

## Nonuniversality and Breakdown of Scaling in a Two-Component Coagulation Model

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We investigate the kinetics of a coagulation process involving two distinct bifunctional monomeric species  $A$  and  $B$  (which can be ascribed a positive and negative "charge," respectively) with bonding allowed only between  $A$  and  $B$ . When the rates for charged-charged, neutral-neutral, and neutral-charged reactions are all distinct, we find, from the solution to the mean-field rate equations, that (i) the kinetic exponents are nonuniversal and (ii) a scaling description of the cluster-size distribution fails. Similarly intriguing results are also found for the kinetic behavior below the upper critical dimension.

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Coagulation is a fundamental kinetic phenomenon in which clusters irreversibly bond, upon colliding, to form clusters of ever-increasing size. This phenomenon underlies a wide variety of nonequilibrium processes in nature, including, e.g., aerosol physics,<sup>1</sup> gelation,<sup>2,3</sup> and galactic clustering,<sup>4</sup> thereby attracting considerable theoretical attention.<sup>5-7</sup> Many current theoretical developments stem from analyses of the (mean-field) rate equations describing the coagulation processes. A coherent theoretical description has now emerged<sup>7</sup> in which the kinetic behavior can be classified according to general features of the dependence of the matrix of reaction rates,  $K(i,j)$ , on the incident cluster masses  $i$  and  $j$ . In general, characteristic physical quantities exhibit power-law temporal behavior, with universal values of the exponents, and with a cluster-size distribution approaching a scaling form at long times. These notions of universality and scaling underlie much of our present understanding of coagulation phenomena.

In this Letter, we consider a two-component coagulation model where fundamentally different behavior occurs: Nonuniversal kinetic exponents are obtained, and scaling is found to be violated. The model involves two distinct<sup>8</sup> bifunctional monomeric species  $A$  and  $B$ , with bonding allowed only between  $A$  and  $B$  (Fig. 1). The physical motivation for considering such a model is that many real gelation processes are of an  $A$ - $B$  form.<sup>9</sup> Our restriction to bifunctional monomers forces clusters to have an alternating linear structure. While this restriction may be somewhat unrealistic, our model exhibits a wide range of novel and surprising behavior, while being sufficiently simple to be tractable analytically.

If we ascribe a unit positive "charge" to the  $A$ 's and a unit negative "charge" to the  $B$ 's, then a very appealing picture of the coagulation process can be developed. According to the  $A$ - $B$  bonding scheme and the linearity of the clusters, only neutral clusters, or clusters with charge  $\pm 1$ , can exist. Furthermore, the types of reactions that may occur can be divided into

three general classes: (a) A positive cluster and a negative cluster can join to form a neutral cluster, (b) two neutral clusters can coalesce to form a larger neutral cluster, and (c) a neutral and a charged cluster can form a heavier charged cluster (with the charge being conserved). Reaction (a) is reminiscent of the two-species recombination process,  $A + B \rightarrow \text{inert}$ ,<sup>10,11</sup> while reaction (c) is similar to a single-species reaction,  $A + A \rightarrow A$ .<sup>10,12</sup>

Even at the level of a mean-field theory, it is natural to consider the general situation in which the rates for reactions (a), (b), and (c) are distinct, as neutral clusters can react with themselves (Fig. 1), while charged clusters cannot. From the mathematical point of view, imposing distinct rates is equivalent to choosing a matrix of reaction rates, in the description of the full coagulation process, in which each element depends only on the relative parity of the matrix indices. The magnitude of the modulation in the matrix elements controls the relative importance of reactions (a), (b), and (c), and this modulation is the source of the novel kinetic phenomena of our model. Our new results are rather unexpected, since  $A$ - $B$  coagulation ostensibly belongs to the universality class of coagulation with a constant matrix of reaction rates<sup>7</sup> (constant-kernel coagulation).

