# Nonuniversality and breakdown of scaling in two-species aggregation

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A simple model of aggregation is presented which is built from two distinct monomeric species, $A$ and $B$, with bonding allowed only between unlike species. This model exhibits novel and unexpected kinetic behavior which depends crucially on whether the mass of the aggregate is odd or even. The kinetics of the even clusters can be accounted for within the framework of the single-species reaction scheme $A + A \rightarrow A$, while the odd clusters can be described by the two-species reaction $A + B \rightarrow$ inert. Consequently, the upper critical dimension, $d_c$, for the kinetics of the even clusters is two, while $d_c = 4$ for the odd clusters. Numerical simulations of this $A$-$B$ model reveal unusual kinetic behavior, including novel dimension dependence below the upper critical dimension, nonuniversality, and a breakdown of scaling for the cluster-mass distribution. The underlying parity dependence of the $A$-$B$ model leads us to introduce a simpler one-component aggregation model in which the reaction rates depend explicitly on the parity of the reacting clusters. The corresponding rate equations are studied and exact expressions for the exponents describing the decay rate of the aggregates are obtained. It is found that the kinetics of clusters of even and odd mass are, in general, quite different, and that the corresponding exponents are also generally nonuniversal. Furthermore, in two special cases, the complete solution to the rate equations can be obtained, and it is thus demonstrated that a conventional scaling description for the cluster-mass distribution breaks down.

## I. INTRODUCTION

Aggregation is the irreversible bonding of clusters to form clusters of indefinitely increasing mass.[1] Typically, such processes are described by the reaction

$$A_i + A_j \xrightarrow{K(i,j)} A_{i+j} ,$$

where $A_i$ denotes a cluster of mass $i$ and $K(i,j)$ is the rate at which $i$-mers and $j$-mers react to form a cluster of mass $i+j$. Much of the current understanding of the kinetics of aggregation is based on the analysis of rate equations.[2,3] These equations represent an approximation in the spirit of a mean-field theory, as fluctuations in the cluster densities and shapes are ignored. Within this approximation, a coherent theoretical description for the possible kinetic behaviors has very recently been proposed by van Dongen and Ernst,[4] in which general features of the dependence of the matrix of reaction rates, $K(i,j)$, on $i$ and $j$, determine the long-time kinetics.

According to this framework, three general classes of behavior may be delineated. In systems of "type I," the reaction rates of large clusters with other large clusters dominate over reactions between small clusters. When this predominance is sufficiently strong, it can lead to a gelation transition in a finite time.[5] Aggregating systems in the type-I class are typically characterized by a cluster-mass distribution which exhibits a power-law dependence on mass, for masses up to the typical cluster mass. On the other hand, in systems of "type III," large-small reactions predominate, a situation which occurs in the aggregation of Brownian particles in solution.[2] This case is typically characterized by a peak in the cluster-mass distribution, which decays faster than any power law on either side of the peak.[1,6,7] Finally, in "type-II" systems, all possible reactions play an equivalent role (in a scaling sense) and marginal-type behaviors can occur. The understanding of this class is not as well developed as the other two classes, although it is worth noting that the simple, exactly soluble case of a constant matrix of reaction rates, "constant-kernel" coagulation, is a type-II system.

In this paper, we consider two simple aggregation models which exhibit rather surprising kinetic behaviors that lie outside of the general framework just discussed. These models are based on very simple modifications of the constant-kernel reaction scheme, and part of their motivation for this study is to understand the effect of these modifications on the kinetics. We find, rather surprisingly, that the exponents characterizing the kinetics may be nonuniversal, depending on the values of the reaction rates. Furthermore, a conventional scaling description of the cluster-mass distribution fails to describe the system adequately. Both of these novel features occur for models which ostensibly are in the universality class of constant-kernel coagulation.

We first investigate the properties of a simple two-component, $A$-$B$, model with constituent monomers $A$ and $B$, in which bonding occurs between unlike species. A model of this type was first introduced by Meakin and Djordjevic[8] to study the aggregation of branched structures with two dissimilar monomeric constituents. In our investigations, we shall restrict ourselves to the simpler situation where the monomers are bifunctional so that the aggregates have the structure of an alternating linear copolymer. If we ascribe a positive "charge" to the $A$'s and a negative charge to the $B$'s, then a very

simple and appealing physical picture of the aggregation process can be developed (Fig. 1). According to the restriction of $A$-$B$ bonding and the linearity of the clusters, the charge is restricted to be equal to 0 or to $\pm 1$. Furthermore, the types of reaction that occur may be divided into three general classes: (a) a positive and a negative cluster can join to form a neutral cluster, (b) two neutral clusters can join to form a larger neutral, and (c) a neutral and a charged cluster can join to form a heavier charged cluster (with the charge being conserved).

Reaction (a) is identical to the two-species reaction

$$A + B \rightarrow \text{inert} ,$$

as the charge is locally conserved, that is, it remains constant at each reaction, while reaction (b) is a single-species fusion reaction,

$$A + A \rightarrow A .$$

These two processes have an upper critical dimension, $d_c$, equal to 4[9,10] and 2,[11] respectively. That is, for spatial dimension $d$ greater than or equal to $d_c$, the kinetics is adequately described by a rate equation approach, while for $d < d_c$, fluctuations in the densities of diffusing reactants give rise to dimension-dependent kinetic behavior at long times. In the $A$-$B$ model, the interplay between the charged and neutral clusters due to reaction

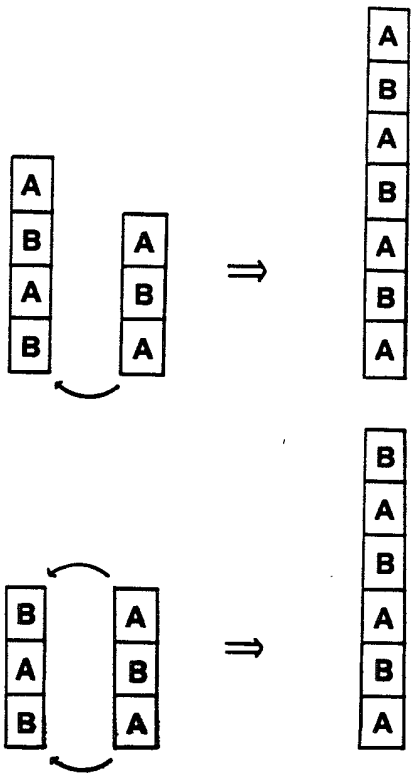



FIG. 1. Pictorial representation of a typical charged-charged and neutral-charged reaction in $A$-$B$ coagulation. Notice that the reaction scheme conserves charge, and that the $A$-$B$ bonding constraint limits the reactivity of neutral clusters with their environment to be $\frac{1}{2}$.

(c), with the individual kinetic behaviors of these two species being very different, is the mechanism underlying many unusual kinetic properties.

One important feature of the $A$-$B$ model is that half of the potential reactions on neutral clusters with their environment are limited by the $A$-$B$ bonding constraint, while this constraint plays no such role in positive-negative reactions. In the diffusion-controlled limit, one therefore expects that the overall rate of neutral-neutral, charged-charged, and neutral-charged reactions will be different. In order to account for the consequences of these induced parity-dependent reaction rates analytically, we therefore introduce a simpler, closely related, one-component aggregation model, in which the reaction rates have an explicit parity dependence and investigate the behavior of this model in the rate equation approximation.[12] We have calculated the exponents describing the temporal behavior of this system, and found them to be nonuniversal in that they depend on the values of the microscopic reaction rates. Furthermore, in two special cases, we can derive a full asymptotic solution for the cluster-mass distribution and thereby show that it does not scale in the conventional sense. The origin of this intriguing feature stems from two competing influences on the time dependence of even clusters: On the other hand, reactions between odd clusters act as an external *source* of even clusters, while processes involving one or two even clusters cause one even cluster to disappear. This again points to the interplay between neutral and charged clusters and the mechanism which leads to new phenomena.

The outline of this paper is as follows. In Sec. II, we give a brief self-contained discussion of the conventional scaling description of aggregation processes and we also define the basic exponents which characterize the long-time kinetic behavior. In Sec. III, we define the two-component, $A$-$B$, coagulation model and the related one-component model with parity-dependent reaction rates (which we term the "alternating model"), and then write the corresponding rate equations for these processes.

In Sec. IV, we present our numerical results for $A$-$B$ coagulation, both in the mean-field limit, and in the diffusion-controlled limit for $d = 1$, 2, and 3. In Sec. V, we calculate the exponents which describe the time dependence of the alternating aggregation process in the mean-field limit, and find them to be nonuniversal. We also present numerical results to provide a more complete picture of the kinetics of this model. In Sec. VI, we solve for the generating function of the alternating model in the case where no reactions are allowed to occur between aggregates of different parity. It is found that the scaling relation derived in Sec. II is in fact violated, and the physical mechanism leading to this violation is identified. In Sec. VII, we solve yet another special case, which can be mapped onto a "sum" kernel form. Evaluation of the exponents in this case shows again that scaling does indeed fail. Furthermore, we are able to identify unambiguously the two contributions to the cluster density which give rise to this breakdown of scaling. In Sec. VIII, we discuss the small-time behavior

of the exactly soluble sum-kernel case of the preceding section. It is found that the small-time behavior is unrelated to the large-time behavior. While it is well known that this is typical of most aggregating systems, no exactly solvable example of this fact has been found previously. In Sec. IX, we give a brief summary. Finally, in an appendix, some of the details leading to the solution of Sec. VII are presented.

## II. SCALING THEORY AND BASIC EXPONENTS OF COAGULATION

In irreversible aggregation processes, the average cluster mass increases indefinitely. It is therefore natural to assume that this typical mass plays a role analogous to that of the correlation length in ordinary critical phenomena. If there is only one such characteristic mass, $s^*(t)$, then we may write the concentration of aggregates of mass $k$,$c_k(t)$, at asymptotically large times in the following scaling form:[1,3,13,14]

$$c_k(t) \simeq k^{-2}\Phi\left[\frac{k}{s^*(t)}\right], \tag{1}$$

where the factor $k^{-2}$ is required by mass conservation, i.e., $\sum_{k=1}^{\infty} k c_k(t)$ is a constant. The long-time kinetics of the system is then completely described by the following three exponents:

$$\begin{aligned} &s^*(t) \propto t^z , \\ &c_k(t) \propto t^{-w} \quad [t \to \infty; k \ll s^*(t)] , \\ &c_k(t) \propto k^{-\tau} \quad [1 \ll k \ll s^*(t)] . \end{aligned} \tag{2}$$

It should be noted, however, that these exponents need not all be defined; in particular, for type-III kernels, the exponents $\tau$ and $w$ do not exist and the kinetics is instead characterized by exponential-type behavior rather than power laws. However, if these exponents do exist, then it is readily seen from Eq. (1) that the function $\Phi(x)$ has the following singular behavior as $x \to 0$:

$$\Phi(x) \sim x^{w/z} \tag{3}$$

from which the following relation between the three basic exponents follows:

$$(2-\tau)z = w . \tag{4}$$

This scaling relation is quite general and its derivation depends mainly on the assumption that a significant amount of the mass of the system is contained in clusters of typical mass [i.e., comparable to $s^*(t)$]. This latter assumption is violated, however, in gelling systems, in percolation, and, quite generally, whenever $\tau > 2$.

