

Kinetics of n -species annihilation: Mean-field and diffusion-controlled limits

D. Ben-Avraham and S. Redner

Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215

(Received 18 February 1986)

We consider the kinetics of a system where n distinct chemical species A_i undergo the reactions $A_i + A_j \rightarrow \text{inert}$ ($i \neq j$). In the rate-equation approximation, a conservation law for the reaction is derived, and an explicit solution for the case $n=3$ is given. At the level of the master equation, Van Kampen's Ω expansion is employed to estimate the magnitude of local fluctuations in density which arise when the basic dynamical variable of the system is the (discrete) particle number, rather than a continuous particle density. We then develop a physical picture for the evolution of the n -species system, when the particles diffuse, which, together with the estimate of the magnitude of the local fluctuations, is used to deduce the form of the decay law when the initial densities of the n species are equal. For a d -dimensional n -species system below an upper critical dimension equal to $4(n-1)/(2n-3)$, the density is predicted to decay as $t^{-\alpha(n)}$, with $\alpha(n) = \frac{1}{2}d\{1 - 1/[2(n-1)]\}$, and this is verified by numerical simulations. In addition, the simulations reveal a striking symmetry breaking, where the equal-density initial state evolves to a long-time state where one species predominates.

I. INTRODUCTION

The kinetics of chemical reactions have been extensively studied both in the mean-field¹⁻³ and in the diffusion-controlled limits.^{4,5} As a general rule, it has been found that the behavior in the diffusion-controlled limit is considerably different than that of the mean-field limit when the spatial dimension d of the system is less than the upper critical dimension.⁶⁻¹¹ This difference stems primarily from the diffusive motion of the particles, which gives rise to fluctuations in the local concentration of the reactants. In contrast, in the mean-field or rate-equation description, it is assumed that the reactants are well-stirred so that the system is always spatially homogeneous. Typical examples where the difference between the diffusion-controlled and the mean-field limits can be easily seen are 1-species annihilation,^{7,9,12} $A + A \rightarrow \text{inert}$, and 2-species annihilation,^{7,8} $A + B \rightarrow \text{inert}$. In the former case, the density decays as $t^{-d/2}$ for $d < d_c = 2$, while in the latter case the decay is $t^{-d/4}$ for $d < d_c = 4$ when the initial density of A and B is equal. Above the upper critical dimension, however, fluctuations become irrelevant and the long-time decay rate for both diffusing particle systems and well-stirred systems will have the same form.

In this work, we study a simple but quite interesting model of bimolecular annihilation of n distinct chemical species whose behavior is considerably richer than the two reactions mentioned above. This model was introduced by Kang in order to understand, from a more general point of view, the fundamental differences between 1-species and 2-species annihilation. In our n -species model, there exist n distinct species which can react only with different species; hence in the limit $n=2$, the reaction reduces to $A + B \rightarrow \text{inert}$, while in the limit $n \rightarrow \infty$, the constraint of reacting only with different species becomes negligible, and the reaction becomes equivalent to the process $A + A \rightarrow \text{inert}$. Our goal in this paper is to understand the

kinetic behavior in the very interesting intermediate case of finite n .

For $n=2$, the reaction has a very simple conservation law, namely the conservation of the density difference, which holds both locally and globally. This *local* conservation law is of great importance in the theoretical understanding of 2-species annihilation.^{7,8,13} For $n > 2$, we shall show that the n -species reaction possesses a conservation law which is valid only *globally*. In order to make use of this form of a conservation law for determining the kinetic behavior, we shall first explore the ramifications that a purely global conservation law has for fluctuations in some very simple examples of bimolecular reactions. These fluctuations originate from the discrete nature of the system, i.e., from the fact that we are dealing with individual particles rather than a continuous concentration of particles, as assumed in the mean-field rate equations.

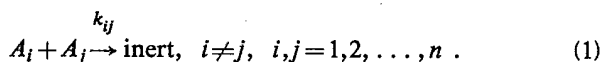
The diffusive character of the particle motion provides another source of concentration fluctuations which are crucial for an understanding of the kinetics. By using information about *both* sources of fluctuations, we shall deduce the decay law for an n -species system of diffusing particles below its upper critical dimension. We find, for equal initial densities of the reactants, that the density decays as $t^{-\alpha(n)}$, with $\alpha(n) = \frac{1}{2}d\{1 - 1/[2(n-1)]\}$ for $d < d_c = 4(n-1)/(2n-3)$.

The outline of the paper is as follows. In Sec. II we present the n -species annihilation model, and discuss its behavior in the mean-field limit. We derive a global conservation law for the densities of the various reactants and present the exact solution to the rate equations for the case of three species; the generalization to an arbitrary number of species is straightforward. We then digress, in Sec. III, to a discussion of the role of global and local conservation laws in determining the kinetics of chemical reactions. We also analyze two closely related simple examples, using the Van Kampen Ω expansion³ of the master

equation as our basic analysis method, in order to illustrate the ramifications of global and local conservation laws in determining local fluctuations in reactant density. In Sec. IV we use the methods presented and developed in the previous sections in order to predict the kinetics of the n -species model in the diffusion-controlled limit, i.e., when the reactants diffuse. The comparison with numerical simulations is presented in Sec. V. Finally, a brief discussion and open questions are given in Sec. VI.

II. THE n -SPECIES MODEL

Consider a chemical system containing n different species of molecules A_1, A_2, \dots, A_n . Any two particles of *different* species are defined to annihilate upon colliding, or equivalently, the particles combine to form an inert species which does not participate in any further reaction. Symbolically, the reaction can be represented as



We shall ignore the possibility of the inverse reaction occurring, and for simplicity, we shall also take all the reaction rates k_{ij} to be equal.

We first investigate the kinetic behavior in the rate equation, or mean-field limit. In this approximation, it is assumed that mixing effects are so strong that fluctuations in the spatial densities of the reactants can be neglected. The system is then described by the rate equations

$$\frac{d}{dt} A_i = -A_i \sum_{j=1}^n{}' A_j, \quad i = 1, 2, \dots, n \quad (2)$$

where A_i denotes the concentration of the i th species, the prime on the summation indicates that the term $j=i$ is excluded, and the reaction rate has been absorbed in the definition of the time.

