

Kinetic description of diffusion-limited reactions in random catalytic media

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We study the kinetics of bimolecular, catalytically-activated reactions (CARs) in d -dimensions. The elementary reaction act between reactants takes place only when these meet in the vicinity of a catalytic site; such sites are assumed to be immobile and randomly distributed in space. For CARs we develop a kinetic formalism, based on Collins–Kimball-type ideas; within this formalism we obtain explicit expressions for the effective reaction rates and for the decay of the reactants' concentrations. © 1998 American Institute of Physics. [S0021-9606(98)50503-X]

I. INTRODUCTION

Many industrial and technological processes depend on catalytically activated reactions (CAR), whose understanding, however, used to be mainly phenomenological.¹ More microscopically inclined approaches emerged only during the last decades. Thus much progress was made in determining how reactions are promoted by specific catalytic substrates.² From the point of view of many-body effects much understanding was gained from an extensive study of the CO-oxidation on metal surfaces.³ The first type of research² is at the molecular level and, ideally, leads to K_{el} , the reaction rate for two molecules which meet at a catalytic site. However, the results of Refs. 3 demonstrate amply that the mere knowledge of K_{el} is not sufficient for determining the time evolution of the global reaction process. Thus the decay forms for the reactants' concentrations in CARs often deviate strongly from the results of formal-kinetics schemes.³ We note that such deviations are not encountered in CARs only, but are widespread,^{4–6} being due to many-body effects, often associated with fluctuations in the spatial distributions of the reacting species. Consequently, a robust, reliable description of CARs has to go beyond formal-kinetic considerations and to take the influence of higher-order particle correlations into account. Here we develop such an approach.

We start from the following system: The catalytic substrate consists of N , immobile catalytic sites (CSs), randomly placed in the d -dimensional reaction volume V . The reacting particles of type A are also randomly positioned; their initial average density is $n_0 = n_A(0)$. The A -particles diffuse with diffusion coefficient D . For simplicity we neglect sterical hindrances between the A s and also between A s and CSs. Furthermore, we assume that the A particles do not get trapped by the CS to form metastable A -CS complexes. Next, pairs of A particles may react upon encounter, if they

meet at a CS (Fig. 1). Formally, the elementary reaction step is



where $K_{el}(\mathbf{r})$, is a random function of the spatial variable \mathbf{r} ; $K_{el}(\mathbf{r})$ is strictly zero everywhere, except in the vicinity of any of the CSs, in which case $K_{el}(\mathbf{r}) = K_{el}$. Here we take the CSs to be randomly distributed in V with a constant average density n_C : thus the CSs' set and V have the same topological dimension. We hasten to add, however, that our approach can be readily extended to other distributions of CSs (i.e., regular or strongly inhomogeneous).

Since in V many microscopic reactions which follow Eq. (1) go on at the same time, the global picture becomes complex, and is, in general, properly described by an infinite hierarchy of coupled, differential equations.^{3,4} The analytical approach for CARs which we pursue here is based on the truncation of this coupled system at the level of third-order correlations; the latter are then accounted for through appropriate boundary conditions. For noncatalytic reactions in $3d$ this method was pioneered by Collins and Kimball⁸ (CK); it generalizes Smoluchowski's treatment of bimolecular chemical reactions (see, e.g., Ref. 6). The CK-approach provides both for the binary reaction $A + A \rightarrow 0$, and for the recombination reaction $A + B \rightarrow 0$ with $n_A(0) \neq n_B(0)$ a reasonable description^{8,9} of the experimentally observed kinetics over the entire time domain. We note, however, that the reaction $A + B \rightarrow 0$ with $n_A(0) = n_B(0)$ requires going beyond the CK-approach, in order to depict the kinetic behavior at very long times, where many-particle effects come into play.^{4–6,10}

Two remarks are here appropriate:

- In the case when the CSs cover V completely, CARs behave exactly as noncatalytic reactions. This special case is equivalent to the original CK-problem.
- Recently, the kinetics of the $A + B + C \rightarrow 0$ diffusion-limited reaction has been analyzed^{11,12} using an extension of the Smoluchowski approach (see, e.g., Ref. 6). Setting $A = B = C$ leads formally to the reaction $A + A + A \rightarrow 0$, for which the procedure shows fair

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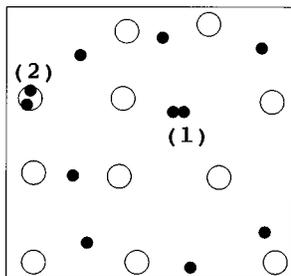


FIG. 1. Reactions in catalytic media. Open circles denote immobile catalytic sites; the filled circles stand for diffusive A particles. Case (1) shows a situation in which an encounter of A particles does not lead to a reaction, while in case (2) the reaction may take place.

agreement¹³ between the analytical predictions and the numerical data. For CARs one may now be tempted to follow a similar course, by setting $A=B$ in $A+B+C\rightarrow 0$, and identifying the C with the CSs. We will show, however, that such a procedure does not describe CARs well; in $1d$ and in $2d$ it does not lead to the proper long-time decay and in $3d$ it accounts only partially for the effect of CSs.

The paper is structured as follows: In Sec. II we formulate the model, by writing its basic equations, which allows us to extend the $3d$ CK-approach to arbitrary d and to CARs. Here we also point out the relation between the CK-CARs kinetics in d -dimensions and the trapping problem in $(d+d)$ -dimensions. In Sec. III we present explicit results for CAR's effective rates and for the reactants' decay; we compare these to the findings for noncatalytic reactions. Finally, we conclude with a summary of results in Sec. IV.

