

## Charged aggregation

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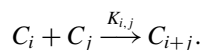
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We introduce an aggregation process that begins with equal concentrations of positively and negatively “charged” monomers. Oppositely charged monomers merge to form neutral dimers. These dimers are the seeds for subsequent aggregation events in which neutral clusters of necessarily even mass join irreversibly to form neutral aggregates of ever-increasing size. In the mean-field approximation with mass independent reaction rates, we solve for the reaction kinetics and show that the concentration of clusters of mass  $k$ ,  $c_k(t)$ , asymptotically scales as  $A_k/t$ , with  $A_k$  having a nontrivial dependence on  $k$ . We also investigate the phenomenon of gelation in charged aggregation when the reaction rate equals the product of the two incident cluster masses. Finally, we generalize our model to the case of three and more types of monomers.

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### I. INTRODUCTION

Aggregation is a fundamental kinetic process in which clusters of various masses irreversibly join to form clusters of ever-increasing mass [1,2]. If we denote a cluster of mass  $i$  by  $C_i$ , each reaction can be written as



Here  $K_{i,j}$  is the reaction kernel, which specifies the rate at which a cluster of mass  $i$  (an  $i$ -mer) joins to a  $j$ -mer to form an  $(i+j)$ -mer. The basic observable in aggregation is the time-dependent cluster-mass distribution whose nature depends on the functional form of the reaction kernel. In the approximation that all reactants are perfectly mixed, the time dependence of the cluster mass distribution is described by an infinite set of rate equations that account for the change in the cluster concentrations due to reactions with other clusters.

The reaction rates  $K_{i,j}$  depend on the properties of the two reacting clusters [3,4]. For diffusion-controlled reactions in three dimensions  $K_{i,j} \sim (D_i + D_j)(R_i + R_j)$ , where  $D_i$  and  $R_i$  are the diffusion coefficient and the radius of a cluster of mass  $i$ , respectively. In turn, the cluster diffusion coefficient is inversely proportional to its mass, which gives  $K_{i,j} \propto 2 + (i/j)^{1/3} + (j/i)^{1/3}$  [4–6]. Because of the complicated form of this reaction rate, aggregation of Brownian clusters is still unsolved [7]. However, a number of idealized exactly soluble cases are known, including the constant kernel ( $K_{i,j} = \text{const.}$ , which has the same homogeneity degree as the Brownian kernel), the sum kernel ( $K_{i,j} = i + j$ ), the product kernel ( $K_{i,j} = ij$ ), and a few other specialized forms [8–10]. The constant-kernel case, in which the reaction rates are independent of the cluster masses, is particularly simple, and investigations of this toy model have helped to develop the concept of scaling in aggregation [11,12].

In this work, we investigate an extension of aggregation that begins with equal concentrations of monomers of two types,  $A$  and  $B$ , that we label as positively charged and negatively charged. There are no physical electrostatic forces

acting, but we invoke the label “charge” to impose the constraint that only positively and negatively charged monomers can merge to form dimers via the reaction  $[A] \oplus [B] \rightarrow [AB]$ , while monomers of the same charge do not interact. Each dimer contains one  $A$  and one  $B$  monomer, and thus are neutral [Fig. 1(a)].

In addition to the interaction between oppositely charged monomers, neutral clusters interact with a rate that is independent of their masses. Thus, dimers constitute the seeds to generate neutral clusters of ever-increasing masses. Once a neutral dimer is created, it can react only with other neutral clusters, and neutral clusters of mass greater than or equal to two can interact among themselves to create neutral clusters of the form  $[(AB)^k]$  for all  $k \geq 2$  [Fig. 1(b)]. No other type of reactions occur. For electrically charged monomers, one should include repulsive interactions between similar monomers and attractive interactions between dissimilar monomers. More importantly, electrostatic interactions are long ranged, and systems with long-range interactions exhibit peculiar behaviors (see, e.g., Refs. [13,14] and references therein). In our modeling, we ignore all electrostatic effects because our main interest is the role that the stoichiometry of our model plays in the reaction kinetics.

