Kinetics of diffusion-limited catalytically-activated reactions: An extension of the Wilemski-Fixman approach

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Abstract

We study kinetics of diffusion-limited catalytically-activated $A + B \rightarrow B$ reactions taking place in three dimensional systems, in which an annihilation of diffusive $A$ particles by diffusive traps $B$ may happen only if the encounter of an $A$ with any of the $B$s happens within a special catalytic subvolumen, these subvolumens being immobile and uniformly distributed within the reaction bath. Suitably extending the classical approach of Wilemski and Fixman (G. Wilemski and M. Fixman, J. Chem. Phys. 58:4009, 1973) to such three-molecular diffusion-limited reactions, we calculate analytically an effective reaction constant and show that it comprises several terms associated with the residence and joint residence times of Brownian paths in finite domains. The effective reaction constant exhibits a non-trivial dependence on the reaction radii, the mean density of catalytic subvolumens and particles’ diffusion coefficients. Finally, we discuss the fluctuation-induced kinetic behavior in such systems.

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I. INTRODUCTION

Catalytically-activated reactions involving diffusive species underly many different processes in physics, chemistry and biology \[1, 2, 3, 4, 5\]. In a general notation, such reactions can be written as

\[ A + B + C \xrightarrow{k} P + C, \]

where \( A \) and \( B \) designate two different types of mobile reactive species, \( C \) denotes a catalytic subvolumen, while \( P \) stands for the reaction product. Catalytic subvolumens \( C \) may form some patterns, be uniformly or regularly spread along a given structure, (e.g., a polymer or polymers in solution), scattered uniformly within or on the boundary (surface) of the reaction bath.

The reaction scheme in Eq. (1) signifies that the bimolecular reaction between the \( A \) and \( B \) molecules may take place, at some finite elementary reaction rate \( k \), if and only if a diffusive encounter of an \( A \) and a \( B \) happens within any catalytic subvolumen \( C \). In some cases, the \( B \) particles may be unaltered by the reaction or their concentration may substantially exceed that of the \( A \) species, in which situation the reaction in Eq. (1) can be viewed as bi-catalytic: that is, one deals with a simplified reaction scheme \( A \rightarrow P \) which requires the presence of two different catalytic subvolumens - \( B \) and \( C \). This is most often the case in biology, as exemplified, for instance, by the transcription of genes induced by the simultaneous presence of several transcription factors on the promoter sequence \[6\].

Most of analytical descriptions of the catalytically-activated reactions have focussed so far on the particular question how reactions are promoted by specific catalytic subvolumens, which was believed to be the most crucial aspect of the problem \[7\]. Within this line of thought, the kinetic behavior has been determined using standard formal-kinetic approaches \[1, 2\]. On the other hand, a few available analytical studies of the catalytically-activated reactions limited both by diffusion of species and by the condition of the simultaneous encounters within the catalytic subvolumens have revealed a non-trivial kinetic behavior in low dimensional systems, and showed that although in three dimensions kinetics follows standard temporal behavior, the effective reaction rates are strongly dependent on particles’ diffusion coefficients, subvolumens’ radii and their concentration \[3, 4, 5\]. These findings are, of course, in an apparent contradiction with the predictions of the formal-kinetic approach.

As a matter of fact, it has been already realized that for reactions taking place in non-
catalytic systems, in many instances, the kinetic behavior can not be adequately described in terms of the formal-kinetics approach. Indeed, it has been known for a long time that diffusion of reactive species limits the reactive process and leads to unusual kinetics in low dimensional systems (see, e.g., Ref. [8] and references therein). Moreover, it has been discovered that in many reactive systems spatial fluctuations in particles concentrations dominate the long-time evolution and entail anomalous, fluctuation-induced behavior. In particular, a pronounced deviation from the conventional descriptions [2] has been predicted for the irreversible, diffusion-controlled recombination reaction $A + B \rightarrow 0$ in case when initially the particles of the $A$ and $B$ species are all distributed at random, independently of each other and with strictly equal mean densities $n_A(0) = n_B(0) = n_0$. It has been first shown [9] that here at long times the mean particle densities follow

$$n(t) \sim n_0^{1/2} (Dt)^{-d/4},$$  \hspace{1cm} (2)

where $d$ is the space dimensionality and $D$ - the sum of particles' diffusion coefficients, $D = D_A + D_B$. This law, which was rigorously proven in Refs. [10, 11], should be contrasted to the conventionally expected Smoluchowski-type form $n(t) \sim 1/\phi_R^{(d)}(t)$ [2], where, as $t \rightarrow \infty$,

$$\phi_R^{(d)}(t) = \int_0^t d\tau K_S(\tau) \sim \begin{cases} 4\sqrt{Dt/\pi}, & d = 1, \\ 4\pi Dt \ln(4Dt/R^2), & d = 2, \\ 4\pi DRt, & (k = \infty) \hspace{0.5cm} d = 3, \end{cases}$$

$K_S(\tau)$ being the $d$-dimensional Smoluchowski-type constant, defined as the flux of diffusive particles through the surface of an immobile sphere of radius $R$ - the reaction radius. Note that both decay laws contradict to the text-book formal-kinetic description based on the "law of mass action", which predicts that regardless of the spatial dimensionality $n(t)$ decays as $n(t) \sim 1/t$ [2].

Therefore, according to the Smoluchowski approach, in diffusion-controlled recombination reaction $A + B \rightarrow 0$ diffusion slows down the decay in low dimensional systems and entails the renormalization of the reaction rates in three-dimensions. On the other hand, in the particular case when initially the particles of the $A$ and $B$ species are all distributed at random, independently of each other and with strictly equal mean densities $n_A(0) = n_B(0) = n_0$, fluctuations in spatial distributions of the reactive species appear as the most important rate controlling factor in spatial dimension $d \leq 4$ and dominate the long-time kinetics.
For trapping reactions $A + B \rightarrow B$ in completely catalytic systems two opposite limiting situations were most thoroughly studied. Namely, the case when the $A$ particles diffuse while the traps $B$ are static, and the situation in which the $A$ particles are immobile while $B$s diffuse - the so-called target annihilation problem (TAP). The case of static traps has attracted most of interest prompted by, in part, an early observation [12] that the long-time survival probability $P_A(t)$ of $A$ particles diffusing in the presence of randomly placed (with mean density $[B]$) traps exhibits highly non-trivial, fluctuation-induced behavior of the form

$$\ln P_A(t) \sim -[B]^{2/(d+2)}(D_At)^{d/(d+2)}, \quad t \rightarrow \infty,$$

which stems from the randomness of $B$ distribution in space and namely, from the presence of large spatial regions devoid of traps where the $A$ particles survive anomalously long times. This fluctuation-induced decay law is intrinsically relevant to the so-called Lifschitz singularities near the edge of the band in the density of states of a particle in quantum Lorentz gas, as first noticed in [12]. Later works (see, e.g., Refs. [10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22]) have also pointed out relevance of the issue to the problems of percolation, self-avoiding random walks or self-attracting polymers, as well as anomalous behavior of the ground-state energy of the Witten’s toy Hamiltonian of supersymmetric quantum mechanics [14].

