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Citation: Vlad, Marcel O., Daniel H. Rothman, and John Ross. “Random Channel Kinetics for Reaction–diffusion Systems.” *Physica D: Nonlinear Phenomena* 239, no. 11 (June 2010): 739–745.

As Published: <http://dx.doi.org/10.1016/j.physd.2009.08.003>

Publisher: Elsevier

Persistent URL: <http://hdl.handle.net/1721.1/101289>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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Random channel kinetics for reaction-diffusion systems

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Abstract

A random channel approach is developed for reaction-diffusion processes in disordered systems. Although the starting point of our research is the kinetic study of the decay and preservation of marine organic carbon, our approach can be used for describing other disordered kinetic catalytic processes with random pathways. We consider a generic catalytic mechanism with two species: a) a catalyst, which is continuously produced by a variable number of independent sources randomly distributed in space; this catalyst diffuses from the sources and is degrading according to a first-order kinetic law; the generation, the degradation and the diffusion of the catalyst balance each other out and a stationary concentration field is generated; b) an active species, which decays according to a second order kinetic law: the decay rate is proportional to the product of the concentrations of the catalyst and the concentration of the active species. We show that the catalyst concentration field can be represented by the sum of a random number of Yukawa-like potentials. The average value of the survival function of the active species can be expressed as a grand canonical average

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of a nonlinear functional of the catalyst field and can be evaluated exactly. We show that a good approximation is given by a nearest neighbor approach, where only the contribution of the closest source is taken into account for the computation of the random concentration field of the catalyst. We discuss the application of the model to the problem of decay and preservation of marine organic carbon. With minor adaptation the model can be applied to other problems of disordered kinetics, such as spatially distributed heterogeneous catalytic processes.

Key words: Disordered kinetics, Random channel kinetics, Reaction-diffusion, Enzyme kinetics

PACS: 82.39.Fk, 82.39.-k, 82.20.Uv, 89.75.Da

1. Introduction

In disordered kinetics there are two different approaches. The first one is the random rate approach [1], which is based on the assumption that the equations of deterministic chemical kinetics can be applied, where we assume that the rate coefficients are no longer constant, but random. The simple case is that of static disorder where the rate coefficients are time-independent random variables. A more complex situation is that of dynamic disorder where the rate coefficients are random functions of time. A second approach is that of random channel kinetics [2, 3, 4], where there are different reaction pathways, which produce the same effect; to each pathway there corresponds a reaction channel and the total reaction rate is the sum of the reaction rates corresponding to the different channels. The random channel approach can also involve static or dynamic disorder.

Although the physical picture in these two approaches are different, in some cases there is a simple mathematical correspondence between them [5]. The random rate approach is less specific and at the same time less informative than the random channel approach. Although formally it is always possible to attach an equivalent random rate model to a random channel model and vice versa, some random rate processes do not have alternate pathways.

Recently Rothman and Forney [6] have introduced a disordered kinetic model for the decay and preservation of marine organic carbon. Surprisingly, even though their physico-chemical model is very close to the random channel approach, their mathematical description

is based on the random rate theory. In this paper we show that the physical picture behind their model can be used as a starting point for a general reaction diffusion approach for catalytic reactions with random channel kinetics. With minor adaptations our approach can be applied for the description of spatially distributed catalytic processes.

The structure of the paper is the following. In Section 2 we give a formulation of our approach, which is solved in Sections 3 and 4. In Section 5 we discuss a nearest neighbor approach, which is somewhat similar to the original approach of Rothman and Forney and which provides a good approximation to our exact solution. Finally, in Section 6, we discuss briefly the implementation of the theory for the description of the kinetics of the decay and preservation of marine organic carbon.

2. Formulation of the problem

We study the decay of an active species with a local concentration g , which decays under the influence of a catalyst with concentration c . The catalyst is produced by a random number of spatially distributed sources. Each source $u = 1, 2, \dots, q$ is characterized by a position vector \mathbf{r}_u and a flux density vector \mathbf{j}_u corresponding to a differential solid angle $d\Omega$ attached to a given orientation. We assume that the emission of catalyst by sources is isotropic and can be characterized by the total fluxes $\mathcal{J}_u = \int \mathbf{j}_u d\Omega$. We consider the case of static disorder for which the number of sources q and their position vectors and total fluxes $\mathbf{r}_1, \mathcal{J}_1; \dots; \mathbf{r}_q, \mathcal{J}_q$ are random variables whose stochastic properties are characterized by a set of grand canonical probability densities (Ref. [7], Ch. 2)

$$Q_0, \dots, Q_1(\mathbf{r}_1, \mathcal{J}_1), \dots, Q_q(\mathbf{r}_1, \mathcal{J}_1; \dots; \mathbf{r}_q, \mathcal{J}_q). \quad (1)$$

Here Q_0 is the probability that there are no sources, Q_1 is the probability density corresponding to exactly one source, at location \mathbf{r}_1 with flux \mathcal{J}_1 , and so on. The entire set of Q 's obey the normalization condition

$$Q_0 + \sum_{q=1}^{\infty} \frac{1}{q!} \int_{\mathbf{r}_1, \mathcal{J}_1} \dots \int_{\mathbf{r}_q, \mathcal{J}_q} Q_q(\mathbf{r}_1, \mathcal{J}_1; \dots; \mathbf{r}_q, \mathcal{J}_q) d\mathbf{r}_1 d\mathcal{J}_1 \dots d\mathbf{r}_q d\mathcal{J}_q = 1. \quad (2)$$

