

## Kinetics of fragmentation-annihilation processes

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We investigate the kinetics of systems in which particles of one species undergo binary fragmentation and pair annihilation. In the latter, nonlinear process, fragments react at collision to produce an inert species, causing loss of mass. We analyze these systems in the reaction-limited regime by solving a continuous model within the mean-field approximation. The rate of fragmentation for a particle of mass  $x$  to break into fragments of masses  $y$  and  $x-y$  has the form  $x^{\lambda-1}$  ( $\lambda > 0$ ), and the annihilation rate is constant and independent of the masses of the reactants. We find that the asymptotic regime is characterized by the annihilation of small-mass clusters, with the cluster density decaying as in pure annihilation and the average cluster mass as in pure fragmentation. The results are compared with those for a model with linear mass loss (i.e., with a sink rather than a reaction). We also study more complex models, in which the processes of fragmentation and annihilation are controlled by mutually reacting catalysts. Both pair and linear annihilation are considered. Depending on the specific model and initial densities of the catalysts, the time decay of the cluster density can now be very unconventional and even nonuniversal. The interplay between the fragmentation and annihilation processes and the existence of a scaling regime are determined by the asymptotic behavior of the average mass and of the mass density, which may either decay indefinitely or tend to a constant value. We discuss further developments of this class of models and their potential applications. [S1063-651X(96)10708-X]

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### I. INTRODUCTION

Irreversible reaction-diffusion processes, such as aggregation or annihilation of species, occur in many physical, chemical, and biological systems. In the past decade they have been investigated extensively. This followed from the realization that spatial fluctuations in the reactant densities slow down the kinetics and lead to an asymptotic behavior at low dimensions that disagrees with the classical reaction-rate equations. (The upper critical dimension  $d_c$  is defined as the spatial dimension below which such disagreement occurs.) Recently, a combined process of aggregation and annihilation of two species has been studied exactly in one dimension by Krapivsky [1], and numerically in higher dimensions by Sokolov and Blumen [2]. A class of related models, but with an arbitrary number of species, has also been investigated at the mean-field level by Ben-Naim and Krapivsky [3]. The power-law decay of the cluster densities has been understood, and in many cases the cluster-mass distributions have been found to approach universal scaling forms.

Fragmentation is another irreversible kinetic process with important applications in nature and technology. These include polymer degradation through shear action [4], chemical attack [5], or exposure to radiation [6], droplet breakup [7], fiber-length reduction [8], fragmentation of colloidal aggregates [9], and rock crushing and grinding [8]. New insight into the statistical mechanics of fragmentation has followed from the work of Ziff and McGrady [10,11], who solved

exactly a class of models with different fragmentation kernels.

The aggregation-fragmentation (or reversible-aggregation) process has been considered by many authors. This has been applied to studying reversible polymerization, for instance, by van Dongen and Ernst [12] and by Sintes, Toral, and Chakrabarti [13]. More generally, mean-field approaches have been used to study the steady-state scaling properties of reversible aggregation, for example, by Family, Meakin, and Deutch [14] and by Blackman and Marshall [15]. In both aggregation annihilation and aggregation-fragmentation processes, rich kinetic behaviors arise due to the competing reaction mechanisms.

In this paper we focus on fragmentation processes with mass loss. A number of authors have considered models combining fragmentation and *linear-annihilation* processes (i.e., a *sink*, where a species “evaporates” at a constant rate in time) (see, e.g., [16–18] and references therein). These models are relevant, for example, to studying oxidation and dissolution of solid porous media [17,18]. However, to the best of our knowledge, the interplay between annihilation and fragmentation remains unexplored in the case of *binary-annihilation* reactions. It is this subject with which we are concerned. The kinetics of these phenomena are *nonlinear*, and therefore more complex and, in principle, more difficult to analyze. Fragmenting systems where fragments react at collision (maybe in the presence of some agent) to produce an inert species would yield potential applications of these combined processes. We investigate, at the mean-field level, a class of (nonlinear) annihilation-fragmentation models, aimed at elucidating the competition between these processes. For all models considered we include, for comparison, an analysis of the corresponding model with linear annihilation (a sink).

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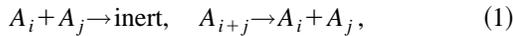
In the simplest situation of a single species, the cluster density decays as in the case of pure annihilation, while the cluster-mass distribution approaches an exponential scaling distribution. An exponential decay of the scaling distribution has also been found in pure fragmentation, aggregation annihilation [3,1], and reversible aggregation [14]. To allow for more interesting, and possibly more realistic behavior, we introduce additional species that work as catalysts for annihilation and/or fragmentation; reactions between the catalysts are also allowed for. We find that the density decay of the main species can be surprisingly unconventional, depending on the specific model and on the initial densities of the catalysts. The decay may be universal but contain logarithmic factors, or it may contain a power law in time with a nonuniversal exponent that depends on the reaction rates. The interplay between annihilation and fragmentation and the existence of a scaling regime are determined by the asymptotic behavior of the mass density and typical cluster mass. These may either decay indefinitely or tend to a constant value, depending on the relative amounts of annihilation and fragmentation catalysts.