II. THE MODEL AND ITS BASIC EQUATIONS

We formulate our model on a d -dimensional ($d=1,2,3$) lattice with lattice spacing a . To each site of the lattice whose position is specified by the vector \mathbf{r} , we assign a time-independent variable $n_C(\mathbf{r})$ which assumes two possible values, namely 0 or 1, depending on whether the site is catalytic, $n_C(\mathbf{r})=1$, or not, $n_C(\mathbf{r})=0$. The catalytic substrate is the set of all N CSs; we denote it by $\{\mathbf{R}_k\}$, where \mathbf{R}_k is the vector of the k th CS. Here we take the \mathbf{R}_k to be random, independent, uniformly distributed variables. The CSs density is $n_C=V^{-1}\sum_{\mathbf{r}}n_C(\mathbf{r})$, where the sum runs over all lattice sites. The case when $\{\mathbf{R}_k\}$ forms different types of ordered geometrical arrays will be discussed elsewhere.

We start at $t=0$ with randomly distributed, identical A particles, with mean density n_0 . Each A particle moves by jumps to nearest-neighboring sites, the average time interval between successive jumps being τ . We disregard any excluded volume interactions; thus all A particles perform independent random walks, with the associated diffusion coefficient $D=a^2/2d\tau$.

Now, whenever an A particle lands on a catalytic site which is already occupied by another A , the two A s may react at a rate K_{el} . Reacting A s are immediately removed

from the system, whereas the corresponding CS remains unaffected. On the other hand, A s never react at noncatalytic sites.

A. Evolution of the local density and of the two-point joint density functions

Let $n(\mathbf{r},t)$ denote the local density of the A s. In continuous-time $n(\mathbf{r},t)$ obeys

$$\frac{d}{dt}n(\mathbf{r},t) = \frac{1}{2d\tau}\Delta_{\mathbf{r}}n(\mathbf{r},t) - K_{el}n_C(\mathbf{r})n(\mathbf{r}_1,\mathbf{r}_2;t)|_{\mathbf{r}_1=\mathbf{r}_2=\mathbf{r}}. \quad (2)$$

Here $n(\mathbf{r}_1,\mathbf{r}_2;t)$ is the two-point joint density function (i.e., the probability of having at time t an A at \mathbf{r}_1 and another A at \mathbf{r}_2), and the symbol $\Delta_{\mathbf{r}}$ stands for the following difference operator acting on \mathbf{r} :

$$\Delta_{\mathbf{r}}n(\mathbf{r},t) = -2dn(\mathbf{r},t) + \sum_{\mathbf{r}',nn}n(\mathbf{r}',t). \quad (3)$$

Here the sum runs over nearest neighbors only, i.e., $|\mathbf{r}'-\mathbf{r}|=a$.

Apart from the factor $n_C(\mathbf{r})$ stemming from the CS, Eq. (2) is the conventional rate equation for $A+A\rightarrow 0$ (see e.g. Ref. 8 for a discussion). On the right-hand side (rhs) of Eq. (2) the first term accounts for the particles' migration, while the second one describes the reaction. In standard fashion, the reaction term is taken to equal the product of the rate K_{el} , of the probability of having a pair of A particles at the same site and at the same time, and of $n_C(\mathbf{r})$; the latter factor is new here and is due to the fact that A s can react only at catalytic sites. We note that Eq. (2) embodies mean-field assumptions. In a more rigorous approach one has to use the three-body probability that two A s encounter each other at a CS; this probability is here decoupled by having it represented as the product of $n_C(\mathbf{r})$ and $n(\mathbf{r},\mathbf{r};t)$.

Before we turn to the analysis of the time evolution of $n(\mathbf{r}_1,\mathbf{r}_2;t)$, it is instructive to consider the result of the simple kinetic approach, which later will serve as reference. Taking the volume average of both sides of Eq. (2) and assuming that the nonlinear reaction term on the rhs of Eq. (2) decomposes into a product of averaged local densities, we arrive at the standard, formal-kinetic "law of mass action" (see, e.g., Ref. 7),

$$\frac{d}{dt}n_A(t) = -K_{el}n_Cn_A^2(t). \quad (4)$$

Here $n_A(t)=V^{-1}\sum_{\mathbf{r}}n(\mathbf{r},t)$ is the average density of the A s. From Eq. (4) the decay of $n_A(t)$ at sufficiently long times, $t\gg 1/n_CK_{el}n(0)$, follows:

$$n_A(t) \approx (n_CK_{el}t)^{-1}. \quad (5)$$

It is important to note that $n_A(t)$ given by Eq. (5) is independent of the spatial dimension and is the same in, say, $1d$ and $3d$. Second, the formal-kinetic approach predicts that

the effective reaction rate constant is $n_C K_{\text{el}}$ and is thus independent of other parameters, such as, e.g., the particles' diffusivities.

We now turn to the analysis of the time evolution of $n(\mathbf{r}_1, \mathbf{r}_2; t)$. We find that this quantity obeys (see, e.g., Ref. 13)

$$\frac{d}{dt} n(\mathbf{r}_1, \mathbf{r}_2; t) = \frac{1}{2d\tau} (\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2}) n(\mathbf{r}_1, \mathbf{r}_2; t) + K_{\text{el}} T, \quad (6)$$

in which the terms in brackets stem from the particles' motion, while T is a combination of joint three-point distributions and arises due to the reaction between the A s.

Equations (2) and (6) are the first two equations of an infinite hierarchy of coupled differential equations (CDE). Such a hierarchy of CDE cannot be solved exactly; in order to compute the evolution of $n(\mathbf{r}, t)$ and thus of its mean value $n_A(t)$ one has to resort to some approximate methods.

