Fluctuation effects in steric reaction-diffusion systems

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We propose a simple model for reaction-diffusion systems with orientational constraints on the reactivity of particles, and map it onto a field theory with upper critical dimension $d_c = 2$. To the two-loop level, long-time particle density $N(t)$ is given by the *same* universal expression as for a nonsteric system, with $N(t) \sim t^{-d/2}$ for $d \leq 2$. For slow rotations of the particles we find an intermediate regime where $N(t) \sim t^{-d/4}$, with the crossover to the nonsteric asymptotics determined by the rates of rotations and reactions. Consequences for experiments are discussed. [S1063-651X(99)50104-9]

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Diffusion-controlled reactions are ubiquitous in nature and span a wide range of phenomena—from chemical catalysis in cell biology to matter-antimatter annihilation in the early universe. In these processes the time t_D for a particle to diffuse to its nearest neighbor is much larger than the characteristic time t_R for the particles to react once in proximity. As a result, large density fluctuations may develop at late times, resulting in anomalous kinetics with universal scaling behavior [1].

Our understanding of diffusion-controlled reactions has advanced significantly in the last few years. Results obtained by new theoretical approaches (like renormalization group methods [2] or mappings to integrable models [3]) can now be tested against high-quality experimental data, including measurements on low-dimensional processes where effects from fluctuations are most pronounced [4]. However, little attention has been paid to the modeling of fluctuation effects in *steric* reaction-diffusion systems, i.e., systems where the reactivity between particles depends on their relative orientation. Examples include diffusion-controlled enzyme reactions [5], effective reaction-diffusion models of protein folding [6], as well as generic solution kinetics of molecules with nonuniform surface reactivity [7]. Here the chemically active part of a reactant is located in a specific region, usually represented by an *active* spot [7] on the sphere modeling the reactant. Two particles react only if their active spots touch, signaling a successful ''docking'' for reaction. Despite the importance of this class of processes, the theoretical effort so far has been limited to estimating how the reaction rates effectively decrease due to orientational constraints [7,8]. The lack of a more comprehensive theory reflects the subtlety of the problem, which here makes a faithful treatment quite difficult.

In this Rapid Communication we propose a *minimal* model for steric reaction-diffusion systems, specifically, annihilation processes. This model—in spirit an ''Ising-type'' model for steric reaction-diffusion—has the advantage that it can be analyzed by field-theoretic renormalization group (RG) techniques, allowing for precise predictions about the long-time kinetics. In spite of its simplicity the model contains some very interesting information. In particular, for sufficiently slow internal rotations of the particles our results reveal that steric reactivity in dimensions $d \leq 2$ drives a crossover from a density decay $N(t) \sim t^{-d/4}$ at large intermediate times to $N(t) \sim t^{-d/2}$ at later times (with logarithmic corrections in $d = 2$).

To define the model we partition configuration space into cells $\Delta \mathbf{r}$, and time into intervals Δt. The particles are represented by spheres with an active spot that is either ''up'' or ''down'' with respect to a fixed reference direction, and ''A'' (''B'') denotes a sphere with the spot up (down) [9]. Thus, the orientation of a sphere is restricted to two states, A and B. The number of A and B particles in the cells at a time step $n\Delta t$, $n = 1,2,...$, are given by the sets of cell occupation numbers $\{a\}_{n\Delta t}$ and $\{b\}_{n\Delta t}$, respectively. We assume that the microscopic dynamics lead to a *Markov* process [10] with waiting time interval Δt, and assign probabilities that within Δt a particle in a given cell will *react* (if the cell is nonempty), *jump* to a neighboring cell *with* or *without* rotation (with rates $\tilde{D}_{tr}$ and $\tilde{D}$ respectively), or *stay* in the cell *with* rotation (with rate $\tilde{D}_{rot}$) or *without*. In the continuum limit $\tilde{D}_{rot}$ and $\tilde{D}_{tr}$ fold into one effective parameter that we refer to as D_{rot}, with the continuum limit translational diffusion constant denoted by D. Disregarding the influence of microscopic rotations at first, we assume that two particles in a cell may react and annihilate with some rate δ_0 only if one is A and the other B, with δ_0 as an average over all possible active (''spot-to-spot'') and nonactive encounters within the time interval Δt. Since microscopic rotations in the time interval Δt may turn a nonactive encounter into an active one we also assign a nonzero reaction rate λ_0 to the cases where both particles initially are of type A or B. The assignment of values to the rate constants is immaterial, but clearly λ_0 will approach δ_0 for sufficiently fast microscopic rotations. Thus, to ''optimize'' effects from steric reactivity we assume that

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$\lambda_0 \ll \delta_0$, and also $D_{\text{rot}}/D \ll 1$. This limit of ''slow'' rotations is indeed realized in many experimental systems [8].