In addition to the three exponents defined in Eqs. (2), a fourth exponent $\alpha$ is generally defined to describe the time dependence of the total number of clusters,

$$\sum_{k=1}^{\infty} c_k(t) \sim t^{-\alpha} . \tag{5}$$

If one substitutes the scaling form (1) for the cluster-mass distribution in Eq. (5) and employs the scaling relation of Eq. (4), then one finds that $\alpha$ satisfies the exponent relations $\alpha = z$, for $\tau \leq 1$, and $\alpha = w$, for $\tau > 1$. These four exponents summarize conveniently the long-time properties of aggregating systems. For the $A$-$B$ and alternating models, however, we shall show that the kinetics of even, or neutral, clusters is generally quite different than the kinetics of the odd, or charged, clusters. For this reason, we will generalize the above exponents by adding the subscript $\pm$ or 0 to denote the exponents of the odd an even clusters, respectively.

## III. DEFINITION OF THE TWO-COMPONENT AND ALTERNATING MODELS

As discussed in the Introduction, these are three types of clusters in the $A$-$B$ model: positively charged, negatively charged, and neutral. Let us denote the concentrations of these three species by $c_{2k+1}^{(+)}$, $c_{2k+1}^{(-)}$, and $c_{2k}^{(0)}$, respectively, where the subscripts denote the cluster mass. Taking into account the restrictions imposed by the $A$-$B$ bonding constraint, and also assuming a reaction rate of unity for each allowed bond, we find that the rate equations for the two-component systems are

$$\begin{aligned} \dot{c}_{2k+1}^{(+)} &= \tfrac{1}{2}\sum_{j=1}^{k} c_{2j-1}^{(+)} c_{2(k-j)+2}^{(0)} - c_{2k+1}^{(+)} \sum_{j=1}^{\infty} (c_{2j-1}^{(-)} + \tfrac{1}{2} c_{2j}^{(0)}) \\ \dot{c}_{2k}^{(0)} &= \sum_{j=1}^{k} c_{2j-1}^{(+)} c_{2(k-j)+1}^{(-)} + \tfrac{1}{4}\sum_{j=1}^{k} c_{2j}^{(0)} c_{2(k-j)}^{(0)} \\ &\quad - c_{2k}^{(0)} \sum_{j=1}^{\infty} (\tfrac{1}{2} c_{2j-1}^{(+)} + \tfrac{1}{2} c_{2j-1}^{(-)} + \tfrac{1}{2} c_{2j}^{(0)}) \end{aligned} \tag{6}$$

and a similar equation can be written for $c_{2k+1}^{(-)}$.

A basic feature of this model is the partitioning of the reactions into three classes: charged-charged, neutral-neutral, and neutral-charged. In the mean-field limit, this partitioning does not give rise to any new physical effects because each cluster "sees" only its average environment (see Sec. IV). However, below the upper critical dimension, fluctuations in the densities of the clusters do arise if the reactants are undergoing local diffusive motion. Most notably, the system segregates into domains which are predominantly positively or negatively charged, with neutral clusters mainly existing along domain boundaries.[9,10] Consequently, the long-time kinetics can be expected to be fundamentally influenced by the partitioning of the possible reactions, as our numerical simulations will confirm.

However, for the purposes of making progress by analytical methods, it is useful to consider a simpler model which mirrors the above partitioning. To this end, we introduce a very simple generalization of the classical one-component constant-kernel coagulation model, by allowing for an explicit parity dependence in the matrix of reaction rates. Thus we define

$$K(i,j) = \begin{cases} K & \text{for } i \text{ and } j \text{ odd} \\ L & \text{for } i \text{ and } j \text{ even} \\ M & \text{otherwise} . \end{cases} \tag{7}$$

This represents an attempt to describe the parity effects

in the $A$-$B$ model induced by spatial fluctuations, by a corresponding parity dependence in the reaction rates of a mean-field model. The rate equations for this "alternating" model are thus given by the conventional form

$$\dot{c}_k=\tfrac{1}{2}\sum_{j=1}^{k-1} K(j,k-j)c_j c_{k-j}-c_k\sum_{j=1}^{\infty} K(k,j)c_j \ . \quad (8)$$

For this model, the exponents $w_\pm$ and $w_0$ are, in general, continuously dependent on the values of the reaction rates $K$, $L$, and $M$. This nonuniversality is in sharp contrast to most previously studied aggregation models, where a rough knowledge of a scaling nature for the dependence of $K(i,j)$ on $i$ and $j$ is sufficient to determine the exponents.[4] Van Dongen and Ernst[15] have, however, pointed out that, for a matrix of reaction rates such that $K(1,j)\sim K(j,j)$, i.e., type-II systems, pathological results can occur, and they have provided examples where a correction term to $K(i,j)$ (i.e., a term that is asymptotically negligible) modifies the exponents in a continuous way.

## IV. KINETICS OF THE $A$-$B$ MODEL

We now study the kinetics of the $A$-$B$ model, both by numerical simulations and by appealing, where possible, to analogies with simple reaction schemes. The simulations employed in this work are simple generalizations of the techniques used previously[7,16] for investigating the kinetics of one-component coagulation models. The basic idea of this simulation method is to regard clusters as being *single* lattice sites, but with a variable mass. When two clusters of mass $i$ and $j$ meet, they coalesce into a single-site cluster of mass $i+j$, at a rate proportional to the reaction rate $K(i,j)$. Since the cluster geometry is trivial, and because we are free to choose the rules for cluster motion arbitrarily, it is therefore possible to specify the reaction rates in our system *exactly*, thus permitting a precise correspondence between a particular simulation and a corresponding system of rate equations.

In the mean-field limit, the cluster concentrations are spatially uniform so that the relative rate of reaction of an $i$-mer and $j$-mer is strictly proportional to $K(i,j)c_i c_j$. Here the product of concentrations gives the probability that an $i$-mer and $j$-mer meet, in the mean-field approximation, while multiplying by $K(i,j)$ gives the overall rate at which $i$-mer and $j$-mer react to form an $i+j$-mer. The requisite spatial uniformity is most conveniently achieved by allowing a cluster to hop to any site of the system with an equal probability. Since the lattice structure is irrelevant in this equivalent-neighbor hopping mode, it is most convenient to perform simulations on a one-dimensional chain. On the other hand, allowing for local diffusive motion of the clusters on a $d$-dimensional lattice, permits a study the diffusion-controlled limit as a function of spatial dimension.

For simulations of the $A$-$B$ model, we regard a cluster as a "stack" of alternating $A$ and $B$ monomers which still continue to occupy a single lattice site. A cluster is chosen sequentially from the current (randomly ordered) list of particles, and this cluster is moved to a neighboring lattice site. If a move is made which leads to a positively charged and negatively charged cluster occupying the same lattice site, then a neutral cluster is formed (Fig. 1). If a move leads to a neutral and charged cluster occupying the same site, then the $A$-$B$ bonding constraint means that only one-half of all encounters will actually lead to a reaction. In such a case, the incident cluster is returned to its original position with probability $\frac{1}{2}$, while a reaction occurs with probability $\frac{1}{2}$. Similarly, if two charged clusters of the same sign to occupy the same site, the incident cluster is returned to its initial position. When an attempt to move all clusters once has been made, the time is incremented by one unit and a new pass through the list of particles is started.

Before presenting our simulations of low-dimensional systems, let us consider the kinetics in the mean-field limit in order to serve as a test of the numerical results. We shall restrict ourselves to the situation where the system has no net charge so that the concentration of positively and negatively charged clusters of given mass will always be equal. Under these conditions, it is straightforward, although a little tedious, to see that the complete solution to the rate equations is trivial. If one defines the generating function

$$f_\pm(z)=\tfrac{1}{2}\sum_{\text{even } k} c_k^{(0)}z^k \pm \sum_{\text{odd } k} c_k^{(+)}z^k \ , \quad (9)$$

then from Eq. (6) these generating functions satisfy the differential equations

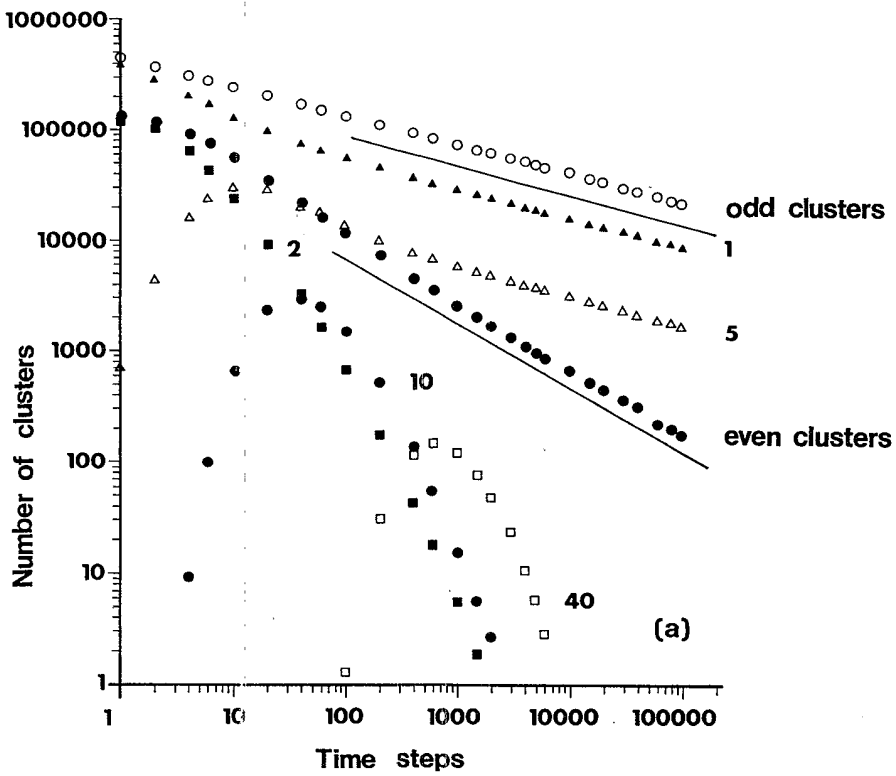
$$\dot{f}_\pm(z)=\tfrac{1}{2}f_\pm(z)^2-f_\pm(z)\mathcal{M} \ , \quad (10)$$

where $\mathcal{M}=f_+(1)$. This closely resembles the equation satisfied by the generating function of the classical constant-kernel model.[2] By following steps similar to those used to solve the constant-kernel problem, the solutions to Eq. (10) may be written as

$$\tfrac{1}{2}[f_+(z)\pm f_-(z)]=\tfrac{1}{2}\mathcal{M}^2 z\sum_k (1-\mathcal{M})^k z^k\frac{[1\pm(-1)^k]}{2} \quad (11)$$

and this immediately leads to the classical constant-kernel solution for the cluster concentrations of each species.

