition (jump) functions of the escaped particles that take into account their energy loss due to interaction with the other escaped ones and with the vacant sites of the substrate. As in [12, 23], spatially inhomogeneous surfaces involve a nonuniform homogeneous and heterogeneous arrangements of reactive and nonreactive sites. In the case of heterogeneous arrangement, the nonuniform homogeneous reactive and nonreactive sites are distributed in domains alternatively. Adsorption, desorption, and diffusion are allowed to proceed at each site, while reaction on reactive ones allows all processes to proceed only at a constant temperature. The product surface diffusion before its desorption is neglected.

The paper is organized as follows. In Sect. 2, we present the model. In Sect. 3, we discuss the numerical results. In Sect. 4, we conclude the paper by a summary of main results.

## 2 The model

As in [23], we assume that reactant  $A$  and product  $B$  of concentrations  $a(t, x)$  and  $b(t, x)$  occupy a bounded domain  $\Omega$  with surface  $S = S_1 \cup S_2$ . Here  $t$  is time,  $x \in \Omega$  is a position,  $S_2$  is a surface of the adsorbent, and  $S_1 = S \setminus S_2$  is a surface

impermeable to the reactant and product. Contrary to the Monte Carlo technique associated with a discrete distribution of adsorption sites, we apply the Langmuir approach and, assuming that adsorption sites are distributed continuously or piecewise continuously, describe their distribution by densities. Let  $s_2(x)$  and  $s_1(x)$ ,  $x \in S_2$ , be the surface density of active and inactive sites in the surface reaction, respectively. Assume that  $s_2\theta_2$  and  $s_1\theta_1$ ,  $\theta_i(t, x) \in [0, 1]$ ,  $i = 1, 2$ , are the densities of active and inactive sites occupied by the reactant molecules. Also, assume that  $s_2\theta_3$  is the density of active sites occupied by the product molecules. Let  $P_{ij}(t, x, y)$  be the rate at moment  $t$  at which the reactant particle adsorbed on a site of type  $j$  located in position  $y \in S_2$ , after its escape from this position, diffuses (jumps) to a vacant site of type  $i$  located in position  $x \in S_2$ . Assume that  $k$  is a reaction rate constant,  $k_r$  is the product desorption rate constant, and  $k_{f1}$ ,  $k_{f2}$ ,  $k_{r1}$ ,  $k_{r2}$  are the reactant adsorption and desorption rate constants. Denoting by  $\kappa_a$  and  $\kappa_b$  the diffusivities of reactant  $A$  and product  $B$  and using the Langmuir mechanism of unimolecular reactions and the law of mass action, we derive the following coupled system for surface coverages  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$ :

$$\left\{ \begin{array}{l} \frac{\partial \theta_1}{\partial t} = (1 - \theta_1) \left\{ k_{f1}a + \int_{S_2} (\theta_1(t, y)s_1(y)P_{11}(t, x, y) \right. \\ \quad \left. + \theta_2(t, y)s_2(y)P_{12}(t, x, y)) dy \right\} \\ \quad - \theta_1 \left\{ k_{r1} + \int_{S_2} ((1 - \theta_1(t, y))s_1(y)P_{11}(t, y, x) \right. \\ \quad \left. + (1 - \theta_2(t, y) - \theta_3(t, y))s_2(y)P_{21}(t, y, x)) dy \right\}, \quad x \in S_2, \quad t > 0, \\ \theta_1|_{t=0} = 0, \quad x \in S_2, \\ \frac{\partial \theta_2}{\partial t} = (1 - \theta_2 - \theta_3) \left\{ k_{f2}a + \int_{S_2} (s_1(y)\theta_1(t, y)P_{21}(t, x, y) \right. \\ \quad \left. + s_2(y)\theta_2(t, y)P_{22}(t, x, y)) dy \right\} \\ \quad - \theta_2 \left\{ k_{r2} + k + \int_{S_2} ((1 - \theta_1(t, y))s_1(y)P_{12}(t, y, x) \right. \\ \quad \left. + (1 - \theta_2(t, y) - \theta_3(t, y))s_2(y)P_{22}(t, y, x)) dy \right\}, \quad x \in S_2, \quad t > 0, \\ \theta_2|_{t=0} = 0, \quad x \in S_2, \\ \frac{\partial \theta_3}{\partial t} = k\theta_2 - k_r\theta_3, \quad x \in S_2, \quad t > 0, \\ \theta_3|_{t=0} = 0, \quad x \in S_2. \end{array} \right. \quad (1)$$

Here  $a = a(t, x)$  is the unknown reactant concentration at point  $x \in S_2$  at the moment  $t$ . The gain term

$$(1 - \theta_1(t, x)) \left\{ \int_{S_2} (\theta_1(t, y)s_1(y)P_{11}(t, x, y) + \theta_2(t, y)s_2(y)P_{12}(t, x, y)) dy \right\}$$

on the right-hand side of the first equation of this system is conditioned by the surface diffusion (jumps) of the adsorbed reactant particles from the inactive and active sites located on surface  $S_2$  to the vacant inactive sites located in the position  $x \in S_2$ . The loss term

$$\theta_1(t, x) \left\{ \int_{S_2} ((1 - \theta_1(t, y))s_1(y)P_{11}(t, y, x) + (1 - \theta_2(t, y) - \theta_3(t, y))s_2(y)P_{21}(t, y, x)) dy \right\}$$

of the first equation is conditioned by the surface diffusion (jumps) of the adsorbed reactant particles from the inactive sites located in position  $x \in S_2$  to vacant inactive and active sites located on  $S_2$ . The rise of the integral gain and loss terms of the second equation of this system can be explained similarly. To close this system, we add the following equations describing the bulk diffusion of reactant  $A$  and product  $B$ :

$$\begin{cases} \frac{\partial a}{\partial t} = \kappa_a \Delta a, & x \in \Omega, t > 0, \\ \partial_n a|_{S_1} = 0, & t > 0, \\ \kappa_a \partial_n a|_{S_2} = -k_{f1}s_1(1 - \theta_1)a|_{S_2} + k_{r1}s_1\theta_1 \\ \quad - k_{f2}s_2(1 - \theta_2 - \theta_3)a|_{S_2} + k_{r2}s_2\theta_2, & t > 0, \\ a|_{t=0} = a_0(x), & x \in \Omega, \end{cases} \tag{2}$$

$$\begin{cases} \frac{\partial b}{\partial t} = \kappa_b \Delta b, & x \in \Omega, t > 0, \\ \partial_n b|_{S_1} = 0, & t > 0, \\ \kappa_b \partial_n b|_{S_2} = ks_2\theta_3, & t > 0, \\ b|_{t=0} = 0, & x \in \Omega. \end{cases} \tag{3}$$

