



# Exactly solvable models of a geminate reaction in the presence of scavengers

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Received 3 February 2004

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## Abstract

The irreversible reaction of a geminate pair  $A + B \rightarrow \text{Product}$  in dilute solution of scavengers is considered. The scavengers react with one of the partners, say  $B$ , thus accelerating its decay and decreasing a geminate reaction yield. The solution of the problem involves certain difficulties due to initial correlations. A many-particle formulation of the problem has been presented. It is based on the consideration of the reacting system in the Fock space. The exact expressions for the kinetics of a geminate pair decay in the presence of scavengers in dilute solutions and for the kinetics of the geminate product accumulation have been derived for arbitrary type of the Markovian motion of the scavengers for the case of immobile  $B$  particle and for the situation of infinite stochastic jumps of  $B$  particle.

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PACS: 82.20.Rp

*Keywords:* Kinetic equations; Many-particle approach; Elementary reactions; Law of mass action; Scavengers problem

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## 1. Introduction

A many-particle approach to the investigation of chemically reacting systems gives most powerful and consequent methods for the derivation of the kinetic equations in liquid solutions. On this way, considerable progress has been achieved in the deriva-

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tion of kinetic equations of a wide class of bulk chemical reactions [1–10], including multistage ones [11–14]. However, most treatments neglect initial spatial correlations between the reacting particles. These correlations can be of two types. One of them is the so-called the same-type correlations [15,16] that correspond to infinite correlation radii between reactants in bulk reacting systems. They have been taken into account in the consideration of simple irreversible reactions [16]. Another type of initial correlations are the correlations with finite correlation radii that are inherent in reactions containing the so-called geminate stages. The irreversible reaction of geminate pairs in dilute solutions of scavengers is of practical interest.

This situation is often realized in radiation chemistry when radiation pulse results in an initial geminate (spatially correlated) pair  $A + B$  one of the partners of which (say  $B$ ) takes part in bulk reactions with  $C$  particles from solution. One has to deal with such reactions, for example, in studies of primary radiation chemical processes in liquid hydrocarbons doped with charge acceptors [17], in studies of irreversible trapping reaction of the hydrated electron and its equilibrated optically excited states and various “precursor states” by different oxidants [18], etc. In these cases the scavengers react with a partner of a single type thus accelerating its decay and decreasing a geminate reaction yield. The problem of adequate description of such systems involves certain difficulties due to spatial correlations and is known as a “scavenger problem” [19,20].

In testing approximate methods of solving the problem commonly used in the literature and searching for new methods for the derivation of kinetic equations in the framework of a many-particle approach, the exactly solvable models are of great interest [15]. Consideration of the exactly solvable models of the scavengers problem is the purpose of this contribution.

The structure of the paper is as follows. In the Section 2 we formulate the problem in terms of a many-particle approach based on the consideration of the reactive system in the Fock space. As a result, we obtain formal expressions for the kinetics of a geminate pair decay in the presence of scavengers, as well as for the kinetics of the geminate product accumulation. In Section 3 we concretize the expressions for the kinetics to the model of immobile  $B$  particles. We show that both kinetics can be expressed through the kinetics of the isolated geminate pair decay and the decay kinetics of immobile  $B$  reactant in the course of the irreversible bulk reaction with scavengers. In Section 4 we obtain the expressions for the kinetics for a more complicated model of a hopping motion of  $B$  particle. The Section 5 summarizes the main results.

## 2. Statement of the problem

Consider the following kinetic scheme describing the competition of geminate and bulk reactions: at the initial instant of time a geminate pair  $AB$  is produced which can then irreversibly recombine



Here  $P$  is the product of a geminate reaction. It can be a molecule originated from a bimolecular association, or two molecules produced by the exchange reaction. The

geminate pair is surrounded by bulk  $C$  particles (scavengers) able to react with one of the geminate partners, namely,  $B$ , detaching it from a geminate partner



so the concentration of  $C$  particles is not changed due to reaction (2.2).

As in most many-particle approaches, we consider all reactants as material points. A finite “size” of the particles can then be taken into account by introducing repulsive force potentials. In the general case, we can consider arbitrary force potentials between particles. However, in the exactly solvable models examined below we neglect the force interaction of any  $C$  particle with  $A$  particle as well as with the products  $P$  and  $D$  of geminate and bulk reactions, respectively.

The most general description of a many-particle system can be performed in the Fock space [7,15,21]. In this space the state of the system considered is determined by the set of distribution functions (DF):

$$\{F_{AB}(\vec{r}^A, \vec{r}^B, r_C^N, t), F_A(r_C^N, t), F_P(r_C^N, t)\}. \quad (2.3)$$

Each of them corresponds to the so-called box in the Fock space. The distribution function  $F_{AB}(\vec{r}^A, \vec{r}^B, r_C^N, t)$  is the probability that at time  $t$   $A$  and  $B$  particles of the initial geminate pair and  $N$   $C$ 's will be found in the macroscopic volume  $\Omega$  at the points  $\vec{r}^A, \vec{r}^B, r_C^N \equiv \{\vec{r}_1^C, \dots, \vec{r}_N^C\}$ , respectively. The distribution function  $F_A(r_C^N, t)$  is the probability that at time  $t$   $A$  particle originated from the initial geminate pair as a result of irreversible bulk reaction (2.2) will be found anywhere in the macroscopic volume  $\Omega$ , and  $N$   $C$  particles will be at the points  $r_C^N$ . The distribution function  $F_P(r_C^N, t)$  is the probability that at time  $t$  the product  $P$  of the geminate reaction appears, and  $N$   $C$  particles will be found in the macroscopic volume  $\Omega$  at the points  $r_C^N$ .