Survival probability $P_{\text{target}}(t)$ of an immobile target $A$ of radius $R$ in presence of point-like diffusive traps $B$ - the target annihilation problem (TAP), allows for an exact solution in any spatial dimension [8, 10, 23, 24, 25, 26]

$$P_{\text{target}}(t) = \exp \left( -[B]\phi_R^{(d)}(t) \right),$$

where $\phi_R^{(d)}(t)$ has been defined in Eq.(3) in which one has to set $D_A = 0$. Extensions to systems with hard-core interactions between traps [27] or fluctuating chemical activities of traps [28] have been also provided.

Now, the general and physically most important case of trapping reactions when both $A$ and $B$s diffuse with diffusion coefficients $D_A$ and $D_B$ was not solved exactly up to the present time. It has been proven [11] that in this case the $A$ particle survival probability
obeys
\[ \ln P_A(t) = -\lambda_d(D_A, D_B) \times \begin{cases} 
  t^{1/2}, & d = 1, \\
  \frac{t}{\ln(t)}, & d = 2, \\
  t, & d = 3, 
\end{cases} \]  
which defines its time-dependence exactly.

On the other hand, the factor \( \lambda_d(D_A, D_B) \) remained for a long time an unknown function of the particles’ diffusion coefficients and spatial dimension. Only very recently some rigorous arguments have been presented showing that for \( A + B \rightarrow B \) reactions in low dimensions \([29, 30, 31, 32]\), the long time decay of \( A \) particles concentration is exactly as in the TAP problem, Eq.(4), and thus is asymptotically independent of the \( A \) particles diffusion coefficient even in the case when both species diffuse.

In three dimensions, however, the precise form of \( \lambda_d(D_A, D_B) \) is still undetermined and still very little is known about it. It has been shown that \( \lambda_d(D_A, D_B) \) is less than the rate constant calculated within the Smoluchowski approach \([10]\) and moreover, it has been realized that in case when \( D_A \) and \( D_B \) are sufficiently small, \( \lambda_d(D_A, D_B) \) may be bounded by a non-analytic function of particles’ diffusion coefficients \([33]\). A perturbation theory approach for calculation of \( \lambda_d(D_A, D_B) \) has been proposed in Ref.[26] and the corrections to the predictions of the Smoluchowski approach have been evaluated. It was also shown that \( \lambda_d(D_A, D_B) \) can not be represented as the function of the combination \( D = D_A + D_B \) only, since the diffusion-reaction equations are not separable. Therefore, even in completely catalytic systems the evaluation of \( \lambda_d(D_A, D_B) \) represents a fairly complicated many-body problem.

In this paper we study the kinetics of the catalytically-activated diffusion-limited reactions in Eq.(1) in the special case when \( B \) particles remain unaltered by reactions, i.e. the case of diffusion-limited catalytically-activated trapping reactions, description of which poses such serious technical difficulties even in the non-catalytic systems (see the discussion above). In order to obtain an effective reaction rate for such bi-catalytic reactions taking place in a homogeneous three-dimensional medium, we first develop an analytical approach, inspired by the work of Wilemski and Fixman \([34]\), which allows one to estimate the reaction rate for non-catalytic bimolecular reactions. Here we extend this Wilemski-Fixman approach (WFA) to catalytically-activated trapping reactions.

We assume that the catalytic subvolumens \( C \) are immobile and are spread uniformly in the
reaction bath. On the other hand, $A$ and $B$ particles are assumed to perform unconstrained diffusion, and react only when they are simultaneously present in a spherical domain of radius $R$ centered around each catalytic subvolumen $C$. As well, we suppose that there is no other interaction between the particles except for the reaction, which enables us to describe the $A$ particle dynamics in terms of a Fokker-Planck-type equation with a sink term which mimics the presence of the traps $B$ and of the catalytic subvolumens $C$. In order to obtain a closed equation, we follow then the well known Wilemski-Fixman approach (WFA) [34]. This approximation relies on the time and space separation of the joint probability density; that is, the probability density is assumed to be a product of the equilibrium density and of a certain time-dependent function, supposing that initially the system is at equilibrium. We hasten to remark, that, although the validity domain of this approximation is still not really known, many researchers have shown that the WFA describes quite correctly reaction kinetics in several general situations [35, 36]. For example, Doi [35] showed that the WFA can be used for the purely diffusion-limited case ($k = \infty$), contrarily to the intuitive expectation that the WFA is appropriate for systems with a weak chemical reaction rate $k$. We will show also in what follows that the effective reaction constant obtained within such an approach reduces to the well-established results in several limiting cases.

Finally, we will present an estimate of the impact of the fluctuation effects on the long-time kinetics of the diffusion-controlled catalytically-activated reactions.

The paper is outlined as follows: In section II, we formulate the model and write down basic equations. Section III is devoted to the solution of the evolution equations within the framework of the suitably extended Wilemski and Fixman approach. Here, we determine an effective reaction rate for the bi-catalytic reaction and show that it can be expressed through different functionals of Brownian motion, known as residence times and joint residence times of Brownian particles in some specified domains. Further on, in Section IV we calculate the residence times involved and obtain an explicit expression for the effective rate constant describing diffusion-limited catalytically-activated trapping reactions. As well, we discuss its asymptotical behavior in several limiting situations. Next, in Section V we present some estimates of the long-time fluctuation-induced behavior in such systems. Finally, in Section VI we conclude with a brief summary of our results and discussion.
II. MODEL AND BASIC EQUATIONS

Consider a three-dimensional reaction bath of volume $V$ comprising a single $A$ particle, $m$ traps $B$, and $q$ immobile catalytic subvolumens $C$ (see Fig.1). These catalytic subvolumens are uniformly distributed in the reaction volume with mean concentration $[C]$. The $A$ and $B$ particles diffuse freely with diffusion coefficients $D_A$ and $D_B$, respectively. For simplicity, we assume that $A$ and $B$s are point-like particles of zero radius such that excluded-volume interactions between them can be safely neglected. Now, the reaction between particles - an annihilation of the $A$ particle by any of the $B$s - takes place with a given probability defining the elementary reaction constant $k$ when both species appear simultaneously within a spherical region of radius $R$ (which can be also thought off as the reaction radius) centered around any catalytic subvolumen $C$. Such a ”reactive” situation is depicted in Fig.2.