Our simulations of the $A$-$B$ model with equivalent-neighbor hopping, do show the anticipated result that the kinetics of the neutral and charged clusters follow the solution of the constant-kernel coagulation model. However, in lower-dimensional systems with nearest-neighbor cluster hopping, the situation is considerably more interesting. Since charged-charged reactions are equivalent to the reaction $A+B\rightarrow$inert, we expect[9,10] that the density of charged clusters will decay as $t^{-d/4}$ for spatial dimension $d<d_c^{(\pm)}=4$. Similarly, neutral-neutral reactions are equivalent to the one-species reaction, $A+A\rightarrow A$. However, neutral charges can also disappear due to their reaction with charged clusters. Therefore, we expect[11] that neutral clusters should decay at least as fast as $t^{-d/2}$ for $d<d_c^{(0)}=2$. In particular, the behavior in three dimensions should be rather pecu-



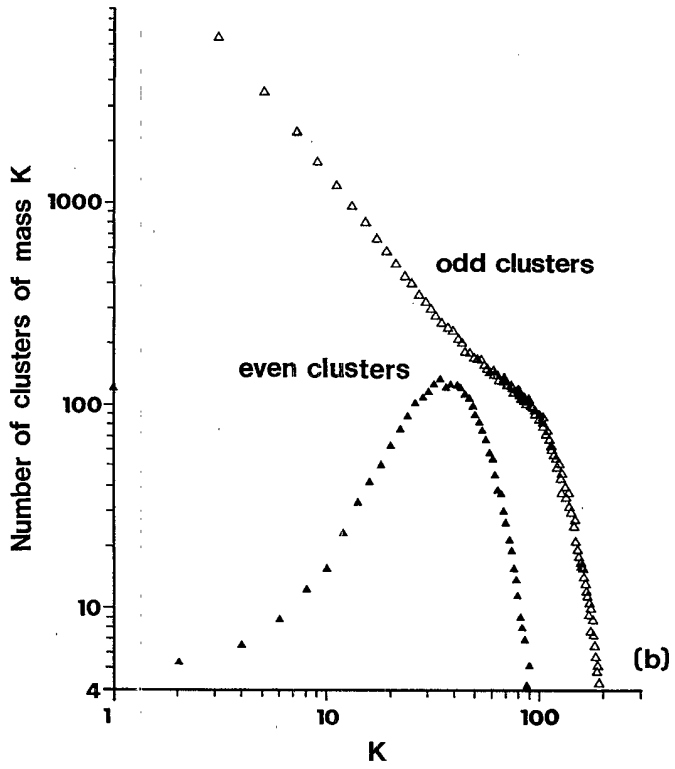
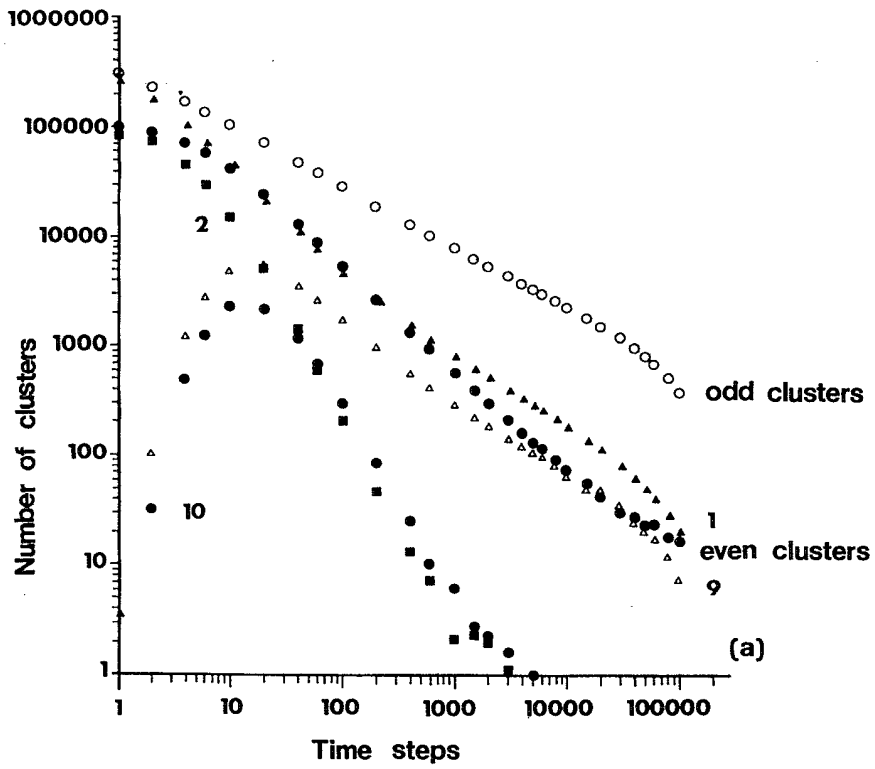




FIG. 2. Numerical results for $A$-$B$ coagulation in the diffusion-controlled limit for a linear chain of $10^6$ sites, with an initial density of $A(0)=B(0)=0.4$. In (a) the dependences of the total number of odd (○) and even (●) clusters are shown, as well as the behavior of selected typical numbers of individual clusters [in this case, monomer (▲), dimer (■), 5-mer (△), 10-mer (●), and 40-mer (□)]. Lines of slope $-\frac{1}{4}$ and $-\frac{1}{2}$ have been drawn to guide the eye. In (b) we show the mass dependence of the even (▲) and odd (△) cluster mass distributions at 1000 time steps and 6000 time steps, respectively.



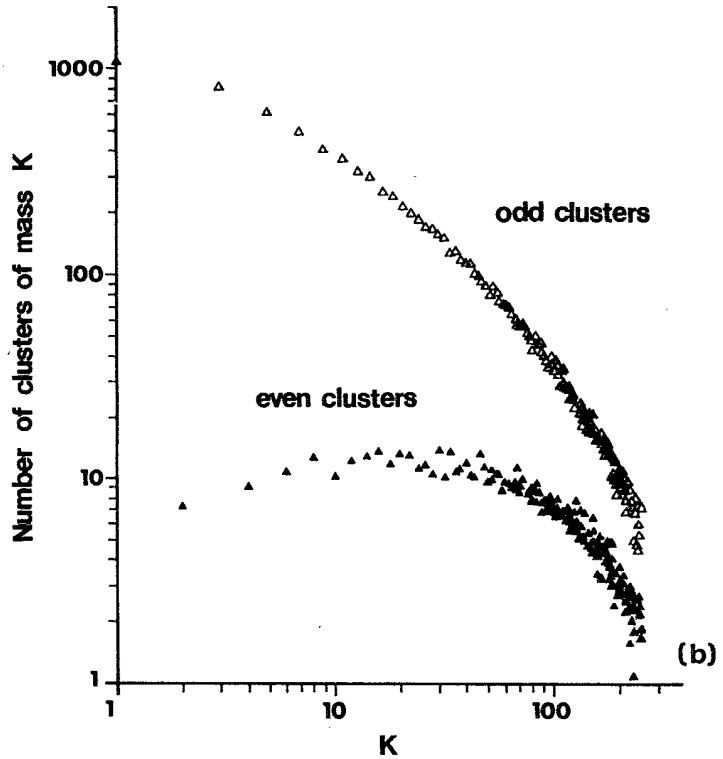




FIG. 3. Numerical results for $A$-$B$ coagulation on a $850\times850$ square, with $A(0)=B(0)=0.4$. In (a) the time dependence of the reaction is shown for selected representative species of clusters. Notice that there is curvature in the data at long times, indicative of finite size effects. In (b) the mass dependence of the even and odd cluster-mass distributions are shown at 600 time steps.

liar as the neutral clusters are predicted to decay according to the mean-field limit, while the charged clusters are predicted to decay according to a diffusion-controlled behavior.

In Figs. 2–4, we outline the kinetic behavior of the $A$-$B$ model for $d=1$, 2, and 3, and numerical estimates for the corresponding exponents are given in Table I. In one dimension, the temporal behaviors of the neutral and charged clusters are quite different from each other. In agreement with our expectations based on the analogy with the reaction $A+B\rightarrow$inert, the density of charged clusters apparently decays as $t^{-1/4}$, that is, $\alpha_{\pm}=\frac{1}{4}$. In more precise terms, the slope given by a double logarithmic least-squares fit to the data yields a slope of $-0.26$ with a rms deviation of about 1%. This is well within numerical uncertainty of the theoretical prediction. The

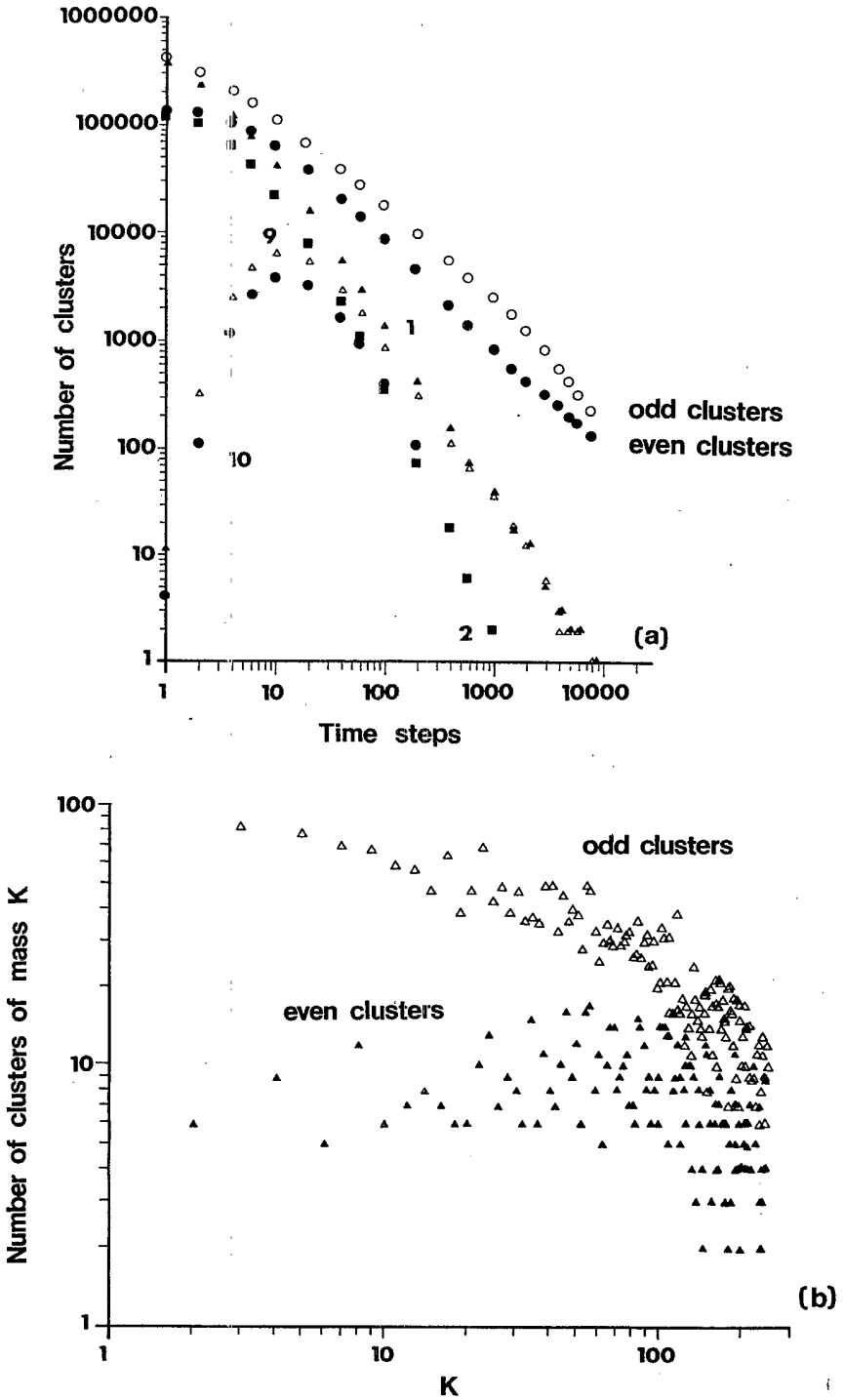



FIG. 4. Numerical results for $A$-$B$ coagulation on a $100\times100\times100$ cube, with $A(0)=B(0)=0.4$, showing both the time dependence of the reaction in (a) and the mass dependence of the cluster-mass distribution at 600 time steps in (b).