This system obeys a conservation law which can be found directly from the rate equations. Without any loss of generality, we may consider the case where initially A_1 is distinct from all the other A_i 's ($i \neq 1$). Of course, if all the densities are initially equal, they will continue to remain so as the reaction proceeds. From (2) we obtain

$$\frac{d}{dt} \ln A_1 = - \sum_{j=2}^n A_j. \quad (3a)$$

On the other hand, we also find from (2),

$$\frac{d}{dt} \ln(A_1 - A_k) = \sum_{j=2}^n{}' A_j \quad (3b)$$

with $k \neq 1$, and the term $j=k$ is excluded in the sum. Now choosing $k=2, 3, \dots, n$ in (3b) and adding the resulting $n-1$ equations and dividing by $n-2$ we find

$$\frac{d}{dt} \ln A_1 = - \frac{1}{(n-2)} \frac{d}{dt} \ln \left[\prod_{j=2}^n (A_1 - A_j) \right]. \quad (4)$$

Thus we obtain the conservation law

$$\left[\prod_{j=2}^n (A_1 - A_j) \right] / A_1^{(n-2)} = \text{const}. \quad (5a)$$

In the special case where all the A_i are distinct initially, then there is no particular reason to single out A_1 in the above derivation. A symmetric form of the conservation law can now be obtained by cyclically permuting the subscript 1 in (5a) over all n and forming the product of the resulting conservation laws. This gives

$$\left[\prod_{\substack{i,j=1 \\ i \neq j}}^n (A_i - A_j) \right] / \left[\prod_{k=1}^n A_k \right]^{n-2} = \text{const}. \quad (5b)$$

We emphasize that these conservation laws hold only in a *global* sense, with the exception of the case $n=2$. For $n=2$, our model reduces to the much simpler scheme of the single reaction $A_1 + A_2 \rightarrow \text{inert}$. For this reaction, the conservation law, $A_2 - A_1 = \text{const}$, [a special case of Eq. (5)], holds locally, i.e., for each reaction, as well as globally.

We now turn to the exact solution of the rate equations (2), for which the conservation law plays a crucial role in the solution. It is possible to find the general solution for arbitrary n , but this solution is rather complicated, and furthermore, it is not particularly relevant to the main point of the paper. However, for the sake of pedagogical completeness, we give the full solution of the case $n=3$, and the generalization to arbitrary n is straightforward.

To simplify the notation for the 3-species case, let us replace A_1, A_2 , and A_3 by A, B , and C , respectively. We also define two auxiliary variables ϕ and ψ by $\phi = B/A$, and $\psi = C/A$, and we redefine the time t in terms of the variable x which is determined by $dx = A dt$. Then it is straightforward to show from the rate equations that

$$\frac{d\phi}{dt} = \left[-\frac{B}{A} + \frac{B^2}{A^2} \right] A, \quad (6a)$$

or equivalently

$$\frac{d\phi}{dx} = -\phi + \phi^2, \quad (6b)$$

with solution

$$\phi(x) = \{ [\phi(0)^{-1} - 1] e^x + 1 \}^{-1}. \quad (7)$$

A similar result holds for ψ . In order to complete the solution, we need to relate x and t . This is most conveniently done by recasting the conservation law

$$\frac{(A-B)(A-C)}{A} = \text{const} \quad (8a)$$

as

$$(1-\phi)(1-\psi) = \frac{\text{const}}{A}. \quad (8b)$$

Then we have

$$t = \int \frac{dx}{A} = \text{const} \times \int dx (1-\phi)(1-\psi), \quad (9)$$

and the constant can be written in terms of the initial conditions. After a number of straightforward steps, we finally obtain

$$t = \frac{(1+r_0)(1+s_0)}{A_0(r_0-s_0)} \left\{ r_0 \ln \left[\frac{e^x+r_0}{1+r_0} \right] - s_0 \ln \left[\frac{e^x+s_0}{1+s_0} \right] \right\}, \quad (10)$$

with $r_0 = \phi(0)/[1-\phi(0)]$ and $s_0 = \psi(0)/[1-\psi(0)]$. From this relatively cumbersome result, the behavior in two interesting limiting cases can be found easily. First, if all the densities are initially unequal [in this case, we choose $A(0) > B(0) > C(0)$], we find that x varies asymptotically linearly with t . Therefore we conclude that both B and C vanish exponentially in time while A approaches its asymptotic value also exponentially in time. If, however, all the densities are equal initially, then x varies logarithmically in time, leading to a density which vanishes as

$$A_i(t) = \frac{A_i(0)}{[1+(n-1)A_i(0)t]}. \quad (11)$$

Finally, it is worth noting that the "symmetric" initial state, where all the species have the same density, is unstable in the rate equation. That is, a small perturbation from this initial condition will grow, leading, at large times, to a situation where the minority species will decay exponentially, as opposed to the pure power-law decay of the symmetric initial state.

III. GLOBAL VERSUS LOCAL CONSERVATION LAWS: THE Ω EXPANSION

A local conservation law can be of great utility in the analysis of the kinetics of reaction processes. Since such a conservation law holds for each reaction, a strong constraint on the nature of the fluctuations in a finite-size system is imposed. As an example, let us recall^{7,8,13} how the conservation law enters into the qualitative argument for deriving the decay rate for two-species annihilation, $A_1 + A_2 \rightarrow \text{inert}$, when the reactants diffuse. Below an upper critical dimension equal to 4, it has been established that fluctuations in the density of the reactants cause the rate-equation approach to fail. This failure stems from the system breaking up into domains which are rich in either A_1 or A_2 . Because of this segregation, recombination takes place only along domain boundaries, and the reaction rate is drastically slower than that predicted by the rate equation.