This paper is organized as follows. In Sec. II we introduce and solve a model with single-species fragmentation annihilation where the fragmentation kernel has a rather general form. The results for the corresponding model with linear annihilation are stated for comparison. In Sec. III we include catalysts in our model and solve it for general time dependences of the catalysts. Specific asymptotic results are presented in the case where the fragmentation and annihilation catalysts mutually annihilate. The conclusions and further comments and suggestions are given in Sec. IV.

## II. SINGLE-SPECIES ANNIHILATION AND FRAGMENTATION

### A. Nonlinear annihilation (model 1)

The more elementary model combining the processes of pair annihilation and fragmentation is that involving a single ‘‘molecular’’ species. This is described by the binary reaction scheme



where  $A_i$  denotes a cluster consisting of  $i$  monomers of species  $A$ . The following calculations could be repeated for a discrete model, but for analytical convenience we shall take the continuous limit, which is standard practice [11,19].

Let  $a(x,t)$  be the density distribution of cluster masses (or sizes)  $x$  at time  $t$ , and

$$A_n(t) = \int_0^\infty dx x^n a(x,t) \quad (2)$$

its moments. In particular, the zeroth and first moments,  $A(t) \equiv A_0(t)$  and  $A_1(t)$ , denote the *total number density* of clusters and the *total mass density*, respectively. For simplicity, we consider linear fragmentation (driven by a homogeneous external agent [19]), neglect multiple breakup, and take the rate that a cluster of mass  $x$  breaks into clusters of mass  $x-y$  and  $y$ ,  $F(y,x-y)$ , to be a constant (which we set to unity by a rescaling of time). Hence, the total rate of

fragmentation of any cluster,  $\int_0^x dy F(y,x-y)$ , is equal to its mass  $x$ . We also envisage the simplest possible reaction, where two clusters of any mass mutually annihilate upon encounter at a rate independent of their masses. Later, we shall see how to generalize our results for a kernel of the form  $F(y,x-y) = x^{\lambda-1}$ , independent of the masses of the fragments.

Treating the annihilation term within the mean-field description, which is valid in the reaction-controlled regime, the kinetic equation for  $a(x,t)$  reads

$$\dot{a}(x) = -xa(x) + 2 \int_x^\infty dy a(y) - Ja(x)A, \quad (3)$$

where  $J/2$  is the relative rate of annihilation (equal rates of fragmentation and annihilation correspond to  $J=2$ ). A set of nonlinear equations for the moments of  $a(x)$  follows immediately:

$$\dot{A}_n = \frac{1-n}{1+n} A_{n+1} - JA_n A. \quad (4)$$

A closed set of equations is found for the first two moments,

$$\dot{A} = A_1 - JA^2, \quad (5)$$

$$\dot{A}_1 = -JAA_1, \quad (6)$$

while the higher moments obey an infinite hierarchy of equations, which are, apparently, not soluble. The absence of a linear term in (6) is a reflection of the conservation of mass in the fragmentation process. Adopting more general rates of fragmentation and annihilation, say  $x^\lambda$  and  $(xy)^\alpha$ , respectively, would yield the following generalization of (4):

$$\dot{A}_n = \frac{1-n}{1+n} A_{n+\lambda} - JA_{n+\alpha} A^\alpha. \quad (7)$$

Clearly, no closed set of equations can be obtained for  $A$  and  $A_1$ , unless  $\lambda=1$  and  $\alpha=0$ , which justifies our present choice.

To solve for  $A(t)$  and  $A_1(t)$ , we proceed as follows. From (5) and (6), the *cluster average mass*,  $M(t) \equiv A_1(t)/A(t)$ , obeys the equation

$$\dot{M} = -M^2, \quad (8)$$

with the solution

$$M(t) = \frac{1}{\delta + t} \simeq \frac{1}{t} \quad (t \rightarrow \infty), \quad (9)$$

where  $\delta \equiv A(0)/A_1(0) = 1/M(0)$ . Using this result, Eqs. (5) and (6) can be solved to give

$$A(t) = \frac{A(0) + A_1(0)t}{1 + J[A(0)t + A_1(0)t^2/2]} \simeq \frac{2}{Jt}, \quad (10)$$

$$A_1(t) = \frac{A(t)}{\delta + t} \simeq \frac{2}{Jt^2}. \quad (11)$$

The asymptotic behavior in (10) and (11), and hereafter, holds at large  $t$ .