One of the motivations for this work is to incorporate compositional constraints on aggregation in a simple way. Physical realizations of aggregation that involve more than one type of monomer have been observed experimentally [1,15,16]. In our charged aggregation model, each aggregate necessarily consists of equal numbers of  $A$  and  $B$  monomers. One can also envision that an  $(m, n)$  aggregate composed of  $m$  monomers of type  $A$  and  $n$  monomers of type  $B$  is allowed only when the ratio  $m/n$  is constrained to be in a certain range. Furthermore, constraints can be geometrical in nature [17], e.g., the merging of the rectangular aggregates  $(m_1, n_1)$  and  $(m_2, n_2)$  could be possible only when one of the “sides” are equal, that is,  $m_1 = m_2 = m$ , for which the reaction is  $(m, n_1) \oplus (m, n_2) \rightarrow (m, n_1 + n_2)$ . Models of aggregation with various compositional constraints have also

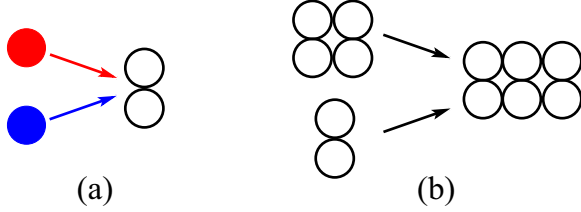


FIG. 1. Charged aggregation: (a) Two oppositely charged monomers merge into a neutral dimer, (b) Two neutral clusters (here a dimer and a 4-mer) merge into a 6-mer.

been proposed [18–25]. The emergent behaviors are often very different from ordinary aggregation, and poorly understood. Our modeling is focused on understanding the role of a particularly simple compositional constraint on the aggregation kinetics.

One of our main results is that when the reaction rates are independent of the cluster masses,  $K_{i,j} = \text{const.}$ , the cluster mass distribution in charged aggregation is quite different from that in classic aggregation with mass-independent reaction rates. For charged aggregation, the density of monomers decays as  $1/(1+t)$ , while the cluster-mass distribution has the asymptotic form

$$c_k \sim t^{-1} e^{-\epsilon k} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k + 1)} \quad (1)$$

for any fixed  $k$  when  $t \gg 1$ , where here  $c_k$  denotes the concentration of neutral clusters of mass  $2k$  (containing  $k$  positive and  $k$  negative monomers). Note that the above ratio of gamma functions decays as  $k^{-3/2}$  for large  $k$ . As we shall discuss in Sec. II B, the exponent  $\epsilon > 0$  depends on the ratio of the monomer-monomer and cluster-cluster merging rates. It is also worth noting that the  $k^{-3/2}$  decay of the cluster density also arises in aggregation with mass-independent reaction rates and with the steady input of monomers [6,26,27]. Our charged aggregation can also be viewed as aggregation with a mass-independent reaction rate and with a time-dependent monomer source.

By way of contrast, for classic aggregation with mass-independent rates, the density of clusters of mass  $k$  at time  $t$ ,  $c_k(t)$ , is [3,4,8]

$$c_k(t) = \frac{1}{(1+t)^2} \left( \frac{t}{1+t} \right)^{k-1} \xrightarrow{t \rightarrow \infty} \frac{1}{t^2} e^{-k/t} \quad (2)$$

when the process begins with a monodisperse initial condition,  $c_k(0) = \delta_{k,1}$ . The latter form is valid in the scaling limit of  $t \rightarrow \infty$  and  $k \rightarrow \infty$ , with the ratio  $k/t$  kept constant. From the scaling form of the cluster-mass distribution, the typical cluster mass grows linearly with time and the distribution of cluster masses is effectively constant for masses smaller than the typical mass. The mass distributions of charged and classic aggregation are quite different in the small-mass limit.

The outline of this paper is as follows. In Sec. II, we investigate charged aggregation within the mean-field framework in which the reactants are assumed to remain perfectly mixed at all times. We also assume that all reaction rates are equal. As we shall show, the primary difference between classic aggregation and charged aggregation is that the latter is driven

by a time-dependent source of dimers. We also treat the more general situation where the reaction rates between monomers is different than the reaction rate between clusters. In Sec. III, we analyze charged aggregation when the reaction kernel has the product form  $K_{i,j} = ij$ . We show that at a finite time, an infinite cluster (gel molecule) is born, and the gel molecule eventually engulfs the finite clusters. In Sec. IV, we generalize to an aggregation process where the elemental building blocks are monomers of three types:  $A$ ,  $B$ , and  $C$ . The reaction starts by the merging of three dissimilar monomers into “neutral” trimers:  $[A] \oplus [B] \oplus [C] \rightarrow [ABC]$ . Neutral clusters of mass three and greater then undergo binary aggregation. We again employ the mean-field framework and determine the cluster mass distribution when the cluster merging rate is independent of the cluster masses.

