


Catalytic coagulation

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We introduce an autocatalytic aggregation model in which the rate at which two clusters merge is controlled by the third “catalytic” cluster, whose mass must equal the mass of one of the reaction partners. The catalyst is unaffected by the joining event and can participate in or catalyze subsequent reactions. This model is meant to mimic the self-replicating reactions that occur in models for the origin of life. We solve the kinetics of catalytic coagulation for the case of mass-independent reaction rates and show that the total cluster density decays as $t^{-1/3}$, while the density of clusters of fixed mass decays as $t^{-2/3}$. These behaviors contrast with the corresponding t^{-1} and t^{-2} scalings for classic aggregation. We extend our model to mass-dependent reaction rates, to situations where only “magic” mass clusters can catalyze reactions, and to include steady monomer input.

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I. INTRODUCTION AND MODEL

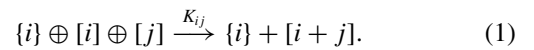
One of the profound mysteries of the natural world is the origin of life. Self-replication has been invoked as a starting point to understand how the complex reactions that underlie a living system might arise; see, e.g., [1–11] and references therein. In such processes, the products of a given reaction serve to catalyze the rate of new products, which, in turn, can catalyze further reactions, leading to potentially complex chemistries.

Various types of random catalytic reaction networks have been proposed and investigated to predict the emergence of autocatalytic cycles in populations of diverse reactants with general types of catalytic activity [12–14]. The outcome of studies such as these is that catalytic activity among a set of reactants is sufficient to promote the appearance of groups of molecules that can replicate themselves through autocatalytic reactions.

While the behavior of many of these autocatalytic reactions is extremely rich, it is often not possible to discern which aspects of the complex chemical reaction networks that have been studied are truly necessary for the emergence of self-replication. A missing element in these models is analytical tractability—most of the models that have been considered thus far typically contain many species and many reaction pathways. These complications make an analytical solution of such models out of reach. Motivated by this disconnect between complexity and analytical tractability, we formulate a simple realization of catalytic kinetics in the framework of irreversible aggregation. While our model is idealized, it might provide a starting point for analytically determining the kinetics of autocatalytic reactions.

In our *catalytic coagulation* model, some fraction of the reactants are catalytic; namely, these catalysts are unaffected by the joining of two other reactants and can subsequently participate in or catalyze further reactions. That is, the rate at which a cluster of mass i , an i -mer, and a j -mer join requires the presence of either another i -mer or another j -mer

to catalyze the reaction (see Fig. 1). We may represent this reaction as



Here, the reactants inside the square brackets undergo aggregation, while the reactant within the braces is unaffected by the reaction. In contrast to ordinary aggregation, where the reaction rates are symmetric in the reactant masses, the reaction rates need not be symmetric in catalytic coagulation, i.e., generically, $K_{i,j} \neq K_{j,i}$.

In the mean-field or perfect-mixing limit where all reactant concentrations are spatially uniform, the catalytic aggregation process (1) has much slower kinetics compared to that in conventional binary aggregation, $[i] \oplus [j] \rightarrow [i + j]$, and even ternary aggregation, $[i] \oplus [j] \oplus [k] \rightarrow [i + j + k]$. We may quantify this slower kinetics by the temporal decay of the total cluster density $c(t)$ when the reaction rates are independent of

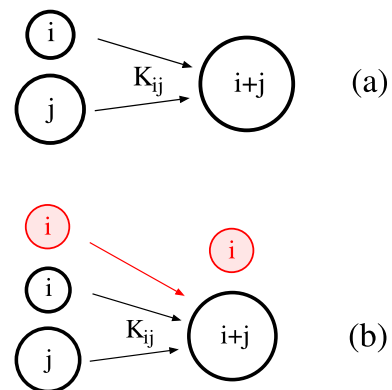


FIG. 1. Schematic of the elemental events in (a) coagulation and (b) catalytic coagulation. In our catalytic coagulation model, the presence of a catalyst (red, shaded) whose mass matches one of the reactants is required. This catalyst is unaffected by the reaction itself.

the mass for all three models. This decay is given by

$$c(t) \sim \begin{cases} t^{-1}, & \text{binary aggregation} \\ t^{-1/2}, & \text{ternary aggregation} \\ t^{-1/3}, & \text{catalytic aggregation.} \end{cases} \quad (2)$$

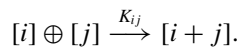
The t^{-1} decay in binary aggregation immediately follows from the closed equation that is satisfied by the total cluster density, $\frac{dc}{dt} = -Kc^2$ (see Sec. II). For ternary aggregation, the decay of the concentration is described by $\frac{dc}{dt} = -Kc^3$, from which $c \sim t^{-1/2}$ (see, e.g., [15]). The catalytic aggregation process (1) also involves a three-body interaction, but this interaction also must satisfy the mass restriction that the catalyst mass matches the mass of one of the two reactants. This restriction is the source of the slower decay in catalytic aggregation compared to ternary aggregation.

