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Analytic approach to the space-time kinetics of annihilation reactions

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Time evolution equations for the density of reactants are derived for the diffusion-limited reaction $A+B\rightarrow 0$ in a d-dimensional space by generalizing the Galanin approach to extended absorbers. The solution of these equations agrees with simulations for the overall time regime. Perfect and imperfect reaction cases are analyzed in d dimensions. With a uniform initial condition a critical dimension of 2 is found for segregation.

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I. INTRODUCTION

The kinetics of the recombination process $A+B\rightarrow 0$ (or inert) has recently attracted considerable interest due to the fact that segregation of like particles occurs, leading to anomalous reaction rate laws [1–10]. The sensitivity of segregation to changes in initial conditions, presence of sources, disorder, external forces, etc., is remarkable. Most of the recent literature is devoted to the analysis of these phenomena under the assumption that some kind of rate equations is valid.

In contrast with other reactions such as $A+A\rightarrow A$ or $A+A\rightarrow 0$, the recombination process does not have exact solutions in one dimension, and in general the analysis of this process is based on approximate schemes. Since it is a many body problem, it is possible to obtain an exact hierarchy of equations involving correlations of higher orders. Truncation of this hierarchy by some approach yields a desirable mesoscopic level description in which an evolution equation for the mean density with effective time dependence coefficients results [11–13].

In this article, we will use a different framework for obtaining evolution equations at the mesoscopic level. Our starting point is a stochastic equation for the density of a species of particles in which the other species acts as an absorber with a given absorption shape function. It is a generalization to extended absorbers of the Galanin methods used in nuclear reactor theory for modeling neutron absorption [14]. This equation can be exactly averaged. Then, by using a diagrammatic technique, it is possible to select and take into account the leading contributions for short and long times. The result is an equation for the density of particles in which the reaction term is given by a convolution in space and time of a kernel with the density. The same method has been recently used for analyzing the evolution of the $A+B\rightarrow B$ reaction [15,16]. As pointed out there, the method has several advantages. On one hand, it is able to describe with good precision the system evolution for any time, while usually only asymptotic results are obtained. On the other hand, the resulting equation is the continuous limit of a master equation directly related to simulations. For this reason, we always obtain a good agreement between simulations and solutions of such an equation.

Since we have used a different scheme, the results obtained yield a new point of view on the problem of segregation in recombination processes. We have the possibility of varying the reaction length by controlling the probability of reaction. Then, it is possible to study perfect and imperfect reaction cases. These changes have no direct consequence for the long-time evolution, but they have a drastic impact on the sensibility to fluctuations on the initial conditions. In fact, we have obtained for segregation a critical dimension of 2 with strictly homogeneous initial conditions. As is known, spatial fluctuations on the initial conditions lead to a critical dimension $d_c=4$ [9].

The paper is organized as follows. In Sec. II, the stochastic equation governing the evolution of the particles is formulated. This equation is exactly averaged in Sec. III. By keeping the leading contribution for short and long times, we obtain the final equations. In Sec. IV, the relation of the equations and comparison of their solutions with simulations is shown. In Sec. V, an extensive analysis of the n-dimensional problem is made for the case of uniform initial conditions. Finally, we present a brief discussion of the results and include in the Appendix a diagrammatic representation of the main equations.

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II. FORMULATION OF THE PROBLEM: STOCHASTIC EVOLUTION EQUATION

We consider two kinds of particles, A and B, with independent motion and with the possibility of annihilation when they are in contact. We assume that the motion of an individual particle is a Markovian process with conditional probability $G(r,t|r',t')$ for the A particles and $W(r,t|r',t')$ for the B ones. These probabilities fulfill the evolution equations

$$\dot{G}=L_A G \ , \tag{1a}$$

$$\dot{W}=L_B W \ , \tag{1b}$$

with $G(r,t|r',t_0)=W(r,t|r',t_0)=\delta(r-r')$ as initial conditions, and with L_A, L_B being linear operators. The Markovian character, which is essential in this formulation, means that a joint probability in position and time for one particle can be factored as

$$\begin{aligned}P(r_1,t_1;r_2,t_2;\ldots;r_n,t_n)&=\langle\delta(r_1-r(t_1))\delta(r_2-r(t_2))\cdots\rangle\\&=W(r_1,t_1|r_2,t_2)\cdots W(r_{n-1},t_{n-1}|r_n,t_n)P(r_n,t_n)\ ,\end{aligned}\tag{2}$$

where the brackets $\langle\ \rangle$ indicate an average over the motion process.