The model thus constructed is equivalent to a generalized two-species annihilation system where A and B particles diffuse by translations and ''flips,'' $A \leftrightarrow B$, and react according to [11]:

$$A + A \xrightarrow{\lambda_0} \emptyset \quad A + B \xrightarrow{\delta_0} \emptyset$$

$$B + B \xrightarrow{\lambda_0} \emptyset. \tag{1}$$
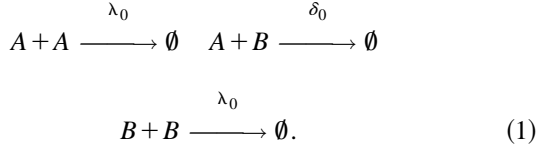
Without rotations ($\lambda_0 = 0$ and $D_{\text{rot}} = 0$) one immediately obtains the well-known $A + B \to 0$ universality class for the asymptotic mean density: $n_a(t) = n_b(t) \sim t^{-d/4}$ [12,2]. To explore the more realistic case including rotations we consider the master equation

$$\frac{d}{dt} P(c,t) = \sum_{c'} R_{c' \to c} P(c',t) - \sum_{c'} R_{c \to c'} P(c,t). \tag{2}$$

Here $P(c,t)$ denotes the probability of a given configuration $c \equiv (\{a\},\{b\})$ at time t, and $R_{c' \to c}$ is the transition rate from state $c' \equiv (\{a\}',\{b\}')$ into c, determined by D, D_{rot}, δ_0, and λ_0. We take $P(c,0)$ as a Poisson distribution, with averages denoted by $n_{a,0}$ and $n_{b,0}$ for A and B particles, respectively. In the absence of anisotropies or external fields we expect that $n_{a,0} = n_{b,0}$, but for now we leave the initial densities unspecified.

Following Refs. [13,14], the master equation (2) can be mapped onto a field theory in the continuum limit, with A and B particles described by scalar fields a and b, respectively. Introducing $\phi \equiv (a+b)/2$, $\psi \equiv (a-b)/2$ (with conjugated fields defined without the factor of $\frac{1}{2}$), and corresponding initial densities $n_{\phi,0} \equiv (n_{a,0} + n_{b,0})/2$, $n_{\psi,0} \equiv (n_{a,0} - n_{b,0})/2$, we obtain the action

$$S = \int d^d x \int dt \left[\bar{\phi}(\partial_t - \nabla^2)\phi + \bar{\psi}(\partial_t - \nabla^2)\psi + \rho\bar{\psi}\psi + (\lambda_0 + \delta_0)\bar{\phi}\phi^2 + (\lambda_0 - \delta_0)\bar{\phi}\psi^2 \right.$$

$$\left. + 2\lambda_0\bar{\psi}\psi\phi + \frac{\lambda_0 + \delta_0}{4}\bar{\phi}^2\phi^2 + \frac{\lambda_0 - \delta_0}{4}\bar{\phi}^2\psi^2 + \frac{\lambda_0 - \delta_0}{4}\bar{\psi}^2\phi^2 + \frac{\lambda_0 + \delta_0}{4}\bar{\psi}^2\psi^2 + \lambda_0\bar{\phi}\bar{\psi}\phi\psi \right]$$

$$- \int d^d x [n_{\phi,0}\bar{\phi}(x,0) + n_{\psi,0}\bar{\psi}(x,0)], \tag{3}$$

where we have rescaled the time variable, $Dt \to t$, and where $\rho \sim D_{\text{rot}}/D$. Using Eq. (3), the mean densities can be calculated as $n_c(t) = \langle c(t) \rangle_S$ ($c = a,b$), where $\langle \ \rangle_S$ denotes an average with respect to the action S. The rate constants, playing the role of coupling constants, here become dimensionless when $d = 2$, suggesting this as the upper critical dimension above which mean field theory (''normal reaction kinetics'' [1]) should be valid, a result confirmed by standard power counting techniques [15]. Hence, we concentrate on $d \leqslant 2$. These dimensions can be explored by using RG improved perturbation theory in $d_c = 2$ and then continuing the results to $d < 2$ via an ϵ expansion. As seen in Eq. (3), rotational diffusion acts as a mass perturbation in the ψ sector, and for simplicity we focus on the ''strong'' steric limit where this term is omitted, commenting on the general case as we go along.