Let the rates for reactions (a), (b), and (c) be  $K$ ,  $L$ , and  $M$ , respectively. Furthermore, let us consider the initial condition of equal concentrations of  $A$  and  $B$

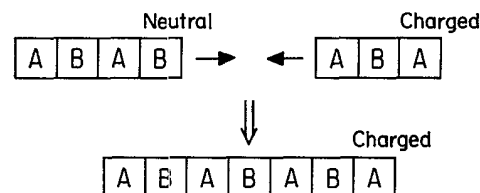


FIG. 1. Schematic representation of a typical reaction in  $A$ - $B$  coagulation. Notice that a neutral cluster can react with itself.

monomer, only. Then the rate equations for  $A$ - $B$  coagulation can be written as

$$\dot{c}_j = \frac{1}{2} \sum_{k=1}^{j-1} K(k, j-k) c_k c_{j-k} - c_j \sum_{k=1}^{\infty} K(j, k) c_k, \quad (1)$$

where  $c_j$  is the concentration of clusters of mass  $j$ ,  $c_{2j+1}^{(+)} = c_{2j+1}^{(-)} = \frac{1}{2} c_{2j+1}$ , and with the matrix of reaction rates given by

$$\begin{aligned} K(i, j) &= K \text{ for } i \text{ and } j \text{ odd,} \\ &= L \text{ for } i \text{ and } j \text{ even,} \\ &= M \text{ otherwise.} \end{aligned} \quad (2)$$

The most direct way to see the nonuniversality in our model is by examining the temporal behavior of the individual cluster densities. In one-component constant-kernel coagulation,  $c_k(t)$  generally decays as a power-law in time,  $t^{-w}$ , with a universal value of the exponent  $w=2$ , for all  $k$ , as  $t \rightarrow \infty$ .<sup>7</sup> Interestingly, in  $A$ - $B$  coagulation, we find that  $c_k(t)$  varies as one power law,  $t^{-w_{\pm}}$ , for all odd values of  $k$ , and as a second power law,  $t^{-w_0}$ , for all even values of  $k$ , with  $w_{\pm} \neq w_0$ , in general.

To show this new behavior, we first consider the total density of neutral and charged clusters, from which the monomer and dimer density, and more generally,  $c_k(t)$ , follows directly. Thus we define the density of charged and neutral mass, respectively,

$$\begin{aligned} \rho_{\pm}(t) &\equiv \rho_{+}(t) + \rho_{-}(t) = \sum_{j=1}^{\infty} c_{2j-1}(t), \\ \rho_0(t) &= \sum_{j=1}^{\infty} c_{2j}(t). \end{aligned} \quad (3)$$

From (1), these quantities satisfy a closed system of differential equations whose solutions for  $L \neq 0$  are

$$\rho_{\pm}(t) = \frac{\rho_{\pm}(0)}{1 + K\rho_{\pm}(0)t}, \quad \rho_0(t) \simeq B_{\infty}\rho_{\pm}(t), \quad (4)$$

where

$$B_{\infty} = 2 \left\{ \frac{K-M}{L} + \left[ \left( \frac{K-M}{L} \right)^2 + \frac{K}{L} \right]^{1/2} \right\},$$

and where corrections to  $\rho_0(t)$ , which vanish as  $t \rightarrow \infty$  have been ignored. Thus  $\rho_{\pm}(t)$  and  $\rho_0(t)$  decay as  $t^{-\alpha_{\pm}}$  and as  $t^{-\alpha_0}$ , respectively, with  $\alpha_{\pm} = \alpha_0 = 1$ . This time dependence coincides with that of the total number of clusters in one-component constant-kernel coagulation,<sup>7</sup> where  $\sum_k c_k(t) \sim t^{-\alpha}$ , with  $\alpha = 1$ .

When  $L = 0$ , the charged-cluster decay is still given as in (4), but there are now three possibilities for the

neutral-cluster decay at long times. They are

$$\begin{aligned} \rho_0(t) &\simeq \frac{\rho_{\pm}(0)}{(M/K-1)[1+K\rho_{\pm}(0)t]}, \\ &M > K, \\ &\simeq \frac{\rho_{\pm}(0)}{[1+K\rho_{\pm}(0)t]} \ln[1+K\rho_{\pm}(0)t], \\ &M = K, \\ &\simeq \frac{1}{(1-M/K)} \frac{\rho_{\pm}(0)}{[1+K\rho_{\pm}(0)t]^{M/K}}, \\ &M < K. \end{aligned} \quad (5)$$

Thus we deduce that  $\alpha_0 = 1$  for  $M \geq K$  (with a logarithmic correction appearing when  $M = K$ ), and  $\alpha_0 = M/K$  for  $M < K$ .