Binary and ternary aggregation processes with mass-independent rates are tractable, which allows for the computation of $c(t)$ in the entire time range. In contrast, for catalytic coagulation, the total cluster density does not satisfy a closed equation even in the simplest case of mass-independent reaction rates. Thus we are able to compute only the decay exponent, $c(t) \sim t^{-1/3}$ (Sec. III), but the amplitude remains unknown. We also derive the scaling solution of the cluster-mass distribution.

In Sec. IV, we extend our theory to treat the case where the efficiency of the catalyst is a function of its mass. Specifically, we analyze a one-parameter family of models with algebraic reaction rates $K_{ij} = i^\nu$. In Sec. V, we treat settings where only clusters of certain “magic” masses can catalyze reactions, as well as the situation where the reaction is augmented by a steady monomer input. In Sec. VI, we give a summary.

II. CLASSICAL COAGULATION

To set the stage for catalytic coagulation, we review some essential features of classical coagulation. Coagulation is a ubiquitous kinetic process in which a population of clusters continuously merge to form clusters of ever-increasing mass [16,17]. This process underlies many physical phenomena, such as blood clotting, gravitational accretion of gas clouds into stars and planets, and gelation. In aggregation, two clusters of mass i and j join irreversibly at rate K_{ij} to form a cluster of mass $i + j$ according to



The basic observables are the densities of clusters of mass k at time t . These k -mer densities depend in an essential way on the reaction rates K_{ij} . Much effort has been devoted to determining these cluster densities in the perfectly mixed or mean-field limit, where the shape and spatial location of the clusters are ignored and the only degree of freedom for each cluster is its mass [18–21].

Let $c_k(t)$ denote the density of k -mers at time t . In the simplest aggregation process with mass-independent reaction rates, the Smoluchowski equations [22–24] that describe the evolution of the densities in the mean-field limit are particu-

larly simple,

$$\frac{dc_k}{dt} = \sum_{i+j=k} c_i c_j - 2c_k c, \quad (3)$$

where

$$c(t) \equiv \sum_{k \geq 1} c_k(t) \quad (4)$$

is the total cluster density. Summing Eq. (3) over all k , one finds that the total cluster density satisfies $\frac{dc}{dt} = -c^2$, with solution $c(t) = (1 + t)^{-1}$.

For the monodisperse initial condition $c_k(t=0) = \delta_{k,1}$, the solution to (3) is

$$c_k(t) = \frac{t^{k-1}}{(1 + t)^{k+1}}. \quad (5)$$

In the scaling limit of $t \rightarrow \infty$ and $k \rightarrow \infty$, with the scaled mass $kc(t)$ kept finite, the mass distribution (5) has the scaling form

$$c_k(t) \simeq c^2 F(ck), \quad (6)$$

with scaled mass distribution $F(x) = e^{-x}$. We will compare these classic results with the corresponding behavior of catalytic coagulation in the following section.

III. CATALYTIC COAGULATION

Various catalytic reaction schemes have been proposed and investigated in the context of building the complex molecules of living systems [1–9]. These models typically invoke some type of constraint in which the size or composition of the catalyst matches, in some way, with the reactants to facilitate a reaction. For example, Ref. [6] proposed the catalytic reaction scheme $\{i + j\} \oplus [i] \oplus [j] \rightarrow \{i + j\} + [i + j]$, i.e., the catalyst mass equals the sum of the two reactant masses. By construction, it is not possible to generate clusters whose masses exceed the largest mass in the initial state. Thus it is necessary to augment this scheme with additional processes, as in [6], to have continuous evolution. The reaction process that we investigate, $\{i\} \oplus [i] \oplus [j] \rightarrow \{i\} + [i + j]$, has the advantage of leading to continuous evolution starting from the monodisperse monomer-only initial condition without the need to invoke additional reaction channels.

We initially assume that the rate of each of these reactions is independent of the reactant masses and we set all reaction rates to 1. The time evolution of the cluster densities now obeys

$$\begin{aligned} \frac{dc_k}{dt} &= \frac{1}{2} \sum_{i+j=k} c_i c_j (c_i + c_j) - c_k \sum_{i \geq 1} c_i (c_i + c_k) \\ &= \sum_{i+j=k} c_i^2 c_j - c_k^2 c - c_k Q, \end{aligned} \quad (7)$$

which involves, in addition to the total cluster density (4), the quadratic moment of the mass distribution,

$$Q(t) \equiv \sum_{k \geq 1} c_k(t)^2. \quad (8)$$

Because the mass is manifestly conserved in each reaction, a useful check of the correctness of the rate Eq. (7) is to verify that $\sum_k k \frac{dc_k}{dt} = 0$.

The presence of this quadratic moment renders the governing Eq. (7) intractable. To understand why, we recall that one can solve the rate Eq. (3) for classical aggregation recursively in terms of the known cluster density. In catalytic coagulation, the governing Eq. (7) are also recurrent, but they require knowledge of both $c(t)$ and $Q(t)$. Using Eq. (7), these quantities obey

$$\frac{dc}{dt} = -cQ, \quad (9a)$$

$$\frac{dQ}{dt} = 2 \sum_{i \geq 1} \sum_{j \geq 1} c_i^2 c_j c_{i+j} - 2c \sum_{k \geq 1} c_k^3 - 2Q^2. \quad (9b)$$

Equation (9b) involves moments higher than quadratic, so Eqs. (9a) and (9b) do not form a closed system and hence are not solvable.