## II. TWO MONOMER TYPES

### A. Equal monomer and cluster reaction rates

We denote the density of monomers with positive charge as  $m(t)$ . We also assume that the density of positively and negatively charged monomers are equal. The time dependence of the monomer density (either positively or negatively charged) is described by the rate equation

$$\frac{dm}{dt} = -m^2, \quad (3)$$

with solution, for the initial condition  $m(0) = 1$ ,

$$m = \frac{1}{1+t}. \quad (4)$$

Let  $c_k$  denote the concentration of neutral clusters of mass  $2k$ . Under the assumption that neutral clusters react with constant and mass-independent rates, the time dependence of the neutral cluster densities is given by the rate equations

$$\frac{dc_1}{dt} = -2c_1c + m^2, \quad (5a)$$

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k c \quad k \geq 2, \quad (5b)$$

where  $c \equiv \sum_{k \geq 1} c_k$  is the total density of neutral clusters. A useful check of the correctness of these equations is to compute the rate of change of the total mass density

$$M \equiv m(t) + \sum_{k \geq 1} k c_k(t).$$

Adding Eq. (3) plus each of Eqs. (5) weighted by their mass, it is immediate to see that  $M$  is manifestly conserved. Since we chose the initial monomer density to equal 1, the total mass  $M = 1$ .

To determine the individual cluster densities, it is necessary to first solve for the total cluster density  $c(t)$ . Summing Eqs. (5), we find that  $c(t)$  satisfies the Riccati equation,

$$\frac{dc}{dt} = -c^2 + m^2 = -c^2 + \frac{1}{(1+t)^2}. \quad (6)$$

This equation should be solved subject to initial condition  $c(0) = 0$ . While Riccati equations are generally unsolvable,

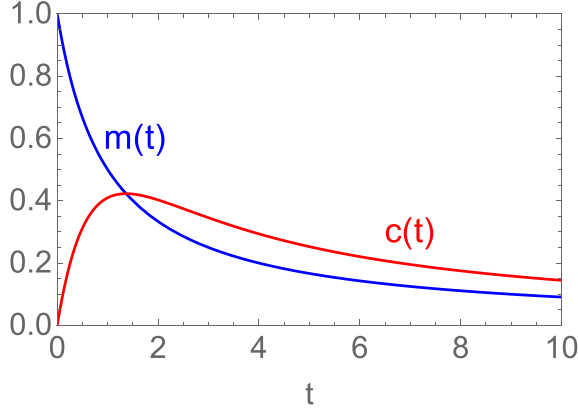


FIG. 2. Time dependence of the monomer density  $m(t)$  from (4) and the cluster density  $c(t)$  from (7). Both densities decay as  $t^{-1}$ , and their ratio  $\frac{c(\infty)}{m(\infty)}$  approaches  $\frac{1}{2}(\sqrt{5} + 1)$ .

some can be solved by first guessing a particular solution,  $c_*(t)$ . If such a solution can be found, no matter how trivial, then the ansatz  $c(t) = c_*(t) + u(t)^{-1}$  reduces the Riccati equation to a linear equation for  $u(t)$  that can be solved by elementary methods [28].

The structure of the Riccati equation (6) suggests seeking a particular solution of the form  $c_* = B/(1+t)$ . Substituting this ansatz into Eq. (6), it is straightforward to verify that this ansatz indeed solves this equation when  $B = (\sqrt{5} + 1)/2$ . Then the function  $u(t)$  satisfies

$$\frac{du}{dt} = 1 + \frac{\sqrt{5} + 1}{1+t} u.$$

Solving this equation subject to the initial condition  $c(0) = 0$ , the full solution to (6) is

$$c(t) = \frac{2}{1+t} \frac{(1+t)^{\sqrt{5}} - 1}{(\sqrt{5} - 1)(1+t)^{\sqrt{5}} + \sqrt{5} + 1}. \quad (7)$$

The densities  $m(t)$  and  $c(t)$  both asymptotically decay as  $t^{-1}$  when  $t \rightarrow \infty$  (Fig. 2). This behavior contrasts with classic constant-kernel aggregation, where  $m(t)$  asymptotically decays as  $t^{-2}$ , while the cluster density asymptotically decays as  $t^{-1}$ . Intriguingly, for  $t \rightarrow \infty$ , the ratio of clusters to monomers in charged aggregation approaches the golden ratio  $\frac{c(\infty)}{m(\infty)} = \frac{1}{2}(\sqrt{5} + 1)$ .