Using dimensional regularization, divergences in perturbation theory show up as poles in $\epsilon = 2 - d$. Analogous to the single-species case $A + A \to 0$ [16], these poles can be removed by simply renormalizing the rate constants: $\lambda_0 \to \lambda_R$ and $\delta_0 \to \delta_R$. The renormalized rate constants are defined by primitively divergent vertex functions evaluated at an arbitrary momentum scale κ, which is further used to define dimensionless bare and renormalized rates $g_0 \equiv \kappa^{-\epsilon}\delta_0$, $h_0 \equiv \kappa^{-\epsilon}\lambda_0$, and $g_R \equiv \kappa^{-\epsilon}\delta_R$, $h_R \equiv \kappa^{-\epsilon}\lambda_R$, respectively. These are related by the exact result

$$g_R = \frac{g_0}{1 + g_0/g^*}, \quad h_R = \frac{h_0}{1 + h_0/h^*}, \tag{4}$$

with $g^* = h^* = \Gamma(\epsilon/2)^{-1}(8\pi)^{d/2}$ as the fixed point to which both rate constants flow. We are interested in the large-time mean densities $n_a(t)$ and $n_b(t)$, which depend, in principle, on the initial densities $n_{a,0}$ and $n_{b,0}$, and the bare rates λ_0 and δ_0, expressed through h_R, g_R, and κ. However, the densities cannot depend on the arbitrarily chosen scale κ, and this implies a Callan-Symanzik equation

$$n_c(t; g_R, h_R; n_{a,0}, n_{b,0}; \kappa)$$

$$= (\kappa^2 t)^{-d/2} n_c[\kappa^{-2}; \tilde{g}_R(t), \tilde{h}_R(t); \tilde{n}_{a,0}(t), \tilde{n}_{b,0}(t); \kappa],$$

$$c = a,b, \tag{5}$$

with running coupling constants

$$\tilde{g}_R(t) = \frac{g^*}{1 + (t/t^*_\delta)^{-\epsilon/2}}, \quad \tilde{h}_R(t) = \frac{h^*}{1 + (t/t^*_\lambda)^{-\epsilon/2}}, \tag{6}$$

and densities $\tilde{n}_{c,0}(t) = (\kappa^2 t)^{d/2} n_{c,0}$, with $c = a,b$. The crossover times are given by $t^*_\delta = (g^*/\delta_0)^{2/\epsilon}$ and $t^*_\lambda = (h^*/\lambda_0)^{2/\epsilon}$, respectively. The fact that the rate constants flow to the *same* fixed point coupling $g^* = h^*$ has some unexpected consequences, and dramatically simplifies calculations as compared to the two-species case $A + B \to 0$, with $\lambda_0 = 0$, a notoriously difficult problem within the RG [2].

To calculate the mean densities $n_a(t)$ and $n_b(t)$, the perturbation series has to be organized in such a way as to make it well behaved when the initial running densities flow to

infinity in Eq. (5). At tree level this can be done by simply "dressing" the initial densities $n_{c,0}$ ($c=a,b$)

$$(7)$$

and free propagators $G_0(t_1-t_2;p)=\theta(t_1-t_2)e^{-p^2(t_1-t_2)}$

$$(8)$$

In these diagrams a thin (thick) line corresponds to a free (dressed) propagator, with a cross representing an initial density. The dressed tree-level densities $\langle a(t)\rangle$ and $\langle b(t)\rangle$ (with averages taken only over tree-level diagrams) are solutions of the coupled *classical* rate equations

$$\frac{d}{dt}\langle a(t)\rangle=-(\lambda_0\langle a(t)\rangle^2+\delta_0\langle a(t)\rangle\langle b(t)\rangle),$$

$$(9)$$

$$\frac{d}{dt}\langle b(t)\rangle=-(\lambda_0\langle b(t)\rangle^2+\delta_0\langle b(t)\rangle\langle a(t)\rangle),$$

which for equal initial densities $n_{a,0}=n_{b,0}=n_0$ yield the prediction

$$\langle a(t)\rangle=\langle b(t)\rangle=\frac{n_0}{1+n_0(\lambda_0+\delta_0)t}.$$