B. The Collins–Kimball's 3d problem and its extension to arbitrary d

Here we continue by recalling Collins and Kimball's (CK) analysis⁸ of reaction kinetics. As discussed, their problem is identical to 3d CARs in a "completely" catalytic medium, i.e., such that $n_C = 1$. In Ref. 8 the hierarchy of CDE is truncated at the level of the third-order correlations, i.e., T in Eq. (6) is set to zero, and the reaction between particles is accounted for by introducing a "radiation" boundary condition on $n(\mathbf{r}_1, \mathbf{r}_2; t)$; CK stipulate that the local reaction rate at any point \mathbf{r} , i.e., $K_{\text{el}} n(\mathbf{r}, \mathbf{r}; t)$, should be exactly equal to the diffusive current of pairs of A particles into this point. Accompanied by the following boundary and initial conditions:

$$n(\mathbf{r}_1, \mathbf{r}_2; t) \Big|_{|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty} \rightarrow n_A^2(t), \quad (7)$$

and

$$n(\mathbf{r}_1, \mathbf{r}_2; t=0) = n_A^2(0) = n_0^2, \quad (8)$$

which signify that correlations in the particles' positions vanish at large separations and that initially the particles are uniformly distributed in V , the CK-approach results in a closed system of linear equations; these allow then calculations of the effective reaction rate and the time evolution of $n_A(t)$. We note that in their original paper⁸ CK have only considered the 3d case. Clearly, however, in the formulation of Eq. (6), extending the CK-approach to systems of arbitrary spatial dimension d is straightforward, as we show in the following.

Solving Eq. (6) (with $T=0$) subject to the radiation boundary condition and the conditions in Eqs. (7) and (8), CK find⁸ that $n_A(t)$ obeys in 3d,

$$\frac{d}{dt} n_A(t) = -K_{\text{eff}}(t) n_A^2(t). \quad (9)$$

Equation (9) is similar to the "law of mass action" displayed in Eq. (4), since for both the rhs are proportional to the second power of $n_A(t)$, in agreement with the elementary reaction act. The difference between Eqs. (9) and (4) is that

now $K_{\text{eff}}(t)$ stands for an effective (in general, time-dependent) rate coefficient, which arises mainly from the particles' diffusion.

Now $K_{\text{eff}}(t)$ can be expressed through its Laplace-transform,

$$K_{\text{eff}}(\lambda) = \int_0^\infty dt \exp(-\lambda t) K_{\text{eff}}(t), \quad (10)$$

for which CK find, for identical reacting particles in the limit $\lambda \ll D/r_0^2$, where r_0 denotes the reaction radius,

$$\frac{1}{K_{\text{eff}}(\lambda)} = \frac{\lambda}{K_{\text{el}}} + \frac{\lambda}{8\pi D r_0}. \quad (11)$$

The second term on the rhs of Eq. (11), i.e., $\lambda/8\pi D r_0$, stems from the Laplace-transformed Smoluchowski constant; the latter equals the particles' current towards the surface of a single, immobile, adsorbing three-dimensional sphere of radius r_0 .

This result is actually a special case of the general, d -dimensional expression for $K_{\text{eff}}(\lambda)$, which can be derived within the framework of the CK approach, as we briefly outline now.

Consider the behavior of the two-point joint density function $n(\mathbf{r}_1, \mathbf{r}_2; t)$. Within the CK approach it obeys Eq. (6) with $T=0$,

$$\frac{\partial}{\partial t} n(\mathbf{r}_1, \mathbf{r}_2; t) = D(\Delta_{\mathbf{r}_1} + \Delta_{\mathbf{r}_2}) n(\mathbf{r}_1, \mathbf{r}_2; t), \quad (12)$$

where $\Delta_{\mathbf{r}_i}$ denote the continuous-space Laplace operators. Note that Eq. (12) is a $(d+d)$ -dimensional diffusion equation. Now, Eq. (12) is to be solved subject to the initial and boundary conditions of Eqs. (7) and (8), as well as to the CK radiation boundary condition

$$K_{\text{el}} n(\mathbf{r}_1, \mathbf{r}_2; t) = D(\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) n(\mathbf{r}_1, \mathbf{r}_2; t) \Big|_{|\mathbf{r}_1 - \mathbf{r}_2| = r_0}. \quad (13)$$

As already observed by CK for noncatalytic reactions, $n(\mathbf{r}_1, \mathbf{r}_2; t)$ depends only on $z = |\mathbf{r}_1 - \mathbf{r}_2|$, the relative distance between \mathbf{r}_1 and \mathbf{r}_2 , and consequently, the $(d+d)$ -dimensional Eqs. (12) and (13) reduce to the effectively d -dimensional equations,

$$\frac{\partial}{\partial t} n(z; t) = 2D \left(\frac{\partial^2}{\partial z^2} + \frac{d-1}{z} \frac{\partial}{\partial z} \right) n(z; t), \quad (14)$$

and

$$K_{\text{el}} n(z; t) = 2D \sigma_d \frac{\partial n(z; t)}{\partial z} \Big|_{z=r_0}. \quad (15)$$

Here $\sigma_d = 2\pi^{d/2} r_0^{d-1} \Gamma^{-1}(d/2)$ denotes the surface area of the d -dimensional sphere of radius r_0 , with $\Gamma(x)$ being the Gamma-function.¹⁴ Equations (14) and (15) generalize to arbitrary dimensions the 3d equations studied by CK.⁸