To determine the individual cluster densities  $c_k(t)$ , it is expedient to introduce the generating function,

$$\mathcal{C}(z, t) \equiv \sum_{k \geq 1} c_k(t) z^k.$$

Multiplying each of Eqs. (5) by  $z^k$  and summing over all  $k$ , we recast the infinite system (5) into the single differential equation,

$$\frac{d\mathcal{C}}{dt} = \mathcal{C}^2 - 2c\mathcal{C} + \frac{z}{(1+t)^2}. \quad (8)$$

As in the case of the generating function solution to constant-kernel aggregation, it proves convenient to subtract (8) from (6) to give the Riccati equation for

$$y(z, t) = c(t) - \mathcal{C}(z, t):$$

$$\frac{dy}{dt} = -y^2 + \frac{1-z}{(1+t)^2}, \quad (9)$$

subject to the initial condition  $y(z, 0) = 0$ . We solve this equation by using the same approach that was used in solving Eq. (6). From this solution, and also using the expression for  $c(t)$  in Eq. (7), we finally obtain

$$\mathcal{C}(z, t) = \frac{2}{1+t} \frac{(1+t)^{\sqrt{5}} - 1}{(\sqrt{5} - 1)(1+t)^{\sqrt{5}} + \sqrt{5} + 1} - \frac{2(1-z)}{1+t} \frac{(1+t)^\zeta - 1}{(\zeta - 1)(1+t)^\zeta + \zeta + 1}, \quad (10)$$

where  $\zeta = \sqrt{5 - 4z}$ .

Expanding (10) in powers of  $z$ , one can, in principle, extract  $c_k(t)$  for any  $k \geq 1$ . However, the expression for  $c_1$  is already cumbersome, and the expressions for  $c_k$  for  $k \geq 2$  are even more so. If we only want the asymptotic behavior, this may be more easily obtained by substituting the ansatz  $c_k = A_k/t$  into (5); one may readily check that this substitution is self consistent. After straightforward steps, we find that the  $A_k$  satisfy the recurrence

$$\sqrt{5}A_k = \sum_{i+j=k} A_i A_j + \delta_{k,1}.$$

For  $k = 1$ , we have  $A_1 = \frac{1}{\sqrt{5}}$ . To obtain the general solution for  $A_k$ , we introduce the generating function  $\mathcal{A}(z) \equiv \sum_{k \geq 1} A_k z^k$ , multiply the above recurrence by  $z^k$ , and sum over all  $k$ . This gives the quadratic equation for the generating function,  $\mathcal{A}^2 - \sqrt{5}\mathcal{A} + z = 0$ , whose solution is

$$\mathcal{A}(z) = \frac{\sqrt{5}}{2} \left( 1 \pm \sqrt{1 - \frac{4}{5}z} \right),$$

where we must choose the negative sign before the square root to have the correct behavior for  $z \rightarrow 0$ . Expanding this expression in a Taylor series gives

$$c_k \simeq \frac{A_k}{t}, \quad (11a)$$

with

$$A_k = \sqrt{\frac{5}{16\pi}} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k + 1)} \left( \frac{4}{5} \right)^k. \quad (11b)$$

The mass distribution decays exponentially in  $k$ , with a time-independent cutoff. This result for  $c_k$  is valid in the limit  $t \rightarrow \infty$  with  $k$  fixed.

It is now instructive to compute the moments of the cluster-mass distribution,

$$M_n \equiv \sum_{k \geq 1} k^n c_k, \quad (12)$$

where we excluded the contribution of monomers for convenience. As we will show below, it is simpler to compute the dependence of the moments on the monomer density rather than as a function of time and then determine the asymptotic time dependence. The exact expressions for the first three

moments are

$$M_1(m) = 1 - m, \quad (13a)$$

$$M_2(m) = \frac{2}{m} + 1 - 3m + 4 \ln m, \quad (13b)$$

$$M_3(m) = \frac{(1-m)(6+24m+19m^2)}{m^2} + \frac{24}{m} \ln m + 24 \ln m + 12(\ln m)^2. \quad (13c)$$

Equation (13a) is just the mass conservation statement. To obtain the second moment, we multiply each of Eqs. (5a) and (5b) by  $k^2$  and sum these equations. This gives the time dependence of the second moment:

$$\frac{dM_2}{dt} = 2M_1^2 + m^2. \quad (14a)$$

It is now helpful to use  $\frac{dm}{dt} = -m^2$  and the mass conservation statement  $M_1 = 1 - m$  to eliminate the time and express  $M_2$  as a function of  $m$ . This gives

$$\frac{dM_2}{dm} = -2(1 - m^{-1})^2 - 1. \quad (14b)$$

The solution to this equation subject to the initial condition  $M_2(m = 1) = 0$  is just (13b).

Similarly, the time dependence of the third moment is

$$\frac{dM_3}{dt} = 6M_1M_2 + m^2. \quad (15a)$$

Once again, we eliminate the time in favor of  $m$  to yield

$$\frac{dM_3}{dm} = -6(1 - m) \left( \frac{2}{m} + 1 - 3m + 4 \ln m \right) - 1. \quad (15b)$$

Solving this equation subject to the initial condition  $M_3(m = 1) = 0$  gives (13b).