Here  $\Delta$  is the Laplace operator,  $\partial_n a$  and  $\partial_n b$  are the outward normal derivatives, and  $a_0$  is the initial distribution of the reactant concentration.

It is easy to prove that system (1)–(3) possesses the mass conservation law

$$\int_{\Omega} (a + b) dx + \int_{S_2} (s_1\theta_1 + s_2\theta_2 + s_2\theta_3) dx = \int_{\Omega} a_0 dx, \quad t \geq 0. \tag{4}$$

We determine the specific catalyst conversion rate of the reactant molecules into the product (turnover rate) by the formula

$$z(t) = k \int_{S_2} s_2(x)\theta_2(t, x) dx \bigg/ \int_{S_2} s_2(x) dx. \tag{5}$$

In the case where  $P_{ij}(t, x, y) = \kappa_{ij}(t, x, y)\delta(x - y)$  with the Dirac delta function  $\delta$ , Eq. (1) reduce, for every interior point of  $S_2$ , to the system of ODEs

$$\begin{cases} \theta'_1 = (1 - \theta_1)\{k_{f1}a + s_2\kappa_{12}(t, x, x)\theta_2\} \\ \quad - \theta_1\{k_{r1} + s_2(1 - \theta_2 - \theta_3)\kappa_{21}(t, x, x)\}, & \theta_1|_{t=0} = 0, \\ \theta'_2 = (1 - \theta_2 - \theta_3)\{k_{f2}a + s_1\kappa_{21}(t, x, x)\theta_1\} \\ \quad - \theta_2\{k_{r2} + k + s_1(1 - \theta_1)\kappa_{12}(t, x, x)\}, & \theta_2|_{t=0} = 0, \\ \theta'_3 = k\theta_2 - k_r\theta_3, & \theta_3|_{t=0}, \end{cases} \tag{6}$$

where prime denotes the time derivative. We emphasize that  $x$  involved in these equations is a parameter. Equation (6) show that, in the limit as  $\alpha_{ij} \rightarrow 0$ , the parameters  $\kappa_{11}$  and  $\kappa_{22}$  do not influence the evolution of  $\theta_1$  and  $\theta_2$ . In the steady-state case, from Eq. (6) we get  $\theta_3 = (k/k_r)\theta_2$  and the following system of algebraic equations for the steady-state values of  $\theta_1$  and  $\theta_2$ :

$$\begin{cases} (1 - \theta_1)\{k_{f1}a + s_2\kappa_{12}(x, x)\theta_2\} \\ \quad - \theta_1\{k_{r1} + s_2(1 - \theta_2(1 + k/k_r))\kappa_{21}(x, x)\} = 0, \\ (1 - \theta_2(1 + k/k_r))\{k_{f2}a + s_1\kappa_{21}(x, x)\theta_1\} \\ \quad - \theta_2\{k_{r2} + k + s_1(1 - \theta_1)\kappa_{12}(x, x)\} = 0 \end{cases} \quad (7)$$

with  $\kappa_{ij}$  independent of  $t$ . In the case where  $q := \kappa_{12} - \kappa_{21}(1 + k/k_r) = 0$ , this system consists of two linear equations. If  $q \neq 0$ , system (7) can be reduced to a quadratic equation for  $\theta_1$  or  $\theta_2$  and solved analytically.

### 3 Numerical results

We study system (1)–(3) in a domain  $\Omega = \{(x_1, x_2, x_3) : x_i \in [0, l], i = 1, 2, 3\}$  with boundary  $S = S_1 \cup S_2$ , where  $S_2 = \{(x_1, x_2, x_3) : x_i \in [0, l], i = 1, 3, x_2 = 0\}$  and  $S_1 = S \setminus S_2$ . To simplify the problem, we restrict ourselves to the case where the densities  $s_1$  and  $s_2$  depend only on variable  $x_1$  and the initial distribution  $a_0$  is a constant. We take into account jumps of adsorbed particles only in the  $x_1$  direction. In this case, the double integrals involved in Eq. (1) reduce to integrals over  $[0, l]$  multiplied by  $l$ . This allows us to consider Eqs. (2) and (3) in  $\tilde{\Omega} = \{(x_1, x_2) : x_i \in [0, l], i = 1, 2\}$  with  $\tilde{S}_2 = \{(x_1, x_2) : x_1 \in [0, l], x_2 = 0\}$ .

The crucial step in the implementation of the present model is the construction of the transition (jump) functions  $P_{ij}(t, x, y)$ ,  $i, j = 1, 2$ , which depend on the geometrical arrangement of the active and nonactive in reaction adsorption sites, local arrangement of the occupied sites, energy exchange between the particle escaped from its adsorption site and substrate (adsorbent), and energy loss due to interaction between the escaped particle and the other escaped ones. The continuous or piecewise-continuous distribution of the adsorption sites makes the problem of the construction of  $P_{ij}(t, x, y)$  too complicated to be solved in detail. Therefore, we restrict ourselves to constructing a model function  $P_{ij}(t, x, y)$  that, as we hope, involves arguments mentioned above indirectly. To this end, we formulate the following hypotheses:

1. The escaped particles are attracted only by vacant adsorption sites (occupied sites do not attract escaped particles).
2. The probability for the escaped particle to be adsorbed on the interval  $[\xi_k, \xi_k + \Delta\xi_k]$  is proportional to the number of the vacant adsorption sites inside the interval, i.e.,

$$\gamma_{ij}[s_1(\xi_k)(1 - \theta_1(t, \xi_k)) + s_2(\xi_k)(1 - \theta_2(t, \xi_k) - \theta_3(t, \xi_k))] \Delta\xi_k, \quad \gamma_{ij} = \text{const.}$$

3. The energy loss of the escaped particle due to interaction with the other escaped ones is an increasing function of their number, which increases as the number of the occupied sites grows.