TABLE I. Numerical estimates of the kinetic exponents for $A$-$B$ coagulation. The equality sign denotes those exponent estimates which are very close to values which we believe are exact. In one dimension, the exponents $w_0$ and $\tau_0$ may not be defined, as discussed in the text. The numbers given in these two cases are the exponents one might reasonably estimate based solely on the data.

| One dimension | | Two dimensions | | Three dimensions | | Mean-field limit | |
|---|---|---|---|---|---|---|---|
| $\alpha_\pm=0.25$ | $\alpha_0=0.5$ | $\alpha_\pm\simeq0.5$ | $\alpha_0\simeq1.0$ | $\alpha_\pm\simeq0.8$ | $\alpha_0\simeq1.0$ | $\alpha_\pm=1.0$ | $\alpha_0=1.0$ |
| $w_\pm=0.25$ | $w_0\simeq2.0$ | $w_\pm\simeq0.5$ | $w_0\simeq2.0$ | $w_\pm\simeq1.5$ | $w_0\simeq2.0$ | $w_\pm=2.0$ | $w_0=2.0$ |
| $\tau_\pm\simeq1.36$ | $\tau_0\simeq-1.6$ | $\tau_\pm\simeq0.75$ | $\tau_0\simeq0.0$ | $\tau_\pm\simeq0.35$ | $\tau_0\simeq0.0$ | $\tau_\pm=0.0$ | $\tau_0=0.0$ |
| $z_\pm\simeq0.5$ | $z_0\simeq0.45$ | $z_\pm\simeq0.75$ | $z_0\simeq0.8$ | $z_\pm\simeq0.95$ | $z_0\simeq0.95$ | $z_\pm=1.0$ | $z_0=1.0$ |

density of each $c_k^{(+)}$ also decays at the same rate, i.e., $w_\pm=\frac{1}{4}$, from which the exponent relations in Sec. II would dictate that $\tau_\pm>1$. Using the observed value of $z_\pm\simeq0.5$, then the natural generalization of the basic scaling relation in Eq. (4), i.e., $w_\pm=(2-\tau_\pm)z_\pm$, yields $\tau_\pm=\frac{3}{2}$, which is in fair agreement with our numerical estimate of $\tau_\pm\simeq1.35$.

The decay of the concentration of neutral clusters can also be understood on the basis of the domain picture for the reaction $A+B\rightarrow$inert. As a function of time, the system segregates into growing domains of oppositely charged clusters, with each domain representing the initial density difference between $A$ and $B$. Reactions between positively and negatively charged clusters then take place only on domain boundaries. This reaction is the only source for neutral clusters in the system, and when a neutral cluster attempts to penetrate a charged domain, it is immediately annihilated. Thus we are led to a scenario where on average, either zero or one neutral cluster exists between each charged domain (Fig. 5). Since the distance between domain boundaries grows as $t^{1/2}$, the density of neutral clusters should therefore decay as $t^{-1/2}$, i.e., $\alpha_0=\frac{1}{2}$. Since the data show appreciable curvature, we need to discard initial points in any estimate of the asymptotic behavior. By successively discarding the early time points, one obtains an estimate of $-0.56$ for the power law, in fair agreement with the prediction made above.

This domain picture can be used to predict the $z$ exponents as well. After a long time has passed, reactions occur only at domain boundaries so that most of the mass in the system is contained in the clusters at the boundaries. Since the number of such clusters varies as $t^{-1/2}$, their average mass should therefore grow as $t^{1/2}$.

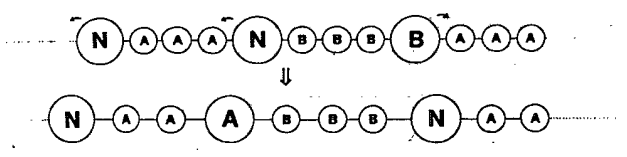



FIG. 5. Schematic "snapshots" of a system undergoing $A$-$B$ coagulation in one dimension at two closely spaced time steps. Note, in particular, the presence of a single relatively massive cluster at each domain boundary, and this cluster rapidly changes between a neutral and charged state upon collisions with the boundary.

In addition, since these massive clusters are rapidly changing between neutral and charged due to the interaction of the massive cluster and its adjoining domains, the typical mass of both the neutral and charged clusters will be the same, so that $z_\pm$ and $z_0$ will be equal to $\frac{1}{2}$. Corresponding to this equality of the $z$ exponents, we observe that asymptotically (for $10^4$ times steps or greater) the ratio of neutral mass to charged mass in the system approaches a constant value of approximately 0.09.

The value of $w_0$ appears to not be defined, however, as the decay rate of individual neutral clusters seems to be faster than a power law. Although our numerical data do not yield this result conclusively, we can give a heuristic argument for a faster than power-law decay. As a preliminary, let us recall the corresponding result for the exponent $w$ in one-component constant-kernel coagulation in one dimension. In this case, the exponent $w$ has been shown[16] to be equal to $\frac{3}{2}$, a result which follows by mapping the problem of the decay of a given cluster to that of studying the three-body problem of the survival probability of a single random walker enclosed in a "cage" of two other random walkers.[17] For the $A$-$B$ model, however, a neutral particle will typically be enclosed by an $A$ on one side an a $B$ on the other. The motion of these two enclosing particles is highly correlated, giving rise to a "cage" which grows in linear dimension only as $t^{1/4}$, rather than as $t^{1/2}$ for uncorrelated enclosing particles. In such a correlated case, we expect that a neutral particle will decay quasi-exponentially with time as $\exp(-t^{1/2})$.

In two dimensions, the behavior of the neutral clusters is fairly close to that of the mean-field limit. Our numerical estimates of the various exponents are typically within 10% of their mean-field values, and we interpret this discrepancy as arising from logarithmic corrections which occur when $d=d_c^{(0)}$. However, the behavior of the charged clusters is extremely interesting. The density of charged clusters does decay as $t^{-1/2}$, in accord with the expected exponent value $\alpha_\pm=d/4$. There is an inconsistency with conventional scaling, however, in that $\tau_\pm$ is less than 1, which dictates $\alpha_\pm=z_\pm$, while we observe $\alpha_\pm=w_\pm$ [see the discussion after Eq. (5)]. Correspondingly, the charged exponents fail to satisfy the scaling relation (4) by an amount which is much larger than the discrepancy in one dimension. Thus in two dimensions, the neutral clusters closely follow a mean-field decay, while the charged clusters follow a decay which is very different from the mean-field form, and which is

also inconsistent with scaling.

In three dimensions, the neutral clusters follow mean-field kinetics to a high degree of accuracy, as should be anticipated. The kinetic behavior of the charged clusters as still distinct from that of the mean-field limit, but, rather surprisingly, it is also qualitatively different from the behavior found in one or two dimensions. In three dimensions, the exponents $\alpha_\pm$ and $z_\pm$ are now very close to each other, rather than the exponents $\alpha_\pm$ and $w_\pm$ coinciding. Corresponding to this change in behavior, the value of $\tau_\pm$ is now considerably less than unity, i.e., the cluster-mass distribution is relatively flat for masses less than the typical mass. Our estimates of the charged exponents still fail to satisfy the scaling relation (4), but by a relatively small amount. Thus as the spatial dimension increases, the kinetic behavior of the $A$-$B$ model approaches that of the mean-field limit, but not in a smooth manner. For the charged clusters, there is an additional transition at $d=2$, as evidenced by the qualitative change in the relations obeyed by the kinetic exponents.

## V. ANALYTICAL RESULTS FOR ARBITRARY VALUES OF THE REACTION RATES IN THE ALTERNATING MODEL

We now study the rate equations of the alternating model in order to calculate the exponents as a function of the reaction rates. Let us first consider the exponent $z$ describing the growth of the typical cluster mass, $s^*(t)$. An appropriate definition of $s^*(t)$ is

$$s^*(t)=\sum_{k=1}^{\infty} k^2 c_k(t) \tag{12}$$

and for the moment, we do not distinguish between even and odd clusters. Combining (12) with (8), one immediately obtains[18]

$$\frac{ds^*}{dt}=\sum_{j,k=1}^{\infty} jkK(j,k)c_j(t)c_k(t) \propto \left[\sum_{j=1}^{\infty} jc_j(t)\right]^2=O(1)\,, \tag{13}$$

and hence the typical mass grows linearly in $t$, so that $z=1$. This is the conventional result for the exponent $z$ in a system where the matrix of reaction rates has no scaling dependence on its arguments. The question as to whether this result also holds for the typical mass of odd (or even) clusters separately is somewhat more difficult, but we shall argue at the end of this section that such is indeed the case.

We now turn to the question of the large-time behavior of the cluster concentrations. By writing the rate equations for the first few $c_k(t)$, it is clear that all the $c_{2k+1}(t)$ have one asymptotic kinetic behavior, while the $c_{2k}(t)$ potentially have a different behavior. Thus it suffices to study the rate equations for $c_1(t)$ and $c_2(t)$. These equations are

$$\dot{c}_1=-c_1(K\rho_\pm+M\rho_0)\,, \tag{14a}$$

$$\dot{c}_2=\frac{K}{2}c_1^2-c_2(M\rho_\pm+L\rho_0)\,, \tag{14b}$$

where

$$\rho_\pm(t)=\sum_{k=1}^{\infty} c_{2k-1}(t)\,, \qquad \rho_0(t)=\sum_{k=1}^{\infty} c_{2k}(t) \tag{15}$$

are the density of odd and even clusters, respectively. Using Eq. (8), the following closed equations for $\rho_\pm$ and $\rho_0$ are obtained:

$$\dot{\rho}_\pm=-K\rho_\pm^2\,, \tag{16a}$$

$$\dot{\rho}_0=\frac{K}{2}\rho_\pm^2-\left[M\rho_\pm+\frac{L}{2}\rho_0\right]\rho_0\,. \tag{16b}$$

By first solving Eqs. (16), it is now possible to solve Eqs. (14), thereby obtain the exponents $w_\pm$ and $w_0$. It also allows us to solve the entire system (8) iteratively, but the expressions for $c_k(t)$ become prohibitively complex as $k$ increases, so that this approach does not allow a direct evaluation of the exponent $\tau$. This is unfortunate, because the breakdown of scaling means that the $\tau$ exponents cannot be generally found by appealing to the scaling relation (4).

With the initial condition, $c_k(t=0)=\delta_{k,1}$, Eq. (16a) is readily solved to give

$$\rho_\pm(t)=\frac{1}{1+Kt}\,, \tag{17}$$

and to solve for $\rho_0$ we introduce the rescaled (dimensionless) variables $\phi$ and $x$,

$$\phi=\rho_0/\rho_\pm,\quad x=-\ln\rho_\pm\,, \tag{18}$$

and substitute into Eqs. (16). This gives

$$\frac{d\phi}{dx}=-\frac{L}{2K}\phi^2+\left[1-\frac{M}{K}\right]\phi+\tfrac{1}{2}\,. \tag{19}$$

It now follows that for $x\to\infty$,

$$\phi(x)\to\phi_\infty=\frac{K}{L}\left\{\left[1-\frac{M}{K}\right]+\left[\left[1-\frac{M}{K}\right]^2+\frac{L}{K}\right]^{1/2}\right\}. \tag{20}$$

This implies, in particular, that both the density of the even and odd clusters decay as $1/t$, namely, $\alpha_\pm=\alpha_0=1$. In addition, if one assumes the generally valid result that the typical cluster mass is inversely proportional to the number of clusters, then the typical masses of odd and even clusters both grow linearly with time. This then leads to $z_\pm=z_0=1$, as mentioned at the beginning of this section.