Each process moves independently, but its existence depends on the evolution of the other particles. We identify each particle with a numerical index. Since the number of particles is not conserved, the set of indices corresponding to the existing particles varies with time $\{i(t)\}$. The density of particles of one kind at time t is given by

$$n_{A,B}(r,t)=\left\langle\sum_{\{i_{A,B}(t)\}}\delta(r_{i_{A,B}}(t))\right\rangle\ , \tag{3}$$

where the average is also taken over all possible annihilation processes. Another important density function is defined as

$$n_{A,B}(r,t'|t)=\left\langle\sum_{\{i_{A,B}(t)\}}\delta(r-r_{i_{A,B}}(t'))\right\rangle\ . \tag{4}$$

This corresponds to the density of particles at time t' that survive until time t. Both densities are related through

$$n_A(r,t)=\int G(r,t|r',t')n_S(r',t'|t)dr'\ , \tag{5a}$$

$$n_B(r,t)=\int W(r,t|r',t')n_B(r',t'|t)dr'\ . \tag{5b}$$

Note that to invert these equations to obtain $n_{A,B}(r',t')|t)$ as a functional of $n_{A,B}(r,t)$ is a quite difficult task. Only when the evolution is essentially diffusive or the density is rather uniform is it feasible.

Having specified the motion of the particles, we consider now the reaction process. We assume that when two particles of different species are close enough to each other, they can annihilate. The rate of probability of such a process when the relative position between the particles to r is given by a function $\gamma_\epsilon H_\epsilon(r)$, where ϵ is a mean interaction length, H_ϵ is a normalized function that tends to $\delta(r)$ when $\epsilon\to 0$, and γ_ϵ is a rate of probability per unit volume of interaction of one particle. Under this notation, the effective interaction time is given by $\epsilon^{-d}\gamma_\epsilon^{-1}$. The reaction will be either perfect (fast) or imperfect (slow) if this time is shorter or longer than the collision time [17]. The different possibilities depend on the kind of motion, dimensionality, initial conditions, etc.

Finally, in order to formulate the evolution equations, we define $n_{A,B}(r,t|\{B,A\})$ as the density of the A or B particles conditioned to the occurrence of a process $\{r_{i_B}(t)\}$ or $\{r_{i_A}(t)\}$ in the evolution of the B and A particles. Hence, the evolution of these densities is governed by

$$\dot{n}_{A,B}(r,t|\{B,A\})=L_{A,B}n_{A,B}(r,t|\{B,A\})-\gamma_\epsilon\sum_{\{i_{B,A}(t)\}}H_\epsilon(r-r_{i_{B,A}}(t))n_{A,B}(r,t|\{B,A\})\ . \tag{6}$$

In this equation, the form of the reaction term is a generalization of the Galanin approach for extended absorbers. In the limit $\epsilon\to 0$, we recover the original Galanin form of point absorbers. The indicated equations are coupled in the sense that the target particles act like an external absorber. The rate of absorption for each particle is then the same only in average. In other words, the annihilation of one particle does not necessarily imply the annihilation of the other. This is the main approximation of the method. As can be seen from the simulations, this approximation is excellent even when the reaction is imperfect. Clearly, in the perfect reaction case nearly all particles react simultaneously, and the effect of the approximation has to be negligible.

III. AVERAGE OF THE EVOLUTION EQUATIONS AND DIAGRAMMATIC EXPANSIONS

A naive approximation for the average of Eq. (6) consists of the factorization of the reaction term

$$\left\langle\sum_{\{i(t)\}}H_\epsilon(r-r_{i_{B,A}}(t))n_B(z|\{A\})\right\rangle\approx n_A^H(z)n_B(z)\ , \tag{7}$$

where the superscript H means a space convolution with the normalized function H:

$$f^H(r,t)=\int H(r-r')f(r',t)dr' \ . \tag{8}$$

This corresponds to a mean field approximation that is only valid at short-time intervals. An exact method for the averaging of this type of equation is given in Ref. [16]. With such a method, it is possible to find a systematic expansion of products and convolutions of conditional probabilities and mean densities. Here we exploit this method with the same notation used therein.