4. The diffusion rate of the escaped particle is a decreasing function of its energy loss due to interaction with the other ones.
5. Attractive forces of vacant adsorption sites acting on the escaped particle decrease as the distance between them increases.

Hence, the diffusion rate of the escaped particle moving from point  $y$  to  $x$  is a decreasing function of  $|x - y|$ . From the second hypothesis it follows that the probability for the particle escaped from point  $y$  to be not adsorbed on the interval  $[y, x]$  is proportional to  $\exp\{-\gamma_{ij}|I_2(t, x, y)|\}$ , where

$$I_2(t, x, y) = \int_y^x [s_1(\xi)(1 - \theta_1(t, \xi)) + s_2(\xi)(1 - \theta_2(t, \xi) - \theta_3(t, \xi))] d\xi.$$

For numerical calculations, we use the model function

$$P_{ij}(t, x, y) = \kappa_{ij}(x, y) \sqrt{\frac{I_1(t, x, y)}{\pi \alpha_{ij}}} \exp \left\{ -\frac{|x - y|^2 I_1(t, x, y)}{\alpha_{ij}} - \gamma_{ij} |I_2(t, x, y)| \right\} \tag{8}$$

with

$$I_1(t, x, y) = 1 + \beta_{ij} \left| \int_y^x (s_1(\xi)\theta_1(t, \xi) + s_2(\xi)(\theta_2(t, \xi) + \theta_3(t, \xi))) d\xi \right|,$$

where  $\beta_{ij} = const$ , and  $\alpha_{ij}/2$ ,  $i, j = 1, 2$ , are the dispersions of jump lengths of adsorbed particles in the case where  $\beta_{ij} = \gamma_{ij} = 0$ ,  $\kappa_{ij}$  are their surface diffusion rate constants, and  $|x - y|$  with  $x, y \in [0, l]$  is the jump length from point  $y$  to  $x$ . The multiplier

$$\sqrt{\frac{I_1(t, x, y)}{\pi \alpha_{ij}}} \exp \left\{ -\frac{|x - y|^2 I_1(t, x, y)}{\alpha_{ij}} \right\}$$

is conditioned by hypotheses 3, 4, and 5. It is evident that

$$\lim_{\alpha_{ij} \rightarrow 0} \frac{1}{\sqrt{\pi \alpha_{ij}}} \exp \left\{ -\frac{|x - y|^2}{\alpha_{ij}} \right\} = \delta(x - y).$$

Using the dimensionless variables  $\bar{t} = t/T$ ,  $\bar{x}_1 = x_1/l$ ,  $\bar{x}_2 = x_2/l$ ,  $\bar{x}_3 = x_3/l$ ,  $\bar{a} = a/a_*$ ,  $\bar{b} = b/a_*$ ,  $\bar{s}_1 = s_1/(la_*)$ ,  $\bar{s}_2 = s_2/(la_*)$ ,  $\bar{k}_{f1} = k_{f1}Ta_*$ ,  $\bar{k}_{f2} = k_{f2}Ta_*$ ,  $\bar{k}_{r1} = k_{r1}T$ ,  $\bar{k}_{r2} = k_{r2}T$ ,  $\bar{k} = kT$ ,  $\bar{k}_r = k_rT$ ,  $\bar{\kappa}_a = \kappa_a T/l^2$ ,  $\bar{\kappa}_b = \kappa_b T/l^2$ ,  $\bar{\kappa}_{ij} = \kappa_{ij} T l^2 a_*$ ,  $\bar{\alpha}_{ij} = \alpha_{ij}/l^2$ ,  $\bar{\gamma}_{ij} = l\gamma_{ij}$ ,  $\bar{\beta}_{ij} = l\beta_{ij}$  where  $T$ ,  $l$ , and  $a_*$  are characteristic dimensional units, we rewrite Eqs. (1)–(8) in the same form, but

in dimensionless variables. The dimensionless Eqs. (1), (4), and (5) involve integration over the interval  $[0, 1]$ . For simplicity, in what follows, we omit the bar and treat Eqs. (1)–(8) as dimensionless. To solve numerically problem (1) with given  $a(t, x_1, 0)$ , we use Euler's scheme with integrals approximated by trapezoidal quadrature formula. To test results obtained by Euler's scheme, we also solved these equations by applying the Runge–Kutta scheme and obtained the same result. To solve problem (1)–(3), we used the implicit finite-difference scheme based on the alternating direction method [25]. As in [23] and [9], for all calculations, we used the following dimensional data:

$$\begin{aligned} T &= 1 \text{ s}, \quad l = 10^{-1} \text{ cm}, \quad a_* = 10^{-11} \text{ mol cm}^{-3}, \\ s_* &= la_* = 10^{-12} \text{ mol cm}^{-3}, \quad k_{f1}, k_{f2} \in [10^9, 10^{11}] \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}, \\ k_{r1}, k_{r2}, k &\in [3 \cdot 10^{-3}, 1] \text{ s}^{-1}, \quad \kappa_a, \kappa_b \in [5 \cdot 10^{-7}, 10^{-3}] \text{ cm}^2 \text{ s}^{-1}. \end{aligned} \quad (9)$$