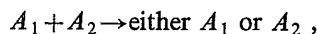
To arrive at the decay law for equal initial densities, consider a domain of linear dimension l within the system. Initially there are of the order of $A_i(0)l^d \pm [A_i(0)l^d]^{1/2}$ particles of each species in the domain. Suppose that one waits a sufficiently long time that the particles can diffuse across and therefore explore the entire domain. For diffusive motion, this characteristic time will vary as l^2 . In this time interval, the A_1 's and A_2 's will mix thoroughly within the domain. Consequently, the extensive portions of the particle numbers will annihilate in pairs, leaving behind only residual fluctuations which are of the order of $[A_i(0)l^d]^{1/2}$ in number, for the species which was initially in the local majority within the domain. This order of magnitude for the residual fluctuation is predicated on the local character of the conservation law. Therefore we conclude that upon

averaging over many realizations of the reaction,

$$\begin{aligned} \langle A_1(t) \rangle &= \langle A_2(t) \rangle \sim [A_i(0)l^d]^{1/2}/l^d \\ &\sim [A_i(0)]^{1/2} t^{-d/4}, \end{aligned} \quad (12)$$

where the angular brackets denote an ensemble average.

Consider now the closely related process



where the two possibilities can occur with equal probabilities. The rate equations for this A_1 or A_2 process are essentially the same as that for 2-species annihilation, except for an overall factor of 2. Consequently, the conservation law $A_2 - A_1 = \text{const}$ still holds, but only in a *global* sense. In a single reaction, however, the quantity $A_2 - A_1$ is certainly not conserved. It is enlightening to compare the kinetics of this A_1 or A_2 reaction with the 2-species annihilation in order to understand the different roles of global and local conservation laws in determining the reaction kinetics. For the A_1 or A_2 process, the number difference $N_2 - N_1$ changes randomly by ± 1 each time a reaction occurs. Thus, instead of a strict conservation of the number difference, we have

$$\begin{aligned} \langle (N_2 - N_1)^2 \rangle &= \text{number of reactions} \\ &= 2[N_2(0) - \langle N_2(t) \rangle]. \end{aligned} \quad (13)$$

It is important to notice that in the mean-field approach, the kinetics of both reactions, $A_1 + A_2 \rightarrow \text{inert}$ and $A_1 + A_2 \rightarrow \text{either } A_1 \text{ or } A_2$, are essentially identical. Thus the mean-field approach is insensitive to the different form of the conservation laws for the two reactions. However, it is clear from (13) that the difference in the kinetics of the two reactions increases at large times. To understand this difference, and to improve over the mean-field approach, we consider the master equation for the state probability of the system. Even without the introduction of diffusion as the mechanism for particle transport, the master equation has an important advantage over the rate equation in that it deals with individual particles rather than with continuous concentrations. Therefore, information about the discrete nature of a real chemical system is retained, and this information allows us to learn more about the ramifications of global and local conservation laws. For this purpose, the Van Kampen Ω expansion³ of the master equation provides the appropriate method of analysis. This is an elegant method for systematically obtaining corrections to rate-equation kinetics which arise from the discreteness of the system. In what follows, we employ Van Kampen's formalism, as well as his notation.³

Consider first the 2-species annihilation process. It is described by the master equation

$$\frac{\partial}{\partial t} P(N_1, N_2, t) = \Omega(E_1 E_2 - 1) \left[\frac{N_1}{\Omega} \right] \left[\frac{N_2}{\Omega} \right] P(N_1, N_2, t), \quad (14)$$

where $P(N_1, N_2, t)$ is the probability distribution function for having N_1 and N_2 particles of type A_1 and A_2 , respectively, at time t , Ω is the volume of the system, and

E_i is a raising operator defined by $E_i f(N_i) = f(N_i + 1)$. Following the Ω expansion, we assume that N_i can be represented by an average value $\Omega\phi_i$, where ϕ_i is the macroscopic density, plus a fluctuating part $\Omega^{1/2}\xi_i$. As written, the fluctuating part of N_i is assumed to scale as the square root of the system volume. The probability distribution function is now defined in terms of ξ_i as

$$P(N_1, N_2, t) = \Pi(\xi_1, \xi_2, t). \quad (15)$$

It then follows that

$$\frac{\partial P}{\partial t} = \frac{\partial \Pi}{\partial t} - \Omega^{1/2} \frac{d\phi_1}{dt} \frac{\partial \Pi}{\partial \xi_1} - \Omega^{1/2} \frac{d\phi_2}{dt} \frac{\partial \Pi}{\partial \xi_2}, \quad (16a)$$

$$E_i = 1 + \Omega^{-1/2} \frac{\partial}{\partial \xi_i} + \frac{1}{2} \Omega^{-1} \frac{\partial^2}{\partial \xi_i^2} \dots \quad (16b)$$

Carrying out these replacements in the master equation (14) yields

$$\begin{aligned} \frac{\partial \Pi}{\partial t} - \Omega^{1/2} \frac{d\phi_1}{dt} \frac{\partial \Pi}{\partial \xi_1} - \Omega^{1/2} \frac{d\phi_2}{dt} \frac{\partial \Pi}{\partial \xi_2} \\ = \Omega^{-1} \left[\Omega^{-1/2} \frac{\partial}{\partial \xi_1} + \Omega^{-1/2} \frac{\partial}{\partial \xi_2} + \frac{1}{2} \Omega^{-1} \frac{\partial^2}{\partial \xi_1^2} \right. \\ \left. + \Omega^{-1} \frac{\partial^2}{\partial \xi_1 \partial \xi_2} + \frac{1}{2} \Omega^{-1} \frac{\partial^2}{\partial \xi_2^2} + \dots \right] \\ \times (\Omega\phi_1 + \Omega^{1/2}\xi_1)(\Omega\phi_2 + \Omega^{1/2}\xi_2)\Pi. \quad (17) \end{aligned}$$