We assume that the different sources are independent. Thus their statistical properties are described by a Poissonian point process for which [7]

$$Q_0 = \exp(-m); \quad Q_q(\mathbf{r}_1, \mathcal{J}_1; \dots; \mathbf{r}_q, \mathcal{J}_q) = \exp(-m) \varphi(\mathbf{r}_1, \mathcal{J}_1) \dots \varphi(\mathbf{r}_q, \mathcal{J}_q), \quad (3)$$

where $\varphi(\mathbf{r}, \mathcal{J})$ is an average density of sources, that is $\varphi(\mathbf{r}, \mathcal{J}) d\mathbf{r} d\mathcal{J}$ is the average number of sources with a position vector between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ and a total flux between \mathcal{J} and $\mathcal{J} + d\mathcal{J}$, and

$$m = \int_{\mathbf{r}, \mathcal{J}} \varphi(\mathbf{r}, \mathcal{J}) d\mathbf{r} d\mathcal{J} \quad (4)$$

is the total number of sources.

The catalyst is undergoing a first order decay process, characterized by a rate constant α and an isotropic diffusion process with a diffusion constant D . We assume that the influx of the catalyst is balanced by the losses through diffusion and decay and that a time-independent and space-dependent concentration field of the catalyst eventually emerges. The mass balance for the catalyst leads to a reaction-diffusion equation with random sources:

$$D\nabla^2 c(\mathbf{r}, t) - \alpha c(\mathbf{r}, t) + \sum_{q=1}^{\infty} \mathcal{J}_q \delta(\mathbf{r} - \mathbf{r}_q) = 0. \quad (5)$$

Eq. (5) is an unusual type of space-dependent Langevin equation, where the stochastic properties of the noise sources are not given in terms of correlation functions, but in terms of a Poissonian point process described by Eqs. (3)-(4)

The concentration $g = g(\mathbf{r}, t)$ of the active species is also a random field. Its decay obeys the second order kinetic equation

$$\partial g / \partial t = -\varepsilon g c, \quad (6)$$

where ε is a second-order rate coefficient. The underlying physical picture is that the decay of g is determined by its contact with the diffusing field c of catalyst. Catalyst is emitted by randomly distributed sources with randomly distributed strength, and remains active over a typical time α^{-1} . The active species g does not diffuse; it is instead fixed in space, e.g., to the solid granular surfaces within a porous medium.

The main observable we intend to evaluate from the theory is the average value of the concentration field g of the active species. In general it is also of interest to know other stochastic properties of this field.

3. Analytic solutions

The first step is to solve the kinetic equations for a given configuration of the sources. The stationary reaction-diffusion (5) is linear and thus the concentration field $c(\mathbf{r}, t)$ can be represented as a linear functional of the sources,

$$c(\mathbf{r}, t) = c_{st}(\mathbf{r}) = \int_{\mathbf{r}'} \chi(\mathbf{r}, \mathbf{r}') \sum_{q=1}^{\infty} \mathcal{J}_q \delta(\mathbf{r} - \mathbf{r}_q) d\mathbf{r}' = \sum_{q=1}^{\infty} \mathcal{J}_q \chi(\mathbf{r}, \mathbf{r}_q), \quad (7)$$

where the susceptibility function $\chi(\mathbf{r}, \mathbf{r}_q)$ can be determined in terms of the Green function $G(\mathbf{r}, t|\mathbf{r}', t')$ of the nonstationary diffusion equation

$$\partial_t G(\mathbf{r}, t|\mathbf{r}', t') = D\nabla^2 G(\mathbf{r}, t|\mathbf{r}', t') + \delta(\mathbf{r} - \mathbf{r}')\delta(t - t'), \quad (8)$$

with proper boundary conditions which express the property that the fluxes at the boundaries of the system vanish. We start out from the nonstationary form of the reaction-diffusion equation for the catalyst,

$$\frac{\partial}{\partial t} c(\mathbf{r}, t) = D\nabla^2 c(\mathbf{r}, t) - \alpha c(\mathbf{r}, t) + \sum_{q=1}^{\infty} \mathcal{J}_q \delta(\mathbf{r} - \mathbf{r}_q), \quad (9)$$

and make the substitution

$$c(\mathbf{r}, t) = \zeta(\mathbf{r}, t) \exp(-\alpha t) \quad (10)$$

resulting in

$$\frac{\partial}{\partial t} \zeta(\mathbf{r}, t) = D\nabla^2 \zeta(\mathbf{r}, t) + \exp(\alpha t) \sum_{q=1}^{\infty} \mathcal{J}_q \delta(\mathbf{r} - \mathbf{r}_q). \quad (11)$$

It follows that

$$\begin{aligned} c(\mathbf{r}, t) &= \exp(-\alpha t) \int_{t'}^t \int_{\mathbf{r}'} \exp(\alpha t') G(\mathbf{r}, t|\mathbf{r}', t') \sum_{q=1}^{\infty} \mathcal{J}_q \delta(\mathbf{r}' - \mathbf{r}_q) d\mathbf{r}' dt' \\ &= \sum_{q=1}^{\infty} \mathcal{J}_q \int_{t'}^t \exp[-\alpha(t - t')] G(\mathbf{r}, t|\mathbf{r}_q, t') dt' \end{aligned} \quad (12)$$

For $t \rightarrow \infty$ we obtain the stationary solution (7) where

$$\chi(\mathbf{r}, \mathbf{r}') = \int_{t'}^{\infty} \exp[-\alpha(t - t')] G(\mathbf{r}, t|\mathbf{r}', t') dt'. \quad (13)$$