Since  $m(t) \simeq t^{-1}$ , the leading time dependence of the moments in (13) comes from the term with the most negative power of  $m$ . Thus, we conclude that

$$M_1(t) \simeq 1, \quad M_2(t) \simeq 2t, \quad M_3(t) \simeq 6t^2. \quad (16)$$

Following the above line of reasoning and with some additional effort, the time dependence of the general  $n$ th moment as  $t \rightarrow \infty$  is

$$M_n(t) \simeq n! t^{n-1}. \quad (17)$$

This leading behavior coincides with the time dependence of the moments in classic constant-kernel aggregation. This equivalence seems to stem from the fact that the reactions of neutral clusters in charged aggregation is the same as reactions of all clusters in constant-kernel aggregation. The fact that neutral clusters are created by a time-dependence source from the reaction of oppositely charged monomers rather than being present in the initial state does not seem to affect the long-time behavior of the moments.

There is a subtlety in the moments that deserves mention. For a fixed value of the mass  $k$ , the asymptotic behavior of the cluster density is given by (11a). If (11a) remained valid for all  $k$ , then all the moments  $M_n(t)$  would decay as  $t^{-1}$ , since  $A_k$  decrease exponentially with mass and the sum  $\sum_{k \geq 1} k^n A_k$  converges for all  $n$ . Thus, it is necessary to take the limits  $k \rightarrow \infty$  and  $t \rightarrow \infty$  in the correct order.

## B. Distinct monomer and cluster reaction rates

Because charged monomers are fundamentally distinct from neutral clusters, it is natural to investigate the aggregation kinetics for the situation in which the rate of cluster-cluster merging is set to one, as before, but the monomer-monomer merging rate is set to  $\lambda$ . We now explore the consequences of this generalization within the mean-field approximation. The rate equations for the monomer and cluster densities now are [compare with Eqs. (3) and (6)]

$$\frac{dm}{dt} = -\lambda m^2, \quad \frac{dc}{dt} = -c^2 + \lambda m^2. \quad (18)$$

The rate equation for the the dimer density now is

$$\frac{dc_1}{dt} = -2c_1c + \lambda m^2, \quad (19)$$

while the rate equations for the cluster densities with  $k \geq 2$  are again given by Eq. (5b).

Solving the equations for  $m(t)$ ,  $c(t)$ , and then  $c_1(t)$ , the resulting expressions for the latter two quantities are extremely cumbersome. However, if we only want the asymptotic behavior, we may perform the same analysis as given above to obtain the amplitude  $A_k$  in the asymptotic expression for  $c_k$ , as well as the ratio of clusters to monomers as a function of  $\lambda$ :

$$A_k = \left( \frac{4}{4 + \lambda} \right)^k \frac{\sqrt{4 + \lambda} \Gamma(k - \frac{1}{2})}{4\sqrt{\pi\lambda} \Gamma(k + 1)},$$

$$\frac{c(\infty)}{m(\infty)} = \frac{\sqrt{\lambda(4 + \lambda)} + \lambda}{2}. \quad (20)$$

From the expression for  $A_k$ , we infer that  $\epsilon$  defined in Eq. (1) is given by  $\epsilon = \ln((4 + \lambda)/4)$ .

The results for  $c(t)$  and  $c_1(t)$  simplify considerably for a number of special cases. For example, when  $\lambda = \frac{1}{2}$ , the above ratio equals 1. In this case, the cluster density becomes the following rational function of time:

$$m = \frac{2}{2 + t}, \quad c = \frac{2t}{2 + t} \frac{12 + 6t + t^2}{24 + 12t + 6t^2 + t^3}, \quad (21a)$$

while the dimer density  $c_1$  is

$$c_1 = \frac{2}{3} \frac{A(t) + B(t) \ln(1 + t/2)}{(2 + t)(24 + 12t + 6t^2 + t^3)^2}, \quad (21b)$$

with

$$A = t(480 + 384t + 184t^2 + 60t^3 + 12t^4 + t^5),$$

$$B = 96(2 + t)^3.$$

Another simple case is  $\lambda = \frac{4}{3}$ , where the ratio  $c(\infty)/m(\infty)$  now equals 2 (Fig. 3). Here, the cluster density is again a rational function of time

$$m = \frac{3}{3 + 4t}, \quad c = \frac{12t}{3 + 4t} \frac{3 + 2t}{9 + 6t + 4t^2}, \quad (22a)$$

and the dimer density  $c_1$  is

$$c_1 = \frac{3}{8} \frac{A(t) + B(t) \ln(1 + 4t/3)}{(3 + 4t)(9 + 6t + 4t^2)^2}, \quad (22b)$$