All figures are drawn for  $k_{f1} = k_{f2} = 0.01661$ ,  $k_{r1} = k_{r2} = 0.001$ , and  $k = 0.03$ . The standard value of  $\kappa_{ij}$  is 1. If the values of  $\kappa_{ij}$  differ from the standard one, then they are given in captures of figures. In what follows, by varying the parameters  $k_r$ ,  $\alpha_{ij}$ ,  $\kappa_{ij}$ ,  $\beta_{ij}$ , and  $\gamma_{ij}$  we study the product desorption rate and long-range surface diffusion influence on the kinetics of catalytic process of surfaces with different arrangements of the active and inactive in reaction adsorption sites. We first discuss the case of surface diffusion where the bulk diffusion of the reactant is neglected and the reactant concentration  $a(t, x_1, 0)$  for  $t \geq 0$  and  $x_1 \in [0, 1]$  is given. Then we analyze the numerical solution of system (1)–(3). In all calculations, we consider three cases of the distribution of active and inactive sites:

Case I.  $s_1 = x_1$ ,  $s_2 = 1 - x_1$  for  $x_1 \in [0, 1]$ .

Case II.

$$s_1 = \begin{cases} 0 & \text{if } x_1 \in (0, 1/2), \\ 1 & \text{if } x_1 \in [1/2, 1], \end{cases}$$

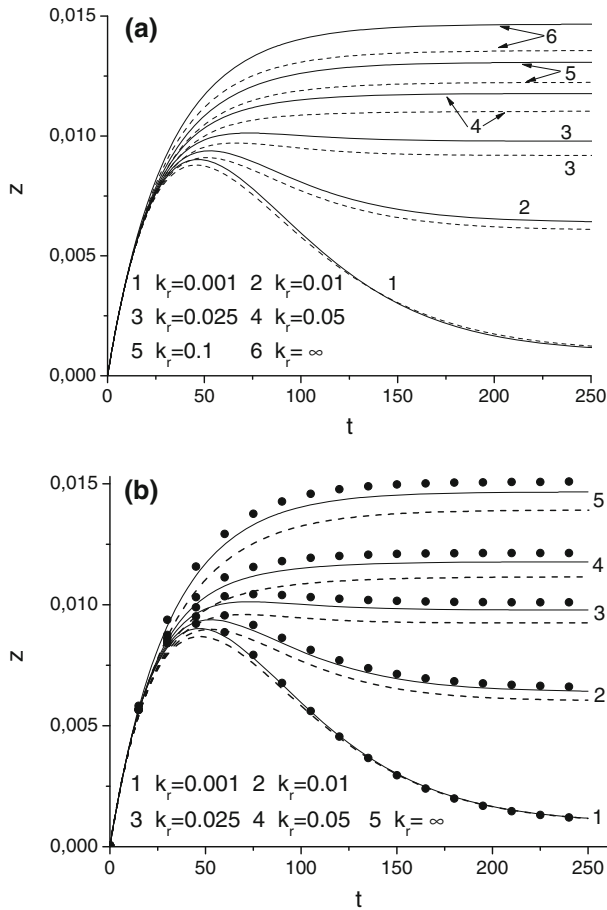
$$s_2 = \begin{cases} 1 & \text{if } x_1 \in [0, 1/2], \\ 0 & \text{if } x_1 \in (1/2, 1]. \end{cases}$$

Case III.

$$s_1 = \begin{cases} 0 & \text{if } x_1 \in (0, 1/8) \cup (2/8, 3/8) \cup (4/8, 5/8) \cup (6/8, 7/8), \\ 1 & \text{if } x_1 \in [1/8, 2/8] \cup [3/8, 4/8] \cup [5/8, 6/8] \cup [7/8, 1], \end{cases}$$

$$s_2 = \begin{cases} 1 & \text{if } x_1 \in [0, 1/8] \cup [2/8, 3/8] \cup [4/8, 5/8] \cup [6/8, 7/8], \\ 0 & \text{if } x_1 \in (1/8, 2/8) \cup (3/8, 4/8) \cup (5/8, 6/8) \cup (7/8, 1]. \end{cases}$$

The densities  $s_1$  and  $s_2$  of all three arrangements of adsorption sites satisfy the condition  $\int_0^1 s_1(x) dx = \int_0^1 s_2(x) dx = 1/2$ . Case I corresponds to the nonuniform homogeneous distribution of adsorption sites, while the other two cases describe a



**Fig. 1** **a** Influence of the product desorption rate constant  $k_r$  on the turnover rate  $z(t)$  determined by Eqs. (1) (solid line) and (6) (dashed line) with densities  $s_1(x_1) = x_1$  and  $s_2(x_1) = 1 - x_1$ . **b** Influence of the product desorption rate constant  $k_r$  and arrangement of adsorption sites on the function  $z(t)$  determined by Eq. (1). Case I—solid line, case II—dashed line, case III—bullets.  $\alpha = 0.02$  and density  $a(t, x_1, 0) = 1$  in both cases (a) and (b)

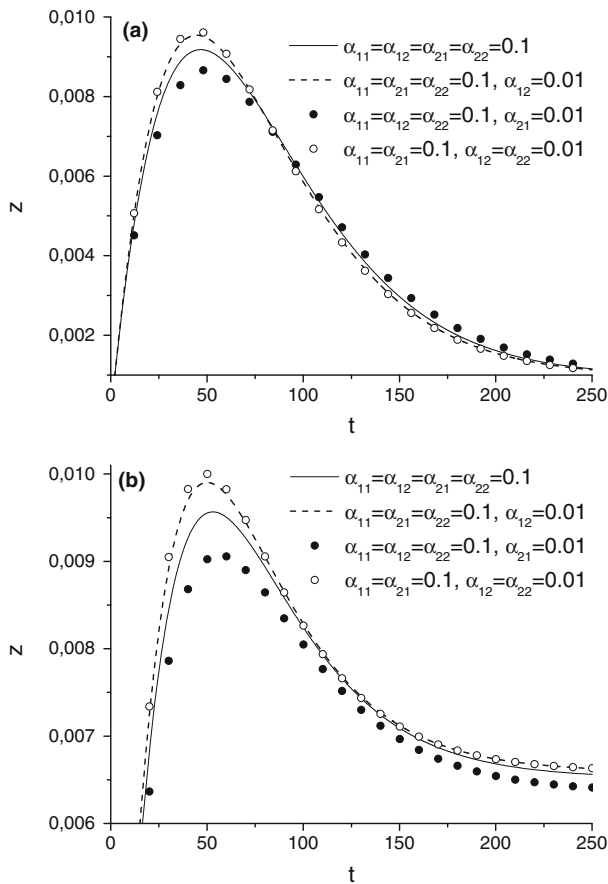
heterogeneous (piecewise homogeneous) arrangement of sites. In the case where all  $\alpha_{ij}$ ,  $\kappa_{ij}$ ,  $\beta_{ij}$ , and  $\gamma_{ij}$  are equal for all  $i, j$ , we use the notations  $\alpha = \alpha_{ij}$ ,  $\kappa = \kappa_{ij}$ ,  $\beta = \beta_{ij}$ , and  $\gamma = \gamma_{ij}$ .