An important particular case is that of unlimited space; in this case the Green function $G(\mathbf{r}, t|\mathbf{r}', t')$ is given by

$$G(\mathbf{r}, t|\mathbf{r}', t') = [4\pi D(t - t')]^{-d_s/2} \exp\{-|\mathbf{r} - \mathbf{r}'|^2/[4D(t - t')]\}, \quad (14)$$

where d_s is the space dimension. In this case the susceptibility function can be expressed in terms of a characteristic reaction-diffusion length r_c and of a relative displacement vector \mathbf{f} :

$$r_c = (D/\alpha)^{1/2}, \quad \mathbf{f} = (\mathbf{r} - \mathbf{r}')/2r_c. \quad (15)$$

We have

$$\chi(\mathbf{r}, \mathbf{r}') = \chi(f) = \alpha^{-1} r_c^{-d_s} I_{d_s}(f), \quad (16)$$

where $f = |\mathbf{f}|$ is the absolute value of the relative displacement vector and

$$I_{d_s}(f) = (4\pi)^{-d_s/2} \int_0^\infty \eta^{-d_s/2} \exp\left(-\eta - \frac{f^2}{\eta}\right) d\eta \quad (17)$$

where $\eta = \alpha t$. As expected, for infinite space with a constant reaction rate, a constant diffusion coefficient, and isotropic diffusion the process is translationally invariant and isotropic and the susceptibility function $\chi(\mathbf{r}, \mathbf{r}')$ depends only on the absolute value of the displacement vector $|\mathbf{r} - \mathbf{r}'|$. In the Appendix we show how the functions $I_{d_s}(f)$ can be computed for different space dimensions d_s . In particular, for three dimensional space we have

$$I_3(f) = (4f)^{-1} \exp(-2f), \quad (18)$$

and thus

$$\chi_3(\mathbf{r}, \mathbf{r}') = \frac{\exp(-|\mathbf{r} - \mathbf{r}'|/r_c)}{2\alpha r_c^2 |\mathbf{r} - \mathbf{r}'|}. \quad (19)$$

The next step is the integration of the kinetic equation for the active species. For a time-independent, stationary concentration field for the catalyst this integration is straightforward:

$$g(\mathbf{r}, t) = g(\mathbf{r}, 0) \exp[-\varepsilon c_{st}(\mathbf{r})t] = g(\mathbf{r}, 0) \exp\left[-\varepsilon t \sum_{q=1}^{\infty} \mathcal{J}_q \chi(\mathbf{r}, \mathbf{r}_q)\right]. \quad (20)$$

The final step is to take an average of the concentration of the active species over all possible values of the positions \mathbf{r}_q of the sources of catalyst and of the corresponding fluxes

\mathcal{J}_q . This average is taken in terms of the grand canonical probability densities (1). We obtain

$$\langle g(\mathbf{r}, t) \rangle = g(\mathbf{r}, 0)Q_0 + g(\mathbf{r}, 0) \times \sum_{q=1}^{\infty} \frac{1}{q!} \int_{\mathbf{r}_1, \mathcal{J}_1} \cdots \int_{\mathbf{r}_q, \mathcal{J}_q} \exp \left[-\varepsilon t \sum_{q=1}^{\infty} \mathcal{J}_q \chi(\mathbf{r}, \mathbf{r}_q) \right] Q_q(\mathbf{r}_1, \mathcal{J}_1; \dots; \mathbf{r}_q, \mathcal{J}_q) d\mathbf{r}_1 d\mathcal{J}_1 \cdots d\mathbf{r}_q d\mathcal{J}_q, \quad (21)$$

where $\langle \dots \rangle$ denotes the ensemble average with respect to the number of sources of catalyst and their positions and output fluxes. All terms in Eq. (21) can be easily factored if we assume that the positions and the intensity of the sources are independently distributed random variables, described by a point process of the Poissonian type (Eqs. (3)). By inserting Eqs (3) into Eq. (21) we obtain

$$\langle g(\mathbf{r}, t) \rangle = \exp(-m)g(\mathbf{r}, 0) + \exp(-m)g(\mathbf{r}, 0) \times \sum_{q=1}^{\infty} \frac{1}{q!} \prod_{q'=1}^q \left\{ \int_{\mathbf{r}_{q'}, \mathcal{J}_{q'}} \varphi(\mathbf{r}_{q'}, \mathcal{J}_{q'}) \exp[-\varepsilon t \mathcal{J}_{q'} \chi(\mathbf{r}, \mathbf{r}_{q'})] d\mathbf{r}_{q'} d\mathcal{J}_{q'} \right\}. \quad (22)$$

From Eq. (22), by merging all terms in an exponential we obtain the following expression for the average concentration of the active species:

$$\langle g(\mathbf{r}, t) \rangle = g(\mathbf{r}, 0) \exp \left\{ - \int_{\mathbf{r}', \mathcal{J}} \varphi(\mathbf{r}', \mathcal{J}) \left\{ 1 - \exp[-\varepsilon t \mathcal{J} \chi(\mathbf{r}, \mathbf{r}')] \right\} d\mathbf{r}' d\mathcal{J} \right\}. \quad (23)$$

Eq. (23) expresses the kinetic behavior of the average concentration at different times and positions in space. It is the main result of this paper, which makes it possible to establish a relation between the theory and observation; for example, by comparing observed concentrations as functions of time, we can extract rate coefficients. This equation is a space-dependent generalization of Huber's basic random channel model [3]. Its derivation can be used as a model for computing the fluctuations of the concentration of the active species. This problem will be dealt with in section 4.