$$(10)$$

This result is drastically changed by fluctuations, as revealed by a loop expansion of the densities. To carry it out we need the dressed tree-level propagators which, for equal initial densities, can be calculated exactly. In the ϕ-ψ basis,

$$G_\xi(p,t_1-t_2)=\theta(t_1,t_2)e^{-p^2(t_1-t_2)}\left(\frac{1+n_0(\lambda_0+\delta_0)t_2}{1+n_0(\lambda_0+\delta_0)t_1}\right)^{\Delta_\xi},$$

$$\xi=\phi,\psi,$$

$$(11)$$

with $\Delta_\phi=2$ and $\Delta_\psi=2\lambda_0/(\lambda_0+\delta_0)$. At the one-loop level there are two diagrams that contribute to $\langle\phi\rangle$ (with $\langle\,\rangle$ now denoting a full average):

$$(12)$$

with a full (dashed) line denoting a $\phi(\psi)$ propagator. After performing the momentum loop integrations and taking $n_0\to\infty$, one obtains

$$\langle\phi\rangle_{1-loop}=\frac{1}{2}(8\pi t)^{-d/2}\int_0^1 dx\, x^{1-d/2}$$

$$\times\int_0^1 dy[y^2+z^2y^{2z}](1-y)^{-d/2},\qquad(13)$$

with $t_1\equiv tx$ and $t_2\equiv txy$, and with $z\equiv(\lambda_R-\delta_R)/(\lambda_R+\delta_R)$. Equations (4) and (6) imply that $z\to0$ for large times, thus killing the second term in the square bracket in Eq. (13). By an ϵ expansion, using that $\langle\psi\rangle=0$ for equal initial densities, we thus obtain for large times,

$$n_a(t)=n_b(t)=\frac{1}{2}\left[\frac{1}{4\pi\epsilon}+\frac{\ln 8\pi-(5/2)}{8\pi}+\cdots\right]t^{-d/2},$$

$$t\to\infty,\ \lambda\neq0,\ d<2.\qquad(14)$$

This result, which we have checked to the two-loop level, yields the *same* universal expression for the total density $N(t)=n_a(t)+n_b(t)$ as for a nonsteric system [16]. The inclusion of rotational diffusion with $\rho\neq0$ in Eq. (3) does not influence the expression in Eq. (14); since ρ does not renormalize, the long-time asymptotics of the theory stay the same [17]. The fact that the asymptotic density is blind to steric effects and exhibits not only the same decay exponent $-d/2$ as a nonsteric system, but also the same *amplitude* is a striking manifestation of universality in reaction-diffusion processes.

Equation (13) reveals how λ_0 controls the universality class of the model. In addition to the pole in $1/\epsilon$, there is a second *potential* divergence coming from the y integration, due to the flow $n_0\to\infty$ under the RG. However, as n_0 flows, z flows as well *unless* $\lambda_0=0$, and the asymptotic value of z determines the fate of the integral: for $z>-\frac{1}{2}$ ($z\leq-\frac{1}{2}$) the y integral is finite (divergent). If $\lambda_0=0$ one has the $A+B\to0$ universality class [2]. For this case $z=-1<-\frac{1}{2}$ for all times and the integral diverges. On the other hand, for *any* $\lambda_0\neq0$, $z\to0$ and, accordingly, $z>-\frac{1}{2}$ for large times, producing a well-behaved expansion. This gives the $A+A\to0$ universality class of Eq. (14). Our results imply that even if λ_0 is arbitrarily small, the system will eventually behave as if $\lambda_0=\delta_0$ (*nonsteric* limit). How long does it take for this to happen? Since $z=-\frac{1}{2}$ is the critical value that controls the n_0 dependence of perturbation theory, and thus the crossover to the $A+A\to0$ universality class, it is natural to define a crossover time t_z such that $z(t_z)=-\frac{1}{2}$. Equation (6), together with the definition of z, shows that
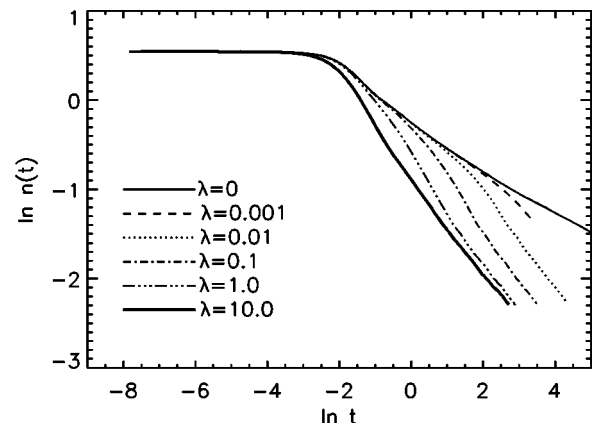