Collecting like powers of Ω , we find that the coefficient of the term which diverges as $\Omega^{1/2}$ vanishes if the concentrations obey the mean-field rate equations $\dot{\phi}_1 = \dot{\phi}_2 = -\phi_1\phi_2$. This feature is a basic consistency requirement of the Ω -expansion approach. Collecting terms of order Ω^0 , one obtains a Fokker-Planck equation for the coefficient of the fluctuating parts of N_1 and N_2 ,

$$\begin{aligned} \frac{\partial \Pi}{\partial t} = \phi_1 \left[\frac{\partial}{\partial \xi_1} + \frac{\partial}{\partial \xi_2} \right] (\xi_2 \Pi) + \phi_2 \left[\frac{\partial}{\partial \xi_1} + \frac{\partial}{\partial \xi_2} \right] (\xi_1 \Pi) \\ + \left[\frac{1}{2} \frac{\partial^2}{\partial \xi_1^2} + \frac{\partial^2}{\partial \xi_1 \partial \xi_2} + \frac{1}{2} \frac{\partial^2}{\partial \xi_2^2} \right] (\xi_1 \xi_2 \Pi). \quad (18) \end{aligned}$$

At this stage, equations of motion for various moments of the probability distribution, Π , are easily derived by multiplying (18) by the desired powers of the ξ_i 's and integrating over all values of these variables. From this procedure, we find

$$\partial_t \langle \xi_1^2 \rangle = -2\phi_1 \langle \xi_1 \xi_2 \rangle - 2\phi_2 \langle \xi_1^2 \rangle + \phi_1 \phi_2, \quad (19a)$$

$$\partial_t \langle \xi_2^2 \rangle = -2\phi_2 \langle \xi_1 \xi_2 \rangle - 2\phi_1 \langle \xi_2^2 \rangle + \phi_1 \phi_2, \quad (19b)$$

$$\begin{aligned} \partial_t \langle \xi_1 \xi_2 \rangle = -(\phi_1 + \phi_2) \langle \xi_1 \xi_2 \rangle - \phi_1 \langle \xi_2^2 \rangle \\ - \phi_2 \langle \xi_1^2 \rangle + \phi_1 \phi_2. \quad (19c) \end{aligned}$$

These equations can be integrated to find the explicit dynamics of the fluctuations arising from the discreteness of the system. Our goal, however, is much more modest, as we are interested primarily in the manifestations of the conservation law. Combining Eqs. (19), we find

$$\partial_t (\langle \xi_2^2 \rangle - 2\langle \xi_1 \xi_2 \rangle + \langle \xi_1^2 \rangle) = \partial_t \langle (\xi_2 - \xi_1)^2 \rangle = 0. \quad (20)$$

Since $\Omega^{1/2}\xi_1$ denotes the fluctuating part of N_i , this last equation indicates that there are no fluctuations in $N_2 - N_1$, as we had already anticipated. We therefore conclude that the conservation law of the particle-number difference holds locally, since even upon consideration of the discreteness of the system, fluctuations in the particle-density difference remain zero.

Consider in contrast the A_1 or A_2 process. The corresponding master equation is

$$\begin{aligned} \frac{\partial}{\partial t} P(N_1, N_2, t) = \Omega(E_1 - 1) \left[\frac{N_1}{\Omega} \right] \left[\frac{N_2}{\Omega} \right] P \\ + \Omega(E_2 - 1) \left[\frac{N_1}{\Omega} \right] \left[\frac{N_2}{\Omega} \right] P. \quad (21) \end{aligned}$$

Performing the Ω expansion, we again obtain the same mean-field rate equations for the ϕ_i 's as in the 2-species annihilation process. However, for the moments of the fluctuating part of the particle number, we find

$$\partial_t \langle (\xi_2 - \xi_1)^2 \rangle = 2\phi_1\phi_2 = -2\partial_t \phi_2, \quad (22)$$

where the last relation is obtained from the rate equation. The solution is clearly that given in (13). Since the conservation law is only globally valid for the A_1 or A_2 process, nonzero fluctuations in density difference are now expected to occur. Thus we see that the Ω expansion provides an accurate picture of the manifestation of the conservation law for this system.

The difference between 2 species annihilation and the A_1 or A_2 reaction was easily deduced without resorting to the formal approach of the Ω expansion. However, this expansion does provide a systematic framework which can be straightforwardly applied to a wide range of more interesting examples. It is with this viewpoint in mind that we now proceed to study the n -species annihilation process.

IV. KINETICS OF n -SPECIES ANNIHILATION

In order to derive the decay law of n -species annihilation, we will focus on a domain of linear dimension l within the system, in analogy with the derivation of the decay law for 2-species annihilation. Initially, particles of all of the n species are present in this domain. However, as the reaction proceeds, there will be successive extinctions of each of the species within this volume. Our first goal is to estimate how many particles of each of the remaining $n-1$ species are left, on average, after one of the species becomes extinct. This information will turn out to be central to our analysis of the decay law when the reactants are diffusing. To obtain this information, we apply the Ω expansion method discussed in the last section.

The master equation for the n -species process is

$$\begin{aligned} \frac{\partial}{\partial t} P(N_1, N_2, \dots, N_n, t) \\ = \Omega \sum_{i>j} (E_i E_j - 1) \\ \times \left[\frac{N_i}{\Omega} \right] \left[\frac{N_j}{\Omega} \right] P(N_1, N_2, \dots, N_n, t). \end{aligned} \quad (23)$$

Following the method outlined previously, we set

$$N_i = \Omega \phi_i + \Omega^{1/2} \xi_i, \quad (24a)$$

$$P(N_1, N_2, \dots, N_n, t) = \Pi(\xi_1, \xi_2, \dots, \xi_n, t). \quad (24b)$$

The master equation is now rewritten in terms of these new variables, and terms containing various powers of $\Omega^{1/2}$ are collected. From the terms of the order of $\Omega^{1/2}$, we obtain the rate equations [compare Eq. (2)]

$$\dot{\phi}_i = -\phi_i \sum_{j(\neq i)} \phi_j. \quad (25)$$

The terms of order Ω^0 yield the Fokker-Planck equation

$$\begin{aligned} \frac{\partial}{\partial t} \Pi = \sum_{\substack{i,j \\ i \neq j}} \left[\phi_i \frac{\partial}{\partial \xi_i} (\xi_j \Pi) + \phi_j \frac{\partial}{\partial \xi_j} (\xi_i \Pi) \right] \\ + \frac{1}{4} \sum_{\substack{i,j \\ i \neq j}} \phi_i \phi_j \left[\frac{\partial^2}{\partial \xi_i^2} + 2 \frac{\partial^2}{\partial \xi_i \partial \xi_j} + \frac{\partial^2}{\partial \xi_j^2} \right] \Pi. \end{aligned} \quad (26)$$