In disordered kinetics it is customary to define an effective reaction rate, which is defined as the time derivative of the logarithm of the relative value of the average concentration of the active species:

$$\kappa_{\text{eff}}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \ln \left[\frac{\langle g(\mathbf{r}, t) \rangle}{g(\mathbf{r}, 0)} \right]. \quad (24)$$

We notice that Eq. (24) can be rewritten as a formal first order kinetic equation, with an apparent rate coefficient dependent on position and time:

$$\frac{\partial}{\partial t} \langle g(\mathbf{r}, t) \rangle = -\kappa_{\text{eff}}(\mathbf{r}, t) \langle g(\mathbf{r}, t) \rangle. \quad (25)$$

For our approach we have

$$\kappa_{\text{eff}}(\mathbf{r}, t) = \frac{\partial}{\partial t} \Psi_1(\mathbf{r}, t) = \varepsilon \int_{\mathbf{r}', \mathcal{J}} \mathcal{J} \chi(\mathbf{r}, \mathbf{r}') \varphi(\mathbf{r}', \mathcal{J}) \exp[-\varepsilon t \mathcal{J} \chi(\mathbf{r}, \mathbf{r}')] d\mathbf{r}' d\mathcal{J}, \quad (26)$$

where

$$\Psi_1(\mathbf{r}, t) = \int_{\mathbf{r}, \mathcal{J}} \varphi(\mathbf{r}', \mathcal{J}) \left\{ 1 - \exp[-\varepsilon t \mathcal{J} \chi(\mathbf{r}, \mathbf{r}')] \right\} d\mathbf{r}' d\mathcal{J}, \quad (27)$$

is the phase of first order of the disordered reaction. We notice that in general the average concentration of the active species as well as the effective rate coefficient and the phase of the disordered reaction depends on both space and time. For our model, this is a finite-size effect; for large systems, for which the boundary effects can be neglected, these three quantities are position-independent.

In conclusion, we have developed a simple approach for computing average values for the concentration of the active species. The results derived in this section will be used in the geochemical application discussed in Section 6.

4. Concentration fluctuations

The method developed in Section 3 for computing the average concentration of the active species can be easily extended for computing other statistical properties of the concentration fluctuations. The generalization is straightforward due to the multiplicative structure of Eq. (20) for the fluctuating concentration field $g(\mathbf{r}, t)$. We start by computing the moments of the concentration field $g(\mathbf{r}, t)$ at a single position and time. We raise Eq. (20) to the w th power, where w is a positive real number, not necessarily an integer, and compute the average value of $g^w(\mathbf{r}, t)$, by using the Poissonian grand canonical probability densities (3). The computation leads to intermediate equations similar to Eqs. (21) and (22); we can also merge the terms of an expansion into an exponential, resulting in a generalization of Eq. (23):

$$\langle g^w(\mathbf{r}, t) \rangle = g^w(\mathbf{r}, 0) \exp[-\Psi_w(\mathbf{r}, t)]. \quad (28)$$

where

$$\Psi_w(\mathbf{r}, t) = \int_{\mathbf{r}', \mathcal{J}} \varphi(\mathbf{r}', \mathcal{J}) \left\{ 1 - \exp[-\varepsilon t w \mathcal{J} \chi(\mathbf{r}, \mathbf{r}')] \right\} d\mathbf{r}' d\mathcal{J}, \quad (29)$$

is a one-position phase of w th order of the disordered reaction. If we restrict the value of w to positive integers, then Eq. (28) makes it possible to evaluate other stochastic properties of the concentration field, for example central moments or cumulants. In particular, we get the following expression for the dispersion of the concentration field of the active species:

$$\begin{aligned} \langle \Delta g^2(\mathbf{r}, t) \rangle &= \langle [g(\mathbf{r}, t) - \langle g(\mathbf{r}, t) \rangle]^2 \rangle \\ &= g^2(\mathbf{r}, 0) [\exp(-\Psi_2(\mathbf{r}, t)) - \exp(-2\Psi_1(\mathbf{r}, t))]. \end{aligned} \quad (30)$$

The computation of the correlation functions at different times and positions can be carried out in a similar way. We express the product $\prod_{w'}^w g(\mathbf{r}_{w'}, t_{w'})$ as

$$\prod_{w'=1}^w g(\mathbf{r}_{w'}, t_{w'}) = \left(\prod_{w'=1}^w g(\mathbf{r}_{w'}, 0) \right) \prod_{q'=1}^q \exp \left[-\varepsilon \sum_{v=1}^w \mathcal{J}_{q'} t_v \chi(\mathbf{r}_v, \mathbf{r}_{q'}) \right], \quad (31)$$

and take an average over all possible numbers, positions, and intensities of the source by assuming that the sources obey the Poissonian statistics of Eq. (3). We obtain

$$\begin{aligned} \left\langle \prod_{w'=1}^w g(\mathbf{r}_{w'}, t_{w'}) \right\rangle &= \exp(-m) \left(\prod_{w'=1}^w g(\mathbf{r}_{w'}, 0) \right) + \exp(-m) \left(\prod_{w'=1}^w g(\mathbf{r}_{w'}, 0) \right) \times \\ &\quad \sum_{q=1}^{\infty} \frac{1}{q!} \prod_{q'=1}^q \left\{ \int_{\mathbf{r}_{q'}, \mathcal{J}_{q'}} \varphi(\mathbf{r}_{q'}, \mathcal{J}_{q'}) \exp \left[-\varepsilon \sum_{v=1}^w \mathcal{J}_{q'} t_v \chi(\mathbf{r}_v, \mathbf{r}_{q'}) \right] d\mathbf{r}_{q'} d\mathcal{J}_{q'} \right\}. \end{aligned} \quad (32)$$