Each function of the set is normalized to the probabilities  $P_{AB}(t)$ ,  $P_A(t)$ , and  $P_P(t)$  to find the system in  $(AB)$ ,  $(A)$ , and  $(P)$ -boxes of the Fock space, respectively,

$$\begin{aligned} P_{AB}(t) &= \int d\vec{r}^A d\vec{r}^B dr_C^N F_{AB}(\vec{r}^A, \vec{r}^B, r_C^N, t), \\ P_A(t) &= \int dr_C^N F_A(r_C^N, t), \quad P_P(t) = \int dr_C^N F_P(r_C^N, t). \end{aligned} \quad (2.4)$$

Thus the probability  $P_{AB}(t)$  is the kinetics of the geminate pair decay in the presence of  $N$  scavengers. Since  $P_A(t)$  is the probability of producing a single  $A$  reactant from the initial geminate pair (as a result of bulk reaction (2.2)), it can be considered as the kinetics of the bulk reaction product  $A$  accumulation. The probability  $P_P(t)$  is the kinetics of the geminate reaction product accumulation. At any time  $t \geq 0$  the normalization condition is fulfilled

$$P_{AB}(t) + P_A(t) + P_P(t) = 1. \quad (2.5)$$

The survival probabilities by time  $t$ ,  $\mathcal{P}_A$  and  $\mathcal{P}_B$ , of  $A$  and  $B$  particles surrounded by  $N$  bulk  $C$  particles in the macroscopic volume  $\Omega$  and the probability of the geminate product accumulation are

$$\mathcal{P}_A(t) = P_{AB}(t) + P_A(t), \quad \mathcal{P}_B(t) = P_{AB}(t), \quad \mathcal{P}_P(t) = P_P(t) \quad (2.6)$$

From Eqs. (2.5) and (2.6) it follows that

$$\mathcal{P}_A(t) + \mathcal{P}_P(t) = 1 . \tag{2.7}$$

For convenience, further we shall use the following shorthand symbols for reactant coordinates as arguments of the functions

$$\vec{r}^A \equiv A, \quad \vec{r}^B \equiv B, \quad \vec{r}_i^C \equiv C_i \quad r_C^N \equiv C^N = \{C_1, \dots, C_N\} . \tag{2.8}$$

Besides, we shall use an extended time interval  $-\infty < t < \infty$ . Then the time evolution of the system considered is described by the set of coupled Liouville-type equations for the distribution functions which obey the balance relations between the Fock boxes

$$\begin{aligned} \left( \partial_t - \hat{L}_A - \hat{L}_B - \sum_{i=1}^N \hat{L}_{C_i} \right) F_{AB}(A, B, C^N, t) &= \hat{V}_{AB} F_{AB}(A, B, C^N, t) \\ &+ \sum_{i=1}^N \hat{V}_{BC}^{(i)} F_{AB}(A, B, C^N, t) + \delta(t) F_{AB}^0(A, B, C^N), \end{aligned} \tag{2.9}$$

$$\begin{aligned} \left( \partial_t - \sum_{i=1}^N \hat{L}_{C_i}^0 \right) F_A(C^N, t) &= - \int dA dB \sum_{i=1}^N \hat{V}_{BC}^{(i)} F_{AB}(A, B, C^N, t), \\ &+ \delta(t) F_A^0(C^N) \end{aligned} \tag{2.10}$$

$$\begin{aligned} \left( \partial_t - \sum_{i=1}^N \hat{L}_{C_i}^0 \right) F_P(C^N, t) &= - \int dA dB \hat{V}_{AB} F_{AB}(A, B, C^N, t) \\ &+ \delta(t) F_P^0(C^N). \end{aligned} \tag{2.11}$$

All operators in Eqs. (2.9)–(2.11) are the integral operators that act on the functions in the infinite (extended time+spatial coordinates) space, i.e., all variables are equal in rights. For this reason, the Dirac delta-function peculiarities reveal themselves in Eqs. (2.9)–(2.11) and in the kernels of the operators. The integral operators  $\hat{L}_A$ ,  $\hat{L}_B$ , and  $\hat{L}_{C_i}$  are the operators specifying the random walks process of  $A$ ,  $B$  and  $C_i$  reactants in the  $(AB)$ -box, respectively. The integral operator  $\hat{L}_{C_i}^0$  specifies random walks in  $(A)$  and  $(P)$ -boxes. For the general type of the Markovian stochastic process they are defined by the kernels

$$\begin{aligned} L_A(A, t|A_0, t_0) &= -\tau_A^{-1} [\delta(A - A_0) - f_A(A|A_0/B)] \delta(t - t_0), \\ L_B(B, t|B_0, t_0) &= -\tau_B^{-1} [\delta(B - B_0) - f_B(B|B_0/A, C^N)] \delta(t - t_0), \\ L_{C_i}(C_i, t|C_{0i}, t_0) &= -\tau_{C_i}^{-1} [\delta(C_i - C_{0i}) - f_C(C_i|C_{0i}/B, C^N(i))] \delta(t - t_0), \\ L_{C_i}^0(C_i, t|C_{0i}, t_0) &= -\tau_{C_i}^{-1} [\delta(C_i - C_{0i}) - f_C(C_i|C_{0i}/C^N(i))] \delta(t - t_0), \end{aligned} \tag{2.12}$$