As an alternative, we specialize to the long-time limit, where the cluster mass distribution should have the scaling behavior (6). We will see that Eqs. (9a) and (9b) can be solved in this scaling limit. For consistency with (4) and with mass conservation, $\sum_{k \geq 1} k c_k = 1$, the scaling function $F(x)$ must satisfy the conditions

$$\int_0^\infty dx F(x) = 1 \quad \text{and} \quad \int_0^\infty dx x F(x) = 1. \quad (10)$$

By substituting the scaling form $c_k(t) \simeq c^2 F(ck)$ into (8), we obtain

$$Q = Ac^3, \quad A = \int_0^\infty dx F^2(x). \quad (11)$$

Finally, we substitute (11) into (9a) and integrate to obtain the cluster density in the long-time limit,

$$c = (3At)^{-1/3}. \quad (12)$$

Now that we have found the cluster density, let us determine the monomer density. Its governing equation is

$$\frac{dc_1}{dt} = -c_1^2 c - c_1 Q = -c_1^2 c - Ac_1 c^3. \quad (13)$$

Dividing (13) by $\frac{dc}{dt} = -cQ = -Ac^4$ yields

$$\frac{dc_1}{dc} = \frac{c_1^2 + Ac_1 c^2}{Ac^3}. \quad (14)$$

The behavior in classical aggregation, $c_1 \simeq c^2$, suggests a similar algebraic scaling, $c_1 \simeq Bc^\beta$, in catalytic coagulation. Substituting this asymptotic into (14) gives

$$(\beta - 1)Bc^{\beta-1} \simeq \frac{B^2}{A} c^{2\beta-3}.$$

Two possibilities emerge: $\beta = 1$, when the left-hand side dominates, and $\beta = 2$, when both terms are of the same order, and we further deduce $B = A$. A more accurate analysis based on substituting $c_1 \simeq Bc$ into (13) leads to inconsistent results, and we thus conclude that

$$c_1 = Ac^2. \quad (15)$$

This equation for c_1 is consistent with the scaling form (6) only if

$$F(0) = A = \int_0^\infty dx F^2(x). \quad (16)$$

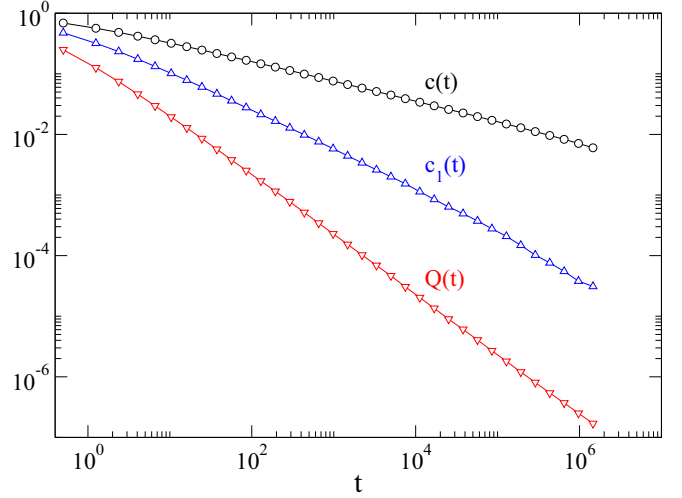


FIG. 2. Simulation data for $c(t)$, $c_1(t)$, and $Q(t)$ for catalytic coagulation on the complete graph of 10^5 sites.

Collecting (11), (12), and (15), we find

$$c \simeq \frac{1}{(3At)^{1/3}}, \quad c_1 \simeq \frac{A^{1/3}}{(3t)^{2/3}}, \quad Q \simeq \frac{1}{3t}. \quad (17)$$

We have thus determined the asymptotic behavior of the quadratic moment (8), while the asymptotic behaviors of the more primary quantities, the densities of monomers and clusters, are known only up to the amplitude A , which we have been unable to compute analytically. Thus we also performed Monte Carlo simulations to verify the asymptotic behaviors (17) and to extract the amplitude A .

In Fig. 2, we show simulation data for $c(t)$, $c_1(t)$, and $Q(t)$ for 10^5 realizations of a system that initially contains 10^5 monomers. Least-squares fits to these data on a double logarithmic scale in the time range $10 \leq t \leq 10^4$ give the respective slopes of -0.327 , -0.654 , and -0.993 compared to our predictions of $-1/3$, $-2/3$, and -1 . We also use the data to infer the amplitude A . From (17), the two combinations Q/c^3 and c_1^3/Q^2 should both approach A for $t \rightarrow \infty$. As a function of time, both these variables converge to a common value up to $t \simeq 10^4$ before fluctuation effects begin to play a significant role. By this analysis, we infer $A \approx 0.517$.