### 3.1 Numerical results of system (1) with $a(t, x_1, 0) = 1$

The numerical results are illustrated by Figs. 1, 2 and 3 in the case where  $\beta_{ij} = \gamma_{ij} = 0$  and depict dynamics of the turnover rate  $z$  for homogeneous and heterogeneous arrangements of sites. The results of the general case are illustrated by Fig. 4.

Figure 1a depicts the comparison of limit values of  $z$  as  $\alpha \rightarrow 0$  and values of  $z$  determined for  $\alpha = 0.02$  and demonstrates the increase of  $z$  as product desorption rate constant  $k_r$  increases from 0.001 till  $\infty$ . This figure also demonstrates the nonmonotonic

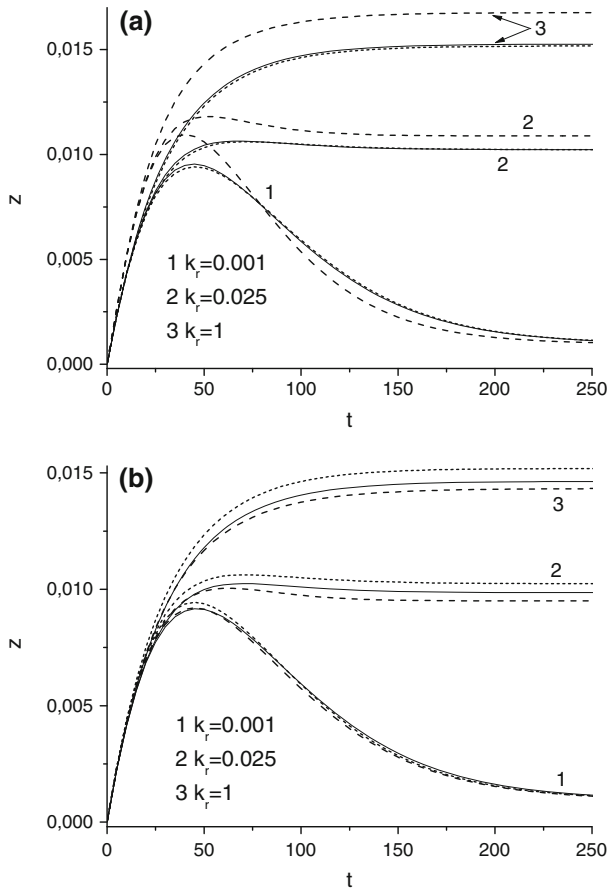




**Fig. 2** Effect of parameters  $\alpha_{ij}$ ,  $i, j = 1, 2$ , on the turnover rate  $z(t)$  determined by Eq. (1) with densities  $a(t, x_1, 0) = 1$ ,  $s_1(x_1) = x_1$ , and  $s_2(x_1) = 1 - x_1$ . **a**  $k_r = 0.001$ , **b**  $k_r = 0.01$

or monotonic behavior of  $z$  in time for small or large values of  $k_r$ , respectively. This result can be explained by the nonmonotonic behavior of  $\theta_2$ . Indeed, calculations show that, for small  $k_r$ ,  $\theta_2(t, x_1)$  grows as  $t$  increases, attains a maximum value depending on  $x_1$ , and then decreases to a positive steady-state function of  $x_1$ . However, in the case of large  $k_r$ ,  $\theta_2$  grows as  $t$  increases, while  $\theta_3$  is a monotonic function of  $t$  for all  $k_r$ . Now from formula (5) the nonmonotonic or monotonic behavior of  $z(t)$  follows.

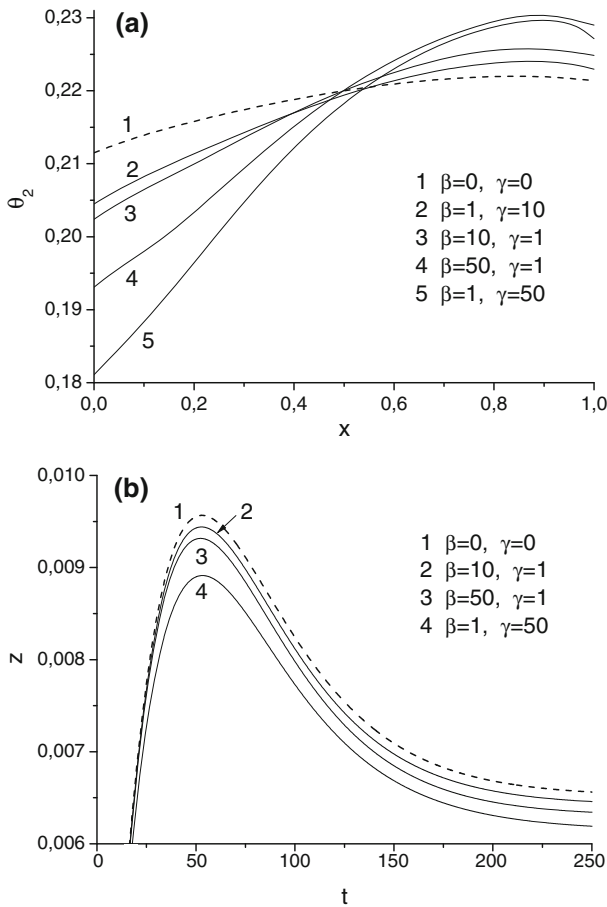
Figure 1b demonstrates the comparison of values of  $z$  that correspond to arrangements I, II, and III of adsorption sites for  $\alpha = 0.02$  and different values of  $k_r$ . For small values of  $k_r$  ( $k_r = 0.001$ ) and large  $t$ , all three distributions of adsorption sites determine approximately the same values of  $z$  (see curves 1), but, for  $k_r \geq 0.01$ , the influence of different arrangements of adsorption sites on the behavior of  $z$  is appreciable. The largest values of  $z$  correspond to arrangement III. Curves 5 correspond to instantaneous product desorption. Calculations show that, for large values of  $\alpha$  ( $\alpha = 0.1$ ), the influence of arrangements I, II, and III on the behavior of  $z$  is small.