with

$$A = t(540 + 504t + 192t^2 + 64t^3), \quad B = 27(3 + 4t)^2.$$

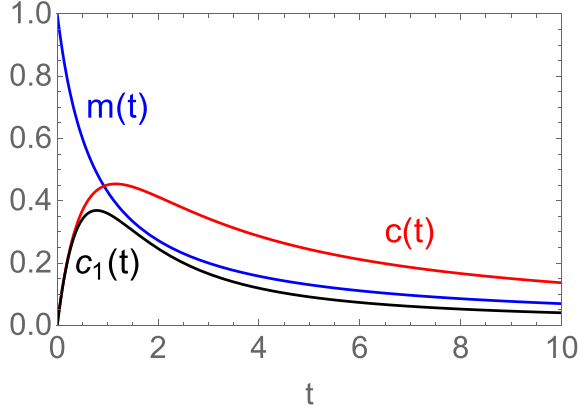


FIG. 3. The monomer density  $m(t)$ , the cluster density  $c(t)$ , and the dimer density  $c_1(t)$  from Eqs. (22) when  $\lambda = \frac{4}{3}$ . All densities decay as  $t^{-1}$ . Asymptotically, the density ratios  $\frac{c(\infty)}{m(\infty)}$  and  $\frac{m(\infty)}{c_1(\infty)}$  both equal 2.

### III. THE PRODUCT KERNEL

We now investigate charged aggregation when the reaction kernel has the product form  $K_{i,j} = ij$ , which leads to a finite-time gelation transition. At a critical gelation time, an infinite cluster (gel molecule) is born that gradually engulfs all the remaining finite-mass clusters as  $t \rightarrow \infty$ .

For generality, we assume that the reaction rate between monomers is  $\lambda$ , so that its rate equation is the first of (18), with solution  $m(t) = 1/(1 + \lambda t)$ . The density of cluster is now given by

$$\frac{dc_1}{dt} = \lambda m^2 - c_1(1 - m), \quad (23a)$$

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} ij c_i c_j - k c_k (1 - m) \quad k \geq 2. \quad (23b)$$

In the loss term in (23b), we have used the fact that the mass density of clusters,  $\sum_{k \geq 1} k c_k$  equals  $1 - m$ .

To find the gelation transition, we study the time dependence of the second moment  $M_2(t)$ . From Eqs. (23), this second moment satisfies

$$\frac{dM_2}{dt} = M_2^2 + \lambda m^2 = M_2^2 + \frac{\lambda}{(1 + \lambda t)^2},$$

whose solution is

$$M_2 = \frac{\Lambda}{1 + \lambda t} \frac{1 - (1 + \lambda t)^{\sqrt{1-4/\lambda}}}{\Lambda - 1 - (1 + \lambda t)^{\sqrt{1-4/\lambda}}}, \quad (24)$$

where  $\Lambda \equiv \frac{1}{2}(\lambda + \sqrt{\lambda(\lambda - 4)})$ . This expression is manifestly real for  $\lambda > 4$  and it can be recast into a real form for  $0 < \lambda \leq 4$ . For the specific cases of  $\lambda = 1$  and  $\lambda = 4$ , we find (Fig. 4)

$$M_2 = \begin{cases} \frac{2}{1+t} \frac{1}{\sqrt{3} \cot[\frac{\sqrt{3}}{2} \ln(1+t)] - 1} & \lambda = 1, \\ \frac{2}{1+4t} \frac{\ln(1+4t)}{2 - \ln(1+4t)} & \lambda = 4. \end{cases} \quad (25)$$

The second moment diverges at the gelation time, whose value is obtained by setting the denominator in Eq. (24) to

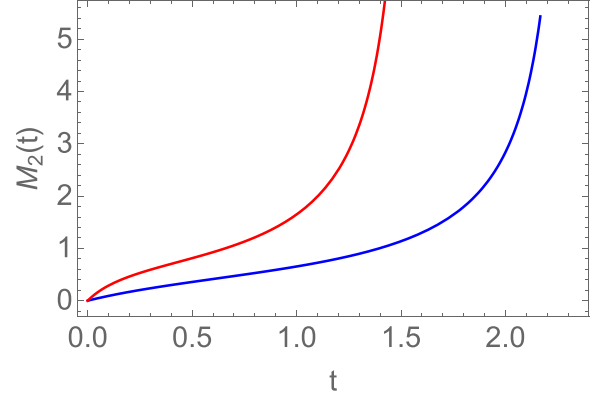


FIG. 4. The second moment  $M_2(t)$  for product kernel charged aggregation for  $\lambda = 1$  (blue) and  $\lambda = 4$  (red).

zero. This gives

$$t_g = \frac{(\Lambda - 1)^{1/\sqrt{1-4/\lambda}} - 1}{\lambda}. \quad (26)$$

For the special cases of  $\lambda = 1$  and  $\lambda = 4$ , the gelation time is  $t_g = e^{2\pi/\sqrt{27}} - 1 = 2.3508\dots$  and  $t_g = \frac{1}{4}(e^2 - 1) = 1.597264\dots$ , respectively. The limiting behaviors of the gel time are  $t_g \rightarrow 1$  for  $\lambda \rightarrow \infty$ , and  $t_g \rightarrow \sqrt{\pi/4\lambda}$  for  $\lambda \rightarrow 0$ .