We now proceed by suitably extending the celebrated approach devised originally by Wilemski and Fixman [34] for non-catalytic trapping $A + B \rightarrow B$ reactions. The basic idea behind this approach is that the presence of traps $B$ can be effectively modelled by introducing a sink function $S$ into the diffusion equation describing dynamics of the $A$ and $B$ particles. Then, the sink term determines the efficiency of the reaction as a function of the instantaneous separation distance between the $A$ particle and the traps $B$.

In the simplest formulation, this sink term can be represented as the Heaviside function, which implies that the reaction takes place with an elementary reaction constant $k$ as soon as the $A$ particle appears in the vicinity of any of the traps $B$. Adapting this line of thought, we describe the $A$ and $B$ particles dynamics in terms of the following multivariant diffusion equation:

$$
\frac{\partial \Psi}{\partial t} = D_A \nabla^2_A \Psi + D_B \sum_i \nabla^2_{B_i} \Psi - k S \Psi
$$

(6)

where $\Psi(\{r\}, t)$ is time-dependent $m + 1$ particles probability density function, $\{r\} = \{r_A, r_{B_1}, \ldots, r_{B_m}\}$ defines the positions of the $A$ particle and all $m$ traps $B$, while the sink function $S$ is represented as a set of Heaviside functions $H(x)$, ($H(x) = 1$ if $x \geq 0$ and $H(x) = 0$ for $x < 0$), centered around $q$ catalytic subvolumens:
\[ S = \frac{1}{V'^2} \sum_{i=1}^{m} \sum_{k=1}^{q} H(R - |r_A - r_{C_k}|) H(R - |r_{B_i} - r_{C_k}|) \]
\[ \equiv \frac{1}{V'^2} \sum_{i=1}^{m} \sum_{k=1}^{q} H_{A,C_k} H_{B_i,C_k}, \quad (7) \]

in which \( V' \) denotes the volume of a "reactive" domain, \( V' = \frac{4}{3} \pi R^3 \), (see Fig. 2).

Consequently, the desired probability \( P(t) \) that the \( A \) particle survives up to time \( t \) obeys:

\[ P(t) = \int d\{r\} \Psi(\{r\}, t), \quad (8) \]

and can be readily evaluated once \( \Psi(\{r\}, t) \) is known.

### III. SOLUTION OF THE EVOLUTION EQUATION.

Equation (6) can be cast into an equivalent form by using the Green function \( G(\{r\}, t; \{r^0\}, t^0) \) of equation (6) without the sink term, the latter being considered as an inhomogeneity [34]. In doing so, we find that the formal solution of equation (6) reads:

\[ \Psi(\{r\}, t) = \int d\{r'\} \Psi(\{r'\}, 0) G(\{r\}, t; \{r'\}, 0) \]
\[ -k \int_0^t dt'^0 \int d\{r^0\} G(\{r\}, t; \{r^0\}, t^0) S(\{r^0\}) \Psi(\{r^0\}, t^0). \quad (9) \]

Note that \( G(\{r\}, t; \{r^0\}, t^0) \) of equation (6) without the sink term factorizes:

\[ G(\{r\}, t; \{r^0\}, t^0) = G_A(\{r_A\}, t; \{r_A^0\}, t^0) \prod_{u=1}^{m} G_B(\{r_{B_u}\}, t; \{r_{B_u}^0\}, t^0). \quad (10) \]

Now, supposing that at \( t = 0 \) the traps \( B \) were uniformly distributed in the reaction bath, i.e. that \( \Psi(\{r'\}, 0) = \Psi(0) \), we find that the first term on the right-hand-side of Eq. (9) reduces to \( \Psi(0) \). Following the reasonings of Wilemski and Fixman, we assume further on that \( \Psi(0) \) is the equilibrium density \( \Psi_{eq} = 1/V^{m+1} \). This corresponds to the physical situation when the system is first brought to equilibrium and the reaction is triggered then at time \( t = 0 \).
Next, multiplying both sides of Eq. (9) by $S(\{r\})$ and integrating it over all spatial variables $\{r\}$, we obtain:

$$v(t) = v_{eq} - k \int_0^t dt' \int d\{r\} \int d\{r^0\} S(\{r\})$$

$$\times G(\{r\}, t; \{r^0\}, t^0) S(\{r^0\}) \Psi(\{r^0\}, t^0)$$

(11)

where, by definition, $v(t) \equiv \int d\{r\} S(\{r\}) \Psi(\{r\}, t)$ and, equivalently, $v_{eq} \equiv \int d\{r\} S(\{r\}) \Psi_{eq}$. Using next the definition of $S(\{r\})$ given in equation (7), we obtain for $v_{eq}$:

$$v_{eq} = \frac{1}{\sqrt{2}} \frac{1}{V^{m+1}} \sum_{i=1}^m \sum_{k=1}^q V^{m-1} \int dA d\{r_B\} H_{A,C_k} H_{B_i,C_k}$$

$$= \frac{1}{\sqrt{2}} \frac{1}{V^{m+1}} \sum_{i=1}^m \sum_{k=1}^q V^{m-1} V'^2 = \frac{mq}{\sqrt{2}} V'^2.$$

Further on, integrating equation (6) over all $\{r\}$, and using the definition of the survival probability (8), we find that:

$$\frac{dP(t)}{dt} = -kv(t).$$

(12)

Consequently, the function $v(t)$ determines the rate of the time evolution of the $A$ particle survival probability.

In order to obtain a closed equation for $v(t)$, we follow again Wilemski and Fixman method, assuming that $\Psi(\{r\}, t)$ can be split into the product of a time-dependent function and the equilibrium density corresponding to the situation without reaction, knowing that initially $\Psi(\{r\}, 0) = \Psi_{eq}$. This approximation is valid $a$ priori for a small enough value of the reaction rate $k$, such that the probability density can be thought of being close to the equilibrium’s one at any time. As a matter of fact, this approximation still holds in much more general situations, for example when the reaction is diffusion-limited ($k = \infty$), as it was shown by Doi [35]. A detailed discussion of this approximation can be found in Refs. [19, 37, 38]. Applying it to our case of the catalytically-activated diffusion-limited trapping reactions, we have:
\[ \Psi(\{r\}, t) \approx \Psi_{eq} \nu(t). \]  

(13)

Noticing next that

\[ \int d\{r\} S\Psi = \nu(t) \int d\{r\} S\Psi_{eq} = \nu(t) v_{eq} \equiv v(t), \]

we get \( \nu(t) = v(t)/v_{eq} \) and hence, the approximated probability density reads:

\[ \Psi = \Psi_{eq} \frac{v(t)}{v_{eq}}. \]  