Now, the solution of Eq. (14) subject to the conditions of Eqs. (7), (8), and (15) can be readily obtained by Laplace transforming with respect to t . The Green's function $G_d(z; \lambda)$ of the equation

$$\lambda G_d(z; \lambda) = 2D \left(\frac{\partial^2}{\partial z^2} + \frac{d-1}{z} \frac{\partial}{\partial z} \right) G_d(z; \lambda) \quad (16)$$

obeys

$$G_d(z; \lambda) = \frac{2}{(8\pi D)^{d/2}} \left(\frac{z^2}{8D\lambda} \right)^{(2-d)/4} \tilde{K}_{1-d/2} \left(\sqrt{\frac{\lambda}{2D}} z \right), \quad (17)$$

in which $\tilde{K}_\nu(x)$ is the modified Bessel function.¹⁴ The solution of the Laplace transformed Eq. (14) [note the occurrence of an additional term, $-n_0^2$, on the lhs, as compared to Eq. (16)], has the form

$$n(z; \lambda) = \frac{n_0^2}{\lambda} [1 + A(\lambda) G_d(z; \lambda)], \quad (18)$$

in which the conditions Eqs. (7) and (8) have already been incorporated. In Eq. (18) $A(\lambda)$ is a constant, which has to be chosen in such a way that the boundary condition, Eq. (15), is also satisfied. Substituting Eq. (18) into Eq. (15) we find that $A(\lambda)$ is

$$A(\lambda) = -G_d^{-1}(r_0; \lambda) \left\{ 1 - \frac{2D\sigma_d}{K_{el}} [\ln G_d(r_0; \lambda)]' \right\}^{-1}, \quad (19)$$

where the prime stands for the derivative with respect to r_0 .

This provides a complete solution of the CK-problem in d -dimensions. In order to calculate the effective rate constant, $K_{eff}(\lambda)$, we have merely to insert Eq. (18) with Eq. (19) into the rhs of Eq. (15). This yields

$$K_{eff}(\lambda) = -\frac{2D\sigma_d}{\lambda} [\ln G_d(r_0)]' \times \left\{ 1 - \frac{2D\sigma_d}{K_{el}} [\ln G_d(r_0)]' \right\}^{-1}. \quad (20)$$

Equation (20) takes a physically more revealing form, if we rewrite it as

$$\frac{1}{K_{eff}(\lambda)} = \frac{\lambda}{K_{el}} + \frac{1}{K_d(D; \lambda)}, \quad (21)$$

where

$$K_d(D; \lambda) = -\frac{2D\sigma_d}{\lambda} [\ln G_d(r_0)]' = \frac{2D\sigma_d}{\lambda} \left(\frac{\lambda}{2D} \right)^{1/2} \frac{\tilde{K}_{d/2} \left(\sqrt{\frac{\lambda}{2D}} r_0 \right)}{\tilde{K}_{1-d/2} \left(\sqrt{\frac{\lambda}{2D}} r_0 \right)}. \quad (22)$$

Equation (21) resembles the electrostatic law of addition of parallel resistances and displays the combined effect of two controlling factors—the effect of the elementary reaction act and the effect of the transport of particles towards each other. Notice now that for $K_{el} = \infty$ the rate $K_d(D; \lambda)$ is the Laplace transform of the diffusive current towards the surface of a single immobile, perfectly adsorbing d -dimensional sphere

of radius r_0 . Consequently, $K_d(D; \lambda)$ is the d -dimensional analog of the Smoluchowski constant and Eq. (21) represents the desired generalization of Eq. (11) to the d -dimensional case. We hasten to remark that Eq. (21) has already been obtained in Ref. 10 in a different framework, based on the analysis of the third-order joint density functions; Eq. (21) also follows from the general results of Ref. 15, which considered reversible reactions.

The behavior of $K_d(D; \lambda)$ depends in a fundamental way on the spatial dimension d . As is well-known (see e.g., Ref. 9), in low dimensions ($d \leq 2$) $\lambda K_d(D; \lambda)$ tends to zero for $\lambda \rightarrow 0$ ($t \rightarrow \infty$). To be explicit, in the limit $\lambda \leq D/r_0^2$ the parameter $K_d(D; \lambda)$ determined by Eq. (22) equals $(8D/\lambda)^{1/2}$ for $d=1$ and $8\pi D/[\lambda \ln(8D/r_0^2\lambda)]$ for $d=2$. In higher dimensions ($d > 2$) $\lambda K_d(D; \lambda)$ approaches constant values at long times; the values for $K_d(D; \lambda)$, for, say $d=3, 4$ and 6 turn out to be $8\pi D r_0/\lambda$, $8\pi^2 D r_0^2/\lambda$ and $8\pi^3 D r_0^4/\lambda$, respectively. The dependence of $K_{eff}(\lambda)$ on d , arising due to the second term in Eq. (21), leads, especially for $d \leq 2$, to deviations of the decay laws from Eq. (5).

C. The CK-approach extended to CARs

After this overview of the CK approach we now extend it to CARs. Following Ref. 8 we truncate the hierarchy at the level of the third-order joint density functions, which yields the continuous-space Eq. (12). Next, in our system only the encounters which happen on a CS may lead to a reaction. Thus, the radiation boundary condition is to be imposed on the CSs only. Denoting by S_k the surface of the k th CS, we hence have that instead of Eq. (13) the following boundary condition should be imposed on $n(\mathbf{r}_1, \mathbf{r}_2; t)$:

$$K_{el} n(\mathbf{r}_1, \mathbf{r}_2; t)|_{\mathbf{r}_1, \mathbf{r}_2 \in S_k} = D(\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) n(\mathbf{r}_1, \mathbf{r}_2; t)|_{\mathbf{r}_1, \mathbf{r}_2 \in S_k}. \quad (23)$$

For simplicity we take in the continuum S_k to be the surface of the d -dimensional sphere of radius r_0 centered at R_k . Equations (12) and (23) are complemented by the initial condition, Eq. (8), and by the boundary condition, Eq. (7); this constitutes a closed system of linear equations which allows the computation of $n(\mathbf{r}_1, \mathbf{r}_2; t)$. In turn, knowing $n(\mathbf{r}_1, \mathbf{r}_2; t)$ and using Eqs. (2) and (23), we have

$$\frac{d}{dt} n_A(t) = -\frac{D}{V} \sum_k (\nabla_{\mathbf{r}_1} + \nabla_{\mathbf{r}_2}) n(\mathbf{r}_1, \mathbf{r}_2; t) \Big|_{\mathbf{r}_1, \mathbf{r}_2 \in S_k}, \quad (24)$$

which defines the evolution of the property of interest, namely of $n_A(t)$, the mean density of As.