By merging the terms into an exponential we then obtain an equation similar to Eq. (28):

$$\left\langle \prod_{w'=1}^w g(\mathbf{r}_{w'}, t_{w'}) \right\rangle = \left(\prod_{w'=1}^w g(\mathbf{r}_{w'}, 0) \right) \Psi_w(\mathbf{r}_1, t_1; \dots; \mathbf{r}_w, t_w), \quad (33)$$

where

$$\Psi_w(\mathbf{r}_1, t_1; \dots; \mathbf{r}_w, t_w) = \exp \left\{ - \left\{ \int_{\mathbf{r}', \mathcal{J}} \varphi(\mathbf{r}', \mathcal{J}) \left\{ 1 - \exp \left[-\varepsilon \sum_{v=1}^w \mathcal{J} t_v \chi(\mathbf{r}_v, \mathbf{r}') \right] d\mathbf{r}' d\mathcal{J} \right\} \right\} \right\} \quad (34)$$

is the w th order multi-position phase of the disordered reaction, which is a generalization of $\Psi_w(\mathbf{r}, t)$ given by Eq. (29). In particular we have

$$\Psi_w(\mathbf{r}, t) = \Psi_w(\mathbf{r}_1, t_1; \dots; \mathbf{r}_w, t_w). \quad (35)$$

The validity ranges of Eqs. (28) and (33) are partially overlapping. Neither is more general than the other, and they become identical if w a positive integer and $\mathbf{r}_1 = \dots = \mathbf{r}_w = \mathbf{r}$ and $t_1 = \dots = t_w = t$. An unexpected feature of Eq. (33) is that it does not contain any singularities if at least two of the positions and/or times are identical. Such singularities occur for the correlations of stochastic additive variables described by random point processes [7]. However, they do not occur in the case of our model because of the multiplicative structure of the equations.

From Eq. (33) we get the following expression for the correlation functions of the concentration field evaluated at different positions and times:

$$\begin{aligned} \langle \Delta g(\mathbf{r}_1, t_1) \Delta g(\mathbf{r}_2, t_2) \rangle = \\ \langle [g(\mathbf{r}_1, t_1) - \langle g(\mathbf{r}_1, t_1) \rangle] [g(\mathbf{r}_2, t_2) - \langle g(\mathbf{r}_2, t_2) \rangle] \rangle = \quad (36) \\ \Delta g(\mathbf{r}_1, 0) \Delta g(\mathbf{r}_2, 0) [\exp(-\Psi_2(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2)) - \exp(-\Psi_1(\mathbf{r}_1, t_1) - \Psi_1(\mathbf{r}_2, t_2))]. \end{aligned}$$

As expected, Eq. (36) includes Eq. (30) as a particular case.

In conclusion, in this section we have developed methods for computing the stochastic properties of the fluctuations of the concentration field for the active species. If the statistical variations of the concentration fields are available experimentally, the equations derived in this section can be used for extracting further kinetic information from experimental data.

5. Nearest neighbor approximation

In this section we suggest a simple approach, based on the assumption that the main contribution of catalyst concentrations comes from the nearest source. We limit ourselves to the evaluation of the average value of the concentration field of the active species. This model is similar to the original model of Rothman and Forney [6]. We assume that the main contribution of the concentration field of the catalyst in Eq. (7) comes from the nearest source so that

$$c_{st}(\mathbf{r}) = \mathcal{J} \chi(\mathbf{r}, \mathbf{r}_n), \quad (37)$$

where \mathbf{r}_n is the position vector of the nearest source and \mathcal{J} is its intensity. We introduce the displacement vector $\Delta \mathbf{r} = \mathbf{r}_n - \mathbf{r}$, which expresses the relative position of the source with respect to the point where the concentrations are evaluated. We denote by ϕ the volume

concentration of sources. The first step is to express the probability $p(\Delta r)d\Delta r$ that the nearest source is at a relative distance between Δr and $\Delta r + d\Delta r$, where $\Delta r = |\Delta \mathbf{r}|$. This probability can be evaluated by expressing the possibility that the first source lies in a shell between two d_s -dimensional spheres of radii Δr and $\Delta r + d\Delta r$. We have

$$p(\Delta r + d\Delta r) = p(\Delta r) \left(1 - \frac{d_s \pi^{d_s/2} (\Delta r)^{d_s-1} d\Delta r}{\Gamma(1 + d_s/2)} \phi \right), \quad (38)$$

from which we get the differential equation:

$$\frac{dp(\Delta r)}{d\Delta r} = \frac{-d_s \pi^{d_s/2} (\Delta r)^{d_s-1} \phi}{\Gamma(1 + d_s/2)} p(\Delta r), \quad \int_{\Delta r_{\min}}^{\Delta r_{\max}} p(\Delta r) d\Delta r = 1, \quad (39)$$

where Δr_{\min} and Δr_{\max} are the minimum and the maximum values of the relative distance Δr . Here Δr_{\min} and Δr_{\max} are cutoff values introduced for physical consistency. In the case of carbon decay [6], Δr_{\min} corresponds to the typical size of a bacterium, whereas Δr_{\max} is the longest distance at which the enzymes released from bacteria have a measurable contribution to the decay process. By solving this equation it follows that