(14)

The latter equation, within the framework of the Wilemski-Fixman approximation, yields the following result for \( v(t) \):

\[ v(t) = v_{eq} - k \Psi_{eq} \int_0^t dt^0 v(t^0) I, \]  

(15)

where the integral \( I \) is given explicitly by:

\[ I = \frac{1}{V^n} \sum_{i,j,k,l} \int d\{r\} \int d\{r^0\} H_{A,C_k} H_{B_i,C_k} H_{A^0,C_l} H_{B_j^0,C_l} G(\{r\}, t; \{r^0\}, t^0). \]  

(16)

In order to obtain an explicit expression for this integral, and thus to get an access to the kinetic behavior of the survival probability, we consider it in more detail below. We note that \( I \) can be split into four parts, when specifying the following different events: the \( A \) particle, initially present in the \( k \)-th subvolumen \( C \) together with the \( i \)-th particle \( B \), will further encounter either the same \( B \) particle \( (i = j) \) or another \( B \) particle \( (i \neq j) \) in either the same subvolumen \( C(k = l) \) or some other subvolumen \( C \ (k \neq l) \).

First, let us consider the integral \( I_{ijkl} \) for \( i \neq j \). Integrating over \( r_{Bu} \) for \( u \neq i \) and over \( r_{Bv}^0 \) for \( v \neq j \), we obtain:

\[ I_{ijkl; i \neq j} = \frac{V^{m-2}}{V^n} \int d\{r\} d\{r^0\} d\{r^0\} H_{A,C_k} H_{B_i,C_k} H_{A^0,C_i} H_{B_j^0,C_l} G(\{r\}, t; \{r^0\}, t^0). \]  

(17)
Next, performing the integration of the Heaviside functions $H_{B^0, C_l}$ and $H_{B_i, C_k}$ over $d\mathbf{r}_{B_i}$ and $d\mathbf{r}_{B_j}^0$, we have:

\[
I_{ijkl;i\neq j} = \frac{V^{m-2}}{V^{r/2}} \int d\mathbf{r}_A d\mathbf{r}_A^0 H_{A,C_k} H_{A^0,C_l} G_A(\mathbf{r}_A, t; \mathbf{r}_A^0, t^0). \tag{18}
\]

Let us now consider the integral $I_{ijkl}$ for $i = j$. Integrating over the variables which do not appear as arguments of the Heaviside functions, we can write that:

\[
I_{ikl} = \frac{V^{m-1}}{V^{r/4}} \int d\mathbf{r}_A d\mathbf{r}_A^0 d\mathbf{r}_{B_i} d\mathbf{r}_{B_j}^0 H_{A,C_k} H_{B_i,C_l} H_{A^0,C_l} H_{B_j^0,C_l}
\times G_A(\mathbf{r}_A, t; \mathbf{r}_A^0, t^0) G_B(\mathbf{r}_{B_i}, t; \mathbf{r}_{B_i}^0, t^0). \tag{19}
\]

Note that when $k = I$, $H_{A,C_k} H_{B_i,C_l} H_{A^0,C_l} H_{B_j^0,C_l}$ reduces to $H_{A,C_k} H_{B_i,C_l}$.

Finally, using the latter decomposition of the integral $I$, and once again splitting it with respect to cases $k = I$ and $k \neq I$, summing over $i, j, k, l$ we obtain:

\[
I = m(m - 1) q I_{ijI; i \neq j} + m q I_{iiE} + m(m - 1)
\times q(q - 1) I_{ijI; i \neq j, k \neq I} + m(q - 1) I_{iiE; k \neq I}. \tag{20}
\]

Now we have to average the integral $I$ over the positions of the catalytic subvolumens $C$. Performing such averaging and denoting it by angle brackets with the subscript $\mathbf{r}_C$, we have the following four terms:

1. \[
\langle I_{ijk; i \neq j} \rangle_{\mathbf{r}_C} = \frac{V^{m-2}}{V^{r/2}} \int d\mathbf{r}_A d\mathbf{r}_A^0 H_A H_{A^0} G_A(\mathbf{r}_A, t; \mathbf{r}_A^0, t^0)
\equiv V^{m-2} \delta(t - t^0)
\]

2. \[
\langle I_{ijk; i \neq j, k \neq I} \rangle_{\mathbf{r}_C} = \frac{V^{m-2} V^{r/2}}{V^2} = \frac{V^{m-2}}{V}
\]

3. \[
\langle I_{iik} \rangle_{\mathbf{r}_C} = \frac{V^{m-1}}{V^{r/4}} \int d\mathbf{r}_A d\mathbf{r}_A^0 d\mathbf{r}_{B_i} d\mathbf{r}_{B_i}^0
\times H_A H_{B_i} H_{A^0} H_{B_i^0} \times G_A(\mathbf{r}_A, t; \mathbf{r}_A^0, t^0) G_B(\mathbf{r}_{B_i}, t; \mathbf{r}_{B_i}^0, t^0)
\equiv \frac{V^{m-1}}{V^{r/2}} \kappa_1(t - t^0)
\]

4. \[
\langle I_{iik; k \neq I} \rangle_{\mathbf{r}_C} = \frac{V^{m-1}}{V^{r/4}} \frac{1}{V}
\int d\mathbf{r}_A d\mathbf{r}_A^0 d\mathbf{r}_{B_i} d\mathbf{r}_{B_i}^0
\times H_A H_{B_i} H_{A^0} H_{B_i^0} \times G_A(\mathbf{r}_A, t; \mathbf{r}_A^0 + \mathbf{u}, t^0) G_B(\mathbf{r}_{B_i}, t; \mathbf{r}_{B_i}^0 + \mathbf{u}, t^0)
\equiv \frac{V^{m-1}}{V V^{r/2}} \kappa_2(t - t^0) \tag{21}
\]

\[12\]
where $\chi(t), \kappa_1(t)$ and $\kappa_2(t)$ are some functionals of time, which will be made explicit in the next section.