where  $C^N(i) \equiv \{C_1, \dots, C_{i-1}, C_{i+1}, \dots, C_N\}$ , and the variables after the sloping line denote a parametric dependence of the functions. The function  $f_A(A|A_0/B)$  is a conditional probability to find  $A$  reactant at the point  $A$  after a stochastic jump on condition

that before the jump it was at the point  $A_0$ , and  $B$  reactant was at the point  $B$ . The parametric dependence of the functions on the coordinate  $B$  is due to the force interaction between  $A$  and  $B$  particles. Other functions in Eqs. (2.12) have the same sense for moving  $B$  or  $C$  particles in different boxes of the Fock space. The parameter  $\tau_n$  ( $n = A, B, C$ ) is the mean time between the jumps of particles of  $n$  type.

The integral operators  $\hat{V}_{AB}$  and  $\hat{V}_{BC}^{(i)}$  are the reactivity operators of geminate and bulk reactions, respectively. As usual, we assume their kernels to be local in space and time

$$\begin{aligned} V_{AB}(A, B, t | A_0, B_0, t_0) &= -w_{AB}(A - B)\delta(A - A_0)\delta(B - B_0)\delta(t - t_0) + O(\Omega^{-1}), \\ V_{BC}^{(i)}(B, C_i, t | B_0, C_{0i}, t_0) &= -w_{BC}(B - C_i)\delta(B - B_0)\delta(C - C_{0i})\delta(t - t_0) \\ &\quad + O(\Omega^{-1}), \end{aligned} \quad (2.13)$$

where  $w_{AB}(A - B)$  and  $w_{BC}(B - C)$  are the elementary event rates of irreversible reactions (2.1)–(2.2) between reactants in infinite volume.

The initial conditions for the DF are taken in the following form:

$$\begin{aligned} F_{AB}^0 &= P_{AB}^0 P(A, B) \prod_{i=1}^N \phi_C(C_i) [1 + O(\Omega^{-1})], \\ F_A^0 &= P_A^0 \prod_{i=1}^N \phi_C(C_i) [1 + O(\Omega^{-1})]; \quad F_P^0 = P_P^0 \prod_{i=1}^N \phi_C(C_i) [1 + O(\Omega^{-1})], \end{aligned} \quad (2.14)$$

where  $P_{AB}^0 = P_{AB}(t=0)$ ,  $P_A^0 = P_A(t=0)$ , and  $P_P^0 = P_P(t=0)$ . Note that  $C$  particles are distributed in the macroscopic volume  $\Omega$  without any correlation, and are described by the normalized single-particle distribution  $\phi_C(C_i)$ . The geminate pair is correlated, and is described by the two-particle probability distribution function  $P(A, B)$ . The integration of this function over the coordinates of one particle gives the normalized single-particle distribution of another geminate partner. Both functions are normalized as

$$\int dA dB P(A, B) = \int dC_i \phi_C(C_i) = 1. \quad (2.15)$$

Since all quantities are considered in a macroscopic but finite volume (taking into account the influence of the walls), the terms of the order  $\Omega^{-1}$  appear on the right-hand side of Eqs. (2.14) and (2.13). To solve Eqs. (2.9)–(2.11), let us introduce the many-particle propagators  $\hat{G}_{AB}$  and  $\hat{G}$ . The propagator  $\hat{G}_{AB}$  describes the evolution of the system in  $(AB)$ -box of the Fock space initially containing the geminate pair  $AB$  and  $N$   $C$  particles, and is the density of the probability of finding the particles at points  $A, B, C^N$  at time  $t$ , provided that at  $t = t_0$  the particles were at points  $A_0, B_0, C_0^N$ , respectively. The propagator  $\hat{G}$  describes the evolution of  $N$   $C$  particles from the points  $C_0^N$  to the points  $C^N$  in  $(A)$  or  $(P)$  boxes of the Fock space. Their kernels obey the following equations:

$$\begin{aligned} &\left( \partial_t - \hat{L}_A - \hat{L}_B - \hat{V}_{AB} - \sum_{i=1}^N \hat{L}_{C_i} - \sum_{i=1}^N \hat{V}_{BC}^{(i)} \right) G_{AB}(A, B, C^N, t | A_0, B_0, C_0^N, t_0) \\ &= \delta(t - t_0)\delta(A - A_0)\delta(B - B_0)\delta(C^N - C_0^N), \end{aligned} \quad (2.16)$$

$$\left( \partial_t - \sum_{i=1}^N \hat{L}_{Ci}^0 \right) G(C^N, t | C_0^N, t_0) = \delta(t - t_0) \delta(C^N - C_0^N). \tag{2.17}$$