To determine the mass distribution  $a(x,t)$ , we map the problem onto a pure fragmentation one using the auxiliary function

$$b(x,t) \equiv a(x,t) \exp \left[ J \int_0^t dt' A(t') \right]. \quad (12)$$

The exponential factor is known and from (10) we see immediately that

$$\exp \left[ J \int_0^t dt' A(t') \right] = 1 + J[A(0)t + A_1(0)t^2/2]. \quad (13)$$

The function  $b(x,t)$  obeys a standard fragmentation equation; i.e., it is the same as (3) but without the nonlinear annihilation term. Its general solution is well known [10,20], and can be written as

$$b(x,t) = \left( b(x,0) + \int_x^\infty dy b(y,0) [2t + t^2(y-x)] \right) \exp(-tx). \quad (14)$$

We find it easier and more illustrative, however, to work from a particular initial condition, and then to extract the asymptotic, universal behavior from the special solution obtained. We adopt the exponential initial distribution

$$a(x,0) = b(x,0) = \beta_0 \exp(-b_0x), \quad (15)$$

where  $b_0 = \delta$  and  $\beta_0 = A(0)\delta$ . The corresponding solution is obtained by substituting (15) into (14) or, equivalently, attempting the ansatz  $b(x,t) = \beta(t) \exp[-b(t)x]$  in the equation for  $b(x,t)$  [21]. This gives, after including the time-dependent factor (13),

$$\begin{aligned} a(x,t) &= \frac{A_1(0)(\delta+t)^2}{1+J[A(0)t+A_1(0)t^2/2]} \exp[-(\delta+t)x] \\ &= \frac{A(t)}{M(t)} \exp[-(\delta+t)x]. \end{aligned} \quad (16)$$

As  $t \rightarrow \infty$ ,  $a(x,t) \approx (2/J) \exp(-tx)$  becomes independent of the initial condition. This universal asymptotic behavior can also be obtained by looking for a scaling solution of the form

$$a(x,t) = M^{-w} \phi(\zeta), \quad \zeta = x/M, \quad (17)$$

which we expect to hold for general initial conditions, in the regime when  $t$  is large and  $x$  is small, with  $xt$  an arbitrary constant. From (10) and (11) at large  $t$ , we find  $w=0$ . Replacing  $a$  by  $\phi$  in Eq. (3) and taking the limit  $t \rightarrow \infty$  yields a linear differential equation with the solution

$$a(x,t) = \phi(\zeta) = \frac{2}{J} \exp(-\zeta). \quad (18)$$

One can calculate all the moments of  $a(x,t)$  given by the special solution (16). This yields for  $A(t)$  and  $A_1(t)$  exactly the same expressions as in (10) and (11), which hold for general initial conditions (One can check that this is also true for modified exponential initial conditions, e.g.,

$x^p \exp[-b_0x]$ ). Since Eq. (4) for all moments is recursive, we conclude that the special solution (16) must have the same moments as the general solution. Hence, we did not need to solve for  $A(t)$  in the first place; rather, we could have solved self-consistently for  $A(t)$  from this special distribution. The rationale is as follows: that one may be able to determine a particular mass distribution even when  $A(t)$  is not known *a priori*, i.e., even when there is not a closed set of equations as in the more general case of Eq. (7).

With this insight, we shall now solve the problem for a more general fragmentation kernel,  $F(y,x-y) = x^{\lambda-1}$ , with  $\lambda > 0$ . There is no reason why the previous statement should not hold here; i.e., we expect that for general  $\lambda$  a particular exponential solution will have the same moments as the general solution. Equation (3) now becomes

$$\dot{a}(x) = -x^\lambda a(x) + 2 \int_x^\infty dy y^{\lambda-1} a(y) - Ja(x)A. \quad (19)$$

Once again we use the auxiliary function  $b(x,t)$ , given by (12), although now the exponential factor is not known. This gives a pure-fragmentation equation for  $b(x,t)$ ,

$$\dot{b}(x) = -x^\lambda b(x) + 2 \int_x^\infty dy y^{\lambda-1} b(y), \quad (20)$$

which has a known, but complicated, general solution [10]. It has been proven that  $\lambda > 0$  is a necessary and sufficient condition for  $b(x,t)$  to have a scaling, universal behavior [19,22]. We are allowed, therefore, to deduce this behavior from a special solution to (19). A simple solution with exponential form [whose initial condition is an obvious generalization of (15)] is

$$b(x,t) = \frac{A_1(0)\lambda}{\Gamma(2/\lambda)} (b_0+t)^{2/\lambda} \exp[-(b_0+t)x^\lambda], \quad (21)$$

with moments

$$B_n(t) = \frac{A_1(0)\Lambda_{n+1}/\Lambda_2}{(b_0+t)^{(n-1)/\lambda}}. \quad (22)$$

In (21) and (22) appropriate normalization has been used. We now have

$$b_0^{1/\lambda} = \delta\Lambda_2, \quad \beta_0 = b_0^{2/\lambda} \frac{A_1(0)\lambda}{\Gamma(2/\lambda)}, \quad (23)$$

with the convenient notation

$$\Lambda_p = \Lambda_p(\lambda) \equiv \frac{\Gamma(p/\lambda)}{\Gamma(1/\lambda)}. \quad (24)$$