From these expressions for  $\rho_{\pm}(t)$  and  $\rho_0(t)$ , we can now solve for  $c_1(t)$  and  $c_2(t)$ , using Eq. (1). When  $L \neq 0$ , the latter quantities decay as  $t^{-w_{\pm}}$  and as  $t^{-w_0}$ , respectively, with

$$\begin{aligned} w_{\pm} &= 1 + \frac{M}{K} B_{\infty}, \\ w_0 &= \frac{M}{K} + \frac{L}{K} B_{\infty}, \quad \text{if } w_0 \leq 2w_{\pm} - 1, \\ &= 2w_{\pm} - 1, \quad \text{otherwise.} \end{aligned} \quad (6)$$

However, when  $L = 0$  and  $M > K$ , we find

$$w_{\pm} = 1 + \frac{1}{2} \frac{1}{(1-K/M)}, \quad w_0 = 1. \quad (7)$$

Finally, when  $L = 0$  and  $M \leq K$ , the cluster densities decay faster than a power law, and the  $w$  exponents are not defined. Instead we obtain

$$\begin{aligned} c_1(t) \sim c_2(t) &\sim \exp[-\ln^2 t], \\ &M = K, \\ c_1(t) \sim c_2(t) &\sim \exp\{-[(\text{const})t]^{1-M/K}\}, \\ &M < K. \end{aligned} \quad (8)$$

Thus we have found the novel result that the exponents  $w_{\pm}$  and  $w_0$  are nonuniversal being, in general, irrational functions of the rate constants.

In order to discuss the breakdown of scaling in two-component coagulation, let us first recall the statement of scaling in conventional one-component coagulation. This is often written in terms of relations involving the basic kinetic exponents of coagulation,  $\alpha$ ,  $w$ ,  $z$ , and  $\tau$ . Here the exponent  $z$  describes the temporal behavior of the average cluster size,  $\sum k^2 c_k(t)$ , which typically varies as the power law  $t^z$ . The exponent  $\tau$  arises in

the mass dependence of the cluster density asymptotically as  $t \rightarrow \infty$  and  $kt^{-z} \rightarrow 0$ , namely,  $c_k(t) \sim k^{-\tau} \times t^{-w}$ . The four exponents  $\alpha$ ,  $w$ ,  $z$ , and  $\tau$  obey the scaling relations<sup>5-7</sup>

$$(2 - \tau)z = w, \quad (9a)$$

together with

$$\alpha = z, \quad \tau < 1; \quad \alpha = w, \quad \tau \geq 1. \quad (9b)$$

In two-component coagulation, we append these exponents with the subscript 0 or  $\pm$  to refer to neutral or charged clusters, respectively. We have already obtained the  $\alpha$  and  $w$  exponents, and it is also immediate to show, for all the kernels we are considering here, that the exponents  $z_0$  and  $z_{\pm}$  are always equal to unity. Thus we require the  $\tau$  exponents in order to demonstrate the loss of scaling in two-component coagulation.

To find these two exponents, consider first the special case  $K, L \neq 0, M = 0$ , which we can solve exactly. Since  $M = 0$ , the only reaction that monomers can undergo is to coalesce into dimers. If the initial state contains only monomers, then the dimers which are formed initially serve as the starting point for a standard one-component constant-kernel coagulation process involving only neutral clusters. The coalescence of monomers serves as a continuous "feed in" of dimers necessary to sustain the reaction. The competition between the feed-in process and the evolution of the system by constant-kernel coagulation is the underlying source of the scaling breakdown.