Using the latter results, we may express the $v(t)$ function in terms of the functionals $\chi(t - t^0), \kappa_1(t - t^0)$ and $\kappa_2(t - t^0)$. This gives

$$v(t) = v_{eq} - k \frac{(m-1)(q-1)}{V^2} \int_0^t dt^0 v(t^0) - k \frac{m-1}{V} \int_0^t dt^0 v(t^0) \chi(t - t^0)$$
$$- \frac{k}{V^2} \int_0^t dt^0 v(t^0) \kappa_1(t - t^0) - k \frac{q-1}{VV^2} \int_0^t dt^0 v(t^0) \kappa_2(t - t^0). \quad (22)$$

Now, defining the Laplace transformation over the time variable of a function $f(t)$ as $\hat{f}(s) \equiv \int_0^\infty dt f(t)e^{-st}$, and performing the Laplace transformation of both sides of Eq. (22), we get:

$$\hat{v}(s) = \frac{v_{eq}}{s} - \frac{k v_{eq} \hat{v}(s)}{s} - k [B] \hat{\chi}(s) - k \frac{q-1}{VV^2} \hat{\kappa_2}(s) - k \frac{|C|}{V^2} \hat{\kappa_1}(s)$$
$$\quad \quad \quad \quad + \frac{k |C| \hat{\kappa_2}(s)}{V^2} + k v_{eq} \hat{v}(s) \hat{\kappa_2}(s) \quad (23)$$

where $\frac{(m-1)(q-1)}{V^2} \simeq [B]|C| = v_{eq}$, which implies that the Laplace-transformed $v(t)$ function is given explicitly by

$$\hat{v}(s) = \frac{v_{eq}}{s \left( 1 + k [B] \hat{\chi}(s) + \frac{k \hat{\kappa_1}(s)}{V^2} + \frac{k |C| \hat{\kappa_2}(s)}{V^2} + k v_{eq} \right)} \quad (24)$$

Now, in virtue of equation (12), $\hat{v}(s)$ and the Laplace-transformed survival probability are related to each other as

$$\hat{P}(s) = \frac{1 - k \hat{v}(s)}{s} \quad (25)$$

Hence, the Laplace-transformed survival probability obeys:

$$\hat{P}(s) = \left[ s + \frac{k v_{eq}}{1 + k [B] \hat{\chi}(s) + \frac{k \hat{\kappa_1}(s)}{V^2} + \frac{k |C| \hat{\kappa_2}(s)}{V^2}} \right]^{-1} \quad (26)$$

It can be shown [2, 34] that $\hat{\chi}(s), \hat{\kappa_1}(s)$ and $\hat{\kappa_2}(s)$ can be replaced by their value for $s = 0$ to obtain the long time behaviour of $P(t)$. Thus, inverting the latter equation in the limit $t \rightarrow \infty$, the $A$ particle survival probability $P(t)$ decays exponentially as:
\begin{equation}
\begin{aligned}
P(t) \simeq \exp \left( -\frac{k[B][C]t}{1 + k[B]\tilde{\chi}(0) + \frac{k[\hat{\kappa}_1(0)}{V^2} + \frac{k[\hat{\kappa}_2(0)}{V^2}} \right), \end{aligned}
\end{equation}

and consequently, comparing the latter equation against the conventional form

\begin{equation}
P(t) \simeq \exp (-k_{\text{eff}}[B]t)\end{equation}

we have that the effective, overall reaction rate $k_{\text{eff}}$ describing the kinetics of diffusion-limited catalytically-activated reactions obeys:

\begin{equation}
\frac{1}{k_{\text{eff}}} = \frac{1}{k[C]} + \frac{[B]\tilde{\chi}(0)}{[C]} + \frac{\hat{\kappa}_1(0)}{V^2[C]} + \frac{\hat{\kappa}_2(0)}{V^2} \tag{29}
\end{equation}

which can be thought of as some "law of addition of inverse resistivities" and resembles (although has a more complex form) the classical result of Collins and Kimball for diffusion-limited trapping reactions with finite elementary reaction constant $k$. \cite{39}

Equation (29) is the central result of our analysis. Functions $\tilde{\chi}(0), \hat{\kappa}_1(0)$ and $\hat{\kappa}_2(0)$ are studied in the next section.

IV. RESIDENCE TIMES

In this section we show that functions $\tilde{\chi}(0), \hat{\kappa}_1(0)$ and $\hat{\kappa}_2(0)$ have an apparent physical interpretation in terms of different residence times of Brownian paths in finite domains and may be evaluated in explicit form.

A. One-particle’s residence time

The function $\tilde{\chi}(0)$ entering the effective reaction rate is defined by:

\begin{equation}
\tilde{\chi}(0) = \frac{1}{V^2} \int_0^\infty dt \int d\mathbf{r}_A d\mathbf{r}_A^0 H_A H_A^0 G(\mathbf{r}_A, t; \mathbf{r}_A^0, 0). \tag{30}
\end{equation}

One notices now that $\tilde{\chi}(0)$ can be interpreted as the total time spent in a sphere of radius $R$ by a Brownian particle $A$, which started its diffusion at time $t = 0$ at position $\mathbf{r}_A^0$ (see figure 3), averaged over all initial positions inside this sphere. In other words, this time is
the cumulative residence time inside the sphere up to an infinite observation time. In one or two dimensions it is infinite since the particle is certain to come back to the sphere, but in three dimensions it is finite since the particle can travel to infinity and thus is not certain to return.

This residence time is well known \[41\], and can be calculated rather straightforwardly. Indeed, integrating first over the time with the change of variable \( y = \frac{1}{t} \), we obtain:

\[
\hat{\chi}(0) = \frac{1}{V^{1/2}} \int dr_A dr_A^0 H_A H_A^0 \frac{1}{4\pi D_A} \frac{1}{||r_A - r_A^0||}
\]  

(31)

Now, since

\[
\int_0^{2\pi} \int_0^\pi \frac{1}{||r_A - r_A^0||} \sin \theta d\theta d\phi = \frac{4\pi}{\max(r_A, r_A^0)},
\]  

(32)

we have:

\[
\hat{\chi}(0) = \frac{1}{V^{1/2}} \frac{4\pi}{D_A} \int_0^R dr_A r_A^2 \int_0^R dr_A^0 (r_A^0)^2 \frac{1}{\max(r_A, r_A^0)}.
\]  

(33)

Splitting next the second integral into the sum \( \int_0^R = \int_0^{r_A^0} + \int_{r_A^0}^R \), we get:

\[
\hat{\chi}(0) = \frac{1}{V^{1/2}} \frac{16\pi R^5}{30D_A},
\]  

(34)

which yields, eventually, the following result:

\[
\hat{\chi}(0)^{-1} = \frac{5}{6} \frac{4\pi D_A R}{6}.
\]  

(35)

We hasten to remark that this expression, up to a numerical factor 5/6, coincides with the famous expression for the Smoluchowski reaction constant in three dimensions, \( K_S = 4\pi D_A R \).

**B. Two-particle’s joint residence time**

Now, we turn to two other functions - \( \hat{\kappa}_1(0) \) and \( \hat{\kappa}_2(0) \), entering equation \[41\]. The first one is formally defined by:
\[ \hat{\kappa}_1(0) = \frac{1}{Vr^2} \int_0^\infty dt \int dr_A dr_B^0 dr_B^0 H_A H_B \]
\[ \quad \times H_{A^0} H_{B^0} G(r_A, t; r_A^0, 0) G(r_B, t; r_B^0, 0). \]  

One may now notice that \( \hat{\kappa}_1(0) \) corresponds to the joint residence time in a sphere of radius \( R \) of particles \( A \) and \( B \), averaged over all initial positions of particles \( A \) and \( B \) inside the sphere (see figure 4).