For the sake of simplicity, we only consider one of the equations (6). The other equation requires an identical treatment. First we take the integral form of Eq. (6) and after iteration and multiplication by $\sum_{\{i(t)\}}H_\epsilon(r-r_{i_B}(t))$, we obtain

$$\begin{aligned}\sum_{\{i(t)\}}\Delta_i(z)n_A(z)=&\sum_{\{i(t)\}}\Delta_i(z)G_{z,\underline{z}'}\delta(t')n_A(z')-\gamma\sum_{\{i(t),i_1(t_1)\}}\Delta_i(z)G_{z,\underline{z_1}}\Delta_{i_1}(z_1)G_{z_1,z'}\delta(t')n_A(z')\\&+\cdots(-\gamma)^n\sum_{\{i(t),i_1(t_1),\ldots,i_n(t_n)\}}\Delta_i(z)G_{z,\underline{z_1}}\Delta_{i_1}(z_1)\cdots G_{z_n,\underline{z}'}\delta(t')n_A(z')+\ldots\ ,\end{aligned}\tag{9}$$

where we have used the following shorthand notation: we denote by z_i the pair (r_i,t_i), $\underline{z_i}$ indicates integration over the variables r_i,t_i for all functions containing them, $G_{z,z'}$ is $G(r,t|r',t')$, and $\Delta_i(z)=H_\epsilon(r-\overline{r}_i(t))$.

Now we average this equation, taking into account the factorization properties of the joint probability [Eq. (2)], obtaining

$$\frac{\partial n_A}{\partial t}=L_An_A-\gamma\mathcal{A}_A\ , \tag{10}$$

where

$$\begin{aligned}\mathcal{A}_A(z)&\equiv\left\langle\sum_{\{i\}}\Delta_i(z)n_A(z)\right\rangle\\&=G_{z,\underline{z}'}n_B^H(z'|t)\delta(t')n_A(z')-\gamma_\epsilon W^H_{z,\underline{z_1}}G_{z,z_1}W^H_{z_1,\underline{z}'}G_{z_1,z'}n_B^H(z'|z)\delta(t')n_A(z')\\&\quad-\gamma_\epsilon W^H_{z,\underline{z_1}}G_{z,z_1}n_B^H(z_1|t)G_{z_1,\underline{z}'}n_B^H(z')\delta(t')n_A(z')\\&\quad+\cdots(-\gamma_\epsilon)^nW^H_{z,\underline{z_1}}G_{z,z_1}G_{z_1,\underline{z_2}}\cdots G_{z_n,\underline{z}'}\delta(t')n_A(z')\\&\qquad\times[n_B^H(z_1|t)n_B^H(z_2)\cdots n_B^H(z')+W^H_{z_1,z_2}\cdots W^H_{z_n,z'}n_B^H(z'|t)]+\ldots\ .\end{aligned}\tag{11}$$

A more complete picture of this expansion is given by means of the diagrammatic representation in the Appendix. Note that all possible combinations of products of n_B^H and W^H are present in the expansion. Since the density is a monotonically decreasing function of time, the long-time behavior will be dominated by the lowest orders in $n_B^H(t)$. These terms can be summed, giving

$$\mathcal{A}_A(z)\approx T(z,z_1)n_B^H(z_1|t)G_{z,\underline{z}'}n_B^H(z_1|t)G_{z,\underline{z}'}\delta(t')n_A(z')\ , \tag{12}$$

with

$$T(z,z')=\delta(z-z')-\gamma_\epsilon G_{z,z'}W^H_{z,z'}+\gamma_\epsilon^2G_{z,\underline{z_1}}W^H_{z,z_1}G_{z_1,z'}W^H_{z_1,z'}+\ldots\ . \tag{13}$$

The remaining terms can also be expressed in terms of these functions in such a way that the overall expansion reads

$$\begin{aligned}\mathcal{A}_A(z)=&T(z,\underline{z_1})n_B^H(z_1|t)G_{z_1,z'}\delta(t')n_A(z')\\&+\cdots(-\gamma_\epsilon)^nT(z,\underline{z_1'})G_{z_1'\underline{z_1}}T(z_1,\underline{z_2'})G_{z_2',\underline{z_2}}\ldots T(z_n,\underline{z_{n+1}'})n_B^H(z_{n+1}')G_{z_{n+1}',\underline{z}'}\delta(t')n_A(z')\\&\qquad\times[n_B^H(z_1')n_B^H(z_2')\cdots n_B^H(z_n')+\cdots n_B^H(z_1')\cdots]\ ,\end{aligned}\tag{14}$$

where the first term corresponds to the asymptotic long-time contribution, terms with consecutive probabilities $W_{z_i,z_{i+1}}W_{z_{i+1},z_{i+2}}$ now being forbidden. A more complete representation of this expansion is given in the Appendix using diagrammatic techniques.