To find the explicit solution to the problem, we must determine the density of clusters  $A(t)$  self-consistently. From (22) and the transformation (12) we obtain an integral equation. This can be recast as the differential equation

$$\dot{A} = \frac{A}{\lambda(b_0+t)} - JA^2, \quad (25)$$

with the solution

$$A(t) = \frac{A(0)[1+t/b_0]^{1/\lambda}}{1+JA(0)b_0[\lambda/(1+\lambda)][(1+t/b_0)^{(1+\lambda)/\lambda}-1]} \\ \simeq \frac{1+\lambda}{\lambda} \frac{1}{Jt} \quad (t \rightarrow \infty). \quad (26)$$

It is easy to see that  $\exp(J\int_0^t dt' A)$  is simply the denominator of  $A$  in (26). From this, (12), and (22), we find

$$M(t) = \frac{\Lambda_2}{(b_0+t)^{1/\lambda}} \sim \frac{1}{t^{1/\lambda}} \quad (t \rightarrow \infty), \\ A_n(t) = \Lambda_{n+1} \frac{A(t)}{(b_0+t)^{n/\lambda}} \sim \frac{\lambda+1}{\lambda} \frac{1}{Jt^{1+n/\lambda}}, \quad (27) \\ a(x,t) = \frac{\lambda\Lambda_2}{\Gamma(1/\lambda)} \frac{A(t)}{M(t)} \exp[-(b_0+t)x^\lambda] \sim \frac{\exp[-\zeta^\lambda]}{JtM(t)},$$

with  $\zeta = \Lambda_2 x/M(t)$ . All results reduce to the previous ones if we set  $\lambda=1$ . Apart from numerical factors, the essential modifications in the asymptotics can be attributed to the time dependence of the average cluster mass,  $M \sim t^{-1/\lambda}$ , and the dependence of  $a(x,t)$  on the scaling variable  $\zeta$ . We see that an increase in  $\lambda$  slows down the decay of  $M$ . This follows from the resulting decrease in the rate of fragmentation of small fragments.

The mass distribution in (27), or (18), is peaked around  $\zeta=0$ , showing that the majority of the clusters have vanishingly small mass at late times due to fragmentation. The factor  $1/J$  indicates that if the annihilation rate increases the mass and cluster densities should decrease. The cluster density  $A(t)$  is the only moment whose decay is independent of  $\lambda$ . We recall that in pure annihilation processes  $A \simeq 1/Jt$ , which differs from Eq. (26) only by a factor of  $(1+\lambda)/\lambda$ , while the cluster-mass distribution remains invariant in time apart from an overall time-dependent factor. The typical fragment mass  $M(t)$ , on the other hand, is always independent of the annihilation rate  $J$  [Eq. (8)] and is asymptotically the same as in pure annihilation, i.e., it becomes independent of  $A(0)$  and  $A_1(0)$ .

Our results indicate, therefore, that at late times the fragmentation-annihilation process consists essentially of the annihilation of small-mass clusters. Furthermore, the fragmentation and annihilation processes effectively decouple from each other. This leads us to conjecture that in this case the upper critical dimension is two, as in pure annihilation. That is clearly true for a discrete system, where there is a minimum cluster mass and the fragmentation process ends before all particles annihilate.

### B. Linear annihilation (model 2)

Here, we briefly discuss model 2: a model with the same fragmentation process as model 1 but with *linear* annihilation. In this case there are no binary reactions and single clusters annihilate at a constant rate in time. We introduce

this model for comparison with model 1 and because in Sec. III we shall make an interesting generalization of it.

The kinetic equation for the cluster-mass distribution is similar to (19), but with the annihilation term replaced by the linear term  $-Ja(x)$ . This yields a trivial modification of the pure-fragmentation model (20) for general  $\lambda$ : the transformation (12) is replaced by  $b(x,t) = a(x,t)\exp[Jt]$ , leading to a simple extra exponential factor in the results. Working once again with the special solution (21), which corresponds to the initial condition  $a(x,0) = b(x,0) = \beta_0 \exp[-b_0 x^\lambda]$ , we obtain

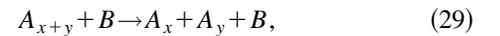
$$A(t) = \frac{A_1(0)}{M(t)} \exp[-Jt] \sim t^{1/\lambda} \exp[-Jt] \quad (t \rightarrow \infty), \\ A_n(t) = \Lambda_{n+1} \frac{A(t)}{(b_0+t)^{n/\lambda}} \sim \frac{\exp[-Jt]}{t^{(n-1)/\lambda}}, \quad (28) \\ a(x,t) = \frac{\lambda\Lambda_2}{\Gamma(1/\lambda)} \frac{A(t)}{M(t)} \exp[-(b_0+t)x^\lambda] \\ \sim \frac{\exp[-\zeta^\lambda] \exp[-Jt]}{M(t)^2},$$

where  $M(t)$  is the same as in model 1 [Eq. (27)]. Similar remarks about the dependence on  $\lambda$  apply here.