The solution of Eqs. (2.9)–(2.11) can be represented as

$$F_{AB}(A, B, C^N, t) = \hat{G}_{AB} | \delta(t) F_{AB}^0(A, B, C^N) \rangle, \tag{2.18}$$

$$F_A(C^N, t) = \hat{G} \left( | \delta(t) F_A^0(C^N) \rangle - \int dA dB \sum_{i=1}^N \hat{V}_{BC}^{(i)} F_{AB}(A, B, C^N, t) \right), \tag{2.19}$$

$$F_P(C^N, t) = \hat{G} \left( | \delta(t) F_P^0(C^N) \rangle - \int dA dB, \hat{V}_{AB} F_{AB}(A, B, C^N, t) \right). \tag{2.20}$$

These solutions will be used for the kinetics calculation in Eq. (2.6). Finally, we shall be interested in the kinetics in the thermodynamic limit

$$\begin{aligned} \mathcal{P}_A^T(t) &= T - \lim \mathcal{P}_A(t), & \mathcal{P}_B^T(t) &= T - \lim \mathcal{P}_B(t), \\ \mathcal{P}_P^T(t) &= T - \lim \mathcal{P}_P(t), \end{aligned} \tag{2.21}$$

where the operator  $T - \lim$  denotes the well-known procedure of the thermodynamic limit [22–24]:  $T - \lim \equiv \lim(N \rightarrow \infty, \Omega \rightarrow \infty, N/\Omega = [C] = \text{const})$ .

Using Eqs. (2.16)–(2.20), one can obtain the final formulae for the kinetics calculation

$$\mathcal{P}_B^T(t) = T - \lim \int dA dB dC^N \hat{G}_{AB} | \delta(t) F_{AB}^0(A, B, C^N) \rangle, \tag{2.22}$$

$$\begin{aligned} \mathcal{P}_P^T(t) &= \theta(t) P_P^{0T} - \left( T - \lim \int dA dB dC^N \right. \\ &\quad \left. \times \int_{-0}^t d\tau \hat{V}_{AB} \hat{G}_{AB} | \delta(\tau) F_{AB}^0(A, B, C^N) \rangle \right), \end{aligned} \tag{2.23}$$

where  $P_P^{0T} = T - \lim P_P^0$ . Further, all quantities in the thermodynamic limit will be designated by additional upper index  $T$ . In the derivation of Eq. (2.23) the condition for the normalization of the function  $G$  has been used

$$\int dC^N G(C^N, t | C_0^N, t_0) = \theta(t - t_0), \tag{2.24}$$

where  $\theta(t)$  is the Heaviside step function. For the calculation of  $\mathcal{P}_A^T(t)$  it is convenient to use the formula following from Eq. (2.7):

$$\mathcal{P}_A^T(t) = \theta(t) - \mathcal{P}_P^T(t). \tag{2.25}$$

Note that for the calculation of kinetics (2.22)–(2.23) the propagator  $\hat{G}$  (i.e., the information about the motion operator  $\hat{L}_{Ci}^0$ ) is not needed.

### 3. The model with immobile B particle

In this section we shall find the kinetics (Eqs. (2.22), (2.23), and (2.25)) in the case of immobile B reactant. Also we assume that there is no force interaction between C particles. Correspondingly, the operators of the particles motion take the following form:

$$\begin{aligned}
 L_A(A, t|A_0, t_0) &= -\tau_A^{-1}[\delta(A - A_0) - f_A(A|A_0/B)]\delta(t - t_0), \\
 L_B &= 0, \\
 L_{C_i}(C_i, t|C_{0i}, t_0) &= -\tau_C^{-1}[\delta(C_i - C_{0i}) - f_C(C_i|C_{0i}/B)]\delta(t - t_0). \tag{3.1}
 \end{aligned}$$

In the case of immobile B particle, the Green function  $G_{AB}$  obeys Eq. (2.16) where one has to assume  $\hat{L}_B \equiv 0$ . It is easily seen that this function takes the form

$$\begin{aligned}
 G_{AB}(A, B, C^N, t|A_0, B_0, C_0^N, t_0) \\
 = G_A(A, t|A_0, t_0/B)\delta(B - B_0) \prod_{i=1}^N G_C(C_i, t|C_{0i}, t_0/B) \tag{3.2}
 \end{aligned}$$

with  $G_A$  and  $G_C$  obeying the equations

$$\begin{aligned}
 (\partial_t - \hat{L}_A - \hat{V}_{AB})G_A(A, t|A_0, t_0/B) &= \delta(t - t_0)\delta(A - A_0), \\
 (\partial_t - \hat{L}_C - \hat{V}_{BC})G_C(C, t|C_0, t_0/B) &= \delta(t - t_0)\delta(C - C_0). \tag{3.3}
 \end{aligned}$$

Here we omitted index  $i$  (the number of C particle). It follows from Eq. (3.3) that the function  $G_A$  is the Green function describing the decay of immobile B particle localized at point B in the reaction with moving A particle. Correspondingly,  $G_C$  are the Green functions describing the decay of immobile B particle localized at point B in the reaction with moving C particle. Using Eq. (3.2) and the distribution from Eqs. (2.14) in Eq. (2.22), we get

$$\mathcal{P}_B^T(t) = T - \lim \int dA dB P_{AB}^0 \hat{G}_A | P(A, B)\delta(t) \rangle \left( \int dC \hat{G}_C | \phi_C(C)\delta(t) \rangle \right)^N. \tag{3.4}$$