Also, in order to get a good approximation for short times, we must keep the contribution of the highest orders in n_B^H. Hence, neglecting the crossed terms of mixed products of W and n_B^H, $\mathcal{A}_A(z)$ will be the solution of the following integral equation:

$$\begin{aligned}\mathcal{A}_A(z)=&T(z,\underline{z_1})n_B^H(z_1|t)G_{z_1,\underline{z}'}\delta(t')n_A(z')\\&+T(z,\underline{z_1'})n_B^H(z_1'|z)G_{z_1',\underline{z_1}}\mathcal{A}_A(z_1)\ .\end{aligned}\tag{15}$$

By substituting (15) into (10) and using the identity

$$n_A(z)=G_{z,\underline{z}'}\delta(t')n_A(z')-\gamma_\epsilon G_{z,\underline{z}'}\mathcal{A}_A(z') , \tag{16}$$

we finally obtain an equation for $n_A(z)$,

$$\frac{\partial n_A}{\partial t}=L_A n_A=\gamma_\epsilon T(z,\underline{z_1})n_B^H(z_1|t)n_A(z_1) , \tag{17a}$$

valid for short and long times. One could obtain a completely similar equation for the averaged density of B particles as

$$\frac{\partial n_B}{\partial t}=L_B n_B-\gamma_\epsilon T(z,\underline{z_1})n_A^H(z_1|t)n_B(z_1) . \tag{17b}$$

Equations (17a) and (17b) are the main result of this paper. As pointed out in the preceding section, the derivation of $n^H(z_1|t)$ as a function of $n(z)$ by means of (5) is not possible, except in a few cases. Then, some approximations are necessary. They will depend on each particular problem, but, as a first approach, two alternatives are possible, either $n(z_1|t)\sim n(z_1)$ or $n(z_1|t)\sim n(z)$. The first (a kind of sudden approximation) seems to be more adapted to problems in which diffusion is the main phenomenon. The second is an adiabatic approximation valid when the shape of the density varies slowly or is rather flat. In any case, the application of these equations to nonhomogeneous situations in cases where the usual rate equations are no longer valid is a very interesting problem, but it goes beyond the scope of the present work. In the next sections, we analyze the uniform solutions of these equations and compare them with simulations.

IV. COMPARISON WITH SIMULATIONS IN THE ONE-DIMENSIONAL HOMOGENEOUS CASE

In this section, we show how our method is very well suited to explain Monte Carlo simulations, even in low dimensions, and for all time regimes. For this comparison, we choose a simple example consisting of a set of particles A and B with the same uniform initial density and with the same diffusion coefficient D. L_A and L_B are diffusion operators $L_A=L_B=\Delta$, and the corresponding Green function has the usual form $G=W=(4\pi Dt)^{-d/2}\exp(-r^2/4Dt)$. In this case, the densities of both species of particles are homogeneous and identical, $n_A(t)=n_B(t)=n(t)$. Then for the two extreme approximations mentioned in the preceding sections, we have the evolution equations

$$\frac{dn}{dt}=\begin{cases}-\gamma n(t)\int_0^t K(t-t')n(t')dt' \quad \text{(adiabatic)} , & (18a)\\ -\gamma \int_0^t K(t-t')n(t')^2 dt' \quad \text{(sudden)} , & (18b)\end{cases}$$

with $K(t)=\int T(r,t)dr$. In any practical application or comparison with simulation, the condition of homogeneity will only hold up to a finite time. At sufficiently long times, inhomogeneities will develop due to the reaction, and the process will end governed by Eq. (18b). Instead of dealing with $T(z,z')$ through the series in (13), it is more convenient to consider its Fourier-Laplace transform $T(k,s)$; then the expression (13) reduces to

$$T(k,s)=\frac{(2\pi)^{-d/2}}{1+\gamma_\epsilon(2\pi)^{d/2}L\left\{\int G(k-k',t)W(k',t)H(k')dk'\right\}} , \tag{19}$$

where $L\{\ \}$ means Laplace transform in time. In terms of this function, $K(t)$ is given by

$$K(t)=(2\pi)^{d/2}L^{-1}\{T(k=0,s)\} . \tag{20}$$

Finally, for the sake of simplicity, we adopt a Gaussian form for the interaction function $H_\epsilon(r)=(\sqrt{2\pi\epsilon})^{-1}\exp(-r^2/4\epsilon^2)$. In a contact interaction, ϵ would correspond to the size of the particles, whereas in simulations it would be the lattice parameter. Substituting H_ϵ, G, and W into (19), and after inversion of the Laplace transform, in the one-dimensional case, for the $\epsilon\rightarrow 0$ limit, we have the following equations:

$$\frac{dn}{dt}=-\gamma n^2+\int_0^t c(t-t')n(t)n(t')dt' , \tag{21a}$$

$$\frac{dn}{dt}=-\gamma n^2+\int_0^t c(t-t')n(t')^2 dt' , \tag{21b}$$

with $c(t)=\gamma[(\pi t)^{-1/2}-\alpha\exp(\alpha^2 t)\text{erfc}(\alpha\sqrt{t})]$, $\alpha=\gamma/\sqrt{8D}$.