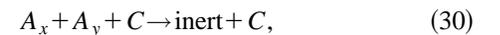
### III. ANNIHILATION AND FRAGMENTATION WITH CATALYSTS

Model 1 has elucidated some of the features in the interplay between the fragmentation and annihilation processes. However, it appears to have a somewhat unrealistic drawback: when two clusters of species  $A$  meet they react to produce a new, inert species, rather than merging into a larger cluster. Such a reaction would seem plausible, though, if another species, say  $C$ , was involved. In a reaction of the form  $A_x + C \rightarrow \text{inert}$ , or  $A_x + A_y + C \rightarrow \text{inert}$ , the kinetic equations of  $A$  and  $C$  would be coupled together. To be able to make progress, however, we envisage a situation where the reactions are induced by the presence of  $C$  but  $C$  does not take part in the reactions; i.e.,  $C$  is a catalyst. In Sec. II, it was implicitly assumed that annihilation was driven by a catalyst of constant concentration. Here we shall allow the concentration of  $C$  to vary in time. Catalysts play a key role in chemical, biological, and ecological systems (see, e.g., [23,24]), so the study of this class of models is potentially of great interest.

With these insights, let us consider the following two models where the fragmentation of  $A$  is controlled by a catalyst  $B$ ,



and the annihilation of  $A$  is induced by a catalyst  $C$ . With a *nonlinear annihilation* reaction (model C1),



while with a *linear annihilation* reaction (model C2)



In addition, we allow the catalysts to undergo the following annihilation reaction, at rate  $R$ :



In the reaction-controlled regime  $B(t)$  and  $C(t)$ , the concentrations of species  $B$  and  $C$ , have the following time dependence (see, e.g., [25]):

$$B(t) = C(t) = \frac{B(0)}{1 + B(0)Rt} \quad [B(0) = C(0)],$$

$$B(t) = \frac{\Delta B(0) \exp[-\Delta Rt]}{C(0) - B(0) \exp[-\Delta Rt]},$$

$$C(t) = \Delta + B(t) \quad [C(0) > B(0)], \quad (33)$$

with  $\Delta \equiv |C(0) - B(0)|$ . Note that if  $B(t)$  and  $C(t)$  were constant in time, then, via a trivial rescaling, models C1 and C2 would reduce to models 1 and 2 without catalysts.

**A. Method of solution**

We shall solve the generalizations of models 1 and 2, with general values of  $\lambda$ , following a similar procedure to that used in Sec. II. The essential difference now is that a formal time variable has to be defined,  $\tau(t)$ , which plays the role of time  $t$  in the previous models.

Model C1, for nonlinear annihilation in the presence of catalysts, is defined by the reaction schemes (29) and (30). The kinetic equation for the cluster-mass distribution, which generalizes (19), is

$$\dot{a}(x) = \left[ -x^\lambda a(x) + 2 \int_x^\infty dy y^{\lambda-1} a(y) \right] B - Ja(x)AC, \quad (34)$$

while the equation for the moments of  $a(x,t)$  now reads [cf. (4) with  $\alpha = 0$ ]

$$\dot{A}_n = \frac{1-n}{1+n} A_{n+\lambda} B - JA_n A C. \quad (35)$$

For  $\lambda = 1$ , a closed set of equations can be obtained once again, from which the general solution for  $A(t)$  and  $A_1(t)$  can be found. For general  $\lambda$ , we map (34) onto a pure-fragmentation equation using the transformation [cf. (12)]

$$b(x,t) \equiv a(x,t) \exp \left[ J \int_0^t dt' A(t') C(t') \right], \quad (36)$$

and redefining time as

$$\tau(t) = \int_0^t dt' B(t'). \quad (37)$$

Clearly, one only expects a scaling regime to occur if  $\tau(t) \rightarrow \infty$  as  $t \rightarrow \infty$ . Then  $b(x,\tau)$  obeys Eq. (20). As usual, we work with the special exponential solution (21) (now with  $\tau$  replacing  $t$ ). Inserting this solution into (36), integrating over  $x$ , and differentiating once with respect to time  $t$  yields the self-consistent equation [cf. (25) and (26)]

$$\dot{A} = \frac{AB}{\lambda(b_0 + \tau)} - JA^2 C, \quad (38)$$

with the solution

$$A(t) = \frac{[A_1(0)/\Lambda_2](b_0 + \tau)^{1/\lambda}}{1 + J[A_1(0)/\Lambda_2] \int_0^t dt' C(t') [b_0 + \tau(t')]^{1/\lambda}}. \quad (39)$$

As in Sec. II,  $\exp(J \int_0^t dt' AC)$  is simply the denominator of  $A$  in (39). Hence, from (21), (22), and (36) we find

$$M(t) = \frac{\Lambda_2}{(b_0 + \tau)^{1/\lambda}},$$

$$A_n(t) = \Lambda_{n+1} \frac{A(t)}{(b_0 + \tau)^{n/\lambda}}, \quad (40)$$

$$a(x,t) = \frac{\lambda \Lambda_2}{\Gamma(1/\lambda)} \frac{A(t)}{M(t)} \exp[-(b_0 + \tau)x^\lambda].$$

The essential differences from (27) are due to the presence of  $\tau(t)$ .