Such a residence time has been amply discussed in another work [42], and here we will merely present the result of these calculations. It has been shown in Ref. [42] that \( \hat{\kappa}_1(0) \) is a complicated function of the diffusion coefficients \( D_A \) and \( D_B \) and is given explicitly by:

\[ \hat{\kappa}_1(0) = \frac{R^2}{20\pi} \left\{ \frac{1}{D_A} m \left( \frac{D_A}{D_B} \right) + \frac{1}{D_B} m \left( \frac{D_B}{D_A} \right) \right\} \]  

where

\[ m(x) = \frac{2 - 10 \ln(1 + x)}{x^{1/2}} - \frac{2 \ln(1 + x)}{x^{3/2}} + 16 \arctan(\sqrt{x}) - \frac{7}{2} x^{1/2}. \]

Finally, the last undetermined function \( \hat{\kappa}_2(0) \) obeys:

\[ \hat{\kappa}_2(0) = \frac{1}{Vr^2} \int_0^\infty dt \int du dr_A dr_A^0 dr_B^0 H_A H_B H_{A^0} H_{B^0} \]
\[ \quad \times G(r_A, t; r_A^0 + u, 0) G(r_B, t; r_B^0 + u, 0). \]  

One notices that it may be interpreted as the joint residence time of particles \( A \) and \( B \) inside a sphere when the particles initially start from a sphere separated by the vector \( u \) from the residence sphere (see figure 5). Note that the joint residence time \( \hat{\kappa}_2(0) \) is obtained when summing over all \( u \).

It is shown in Appendix that:

\[ \frac{Vr^2}{\hat{\kappa}_2(0)} = 4\pi R(D_A + D_B)^{385/334} \approx 1.15 \times 4\pi R(D_A + D_B). \]  

16
C. Effective reaction rate

Eventually, summing up the results of this section, we present an explicit expression for the effective reaction rate describing the kinetics of diffusion-limited catalytically-activated trapping reactions in terms of a suitably extended Wilemski and Fixman approach:

\[
\frac{1}{k_{\text{eff}}} = \frac{1}{k[C]} + \frac{[B]}{4\pi D_A R[C]} + \frac{1}{g(D_A, D_B)\pi^3 R^4[C]} + \frac{385}{334} \frac{1}{4\pi R(D_A + D_B)}
\]

(41)

where \( g^{-1}(D_A, D_B) = \frac{9}{320} \left\{ \frac{1}{D_A} m \left( \frac{D_A}{D_B} \right) + \frac{1}{D_B} m \left( \frac{D_B}{D_A} \right) \right\}, m(x) \) being defined in equation (38). Note that the correlations that are neglected in the Wilemski-Fixman approximation cannot be estimated precisely, so that it is difficult to find how they affect the different terms included into the reaction constant. However, these terms should not be considered as successive corrections to the usual expression for a bimolecular reaction. In fact, the joint residence time of two molecules on a catalytic site cannot be treated as a perturbation of the residence time of one molecule on this site, except in some limit cases. Clearly, our results should be compared to experimental or numerical results in order to be discussed.

Consider now the behavior of the effective reaction constant in Eq.(41) in several limiting cases. In non-catalytic systems, in which the \( A \) and \( B \) particles may react at any point, which corresponds to an evident situation with \([C] \to \infty\) (but \(k[C] = K\) is kept finite), we find from Eq.(41) that

\[
\frac{1}{k_{\text{eff}}} \approx \frac{1}{K} + \frac{385}{334} \frac{1}{4\pi R(D_A + D_B)}
\]

(42)

which represents, up to a numerical factor \(385/334 \approx 1.15\) in the second term, the classical Collins and Kimball result \(39\) describing the effective reaction rate for trapping reactions involving diffusive \( A \) and \( B \) particles in non-catalytic systems. Note that the numerical factor \(385/334\) comes from the description of the reactive process which differs between the Collins-Kimball approach and the present case.

Next, we turn to a different trivial situation when the particles \( B \) are present in a great excess, i.e. \([B] \to \infty\), such that their diffusion becomes irrelevant. In this limiting case we
find from Eq. (41) the following result:

$$k_{\text{eff}} \simeq \frac{5}{6} \frac{4\pi D_A R[C]}{[B]},$$

(43)

such that the $A$ particle survival probability follows

$$P(t) \simeq \exp \left( -\frac{5}{6} 4\pi D_A R[C] t \right)$$

(44)

This is, again, a standard Smoluchowski-type (up to a numerical factor $5/6$) prediction for trapping $A + C \rightarrow C$ reactions with immobile traps $C$.

Finally, some simple analysis shows that for sufficiently small $D_B$ the third term on the right-hand-side of Eq. (41) dominates and the effective reaction constant follows

$$k_{\text{eff}} \simeq g(D_A, D_B) \pi^3 R^4[C]$$

(45)

Surprising feature of this result is that $k_{\text{eff}}$ is proportional not to the first power of the reaction radius $R$, but to the fourth power of it! Curiously enough, this prediction coincides with earlier results obtained for trimolecular reaction of the form $A + A + C \rightarrow P + C$ using an extended Collins-Kimball approach [4]. This anomalous dependence has been confirmed by Molecular Dynamics simulations in Ref. [5].

V. FLUCTUATION-INDUCED LONG TIME BEHAVIOR

As shown in the introduction for trapping reactions involving diffusive particles, some fluctuation states can change significantly the kinetics of diffusion-limited, catalytically-activated trapping reactions. The particular systems with random placement of the catalytic subvolumens the long-time kinetic behavior is described by a stretched-exponential function, so that the usual kinetic laws do not hold.

Suppose that the $A$ particle is initially at the origin, the traps $B$ are also initially uniformly spread in the reaction bath and the immobile catalytic subvolumens $C$ are randomly distributed in the reaction bath such that the closest to the origin (i.e. to the $A$ particle) subvolumen is at the distance $\rho$ apart from it. Then, the $A$ particle survival probability is evidently bounded from below by

$$P(t) \geq P_{\text{lac}} \times P_A(\rho, t),$$

(46)
where $P_{lac}$ is the probability of having a spherical region of radius $\rho$ completely devoid of the catalytic subvolumes $C$ and $P_A(\rho, t)$ is, again, the probability that the $A$ particle will not leave this region up to time $t$; in these conditions, the diffusive $A$ particle may meet the diffusive traps $B$ many times but the reaction can not take place since the necessary ingredient of the elementary act - the presence of the catalytic subvolume $C$, will not be fulfilled.