D. Relation between CARs and the trapping reaction

We note now that it is expedient to view Eqs. (12), (23), (7), and (8) from a somewhat different perspective, which will allow us to find eventually an approximate analytical solution for them, and to explain, on simple physical grounds, some seemingly surprising results. As a matter of fact, what the CK approach enables us to do it is to reduce the problem of computing the rates of binary reactions, tak-

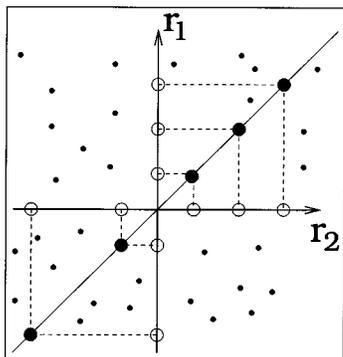


FIG. 2. Open circles on the r_1 and r_2 -axis denote the catalytic sites; filled circles give the corresponding positions of traps and small black circles denote diffusive compound particles.

ing place in d -dimensional catalytic systems, to the analysis of (imperfect) trapping in $(d+d)$ -dimensional systems. The latter problem, and especially its quantum mechanical counterpart, the scattering of quantum particles by immobile impurities, have been extensively investigated (see, e.g., Refs. 15–18, and references therein).

The relation between the CAR and the trapping problem can be mostly simply illustrated for the binary CAR in $d = 1$. Note that Eqs. (12) and (23) describe the evolution of the local density of some compound particles, moving with diffusion coefficient¹⁹ D on a two-dimensional plane (r_1, r_2) , where r_1 and r_2 are scalar variables. The particles may disappear at the locations (R_k, R_k) of the traps, placed on the diagonal $r_1 = r_2$ (Fig. 2). Physically, each compound particle is a pair of A particles, whose coordinates on the one-dimensional line are r_1 and r_2 , respectively; consequently, $r_1 = r_2 = R_k$ are the only points where two A s may enter into reaction, in which case the compound particle may be destroyed by the trap at R_k with a finite probability related to K_{el} . In this language, the reaction rate of the CAR, i.e. the rhs of Eq. (24), attains a quite lucid meaning: It equals the volume-averaged diffusive current of compound particles through the S_k . One can now note the fundamental distinction between systems with $n_C = 1$ and with $n_C < 1$: The former case corresponds to a situation in which the traps cover the diagonal $r_1 = r_2$ completely; here $n(r_1, r_2)$ depends only on the relative distance between r_1 and r_2 , i.e., one has $n(r_1, r_2) = n(r_1 - r_2)$, which then reduces the problem to $1d$. On the other hand, in the case $n_C < 1$ the traps fill only some portion of the diagonal, and thus the kinetics remains essentially two-dimensional, since $n(r_1, r_2)$ depends on both spatial variables; compound particles can cross the diagonal harmlessly, i.e., with zero reaction probability, through the gaps between the traps.

Returning now to the general problem of CARs in d -dimensional media, the corresponding mapping leads to considering a trapping problem involving compound particles diffusing in a $(d+d)$ -dimensional space in the presence of imperfect traps placed on a d -dimensional substrate.

Several analytical approaches have been developed to describe the kinetics of trapping in systems with nonuniform

spatial distributions of traps (see, e.g., Refs. 6 and 15). We will search for the solution of Eqs. (12) and (23) in the spirit of the Green's function method.¹⁷ Here we merely outline the steps involved, and address the reader for more details to Refs. 15 and 17.

One starts with the Laplace-transformed Green's function solution $G_{d+d}(\boldsymbol{\rho}; \lambda)$ of the $(d+d)$ -dimensional diffusion, Eq. (12),

$$G_{d+d}(\boldsymbol{\rho}; \lambda) = \frac{2}{(4\pi D)^d} \left(\frac{|\boldsymbol{\rho}|^2}{4D\lambda} \right)^{(1-d)/2} \tilde{K}_{1-d} \left(\sqrt{\frac{\lambda}{D}} |\boldsymbol{\rho}| \right), \quad (25)$$

in which $\boldsymbol{\rho} = (\mathbf{r}_1, \mathbf{r}_2)$. Furthermore, the Laplace-transform of $n(\mathbf{r}_1, \mathbf{r}_2; t)$ is represented as a series in which each term is the Green's function solution of Eq. (12), centered around the position of the k th trap,

$$n(\mathbf{r}_1, \mathbf{r}_2; \lambda) = \frac{n_0^2}{\lambda} + \sum_k C_k(\lambda) G_{d+d}(\boldsymbol{\rho} - \boldsymbol{\Theta}_k; \lambda), \quad (26)$$

with the $d+d$ -dimensional vector $\boldsymbol{\Theta}_k = (\mathbf{R}_k, \mathbf{R}_k)$. Equation (26) obeys automatically Eqs. (12), (7), and (8); the coefficients $C_k(\lambda)$ are to be chosen in such a way that Eq. (23) is satisfied. Substituting Eq. (26) into Eq. (23) we arrive at the following system of N linear equations for the $C_k(\lambda)$:

$$-\frac{n_0^2}{\lambda} = [K_{el}^{-1} + G_{d+d}(r_0; \lambda)] C_j(\lambda) + \sum_k ' C_k(\lambda) G_{d+d}(\boldsymbol{\Theta}_k - \boldsymbol{\Theta}_j; \lambda), \quad (27)$$

where $j = 1, \dots, N$, and the prime indicates that the sum in Eq. (27) runs over all k with the exception of $k = j$.