$$p(\Delta r) = Z^{-1} \frac{d_s \pi^{d_s/2} (\Delta r)^{d_s-1} \phi}{\Gamma(1 + d_s/2)} \exp \left[-\frac{\pi^{d_s/2} (\Delta r)^{d_s} \phi}{\Gamma(1 + d_s/2)} \right], \quad (40)$$

where

$$Z = \exp \left[-\frac{\pi^{d_s/2} (\Delta r_{\min})^{d_s} \phi}{\Gamma(1 + d_s/2)} \right] - \exp \left[-\frac{\pi^{d_s/2} (\Delta r_{\max})^{d_s} \phi}{\Gamma(1 + d_s/2)} \right] \quad (41)$$

is a partition function which ensures that the probability density is properly normalized to unity and $\Gamma(x) = \int_0^\infty y^{x-1} \exp(-y) dy$, $x > 0$, is Euler's gamma function. We also assume that we know the probability density of the intensity of a source:

$$B(\mathcal{J})d\mathcal{J}, \quad \text{with} \quad \int B(\mathcal{J})d\mathcal{J} = 1. \quad (42)$$

Now we have all elements necessary for computing the average concentration field of the active species. Eqs. (20) and (37) lead to

$$g(\mathbf{r}, t) = g(\mathbf{r}, 0) \exp[-\varepsilon \mathcal{J} \chi(\mathbf{r}, \mathbf{r}_n) t], \quad (43)$$

from which we obtain the following expression for the average concentration field:

$$\langle g(\mathbf{r}, t) \rangle = g(\mathbf{r}, 0) \exp[-\Psi_{\text{MF}}(\mathbf{r}, t)], \quad (44)$$

where the mean field phase factor $\Psi_{\text{MF}}(\mathbf{r}, t)$ is given by:

$$\Psi_{\text{MF}}(\mathbf{r}, t) = -\ln \left\{ \int d\mathcal{J} B(\mathcal{J}) \int d\Delta r p(\Delta r) \exp[-\varepsilon \mathcal{J} \chi(\mathbf{r}, \mathbf{r} + \Delta \mathbf{r}) t] \right\}. \quad (45)$$

This nearest neighbor theory is attractive for its simplicity. However its validity range is limited; in particular, it is a mean field theory which cannot be used for computing position-position correlation functions or other stochastic properties of the concentration field attached to two or more positions in space.

6. Application to the decay and preservation of marine organic carbon

Finally we apply our theory to the problem which motivated its study: the decay and preservation of marine organic carbon [6]. In this problem, organic detritus mixed within granular sediment (e.g., mud) beneath the seafloor is degraded through contact with diffusing hydrolytic enzymes emitted by bacteria. Our assumption of randomly distributed catalytic sources therefore corresponds to randomly dispersed microbes, and the active species is the organic carbon undergoing decay.

We assume a given volume concentration ϕ of bacteria (which can be as high as 10^9 cm^{-3}), and neglect the fluctuations of the intensity of the emitted enzyme flux. Under these circumstances the average density of sources is given by

$$\varphi(\mathbf{r}', \mathcal{J}) = \delta(\mathcal{J} - \mathcal{J}_m) \phi, \quad (46)$$

where \mathcal{J}_m is the typical value for the flux of hydrolytic enzymes. The susceptibility function $\chi_3(\mathbf{r}, \mathbf{r}')$ is given by Eq. (19), which is derived in the Appendix for isotropic diffusion in unlimited three-dimensional space. Following Rothman and Forney we employ the two cutoff distances Δr_{\min} and Δr_{\max} (see Eq. (39)) to compute the the average concentration fields.

The stochastic properties of the concentration of the organic matter are determined by the different phase factors of the disordered reaction. These phase factors are dimensionless quantities; their expressions can be considerably simplified by introducing a few dimensionless variables. The one-position, w th order phase factor is given by

$$\Psi_w(\tau) = \tilde{\phi} \int_{x_{\min}}^{x_{\max}} \left\{ 1 - \exp \left[-\tau w \frac{\exp(-x)}{2x} \right] \right\} 4\pi x^2 dx. \quad (47)$$

Here we have used the characteristic diffusion length $r_c = (D/\alpha)^{1/2}$ (where α is the enzyme inactivation rate) to form the dimensionless average concentration

$$\tilde{\phi} = \phi r_c^3 \quad (48)$$

of hydrolytic bacteria, and the dimensionless distances

$$x = \Delta r / r_c, \quad x_{\min} = \Delta r_{\min} / r_c, \quad \text{and} \quad x_{\max} = \Delta r_{\max} / r_c. \quad (49)$$

Dimensionless time is given by

$$\tau = \frac{\varepsilon \mathcal{J}_m t}{\alpha r_c^3}. \quad (50)$$

A dimensionless equation for the w th-order multi-position phase can also be derived. The computations are more complicated because the integrals over position vectors cannot be fully reduced to integrals over distances, because the cosine theorem applied to differences among vectors leads to angle-dependent integrals; an expansion in spherical and Bessel functions is required.