From the rate equations (23a) and (23b), the time dependence of the total cluster density is

$$\frac{dc}{dt} = \lambda m^2 + \frac{g^2 - (1 - m)^2}{2}, \quad (27)$$

where  $g$  is mass in the gel phase. This gel mass is defined via

$$M_1 = \sum_{k \geq 1} k c_k = 1 - m - g, \quad (28)$$

where the sum is over finite-mass clusters. When  $t < t_g$ , we integrate (27) with  $g = 0$  to yield

$$c = \frac{\ln(1 + \lambda t)}{\lambda} - \frac{1 - \lambda(1 - t/2)}{1 + \lambda t} t. \quad (29)$$

This cluster density has a maximum for  $t = \sqrt{2/\lambda}$ . In the postgel phase,  $t > t_g$ , we formally integrate (27) to give

$$c = \frac{\ln(1 + \lambda t)}{\lambda} - \frac{1 - \lambda(1 - t/2)}{1 + \lambda t} t + \frac{1}{2} \int_{t_g}^t dt' g^2(t'). \quad (30)$$

### IV. THREE TYPES OF MONOMERS

Given the rich dynamics of charged aggregation with two types of monomers, it is natural to generalize to the case of three types of monomers,  $A$ ,  $B$ , and  $C$ , that are each initially present with equal densities. In the same spirit as the two-monomer model, we postulate that the only possible monomer reaction event is the merging of three dissimilar monomers,  $[A] \oplus [B] \oplus [C] \rightarrow [ABC]$ , which results in a neutral trimer (Fig. 5). Neutral clusters of mass greater than or equal to three continue to merge to create neutral clusters of the form  $[(ABC)^k]$  with  $k \geq 2$ . If we ascribe a complementary color to each monomer species, the trimer is neutral since it has no net color.



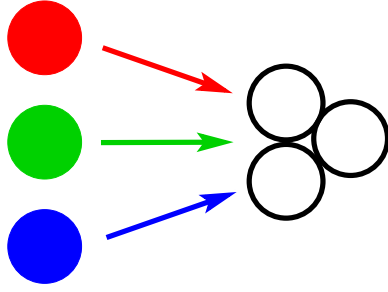


FIG. 5. Aggregation with three monomer species. The elemental event where three distinct monomer types merge into a neutral trimer is shown.

Adopting the language from particle physics, we can think of monomers as quarks with colors  $A = \text{red}$ ,  $B = \text{green}$ , and  $C = \text{blue}$ . A baryon is composed of three quarks, which must contain one monomer each of red, green, and blue colors. Hence, a trimer plays the role of an elementary baryon. We may also envision a more general stoichiometry in which there are both quarks and antiquarks. In the context of particle physics, a quark-antiquark pair corresponds to a meson. In the framework of aggregation, one can imagine a rich range of phenomena with both baryonic aggregation, mesonic aggregation, and possibly mixed aggregation of baryons and mesons.

Returning to our minimal three-species model, the density  $m$  of monomers of each type decays according to

$$\frac{dm}{dt} = -m^3, \tag{31}$$

whose solution, subject to  $m(0) = 1$ , is

$$m = \frac{1}{\sqrt{1 + 2t}}. \tag{32}$$

The density  $c_1$  of trimers now satisfies

$$\frac{dc_1}{dt} = -2c_1c + m^3, \tag{33}$$

while the density  $c_k$  of clusters of mass  $3k$  satisfies Eq. (5b) for  $k \geq 2$ .