The exact solution of Eqs. (27) for a given distribution of $\{\mathbf{R}_k\}$ requires the inversion of the random matrix $\|G_{d+d}(\boldsymbol{\Theta}_k - \boldsymbol{\Theta}_j; \lambda)\|$, see Ref. 17. Neglecting fluctuations in the distribution of the CSs, in which case the Eqs. (27) simplify considerably, one obtains

$$C(\lambda) \approx - \frac{n_0^2}{\lambda [K_{el}^{-1} + G_{d+d}(r_0; \lambda) + M_{scr}]}, \quad (28)$$

where M_{scr} denotes the screening integral (or "shielding" integral in the formulation of Ref. 15),

$$M_{scr} = \left\langle \sum_k ' G_{d+d}(\boldsymbol{\Theta}_k - \boldsymbol{\Theta}_j; \lambda) \right\rangle \approx n_C \int \int d\mathbf{r}_1 d\mathbf{r}_2 \delta(\mathbf{r}_1 - \mathbf{r}_2) G_{d+d}(\boldsymbol{\rho}; \lambda). \quad (29)$$

In Eq. (29) the brackets denote averaging over the distribution of $\{\mathbf{R}_k\}$, and the integrations with respect to the variables \mathbf{r}_1 and \mathbf{r}_2 extend over the whole volume occupied by CSs, excluding the volume of a d -dimensional sphere of radius r_0 . In the following we turn to the limit $N, V \rightarrow \infty$, while keeping the ratio N/V fixed, $N/V = n_C$. We note that Eq. (29) is only approximate, since excluded-volume aspects between the CSs are neglected; this limits the applicability of the expression to n_C sufficiently small. We note also that

within our CK-type description the dependence of the effective reaction rate on the geometry of the catalytic substrate and/or the distribution of the CSs enters only through the screening integral M_{scr} . Consequently, any other geometry of the substrate (it can be, for instance, a two-dimensional convoluted surface of porous materials, imperfect crystallites with broken faces, kinks and steps, or polymers in solution¹) can be accounted for by the use of the appropriate distribution functions and by corresponding integrations in Eqs. (29). In particular, the details of the averaging procedure in the case when the integrations extend over Gaussian polymer chains in solution have been discussed in Ref. 20.

III. RESULTS

Now, combining Eqs. (26), (28), and (29), we find from Eq. (24) that $n_A(t)$ obeys the effective ‘‘law of mass action’’ in Eq. (9). In the limit $\lambda \ll \lambda_D = D/r_0^2$, ($t \gg \tau_D = r_0^2/D$), when M_{scr} and $G_{d+d}(r_0; \lambda)$ reduce to $M_{\text{scr}} \approx n_C [\lambda K_d(D; \lambda)]^{-1}$ and $G_{d+d}(r_0; \lambda) \approx [\lambda K_{d+d}(D/2; \lambda)]^{-1}$, the effective rate constant attains for $n_C r_0^d \ll 1$ the form

$$\frac{1}{K_{\text{eff}}(\lambda)} = \frac{\lambda}{n_C K_{\text{el}}} + \frac{1}{K_d(D; \lambda)} + \frac{1}{n_C K_{d+d}(D/2; \lambda)}, \quad (30)$$

which represents the desired generalization of the CK-type result, Eq. (21), to CARs. Equation (30) is the main result of our analysis and allows to compute $n_A(t)$, which is related to $K_{\text{eff}}(t)$ through Eq. (9). Hence,

$$n_A(t) = n_0 \left[1 + n_0 \int_0^t d\tau K_{\text{eff}}(\tau) \right]^{-1}. \quad (31)$$

Let us consider first the 3d case. We recall the explicit forms of the parameters $K_d(D; \lambda)$, presented in the text after Eq. (22), so that in 3d Eq. (30) takes the following form ($n_C r_0^3 \ll 1$):

$$\frac{1}{K_{\text{eff}}(\lambda)} = \frac{\lambda}{n_C K_{\text{el}}} + \frac{\lambda}{8\pi D r_0} + \frac{\lambda}{4\pi^3 D r_0^4 n_C}, \quad (32)$$

which signifies that in the limit $t \rightarrow \infty$ the effective rate constant $K_{\text{eff}}(t)$ approaches a constant value,

$$\frac{1}{K_{\text{eff}}} = \frac{1}{n_C K_{\text{el}}} + \frac{1}{8\pi D r_0} + \frac{1}{4\pi^3 D r_0^4 n_C}. \quad (33)$$

Consequently, from Eq. (31) we have for $n_A(t)$ in three-dimensions and large t ,

$$n_A(t) \approx (K_{\text{eff}} t)^{-1}, \quad (34)$$

where K_{eff} is given by Eq. (33). Equation (34) signifies that in 3d catalytic systems $n_A(t)$ is inversely proportional to t , i.e., is qualitatively the same as the formal-kinetic Eq. (5). Now, Eq. (33) differs from Eq. (5), since here K_{eff} replaces $n_C K_{\text{el}}$. Note from Eq. (33) that K_{eff} reduces to $n_C K_{\text{el}}$ only for $D \rightarrow \infty$. Thus for finite D , the rate K_{eff} depends both on the reaction radius and on the mean density of CSs. The difference between the CK-result for $n_C r_0^3 \sim 1$ and for CARs with $n_C r_0^3 \ll 1$ is the last term in Eq. (30), which is due to the Green’s function solution of the diffusion equation in 6d.