We now turn to model C2, for linear annihilation in the presence of catalysts, defined by the reaction schemes (29) and (31). The kinetic equation for  $a(x,t)$  is similar to (34), but with the nonlinear term replaced by  $-Ja(x)C$ . Defining

$$b(x,t) \equiv a(x,t) \exp \left[ J \int_0^t dt' C(t') \right], \quad (41)$$

and using the same formal time variable  $\tau(t)$ ,  $b(x,\tau)$  obeys Eq. (20) once again, and we work with the special exponential solution as before. The results, therefore, follow from (21) and (22) (with  $\tau$  replacing  $t$ ) multiplied by  $\exp[-J \int_0^t dt' C']$ . This gives [cf. (28)]

$$A(t) = \frac{A_1(0)}{M(t)} \exp \left[ -J \int_0^t dt' C(t') \right], \quad (42)$$

with  $M(t)$ ,  $A_n(t)$ , and  $a(x,t)$  still given by (40).

**B. Asymptotic results for  $B + C \rightarrow \text{inert}$**

The results derived in Sec. III A for models C1 and C2 hold for any time dependence of the catalysts. To obtain the asymptotic behaviors corresponding to catalysts  $B$  and  $C$  mutually annihilating according to (32), we insert the mean-field expressions (33) into the previous results and look for the dominant contributions in the limit  $t \rightarrow \infty$ . There are three qualitatively different cases, depending on the relative values of the initial densities of the catalysts.

**I.  $B(0) = C(0)$**

With balanced amounts of the two catalysts, we have

$$\tau = \ln[1 + RB(0)t]^{1/R} \simeq \ln(t^{1/R}) \quad (t \rightarrow \infty). \quad (43)$$

This gives

$$M(t) \simeq \frac{\Lambda_2 R^{1/\lambda}}{[\ln(t)]^{1/\lambda}} \quad (t \rightarrow \infty),$$

$$A_n(t) \sim M(t)^n A(t), \quad (44)$$

$$a(x,t) \sim \frac{A(t)}{M(t)} \exp[-\zeta^\lambda], \quad \zeta = \Lambda_2 x / M(t)$$

for models C1 and C2, and

$$A(t) \simeq \begin{cases} \frac{1+\lambda}{\lambda} \frac{R}{J \ln(t)} \sim \frac{1}{\ln(t^{J/R})} & (\text{model C1}) \\ \frac{A_1(0)}{M(t)} \frac{1}{[B(0)Rt]^{J/R}} \sim \frac{[\ln(t)]^{1/\lambda}}{t^{J/R}} & (\text{model C2}). \end{cases} \quad (45)$$

As in models 1 and 2 without catalysts, the late-time regime is dominated by the annihilation of small-mass clusters, the two underlying processes decouple from each other, and there is scaling. The cluster-number density, however, decays logarithmically in model C1 and with a nonuniversal power law in model C2: the nonuniversal exponent depends on the annihilation rates  $J$  and  $R$  of species  $A$  and of the catalysts. We conclude that, although different time dependences emerge, the balance between the annihilation and fragmentation processes in this symmetric case is analogous to that occurring in the absence of catalysts.

## 2. $B(0) > C(0)$

If there is a majority of the fragmentation catalyst the auxiliary time  $\tau$  behaves essentially like  $t$ :

$$\begin{aligned} \tau &= \Delta t + \ln\{[B(0) - C(0)\exp(-\Delta Rt)]/\Delta\}^{1/R} \\ &\simeq \Delta t \quad (t \rightarrow \infty). \end{aligned} \quad (46)$$

The key point to notice when evaluating the integral in the denominator of (39) and the exponential term in (42) is that  $\int_0^t dt' C(t') \rightarrow \ln[B(0)/\Delta]^{1/R}$  as  $t \rightarrow \infty$ . This yields, for models C1 and C2,

$$\begin{aligned} M(t) &\simeq \frac{\Lambda_2}{(\Delta t)^{1/\lambda}} \quad (t \rightarrow \infty), \\ A(t) &\simeq [A_1(0)/\Lambda_2] F(\lambda) (\Delta t)^{1/\lambda}, \\ A_1(t) &\rightarrow A_1(0) F(\lambda), \end{aligned} \quad (47)$$

$$a(x,t) \sim \frac{1}{M(t)^2} \exp[-\zeta^\lambda], \quad \zeta = \Lambda_2 x / M(t),$$

where

$$F(\lambda) = \begin{cases} \frac{1}{1 + JA_1(0)I_\infty/\Lambda_2} & (\text{model C1}) \\ \left(\frac{\Delta}{B(0)}\right)^{J/R} & (\text{model C2}), \end{cases} \quad (48)$$

$$\begin{aligned} I_\infty &\equiv \int_0^{\ln[B(0)/\Delta]^{1/R}} dx [b_0 + x + \ln\{C(0)/[B(0) \\ &\quad - \Delta \exp(Rx)\}]^{1/R} \quad (49) \end{aligned}$$