**Fig. 3** Effect of parameter  $k_r$  and arrangement of adsorption sites on the turnover rate  $z(t)$  determined by Eq. (1) with density  $a(t, x_1, 0) = 1$ : **a**  $\alpha_{11} = \alpha_{21} = \alpha_{22} = 0.1, \alpha_{12} = 0.01$ ; **b**  $\alpha_{11} = \alpha_{21} = \alpha_{22} = 0.02, \alpha_{12} = 0.01$ . Nonuniform homogeneous distribution of sites ( $s_1(x_1) = x_1, s_2(x_1) = 1 - x_1$ )—solid line, heterogeneous distribution of sites: case II—dashed line, case III—short dashed line

Figure 2 depicts the influence of the parameters  $\alpha_{12}, \alpha_{21},$  and  $\alpha_{22}$  on the dynamics of  $z$  for  $k_r = 0.001$  (Fig. 2a) or  $k_r = 0.01$  (Fig. 2b) and, because of the smallness of  $k_r$ , demonstrate the nonmonotonic behavior of  $z$  in time. Both figures present a small influence of  $\alpha_{22}$  and essential influence of parameters  $\alpha_{21}$  and  $\alpha_{12}$ . From Fig. 2a we observe that, for  $t < t_*, t_* \approx 100$  s,  $z$  increases as  $\alpha_{12}$  decreases or  $\alpha_{21}$  increases but, for  $t > t_*, z$  behaves vice-versa. Figure 2b demonstrates the increase of  $z$  for all  $t > 0$  as  $\alpha_{12}$  decreases or  $\alpha_{21}$  increases. From Fig. 2a, b we also observe that, as  $t$  grows,  $z$  tends to asymptotic values that, for small  $k_r$  ( $k_r = 0.001$ ), practically do not depend on  $\alpha_{ij}$ .

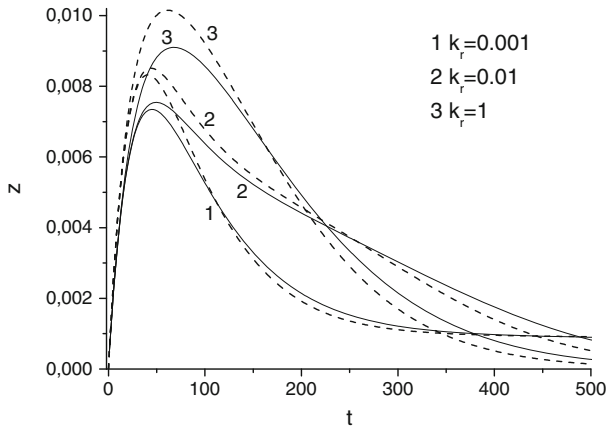
Figure 3a, b together demonstrate the cooperative influence of parameters  $\tilde{\alpha} := \alpha_{11} = \alpha_{21} = \alpha_{22}$  and  $k_r$  and arrangements I, II, and III of the adsorption sites on the dynamics of  $z$  for  $\alpha_{12} = 0.01$ . Numerical experiments show that, in the case where  $\tilde{\alpha} \lesssim 0.025$ , the largest maximal values of  $z$  for small  $k_r$  and all values of  $z$  for large  $k_r$ ,



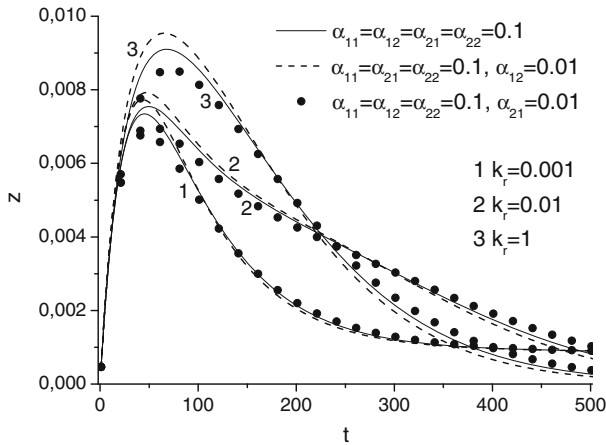
**Fig. 4** Dependence of coverage  $\theta_2(t)$  and function  $z(t)$  determined by Eq. (1) with densities  $a_0(x_1, x_2) = 1$  and  $s_1(x_1) = x_1, s_2(x_1) = 1 - x_1$  on the parameters  $\beta$  and  $\gamma$  in the case  $\alpha = 0.1$

correspond to arrangement III of adsorption sites. But, in the case where  $\tilde{\alpha} > 0.025$ , the maximal values of  $z$  for small  $k_r$  and all values of  $z$  for large  $k_r$  correspond to arrangement II. This can be explained by different numbers of adsorbed particles that because of jumps leave and arrive at active sites of arrangements II and III in the cases of small and large values of  $\tilde{\alpha}$ . Calculations show that the values of  $z$  determined by arrangements I and III for large  $k_r$  ( $k_r \approx 0.1$ ) are approximately equal.