It is worth highlighting that we absorbed the factor $(c_i + c_j)$ in the right-hand side of Eq. (7) into the time increment in the simulation. By this device, we are merely simulating binary aggregation, but with a density-dependent time increment. This construction makes the simulation easy to code, as only minor modifications of our previous simulation codes for binary aggregation are needed, and also quite efficient.

One can, in principle, continue this analysis to determine the k -mer densities one by one. However, it is more expedient to invoke scaling. Thus we substitute the scaling form (6) into the rate equations (7), from which we can directly obtain the entire scaled mass distribution. After some straightforward algebra, the rate equations transform to the integro-differential equation

$$F^2 - A \left[x \frac{dF}{dx} + F \right] = \int_0^x dy F^2(y) F(x-y). \quad (18a)$$

Notice that for $x = 0$, the condition (16) that $F(0) = A$ is automatically satisfied.

The transformation $\xi = Ax$ and $F(x) = A\Phi(\xi)$ recasts (19) into

$$\Phi^2 - \Phi - \xi \Phi' = \int_0^\xi d\eta \Phi^2(\eta)\Phi(\xi - \eta), \quad (18b)$$

where the prime denotes differentiation with respect to ξ . In these new variables, Eq. (16) becomes

$$1 = \Phi(0) = \int_0^\infty d\xi \Phi^2(\xi). \quad (19)$$

The scaled mass distribution approaches to $\Phi(0) = 1$ in the small-mass limit of $\xi \rightarrow 0$. To find the next correction, we write $\Phi = 1 - \epsilon$ with $\epsilon \ll 1$, and substitute this ansatz into (18b) to find

$$\xi \epsilon' - \epsilon = \xi, \quad (20)$$

to leading order. The solution is $\epsilon = \xi(\ln \xi + a)$, with a some constant. Thus we conclude that the scaled mass distribution has the small-mass tail,

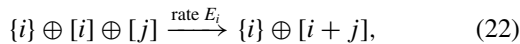
$$\Phi = 1 - \xi(\ln \xi + a) + \dots, \quad (21)$$

as $\xi \rightarrow 0$. This small-mass behavior suggests that the scaled mass distribution is more complicated than the scaled distribution $\Phi = e^{-\xi}$ in classical aggregation. While we have found the small-mass tail of the scaled mass distribution, we have been unable to determine the large-mass tail.

IV. ALGEBRAIC MERGING RATES

We can extend the approach of Sec. III to treat catalytic coagulation in which the reaction rate depends on the mass of the catalyst: $K_{ij} = E_i$. Such a generalization accounts for the possibility that the efficacy of the catalyst depends on geometrical constraints; for example, if the catalyst serves as a physical scaffold upon which the reaction takes place and a larger-area scaffold is more efficient.

We may write this mass-dependent catalytic reaction as



in which the reaction rate E_i is mass dependent. A natural situation is when the reaction rate is algebraic in the mass: $E_i = i^\nu$. On the physical grounds, the reaction rate cannot grow faster than linearly in the mass, i.e., the exponent should satisfy $\nu \leq 1$. The $\nu > 1$ range is not merely questionable physically, but the resulting behaviors are often mathematically pathological. In an infinite system, the process completes, that is, all clusters merge into one, in zero time. This phenomenon of instantaneous gelation has been studied in the context of classical aggregation; see, e.g., [25–29]. While instantaneous gelation also seems to occur in catalytic coagulation, we limit ourselves to the physically relevant range of $\nu \leq 1$.

For the catalytic reaction (22) with the reaction rate $E_i = i^\nu$, the k -mer densities obey

$$\frac{dc_k}{dt} = \sum_{i+j=k} i^\nu c_i^2 c_j - kc_k^2 c - c_k Q_\nu, \quad (23)$$

with

$$Q_\nu = \sum_{k \geq 1} k^\nu c_k^2. \quad (24)$$

Similarly, the cluster density evolves according to

$$\frac{dc}{dt} = -c Q_\nu. \quad (25)$$

When $\nu < 1$, this mass-dependent catalytic coagulation admits a scaling treatment parallel to that given in Sec. III for the model with mass-independent rates ($\nu = 0$). Combining (24) with the scaling form (6), we obtain the analog of Eq. (11),

$$Q_\nu = A_\nu c^{3-\nu}, \quad A_\nu = \int_0^\infty dx x^\nu F^2(x). \quad (26)$$

Substituting (26) into (25) and integrating, we obtain

$$c = [(3 - \nu)A_\nu t]^{-1/(3-\nu)} \quad (27)$$

for the density of clusters in the long-time limit. Substituting (27) into (26), we find the asymptotic behavior,

$$Q_\nu = \frac{1}{(3 - \nu)t}. \quad (28)$$

Thus we know the exact asymptotic behavior of the moment Q_ν , while the asymptotic of the more natural moment, the cluster density, is solved only up to an unknown amplitude A_ν .