To obtain the exponents describing the decay of $c_1$ and $c_2$, we use the result of Eq. (20) in Eqs. (14a) and (14b) to yield the approximate large-time equations $c_1(t)$ and $c_2(t)$,

$$\dot{c}_1 = -c_1\rho_\pm(K+M\phi) \sim -c_1\frac{1}{1+Kt}(K+M\phi_\infty)\,, \tag{21a}$$

$$\dot{c}_2 = \frac{K}{2}c_1^2 - c_2\rho_\pm(M+L\phi) \sim \frac{K}{2}c_1^2 - c_2\frac{1}{1+Kt}(M+L\phi_\infty)\,. \tag{21b}$$

Now solving Eqs. (21a) and (21b) in their asymptotic form one obtains for the exponents $w_\pm$ and $w_0$,

$$w_\pm = 1+\frac{M}{K}\phi_\infty\,,$$

$$w_0 = \begin{cases} \bar{w}_0 \quad \text{if } \bar{w}_0 \equiv \dfrac{M}{K}+\dfrac{L}{K}\phi_\infty \le 2w_\pm - 1 \\ 2w_\pm - 1 \quad \text{otherwise}\,. \end{cases} \tag{22}$$

The two possible values for $w_0$ stem from the two different contributions to $\dot{c}_2$ in Eq. (21b), namely, production and loss terms. The full solution to this equation is of the form $t^{1-2w_\pm}+t^{-\bar{w}_0}$, so that the true exponent $w_0$ arises from the asymptotically dominant of the two terms. Numerically, we have determined which of the two values, either $1-2w_\pm$ or $\bar{w}_0$, gives the asymptotic value of $w_0$ in the two-dimensional parameter space spanned by $L/K$ and $M/K$ (cf. Fig. 6). The values of $w_\pm$ and $w_0$ are conveniently summarized by the contour plots given in Figs. 6(a) and 6(b). The exponent $w_\pm$ has a large variation as a function of $L/K$ and $M/K$, while $w_0$ has a much smaller variation. In particular, $w_\pm$ is quite large close to the vertical axis for $L/K<1$. Since both the $z$ and $\alpha$ exponents are equal to 1, and since the integral of the cluster-mass distribution must give the total number of clusters, a very large value of $w$ must correspond to a nonmonotonic cluster-mass distribution, namely, $\tau<0$. The strong anomaly in the value of $w_\pm$ near the vertical axis also indicates that the special case $L=0$ will have very different behavior from that of the interior of the parameter space, as we will show below.

It is also interesting that there is an infinite set of points in the parameter space where the $w$ exponents take on *rational* values. For such points, one might anticipate that the reaction matrix can be written in a form that facilitates an exact solution. One such case is the situation where $M=(K+L)/2$ which can be mapped onto a "sum" kernel form (cf. Sec. VII). Another very striking case is $L=4M$, where the exponents $w_\pm$ and $w_0$ now take on the *universal* values of 1.5 and 2.0, respectively. At the present time, we do not have a satisfactory description of the behavior at these "rational" points.

Let us now turn to the special case of $L=0$, which is expected to have especially interesting behavior. From (20), we see that this case is singular, and in general, an alternative derivation is needed to obtain the exponents. The rate equations remain easily soluble by elementary means, however, and we find that the density of odd clusters still continues to decay as $1/t$, while the decay of the even clusters is given by

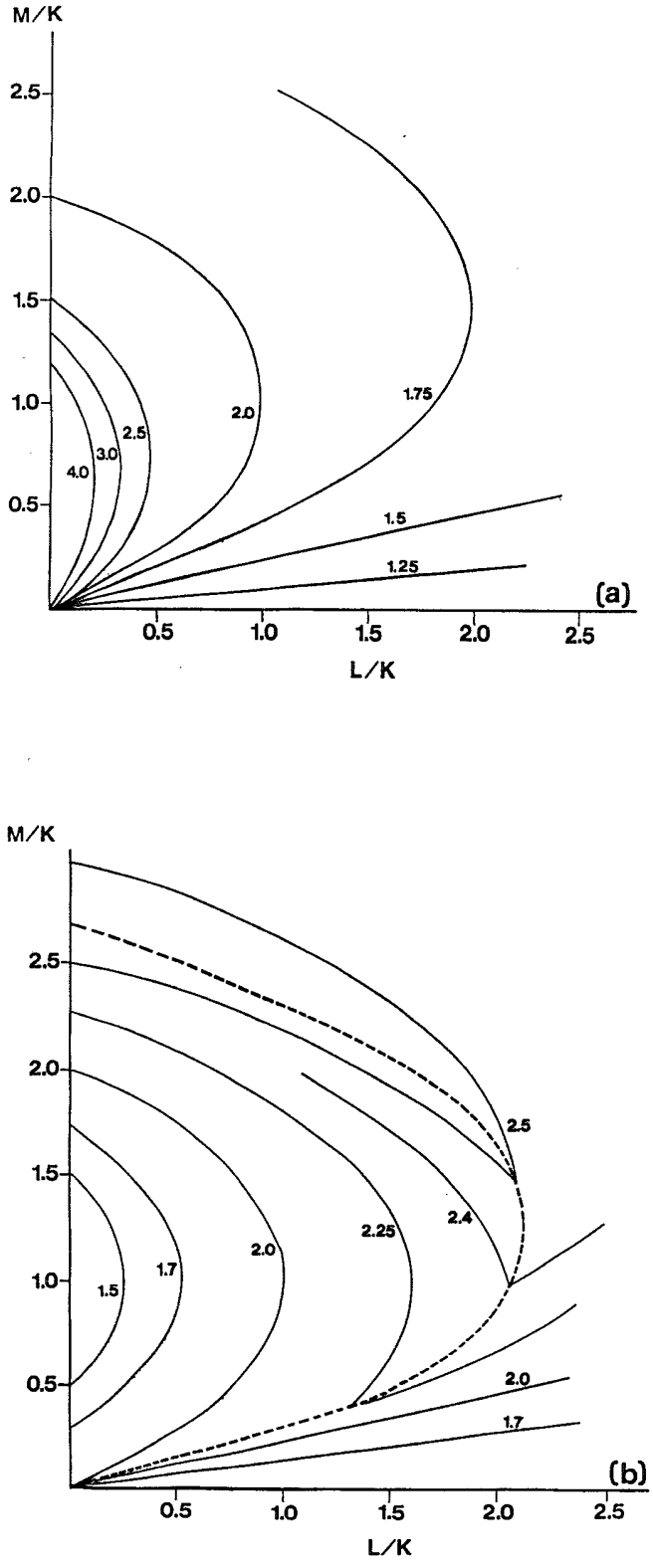



FIG. 6. Contour plots of constant values of the exponent $w_\pm$ in (a), and the exponent $w_0$ in (b), in the $(L/K)$-$(M/K)$ parameter space. Also shown in (b) (dashed curve) is the locus of points separating the region where $w_0=\bar{w}_0$ (to the left of the curve), from the region where $w_0=2w_\pm-1$.

$$\rho_0(t)\simeq\begin{cases}\dfrac{1}{2(M/K-1)(1+Kt)}, & M>K\\ \dfrac{1}{2(1+Kt)}\ln(1+Kt), & M=K\\ \dfrac{1}{2(1-M/K)}\dfrac{1}{(1+Kt)^{M/K}}, & M<K\ .\end{cases}\tag{23}$$

Thus for $M\geq K$, $\alpha_0=1$ (with a logarithmic correction appearing when $M=K$), and for $M<K$, $\alpha_0=M/K$. This last result demonstrates the rather strong competing effects of the "source" and "sink" terms in Eq. (16b). In particular, for $M<K$, charged clusters are decaying sufficiently quickly that a decay slower than $1/t$ is admissible in a simple bimolecular reaction scheme, a most unusual result.

For the $w$ exponents we obtain the following.[19] When $M>K$,

$$w_\pm=1+\frac{1}{2}\frac{1}{(1-K/M)},\quad w_0=\frac{M}{K}\ .\tag{24}$$

These exponent values could also have been obtained simply by taking the limit $L\to 0$ in Eqs. (20) and (22). However, when $M\leq K$, the individual cluster densities decay faster than a power law, so that the $w$ exponents are not defined. Instead, we find

$$c_1(t)\sim\begin{cases}c_2(t)\sim\exp(-\ln^2 t), & M=K\\ c_2(t)\sim\exp[-(\text{const}\times t)^{1-M/K}], & M<K\ .\end{cases}\tag{25}$$

We see, therefore, that the $w$ exponents in the alternating model are not universal, i.e., they depend on rather detailed information concerning the reaction rates. This is contrary to the general expectation[4] that a limited amount of information of a scaling nature about the reaction rates is sufficient to obtain all the exponents.

To complete the description of the behavior in the alternating model, we need to determine the values of the $\tau$ exponents. This exponent is, in general, very difficult to determine analytically, and we therefore resort to numerical simulations in an attempt to accomplish this task. Our simulations of the alternating model are very similar, although simpler, than those performed for the $A$-$B$ model. For the alternating model, when two (single-site) clusters come to occupy the same lattice site, a reaction is defined to occur with a probability given by the reaction rate appropriate for the two colliding clusters. If a reaction does not occur, then the incident cluster is returned to its initial position. With this numerical approach, then, we have studied the kinetics for general points in the alternating-parameter space.

The simulation results generally confirm the physical picture outlined thus far. We have verified the predicted values of the $\alpha$, $w$, and $z$ exponents quite accurately. It does not appear possible, however, to estimate the $\tau$ exponents, with any degree of precision. We do observe that wherever a $w$ exponent is greater than 2, the corresponding $\tau$ exponent is negative, as discussed above. However, the $\tau$ exponents appear to be fairly small in general, so that it is not feasible to estimate an exponent accurately by a direct measurement of the shape of the cluster-mass distribution.

## VI. THE CASE $M=0$

In the following, we shall completely solve the case where $M$ is equal to zero. This will then enable us to calculate the remaining exponents $\tau_\pm$ and $\tau_0$ explicitly. We will find that scaling is, in fact, violated, so that it is not generally valid to infer the value of $\tau_\pm$ and $\tau_0$ by combining the expressions of Eq. (22) with the scaling relation of Eq. (4).