The time dependence of the total cluster density is accounted for by the Riccati equation,

$$\frac{dc}{dt} = -c^2 + (1 + 2t)^{-3/2}. \tag{34}$$

While this equation is unsolvable, it is not difficult to determine the relevant large-time behavior. We first note that it is not possible that all three terms in (34) have the same time dependence. If one assumes that  $c \sim t^{-\alpha}$ , then the terms in this equation are of order  $t^{-(1+\alpha)}$ ,  $t^{-2\alpha}$ , and  $t^{-3/2}$ , which can never be of the same order. Thus, we seek a solution in which two of the three terms in (34) are dominant. The only consistent solution arises when the terms on the right-hand side are dominant, while the left-hand side is negligible. With this assumption, we immediately find

$$c \simeq (1 + 2t)^{-3/4}. \tag{35}$$

Hereinafter we keep only the leading term and merely mention that the correction terms can be also computed:

$$c = (1 + 2t)^{-3/4} + \frac{3}{4}(1 + 2t)^{-1} + \dots$$

By keeping the two dominant terms in (33), we find that the leading asymptotic behavior of the trimer density is simply  $c_1 = c/2$ . Using (5b) we can then find the leading asymptotic behavior of the densities  $c_k$  for the first few  $k$  values, from which we deduce that all the  $c_k$  are of the same order as  $c$  itself. Using this fact, we therefore write

$$c_k = A_k c \tag{36}$$

for any fixed  $k$  and  $t \rightarrow \infty$ . Substituting this ansatz into (5b) and keeping only the leading terms gives the recurrence

$$2A_k = \sum_{i+j=k} A_i A_j + \delta_{k,1},$$

whose solution is [6]

$$c_k = \frac{c}{\sqrt{4\pi}} \frac{\Gamma(k - \frac{1}{2})}{\Gamma(k + 1)} \simeq \frac{c}{\sqrt{4\pi}} k^{-3/2} \quad k \gg 1. \tag{37}$$

Let us now determine the asymptotic behavior of the moments  $M_n$  as defined in Eq. (12). The first moment is given by Eq. (13a) due to mass conservation. Following the same steps as those used for monomers with two types of charges, the next two moments are

$$M_2(m) = (2 - m^{-1})^2 - m - 2 \ln m, \tag{38a}$$

$$M_3(m) = \frac{3}{2m^4} - \frac{10}{m^3} + \frac{21}{m^2} - \frac{18}{m} + \frac{13}{2} - m - 6(1 - m^{-1})^2 \ln m. \tag{38b}$$

We now substitute the asymptotic form  $m(t) \simeq 1/\sqrt{2t}$  for the monomer density into Eqs. (38) and find that the leading time dependence of the moments are the same as in the case of two types of monomers:  $M_n(t) \simeq n! t^{n-1}$ .

If there are  $n + 1$  types of monomers with  $n \geq 2$ , the same considerations as those used for the three-species model lead to

$$m = (1 + nt)^{-1/n}, \quad c \simeq (1 + nt)^{-(n+1)/2n}. \tag{39}$$

The solution for the cluster-mass density is still given by Eq. (37), but with  $c$  now given by (39). We also find that the asymptotic time dependence of the moments is independent of the number of monomer types.

## V. SUMMARY AND DISCUSSION

We investigated the kinetics in a model of ‘‘charged’’ aggregation, in which the reaction begins with equal concentrations of positively charged and negatively charged monomers. Oppositely charged monomers join to form neutral dimers, and neutral clusters of any mass greater than or equal to two react freely with other neutral clusters to form aggregates of ever-increasing size. Within the mean-field approximation, we obtained the time dependences of the concentration of monomers and the concentration of clusters of any size.

At a qualitative level, charged aggregation is a version of classic aggregation, but with a time-dependent source of

dimers (effectively the elemental constituents of charged aggregation) that is decaying with time. This mechanism leads to the densities of clusters of mass  $k$  decaying with time as  $t^{-1}$  in the small-mass limit. We also explored the kinetics of charged aggregation with a product reaction kernel. We found that this model undergoes a conventional second-order gelation transition at a gelation time that depends on  $\lambda$ , the monomer-monomer reaction rate.

It should be worthwhile to explore the kinetics of charged aggregation in finite spatial dimensions, where fluctuation effects should play a significant role. The simplest case and the one with the largest departures from mean-field behavior is the case of one dimension. There are two natural situations that may be worthwhile to explore: (i) a spatially homogeneous system, and (ii) positive and negative monomers initially occupying the positive and negative infinite half-lines. Another natural situation is a steady and spatially localized monomer input in a  $d$ -dimensional space.

For the first scenario, charged aggregation involves a superposition of a two-species reaction, the conversion of oppositely charge monomers to neutral dimers, and single-species reactions, the merging to neutral clusters of any size. In one dimension, these two constituent reactions have very different kinetics and their melding could lead to unusual kinetics.

If the monomers of each type are spatially separated, then their reaction is identical to the well-studied problem of two-species annihilation with the same initially separated initial condition. In charged aggregation, the localized zone where monomers react leads to a spatially localized and time-dependent source of dimers. It is natural to also treat a steady, but spatially localized source of dimers in general spatial dimension.

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