These are the final equations governing the evolution of the density to be compared with simulations. By simple inspection of these equations, we can see that at short times the mean field approximation holds. It is also evident that the memory term dominates the long-time behavior. At long time, the following asymptotic behaviors are found:

$$n(t)\sim\frac{\ln t}{2\gamma\Gamma(\frac{1}{2})\sqrt{8D}}t^{-1/2} , \tag{22a}$$

$$n(t)\sim\left[\frac{n(0)}{\gamma\Gamma(\frac{1}{2})\sqrt{8D}}\right]^{1/2}t^{-1/4} . \tag{22b}$$

We have simulated the equivalent system on a one-dimensional lattice. We have distributed uniformly an equal number of A and B particles through the lattice. One particle has a probability $\lambda\Delta t$ of moving to either the left or right. Several particles of the same class can coexist in the same site, to avoid the extra interaction of the volume effect. When two particles A and B meet in the same place, they can annihilate with a probability $\beta\Delta t$. Concerning this point, we have considered two cases, one with correlate annihilation (CA) and the other with in-

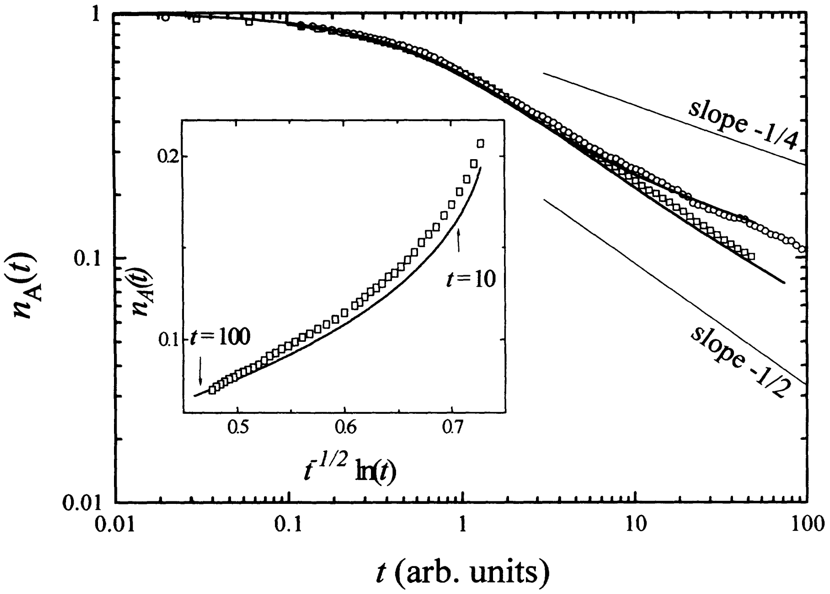

FIG. 1. Evolution of the mean density of A particles in one dimension. The continuous lines are the solutions of Eqs. (18) and (19). Circles and squares are the result of the simulation of the system on a 10 000 site grid, with periodic boundary conditions. The circles show the average of ten realizations with the particles distributed randomly over the whole system. The squares show the average of 30 realizations with the particles initially distributed within ten cells. The inset shows the two lower curves on another scale, showing the behavior of Eq. (22a). The parameters are $D=1, \gamma=1$.

dependent annihilation (IA). In the first situation, both particles annihilate simultaneously with the indicated probability. In the second case, each particle annihilates independently of the other, with the same probability. The IA case corresponds exactly to the simulation of the following master equation:

$$\frac{\partial P(r,t)}{\partial t}=\lambda P(r-1,t)+\lambda P(r+1,t)-2\lambda P(r,t)$$
$$-\sum_{\{j\}}\beta\delta_{r,r_{B_j}}P(r,t)\ , \tag{23}$$

where $P(r,t)$ is the probability for the ith particle of class A of being at site r, and r_{B_j} is the position of the jth particle of class B. By taking a length scale Δ, it is straightforward to obtain the continuous limit of (23) which, under the constraints $(\Delta\to 0;\lambda,\beta\to\infty)$, gives $D=\lambda\Delta^2$ and $\gamma=\beta\Delta$, and with $P(r,0)=\delta_{r,0}$, reproduces Eq. (6) with $H_\epsilon(r)=\delta(r)$ and $n(r,0)=\delta(r)$.