Equations of motion for the moments of the fluctuating part of the particle density are obtained by multiplying (26) by the desired powers of ξ_i and integrating. We therefore find for all the independent moments up to the quadratic order,

$$\partial_t \langle \xi_i \rangle = -\phi_i \sum_{j(\neq i)} \langle \xi_j \rangle - \langle \xi_i \rangle \sum_{j(\neq i)} \phi_j, \quad (27a)$$

$$\begin{aligned} \partial_t \langle \xi_i \xi_m \rangle = -\phi_m \sum_{j(\neq m)} \langle \xi_i \xi_j \rangle - \phi_i \sum_{j(\neq i)} \langle \xi_j \xi_m \rangle \\ - \langle \xi_i \xi_m \rangle \left[\sum_{i(\neq m)} \phi_i + \sum_{i(\neq i)} \phi_i \right] + \phi_i \phi_m, \end{aligned} \quad (27b)$$

$$\begin{aligned} \partial_t \langle \xi_i^2 \rangle = -2 \sum_{j(\neq i)} \phi_j \langle \xi_i \xi_j \rangle - 2 \sum_{j(\neq i)} \phi_j \langle \xi_i^2 \rangle \\ + \sum_{j(\neq i)} \phi_j \phi_i. \end{aligned} \quad (27c)$$

Since we are considering only the initial condition where the number of particles of each species is the same, we have that all the ϕ_i 's are equal. This simplifies the equations considerably, leading to

$$\dot{\phi} = -(n-1)\phi^2, \quad (28a)$$

and

$$\begin{aligned} \partial_t \langle (\xi_i - \xi_m)^2 \rangle = -2(n-2)\phi \langle (\xi_i - \xi_m)^2 \rangle \\ + 2(n-2)\phi^2. \end{aligned} \quad (28b)$$

Equation (28b) can be easily integrated without explicitly solving for ϕ (this method is especially useful when the rate equations yield a cumbersome time behavior of ϕ). Using (28a) we express the ϕ 's in (28b) in terms of time derivatives. Thus,

$$\frac{\partial}{\partial t} \langle (\xi_i - \xi_m)^2 \rangle = 2 \frac{(n-2)\dot{\phi}}{(n-1)\phi} \langle (\xi_i - \xi_m)^2 \rangle - 2 \frac{(n-2)}{(n-1)} \dot{\phi}. \quad (29)$$

We find, by inspection, an integrating factor, $\phi^{-2(n-2)/(n-1)}$, with the final result

$$\langle (\xi_i - \xi_m)^2 \rangle = \begin{cases} 2 \frac{(n-2)}{(n-3)} \phi \left\{ 1 - (1 - \Delta^2) \left[\frac{\phi}{\phi(0)} \right]^{(n-3)/(n-1)} \right\}, & n > 3 \\ \phi \left[\ln \left[\frac{\phi}{\phi(0)} \right] + \frac{\Delta^2}{\phi(0)} \right], & n = 3 \\ \Delta^2, & n = 2. \end{cases} \quad (30)$$

Here Δ^2 is an integration constant equal to the square of the initial particle-number difference over the volume of the system. We see that the conservation law for the number of particles difference holds locally for $n=2$, but not for $n>2$.

We now focus on our primary result, namely, the decay law for the n -species process when particles move by diffusion. Our approach is based on the physical picture that within a sufficiently large domain, species are eliminated successively. We will use the results derived above to estimate how many particles of the remaining species are left at each stage of this elimination process. Carrying this line of reasoning through all stages of elimination, we

will thereby infer the decay law for n -species annihilation.

For an initially symmetric state in which all the concentrations are equal, Δ^2 is zero, so that the initial differences of the particle numbers (represented by $[\Omega \langle (\xi_i - \xi_m)^2 \rangle]^{1/2}$) are also zero. However, as the system evolves, there will develop asymmetries in the density, even if the initial state was locally symmetric. These asymmetries are characterized by the terms involving the Δ^2 factor. This holds, in particular, for the case of our finite-size domain, after one of the species has become extinct. We conclude that the average number of particles in the remaining species is of the order of the square root of these " Δ^2 " terms. Thus, we find from (30), that for

$n > 3$, after the reaction has progressed to the point where one of the species is eliminated, there remain, not zero, but rather of the order of $(\langle N \rangle \langle N \rangle^{(n-3)/(n-1)})^{1/2} = \langle N \rangle^{(n-2)/(n-1)}$ particles of each of the remaining $n-1$ species. Notice that this source of fluctuations is larger than the conventional $\sqrt{\langle N \rangle}$ fluctuations possibly present in an initial Poisson distribution, and hence the latter may be neglected.

We are now left with only $n-1$ species in the domain, each containing of the order of $\langle N \rangle^{(n-2)/(n-1)}$ particles, where $\langle N \rangle$ is the average initial number of particles of any of the species. We can apply the above reasoning a second time, except that n is replaced by $n-1$ in (30). Now by the time that the second space is eliminated, we are left with of the order of

$$(\langle N \rangle^{(n-2)/(n-1)})^{(n-3)/(n-2)} = \langle N \rangle^{(n-3)/(n-1)}$$

particles for each of the remaining $n-2$ species. In this fashion, species are eliminated successively, and as long as the number of species remaining exceeds 3, we can employ the reasoning just described.