Let us pass to the thermodynamic limit in Eq. (3.4). To do this, we assume that the following expansion takes place:

$$P(A, B) \underset{\Omega \rightarrow \infty}{\sim} \Omega^{-1} \Theta_h(A) \Theta_h(B) P^T(A, B), \quad \phi_C(C) \underset{\Omega \rightarrow \infty}{\sim} \Omega^{-1} \Theta_h(C) \phi_C^T(C), \tag{3.5}$$

where  $\Theta_h(\vec{r})$  is the characteristic function of the volume  $\Omega$ :

$$\Theta_h(\vec{r}) = \int_{\Omega} d\vec{r}_0 \delta(\vec{r} - \vec{r}_0) = \begin{cases} 1, & \vec{r} \in \Omega, \\ 0, & \vec{r} \notin \Omega. \end{cases} \tag{3.6}$$

The functions  $P^T(A, B)$  and  $\phi_C^T(C)$  are not equal to zero in the whole infinite space, and have no dependence on the boundary of the volume  $\Omega$ . They are called a two-particle local probability of A and B reactants and one-particle local probability of C reactants,

respectively. A one-particle local probability of  $A$  and  $B$  reactants can be obtained from a two-particle local probability by the integration over the coordinates, i.e., as in a usual probability theory

$$\phi_A^T(A) = \int dB P^T(A, B), \quad \phi_B^T(A) = \int dA P^T(A, B). \quad (3.7)$$

A two-particle probability  $P^T(A, B)$  depends not only on relative coordinates of  $A$  and  $B$  reactants, since, generally speaking, nonuniform reacting systems are considered. One-particle local probabilities under standard procedure of averaging over the volume give

$$\lim_{v \rightarrow \infty} \int_v \frac{dA}{v} \phi_A^T(A) = \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} \phi_B^T(B) = \lim_{v \rightarrow \infty} \int_v \frac{dC}{v} \phi_C^T(C) = 1. \quad (3.8)$$

Here  $v$  under the integral sign denotes that integration is performed solely within the limits of the volume  $v$ .

Substituting Eq. (3.5) in Eq. (3.4), passing to the thermodynamic limit and using the method from our previous works [15,21], we obtain

$$\mathcal{P}_B^T(t) = P_{AB}^{0T} \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} \Omega(t/B) N_B(t/B), \quad (3.9)$$

where the survival probability  $\Omega(t/B)$  of a geminate pair without scavengers on fixed coordinates of  $B$  particle is defined in the following way:

$$\Omega(t/B) = \int dA \hat{G}_A^T | \delta(t) P^T(A, B) \rangle. \quad (3.10)$$

The survival probability  $N_B(t/B)$  of immobile  $B$  particle in a bulk reaction with scavengers is

$$N_B(t/B) = \theta(t) \exp \left\{ -[C] \int dC (\phi_C^T(C) - \hat{G}_C^T | \delta(t) \phi_C^T(C) \rangle) \right\}. \quad (3.11)$$

In the literature it is known as the exact solution of the “target problem” [15,21,25–27].

The propagators  $\hat{G}_A^T$  and  $\hat{G}_C^T$  in Eqs. (3.10), and (3.11) obey the equations following from Eqs. (3.3) after the thermodynamic limit:

$$\begin{aligned} (\partial_t - \hat{L}_A^T - \hat{V}_{AB}^T) G_A^T(A, t | A_0, t_0/B) &= \delta(t - t_0) \delta(A - A_0), \\ (\partial_t - \hat{L}_C^T - \hat{V}_{BC}^T) G_C^T(C, t | C_0, t_0/B) &= \delta(t - t_0) \delta(C - C_0). \end{aligned} \quad (3.12)$$

The operators  $\hat{L}_A^T$ ,  $\hat{V}_{AB}^T$ ,  $\hat{L}_C^T$ , and  $\hat{V}_{BC}^T$  describe the evolution of reactants in the infinite space, and do not depend on the boundary of the volume  $\Omega$ . In particular, the kernels of the operators  $\hat{V}_{AB}^T$  and  $\hat{V}_{BC}^T$  coincide with the first terms in Eq. (2.13).

Eqs. (3.9)–(3.11) become simpler for homogeneous distribution of scavengers  $C$ :  $\phi_C^T(C) = 1(C)$ . Using the shift symmetry

$$G_C^T(C, t | C_0, t_0/B) = G_C^T(C - B, t | C_0 - B, t_0/0) \quad (3.13)$$



we obtain

$$N_B(t/B) \equiv N_B(t) = \theta(t) \exp\{-[C] \int dC(\phi_C^T(C) - \hat{G}_C^T | \delta(t)1(C))\} \tag{3.14}$$

i.e., it does not depend on  $B$  coordinates. Thus introducing the volume-averaged survival probability of a geminate pair without scavengers

$$\bar{\Omega}(t) = \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} \Omega(t/B) \tag{3.15}$$

we have

$$\mathcal{P}_B^T(t) = P_{AB}^{0T} \bar{\Omega}(t) N_B(t), \quad (\phi_C^T(C) = 1(C)). \tag{3.16}$$

For the calculation of  $\mathcal{P}_P^T(t)$  we substitute Eq. (3.2) into Eq. (2.23), and obtain the following expression:

$$\begin{aligned} \mathcal{P}_P^T(t) = \theta(t) P_P^{0T} - P_{AB}^{0T} & \left( T - \lim \int dA dB \int_{-0}^t d\tau \hat{V}_{AB} \hat{G}_A | \delta(\tau) P(A, B) \right) \\ & \times \left( \int dC \hat{G}_C | \delta(\tau) \phi_C(C) \right)^N \end{aligned} \tag{3.17}$$