In this case the fragmentation process is much faster than the annihilation one, which is suppressed as the mass density tends to a fraction  $F(\lambda)$  of its initial value  $A_1(0)$ . Once again there is a scaling regime. In conclusion, the asymptotic behaviors of models C1 and C2 are similar to that of a pure fragmentation process with rescaled initial mass density  $A_1(0)F(\lambda)$  and rescaled time  $\Delta t$ , where  $\Delta$  is the residue of catalyst  $B$ . Hence, the smaller the value of  $\Delta$  the longer the time needed to reach this regime. The value of  $F(\lambda)$  is determined not only by the kinetic parameters  $J$ ,  $R$ , and  $\lambda$ , but also by the initial densities  $B(0)$  and  $C(0)$ .

## 3. $C(0) > B(0)$

With a majority of the annihilation catalyst  $\tau$  tends to a finite value,

$$\begin{aligned} \tau &= \ln\{[C(0) - B(0)\exp(-\Delta Rt)]/\Delta\}^{1/R} \\ &\rightarrow \tau_\infty = \ln[C(0)/\Delta]^{1/R} \quad (t \rightarrow \infty). \end{aligned} \quad (50)$$

Noticing that the integral in the denominator of (39),  $\int_0^t dt' C(t') [b_0 + \tau(t')]^{1/\lambda}$ , is dominated by the large- $t$  contribution, we obtain

$$\begin{aligned} M(t) &\rightarrow M_\infty = \Lambda_2 / (b_0 + \tau_\infty)^{1/\lambda} \quad (t \rightarrow \infty), \\ A_n(t) &\sim A(t), \end{aligned} \quad (51)$$

$$a(x,t) \sim A(t) \exp[-(b_0 + \tau_\infty)x^\lambda]$$

for models C1 and C2, and [cf. (26) and (28)]

$$A(t) \simeq \begin{cases} \frac{1}{J\Delta t} & (\text{model C1}), \\ \frac{A_1(0)}{M_\infty} \left(\frac{\Delta}{C(0)}\right)^{J/R} \exp[-J\Delta t] & (\text{model C2}). \end{cases} \quad (52)$$

Here, the annihilation process dominates over fragmentation. The latter is suppressed as the average cluster mass tends to a nonzero value  $M_\infty$  and the mass distribution becomes stationary (up to an overall time-dependent factor) and identical to its initial form  $a(x,0)$ . This form of  $a(x,t)$  follows from all fragments being equally likely to annihilate, and the prefactor  $A(t) \rightarrow 0$  indicates the eventual loss of all mass. This situation differs from  $B(0) = C(0)$ , where annihilation occurs between increasingly smaller clusters. As expected, there is no scaling regime since  $\tau$  has a finite limit. In addition, the behavior of  $a(x,t)$  may not be universal in this case. In conclusion, the asymptotic behavior of models C1 and C2 is similar to that of a pure-annihilation process with  $M = M_\infty$  and rescaled time  $\Delta t$ : the process being a binary reaction for model C1, and linear with initial mass  $A_1(0) \times [\Delta/C(0)]^{J/R}$  for model C2. The asymptotic average mass  $M_\infty$  is determined by the kinetic parameters  $R$  and  $\lambda$ , and by the initial values  $A(0)/A_1(0)$ ,  $B(0)$ , and  $C(0)$ .

It should be stressed that the validity of the continuous-mass description used throughout is subject to restrictions in the long-time regime. In the cases  $B(0)=C(0)$  and  $C(0)>B(0)$ , where the cluster number  $A(t)\rightarrow 0$  and the system eventually reaches an empty state, the description holds while the system still contains a sufficiently large number of particles. This condition ensures the smoothness of the cluster mass distribution. In the cases  $B(0)=C(0)$  and  $B(0)>C(0)$ , where the average cluster mass  $M(t)\rightarrow 0$  and increasingly smaller fragments are produced, the usual restrictions to a pure-fragmentation process apply [11]. The essential difference within a discrete description lies in the behavior of the density of the smaller fragments, or monomers.

#### IV. CONCLUSIONS

We have solved a class of fragmentation models with nonlinear mass loss, at the mean-field level, and elucidated the competition between fragmentation and annihilation processes. Simultaneously, we have analyzed the corresponding models with linear mass loss. Although the solutions for the cluster-mass distribution hold for exponential initial conditions, we expect their moments to be identical to those of the corresponding general solutions.

Asymptotically, models 1 and 2 (without catalysts) are characterized by the annihilation of small-mass clusters and by the effective decoupling of the two underlying processes. We believe that in this case the upper critical dimension is 2 (but see [14]).