The monomer density satisfies

$$\frac{dc_1}{dt} = -c_1^2 c - c_1 Q_\nu. \quad (29)$$

Dividing (29) by (25) and using $Q_\nu = A_\nu c^{3-\nu}$, we obtain

$$\frac{dc_1}{dc} = \frac{c_1}{c} + \frac{c_1^2}{A_\nu c^{3-\nu}}. \quad (30)$$

There are three possible alternatives for the asymptotic solution of this equation: (i) The first term on the right-hand side of (30) is asymptotically dominant; (ii) the second term is dominant; (iii) both terms are comparable. A straightforward analysis shows that only the third possibility is consistent. Thus, $c_1 \sim c^{2-\nu}$. Substituting this asymptotic into (30), we fix the amplitude

$$c_1 = (1 - \nu)A_\nu c^{2-\nu}. \quad (31)$$

Equation (31) is compatible with the scaling prediction $c_1 = c^2 F(x)$ if

$$F(x) = \frac{(1 - \nu)A_\nu}{x^\nu} \quad \text{as } x \rightarrow 0. \quad (32)$$

We can now obtain the governing equation for the scaled mass density $F(x)$ by substituting the scaling form $c_k(t) \simeq c^2 F(x)$ into (23) to give the analog of Eq. (18a),

$$x^\nu F^2 - A \left[x \frac{dF}{dx} + F \right] = \int_0^x dy y^\nu F^2(y) F(x - y). \quad (33)$$

As in the case of Eq. (18a), the full equation is not analytically tractable, but it is possible to extract partial information about the scaling functions in the limits of small and large x .

The asymptotic behaviors (27) and (28) are valid for all $\nu \leq 1$, while (31) is valid for $\nu < 1$. A more careful analysis

is required to establish the decay of the monomer density in the model with $\nu = 1$, i.e., with linear rates $E_i = i$. Specializing (30) to $\nu = 1$, we obtain

$$\frac{dc_1}{dc} = \frac{c_1}{c} + \frac{1}{A_1} \left(\frac{c_1}{c} \right)^2. \quad (34)$$

Substituting $c_1 = cu$ into (30) gives

$$c \frac{du}{dc} = \frac{u^2}{A_1},$$

from which $u = A_1 / \ln(1/c)$ when $c \rightarrow 0$. Using this together with (27) and (28) specialized to the case $\nu = 1$ yields

$$Q_1 = \frac{1}{2t}, \quad c = \frac{1}{\sqrt{2A_1 t}}, \quad c_1 = \sqrt{\frac{2A_1}{t}} \frac{1}{\ln(2A_1 t)}, \quad (35)$$

when $t \gg 1$.

V. CATALYSTS WITH MAGIC MASSES

In many catalytic reactions, only a small subset of the reactants is catalytic. Since the cluster mass is the only parameter in our modeling, the spectrum of masses for the catalytic reactants should be sparse, so that catalysts are rare. Here we treat an extreme model where only monomers are catalytic. In Appendix A, we briefly consider the model where clusters with “magic” masses 2^n are catalytic.

A. Only monomers are catalytic

If only monomers are catalytic, the reaction now is $\{1\} \oplus [1] \oplus [j] \xrightarrow{\text{rate}1} \{1\} \oplus [1+j]$. The class of models (22) with algebraic reaction rates $E_i = i^\nu$ reduces to the model where only monomers are catalytic in the $\nu \rightarrow -\infty$ limit.

The cluster densities now evolve according to

$$\frac{dc_1}{dt} = -c_1^2(c + c_1), \quad (36a)$$

$$\frac{dc_k}{dt} = c_1^2(c_{k-1} - c_k), \quad k \geq 2. \quad (36b)$$

Essentially the same equations describe the phenomenon of submonolayer islanding [17,26]. In the islanding reaction, monomers adsorb and diffuse freely on a surface. When two monomers meet or a monomer meets a cluster of mass $k \geq 2$, merging takes place and all clusters of mass $k \geq 2$ are immobile [17,26]. The only difference between submonolayer islanding and catalytic coagulation with catalytic monomers is the factor c_1^2 instead of c_1 on the right-hand sides of Eq. (36).

By introducing the modified time variable

$$\tau = \int_0^t dt' c_1^2(t'), \quad (37)$$

we linearize (36) and obtain

$$\begin{aligned} \frac{dc_1}{d\tau} &= -c - c_1, \\ \frac{dc_k}{d\tau} &= c_{k-1} - c_k, \quad k \geq 2, \\ \frac{dc}{d\tau} &= -c. \end{aligned} \quad (38)$$

The last equation is not independent, as it is obtained by summing the rate equations for all the c_k . Solving this last equation gives

$$c(\tau) = e^{-\tau}. \quad (39a)$$

Then we solve the equation for c_1 and find

$$c_1(\tau) = (1 - \tau)e^{-\tau}. \quad (39b)$$

Finally, we solve the rate equations for c_k for $k \geq 2$ recursively and find

$$c_k(\tau) = \left(\frac{\tau^{k-1}}{(k-1)!} - \frac{\tau^k}{k!} \right) e^{-\tau}, \quad (39c)$$

for the monodisperse initial condition.