Passing to the thermodynamic limit, we get

$$\mathcal{P}_P^T(t) = \theta(t) P_P^{0T} + P_{AB}^{0T} \int_{-0}^t d\tau \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} K_g(\tau/B) N_B(\tau/B). \tag{3.18}$$

As usual, the geminate reaction  $K_g(t/B)$  rate depending on the fixed position of  $B$  particle is determined here by the formula [28,29]

$$K_g(t/B) = - \int dA \hat{V}_{AB}^T \hat{G}_A^T | \delta(t) P^T(A, B). \tag{3.19}$$

For initially uniform distribution of  $C$  reactants Eq. (3.17) reduces to

$$\mathcal{P}_P^T(t) = \theta(t) P_P^{0T} + P_{AB}^{0T} \int_{-0}^t d\tau \bar{K}_g(\tau) N_B(\tau), \quad (\phi_C^T(C) = 1(C)). \tag{3.20}$$

Here we introduce the volume-averaged geminate reaction rate

$$\bar{K}_g(t) = \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} K_g(t/B). \tag{3.21}$$

The well-known relation connects the survival probability of the geminate pair  $\bar{\Omega}(t)$  and  $\bar{K}_g(t)$  [30,31]:

$$\partial_t \bar{\Omega}(t) = \delta(t) - \bar{K}_g(t) \tag{3.22}$$

that follows from Eqs. (3.12), (3.10), (3.15), (3.19) and (3.21).

#### 4. The model with the hopping motion of $B$ particle

In exactly solvable model with mobile  $B$  particle we, as in Ref. [15], have to restrict ourselves to three additional assumptions.

First, we shall consider the reacting systems with the uniform distribution of bulk  $C$  reactants

$$\phi_C^T(C) = 1(C). \quad (4.1)$$

Second, we additionally (compared to the above Section) neglect the force interaction between  $B$  and  $C$  particles. Then, instead of Eqs. (3.1), we have from general equations (2.12)

$$\begin{aligned} L_A(A, t|A_0, t_0) &= -\tau_A^{-1}[\delta(A - A_0) - f_A(A|A_0/B)]\delta(t - t_0), \\ L_B(B, t|B_0, t_0) &= -\tau_B^{-1}[\delta(B - B_0) - f_B(B|B_0/A)]\delta(t - t_0), \\ L_C(C, t|C_0, t_0) &= -\tau_C^{-1}[\delta(C - C_0) - f_C(C|C_0)]\delta(t - t_0). \end{aligned} \quad (4.2)$$

The third necessary assumption is that random walks of  $B$  reactants can be considered as an uncorrelated Markovian process

$$f_B(B|B_0/A) = \psi_B(B/A), \quad \int dB \psi_B(B/A) = 1, \quad (4.3)$$

where  $\psi_B(B/A)$  is the equilibrium distribution of  $B$  reactants at fixed  $A$  particle coordinate. Physically this means that, as result of a jump,  $B$  particle will be far away from its initial point [32]. This assumption considering infinite jumps of  $B$  reactant in the thermodynamic limit corresponds to the so-called hopping mechanism of a chemical reaction [32] in liquid solutions. It has been established in experimental investigation of a chemical reaction of an excess electron with scavengers in nonpolar liquid solutions [33].

As in Ref. [15], the many-particle Green function  $G_{AB}$  can be represented as a sum of all possible realizations of the stochastic trajectories of  $B$  particle

$$G_{AB}(A, B, C^N, t | A_0, B_0, C_0^N, t_0) = \sum_{k=0}^{\infty} G_{AB}^{(k)}(A, B, C^N, t | A_0, B_0, C_0^N, t_0). \quad (4.4)$$

Here the index  $k$  denotes the number of the stochastic jumps in a time interval  $t - t_0$ . The first term in Eq. (4.4) describes the part of the trajectories in which  $B$  particle remains at the point of the start  $B_0$  at time  $t_0$ :

$$\begin{aligned} G_{AB}^{(0)}(A, B, C^N, t | A_0, B_0, C_0^N, t_0) \\ = \delta(B - B_0) G_A(A, t | A_0, t_0/B) e^{-(t-t_0)/\tau_B} \prod_{i=1}^N G_C(C_i, t | C_{0i}, t_0/B). \end{aligned} \quad (4.5)$$

It is the product of the Green functions of  $A$  and  $C$  particles on condition of a fixed  $B$  particle and the Poisson waiting time distribution with the mean time  $\tau_B$  between

sequential jumps. Other terms can be represented in the following form:

$$\hat{G}_{AB}^{(1)} = \hat{G}_{AB}^{(0)}(\tau_B^{-1} \hat{f}_B) \hat{G}_{AB}^{(0)}; \quad \hat{G}_{AB}^{(k)} = [\hat{G}_{AB}^{(0)}(\tau_B^{-1} \hat{f}_B)]^k \hat{G}_{AB}^{(0)}, \quad (4.6)$$