When 3 species are left, the magnitude of the fluctuations arising from the discrete nature of the particles equals that of local fluctuations in concentration for the very first time. It is interesting, also, that this feature is accompanied by the presence of a logarithmic term in (30). Thus when the third-to-last species is eliminated, we can conclude that by either mechanism (discrete fluctuations or local concentration fluctuations) the number of particles remaining in a domain is proportional to the square root of the number of particles when $n=3$. When the last two species are left, the conservation law becomes strictly local, and as a result, no fluctuations are predicted because of discreteness. However, fluctuations in local concentration will now be of primary importance (as in the 2-species reaction) thus leaving a final residue proportional to the square root of the number of the remaining two species. The evolution of $N_i(t)$ through the various elimination stages can be summarized as follows:

$$\begin{aligned} \langle N_i \rangle &= \langle N_i(0) \rangle, \text{ initial condition} \\ \langle N_i \rangle &\sim \langle N_i(0) \rangle^{(n-2)/(n-1)}, \quad n-1 \text{ species remaining} \\ \langle N_i \rangle &\sim [\langle N_i(0) \rangle^{(n-2)/(n-1)}]^{(n-3)/(n-2)} \\ &= \langle N_i(0) \rangle^{(n-3)/(n-1)}, \quad n-2 \text{ species remaining} \\ &\vdots \\ \langle N_i \rangle &\sim \langle N_i(0) \rangle^{2/(n-1)}, \quad \text{three species remaining} \\ \langle N_i \rangle &\sim \langle N_i(0) \rangle^{1/(n-1)}, \quad \text{two species remaining} \\ \langle N_i \rangle &\sim \langle N_i(0) \rangle^{1/[2(n-1)]}, \quad \text{last species remaining} \end{aligned}$$

In terms of the concentration in the domain,

$$\begin{aligned} A_i(t) &\sim \frac{N_i(t)}{l^d} \sim \frac{\langle N_i(0) \rangle^{1/[2(n-1)]}}{l^d} \\ &\sim [A_i(0)]^{1/[2(n-1)]} l^{d\{1-1/[2(n-1)]\}} \end{aligned} \quad (31)$$

Finally, since the particle motion is diffusive, the time required for all stages of the reaction to occur will scale as l^2 , so that

$$A_i(t) \sim [A_i(0)]^{1/[2(n-1)]} t^{-(d/2)\{1-1/[2(n-1)]\}} \quad (32)$$

This is our main quantitative result. We note that this decay law for the n -species process interpolates smoothly between the decays for two basic special cases: For the reaction $A+B \rightarrow \text{inert}$ (i.e., $n=2$), the density decays as $A_i(0)^{1/2} t^{-d/4}$ for spatial dimension d less than an upper critical dimension d_c equal to 4, while for the reaction $A+A \rightarrow \text{inert}$ (i.e., $n \rightarrow \infty$), the density decays as $t^{-d/2}$ for $d < d_c = 2$. By finding the spatial dimension where the decay law (32) matches that of the mean-field limit, we also deduce that the upper critical dimension of n -species decay is equal to $4(n-1)/(2n-3)$.

V. NUMERICAL RESULTS

We have performed numerical simulations of n -species decay to test our theoretical prediction (32). Our simulation method is quite simple, but it is worthwhile to outline its main features. First, our choice of initial conditions is somewhat unconventional. Usually, one simulates a Poisson distribution where the density of each species is fixed. Thus for a finite-size system, the initial number of particles will fluctuate from realization to realization. However, if we are interested in the symmetric initial condition (equal densities of all species), a Poisson distribution does not give satisfactory results. This happens because, in a finite-size system, the initial differences in particle number will eventually drive the system away from the behavior of the symmetric initial state, as the species that is initially in the majority is likely to predominate at long times. Clearly, this effect can be made small if an average is taken over many realizations of the reaction. We have found, however, that for a fixed amount of computer time, it is preferable to build an initial state where the number of particles is fixed. In this way, we can force the number of particles of the n species to be equal, and thus greatly reduce deviations away from the symmetric initial state arising from the fluctuations in Poisson statistics. This choice of an initial state is justified by the fact that the numerical results from the two types of initial states are essentially identical.

To construct our initial state, define

$$u_i(0) = A_i(0) / \sum_j A_j(0),$$

the initial fraction of particles that are of the i th species. Then with probability $u_i(0)$ a particle of the i th species is placed at random on the unoccupied portion of the lattice. This particle placement is continued until the number of particles of each species, $N_i(0)$, reaches the value $A_i(0)L^d$, where L is the linear dimension of the lattice.

After the initial state has been constructed, particles are selected one at a time, at random, from the occupied portion of the lattice, and moved to a neighboring lattice site. To model diffusion, the particle is moved one lattice spacing in a random direction (with periodic boundary conditions being employed). To model the mean-field limit, we move the particle to *any* site of the lattice equiprobably.^{13,14} This corresponds exactly with the infinite mobility implicit in the rate equations. Since each site is

equidistant from all other sites, the lattice structure in the mean-field limit is irrelevant, and it is simplest to consider a one-dimensional chain.

When the particle is moved, there are three possibilities. If the new site is unoccupied the move is accepted, while if the new site is occupied by a particle of the same species the initial particle is returned to its previous position, and this is defined as a "move." Thus we have also introduced an excluded-volume interaction into the problem. However, we have checked that there is a negligible difference with the behavior of a system in which unlimited occupancy of sites by particles of the same species is allowed. This is especially true at long times when the density is low. We have therefore incorporated this excluded volume interaction in our modeling of the reaction, because it gives rise to a simpler and faster executing program. Finally, if the new site is occupied by a particle of a different species, a reaction takes place in which both particles are removed from the lattice. After each move, the time is incremented by $1/(\text{current number of particles})$.

Several very useful checks of the mean-field version of the simulation program can be performed. One basic test is to verify that the conservation law from the rate equations, Eq. (5), does actually hold. For a single realization containing $\sim 5 \times 10^5$ particles, we found that the conservation law held to an accuracy of the order of 10^2 particles or less during the course of the reaction for a variety of initial conditions. A second, very detailed check is to compare the fluctuations in the particle density from realization to realization of the reaction, with those predicted by the Van Kampen Ω expansion. This also allows us to assess the influence of the initial condition of fixed particle number on the reaction kinetics, as the Van Kampen approach is based on an initial condition of fixed particle density. We have therefore monitored the diagonal and off-diagonal terms in the correlation matrix, $\langle \xi_i^2 \rangle$ and $\langle \xi_i \xi_j \rangle$, respectively [see Eqs. (27a) and (27b)]. The agreement between the numerical data and the theoretical values, which can be straightforwardly obtained from (27), is quite good (Fig. 1). We believe that this agreement, especially for the correlations, is quite satisfactory, given the very detailed nature of the information being investigated, and the possible corrections stemming from the fixed-particle-number initial condition.