To obtain the exact solution for  $M = 0$ , we introduce the generating function<sup>13</sup>

$$G(z, t) = \sum_{j=1}^{\infty} c_{2j}(t)(z^j - 1). \quad (10)$$

With the boundary condition  $G(z, 0) = z - 1$  [corresponding to  $c_j(0) = \delta_{j1}$ ], we find that  $G(z, t)$  satisfies a simple differential equation whose solution is

$$G(z, t) = \frac{A_{\infty}}{(1 + Kt)} + \left[ \frac{C_{\infty}}{(1 + Kt)^{A_{\infty}/2}} - \frac{(1 + Kt)}{4(1 + A_{\infty}/2)} \right]^{-1}, \quad (11)$$

where

$$A_{\infty} = -(K/L) \{1 - [1 + (L/K)(1 - z)]^{1/2}\}, \quad (12)$$

$$C_{\infty} = -\frac{(1 + LA_{\infty}/4K)}{A_{\infty}(1 + LA_{\infty}/K)}.$$

The singularity in  $G(z, t)$  as a function of  $z$  is determined solely by the divergence of the second factor which can be shown to be a simple pole located at  $z_c(t) \sim 1 + (\text{const})t^{-1}$ . As a result of this singularity, we conclude that  $\tau_0 = 0$ , while from the  $1/t$  time

dependence of  $z_c(t)$ , we also deduce that  $z_0 = 1$ . Thus for the neutral clusters, we have found the kinetic exponents  $\tau_0 = 0$ ,  $z_0 = \alpha_0 = 1$ , and from (6),  $w_0 = 1$ , in contradiction with the scaling relations given in (9).

We can gain further insight into the mechanism underlying the loss of scaling by expanding  $G(z, t)$  in a power series in  $z$ , thus yielding the complete expression for  $c_j(t)$ . This gives the following approximate long-time expression for  $c_j(t)$ :

$$c_j(t) \sim j^{-3/2}(1 + K/L)^{-j}(1 + Kt)^{-1} + (\text{const})t^{-2}z_c(t)^{-j}, \quad (13)$$

where the factor arises solely from the feed-in process, while the second factor arises from the evolution of the system by constant-kernel coagulation. At long times,  $c_j(t)$  is dominated by the term decaying as  $1/t$ , implying that  $w_0 = 1$ . However, because of the exponential mass cutoff in this first factor, it makes a negligible contribution to any measure of the typical cluster size at finite times, even though this factor dominates asymptotically at fixed  $j$ .

When  $M \neq 0$ , we are no longer able to derive a complete solution for the generating function, but numerical simulations (described below) clearly indicate that scaling continues to be violated over a wide range of  $K$ ,  $L$ , and  $M$  values.

There is a second special case where considerable analytic progress can be made in solving the rate equations and in demonstrating the loss of scaling. When the reaction rates satisfy the condition  $M = (K + L)/2$ ,  $K(i, j)$  can be written as a "sum" kernel

$$K(i, j) = \frac{1}{4}(K + L) + \frac{1}{4}(L - K)[(-1)^i + (-1)^j]. \quad (14)$$

With the kernel in this form, we have made use of a number of specialized techniques<sup>14</sup> to give a formal solution for the generating function. The details are quite complicated, and we merely quote the final result for the  $\tau$  exponents. We find

$$\tau_{\pm} = 2(L - K)/L,$$

$$\tau_0 = (K - L)/2K, \quad \text{for } K \leq L/2, \quad (15)$$

$$= -K/L, \quad \text{for } K \geq L/2,$$

Corresponding to this relatively simple behavior for  $\tau_0$  and  $\tau_{\pm}$ , the  $w$  exponents, quoted in (6) and (7), now become simple rational functions of the reaction rates.

From the generating function we find that the loss of scaling for the neutral clusters stems from a mechanism similar to the one discussed in Eq. (13). Asymptotically,  $c_{2j}(t)$  turns out to be the sum of two factors, with one factor characterized by the exponent set  $(\tau_0, w_0)$ , and the other factor characterized by a different exponent set  $(\tau'_0, w'_0)$ . Using the general result

that  $z = 1$ , it turns out that each exponent set is consistent with scaling, namely  $2 - \tau_0 = w_0$  and  $2 - \tau'_0 = w'_0$ . However, the asymptotic form of  $c_{2j}(t)$  is dominated by one of the composite-exponent sets  $(\tau_0, w_0)$  or  $(\tau'_0, w'_0)$ , neither of which is consistent with scaling.