The influence of  $\beta_{ij}$  and  $\gamma_{ij}$  on the behavior of  $z$  and  $\theta_2$  is depicted in Fig. 4 for the homogeneous arrangement of adsorption sites. The curves corresponding to positive and zero values of  $\beta_{ij}$  and  $\gamma_{ij}$  demonstrate a similar qualitative behavior of turnover rate  $z$  and coverage  $\theta_2$ . This figure also demonstrates the decrease of  $z$  as  $\beta_{ij}$  and  $\gamma_{ij}$  increase, but the influence of  $\gamma_{ij}$  is more significant. Moreover, the difference  $z(t, \beta_{ij}, \gamma_{ij}) - z(t, 0, 0)$  is small for small values of  $\beta_{ij}$  and  $\gamma_{ij}$ . We also used function (8) with  $I_1(t, x, y)$  replaced by  $I_1(t, 1, 0)$  and get that the qualitative behavior of  $z$  in both cases is similar, but the values of  $z$  that correspond to modified formula (8)



**Fig. 5** Dependence of the turnover rate  $z(t)$  determined by Eqs. (1)–(3) with densities  $a_0(x_1, x_2) = 1$  and  $s_1(x_1) = x_1, s_2(x_1) = 1 - x_1$  on the parameters  $k_r$  and  $\kappa_{12} = \kappa_{22}$  in the case  $\alpha = 0.1, \kappa = 1$ —solid line,  $\kappa_{11} = \kappa_{21} = 1, \kappa_{12} = \kappa_{22} = 0.5$ —dashed line

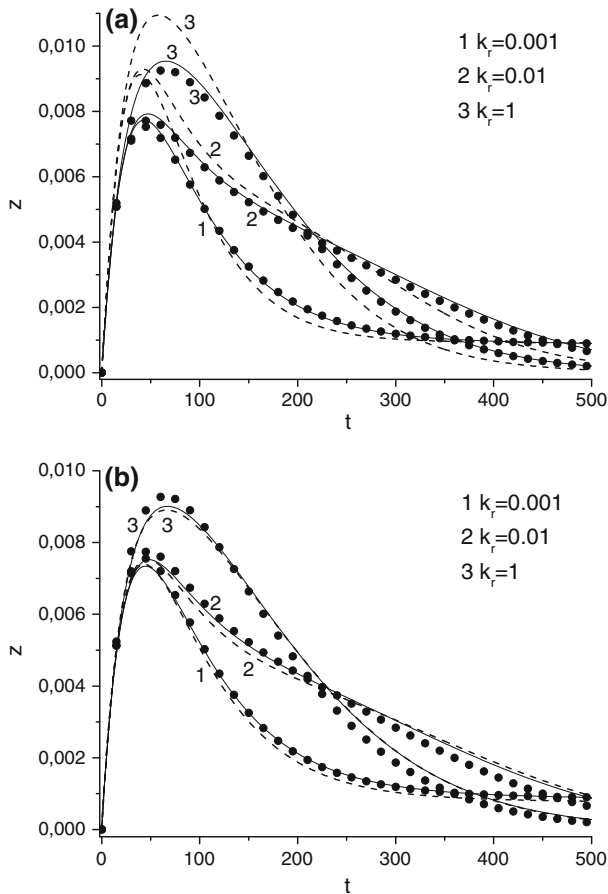


**Fig. 6** Influence of parameters  $k_r, \alpha_{12}$  and  $\alpha_{21}$  on the turnover rate  $z(t)$  determined by Eqs. (1)–(3) with densities  $a_0(x_1, x_2) = 1$  and  $s_1(x_1) = x_1, s_2(x_1) = 1 - x_1$

are smaller than those determined by the previous version of formula (8). This is not surprising because the modified function determines a smaller dispersion.

3.2 Numerical results of system (1)–(3)

The results are depicted in Figs. 5, 6, 7 and 8 only for  $\beta_{ij} = \gamma_{ij} = 0$ . For all values of  $k_r$ , the figures show the nonmonotonic behavior of  $z$  in time, which is conditioned by the cooperation of the decrease of reactant concentration  $a(t, x_1, 0)$  and poisoning effect of  $k_r$ . Note that the instantaneous product desorption and decrease of the reactant concentration also determines a nonmonotonic behavior of  $z$  in time (see [9]). Figure 5 presents the dependence of  $z$  on parameters  $\kappa_{12} = \kappa_{22}$  and  $k_r$ . For small  $t$  and all