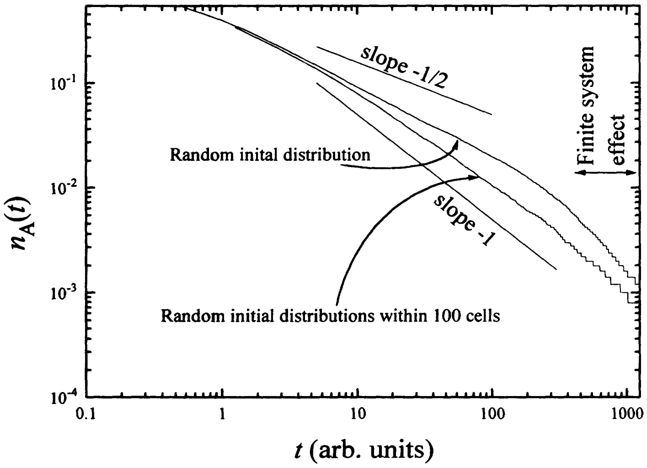

FIG. 2. Evolution of the mean density of A particles in two dimensions. The curves correspond to the simulation of the process on a grid of 200×200 with periodic boundary conditions and 5000 particles. The upper cure corresponds to a random initial distribution over the whole square, while the lower one corresponds to the distribution within 100 cells.

Since the averaging of (23) can be done exactly, it is not surprising to find rather good agreement between the simulations in the IA case and the solutions of (21a) and (21b). Simulations with CA would correspond to a more complicated master equation in which all particles enter simultaneously. It is not the aim of this work to deal with this complicated master equation but to show that simulations with IA are good approximations to the more usual case of CA. Consequently our analytical method turns out to be well suited to explain Monte Carlo simulations (see Fig. 1). Simulations on this figure correspond to a case with IA and imperfect reaction $(\Delta \ll D/\lambda)$. The curves (a) correspond to a random initial condition with a Poisson interparticle distribution, while the curves (b) correspond to a still random initial distribution but with lower spatial fluctuations, generated by a random setting of particles within cells. It can be seen that the solutions of (21a) and (21b) agree quite well with the simulation of these cases.

V. ASYMPTOTIC ANALYSIS IN N DIMENSIONS

Most papers in the recent literature on diffusion-dominated annihilation have focused on the study of propagation of initial fluctuations and their relation with other phenomena [1–10]. However, the apparently easier problem of uniform evolution and comparison with simulations has scarcely been treated. This is mainly due to the lack of simple equations taking into account the fluctuations in the evolution process that arise from the reaction itself. Equations (17a) and (17b) have the leading contributions of these fluctuations and, as we show in the following, can be easily analyzed.

In more than one dimension, and due to the complications of inverting the Laplace transform of $T(k=0,s)$, it is more difficult to obtain a time evolution equation like

(21a). However, it is possible to perform an asymptotic analysis. In order to do it, we consider Eq. (18a) with the corresponding kernel in each dimension:

$$K_1(s)=\frac{\gamma_\epsilon}{1+\frac{\gamma_\epsilon}{\sqrt{8Ds}}\exp\left[\frac{s\epsilon^2}{2D}\right]\left\{1-\Phi\left[\left[\frac{s}{2D}\right]^{1/2}\epsilon\right]\right\}}\,, \tag{24a}$$

$$K_2(s)=\frac{\gamma_\epsilon}{1-\frac{\gamma_\epsilon}{8\pi D}\exp\left[\frac{s\epsilon^2}{2D}\right]E_i\left[-\frac{\epsilon^2 s}{2D}\right]}\,, \tag{24b}$$

$$K_3(s)=\frac{\gamma_\epsilon}{1+\frac{\gamma_\epsilon}{8\pi D}\frac{1}{\epsilon\sqrt{\pi}}-\left[\frac{s}{2D}\right]^{1/2}\exp\left[\frac{s\epsilon^2}{2D}\right]\left\{1-\Phi\left[\left[\frac{s}{2D}\right]^{1/2}\epsilon\right]\right\}}\,, \tag{24c}$$

where E_i and Φ are the exponential integral and the Fresnel functions, respectively.

The first point to note is that in all cases the short-time behavior leads to the mean field equation:

$$\frac{dn}{dt}=-\gamma_\epsilon n^2\,. \tag{25}$$

Hence, if we introduce as usual the equivalent rate coefficient $K_{\rm eff}$ as the necessary coefficient to validate the classical equation

$$\frac{dn}{dt}=-K_{\rm eff}n^2\,, \tag{26}$$

we can conclude that the short-time behavior is controlled by the usual coefficient of chemical kinetics $\gamma_\epsilon=\beta V$, V being the volume of the particle.