FIG. 1. Density decay obtained from a numerical simulation of the master equation in Eq. (2) in $d=1$ with 10^5 cells. Here $\delta=10$ and $n_A^0=n_B^0=3.5$ particles/site.

$$t_z = \left[\frac{g*}{2} \left(\frac{1}{\lambda_0} - \frac{3}{\delta_0} \right) \right]^{2/\epsilon}. \tag{15}$$

Since $t_\delta^* \ll t_z \sim t_\lambda^*$ for small λ_0, there is a large intermediate time interval with a strong n_0 dependence where $\widetilde{g}_R$ is close to its fixed point value $g*$, while $\widetilde{h}_R$ is still small. A strong n_0 dependence with $\widetilde{g}_R \sim g*$ implies scaling with the exponent $-d/4$ when $\widetilde{h}_R = 0$ (no rotations) [2]. Since a small $\widetilde{h}_R$ cannot change this behavior, it will also be present for slow rotational modes with $\lambda_0 \neq 0$. The inclusion of rotational diffusion with $\rho \neq 0$ in Eq. (3) will decrease t_z, but for sufficiently small ρ there will still be an intermediate regime with a strong n_0 dependence, supporting scaling with the exponent $-d/4$ [17]. We expect this property to hold generically, also for more realistic systems with continuous degrees of freedom. By analogy, we also expect a similar crossover from $n(t) \sim t^{-d/4}$ to the usual mean-field behavior $n(t) \sim t^{-1}$ for steric systems in dimensions $d > 2$. Work on this problem is in progress.

What causes the crossover from the $t^{-d/4}$ decay to the $t^{-d/2}$ decay for small λ_0? The most probable scenario is that A and B particles begin to segregate into A- and B-rich regions, a process during which the $A + B \rightarrow 0$ reaction is dominant ($-d/4$ decay exponent). Once A and B regions are formed, however, the $A + B \rightarrow 0$ reaction becomes unimportant and the $A + A \rightarrow 0$ and $B + B \rightarrow 0$ reactions become dominant despite the small value of λ_0, resulting in the $-d/2$ decay exponent.

Figure 1 shows the results of a numerical simulation of the master equation (2) in $d = 1$ [18]. The uppermost curve corresponds to $\lambda = 0$ and $\delta = 10$ ($A + B \rightarrow 0$ model with decay exponent $-d/4$), while the lowest curve corresponds to the case with equal reaction rates $\lambda = \delta = 10$, representing the asymptotic limit of equal rate constants as given in Eq. (6). As predicted, for small values of λ (intermediate curves) the decay exponent (slope of the curves) changes from $-d/4$ for early times to $-d/2$ at late times, with crossovers consistent with Eq. (15) (scaling with $1/\lambda^2$ for small λ).

The present model can be generalized to an arbitrary number of orientations N by introducing the ''particles'' $A_1, \ldots, A_N$, and reactions $A_\alpha + A_\beta \xrightarrow{\lambda_{\alpha,\beta}} \emptyset$. This generalized system can be shown to belong to the same universality class as the present $N = 2$ model as long as all rates $\lambda_{\alpha,\beta}$ are nonzero [17]. However, if one or several of the rates $\lambda_{\alpha,\beta}$ vanish, a different scaling behavior results (most probably the $t^{-d/4}$ asymptotics of the ''$A + B$'' model, although this is still to be established).

A recent breakthrough in preparing and monitoring low-dimensional chemical reactions—using carbon nanotubes as effectively one-dimensional ''test tubes'' [19,20]—opens up the possibility to experimentally test our predictions. The essential elements to be present in a laboratory setup are that (i) the reactions are sufficiently fast to ensure the diffusion-controlled condition $t_R \ll t_D$, (ii) the reactants have a highly anisotropic surface reactivity with sufficient slow rotational diffusion to make the system strongly steric, and (iii) the reactive products precipitate out of the system on a short time scale compared to t_D and hence do not influence the kinetics [21]. An observation of the crossover behavior predicted in the present work would be extremely interesting as it would exhibit a reaction-diffusion process supporting two distinct time scales with different anomalous scaling.

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