To solve this case, we first note that if there is no reaction between chains of even and odd length, then the odd chains have no means of growing. This follows because odd chains grow in size only by reacting with even chains, whereas a reaction of two odd chains removes both of them from the population of odd chains. If the initial condition is $c_k(0)=\delta_{k,1}$ (i.e., monodisperse monomer-only initially), then no odd chains will ever be formed, apart from the original monomer. It is therefore convenient to define new variables $\gamma_k(t)$ as $c_{2k}(t)$, thus reducing the rate equations to

$$\begin{aligned}&\dot c_1=-Kc_1^2\ ,\\ &\dot\gamma_k=L\left[\tfrac{1}{2}\sum_{j=1}^{k-1}\gamma_j\gamma_{k-j}-\gamma_k\sum_{j=1}^{\infty}\gamma_j\right]+\frac{K}{2}c_1^2\delta_{k1}\ ,\end{aligned}\tag{26}$$

that is, a conventional constant-kernel rate equation, but driven by a source term whose time dependence is known [since the equation for $c_1(t)$ can be readily integrated]. This problem can be solved by the method developed by Leyvraz and Tschudi.[20] Define the following generating functions:

$$F(z,t)=\sum_{k=1}^{\infty}\gamma_k(t)z^k\ ,\tag{27a}$$

$$G(z,t)=F(z,t)-F(1,t)\ .\tag{27b}$$

Combining Eqs. (26) and (27b), one obtains

$$\frac{dG}{dt}=\frac{L}{2}G^2+\frac{K}{2}(z-1)c_1^2\ ,\tag{28}$$

$$G(z,0)=0\ .$$

To solve this equation we introduce the auxiliary variables

$$\phi(z,t)=G(z,t)/c_1(t),\quad x=-\ln c_1(t)\tag{29}$$

which gives the following equation for $\phi(z,t)$:

$$\frac{d\phi}{dx}=\frac{L}{2K}\phi^2+\phi+\frac{z-1}{2}\ .\tag{30}$$

It is easily seen that for large times (i.e., as $x\to\infty$), $\phi(z,t)$ goes to an equilibrium value, $\phi_\infty(z)$, given by

$$\phi_\infty=-\frac{K}{L}\left[1+\left[1+\frac{L}{K}(1-z)\right]^{1/2}\right]\ .\tag{31}$$

Therefore $\phi_\infty(z)$ has the singularity structure $(z-z_c)^{1/2}$, with $z_c=1+K/L$. This means that the cluster concen-

trations *at infinite time,* suitably normalized by the monomer concentration, have the following asymptotic form:

$$\frac{c_{2k}}{c_1}(t=\infty)\sim k^{-3/2}\left[1+\frac{K}{L}\right]^{-k}. \tag{32}$$

Note also that this result goes over to the well-known[21] $k^{-3/2}$ power-law decay for the steady-state solution of a system with constant reaction rate and a constant monomer source if $K$ is negligible compared to $L$. Finally, since Eq. (26) gives $c_1(t)$ decaying as $t^{-1}$, Eq. (32) implies that $c_{2k}(t)$ also decays at the same rate, thus yielding $w_0=1$.

To obtain the value of $\tau$, however, one must look into the time dependence of $\phi(z,t)$ in greater detail. Defining $\psi(z,t)$ as $\phi(z,t)-\phi_\infty(z)$ and eliminating the time in favor of $dx=c_1dt$, one obtains the following differential equation for $\psi(z,x)$:

$$\frac{d\psi}{dx}=\frac{L}{2K}\psi^2+\left[1+\frac{L}{K}\phi_\infty(z)\right]\psi,$$
$$\psi(z,0)=-\phi_\infty(z). \tag{33}$$

This equation is readily solved to yield

$$\psi(z,x)=\left[-[\phi_\infty(z)^{-1}+u_\infty(z)]\exp\left[\frac{Lx}{2Ku_\infty(z)}\right]+u_\infty(z)\right]^{-1}, \tag{34}$$

where $u_\infty(z)$ is defined as

$$u_\infty(z)=\lim_{x\to\infty}\{[\psi(z,x)]^{-1}\}=-\frac{L}{2[K+L\phi_\infty(z)]}. \tag{35}$$

Note that $u_\infty(z=1)=-1/\phi_\infty(z=1)$ so that the coefficient in front of the exponential in Eq. (34) vanishes for $z=1$ and becomes a very small negative number for $z$ somewhat larger than 1. This means that for large times (i.e., large $x$) there is a simple pole in $\psi(z,x)$ close to $z=1$. This implies that $\tau=0$, in contradiction to the scaling relation given in Eq. (4).

The reason for this anomalous behavior is readily understood from a careful consideration of the solution presented above. It is well known that the classical one-component system with constant rate and no source term satisfies scaling. The source term is a perturbation to the scaling solution which, for a given mass $k$ decays more slowly than the scaling solution itself. This remarkable mechanism has the effect that the exponent $w$ as defined in Eq. (2) is determined by the slowly decaying effects of a *nonscaling* contribution to the concentration $c_k(t)$, which makes a negligible contribution to the mass, so that the very basis for deriving the scaling relation is absent.

To amplify the above arguments, consider how $G(z,t)$ evolves in time. The first, and most obvious, remark is that $G(z,t)/c_1$ tends to a limit as $t\to\infty$. This fact is the origin of the value $w_0=1$, since the presence of a limit means that, eventually, *all* concentrations will behave exactly as $c_1(t)$. This contribution, however, is *not* scaling, as is evident by the fact that the corresponding generating function has no singularity at $z=1$. This implies that any measure of "typical mass" for this contribution will remain finite. In fact, the mass contained in this contribution to the concentration is asymptotically zero, since it is equal to $[\partial\phi_\infty(z=1,t)/\partial z]c_1(t)$. This means that the scaling behavior is determined by the *correction* to the leading behavior of the generating function. This correction, however, is simply $\psi(z,x)c_1$ as defined in Eq. (34). If we examine the large time behavior of $\psi(z,x)$ we find

$$\psi(z,x)\simeq\exp\left[-\frac{L}{2Ku_\infty(z)}x\right]=(1+Kt)^{-(L/2Ku_\infty(z))} \tag{36}$$

from which we infer that the behavior of the correction to $G(z,t)$ is

$$G(z,t)-\phi_\infty(z)c_1\simeq(1+Kt)^{-(L/2Ku_\infty(z)-1)}. \tag{37}$$

Since $u_\infty(z=1)=L/2K$, we find that for $z$ close to unity the relevant contribution to the generating function (i.e., the one responsible for the singular behavior at large times) goes approximately as $(1+Kt)^{-2}$. Since $z$ is the variable conjugate to the mass of the aggregates, large aggregates have a scaling behavior corresponding to a $t^{-2}$ decay law, in agreement with the value of $w$ obtained from Eq. (4), and the already obtained values for the exponents $\tau$ and $z$. In other words, the asymptotic form describing the behavior of $c_k(t)$ at large times is approximately given by an expression of the form

$$c_k(t)\sim k^{-3/2}\left[1+\frac{K}{L}\right]^{-k}\frac{1}{1+Kt}+\text{const}\times t^{-2}z_c(t)^{-k}, \tag{38}$$

where $z_c(t)$ is the nearest singularity of the generating function $G(z,t)$. It is easily seen that $z_c(t)\sim 1+\text{const}\times t^{-1}$, in agreement with the general result that the typical mass of the clusters grows linearly in time.

## VII. THE CASE $M=(K+L)/2$

In the following, we will discuss some of the features of the exact solution for the case where $M=(K+L)/2$. As the solution itself is quite complicated, we present it as an appendix, giving here those results that pertain to the critical behavior and the value of the exponents $\tau_0$ and $\tau_\pm$.

First, let us see why the case $M=(K+L)/2$ has special significance. We write the reaction kernel $K(i,j)$ in the suggestive form

$$K(i,j)=\begin{cases}K=2a-2b & \text{for } i \text{ and } j \text{ odd}\\ L=2a+2b & \text{for } i \text{ and } j \text{ even}\\ M=(K+L)/2=2a & \text{otherwise},\end{cases} \tag{39}$$

which can be rewritten as

$$K(i,j)=f(i)+f(j)\ ,$$
$$f(i)=a+b(-1)^i\ . \tag{40}$$

That is, $K(i,j)$ can be recast as a sum kernel, and the solution of the rate equations can always be reduced (see, e.g., Hendriks, Ernst, and Ziff[5]) to the simpler problem of recursively solving an infinite set of equations for the following dimensionless variables:

$$\phi_k=c_k\Big/\left[\sum_{k=1}^{\infty}c_k\right]\ ,$$
$$dx=dt\sum_{k=1}^{\infty}c_k,\quad x(0)=0\ . \tag{41}$$

We now introduce generating functions for the even and odd clusters, respectively, as follows:

$$V(z,x)=2\sum_{k=1}^{\infty}\phi_{2k}(x)z^{2k}-2\ ,$$
$$T(z,x)=2\sum_{k=1}^{\infty}\phi_{2k-1}z^{2k-1}\ . \tag{42}$$

To determine $\tau_0$ and $\tau_\pm$, we require the singular behavior of these generating functions in the limit where $1\ll(1-z)^{-1}\ll s^*(t)$. This follows from the definition of the exponent $\tau$ given in Sec. II, where it is defined as giving the behavior of the cluster mass distribution $c_k(t)$ for $1\ll k\ll s^*(t)$. To determine this singular behavior from the exact solution is a nontrivial task which we will only sketch here, again leaving the details to the Appendix.

From a detailed analysis of the differential equations satisfied by the functions $T(z,x)$ and $V(z,x)$, we find the following behavior: We consider the ratio $\phi(z,x)=V(z,x)/T(z,x)$ of the two generating functions. It then appears that if $z$ is very close to (but *less*) than 1, one obtains over a fairly long range of times

$$T(z,x)\approx(a+b)/a,\quad V(z,x)\approx-(a+b)/a\ ,$$
$$\phi(z,x)\approx-1\ . \tag{43}$$

Inserting these approximate expressions into the exact equation for $\phi(z,x)$ derived in the Appendix [Eq. (A10)], one obtains

$$\frac{d\phi}{dx}=\frac{a^2-b^2}{2a}(1-\phi^2)\ ,$$
$$\phi(z,0)=-1/z\ . \tag{44}$$

To determine the range of validity of Eq. (44)—in particular for $\phi(z,x)$—we solve the approximate equation (45) for $\phi(z,x)$ exactly and obtain

$$\phi(z,x)=\coth\left[\frac{a^2-b^2}{2a}[x-x_c(z)]\right]\ ,$$
$$x_c(z)=\frac{2a}{a^2-b^2}\operatorname{arccoth}\left[\frac{1}{z}\right]\approx\frac{a}{a^2-b^2}\ln[(1-z)^{-1}]\ . \tag{45}$$

This latter equation gives a natural time scale dependent on $z$, beyond which the approximation with which Eq. (43) was derived must break down. Far beyond this time scale, the behavior of the generating functions is very different. From the conditions imposed on $z$ and $t$, respectively, however, it is quite clear that we need to know the singular $z$ dependence of the generating functions in this regime. For large times, however, the various equations can also be closed, as shown in the Appendix. One then obtains, for example, for $T(z,x)$,

$$\frac{dT}{dx}\approx-(a-b)T\ . \tag{46}$$

This yields a large-time expression for $T(z,x)$ of the form

$$T(z,x)\approx\frac{a+b}{a}e^{-(a-b)[x-x_c(z)]}$$
$$\sim\text{const}\times(1-z)^{-a/(a+b)}\ . \tag{47}$$

The singular $z$ dependence in the large-time regime therefore arises from the $z$ dependence of the "turnover time" $x_c(z)$ at which the approximation $\phi(z,x)\approx-1$ breaks down. The detailed analysis of these singularities, carried out in the Appendix, yields

$$\tau_\pm=\frac{b}{a+b}\ ,$$
$$\tau_0=\begin{cases}-\dfrac{b}{a-b} & \text{for } a\le 3b\\[2mm] -\dfrac{a-b}{a+b} & \text{for } a\ge 3b\ .\end{cases} \tag{48}$$

For reference, let us evaluate the exponents $w_\pm$ and $w_0$. Using Eq. (22), one obtains, in the notation defined for the rate constants

$$w_\pm=\frac{2a+b}{a+b}\ ,$$
$$w_0=\begin{cases}\dfrac{2a-b}{a-b} & \text{if } a\ge 3b\\[2mm] \dfrac{3a+b}{a+b} & \text{if } a\le 3b\ .\end{cases} \tag{49}$$

We now notice the following remarkable facts: Firstly, the value given for $\tau_\pm$ does indeed satisfy scaling. Further, both values of $\tau_0$ satisfy scaling with respect to *one* of the admissible values for $w_0$, but never the dominant one. Going back to Eq. (21b), we notice that there are in fact two contributions to $c_2(t)$, namely, the one arising from the production term, $c_1^2$, and the one arising from the usual loss term. Both give power-law contributions to $c_2(t)$. Denoting the exponent of the first contribution as $w_0'$ and the second by $w_0''$, we now see from the above that at least in the case $M=(K+L)/2$ we have

$$c_{2k}(t)\simeq k^{-\tau_0'}t^{-w_0'}+k^{-\tau_0''}t^{-w_0''}\ , \tag{50}$$

where $\tau_0'=2-w_0'$ and $\tau_0''=2-w_0''$. We therefore have two different behaviors, both of which internally satisfy

scaling, contributing to $c_{2k}(t)$. This, however, implies that the asymptotic exponents $\tau_0=\min(\tau_0',\tau_0'')$ and $w_0=\min(w_0',w_0'')$ cannot satisfy the scaling relation (4). We have, therefore, found a very natural explanation for the violations of scaling observed in this system. From Eq. (21b) we see that the existence of two contributions to the behavior of even clusters is a completely general phenomenon. The existence of corresponding power-law behaviors in the cluster-mass distribution, each satisfying scaling with respect to the corresponding $w$ exponent, does not necessarily follow, in general, but we have been able to discover their existence in a special case which one may hope is typical. Should this be a general phenomenon, it would follow that the dominant value of $\tau_0$ corresponds to a subdominant value for $w_0$ and vice versa, so that the dominant values do not obey scaling with respect to one another. As a final remark, it should be pointed out that this does not completely invalidate the scaling form (1), but rather indicates that the conventional definitions of the exponents $\tau$ and $w$ become ambiguous in the presence of nonanalytic corrections to scaling, i.e., when the small-$x$ behavior of the scaling function $\Phi$ is not given by one single power law.