The long-time behavior is more involved and needs a separate analysis for each dimension. However, there are general features that are worth mentioning. For long times, $s\rightarrow 0$, the parameter γ_ϵ is irrelevant since it does not appear in the kernel. This means that for long times, perfect or imperfect reactions give the same result. Moreover, since reactions with IA and CA are equivalent when the reaction is perfect, one can expect that for long times both cases behave identically. Then the essential difference between perfect and imperfect reactions is the sensitivity to the initial conditions. An imperfect reaction is less sensitive to fluctuations in the initial conditions since the time between reactions is longer and there is more time for diffusion to homogenize initial fluctuations.

Recalling the asymptotic analysis in one dimension and taking into account the behavior of K_1 for $s\rightarrow 0$, $K_1(s)\sim\sqrt{8Ds}$, it is easy to deduce the asymptotic form of $n(t)$,

$$n(t)\sim\left[\frac{n(0)}{\gamma\Gamma(\frac{1}{2})\sqrt{8D}}\right]^{1/2}t^{-1/4}\,,$$

which agrees with simulations [18]. As we have shown above, this is a typical behavior indicating segregation of like particles. From (24a), one deduces an effective coefficient given by $K_{\rm eff}\sim n(t)^3/4a^2$. Due to its time dependence, it is an anomalous coefficient. In one dimension the reaction time is given by $\beta^{-1}=\epsilon\gamma^{-1}$, whereas the collision time, which is the same for any number of dimensions, is $\lambda^{-1}=\epsilon^2/D$. So the reaction is perfect whenever $\epsilon\geq D/\gamma$. The relative probability of reaction is $\beta/(\lambda+\beta)=\gamma\epsilon/(D+\gamma\epsilon)$. When γ is finite and ϵ is small (very slow reaction), the time between reactions is very large, $(D+\gamma\epsilon)/\gamma\epsilon n^{-1}$, and any initial condition becomes uniform in this time. Hence the evolution must be independent of the initial conditions. However, despite its long homogenization time ($\sim\epsilon^{-1}$), segregation occurs due to the compactness of diffusion in one dimension. The number of times a given site is visited is also of order ϵ^{-1}.

The two-dimensional (2D) case can be analyzed in a similar manner. The asymptotic behavior of the kernel is now $K_2(s)\sim -8\pi D\ln(\epsilon^2 s/2D)$, leading to an asymptotic behavior of the Laplace transformed density as $n(s)\sim -[8\pi D\ln(\epsilon^2 s/2D)]^{-1}$. This expression has the logarithmic correction typical of a marginal dimension. However, for the time dependent behavior, this correction does not exist, $n(t)\sim t^{-1}$. Hence the effective coefficient is constant and the result is not anomalous. We conclude that in the case of a uniform initial condition, the critical dimension for segregation is 2. This conclusion requires some explanation since it is in apparent contradiction with most of the analysis and simulations appearing in the literature. The problem arises because all distributions used for modeling uniform initial conditions are Poissonian. Then a simple scaling argument leads to the conclusion that in two dimensions the propagation of the initial spatial fluctuations gives segregation and, consequently, a $n(t)\sim t^{-1/2}$ behavior must be observed [4]. This is in agreement with the simulations. The apparent contradiction can be solved by choosing a distribution, other than Poissonian, with smaller spatial fluctuations. When doing that, a $n(t)\sim t^{-1}$ asymptotic behavior is obtained (see Fig. 2). For a continuous and completely uniform initial density, no segregation should develop.

Finally, in the three-dimensional case, one has $K_3(s)\sim 8\pi D(\epsilon\sqrt{\pi})$, obtaining for the temporal evolution of the density $n(t)\sim 8\pi D(\epsilon\sqrt{\pi})^{-1}$, and for the effective coefficient the classical result of Smoluchovsky, $K_{\rm eff}=8\pi D(\epsilon\sqrt{\pi})$ [19], where we identify the radius of the particle with $\sqrt{\pi}\epsilon$. The reaction time is $\beta^{-1}=\gamma^{-1}\epsilon^3$, and the reaction is perfect when $\gamma \gg \epsilon/D$, For finite γ and small ϵ the reaction is very fast; the relative probability of the reaction $(1+\gamma\epsilon D)^{-1}$ is large, and there will be great sensitivity to the initial conditions.