Consequently, the $A$ particle survival probability obeys

$$P(t) \geq \exp \left( -\frac{4}{3} \pi \rho^3 [C] \right) \times \exp \left( -\frac{D_A t}{\rho^2} \right)$$

(47)

This bound is valid for any $\rho$ and we have to choose such value of it, which provides the maximal lower bound. Maximizing the right-hand-side of the latter equation, we find that the optimal $\rho$ is $\rho \sim \left( \frac{D_A t}{2\pi [C]} \right)^{1/5}$, which yields

$$P(t) \geq \exp \left( -\frac{3}{5} \left( \frac{2\pi}{(2\pi)^{2/5}} \right)^{2/5} \left( \frac{2\pi [C]}{D_A t} \right)^{3/5} \right),$$

(48)

i.e. the law similar to the one in Eq.(3) describing the long-time evolution of the survival probability of a particle diffusing in presence of immobile, randomly placed traps.

Since the right-hand-side of Eq.(48) decays slower than exponentially, we may infer that at long-times the kinetics of diffusion-limited catalytically-activated trapping reactions will be supported by such fluctuation states and will be described by a stretched-exponential function of time. The comparison of Eq.(48) with the classical kinetic law given by Eq.(31) shows that in all conditions the bound Eq.(48) should only be considered for exceedingly long times, so that the classical law usually holds.

VI. CONCLUSION

To conclude, in this paper we have studied the kinetics of the catalytically-activated diffusion-limited reactions in Eq.(1) in the special case when $B$ particles remain unaltered by reactions, i.e. the case of diffusion-limited catalytically-activated trapping reactions. In order to obtain an effective reaction rate for such bi-catalytic reactions, we have developed an analytical approach based on the work of Wilemski and Fixman [34], which allowed us to calculate analytically the effective reaction constant. We have shown that this effective reaction constant comprises several terms which may be interpreted in terms of the residence and
joint residence times of Brownian paths in finite domains. We have demonstrated that the effective reaction constant exhibits a non-trivial dependence on the reaction radii, the mean density of catalytic subvolumes and particles’ diffusion coefficients. Finally, we have discussed the impact of several fluctuation states giving rise to anomalous fluctuation-induced contributions to the long-time kinetic behavior in such systems. Except in this asymptotic case, however, the usual kinetic laws hold with the effective reaction constant calculated previously. These results can be very useful not only in the theory of heterogeneous catalysis, but also in biology, when reactions can only take place on specific sites.

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VIII. APPENDIX: JOINT RESIDENCE TIME IN A DISTANT SPHERE

In order to evaluate explicitly the function given in (39), we first integrate the two propagators over $u$:

$$
\int d\mathbf{u} G(\mathbf{r}_A + \mathbf{u}, t | \mathbf{r}_A^0, 0) G(\mathbf{r}_B + \mathbf{u}, t | \mathbf{r}_B^0, 0)
= \int d\mathbf{X} G_{D_A + D_B}(\mathbf{X}, t | \mathbf{X}^0, 0) G_{D_A + D_B}(\mathbf{r}_B - \mathbf{r}_A, t | \mathbf{r}_B^0 - \mathbf{r}_A^0, 0)
= G_{D_A + D_B}(\mathbf{r}_B - \mathbf{r}_A, t | \mathbf{r}_B^0 - \mathbf{r}_A^0, 0),
$$

(49)

where

$$
\mathbf{X} = \frac{D_B}{D_A + D_B}(\mathbf{r}_A + \mathbf{u}) + \frac{D_A}{D_A + D_B}(\mathbf{r}_B + \mathbf{u}),
$$

$$
\mathbf{X}^0 = \frac{D_B}{D_A + D_B}(\mathbf{r}_A^0 + \mathbf{u}) + \frac{D_A}{D_A + D_B}(\mathbf{r}_B^0 + \mathbf{u}),
$$

(50)

and $G_D$ is the Gaussian propagator associated to the diffusion coefficient $D$.

Then, the integral defined in (39) attains the following form:
\[ V'^2\hat{\kappa}_2(0) = \int_0^\infty dt d\mathbf{r}_A d\mathbf{r}_B d\rho_A d\rho_B H_{A^0} H_{B^0} \]
\[ = H_{\rho_A^0} H_{\rho_B^0} B^0 G_{D_A + D_B} (\rho_B - \rho_A, t|0, 0) \]  
(51)

where \(\rho_B = \mathbf{r}_B - \mathbf{r}_B^0\) and \(\rho_A = \mathbf{r}_A - \mathbf{r}_A^0\). The calculation of this equation requires the analysis of integrals of the following type:

\[ \int d\mathbf{r}_A H_{A^0} H_{\rho_A^0} \]  
(52)

which represent the overlapping area between two spheres (see figure 6).

This area can be straightforwardly obtained:

\[ \mathcal{A} = 2 \int_{\rho_A/2}^R dr \pi (R^2 - r^2) = \frac{\pi}{3} (R - \rho_A/2)^2 (4R + \rho_A). \]  
(53)

Next, we have to calculate the integral

\[ V'^2\hat{\kappa}_2(0) = \int_0^\infty dt d\mathbf{r}_A d\mathbf{r}_B H(2R - |\rho_A|)H(2R - |\rho_B|) \]
\[ \left[ \frac{\pi}{3} (R - \rho_A/2)^2 (4R + \rho_A) \right] \left[ \frac{\pi}{3} (R - \rho_B/2)^2 (4R + \rho_B) \right] \]
\[ \times G_{D_A + D_B} (\rho_B - \rho_A, t|0, 0). \]  
(54)

Using the explicit expression for the propagators and integrating them over the time variable, we obtain

\[ I = \int d\rho_A d\rho_B H(2R - |\rho_A|)H(2R - |\rho_B|) \frac{\rho_A^m \rho_B^n}{||\rho_B - \rho_A||} \]  
(55)

and

\[ \int_0^{2\pi} \int_0^\pi \frac{1}{||\rho_B - \rho_A||} \sin \theta_B d\theta_B d\phi_B = \frac{4\pi}{\max(\rho_A, \rho_B)} \]  
(56)

which yields
\[ I = (4\pi)^2 \int_0^{2R} d\rho_A \rho_A^{n+2} \int_0^{2R} d\rho_B \rho_B^{m+2} \frac{1}{\text{max}(\rho_A, \rho_B)} \]  

(57)

Consequently, the latter equation enables us to evaluate an explicit expression for \( \tilde{\kappa}_2(0) \):

\[ \frac{V'^2}{\tilde{\kappa}_2(0)} = 4\pi R(D_A + D_B) \frac{385}{334} \approx 1.15 \times 4\pi R(D_A + D_B). \]  