## VIII. THE SMALL-TIME BEHAVIOR

It is a remarkable fact[22,23] that the small-time behavior of exactly solved systems is usually identical (in a sense that will be defined below) to its long-time behavior. By the small-time behavior, one means the exponent characterizing the cluster-mass distribution in the regime $k \gg s^*(t)$. In other words, if one recalls the scaling function defined in Sec. II [see, e.g., Eq. (1)], then one can define a small-time exponent $\theta$ as follows:

$$\Phi(x)\sim x^{2-\theta}e^{-ax} \quad (x\gg 1)\,, \tag{51}$$

whereas the exponent $\tau$ is similarly defined, but for $x \ll 1$. There is no reason whatever to expect any relation between these two exponents, since they describe two completely unconnected parts of the same phenomenon. Nevertheless, it is well known that *all* exactly solved systems known to date satisfy the relation $\tau=\theta$. However, this phenomenon need not hold universally, as demonstrated by numerous scaling arguments for systems which cannot be solved exactly. It is the aim of this section to discuss the small-time behavior of the sum-kernel system solved in the preceding section and to show that it does not share this peculiarity with the other exactly solved models. We find that for the sum kernel system, $\theta=0$ independent of the parity, so that we have $\theta\neq\tau$.

Before we proceed to calculate $\theta$, however, we want to discuss a possible reason for this very strange coincidence of $\theta$ and $\tau$ that is characteristic of previously exactly solved systems. It is well known that almost all examples of exactly solved systems have been solved by the method of generating functions. The simplest behavior that a generating function can possibly have while still describing a process where the typical cluster-mass goes to infinity is the following: as $t\to\infty$, a singularity $z_c(t)$ of the generating function approaches unity, and this determines the rate of growth of the typical mass through the relation $z_c(t)\sim 1+1/s^*(t)$. Assuming that the singularity does not change its nature with time, one finds that the function $F(z,t)$ behaves as $[z-z_c(t)]^{\theta-1}$. This follows immediately from the fact that the singular behavior of a function at its radius of convergence is determined by the asymptotic behavior of the coefficients of the corresponding power-series representation. This behavior is given by $\theta$, the exponential decay being compensated by the fact that $z_c(t)>1$. If $z_c(t)$ is the *only* singularity, however, then it is clear that the behavior for $z$ close to 1 will be determined by the same singularity. Such systems, being analytically the simplest of all, are most naturally the first exactly solved ones. As has been shown by many scaling arguments, however, this simple behavior is by no means typical. It is therefore pleasing to have a system that goes somewhat beyond this level of simplicity and displays a richer singularity structure than previously exactly solved systems. It is only to be regretted that this point cannot be made in a more elementary manner.

To find the small-time behavior, we proceed as follows: We consider the generating functions defined in the preceding section, but we evaluate them now for a value of $z$ slightly above 1. This means, of course, that the generating function will diverge at some finite time. We then want to find out how this generating function diverges as a function of $z$. This gives the exponent $\theta$, just as the procedure outlined in Sec. VII gave $\tau$. It is readily seen, however, that the only difference with Sec. VII is that the equations for $\phi(z,w)$ have different solutions: Eq. (45) must now be replaced by

$$\begin{aligned}\phi(z,x)&=\tanh\left[\frac{a^2-b^2}{2a}[x-x_c(z)]\right],\\ x_c(z)&=\frac{2a}{a^2-b^2}\operatorname{arctanh}\left[\frac{1}{z}\right].\end{aligned} \tag{52}$$

This means that the function $\phi(z,x)$ does *not* diverge as $x\to\infty$ but rather goes to 1. This implies that the large-time behavior of $T(z,x)$ will be well approximated by the following:

$$\frac{dT}{dx}\approx aT^2\,. \tag{53}$$

This confirms the previous claim that for $z>1$ the generating functions will diverge at finite time. The divergence is clearly of the form $[x-x_\infty(z)]^{-1}$, where $x_\infty(z)$ is of the same order of magnitude as $x_c(z)$, since $T(z,x)$ cannot diverge before $\phi(z,x)$ starts to deviate strongly from its original value of $-1$. From this, it follows that the singular dependence of $T(z,x)$ on $z$ is a simple pole, since a change in $z$ will change the location of the pole $x_\infty(z)$ by an amount proportional to the change in $z$. This implies the assertion made above, that $\theta=0$, at least for odd clusters. The statement for even clusters then immediately follows from the fact that $\phi(z,x)=V(z,x)/T(z,x)\to 1$ as $x\to x_\infty(z)$.

The same claim can also be derived in a more rigorous way as follows: For the small-time behavior of the $c_k(t)$

one can make the following ansatz:

$$c_k(t)=a_k t^{k-1}+O(t^k)\ , \tag{54}$$

where the $a_k$'s are constants, for which the following recursion can be derived for arbitrary rates $K(i,j)$:

$$(k-1)a_k=\tfrac{1}{2}\sum_{j=1}^{k-1} K(j,k-j)a_j a_{k-j}\ . \tag{55}$$

These can be solved for the case $M=(K+L)/2$ with the same result as described above, that is, $\theta=0$, independently of the parity of the cluster. This also confirms general scaling results concerning the recursion (59), which predict that for rates which are approximately constant, the result $\theta=0$ should be quite universal.

## IX. SUMMARY

In summary, we have found that rather unexpected and rich kinetic behaviors arise in two models of coagulation which are relatively simple generalizations of the classical one-component coagulation process. In the $A$-$B$ model, we considered a coagulation process involving two distinct types of monomers, with bonding allowed only between unlike species. This bonding constraint naturally imposed the division of clusters into two classes: "Charged" clusters, in which the number of $A$'s and $B$'s differ by 1, and "neutral" clusters, containing equal numbers of $A$'s and $B$'s. The kinetics of the system can be visualized as a superposition of the fusion reaction, $A+A\rightarrow A$, and the recombination reaction $A+B\rightarrow$inert. These two constituent reactions have very different kinetic behaviors, and the interplay between these two reactions in the $A$-$B$ coagulation process is the source of the many very interesting features of the model. In particular, we found that the kinetics of the neutral and charged clusters were distinct in low-dimensional systems, and that the exponents of each subpopulation were inconsistent with scaling.

In the diffusion-controlled limit, the inhomogeneities in cluster densities that arise during the course of the reaction induce an effective parity dependence of the reaction rates. This feature led us to introduce a purely mean-field model, where the parity dependence of the reaction rates was explicit. This one-component alternating model represents a very simple generalization of the classical "constant-kernel" coagulation process. Ostensibly, this alternating model should be in the same universality class as the constant-kernel model, as the matrix of reaction rates has no scaling dependence on the matrix indexes for both cases.

However, within this constant-kernel universality class a very rich universe of possible kinetic behaviors has been found. By explicit solutions to the rate equations, we showed that the alternating model possessed exponents which were nonuniversal in that they depended on the values of the reaction rates. Furthermore, in two special cases, namely, for $M=0$ ("feed-in" case), and for $M=(K+L)/2$ (sum kernel), a complete solution for the generating function of the cluster-mass distribution was obtained. These solutions demonstrate that the scaling relation linking the basic exponents of coagulation do indeed fail in the alternating model.

The peculiar behavior of in the alternating model raises the interesting question of what is the minimal perturbation on a constant kernel coagulation scheme that leads to nonuniversality and a breakdown of scaling. It may be worthwhile to systematically classify the possible behaviors resulting from generic types of perturbations of the constant-kernel reaction scheme.

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## APPENDIX: GENERATING FUNCTION SOLUTION FOR THE CASE $M=(K+L)/2$

In the following, we shall perform the detailed computations, referred to in Sec. VII, to solve the case $M=(K+L)/2$ exactly. In this case, as was pointed out previously, the kernel $K(i,j)$ can be written in the form

$$\begin{aligned} &K(i,j)=f(i)+f(j)\ , \\ &f(i)=a+b(-1)^i\ . \end{aligned} \tag{A1}$$

For such a sum kernel, it is expedient to introduce the following dimensionless quantities:

$$\begin{aligned} &\phi_j=c_j\Big/\left[\sum_{k=1}^{\infty} c_k\right]\ , \\ &dx=dt\sum_{k=1}^{\infty} c_k,\quad x(0)=0\ , \end{aligned} \tag{A2}$$

which then satisfy the following equations:

$$\begin{aligned} &\frac{d\phi_j}{dx}=\sum_{k=1}^{j-1} f(k)\phi_k\phi_{j-k}-f(j)\phi_j\ , \\ &\phi_j(0)=0\ . \end{aligned} \tag{A3}$$

This system of equations is recursively solvable, as pointed out by Hendriks, Ernst, and Ziff,[5] so that $\phi_j(x)$ can be obtained in closed form, at least in principle, for any given $j$. Note also, that a solution for $\phi_j(x)$ as a function of $x$ is sufficient to describe the system completely, since $x(t)$ is known exactly from the expressions derived in Sec. V for $\sum_{j=1}^{\infty} c_j(t)$. This is in contrast to the general case of a kernel of type $f(i)+f(j)$, where $x(t)$ is not generally known, so that a solution in terms of $x$ does not provide the temporal behavior of the system. The recursive approach, however, rapidly becomes unwieldy and does not, in any case, give a closed expression for $\phi_j(x)$ for arbitrary $j$. To accomplish this task, we introduce the generating functions

$$F_1(z,x)=\sum_{j=1}^{\infty}\phi_j(x)z^j,\quad F_2(z,x)=F_1(-z,x)\ . \tag{A4}$$

For these two quantities one obtains from Eq. (A3)

$$\frac{dF_1}{dx}=(aF_1+bF_2)(F_1-1),\quad F_1(z,0)=z\ ,$$
$$\frac{dF_2}{dx}=(aF_2+bF_1)(F_2-1),\quad F_2(z,0)=-z\ . \tag{A5}$$