For small values of the parameter $n_C r_0^3$ and for $D r_0^4 \ll K_{\text{el}}$, the last term in Eq. (30) provides the dominant contribution to the effective rate constant K_{eff} . In this case Eq. (30) reduces to the result of Ref. 12, obtained for the three-body problem.

Consider next the evolution of $n_A(t)$ in low dimensional systems, i.e., for $d=1$ and $d=2$. We have from Eq. (30) that in 1d $K_{\text{eff}}(\lambda)$ is given by ($n_C r_0 \ll 1$)

$$\frac{1}{K_{\text{eff}}(\lambda)} = \frac{\lambda}{n_C K_{\text{el}}} + \left(\frac{\lambda}{8D} \right)^{1/2} + \frac{\lambda \ln(4D/\lambda r_0^2)}{4\pi D n_C}. \quad (35)$$

Now, Eq. (35) shows that in 1d catalytic systems the kinetics is richer than in the 3d case; comparing the different terms in Eq. (35) one readily notices that depending on λ each of these terms may dominate $K_{\text{eff}}(\lambda)$; hence a succession of different kinetic regimes may be observed in the time domain. When $4\pi D/K_{\text{el}}$ is sufficiently large and $n_C r_0$ is sufficiently small, so that $n_C r_0 \ll \exp(-4\pi D/K_{\text{el}})$, we can consider three different intervals, namely,

$$\lambda_D \exp(-4\pi D/K_{\text{el}}) \ll \lambda \ll \lambda_D, \quad (36a)$$

$$\lambda_D (n_C r_0)^2 \ll \lambda \ll \lambda_D \exp(-4\pi D/K_{\text{el}}), \quad (36b)$$

and

$$\lambda \ll \lambda_D (n_C r_0)^2. \quad (36c)$$

- In the regime described by Eq. (36a), the main contribution to $K_{\text{eff}}(\lambda)$ comes from the first term on the rhs of Eq. (35); in this kinetically-controlled regime $K_{\text{eff}}(t) = n_C K_{\text{el}}$ and hence coincides with the result of the formal-kinetic approach. This behavior persists until $t_{kc} \approx \tau_D \exp(4\pi D/K_{\text{el}})$, which can be rather large for $D \gg K_{\text{el}}$. On the other hand, such a behavior is unobservable for $K_{\text{el}} \gg 4\pi D$, exemplified by instantaneous reactions in Eq. (1).
- In the regime described by Eq. (36b) $K_{\text{eff}}(\lambda)$ is dominated by the third term on the rhs of Eq. (35), so that $K_{\text{eff}}(t) \approx 4\pi D n_C / \ln(4t/\tau_D)$. This 1d CAR expression is reminiscent (apart of the factor n_C and the replacement $D \rightarrow D/2$) of the classical result of Ref. 9 for the kinetics of binary reactions in 2d. One thus expects that at this stage $n_A(t) \sim \ln(t)/t$. The appearance of such an effectively 2d regime for CAR in 1d constitutes the principal difference between the CAR kinetics for $n_C r_0 \ll 1$ and the kinetics of noncatalytic binary reactions in 1d. We also note that such an effectively 2d behavior was predicted in Ref. 12 for 1d reactions of $A+B+C \rightarrow 0$ type as the final kinetic stage; in our case, when C does not disappear in the reaction act, Eq. (36b) determines only an intermediate transient stage, which may be observed for times smaller than a typical time t_{tr} , where $t_{tr} = 1/D n_C^2$. Consequently, for 1d systems with very low densities of catalytic sites ($n_C r_0 \ll 1$) such an effectively 2d behavior can last over extended time periods.
- Finally, in the limit of very small λ , Eq. (36c), $K_{\text{eff}}(\lambda)$ is determined by the second term on the rhs of Eq. (35), i.e., $K_{\text{eff}}(\lambda) \approx (8D/\lambda)^{1/2}$. Thus for large t the rate

$K_{\text{eff}}(t) \approx (8D/\pi t)^{1/2}$ is independent of n_C . Hence for large times the qualitative decay behavior is the same for CARs and for noncatalytic reactions. Actually, this seemingly surprising behavior has already been observed numerically²¹ and has a simple physical interpretation, which we will discuss below. Explicitly, we find that the mean density of A particles decays in the limit $t \gg t_{\text{tr}}$ as

$$n_A(t) \sim (\pi/32Dt)^{1/2}. \quad (37)$$

We turn next to the analysis of CAR in $2d$. Now Eq. (30) reads

$$\frac{1}{K_{\text{eff}}(\lambda)} = \frac{\lambda}{n_C K_{\text{el}}} + \frac{\lambda \ln(8D/r_0^2 \lambda)}{8\pi D} + \frac{\lambda}{4\pi^2 D r_0^2 n_C}. \quad (38)$$

On comparing different terms on the rhs of Eq. (38) we infer that in $2d$ two different kinetic stages may take place. Namely, for λ from the interval

$$\lambda_D \exp\left(-\frac{8\pi D}{n_C K_{\text{el}}} - \frac{1}{\pi n_C r_0^2}\right) \ll \lambda \ll \lambda_D, \quad (39a)$$

the sum of the first and of the third term, which both have the same λ -dependence, determines $K_{\text{eff}}(\lambda)$, while for smaller λ , such that

$$\lambda \ll \lambda_D \exp\left(-\frac{8\pi D}{n_C K_{\text{el}}} - \frac{1}{\pi n_C r_0^2}\right), \quad (39b)$$

the main contribution to the effective rate constant is given by the second term on the rhs of Eq. (38).