where  $\hat{G}_{AB}^{(0)}$  is the integral operator defined by kernel (4.5), and  $\hat{f}_B$  is the integral operator defined by the kernel  $f_B(B|B_0/A)\delta(A - A_0)\delta(C^N - C_0^N)\delta(t - t_0)$ . Substituting Eqs. (4.3) and (4.5) into Eq. (2.22), we obtain

$$\mathcal{P}_B^T(t) = T - \lim \int dC^N \hat{\mathcal{P}} | \delta(t) F_{AB}^0(A, B, C^N) \rangle, \quad (4.7)$$

where the kinetics operator is introduced [15,21]

$$\hat{\mathcal{P}} = \int dA dB \sum_{k=0}^{\infty} \hat{G}_{AB}^{(k)} = \int dA dB \sum_{k=0}^{\infty} [\hat{G}_{AB}^{(0)}(\tau_B^{-1} \hat{f}_B)]^k \hat{G}_{AB}^{(0)} \equiv \sum_{k=0}^{\infty} \hat{\mathcal{P}}^{(k)}. \quad (4.8)$$

The calculation of  $\hat{\mathcal{P}}^{(k)}$  with  $f_B(B|B_0/A)$  from Eq. (4.3) gives the following results for the first two terms of the sum in Eq. (4.8):

$$\begin{aligned} &\mathcal{P}^{(0)}(C^N, t | A_0, B_0, C_0^N, t_0) \\ &= \int dA G_A(A, t | A_0, t_0/B_0) e^{-(t-t_0)/\tau_B} \prod_{i=1}^N G_C(C_i, t | C_{0i}, t_0/B_0), \end{aligned} \quad (4.9)$$

$$\begin{aligned} &\mathcal{P}^{(1)}(C^N, t | A_0, B_0, C_0^N, t_0) = \tau_B^{-1} \int dA dB dA_1 dC_1^N dt_1 \\ &\quad \times G_A(A, t | A_1, t_1/B) e^{-(t-t_1)/\tau_B} \psi_B(B/A_1) \prod_{i=1}^N G_C(C_i, t | C_{1i}, t_1/B) \\ &\quad \times G_A(A_1, t_1 | A_0, t_0/B_0) e^{-(t_1-t_0)/\tau_B} \prod_{i=1}^N G_C(C_{1i}, t_1 | C_{0i}, t_0/B_0). \end{aligned} \quad (4.10)$$

At the thermodynamic limit  $\Omega \rightarrow \infty$  the region of a large  $B$  gives the main contribution to the integral over  $dB$ . Then one can use the following asymptotic estimation in this region:

$$G_A(A, t | A_1, t_1/B)_{B \rightarrow \infty} \sim G_A^\infty(A, t | A_1, t_1), \quad \psi_B(B/A)_{A \rightarrow \infty} \sim \psi_B^\infty(B), \quad (4.11)$$

where  $G_A^\infty$  is the propagator of a free stochastic motion of  $A$  reactant far from  $B$  reactant, and  $\psi_B^\infty(B)$  is the equilibrium distribution (static contour) for the free propagator [31] of  $B$  reactants far away from  $A$  reactants. Using the normalization condition

$$\int dA G_A^\infty(A, t | A_0, t_0) = \theta(t - t_0) \quad (4.12)$$

in Eq. (4.10), we obtain

$$\mathcal{P}^{(1)}(C^N, t | A_0, B_0, C_0^N, t_0) = \tau_B^{-1} \hat{\mathcal{P}}_\infty | \mathcal{P}^{(0)}(C^N, t | A_0, B_0, C_0^N, t_0) \rangle, \quad (4.13)$$

where the operator  $\hat{\mathcal{P}}_\infty$  is defined by the kernel

$$\mathcal{P}_\infty(C^N, t | C_0^N, t_0) = e^{-(t-t_0)/\tau_B} \int dB \psi_B^\infty(B) \prod_{i=1}^N G_C(C_i, t | C_{0i}, t_0/B). \tag{4.14}$$

Accordingly, one can get for the  $k$ -term

$$\mathcal{P}^{(k)}(C^N, t | A_0, B_0, C_0^N, t_0) = [\tau_B^{-1} \hat{\mathcal{P}}_\infty]^k | \mathcal{P}^{(0)}(C^N, t | A_0, B_0, C_0^N, t_0) \rangle. \tag{4.15}$$

Thus the structure of the kinetics operator (4.8) coincides with the structure of the kinetics operator from paper [15]. So, as in paper [15], we can derive the closed integral equation for the kinetics  $\mathcal{P}_B^T(t)$ :

$$\mathcal{P}_B^T(t) = P_{AB}^{0T} \bar{\mathcal{Q}}(t) N_B(t) e^{-t/\tau_B} + \frac{1}{\tau_B} \int_{-0}^t d\tau N_B(t - \tau) e^{-(t-\tau)/\tau_B} \mathcal{P}_B^T(\tau). \tag{4.16}$$

Thus the determination of the survival probability of  $B$  particle moving by infinite jumps in our many-particle system is reduced to solving the closed integral equation for this value. The kernel of the equation  $e^{-t/\tau_B} N_B(t)$  is the product of the Poisson waiting time distribution of  $B$  particle with the mean time  $\tau_B$  between sequential jumps and the survival probability of  $B$  particle in a “target problem” (immobile  $B$  reacts with the ensemble of  $C$  particles moving in an arbitrary way by Markovian random walks). The inhomogeneous part of Eq. (4.16) is the product of the kernel and the survival probability  $\bar{\mathcal{Q}}(t)$  (defined in Eq. (3.15)) of immobile  $B$  particle in a geminate pair with mobile  $A$  particle. It is remarkable that initial geminate correlations reveal themselves only in the inhomogeneous part of Eq. (4.16) that describes the process before the first jump of the  $B$  particle. After the first jump  $B$  particle leaves the geminate pair forever and reacts with bulk  $C$ -particles only. The last processes are described by the integral term of Eq. (4.16). Note that at  $\tau_B \rightarrow \infty$  Eq. (4.16) is transformed to Eq. (3.16).