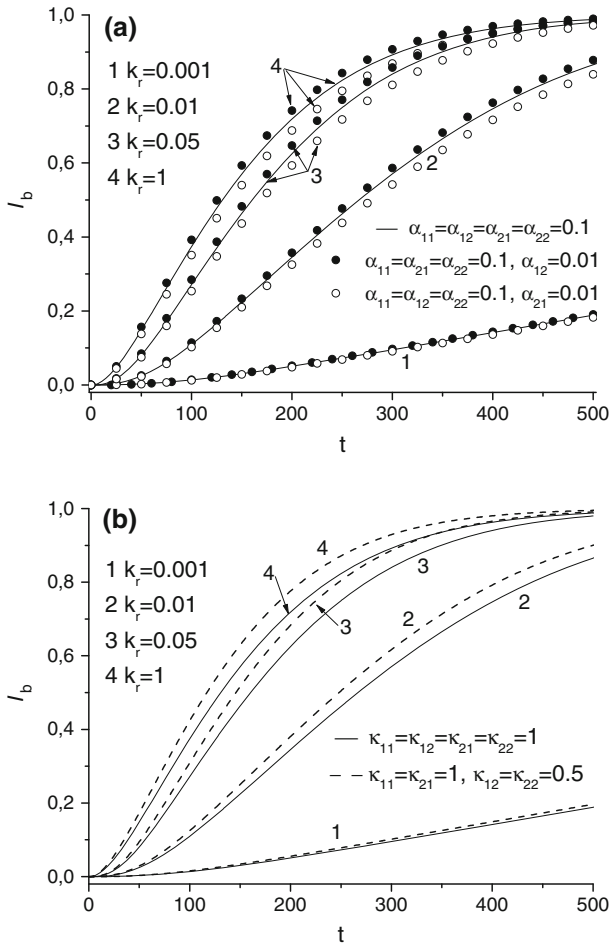


**Fig. 7** Effect of the parameters  $k_r$ ,  $\alpha_{12}$  and arrangement of adsorption sites on the function  $z(t)$  determined by Eqs. (1)–(3) for nonuniform homogeneous distribution of sites (case I, solid line) and for heterogeneous distribution of sites (cases II, dashed line, and III, bullets): **a**  $\alpha_{11} = \alpha_{21} = \alpha_{22} = 0.1$ ,  $\alpha_{12} = 0.01$ ; **b**  $\alpha_{11} = \alpha_{21} = \alpha_{22} = 0.02$ ,  $\alpha_{12} = 0.01$

values of  $k_r$  we used, the decrease of parameter  $\kappa_{12} = \kappa_{22}$  increases  $z$ , but, for large  $t$ , its influence is vice-versa. The growth of  $k_r$  increases the maximal values of  $z$ , but, for large  $t$ , because of the rapid decrease of the reactant concentration, its influence on the behavior of  $z$  is opposite.

Figure 6 presents the influence of parameters  $k_r$ ,  $\alpha_{12}$ , and  $\alpha_{21}$  on the behavior of  $z$ . For each value of  $k_r$ , we demonstrate three curves that correspond to fixed values of parameters  $\tilde{\alpha}$ ,  $\alpha_{12}$ , and  $\alpha_{21}$ . For small  $t$ , the decrease of  $\alpha_{12}$  or increase of  $\alpha_{21}$  increases  $z$ , but, for large  $t$ , their influence is opposite. This effect can be explained by the fast decrease of the reactant concentration.

In Fig. 7, the comparison of the values of  $z$  that correspond to different arrangements of adsorption sites is demonstrated for  $\alpha_{12} = 0.01$ ,  $k_r = 0.001, 0.01, 0.1, 1$ ,  $\tilde{\alpha} = 0.1$  (Fig. 7a), and  $\tilde{\alpha} = 0.02$  (Fig. 7b). Both figures depict the different influences of the different arrangements of adsorption sites on the behavior of  $z$ . Numerical experiments



**Fig. 8** Dependence of the total amount of the product  $I_b$  on  $k_r$  and parameters: **a**  $\alpha_{12}$  and  $\alpha_{21}$ ; **b**  $\kappa_{12} = \kappa_{22}$  in the case where  $a_0(x_1, x_2) = 1$  and  $s_1(x_1) = x_1, s_2(x_1) = 1 - x_1$

show that the largest maximal values of  $z$  correspond to arrangement III of adsorption sites if  $\tilde{\alpha} \lesssim 0.025$  and to type II if  $\tilde{\alpha} > 0.025$ . For large  $k_r$  and large  $t$ , this behavior is opposite.

Figure 8 depicts the influence of the parameters  $k_r, \alpha_{12}$ , and  $\alpha_{21}$  (Fig. 8a) and parameters  $k_r$  and  $\kappa_{12} = \kappa_{22}$  (Fig. 8b) on the dynamics of the total amount of the product  $I_b = \int_0^1 \int_0^1 b(t, x_1, x_2) dx_1 dx_2$ . We observe that the decrease of  $\kappa_{12} = \kappa_{22}$  or  $\alpha_{12}$  and increase of  $k_r$  or  $\alpha_{21}$  increase  $I_b$ .

### 4 Conclusions

To conclude, we summarize the main results. In this paper, we have presented simulations of a phenomenological mathematical model of unimolecular reactions

proceeding on inhomogeneous (nonuniform homogeneous and heterogeneous) planar surfaces in the two-dimensional space, taking into account the following: the bulk diffusion of the reactant from the bounded vessel toward the adsorbent and the product bulk one from the adsorbent into the same vessel, different arrangements of active and inactive in reaction adsorption sites, the adsorption and desorption of reactant particles, long-range surface diffusion of the adsorbate, and the slow product desorption from the adsorbent.

The present model generalizes that given in [23] by including the slow product desorption and using more complicated transition functions  $P_{ij}(t, x, y)$  of escaped particles. The main characteristic we have studied is the reactivity of the surfaces.

In the case of  $P_{ij}(t, x, y)$  with  $\beta_{ij} = \gamma_{ij} = 0$ :

- (a) we have investigated theoretically the role of dispersions of jump lengths of escaped particles and both the surface diffusion and product desorption rate constants,  $\kappa_{ij}$  and  $k_r$ , on the reactivity of inhomogeneous surfaces;
- (b) we have shown that dispersions of jump lengths of escaped particles and the arrangement of adsorption sites strongly influence catalytic activity of the system resulting in different turnover rate values of different arrangements of adsorption sites at different values of dispersions of jumps lengths and product desorption rate constant  $k_r$ . For large values of dispersion  $\alpha$ , this difference is small. But if  $\alpha_{12}$  is small or  $\alpha_{21}$  is large and the other equal dispersions of jumps lengths are small or large, then this difference is large. Moreover, there exist different domains of parameters for which the largest maximal values of  $z$  correspond to arrangement II or III of adsorption sites. In all cases, the decrease of the product desorption rate constant  $k_r$  decreases the values of  $z$ ;
- (c) we have demonstrated that the nonmonotonic behavior of  $z$  is conditioned by the cooperative effect of the product desorption rate and decrease of the reactant concentration in the case of model (1)–(3) and by a poisoning effect of small values of the product desorption rate constant in the case of system (1) with  $a(t, x_1, 0) = 1$ .

We also have shown that  $z$  that correspond to zero or positive values of  $\beta_{ij}$  and  $\gamma_{ij}$  behave similarly.

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