Models  $C1$  and  $C2$ , with fragmentation and annihilation catalysts, have been solved for a general time dependence of the catalyst densities. The linear annihilation model, in particular, shows much more interesting and less trivial behavior in this case. When  $B$  and  $C$  undergo mutual annihilation, we have found that different interplays arise between the two intervening processes depending on the initial densities  $B(0)$  and  $C(0)$ . As a result, unconventional and/or nonuniversal asymptotic behavior may occur [ $B(0)=C(0)$ ], or the scaling regime may be absent [ $C(0)>B(0)$ ]. In these models, the upper critical dimension is likely to be 4, as a consequence of the spatial structure induced by the catalytic reactants at late times: in  $B$ -rich regions fragmentation (annihilation) will be frequent (absent) producing a high concentration of  $A$ , while in  $C$ -rich regions the roles of these processes will be reversed, producing voids of  $A$ . With simultaneous fragmentation and annihilation it seems difficult, however, to develop more quantitative arguments determining  $d_c$ . In any case, new, unusual behavior should also appear at *lower dimensions* in the presence of catalysts. Even here, the mean-field description may prove adequate up to moderate times, before significant spatial fluctuations set in.

Instead of the mean-field expressions (33) for the catalyst densities, one may use the corresponding ones in the diffusion-controlled regime ( $d<4$ ), which can be deduced, e.g., from Ref. [25]. In addition, other reactions or time dependences of the catalysts may be investigated. One may even replace one of the catalysts by an *inhibitor*. For these purposes one simply needs to use the results of Sec. III A. In practice, it may be that both linear and nonlinear mass-loss processes operate. In such cases, models 1 and 2, or  $C1$  and

$C2$ , would merge to yield a model with linear and nonlinear annihilation terms. It should be possible to solve such a model using the methods of Secs. II and III. It may also be that one has a source rather than a sink term, in which case the previous terms will have opposite signs leading to a competition between linear and nonlinear contributions.

Further directions of work are possible, in addition to those just mentioned. One may look for mass-dependent reaction rates, the generic form for the annihilation terms then being  $-Ja(x)\int_0^\infty dy f(x,y)a(y)$  for model 1, and  $-Ja(x)f(x)$  for model 2. [In Sec. II A we mentioned the case  $f(x,y)=(xy)^\alpha$ .] Another research avenue would be to investigate two species, say  $A$  and  $B$ , undergoing fragmentation and mutual annihilation. When  $A(0)=B(0)$  this model is identical to the single-species model of Sec. II A. With two species, a ‘‘charge’’ conservation law may also be present, e.g.,  $A_x+B_y\rightarrow A_{x-y}$  ( $B_{y-x}$  for  $y>x$ ) [1]. We have found [26] that in the absence of such a constraint both cluster densities  $A(t)$  and  $B(t)$  decay as  $2/(Jt)$  ( $\lambda=1$ ), independently of the initial masses  $A_1(0)$  and  $B_1(0)$ ; i.e., there is no mass difference residue.

We expect the classes of models studied here, and their further developments, to have applications in various subjects, such as physics, chemistry, biology, and, to some extent, population dynamics (see, e.g., [23,24]). Model 1 (without catalysts) is suitable to describe fragmenting systems with nonlinear (reaction) mass loss. Models  $C1$  and  $C2$ , on the other hand, have the potential to describe a broad range of phenomena, with linear or nonlinear mass loss and with arbitrary time dependences of the catalysts. We describe one particularly important generalization to these models. In many processes of industry, heterogeneous chemistry, or biochemistry, such as food processing or food digestion (where the catalysts are enzymes), the efficiency of the reactions may depend on the available surface area of the reacting fragments (see, e.g., [27]). It would be of great interest, therefore, to develop fragmentation models whose clusters are characterized not only by their *volume* (or mass), but also by their *surface area*. From these, one could then build up fragmentation-annihilation models with surface-area-dependent annihilation rates. An obvious difficulty in constructing such models is the dependence of the surface area on the shape of the fragments. First steps towards this goal have been taken in very recent work on multivariable fragmentation [28].

It is interesting to note that there is some resemblance between fragmentation-annihilation processes and branching-annihilating random walks [29]. In the latter, particles diffuse and annihilate upon encounter and each particle gives birth to  $n$  offspring, at prescribed rates. A difference, though, is that the particles do not have a mass distribution. Depending on the branching and annihilating rates, these systems may evolve towards an empty state or an active steady state. The existence of phase transitions in the long-time behaviour has been investigated for different values of  $n$  [29]. Depending on the densities of catalysts (which control the rates of the two processes involved), we have found that models  $C1$  and  $C2$  can also exhibit quite opposite asymptotic behavior:  $A\rightarrow 0$  for  $C(0)\geq B(0)$ , and  $A\rightarrow\infty$  for  $B(0)>C(0)$ . Although we have not seen evidence for states characterized by steady values of the cluster-number density

$A(t)$ , steady-state values were obtained for the cluster-mass density  $A_1(t)$  [ $B(0) > C(0)$ ] and for the average cluster mass  $M(t)$  [ $C(0) > B(0)$ ].

In conclusion, we hope that this paper will stimulate future work on fragmentation-annihilation processes, and believe that fruitful applications of the present or related models (especially those with catalysts), can be found in various fields.

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