The derivation of the kinetic equations for  $\mathcal{P}_P^T(t)$  can be done in a similar manner. Using Eqs. (2.23) and (4.4), it is easy to see that the terms with  $k > 0$  vanish since even the first jump of  $B$  reactant interrupts the geminate reaction. The mathematical proof of the last statement is based on the following: as a result of the operator  $\hat{V}_{AB}$  action (for example,  $\hat{V}_{AB} \mathcal{P}^{(1)}$ ), the region of the integration over  $dB$  is restricted to the reaction volume of a geminate reaction. So in the thermodynamic limit the contribution of these terms will tend to zero. Thus the equation for  $\mathcal{P}_P^T(t)$  takes the form

$$\mathcal{P}_P^T(t) = P_P^{0T} \theta(t) + P_{AB}^{0T} \int_{-0}^t d\tau \bar{K}_g(\tau) N_B(\tau) e^{-\tau/\tau_B}. \tag{4.17}$$

At  $\tau_B \rightarrow \infty$  Eq. (4.17) reduces to Eq. (3.20), just as it should be.

### 5. Summary

Let us summarize the main results. For the scavengers problem two many-particle exactly solvable models are considered, and expressions for the kinetics of a geminate pair decay in the presence of scavengers in dilute solutions and for the kinetics of the geminate product accumulation are obtained.

In the first model one of the geminate pair particles (say  $B$ ) is immobile, and the force and chemical interactions of scavengers between each other and with  $A$  particle of the geminate pair are neglected. Then we derive for the kinetics of the geminate pair decay

$$\mathcal{P}_B^T(t) = P_{AB}^{0T} \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} \Omega(t/B) N_B(t/B), \tag{5.1}$$

where the survival probability  $\Omega(t/B)$  of the geminate pair without scavengers on fixed coordinates of  $B$  particle is defined in the following way:

$$\Omega(t/B) = \int dA \hat{G}_A^T | \delta(t) P^T(A, B) \rangle \tag{5.2}$$

and the survival probability  $N_B(t/B)$  of immobile  $B$  particle in a bulk reaction with scavengers is

$$N_B(t/B) = \theta(t) \exp \left\{ -[C] \int dC (\phi_C^T(C) - \hat{G}_C^T | \delta(t) \phi_C^T(C) \rangle) \right\}. \tag{5.3}$$

For the kinetics of the geminate reaction product accumulation we have

$$\mathcal{P}_P^T(t) = \theta(t) P_P^{0T} + P_{AB}^{0T} \int_{-0}^t d\tau \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} K_g(\tau/B) N_B(\tau/B). \tag{5.4}$$

As usual, the geminate reaction rate  $K_g(t/B)$  depending on fixed position of  $B$  particle is determined by the formula [28,29]

$$K_g(t/B) = - \int dA \hat{V}_{AB}^T \hat{G}_A^T | \delta(t) P^T(A, B) \rangle. \tag{5.5}$$

For initial uniform distribution of  $C$  reactants Eq. (5.4) reduces to

$$\mathcal{P}_P^T(t) = \theta(t) P_P^{0T} + P_{AB}^{0T} \int_{-0}^t d\tau \bar{K}_g(\tau) N_B(\tau), \quad (\phi_C^T(C) = 1(C)). \tag{5.6}$$

Here we introduce the volume-averaged geminate reaction rate  $\bar{K}_g(t)$ :

$$\bar{K}_g(t) = \lim_{v \rightarrow \infty} \int_v \frac{dB}{v} K_g(t/B). \tag{5.7}$$

In the model of a mobile  $B$  particle moving by infinite stochastic jumps we also took that in the reacting system the distribution of bulk reactants was uniform. Besides, we neglected the force interactions of  $B$  particle with bulk reactants. So we have for the kinetics of the geminate pair decay and the geminate reaction product accumulation

$$\mathcal{P}_B^T(t) = P_{AB}^{0T} \bar{\Omega}(t) N_B(t) e^{-t/\tau_B} + \frac{1}{\tau_B} \int_{-0}^t d\tau N_B(t - \tau) e^{-(t-\tau)/\tau_B} \mathcal{P}_B^T(\tau) \tag{5.8}$$

and

$$\mathcal{P}_P^T(t) = P_P^{0T} \theta(t) + P_{AB}^{0T} \int_{-0}^t d\tau \bar{K}_g(\tau) N_B(\tau) e^{-\tau/\tau_B}, \tag{5.9}$$

respectively.

Note that the internal degree of freedom can immediately be taken into account in the case of the absence of the interaction between these degrees in geminate and bulk reactions.

## Acknowledgements

We are grateful to the Russian Foundation of Basic Research for the support of this work (project 02-03-32182).

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