Having successfully tested the simulation method in the mean-field limit, we now turn to the behavior below the upper critical dimension in order to test our basic theoretical prediction (32). In Fig. 2 we plot the total density of particles as a function of time for both the 3- and 4-species reactions in one dimension. For equal initial densities of all species, Eq. (32) predicts that the exponent of the power-law in the decay of the density, $\alpha(n, d=1)$, should be equal to $\frac{3}{8}$ and $\frac{5}{12}$, respectively. From a least-squares fit to the data on a logarithmic scale, we estimate $\alpha(3, d=1) = 0.370 \pm 0.007$ and $\alpha(4, d=1) = 0.406 \pm 0.004$, respectively, where the error bars represent statistical uncertainties to a straight-line fit. Systematic sources of uncertainties have not been accounted for in this error estimate. Thus while the purely statistical error in $\alpha(4, d=1)$ nominally excludes the theoretical prediction for this ex-

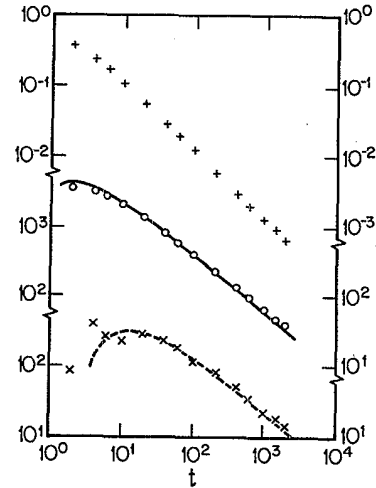


FIG. 1. Kinetic behavior of the 3-species reaction in the mean-field limit for the case of a "symmetric" initial state. Shown are the results for a linear chain containing 10^5 sites in which the initial density of each species is 0.2. An average is taken over 200 initial configurations which evolve for 2000 time steps. Plotted is the average density of each species (+), together with the diagonal correlations, $\Omega\langle \xi_i^2 \rangle$ (O), and the off-diagonal correlations, $\Omega\langle \xi_i \xi_j \rangle$ (x). For comparison, the prediction for these correlations from the Ω expansion are also shown (— and — — —, respectively). Note the breaks in the vertical scale.

ponent, we believe that, overall, the agreement between the data and the theory is excellent. As a further test of our theory, we show in Fig. 3 the scaled density $A_i(t)/[A_i(0)]^{1/4}$ versus time on a double logarithmic scale for the 3-species reaction. According to (32), this scaled density should be a universal function, independent of the initial density. At long times, the data does exhibit the requisite data collapsing to a high accuracy, thus providing additional evidence to support our prediction of the decay law.

In two dimensions, the agreement between the data and the theory is still quite reasonable (Fig. 4). However, at the longest times that we investigated, finite size effects,

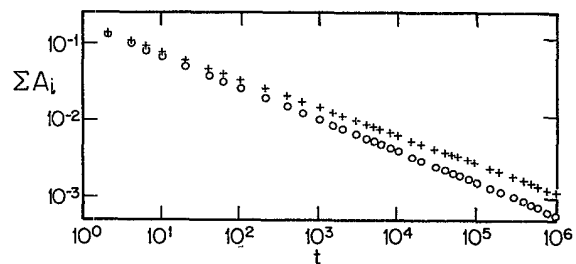


FIG. 2. Total density $\sum_i A_i$ vs time on a double-logarithmic scale for both the 3- and 4-species reaction in one dimension (+ and O, respectively). The initial density of each species was 0.2 for $n=3$ and 0.15 for $n=4$. Both results are based on a single realization of 10^6 steps on a linear chain of 5×10^5 sites.

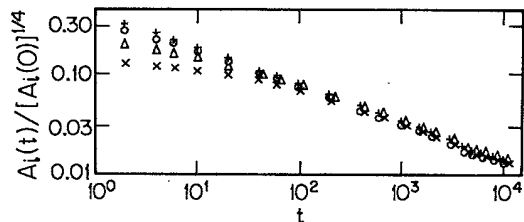


FIG. 3. Scaled density $A_i(t)/[A_i(0)]^{1/4}$ vs time on a double-logarithmic scale for the 3-species reaction in one dimension with an initial symmetric state. Shown are the cases $A_i(0)=0.2$ on a chain of $L=2 \times 10^4$ sites (+), $A_i(0)=0.1$ with $L=2 \times 10^4$ (o), $A_i(0)=0.05$ with $L=2 \times 10^5$ (Δ), and $A_i(0)=0.025$ with $L=4 \times 10^5$ (x).

due to particles diffusing across the entire lattice, will not be entirely negligible. Nevertheless, the numerical data for the decay is fairly linear on a double logarithmic scale and we estimate $\alpha(n, d=2)$ to be approximately 0.8 for $n=3$, and 0.86 for $n=4$. These two estimates are consistent with the theoretical values for these exponents of $\frac{3}{4}$ and $\frac{5}{6}$, respectively.

Although we have developed a reasonable quantitative description for the behavior of the average density in n -species decay, there are other, perhaps more interesting, properties for which we have little theoretical understanding. For example, consider the mean-square of the differences in particle number between unlike species, $\langle (N_i - N_j)^2 \rangle$. Starting with the symmetric initial condition, we expect from (30) that the size of these differences, relative to the total number of particles, increases during the initial stages of the reaction, then decays to zero at long times. Thus the symmetry of the initial condition is evidently spontaneously broken during the course of the reaction. This feature is illustrated in Fig. 5, where we plot this mean-square number difference for the 3-species reaction in one dimension, together with the value of this

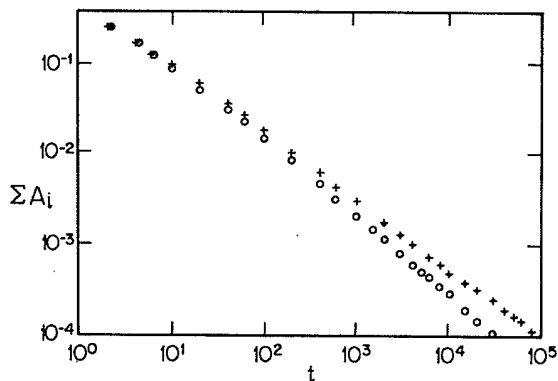


FIG. 4. Total density vs time on a double-logarithmic scale for the 3- and 4-species reaction in two dimensions (+ and o, respectively). The initial density of each species was 0.2 for $n=3$ and 0.15 for $n=4$. Both results are based on a single realization of 10^5 steps on a $10^3 \times 10^3$ square.