Finally, let us investigate  $A$ - $B$  coagulation in a system which is below the upper critical dimension, where fluctuations in cluster density give rise to kinetic behavior different from that predicted by mean-field theory. For simplicity, consider only the simplest case of the purely constant kernel, i.e.,  $K = L = M$ . As mentioned previously, the coalescence of two charged clusters to form a neutral cluster is analogous to the reaction  $A + B \rightarrow \text{inert}$ , where the product neutral cluster plays the role of an inert species with respect to the charged clusters. Consequently, we expect<sup>10,11</sup> that for spatial dimension  $d$  less than an upper critical dimension equal to 4, the density of the charged clusters will decay as  $t^{-d/4}$ . Similarly, the coalescence of neutral clusters can be thought of as the reaction  $A + A \rightarrow A$ , which is of the general form of the single-species reaction  $A + A \rightarrow \text{inert}$ . As a result, we expect<sup>10,12</sup> that the density of neutral clusters will decay as  $t^{-d/2}$  below an upper critical dimension equal to 2. Since  $A$ - $B$  coagulation is a superposition of these two rather disparate reactions, very unusual kinetic behaviors might be anticipated below the upper critical dimension of either or both constituent reactions.

We have therefore performed numerical simulations of  $A$ - $B$  coagulation in one, two, and three dimensions.

TABLE I. The kinetic exponents for  $A$ - $B$  coagulation for the case  $K = L = M$ . An equality sign denotes those exponent estimates which are very close to values which we believe are exact.

One dimension	
$\alpha_{\pm} = 0.25$	$\alpha_0 = 0.5$
$w_{\pm} = 0.25$	$w_0 = 2.0$
$\tau_{\pm} \approx 1.36$	$\tau_0 \approx -1.6$
$z_{\pm} = 0.5$	$z_0 = 0.45$
Two dimensions	
$\alpha_{\pm} \approx 0.5$	$\alpha_0 \approx 1.0$
$w_{\pm} \approx 0.5$	$w_0 \approx 2.0$
$\tau_{\pm} \approx 0.75$	$\tau_0 = 0.0$
$z_{\pm} \approx 0.75$	$z_0 \approx 0.8$
Three dimensions	
$\alpha_{\pm} \approx 0.8$	$\alpha_0 = 1.0$
$w_{\pm} \approx 1.5$	$w_0 = 2.0$
$\tau_{\pm} \approx 0.35$	$\tau_0 = 0.0$
$z_{\pm} \approx 0.95$	$z_0 = 0.95$
Mean-field limit	
$\alpha_{\pm} = 1.0$	$\alpha_0 = 1.0$
$w_{\pm} = 2.0$	$w_0 = 2.0$
$\tau_{\pm} = 0.0$	$\tau_0 = 0.0$
$z_{\pm} = 1.0$	$z_0 = 1.0$

Our method is a simple extension of the techniques previously developed for one-component coagulation processes,<sup>15</sup> suitably modified to account for the constraint of  $A$ - $B$  bonding. The simulations exhibit a rich phenomenology. In one dimension,  $\rho_{\pm}(t)$  and  $\rho_0(t)$  appear to decay as  $t^{-1/4}$  and as  $t^{-1/2}$ , respectively, as expected on the basis of the analogy with related bimolecular reactions. There is a similar division of the temporal behavior of the individual charged- and neutral-cluster densities:  $c_j(t)$  varies as  $t^{-w_{\pm}}$  with  $w_{\pm} \sim -\frac{1}{4}$ , and with  $w_0 \sim 2$ , or greater. Our numerical results are summarized in Table I. In general, the exponent set characterizing the kinetics of the charged and neutral clusters each violate scaling. The behavior in three dimensions is particularly intriguing, as the charged-cluster kinetics is still rather different from that of mean-field theory, while the neutral-cluster kinetics roughly coincides with the mean-field results.

In a future publication, we will discuss the behavior of two-component coagulation in greater detail, and treat the interesting case where the system is initially charged.

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