The application of the nearest neighbor theory leads to a simplified equation for the first order phase factor

$$\Psi_{\text{MF}}(\tau) = -\ln \left\{ \int_{x_{\min}}^{x_{\max}} \tilde{p}(x) \exp \left[-\tau \frac{\exp(-x)}{2x} \right] dx \right\}, \quad (51)$$

where

$$\tilde{p}(x) = 4\pi Z^{-1} \tilde{\phi} x^2 \exp \left[-\frac{4}{3} \pi x^3 \tilde{\phi} \right], \quad (52)$$

is the probability density of the dimensionless distance x and the partition function Z is given by

$$Z = \exp \left[-\frac{4}{3} (x_{\min})^3 \tilde{\phi} \right] - \exp \left[-\frac{4}{3} (x_{\max})^3 \tilde{\phi} \right]. \quad (53)$$

The range of variation Δr covers a few orders of magnitude and, under these circumstances, it makes sense to consider a uniform distribution for Δr between Δr_{\min} and Δr_{\max} . In terms of dimensionless variables we have

$$p(x) = \frac{\vartheta(x - x_{\min}) - \vartheta(x - x_{\max})}{x_{\max} - x_{\min}} \quad (54)$$

where $\vartheta(x)$ is Heavisides step function.

The first observable we want to evaluate is the effective rate of decay $\kappa_{\text{eff}}(\mathbf{r}, t)$ defined by Eq. (26) or the corresponding dimensionless variable

$$\tilde{\kappa}_{\text{eff}}(\tau) = \frac{\alpha r_c^3}{\varepsilon \mathcal{J}_m} \kappa_{\text{eff}} = \frac{\partial}{\partial \tau} \Psi(\tau), \quad (55)$$

where the phase factor $\Psi(\tau) = \Psi_1(\tau)$ is given by Eq. (47) for $w = 1$ for the random channel model, and by Eq. (51) (i.e., $\Psi(\tau) = \Psi_{\text{MF}}(\tau)$) for the nearest neighbor model. Other quantities of interest include the phase of the reaction Ψ and the survival function $g/g(0) = \exp(-\Psi)$. In the following we focus on time dependent behavior rather than absolute values and for this reason we consider the dependence of these variables in terms of the dimensionless time τ rather than the dimensional time t . Going back to dimensional time it may be possible to evaluate some of the parameters of the model, but here we do not pursue this problem.

We start out from the experimental data. Rothman and Forney showed that the effective decay rate can be approximately fit to a hyperbolic law in time (Ref. [6], Fig. 4):

$$\kappa_{\text{eff}}(t) \sim t^{-1}. \quad (56)$$

Eq. (56) holds for many orders of magnitude for the time scale, but is not valid for very small times and displays a singularity for $t = 0$, which is obviously an artifact. To avoid the effects of this singularity we introduce a small cutoff value corresponding to a minimum time t_{min} and consider that Eq. (56) describes the data adequately for any times larger than t_{min} . In terms of dimensionless time, we have

$$\tilde{\kappa}_{\text{eff}}(\tau) = \gamma \tau^{-1} \quad \text{for} \quad \tau \geq \tau_{\text{min}} = \frac{\varepsilon \mathcal{J}_m t_{\text{min}}}{\alpha r_c^3}, \quad (57)$$

where γ is a dimensionless proportionality factor.

A first case corresponds to the mean field theory with the uniform distribution of distances given by Eq. (54). In this case our approach reduces to the original model considered by Rothman and Forney. By using the properties of the exponential integral function, they showed that the tail of the effective decay rate should behave approximately as t^{-1} , that is, they provided a theoretical justification of the experimental equation (56). They showed that there is a small logarithmic correction to this hyperbolic law, but its contribution to the data is less important compared to the main $\sim t^{-1}$ term.

The other two cases correspond to the nearest neighbor model with the probability density (52) for the dimensionless distance x and to the random channel model. In both cases we failed to find simple analytical estimates for the asymptotic behavior at large times. However, the time-dependent behavior can be easily estimated numerically. In both cases the dimensionless functions of interest depend on three different parameters, which makes an exhaustive investigation difficult. By sampling random values of these three variables we have shown that the tail of $\tilde{\kappa}_{\text{eff}}(\tau)$ can be represented reasonably by two simple fit functions:

$$\tilde{\kappa}_{\text{eff}}(\tau) \sim \tau^{-1} \quad (58)$$

and

$$\tilde{\kappa}_{\text{eff}}(\tau) \sim \tau^{-\lambda}. \quad (59)$$

We carried out 128 computations for each model, by randomly sampling values for the three parameters. For both models, plots of $\ln \tilde{\kappa}_{\text{eff}}(\tau)$ versus $\ln \tau$ are slightly curved, roughly indicative of the logarithmic correction in the model of Rothman and Forney, but the simulation data can nevertheless be fit with good accuracy to straight lines. The range of the correlation coefficient for the fit was $0.972 \leq R \leq 0.991$ (Eq. (58)) and $0.980 \leq R \leq 0.989$ (Eq. (59)) for the nearest neighbor model and $0.977 \leq R \leq 0.996$ (Eq. (58)) and $0.984 \leq R \leq 0.999$ (Eq. (59)) for the random channel model. For both models the equation with an arbitrary exponent, Eq. (59), leads to a better fit, but the difference is rather small. The exponent λ tends to be slightly smaller than unity; in our simulations the range of variation for λ was $0.89 \leq \lambda \leq 0.96$ for the nearest neighbor model and $0.81 \leq \lambda \leq 0.98$ for the random channel model.

The two fitting equations, Eqs. (58) and (59), lead to different types of kinetic behavior for the survival function $g/g(0)$. From Eq. (58) we find

$$\frac{g(\tau)}{g(0)} = \exp\left(-\int_0^t \tilde{\kappa}_{\text{eff}}(\tau) d\tau\right) = \left(\frac{\tau_{\text{min}}}{\tau}\right)^\gamma \exp(\Psi(\tau_{\text{min}})), \quad \tau \geq \tau_{\text{min}}. \quad (60)$$

Consequently the kinetics of the process are fractal, characterized by the scaling exponent γ .