VI. CONCLUSIONS

By extending a previous result for the reaction $A+B \rightarrow B$ [16], we have derived a systematic method for obtaining evolution equations for the densities in two species annihilation reactions. We have assumed that the evolution between collisions is diffusive, and that there is a finite probability of annihilation in any collision of unlike particles. Our results describe the behavior of the densities, not only asymptotically but in the whole range of times. The predicted behavior was verified *via* numerical simulations in one and two dimensions. We have found a critical dimension of 2 for absolutely uniform initial conditions, meaning that in three dimensions mean field approximations are valid at all times. This apparent contradiction with previous results (e.g., [(1e),9]) is due exclusively to the character of the initial condition. In two dimensions, the time needed for the system to blur the initial condition is extremely large. The segregation observed in two-dimensional simulations is due to the inevitable initial fluctuations of discrete distributions. However, the true asymptotic stage of the evolution is finally achieved, and the crossover from the $t^{-1/2}$ to the t^{-1} behavior is seen in our simulations. This controversy will be discussed in detail elsewhere [20]. Spatial problems, such as the propagation of reaction fronts [21–29], can be adequately treated by this procedure [30]. Similar methods can be set up to analytically treat other related reactions (e.g., annihilation or coagulation of like particles, etc.). These and other extensions are the subject of further work.

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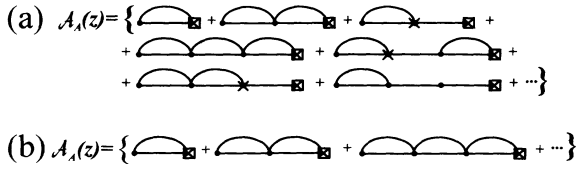

FIG. 4. Diagrammatic representation of the absorption function. See the Appendix.

APPENDIX

In order to make a representation of (11) in diagrammatic form, we consider the following criteria for the construction of diagrams. The basic structure of a diagram of nth order is a sequence of $n+2$ points $(z,z_1,z_2,\ldots,z_n,z')$ joined by a solid line, which represents the Green function G. The square in the last point z' corresponds to the initial condition $n_B^H(z'|\cdot)\delta(t')n_A(z')$ [Fig. 3(a)].

As shown in Fig. 3(b), on top of this structure there are clusters. A loop from a point z_{i_1} to another point z_{i_2} represents the $W^H_{z_{i_1},z_{i_2}}$ function. The last point of the cluster (with a cross) represents the function $n_B^H(z_{i_4}|t_{i_1})$. The cluster is built by several joined loops finishing with a crossed point.

A general diagram consists of the superposition of clusters. All points of the basic structure must be occupied by either loops or crosses. Each point belongs to one cluster only. The extreme cases of expression (11) are depicted in Figs. 3(c) and 3(d). In this figure, we also present, as an example, a mixed term of fourth order given by

$$(-\gamma_\epsilon)^4 G_{z,z_1}\ldots G_{z_4,z'} W^H_{z,z_2} n_B^H(z_1,z) W^H_{z_1,z_3} W^H_{z_3z'}(z'|t_1) n_B(z_4)$$

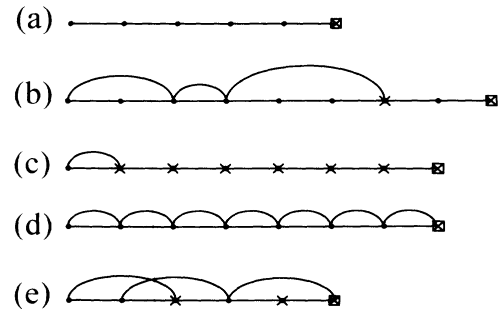

FIG. 3. Basic diagrams that represent the process of diffusion and reaction. See the Appendix.

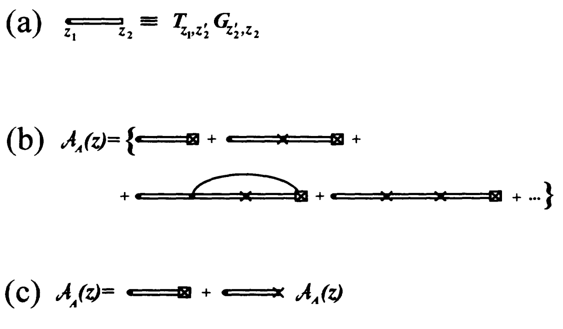

FIG. 5. Diagrammatic representation of the approximation of the absorption function. See the Appendix.

[Fig. 3(e)].

Equation (14) in this diagrammatic representation is represented in Fig. 4(a). The leading contribution for long times [Eq. (12)] is given in Fig. 4(b). The cluster in this figure can be summed up [Eq. (13)] giving a new basic structure in which the solid line is substituted by a double solid line representing a new propagator given by $T_{z_1,z_2'}G_{z_2',z_2}$. The rest of the representation remains unchanged, but now clusters with loops between nearest neighbors do not appear [see Fig. 5(b)]. Finally, the leading contribution for short times given by diagrams without loops can also be taken into account through the integral equation (15), which in diagrammatic representation is given in Fig. 5(c).

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