Now, we introduce the generating functions for the odd and even clusters, respectively, as follows:

$$V(z,x)=F_1+F_2-2=2\sum_{j=1}^{\infty}\phi_{2j}(x)z^{2j}-2\ ,$$
$$T(z,x)=F_1-F_2=2\sum_{j=1}^{\infty}\phi_{2j-1}(x)z^{2j-1}\ . \tag{A6}$$

From (A5), these generating functions are then seen to satisfy

$$\frac{dV}{dx}=\tfrac{1}{2}(a+b)V^2+\tfrac{1}{2}(a-b)T^2+(a+b)V\ ,$$
$$V(z,0)=-2\ ,$$
$$\frac{dT}{dx}=aVT+(a+b)T\ , \tag{A7}$$
$$T(z,0)=2z\ .$$

Now, since the linear terms in these equations can be removed by multiplying $T$ and $V$ by an appropriate exponential (the integrating factor) and then reparametrizing $x$ in terms of this integrating factor, it is clear that we may transform these equations into a homogeneous form. This means it is possible to introduce a new set of dimensionless variables as follows: We define

$$\phi=\frac{V}{T},\quad dw=T(z,x)=dx,\quad w(0)=0\ . \tag{A8}$$

This yields the following equation for $\phi$:

$$\frac{d\phi}{dw}=\tfrac{1}{2}(a-b)(1-\phi^2),\quad \phi(0)=-\frac{1}{z}\ , \tag{A9}$$

which gives for $\phi(z,w)$,

$$\phi(z,w)=\coth\{\tfrac{1}{2}(a-b)[w-w_c(z)]\}\ ,$$
$$w_c(z)=\frac{2}{a-b}\operatorname{arccoth}\left[\frac{1}{z}\right]\ . \tag{A10}$$

This, however, does not yet constitute a solution of the problem, since $w(z,x)$ is an unknown function of $x$ and $z$. Thus, in order to close the equations, we rewrite equations (A7) in the $(z,w)$ variable as follows:

$$\frac{dT}{dw}=a\phi T+(a+b)\ ,$$
$$T(0)=2z\ ,$$
$$\frac{dV}{dw}=\tfrac{1}{2}(a+b)\phi V+\tfrac{1}{2}(a-b)T+(a+b)\phi\ , \tag{A11}$$
$$V(0)=-2\ ,$$
$$dw=T\,dx,\quad w(0)=0\ .$$

The two differential equations for $T(z,w)$ and $V(z,w)$ are linear and inhomogeneous, and $T(z,w)$ can be expressed in closed form (in terms of quadratures), since $\phi(z,w)$ is known explicitly. From the closed-form solution for $T(z,w)$, the final equation in (A11) can now be solved by separation of the variables, thereby yielding a closed expression for $w(z,x)$, thus demonstrating that the model can indeed be solved by quadratures.

However, it should now be clear that the exact solution is not really transparent enough to yield much useful information. In order to evaluate the exponents $\tau_\pm$ and $\tau_0$ we need to find the singularities of the functions $T(z,x)$ and $V(z,x)$ at fixed (very large) $x$ for values of $z$ satisfying the inequalities

$$1\ll(1-z)^{-1}\ll s^*(t)\ . \tag{A12}$$

To find these singularities, it turns out to be useful to obtain large- and small-time approximations to the generating functions $T(z,x)$ and $V(z,x)$ in terms of the variables $z$ and $x$. However, since (A11) is written conveniently in terms of the variables $z$ and $w$, it is necessary to investigate the relation between $x$ and $w$. It is easy to see that $x(t)$ is small for small $t$ [since $x(0)=0$] and that $x\sim\ln t$ as $t\to\infty$ since

$$\sum_{j=1}^{\infty}c_j(t)=\mathcal{O}(t^{-1})\quad(t\to\infty)\ . \tag{A13}$$

If $z$ is assumed to be very near to 1, then it follows from the equation for $\phi(z,w)$ that, over a long range of $w$, and hence also of $x$,

$$T(z,x)\approx a/(a+b),\quad V(z,x)\approx -a/(a+b)\ ,$$
$$\phi(z,x)\approx -1\ , \tag{A14}$$

where the results for $T(z,x)$ and $V(z,x)$ follow from rewriting Eq. (A7) for $T(z,x)$ as follows:

$$\frac{dT}{dx}=a\phi T^2+(a+b)T\ , \tag{A15}$$

and using the approximation $\phi\approx -1$ for small times. We now wish to compute the "turnover time" at which the above small-time approximation for the generating functions breaks down. Using Eq. (A10) for $\phi(z,w)$, one sees that the approximation must fail when $w\approx w_c(z)$, since at that point $\phi(z,w)$ diverges. However, as long as Eq. (A14) remains a good approximation, one has $w\approx ax/(a+b)$ and hence the turnover time $x_c(z)$ is given by

$$x_c(z)=\frac{a+b}{a}w_c(z)=\frac{2a}{a^2-b^2}\operatorname{arccoth}\left[\frac{1}{z}\right]$$
$$\approx\frac{a}{a^2-b^2}\ln[(1-z)^{-1}]\ . \tag{A16}$$

Now we proceed to derive a large-time approximation for the generating functions. To help accomplish this task, it is very helpful to first show that

$$\lim_{x\to\infty}\phi(z,x)T(z,x)=-2\ . \tag{A17}$$

This is most easily seen as follows: The limit $x\to\infty$ cor-

responds in the $w$ variables to the limit $w \to w_c(z)$. This follows from the definition of $w$ in Eq. (A8), together with the remark that $T[z,w_c(z)]$ is equal to zero, as is seen from Eq. (A11). If we now examine the behavior of $w$ very close to $w_c(z)$, we obtain, using a Taylor expansion, together with Eq. (A11),

$$\begin{aligned}\frac{dT(z,w)}{dw} &\approx \frac{T(z,w)}{w-w_c(z)} \\ &= a\phi T + (a+b) \\ &\approx \frac{2a}{a-b}\frac{T}{w-w_c(z)} + (a+b) \\ &\approx \frac{2a}{a-b}\frac{dT}{dw} + (a+b) ,\end{aligned} \tag{A18}$$

from which it immediately follows that

$$\frac{dT[z,w_c(z)]}{dw} = -(a-b), \quad \lim_{w \to w_c(z)} \phi(z,w) T(z,w) = -2 . \tag{A19}$$

From this, it therefore follows that for large times

$$\frac{dT}{dx} = a\phi T^2 + (a+b)T \approx -(a-b)T . \tag{A20}$$

This gives the large-time behavior already stated in Sec. VII, and matching it at the turnover time $x_c(z)$ to the small-time behavior $T(z,x) \approx a/(a+b)$ yields

$$\begin{aligned}T(z,x) &\approx \frac{a+b}{a} e^{-(a-b)[x-x_c(z)]} \\ &\approx \text{const} \times (1-z)^{-a/(a+b)} ,\end{aligned} \tag{A21}$$

thus giving the desired result for $\tau_{\pm}$.

The calculations for $\tau_0$ are performed entirely similarly, so we shall not do more than merely sketch them. We consider the generating function for the even clusters given by

$$S(z,x) = \sum_{j=1}^{\infty} \phi_{2j}(x) z^{2j} = V(z,x) + 2 , \tag{A22}$$

for which the following equation holds

$$\frac{dS}{dx} = \tfrac{1}{2}(a-b)T^2 + \tfrac{1}{2}(a+b)S^2 - (a+b)S . \tag{A23}$$

As we have seen above, $T(z,x)$ is approximately constant for small times. Using this in Eq. (A23), it is found that $S(z,x)$ also remains constant for small times. By the same token, the turnover time $x_c(z)$ remains the same. For large $x$, $S(z,x)$ rapidly becomes extremely small, so that the quadratic term in $S$ can be neglected. Thus the large-time regime is given by the following approximate equation:

$$\frac{dS}{dx} \approx \tfrac{1}{2}(a-b)e^{-2(a-b)x} - (a+b)S , \tag{A24}$$

so that $S(z,x)$ has one of two possible different exponential behaviors in $x$, depending on whether the first or second term dominates the equation. This corresponds, in fact, exactly to the existence of two different contributions to $\rho_0(t)$ observed in Sec. V, the exponentials being due to the fact that $x \sim \ln t$ as $t \to \infty$. The same matching procedure as above now yields two different singularities, of which we only retain the one that is dominant (i.e., most singular in $z$). This gives the values of $\tau_0$ already reported in Sec. VII.


[1] S. K. Friedlander, *Smoke, Dust and Haze: Fundamentals of Aerosol Behavior* (Wiley, New York, 1977); see also the collection of articles in *Kinetics of Aggregation and Gelation,* edited by F. Family and D. P. Landau (North-Holland, Amsterdam, 1984).

[2] M. V. von Smoluchowski, Z. Phys. **17**, 557 (1916); S. Chandrasekhar, Rev. Mod. Phys. **15**, 1 (1943); R. L. Drake, in *Topics in Current Aerosol Research,* edited by G. M. Hidy and J. R. Brock (Pergamon, New York, 1972).

[3] M. H. Ernst, in *Fundamental Problems in Statistical Physics VI,* edited by E. G. D. Cohen (Elsevier, New York, 1985).

[4] P. G. J. van Dongen and M. H. Ernst, Phys. Rev. Lett. **54**, 1396 (1985).

[5] F. Leyvraz and H. R. Tschudi, J. Phys. A **14**, 3389 (1981); **15**, 1951 (1982); E. M. Hendriks, M. H. Ernst, and R. M. Ziff, J. Stat. Phys. **31**, 519 (1983); M. H. Ernst, R. M. Ziff, and E. M. Hendriks, J. Colloid Interface Sci. **97**, 266 (1984).

[6] P. Meakin, T. Vicsek, and F. Family, Phys. Rev. B **31**, 564 (1985).

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

[8] For a closely related model, see P. Meakin and Z. Djordjevic, J. Phys. A **19**, 2137 (1986).

[9] D. Toussaint and F. Wilszek, J. Chem. Phys. **78**, 2642 (1983).

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

[11] D. C. Torney and H. M. McConnell, J. Chem. Phys. **87**, 1441 (1983).

[12] A preliminary account of this work appeared in F. Leyvraz and S. Redner, Phys. Rev. Lett. **57**, 163 (1986); **57**, 3123(E) (1986).

[13] A. A. Lushnikov, J. Coll. Interface Sci. **46**, 549 (1973); **48**, 400 (1974).

[14] T. Vicsek and F. Family, Phys. Rev. Lett. **52**, 1669 (1984).

[15] P. G. J. van Dongen and M. H. Ernst (private communication).

[16] K. Kang and S. Redner, Phys. Rev. A **30**, 2833 (1984).

[17] M. E. Fisher, J. Stat. Phys. **34**, 667 (1984).

[18] See, e.g., F. Leyvraz, in *On Growth and Form,* edited by H. E. Stanley and N. Ostrowsky (Martinus Nijhoff, Dordrecht, 1986), p. 136.

[19] Note that the value of the exponent $w_0$ for the case $L=0$ was erroneously reported in Ref. 12.

[20] F. Leyvraz and H. R. Tschudi, J. Phys. A **13**, 1817 (1980).

[21] This result was apparently first obtained by G. B. Field and W. C. Saslaw, Astrophys. J. **142**, 568 (1965).

[22] M. H. Ernst, E. M. Hendriks, and F. Leyvraz, J. Phys. A **17**, 2137 (1984).

[23] A. A. Lushnikov and V. N. Piskunov, Kolloidn. Zh. **37**, 251 (1975); A. A. Lushnikov and V. N. Piskunov, Dokl. Phys. Chem. **231**, 1266 (1976).