In the second case we introduce a proportionality factor ζ in Eq. (59):

$$\tilde{\kappa}_{\text{eff}}(\tau) = \zeta \tau^{-\lambda}. \quad (61)$$

Our simulations suggest that the fractal exponent λ is smaller than one and thus the singularity in Eq. (61) for $\tau = 0$ does not lead to a singularity in the phase factor and there is no need for a cutoff value. In this case the kinetics of the process are described by a stretched exponential survival function:

$$\frac{g(\tau)}{g(0)} = \exp\left(-\frac{\zeta}{1-\lambda}\tau^{1-\lambda}\right), \quad (62)$$

where the scaling exponent $1 - \lambda$ is between zero and one.

An interesting aspect, not clarified by our limited simulations, is related to the proportionality coefficients in Eqs. (58) and (59). These two equations only describe the main trend of the time dependence of the effective rate coefficients. Indeed, the proportionality factors are not constants, but slowly varying functions of time.

In conclusion, our simulations suggest that both fractal and stretched exponential kinetics are able to fit the theoretical predictions of our models. This situation appears to apply also to some extent to the experimental data: interpretations have been given in terms of fractal kinetics [6], but the data do not easily distinguish between $\lambda = 1$ and λ somewhat smaller than one. For similar reasons we cannot yet determine the relative efficacy with which the two versions of the nearest neighbor model and the random channel model fit the data. In order to learn more, further geochemical investigations are needed. The theoretical approaches developed in this paper should serve as a starting point for new research.

7. Conclusions

In this paper we have developed techniques for analyzing random channel kinetics for reaction diffusion systems. Although our research has been motivated mainly by the study of the decay and preservation of marine organic carbon, the methods developed here can be adapted to other reaction-diffusion systems with random channel kinetics. Possible applications are the study of heterogeneous catalytic reactions with surface reconstruction [8], recombination kinetics in subdiffusive media [9], or inhomogeneous reactions in cell biochemistry.

Dedication

We dedicate this article to Professor Stefan C. Müller on his 60th birthday in recognition of his great contributions to the study of reaction-diffusion kinetics and of nonlinear systems.

Acknowledgments

This project was supported in part by the National Science Foundation, grants EAR-0420592 and CHE-0847073, the NASA Astrobiology Institute, the CEEEX grant M1-C2-3004/2006-Response of the Romanian Ministry of Research and Education, the Alexander von Humboldt Foundation, BayGene and the ReForM program of the Medical School Regensburg. We thank Robert Vlassa and Dr. Alexandru Corlan for useful discussions and help with numerical simulations. We also thank Dr. Corlan for invaluable technical assistance in the revision of the original manuscript.

Appendix

We start out by expressing Eq. (17) in a more symmetrical form, by carrying out the transformation of variable $\eta = x^2$:

$$I_{d_s}(f) = 2(4\pi)^{-d_s/2} \int_0^\infty x^{1-d_s} \exp\left(-x^2 - \frac{f^2}{x^2}\right) dx. \quad (\text{A1})$$

The integral $I_1(f)$ can be computed directly, because for $d_s = 1$ the integral in Eq. (A1) has a symmetric structure. By putting $y = f/x$ we come to:

$$I_1(f) = 2(4\pi)^{-1/2} \int_0^\infty \exp\left(-x^2 - \frac{f^2}{x^2}\right) dx = \int_0^\infty f y^{-2} \exp\left(-y^2 - \frac{f^2}{y^2}\right) dy. \quad (\text{A2})$$

It follows that, through differentiation with respect to f , we obtain:

$$\frac{\partial}{\partial f} I_1(f) = -2(4\pi)^{-1/2} \int_0^\infty f x^{-2} \exp\left(-x^2 - \frac{f^2}{x^2}\right) dx, \quad (\text{A3})$$

from which, by using the integral expression in Eq. (A2), we can derive a differential equation in $I_1(f)$:

$$\frac{\partial}{\partial f} I_1(f) = -2I_1(f). \quad (\text{A4})$$

The integral $I_1(f)$ can be easily evaluated in the particular case $f = 0$. From Eq. (17) it follows that:

$$I_1(0) = (4\pi)^{-1/2} \int_0^\infty \eta^{-1/2} \exp(-\eta) d\eta = (4\pi)^{-1/2} \Gamma(1/2) = 1/4. \quad (\text{A5})$$

By integrating Eq. (A4) with the initial condition (A5) we come to:

$$I_1(f) = I_1(0) \exp(-2f) = 2^{-2} \exp(-2f). \quad (\text{A6})$$

By differentiating Eq. (A1) with respect to f , we obtain:

$$\frac{\partial}{\partial f} I_{d_s}(f) = -2f 2(4\pi)^{-d_s/2} \int_0^\infty x^{1-(d_s+2)} \exp\left(-x^2 - \frac{f^2}{x^2}\right) dx = -2f I_{d_s+2}(f). \quad (\text{A7})$$

From Eq. (A7) we can compute $I_2(f)$ in terms of $I_1(f)$. We have:

$$I_2(f) = -(2f)^{-1} \frac{\partial}{\partial f} I_1(f) = (4f)^{-1} \exp(-2f). \quad (\text{A8})$$

The integral $I_2(f)$ for two dimensions can be computed in a similar way. We start out by formally introducing an integral $I_0(f)$ defined by Eq. (A1) and finally computing from Eq. (A7) applied for $d_s = 0$. Since in this article we do not use the expression for $I_2(f)$, we skip the derivation in order to save space.

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