The time evolution ends at $\tau_{\max} = 1$, which corresponds to $t = \infty$. At this moment, the density of monomers vanishes and the reaction freezes. The k -mer densities at this final time are

$$c_k(t = \infty) = \frac{k-1}{k!} e^{-1}, \quad c(t = \infty) = e^{-1}. \quad (40)$$

While the dependence of the densities in Eq. (39) in terms of the modified time τ is the same as in submonolayer islanding [17,26], the dependence on the physical time is different. To determine the dependence on physical time, we exploit the fact that the monomer density vanishes, $c_1(t) \rightarrow 0$, as $t \rightarrow \infty$. Using this fact, together with $c(\infty) = e^{-1}$, we simplify (36a) to

$$\frac{dc_1}{dt} \simeq -\frac{c_1^2}{e},$$

from which

$$c_1(t) \simeq \frac{e}{t}. \quad (41)$$

In contrast, for submonolayer islanding, the density of monomers decays exponentially with time, $c_1 \sim e^{-t/e}$. The asymptotic approach of all the other k -mer densities to their final values is also algebraic,

$$c_k(t) - c_k(\infty) \simeq -\frac{k^2 - 3k + 1}{k!} \frac{e}{t}. \quad (42)$$

While catalytic coagulation with an initial population of catalytic monomers is solvable, it has the obvious limitation that all reactions terminate in a finite time. For this reaction with only monomers being catalytic to continue ad infinitum, it is necessary to postulate the existence of a source of monomers. This is the subject of the next section.

B. Input of monomers

We now extend the model (36) and postulate that monomeric catalysts are injected at a constant rate. Indeed, in mimicking the origin of life, it is natural to consider open systems. Clusters can spontaneously arise via external processes which we do not describe; instead, we merely account for them as a steady input of catalysts. One may anticipate that the balance between input and the increase of mass due to aggregation manifests itself by driving the system to a steady

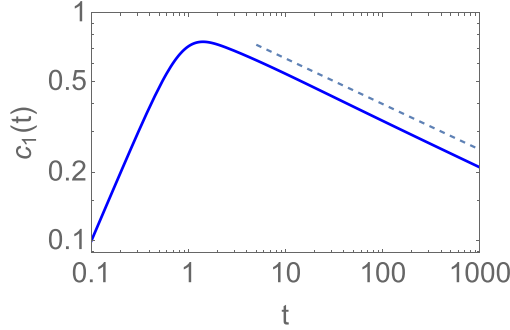


FIG. 3. The evolution of the monomer density from the numerical solution to Eqs. (45a) and (45b) with $J = 1$, subject to $c_1(0) = N(0) = 0$. The dashed line has slope $-1/5$.

state. This steady-state behavior often arises in classical aggregation (see, e.g., [30–32]). However, the outcome in the present case is continuous evolution, as we now demonstrate.

With monomer input, we add the source term to Eq. (36a),

$$\frac{dc_1}{dt} = -c_1^2 c - c_1^3 + J, \quad (43)$$

where J is the source strength. The k -mer densities with $k \geq 2$ again satisfy Eq. (36b). The time dependence of the density of noncatalytic clusters,

$$N = \sum_{k \geq 2} c_k, \quad (44)$$

can be found by summing Eq. (36b) for $k \geq 2$ and gives

$$\frac{dN}{dt} = c_1^3. \quad (45a)$$

It is also useful to rewrite (43) as

$$\frac{dc_1}{dt} = -c_1^2 N - 2c_1^3 + J. \quad (45b)$$

The pair of Eqs. (45a) and (45b) does not admit an exact solution, but we can determine the asymptotic behavior. The analysis is parallel to that given for the case of submonolayer island growth [17,26,33]. It turns out (which can be justified *a posteriori*) that $c_1 \rightarrow 0$ and $N \rightarrow \infty$. Hence, from (45b), we obtain $c_1^2 N \simeq J$, so that (45a) has the asymptotic form $\frac{dN}{dt} = (\frac{J}{N})^{3/2}$ leading to

$$c \simeq J^{3/5} \left(\frac{5t}{2}\right)^{2/5}, \quad c_1 \simeq J^{1/5} \left(\frac{5t}{2}\right)^{-1/5}. \quad (46)$$

To verify these asymptotic behaviors and to determine the small-time behavior, we used *Mathematica* and numerically solved Eqs. (45a) and (45b) subject to $c_1(0) = N(0) = 0$. The results agree with the asymptotic behaviors (46). In Fig. 3, we show the initial growth of the density of monomers and the decay at large times. The asymptotic behaviors (46) imply that $c_1^2 c \rightarrow J$ when $t \rightarrow \infty$, and this is also readily confirmed by the numerical integration of Eqs. (45a) and (45b).

By substituting $c_1 \simeq (2J/5t)^{1/5}$ into (37), we express the modified time in terms of the physical time and thereby

express the density in terms of the modified time,

$$c_1 \simeq \left(\frac{2J}{3\tau}\right)^{1/3}. \quad (47)$$

Next we solve

$$\frac{\partial c_k}{\partial \tau} = c_{k-1} - c_k \simeq -\frac{\partial c_k}{\partial k}.$$

The solution to this wave equation is $c_k \simeq c_1(\tau - k)$. Therefore,

$$c_k \simeq \left(\frac{2J}{3(\tau - k)}\right)^{1/3}, \quad (48)$$

which is valid when $\tau - k \gg 1$.