(58)

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[1] G.C. Bond, *Heterogeneous Catalysis: Principles and Applications*, (Clarendon Press, Oxford, 1987)

[2] S.A. Rice, *Diffusion-Limited Reactions*, eds.: C.H Bamford et al, Comprehensive Chemical Kinetics 25, 1985

[3] S.F. Burlatsky and M. Moreau, Phys. Rev. E 51, 2363 (1995)

[4] G. Oshanin and A. Blumen. J. Chem. Phys. 108, 1140 (1998)

[5] S. Toxvaerd, J. Chem. Phys. 109, 8527 (1998)

[6] Calkhoven CF and Ab G, Biochem J. 317, 329-42. (1996)

[7] P.J. Feibelman and J. Harris, Nature (London) 372, 135 (1994)

[8] A. Blumen, J. Klafter and G. Zumofen, in: Optical Spectroscopy of Glasses, ed.: I. Zschokke, (Reidel Publ., Dordrecht, 1986)

[9] A.A. Ovchinnikov and Ya.B. Zeldovich, Chem. Phys. 28, 214 (1978); S.F. Burlatsky, Teor. Exp. Chem. 14, 343 (1978); D. Toussaint and F. Wilczek, J. Chem. Phys. 78, 2642 (1983); S. Redner and K. Kang, Phys. Rev. Lett. 51, 1729 (1983)

[10] S.F. Burlatsky and A.A. Ovchinnikov, Zh. Eksp. Teor. Fiz. 92, 1618 (1987) [Sov. Phys. JETP 65, 908 (1987)]

[11] M. Bramson and J. L. Lebowitz, Phys. Rev. Lett. 61, 2397 (1988); J. Stat. Phys. 62, 297 (1991)

[12] B. Ya. Balagurov and V. T. Vaks, Zh. Eksp. Teor. Fiz. 65, 1939 (1973) [Sov. Phys. JETP 38, 968 (1974)]

[13] T. C. Lubensky, Phys. Rev. A 30, 2657 (1984); S. R. Renn, Nucl. Phys. B 275, 273 (1986); Th. M. Nieuwenhuizen, Phys. Rev. Lett. 62, 357 (1989)

[14] C. Monthus, G. Oshanin, A. Comtet and S.F. Burlatsky, Phys. Rev. E 54, 231 (1996)
[15] M.D. Donsker and S.R.S. Varadhan, Commun. Pure Appl. Math. 28, 525 (1975)

[16] L.A. Pastur, Theor. Math. Phys. 32, 88 (1977)

[17] P. Grassberger and I. Procaccia, J. Chem. Phys. 77, 6281 (1982)

[18] R.F. Kayser and J.B. Hubbard, Phys. Rev. Lett. 51, 6281 (1982)

[19] F. den Hollander and G.H. Weiss, in: Contemporary Problems in Statistical Physics, ed. G.H. Weiss (SIAM, Philadelphia, 1994)

[20] M. Fixman, J. Chem. Phys. 81, 3666 (1984)

[21] S.F. Burlatsky, O. Ivanov and J.M. Deutch, J. Chem. Phys. 97, 156 (1992)

[22] G. Oshanin, S.F. Burlatsky and M. Moreau, Adv. Colloid and Interface Sci. 49, 1 (1994)

[23] M. Tachiya, Radiat. Phys. Chem. 21, 167 (1983)

[24] A. Blumen, G. Zumofen and J. Klafter, Phys. Rev. B 30, 5379 (1984)

[25] S. Redner and K. Kang, J. Phys. A 17, L451 (1984)

[26] A. Szabo, R. Zwanzig and N. Agmon, Phys. Rev. Lett. 61, 2496 (1988)

[27] S.F. Burlatsky, M. Moreau, G. Oshanin and A. Blumen, Phys. Rev. Lett. 75, 585 (1995); D.P. Bhatia, M.A. Prasad and D. Arora, Phys. Rev. Lett. 75, 586 (1995)

[28] O. Bénichou, M. Moreau and G. Oshanin, Phys. Rev. E 61, 3388 (2000)

[29] A.J. Bray and R.A. Blythe, Phys. Rev. Lett. 89, 150601 (2002)

[30] G. Oshanin, O. Bénichou, M. Coppey and M. Moreau, Phys. Rev. E. 66, 060101(R) (2002)

[31] M. Moreau, G. Oshanin, O. Bénichou and M. Coppey, Phys. Rev. E 67, 045104(R) (2003)

[32] A.J. Bray, S.N. Majumdar and R.A. Blythe, Phys. Rev. E 67, 060102(R) (2003)

[33] A.M. Berezhkovskii, Yu.A. Makhnovskii and R.A. Suris, J. Stat. Phys. 57, 333 (1989); A.M. Berezhkovskii, Yu.A. Makhnovskii and R.A. Suris, J. Phys. A 22, L615 (1989)

[34] G. Wilemski and M. Fixman, J. Chem. Phys. 58, 4009 (1973)

[35] M. Doi, Chem. Phys. 11, 107 (1975)

[36] G.H. Weiss. J. Chem. Phys. 80, 2880 (1984)

[37] A. Perico and M. Battezzati, J. Chem. Phys. 75, 4430 (1981)

[38] M. Battezzati, and A. Perico. J. Chem. Phys. 74(8), 4527 (1981)

[39] F.C. Collins and G.E. Kimball, J. of Colloid Science. 4, 425 (1949)

[40] G. Oshanin, M. Moreau and S.F. Burlatsky, Adv. Colloid Inter. Sci. 49, 1 (1994)

[41] A. M. Berezhkovskii, V. Zaloj and N. Agmon, Phys. Rev. E 57, 3937 (1998)

[42] O. Bénichou, M. Coppey, Y. Klafter, M. Moreau, and G. Oshanin, J. Phys. A 38, 7205 (2005)
FIG. 2:
FIG. 3:
FIG. 4:
FIG. 5:
FIG. 6:
Figure legend

**Figure 1.** Schematic representation of the bi-catalytic reaction: volume $V$, comprising a single $A$ particle, $m$ diffusing $B$ particles and $q$ immobile subvolumen $C$.

**Figure 2.** Trimolecular reaction: the trajectories in bold type are those for which the reaction takes place, i.e. when one particle $A$ and one $B$ are jointly present in a catalytic domain.

**Figure 3.** Residence time of a Brownian particle in a sphere.

**Figure 4.** Joint residence time in a sphere. Blod lines: trajectories during common residence time.

**Figure 5.** Joint residence time in a distant sphere.

**Figure 6.** Overlapping area between two spheres.