- (a) In the regime described by Eq. (39a) $K_{\text{eff}}(\lambda)$ is controlled by the constraints imposed by the elementary reaction act and by the diffusion in $4d$. For such a regime we obtain

$$n_A(t) \approx \left(\frac{1}{K_{\text{el}}} + \frac{1}{4\pi^2 D r_0^2}\right) (n_C t)^{-1}. \quad (40)$$

According to Eq. (39a), the regime described by Eq. (40) is a transient one and persists until $t_{\text{tr}} \approx \tau_D \exp[(D/n_C K_{\text{el}}) + (1/r_0^2 n_C)]$.

- (b) In the final stage described by Eq. (39b), the main contribution to $K_{\text{eff}}(\lambda)$ comes from the second term in Eq. (38). Thus, similarly to the behavior in $1d$, $K_{\text{eff}}(\lambda)$ in the limit $\lambda \rightarrow 0$ is independent of n_C . This implies that also in $2d$ for large times the kinetics for CARs is the same as for noncatalytic reactions. We find here

$$n_A(t) \sim \frac{\ln(8Dt/r_0^2)}{8\pi Dt}, \quad (41)$$

which coincides with the result of Ref. 9 obtained for the long-time kinetics of noncatalytic reactions. We furthermore note that the very long time decay behavior is reached much more slowly in $2d$ than in $1d$; the crossover time t_{tr} is in $2d$ an exponential function of n_C^{-1} and is thus substantially larger than its $1d$ counterpart, which goes as n_C^{-2} .

Lastly, we discuss the physical origin of the fact that in low dimensions the CARs long-time decay is independent of

n_C . Here, the analogy between the CAR kinetics in d -dimensions and the trapping problem in $(d+d)$ -dimensions again turns out to be very fruitful. Let us consider first the case $d=1$. The equivalent problem is a $d=2$ system with compound particles diffusing in the presence of traps placed on the diagonal $r_1=r_2$, (see Fig. 2). Now, it is well-known⁹ that even in the presence of a single trap the particles' density profile around the trap is not stationary; there is a zone around the trap, which is depleted of particles and whose size grows with time as \sqrt{t} . For the situation depicted in Fig. 2 at short times (such that $n_C \sqrt{Dt} \ll 1$) the depletion zones of different traps are well separated from each other. Consequently, at short times the traps act independently and the Laplace-transformed particle current towards a given trap is given by Eq. (21), $J(\lambda) \approx K_{\text{el}} K_2(D/2; \lambda) / [K_{\text{el}} + K_2(D/2; \lambda)]$. The effective rate, which is given by Eqs. (23) and (24), is now $K_{\text{eff}}(\lambda) = n_C J(\lambda)$; the CAR decay shows in this time-domain an effectively two-dimensional behavior going as $n_A(t) \sim n_C \ln(t)/t$. This behavior also shows up in the results of Ref. 12. At longer times, the depletion zones of different traps start to overlap and the probability $n(r_1, r_2)$ of finding a compound particle on the diagonal $r_1=r_2$ decreases substantially even in the gaps between the traps. This results in a situation in which the array of traps distributed on the diagonal $r_1=r_2$ acts as an adsorbing line. It is not surprising then that the current of particles per trap attains a one-dimensional form $J(\lambda) \approx K_{d=1}(D; \lambda)/n_C$, and that even for $n_C r_0 \ll 1$ at very long times the evolution of $n_A(t)$ proceeds essentially in the same fashion as for noncatalytic reactions. Similarly, for $2d$ CARs we have to analyse the kinetics of trapping in $4d$, the traps being now distributed on a $2d$ plane. As before, one can now distinguish between two different temporal regimes; one finds first a situation in which the traps act independently, which gives rise to an effectively $4d$ behavior.¹² This regime crosses over to a stage at long times, where the depletion zones of the different traps overlap, so that the array of traps acts as an effectively $2d$ adsorbing plane; the decay of $n_A(t)$ is then given by Eq. (41), and is independent of n_C . We note finally, that such a peculiarity of the trapping kinetics in low dimensional system, associated with the formation of nonstationary depletion zones around traps, has already been demonstrated in Ref. 15. In particular, it was shown¹⁵ that for $2d$ systems in which N traps are located inside a circular area of radius R one finds two different temporal regimes; in the first, intermediate time regime all traps act independently and the effective rate constant is proportional to N . This regime crosses over into a long-time stage, in which the depletion zones around different traps overlap; at this stage an array of traps acts as a single trap of radius R and the effective rate constant is independent of N .

IV. CONCLUSIONS

We now conclude with the discussion of the obtained results. We find for $3d$ CARs that $n_A(t)$ decreases inversely proportional to t , Eq. (34), which agrees with the formal-

kinetic picture, Eq. (5). Distinct from it, the effective rate constant is less than the formal-kinetic value, $n_C K_{el}$, and depends both on the particles' diffusion constant D and on the reaction radius r_0 . We also note that in the diluted case, when $n_C r_0^3 \ll 1$, the result in Eq. (33) shows the same dependence on the system's parameters as the one predicted in Ref. 12. The very long-time behavior in low dimensions is somewhat surprising, since the decay turns out to be essentially independent of n_C . The approach to this asymptotic domain is, however, very slow for low densities of CSs, $n_C r_0^3 \ll 1$, and thus different decay forms appear at intermediate times. The crossover times t_{tr} may be very large, since we find that $t_{tr} \sim 1/n_C^2$ in $1d$ and $\ln(t_{tr}) \sim 1/n_C$ in $2d$. For $n_C r_0^d \ll 1$ and for extended period of time the decay laws obey in $1d$ and $2d$ $n_A(t) \sim n_C \ln(t)/t$ and $n_A(t) \sim n_C/t$, respectively.

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¹⁹To generalize our mean-field-type approach to the analysis of the recombination reaction $A + B \rightarrow 0$, we have merely to assume anisotropic diffusion, where the diffusion coefficient of the compound particle along the r_1 -axis is D_A , while it is D_B along the r_2 -axis.

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