VI. SUMMARY

We introduced an aggregation process in which the reaction requires the presence of catalysts to proceed. These catalysts both facilitate the aggregation process and they can also directly participate in the aggregation reactions. While we vaguely have in mind the self-replicating reactions that occur in models for the origin of life, our modeling is more naive in character and is focused on devising a set of reactions that both relies on catalytic action and is analytically tractable. In this setting of aggregation, larger mass clusters are meant to imply molecules of greater complexity.

By imposing the constraint that the mass of the catalyst equals that of either of the participants in the aggregation reaction, we formulated a process that turns out to be analytically tractable. For the case where the reaction starts with a population of monomers, we solved for the k -mer densities in the scaling limit and found that c_k asymptotically decays as $t^{-2/3}$, while the total cluster density decays as $t^{-1/3}$. We generalized our catalytic coagulation model to allow for the efficacy of the catalysts to grow with their mass.

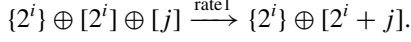
We also extended our approach to deal with open systems. The input of elemental reactants is a necessary ingredient to devise complex chemistries that underlie models of the origin of life. In our modeling, we treated the situation where only monomers are catalytic and they are injected into the system at a fixed rate to sustain a continuously evolving set of reactions. For this process, we again solved for the reaction kinetics by using classical tools of nonequilibrium statistical physics. We found that the cluster density continuously evolves, rather than reaching a steady state, with $c(t)$ growing with time as $t^{2/5}$, while the k -mer densities for fixed k all decay with time as $t^{-1/5}$. This continuous evolution of the aggregating system crudely mimics the increasing complexity necessary for the origin of life.

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APPENDIX A: ONLY CLUSTERS OF MASS 2^n ARE CATALYTIC

Here we study the process in which only reactants with “magic” masses 2^n are catalytic. This leads to the following generalization of the reaction (7):



The time evolution of cluster densities with nonmagic masses, $k \neq 2^n$, obeys

$$\frac{dc_k}{dt} = \sum_{2^i+j=k} b_i^2 c_j - c_k Q, \quad (\text{A1a})$$

where $b_i \equiv c_{2^i}$ are the densities of clusters with magic masses, while the density of magic-mass clusters obeys

$$\frac{db_i}{dt} = \sum_{2^l+m=2^i} b_l^2 c_m - b_i^2 c - b_i Q. \quad (\text{A1b})$$

Here, we still denote the cluster density by c , while Q is now the quadratic moment of the mass distribution of magic-mass clusters,

$$Q = \sum_{n \geq 0} b_n^2. \quad (\text{A2})$$

With this definition of catalytic clusters, the first of Eqs. (9a) still remains valid,

$$\frac{dc}{dt} = -cQ. \quad (\text{A3})$$

The validity of scaling is questionable. To appreciate this assertion, consider the evolution of the densities of small-mass clusters. For $k = 1, 2, 3$, we obtain

$$\begin{aligned} \frac{dc_1}{dt} &= -c_1^2 c - c_1 Q, \\ \frac{dc_2}{dt} &= c_1^3 - c_2^2 c - c_2 Q, \\ \frac{dc_3}{dt} &= c_1^2 c_2 + c_2^2 c_1 - c_3 Q. \end{aligned} \quad (\text{A4})$$

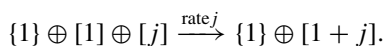
The asymptotic behavior seemingly is

$$\begin{aligned} \frac{dc_1}{dt} &\simeq -c_1^2 c, \\ \frac{dc_2}{dt} &\simeq -c_2^2 c, \\ \frac{dc_3}{dt} &\simeq -c_3 Q. \end{aligned} \quad (\text{A5})$$

The decay of the densities of magic clusters c_1 and c_2 is apparently qualitatively faster than the decay of c_3 . This apparently different temporal behaviors for small-mass clusters indicates that there no longer is a scaling description for the cluster-mass distribution.

APPENDIX B: CATALYTIC MONOMERS WITH MASS-DEPENDENT REACTION RATES

The reaction scheme for this process is



In contrast to models that we considered previously when the rate could depend on the mass of the catalyst, we now assume that the rate depends on the mass of the reactant. The cluster densities now obey

$$\frac{dc_1}{dt} = -c_1^2(1 + c_1), \quad (\text{B1a})$$

$$\frac{dc_k}{dt} = c_1^2[(k-1)c_{k-1} - kc_k], \quad k \geq 2. \quad (\text{B1b})$$

In terms of the modified time (37), we rewrite (B1) as

$$\frac{dc_1}{d\tau} = -1 - c_1, \quad (\text{B2a})$$

$$\frac{dc_k}{d\tau} = (k-1)c_{k-1} - kc_k, \quad k \geq 2. \quad (\text{B2b})$$

Solving these equations recursively subject to the monodisperse initial condition yields [26]

$$c_k(\tau) = e^{-\tau}(1 - e^{-\tau})^{k-1} - k^{-1}(1 - e^{-\tau})^k. \quad (\text{B3})$$