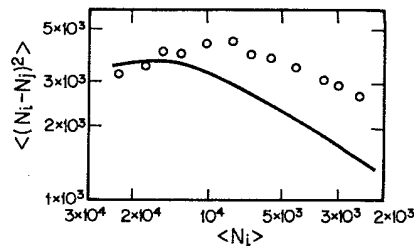


FIG. 5. Plot of the quantity $\langle (N_i - N_j)^2 \rangle$ (o) plotted vs $\langle N_i \rangle = \Omega \langle \phi_i \rangle$ on a double-logarithmic scale for the 3-species reaction in one dimension. For comparison, we also show the value of this quantity expected by taking the value of the density from the simulations, and using this in the Ω expansion expression for the mean-square number difference [from Eq. (30)]. The data are based on averaging over 50 realizations for a linear chain of 5×10^4 sites in which the initial density of each species is 0.2.

quantity expected for the same reaction in mean-field theory [Eq. (30)]. The size of this quantity is surprisingly large in one dimension, compared to the behavior of the mean-field limit. Moreover, on the basis of the numerical results, we would conclude that at long times, one species predominates in the long-time limit, as opposed to the mean-field prediction of a symmetric final state. We believe that this behavior is on the same footing as that of the spontaneous magnetization below the critical temperature, where one particular spatial direction is picked out.

VI. DISCUSSION AND CONCLUSIONS

We have presented an idealized chemical-reaction model of n -species annihilation. This model reduces to the important 1- and 2-species annihilation processes, $A + A \rightarrow \text{inert}$ and $A + B \rightarrow \text{inert}$, respectively, in the limits $n \rightarrow \infty$ and $n=2$. In the intermediate case of $2 < n < \infty$, the n -species annihilation model exhibits a number of new and interesting features.

In the mean-field limit, we derived a conservation law for the densities of the various species. We also showed that the nature of the conservation law changes as the number of species increases: it is *locally* valid for $n=2$, then only *globally* valid for finite $n > 2$, and finally no trace of the conservation law remains in the limit of $n \rightarrow \infty$. We argued that to understand the kinetic behavior of the n -species reaction below the upper critical dimension, the scaling arguments which were formulated in terms of local fluctuations in density and previously applied to 2-species decay, have to be modified to include fluctuations arising from the discreteness of the particles. We believe that our model is a first example where this feature plays such an important role.

Fluctuations arising from discreteness were shown to be most conveniently captured by the Van Kampen Ω expansion of the master equation for the reaction process. Moreover, this method was shown to provide us with an accurate description of the manifestations of a conservation law for the system (whenever such a law exists). Us-

ing this approach, together with a domain picture for the evolution of the particle densities in the n -species reaction, we proposed a decay law for this reaction below the upper critical dimension. Our primary result, Eq. (32), for the decay law appears to be well-supported by numerical simulations.

There remain, still, some open questions. First, we have specialized only to the very restricted symmetrical case of equal reaction rates, k_{ij} , and equal initial densities. The general case may be expected to have some qualitatively different features compared to the special case considered in this paper. Also, our theoretical analysis makes use of some rather qualitative scaling arguments. As a result, we expect that our predictions will display the correct *scaling* asymptotic form, but a full theoretical solution, similar to that given by Toussaint and Wilczek⁷ for the 2-species annihilation, is still lacking. Such a solution should also include a quantitative understanding of

the striking symmetry breaking discussed in the end of Sec. V.

Finally, we would welcome more examples of systems exhibiting global conservation laws, and of systems for which fluctuations arising from discreteness are essential to an understanding of their kinetics. The question of whether these two properties are necessarily related or not, remains completely unanswered.

ACKNOWLEDGMENTS

One of us (S.R.) acknowledges Kiho Kang (now deceased), who proposed the n -species model studied in this paper, for stimulating discussions and for his deep and creative physical insights. We also thank Dr. F. Leyvraz and Professor I. Oppenheim for a number of very informative discussions. One of us (D.B.A.) acknowledges the support of the Weizmann Foundation.

¹K. J. Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1965).

²S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).

³N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

⁴D. F. Calef and J. M. Deutch, *Annu. Rev. Phys. Chem.* **34**, 493 (1983).

⁵R. M. Noyes, *Prog. React. Kinet.* **1**, 128 (1961).

⁶P. Grassberger, *Z. Phys. B* **47**, 365 (1982).

⁷D. Toussaint and F. Wilczek, *J. Chem. Phys.* **78**, 2642 (1983).

⁸K. Kang and S. Redner, *Phys. Rev. Lett.* **52**, 955 (1984).

⁹P. Meakin and H. E. Stanley, *J. Phys. A* **17**, L173 (1984).

¹⁰K. Lee and E. J. Weinberg, *Nucl. Phys.* **B246**, 354 (1984).

¹¹G. Zumofen, A. Blumen, and J. Klafter, *J. Chem. Phys.* **82**, 3198 (1985).

¹²D. C. Torney and H. M. McConnell, *J. Phys. Chem.* **87**, 1441 (1983); D. C. Torney and H. M. McConnell, *Proc. R. Soc. London, Ser. A* **387**, 147 (1983).

¹³K. Kang and S. Redner, *Phys. Rev. A* **32**, 435 (1985).

¹⁴K. Kang, S. Redner, P. Meakin, and F. Leyvraz, *Phys. Rev. A* **33**, 1171 (1986).