The density of monomers is

$$c_1(\tau) = 2e^{-\tau} - 1, \quad (\text{B4})$$

and it vanishes at $\tau_{\text{max}} = \ln 2$, corresponding to $t = \infty$. At this moment, the process freezes. The final densities are

$$c_k(t = \infty) = \frac{k-1}{k} 2^{-k}, \quad c(t = \infty) = 1 - \ln 2. \quad (\text{B5})$$

The latter formula follows from $c(\tau) = 1 - \tau$ that follows by summing all the k -mer densities (B3). In terms of the physical time, the asymptotic approach of the k -mer densities to their final values is algebraic. The leading behavior of these corrections is inversely proportional to time,

$$c_k(t) - c_k(\infty) \simeq -\frac{k-3}{2^k} t^{-1}. \quad (\text{B6})$$

The only exception is the density of 3-mers:

$$c_3(t) - c_3(\infty) \simeq -\frac{1}{4t^2}. \quad (\text{B7})$$

We now inject catalysts with rate J to counterbalance freezing. In the system of Eq. (B1), only Eq. (B1a) is affected. In the case of an initially empty system, we find

$$\frac{dc_1}{dt} = -c_1^2(Jt + c_1) + J. \quad (\text{B8})$$

Thus, $c_1 \simeq t^{-1/2}$ as $t \gg 1$.

In the long-time limit, $c_k(t)$ approaches the scaling form,

$$c_k(t) \simeq t^{-1} F(k/t). \quad (\text{B9a})$$

More precisely, this happens in the scaling limit,

$$t \rightarrow \infty, \quad k \rightarrow \infty, \quad \frac{k}{t} = \text{finite}. \quad (\text{B9b})$$

The scaled mass distribution can be extracted from the exact formula in Ref. [26] (which is valid for all $k \geq 2$),

$$c_k(\tau) = (k-1) \int_0^\tau du c_1(\tau-u) e^{-2u} [1 - e^{-u}]^{k-2}. \quad (\text{B10})$$

Suppose $k = O(1)$. By substituting $c_1 \simeq t^{-1/2}$ into (37) and dropping terms that vanish as $t \rightarrow \infty$, we get

$$\tau = \ln t + \ln C. \quad (\text{B11})$$

[Fixing the constant C requires an exact solution of (B8), which looks intractable.] The asymptotic $c_1 \simeq t^{-1/2}$ becomes $c_1(\tau) \simeq \sqrt{C} e^{-\tau/2}$ in the modified time variable τ when $\tau \gg 1$. Substituting this latter form into (B10) and using $U \equiv e^{-u}$, we deduce

$$\begin{aligned} c_k(\tau) &\simeq c_1(\tau)(k-1) \int_0^1 dU \sqrt{U} [1-U]^{k-2} \\ &= c_1(\tau) \frac{\Gamma(\frac{3}{2}) \Gamma(k)}{\Gamma(k + \frac{1}{2})}, \end{aligned}$$

in the long-time limit. When $1 \ll k \ll t$, we get

$$c_k(t) \simeq \sqrt{\frac{\pi}{4kt}}, \quad (\text{B12})$$

which is consistent with the scaling form (B9) and gives the small-mass asymptotic of the scaled mass distribution,

$$F(x) \simeq \sqrt{\frac{\pi x}{4}} \quad \text{when } x \rightarrow 0. \quad (\text{B13})$$

To extract the asymptotic behavior of the scaling function for $x \gg 1$, we simplify the last factor in the integrand in (B10).

Namely, we write $v = \tau - u$ and obtain

$$c_k(\tau) \simeq k e^{-2\tau} \int_0^\tau dv c_1(v) e^{2v - k e^v e^{-\tau}}. \quad (\text{B14})$$

Using (B11), we find $k e^{-\tau} = x/C$. Hence, in the exponent, we have $2v - k e^v e^{-\tau} = 2v - e^v x/C$. Since $x \gg 1$, we only need the small- v behavior. We obtain

$$c_k(\tau) \simeq k e^{-2\tau - x/C} \int_0^\infty dv c_1(v) e^{-xv/C}. \quad (\text{B15})$$

To compute the integral, we need to know the asymptotic behavior of $c_1(v)$ when $v \ll 1$, as the integrand vanishes exponentially quickly when $v > 1/x$. Using (B8) and (37) one can deduce that when the modified time v is small, the density of monomers scales as $c_1(v) \simeq (3Jv)^{1/3}$. Substituting this asymptotic into (B15) and using the original time variable yields

$$\begin{aligned} c_k(t) &\simeq \frac{k}{(Ct)^2} e^{-x/C} \int_0^\infty dv (3Jv)^{1/3} e^{-xv/C} \\ &= t^{-1} \left(\frac{3J}{C^2}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) x^{-1/3} e^{-x/C}, \end{aligned} \quad (\text{B16})$$

which is compatible with the scaling form (B9) and gives the large-mass asymptotic of the scaled mass distribution,

$$F(x) \simeq \left(\frac{3J}{C^2}\right)^{1/3} \Gamma\left(\frac{4}{3}\right) x^{-1/3} e^{-x/C}, \quad (\text{B17})$$

as $x \rightarrow \infty$.

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